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Structure and Mechanism in Macrocyclic Systems

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requirements of The Nottingham Trent University
for the Degree of Doctor of Philosophy.

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I would like to acknowledge the staff members of the Department of Chemistry and Physics at the Nottingham Trent University for their help and assistance.

I am also extremely grateful to the past and present members of the Organic Research Laboratory for their good humour and support.

Thanks also to my family for their never-ending support and to my friends for their encouragment.

Finally, I would like to thank the Nottingham Trent University for providing me with financial support throughout the course of this work.

Abstract

The aim of this work was to produce a range of crystalline thiophene-based macrocycles and macrocyclic complexes and to investigate their structure-property relationships. This involved studies of the structures of macrocycles and also their mechanism of complexation with metals including nickel, copper, aluminium, and silver. The macrocycles and relevant complexes were prepared and crystallised from solution, and their structure-property relationships investigated by using X-ray crystallography and spectroscopy, in addition to theoretical calculations of molecular geometry and binding energy, and optimisation of molecular geometry using suites of molecular modelling programs.

The synthesis of macrocycles 15-ethyl-2,5,8-trioxa-12,18-dithia-15-aza-tricyclo-tricosa-1(18),9(13)-10-19-tetraene **10a**; 18,24-bis-(methyl)-2,5,8,11.21-pentaoxa-15,27-dithia-18,24-diaza-tricyclo-nonacosa-1(26),12(16),13,28-tetraene **22** and 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene **24**, involved the synthesis of intermediate molecules such as thiophene open-chains. These intermediates are: diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate **15**; thiophene bisester; thiophene bisacid; α,ω-bis-(3-oxythienyl)ethane **16**; α,ω-bis-(3-ethyloxythienyl)ethane **20**; 18-carboxylic-α,ω-bis-(3-oxythienyl)ethane **16**; thiophene bisaldehyde or α,ω-bis-(2-formyl-3-oxythienyl)ethane **19**; α,ω-bis-(2-propylimine3-oxythienyl)ethane and α,ω-bis-(2-propylamine3-oxythienyl)ethane. The structure of compounds 18,21-bis-(methyl)-2,5,8,11-tetraoxa-15,24-dithia-18,21-diaza-tricyclo-hexacosa-1(26),12(16),13,25-tetraene **8b**; **10a**; 18-ethyl-2,5,8,11-tetraoxa-15,21-dithia-azatricyclo-tricosa-1,22,12,13-tetraene **10b**; **15**; **16**; 5,17-dimethyl- α,ω-bis-(3-oxythienyl)ethane **17**; **18**; **19**; **20**; 2,5,8,11-tetraoxa-15,26-dithia-18,21-diaza-tricyclo-nonacosa-1(26),12(16),13,28-tetraene **23** and **24** were characterised by X-ray crystallography as well as the structure of macrocycle **24** complexed with $Cu(ClO_4)_2$ **50** and with $Co(ClO_4)_2$ **54**. The other thiophene-based macrocycles which were not characterised by x-ray crystallography as well as **10a** were geometrically optimised by molecular modelling.

The results obtained showed that metal complexation did not always occur in macrocycle cavities of apparently optimum size and that in the case of silver the metal did not enter the macrocycle, but bonded externally to an electronegative atom from the ring. The infrared spectroscopy showed some peaks that were characteristic of the counterion (for example perchlorate and isocyanate), but it was also possible to identify

some new peaks and some peak shifts due to complexation of the metal ions with the ligand (for example Al(III)-O). Moreover, the ^1H and ^{13}C NMR spectroscopy revealed several significant peak shifts between the free ligands and the complexed ligand due to interactions between the ligand and the metal ion, which depend on through which atoms and how strongly the metal ion is complexed with the ligand.

Abbreviations

^{13}C : carbon 13

d : doublet

DCM : dichlomethane

dd : double doublet

ΔH : enthalpy

ΔG : free energy

DMF : N,N' dimethyl formamide

ΔS : entropy

eq. : equivalent

esd : estimated standard deviation

ethylenediamine : 1,2-diaminoethane

g.AcOH : glacial acetic acid

^{1}H : proton

IR : (FTIR) Fourier Transform Infrared Spectroscopy (υ_{max}/cm^{-1})

KOH : potassium hydroxide

m : multiplet

M : molecular weight

M.F. : molecular formula

NMR : Nuclear Magnetic Resonance Spectroscopy (δ_H and δ_C)

Ph : C_6H_4

q : quartet

s : singlet

t : triplet

Th : thiophene

THF : tetrahydrofuran

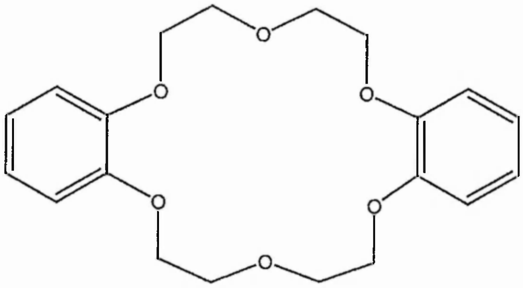
Contents

Introduction

1. Macrocyclic Chemistry

1.1. Discovery

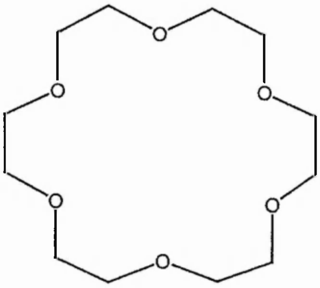
The crown ethers were accidentally discovered by Pedersen[9] when "white fibrous crystals" were obtained in 0.4% yield from a reaction between partially protected catechol and bis(2-chloroethyl)ether. This first crown ether was 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-ine.



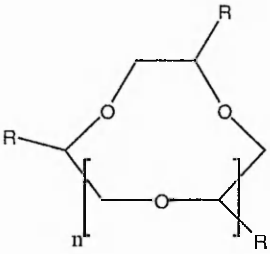
1.2. Different Macrocycles

1.2.1. Cyclic Polyethers

By consideration of the factors involved in the stability of the salt complexes (such as the relative sizes of the hole and the cation, and the number and symmetrical arrangement of the oxygen atoms in the polyether ring), Pedersen synthesized a range of macrocyclic polyethers varying the numbers of atoms in the polyether ring and the donor atoms (oxygen, nitrogen, sulfur)[10-13]. These served to define the effective ones which proved to be compounds containing 5 to 10 oxygen atoms in the ring, each separated from the next by 2 carbon atoms. Truter and her collaborators were the first to determine the structures of a number of crystalline salt complexes of crown compounds by X-ray diffraction methods[14]. In 1974 and 1979, Dunitz and Seiler[15,16] determined several times the X-ray structure of the most well known macrocycle, which is 1,4,7,10,13,16-hexaoxacyclooctadecane or 18-crown-6 (18C6), at different temperatures. They published at the same time the first complete series of X-ray structures of 18-crown-6, which includes complexes as well as the free ligand[17]. This series of structures was the second available so far after those of the macrobicyclic [2,2,2] cryptate studied by Moras et al[18].

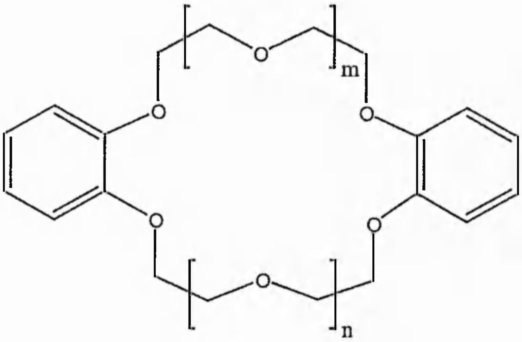


The crown ethers created considerable interest due to their proven ability to form stable complexes with alkali and alkali earth cations. Since Pedersen reported the synthesis and cation-complexing characteristics of the crown ethers in 1967, there has been increasing interest in these compounds as complexing agents for various metal and organic cations. Many different modifications of the crowns have been made to enhance their cation-complexing properties. A compilation of cation complexing properties of the crown ethers has been published[8,19-36]. Those macrocycles can contain from zero to four aromatic rings.

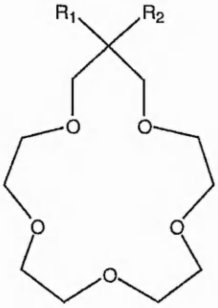


n= 1 9C3
n= 2 12C4
n= 3 15C5
n= 4 18C6
...

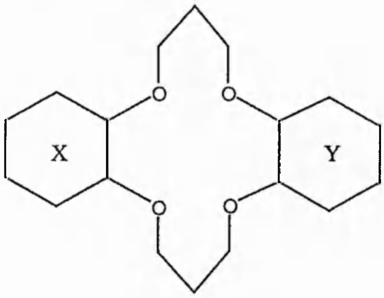
R= H, Me...



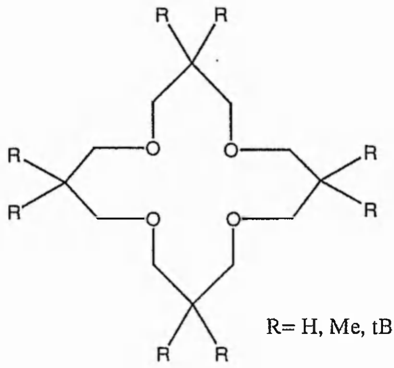
n, m= 0,1,2,3,4,5,9...
X,Y=C_2H_4,C_3H_6,C_6H_4,C_6H_{10},C_4SH_2
phenanthroline...



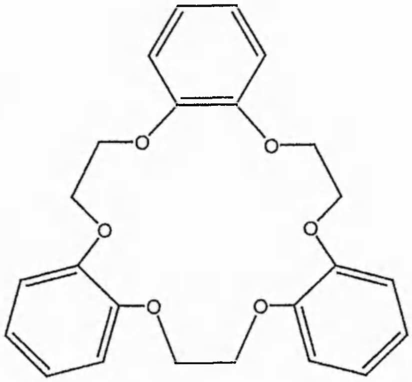
R_1, R_2= H, Me...

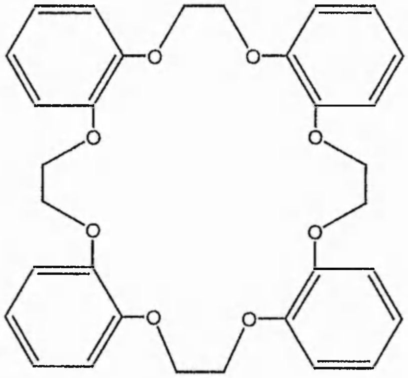


X,Y=C_2H_4,C_2H_2,C_6H_4,C_8H_{10}...



R= H, Me, tBu...





In a more recent review, Liu and al.[37] stress that studies of the complexation thermodynamics of lanthanide ions with crown ethers are limited, whereas the bonding abilities of a large number of synthetic coronands, towards a wide variety of cations have been thoroughly investigated[19,24,27,34-36,38-41].

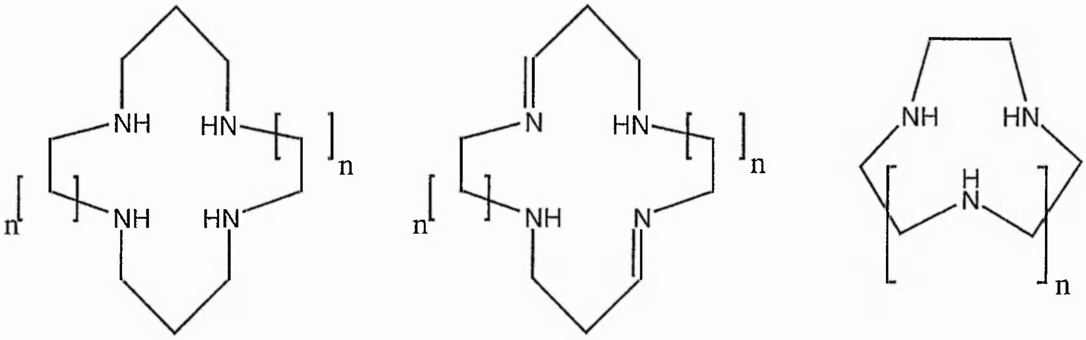
1.2.2. Cyclic Polyamines and Polyimines

A large variety of cyclic polyamines and polyimines having three to six functional groups in the ring have been synthesized. However, the majority have four functional groups, which are more or less evently spaced in a ring containing between 12 and 16 atoms. The macrocycles can be synthesised either "free" or bound to a given metal ion.

The preparation of the free macrocycle has certain advantages in many cases, for example the purification of the organic product may be more readily accomplished than its complexes. The characterization by such physical techniques as gas-liquid chromatography, mass spectrometry, infrared spectroscopy and nuclear magnetic resonance spectroscopy also tends to be less involved for the metal-free macrocycle. However, preparation of the free macrocycle has disadvantages in that the method usually gives only low yields of the desired products.

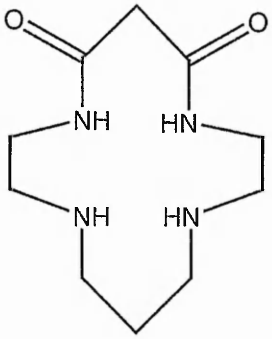
In general, cyclic polyamines are formed by one of a number of different kinds of condensation reactions in which metal ions function as a template, holding the condensing molecules in a suitable orientation to facilitate the formation of products[42-44]. Typical of macrocycles prepared by condensation in the presence of transition metal salts are those formed by reaction of certain metal-amine complexes with aliphatic carbonyl compounds[42,44].

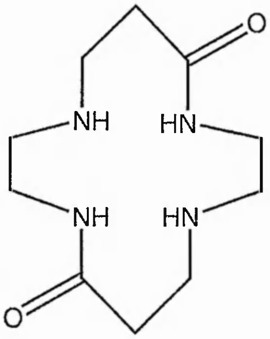
It is possible to vary the unsaturation of the macrocycles from imine function to the amine by oxidation or reduction, respectively. Several reviews and papers have been published describing the synthesis of polycyclic polyamines[42-46]. Most of the cyclic polyamines and polyimines are derived from the 1,4,8,11-tetraazacyclotetradecane or "cyclam".

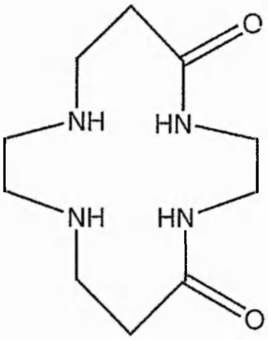


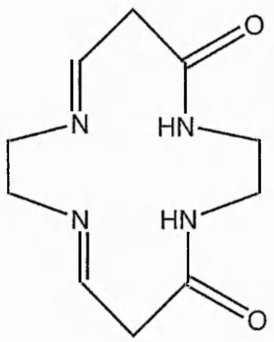
n= 1,2,3...

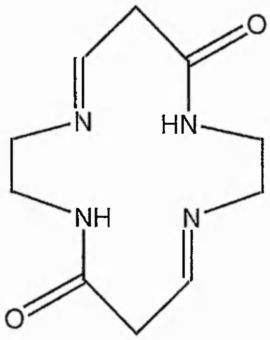
The ion binding ability of the polyamines and polyimine macrocycles has been thoroughly investigated in several reviews and papers[19,35-47]. For example, the dioxocyclam has been substituted and its complexation ability has been widely studied[48-53].

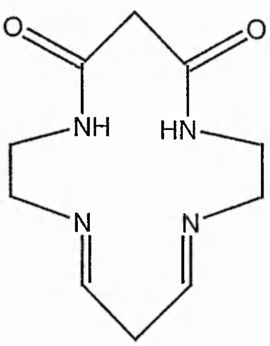




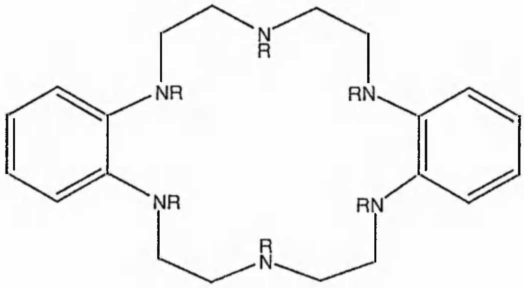




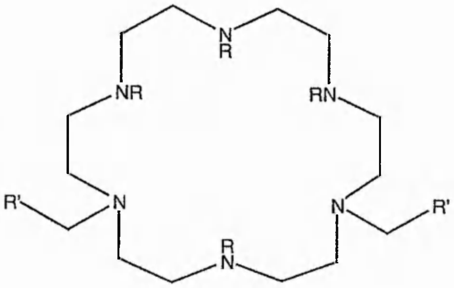




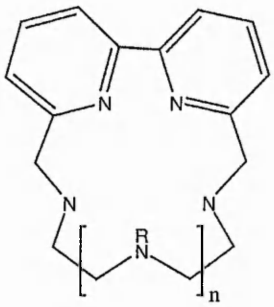
The cyclam has also been substituted by the incorporation of alkyl groups[54], aromatic groups such as pyridine[54,55], naphthalene[47], phenanthroline[56] or containing heteroaromatic units[57] as pendant arms such as thiophene.



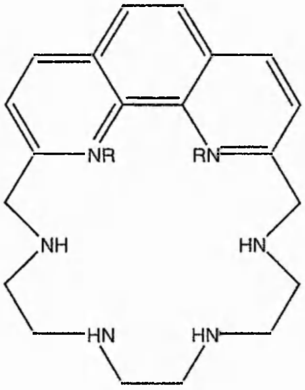
R= H, Me...

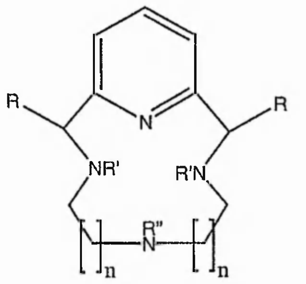


R= H, Me, CO_2H...
R'= H, Me, CO_2H, Th, Ph-NO_2...

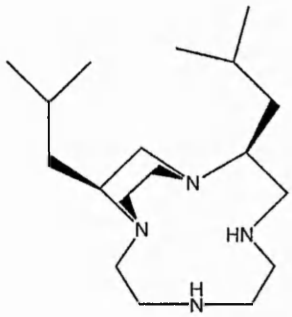


n= 1,2,3...
R= H, Me...

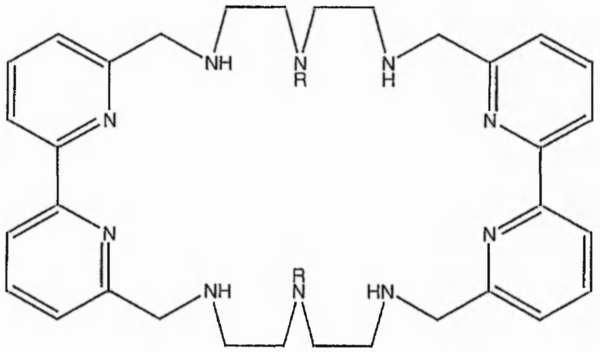




n= 1,2...
R, R', R''= H,Me,CH_2CO_2H,$(CH_2)_2CO_2H$...



n= 1,2,3...
R= H, Me...



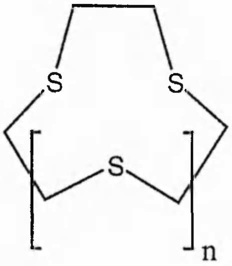
R= H, Me...

In particular, large polyazacycloalkanes containing six or more nitrogen donors are able to form very stable metal complexes, containing one or more metal ions, due to their large number of nitrogens[58,59]. The coordination properties of these polyamines may be modulated through nitrogen functionalization.

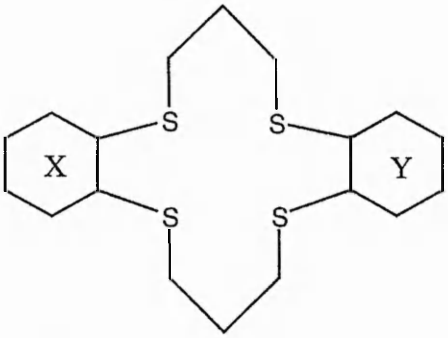
1.2.3. Cyclic Polythioethers

The past decade has witnessed a phenomenal growth in research into the coordination chemistry of macrocyclic thioether ligands such as 1,4,7-trithiacyclononane (9S3) and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6). Reports on these and related thioether ligand systems have appeared[60-68].

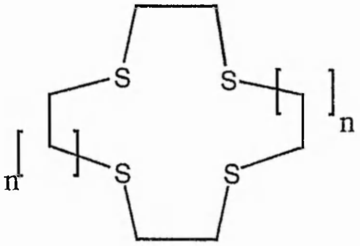
The complexing properties of macrocyclic polythioethers have been widely studied and metal complexes with these ligands have also been isolated and characterized[62,69-76]. The analytical applications of macrocyclic polythioethers in areas such as solvent-solvent extraction[76-78], solid-phase extraction[79], and PVC-membrane selective electrodes have also been reported in the literature[79-82].



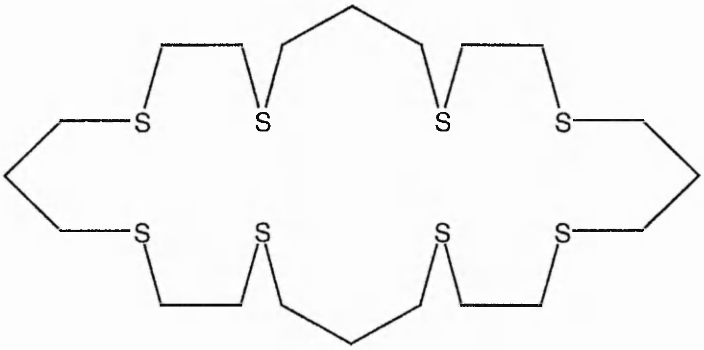
n=1 9S3
n=2 12S4
n=3 15S5
n=4 18S6
...



X,Y= C_2H_4,C_2H_2,C_6H_4,C_6H_{10}...



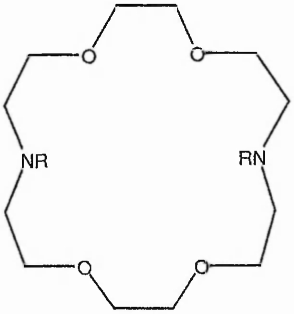
n= 1,2,3...



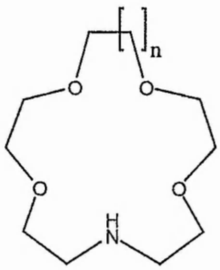
1.2.4. Mixed donor atoms

1.2.4.1. Nitrogen-Oxygen

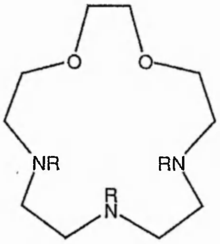
The coordination chemistry of aza and mixed oxa-aza macrocycles containing different pendant arms attached to the aza centers has attracted the attention of many researchers over the past twenty years[83-91]. These ligands can exhibit remarkable metal ion selectivity and show specific complexation behavior forming metal complexes with unusual structures[86-93].



R= H, Me,C_6H_5,$CH_2C_6H_5$...

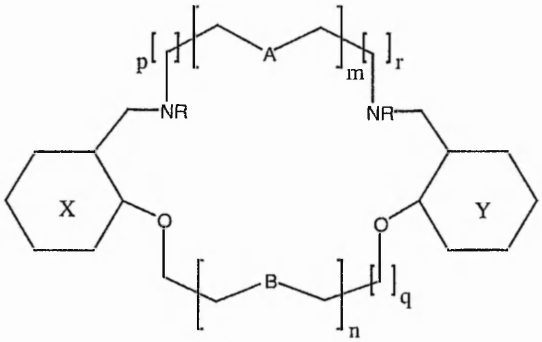


n= 1,2,3...

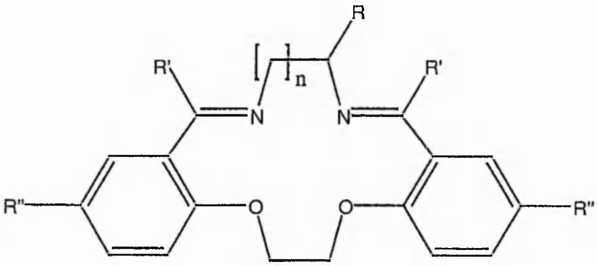


R= H, Me,CH_2CN,$C_2H_4NH_2$,CO_2H,C_6H_4...

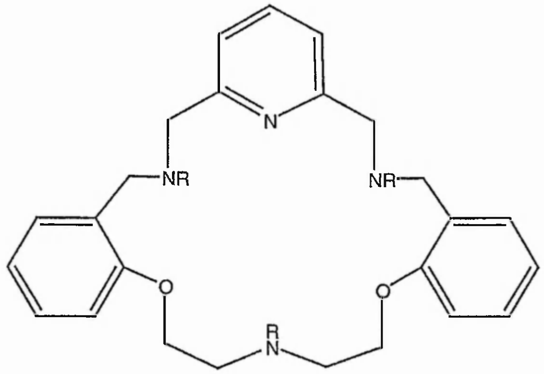
Macrocyclic crown ethers and other ionophores can bind cations[94], anions and small neutral organic molecules[95]. The initial design of macrocycles focused on simple ether and amine donors that were essential for efficient substrate binding. Progress has led to the incorporation of different structural moieties such as benzene[34,36,96-122], thiophene[1-7,29,30,123], pyridine[124,125], bipyridine[126,127], and tetrapyridine[128], which has allowed a greater selectivity in substrate binding. Lindoy and co-workers[34,36,96-109,111,112,114,115,117,119] have specially focused their study on the variation of: the macrocyclic ring size, the donor set present and/or the degree of substitution of the parent ring structure to 'tune' the affinity of a given ring type for the metal ions of interest, in order to document structure-function relationships underlying the observed respective thermodynamic stabilities of the resulting complexes.



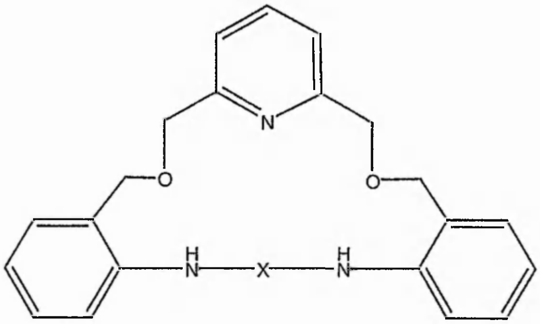
n, m= 0,1,2,3...
p, q,r= 1,2...
A,B= O,NH,S
R= H,Me...
X,Y=C_2H_4,C_6H_4,C_6H_{10}...



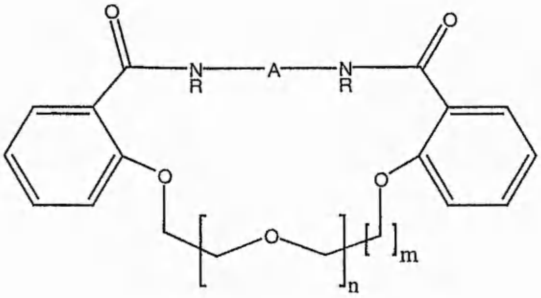
n=1,2,3...
R= H,Me...
R'= H,C_6H_4...
R''= H,Cl...



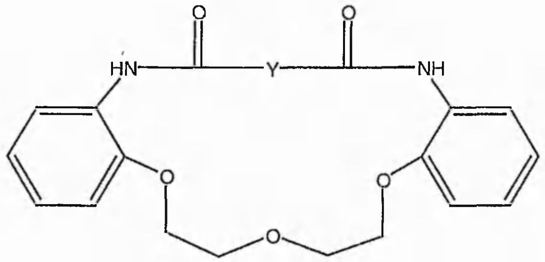
R= H, $C_6H_4NO_2$...



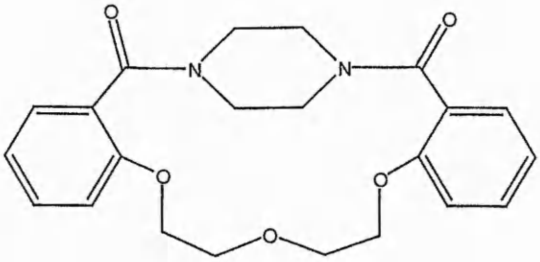
X= CH_2-C_5H_3N-CH_2,C_2H_4...

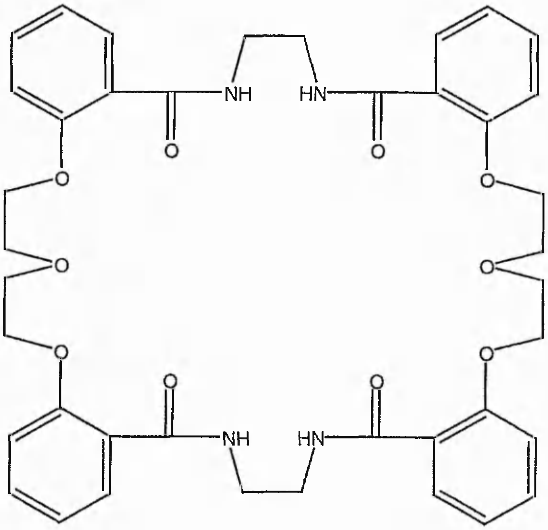


m,n= 1,2,3...
A= CH_2-C_6H_4-CH_2,$(CH_2)_p$...
p= 2,3,4...
R= H,Me...

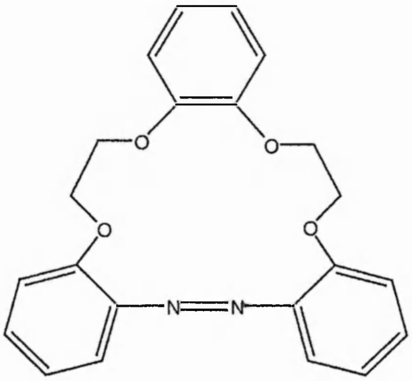


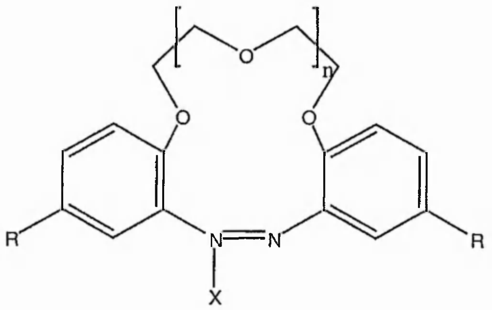
Y= $(CH_2)_2$,$(CH_2)_4$,C_6H_4,C_5H_3N,$(CH_2)_2OC_6H_{40}(CH_2)_2$...





L.M. Goldenberg and N.N. Denisov[129] showed that the introduction of photo and electroactive –N=N– or –N(O)=N– residues into crown ether macrocycles can result in highly selective chemical sensors. Over recent years, they have been studying the family of 13 and 16 membered aza and azoxycrowns[130-141].

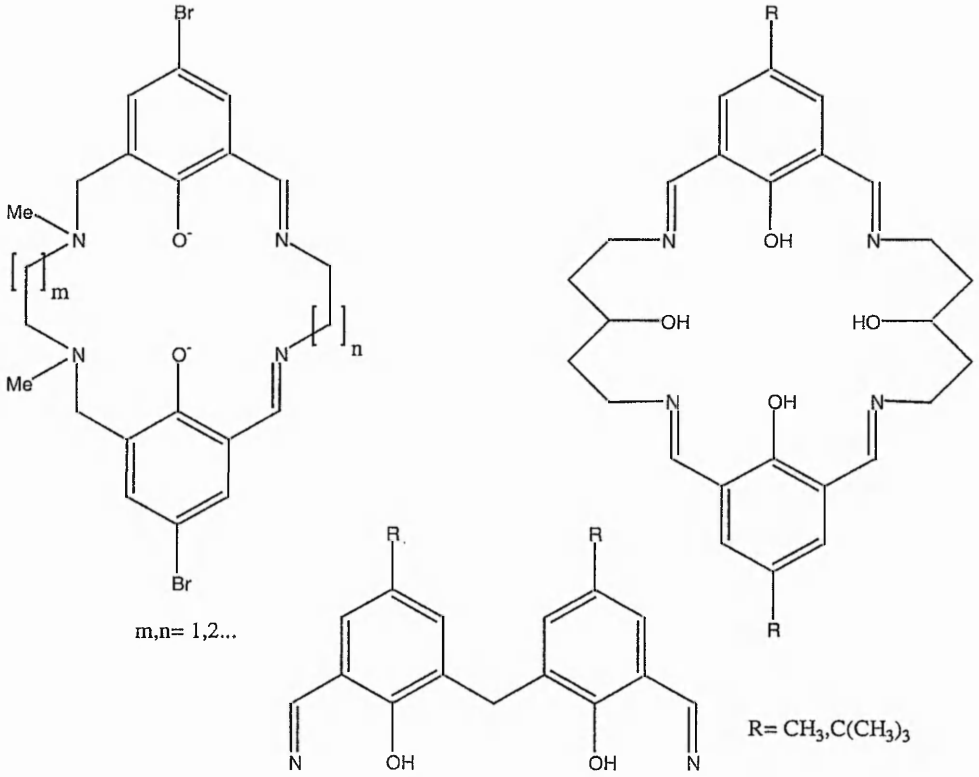




n= 1,2...
X= nil,O
R= $(CH_3)_3CCH_2C(CH_3)_2$,n-$C_{12}H_{25}$

The search for novel macrocyclic ligands that are capable of selectively binding metal ions is a major area of modern coordination chemistry research. A great deal of work has been carried out on crown-like macrocycles containing azole or azine fragments in this context[142,143]. Macrocycles containing pyrazole[144], imidazole[145], 1,2,4-triazole[146], pyridine[147] and 1,3,5-triazine[148] are well known.

More recently, the study of heterodinuclear metal complexes has become important because of unprecedented physicochemical properties and functions arising from a pair of dissimilar metal ions in close proximity[147-155]. In order to provide discrete heterodinuclear core complexes, many efforts have been devoted to the design of unsymmetric compartmental ligands whose two metal-binding sites are not equivalent with respect to the cavity size[156], coordination mode[157], or the nature of the donor atoms[158-166]. Macrocyclic compartmental ligands have a great advantage over acyclic ligands for this purpose because macrocyclic heterodinuclear cores can be thermodynamically stabilized and kinetically retarded toward metal dissociation and substitution by the so-called 'macrocyclic effect'[167].



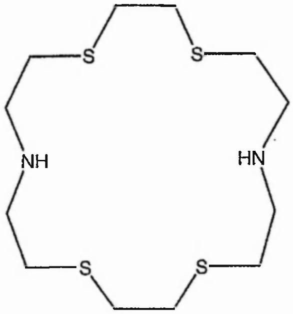
m,n= 1,2...

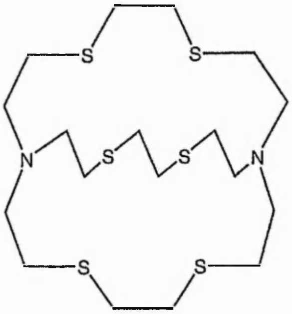
R= CH_3,$C(CH_3)_3$

...

1.2.4.2. Sulfur-Nitrogen

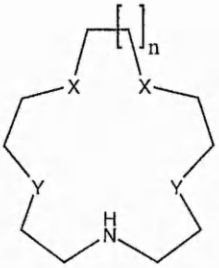
The first mixed sulfur-nitrogen donor crown macrocycles were synthesized by Dietrich, Lehn, and Sauvage[168] and by Black and Mc Lean[169,170].



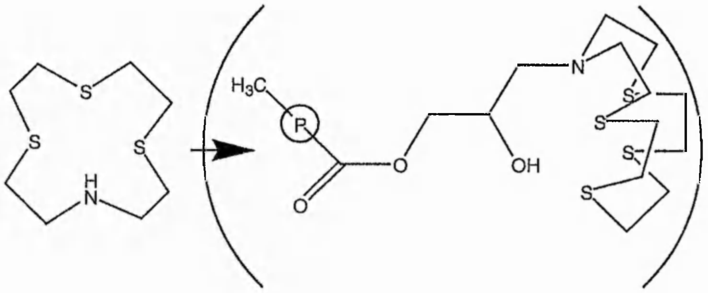


Busch and co-workers[44,171-174] also synthesized several sulfur-nitrogen containing macrocycles by in situ methods where a metal ion was present, yielding the metal complex directly.

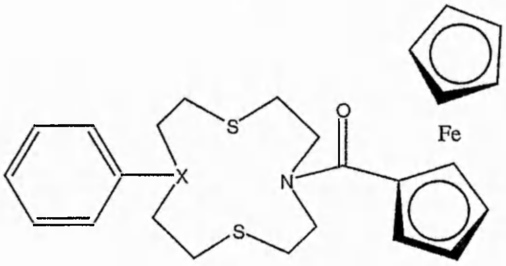
Crown ethers containing nitrogen and/or sulfur donor atoms are of interest as their affinity to coordinate to specific cations is directed more towards (heavy) transition metal ions. This affinity can be fine-tuned by altering the composition of the donor-atom set[175]. Selectively chelating ion exchangers for the complexation and subsequent separation of heavy metals ions can be obtained, via the immobilization of mixed-donor crown ethers on highly cross-linked glycidyl methacrylate copolymers[176-179].



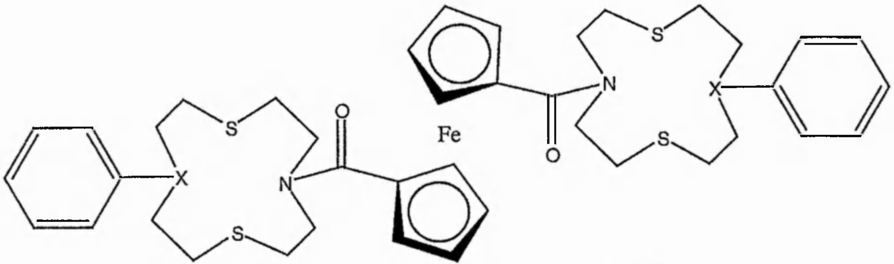
n= 1,2...
X,Y= S,O



The exocyclic functionalization of macrocycles with redox active or luminiscent centers is also a well known strategy, used in the design of sensoring systems based on ion-selective macrocyclic ligands[180].

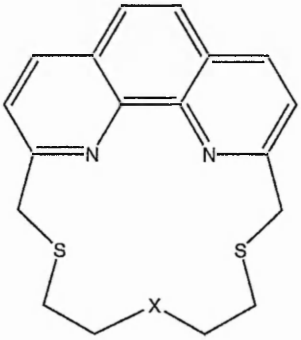


X= N,P



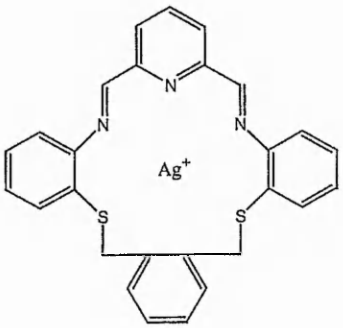
X= N,P

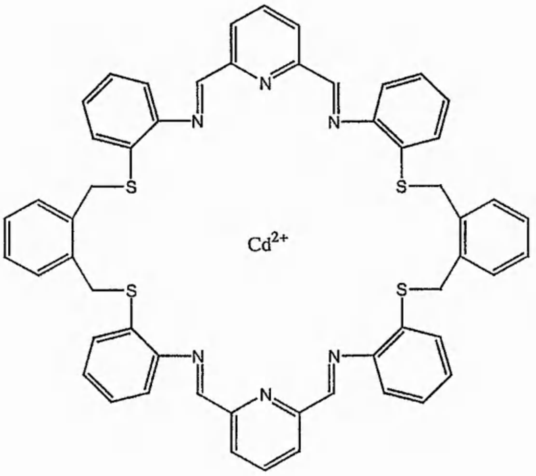
It is well known that the formation constant of complexes of group I and II ions with crown ethers drastically decreases upon replacement of some of the oxygen atoms of the cyclic ligands with the sulfur donors[39]. On the other hand, thioether macrocycles have come to great prominence in the last decade due to their ability to stabilize unusual oxidation states and coordination geometries of soft metal ions such as transition metals and coinage metals[61,181]. Some thioether crowns containing rigid aromatic and heteroaromatic units fused with thioether linkers have also been tested as sensors in solid-state electrodes, resulting in particularly selective detection of Ag (I)[182-185].



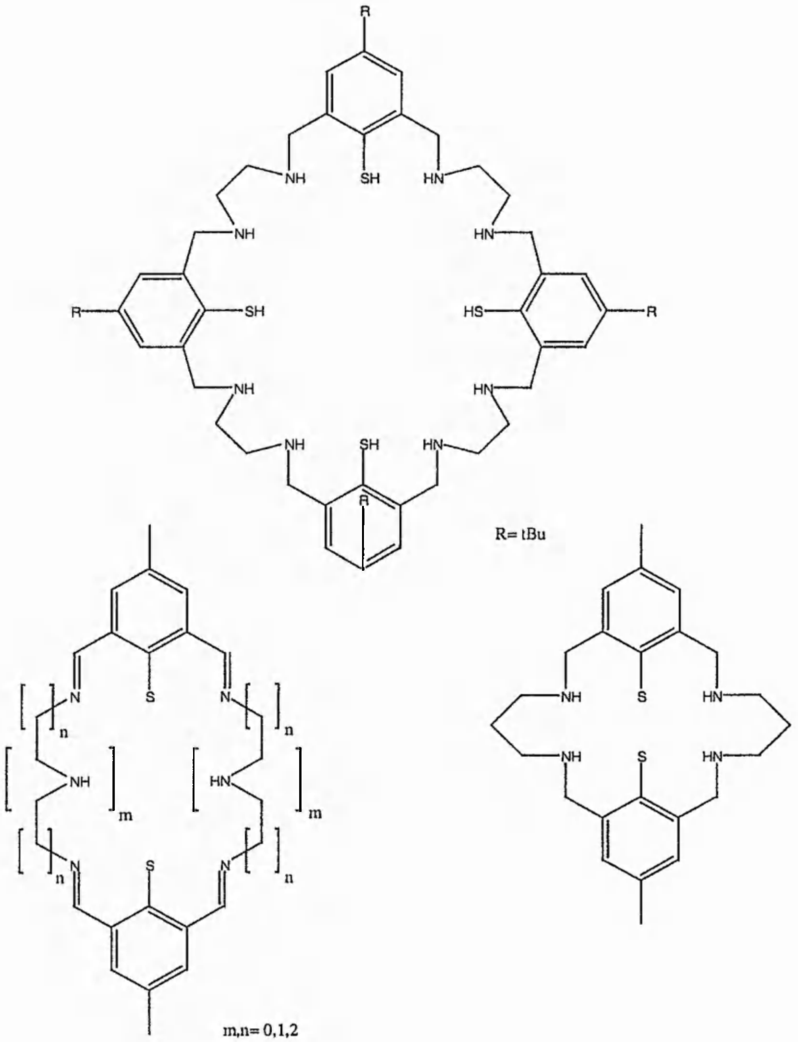
X,Y= S,O

Substantial interest surrounds the application of metal ions in the control entwined molecular architectures and in particular in the production of helical metal complexes, the helicates[186-189]. While a large number of single, double and even triple-helicate species are now known, relatively few macrocyclic helicate systems, which are potentially more robust in solution, have been reported[190-198]. Matthews and co-workers[199] are now incorporating sulfur donors into related macrocylic species, envisaging that, in addition to changing the binding characteristics of the ligands, these donors may affect the folding characteristics of the macrocycle, thereby influencing the secondary structures of any helical products.

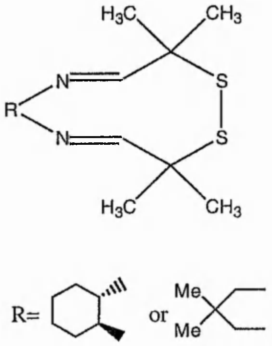


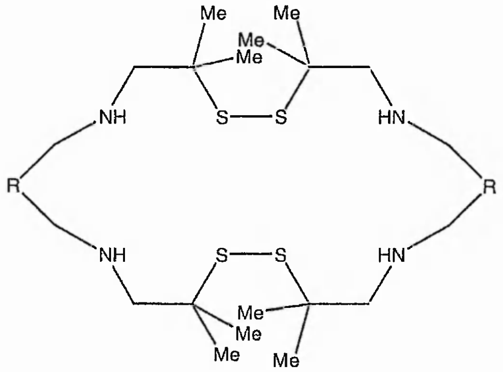


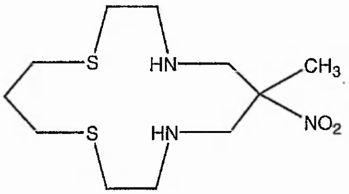
In contrast to the large number of macrocyclic amine-phenolate ligands, there exist only a few examples of the corresponding imine and amino-thiophenolates[200]. This is true in particular for larger macrocyclic N_xS_y compounds[201-204]. Added impetus for studying complexes of such macrocycles is coming from the increasing numbers of biologically active sites which contain bridging thiolates.

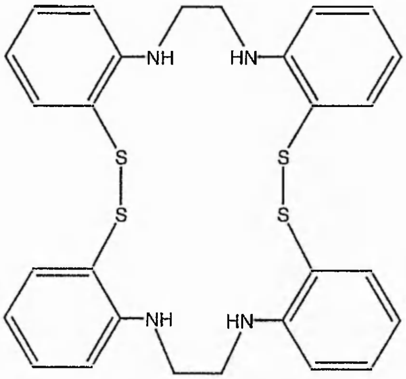


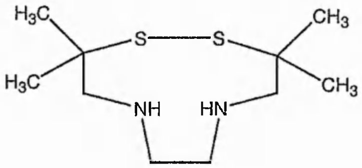
The extensive literature of mixed-donor macrocyclic ligands[205,206] includes only a few examples in which a metal ion is bound to the disulfide incorporated in the macrocycle. Although cystine cross-linked peptides constitute an enormous class of macrocycles containing one or more disulfide groups, the ligating roles of such disulfide units have apparently been neither demonstrated nor widely investigated[206,207].



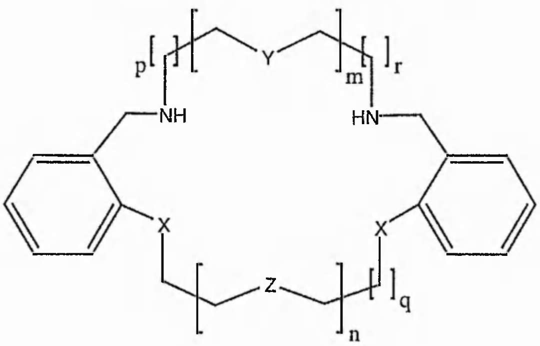




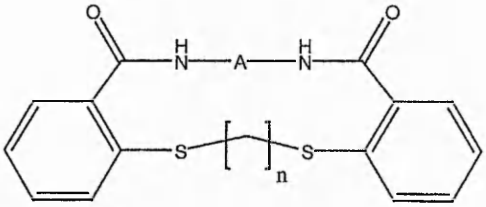




The complexing ability of macrocyclic crown ethers containing nitrogen donors such as imine or amine and aromatic moieties, have been compared with the corresponding macrocycles containing sulfur donors instead of oxygen donors[96-98,117,120].



n, m= 0,1,2,3...
p, q,r= 1,2...
X,Y,Z= O,NH,S

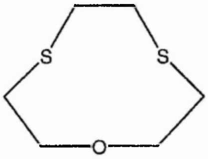


n= 1,2,3...
A= $CH_2C_6H_4CH_2$

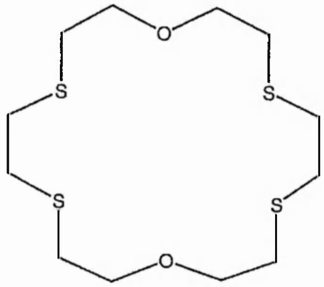
1.2.4.3. Sulfur-Oxygen

Less developed, however, is the coordination chemistry of crown thioethers, which incorporate a second type of heteroatom into the macrocycle ring. Several contemporary examples of these crown ligands include tridentate macrocycles containing either one or two nitrogen donor atoms[68,208], a single phosphorus atom[209,210], and an 18-membered ring system with two nitrogen atoms[211]. Of particular interest are mixed ether-thioether ligands since these systems incorporate hard and soft donor atoms into the macrocyclic ring, and therefore can potentially bind to both hard and soft guest ions simultaneously. These systems have potential applications as liquid crystals, synthetic selective ionophores, and model compounds for biological systems[212,213].

Several reports have appeared dealing with the complexation behavior of macrocyclic oxathioethers[214-216]. The tetrathioether 1,4,10,13-tetrathia-7,16-dioxa-cyclooctadecane ($18S_4O_2$) was first synthesized[169] by reaction of 1,2-dibromoethane with the disodium salt of 3-oxapentane-1,5-dithiol in ethanol at high dilution with a yield of 7%. Bradshaw et al.[217] have prepared 11 different thioethers in a manner similar to that reported by Dann, Chiesa, and Gates[218], in which the appropriate oligo ethylene glycol dichloride was allowed to react with a dithiol or sodium sulfide.

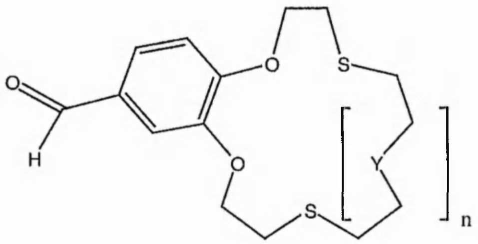


$9S_2O$

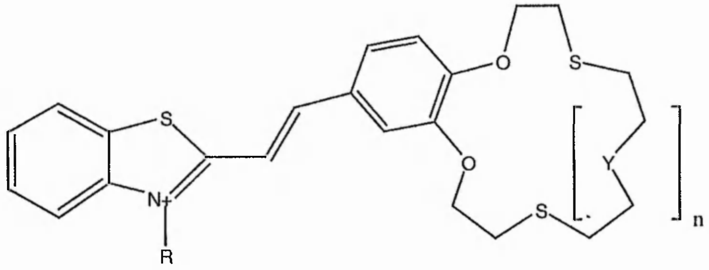


$18S_4O_2$

Recently, a facile method for the preparing crown compounds with different combination of oxygen and sulfur atoms in the macrocycle has been developed and styryl dyes based on these crown compounds were obtained[219].

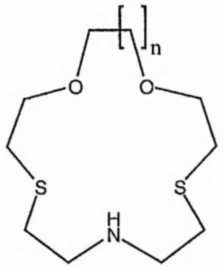


n= 0,1,2...
Y= S,O
R= Me and ClO_4^-, $(CH_2)_2SO_3^-$

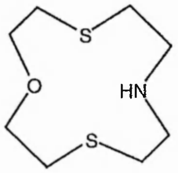


1.2.4.4. Nitrogen-Sulfur-Oxygen

Black and Mc Lean[169], and earlier Bobranski et al.[220] prepared the [12]ane O_2S_2N crown ether macrocycle by the reaction of the disodium salt of 3-oxapentane-1,5-dithiol with di(2-bromoethyl)amine in ethanol at high dilution.

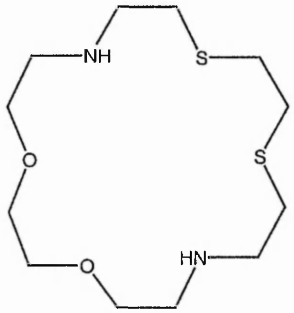


n= 1 [15] ane O_2S_2N
n=2 [16] ane O_2S_2N



[12] ane OS_2N

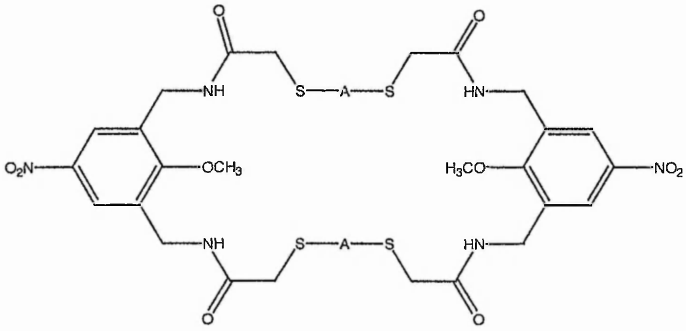
Then, Dietrich et al.[168] synthesized their first N,S,O three mixed donor atoms crown ether macrocycle [18]ane $O_2S_2N_2$, using the same method as for the synthesis of N,S and N,O mixed donor atoms crown ether macrocycles.



[18] ane $O_2S_2N_2$

Afterwards, series of three mixed donor crown ethers, with the common formula [X]ane $O_mS_nN_p$ (with X= ring size; m, n, p= 0,1,2,3,4...) were prepared and studied[176,221-223].

As for crown ethers, two rigid aromatic[117,120] or heteroaromatic[185,224] moieties have been included in N,S,O three mixed donor atoms crown ethers and their properties have been studied and compared.

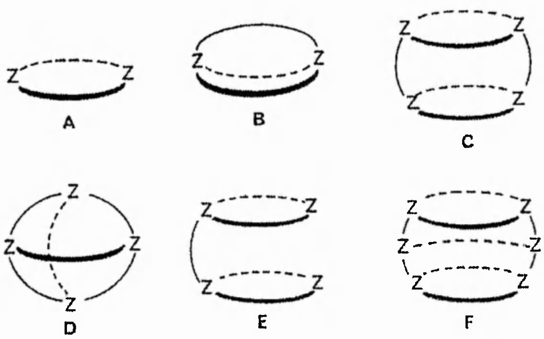


A= $((CH_2)_2OCH_2)_2$

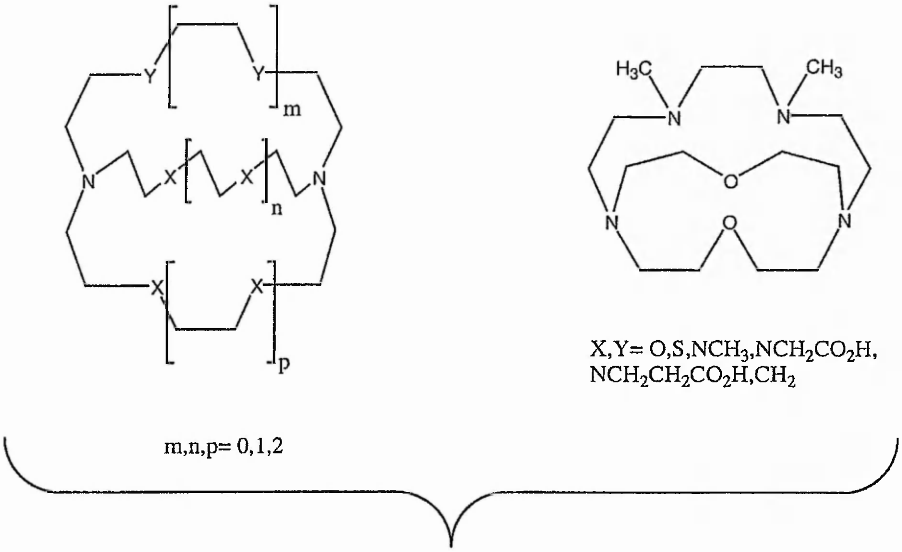
1.2.5. Polycyclic Macrocycles

Macropolycyclic molecules[225,226] are molecules of intermediate size, mesomolecules[227,228], which may present a multitude of new properties. Having novel structures, they are often challenging synthetic targets. Whereas macrocycles have been extensively studied for several decades, the chemistry of macropolycyclic systems is much more recent.

Since macropolycycles contain intramolecular cavities delineated by molecular segments, which may bear various sites for binding and reaction, the most fascinating aspects of their chemistry lie in their ability to form inclusion complexes, to bind substrates selectively, and eventually to perform transport or reactions on the bound substrate. Thus, a field of supramolecular chemistry emerges which, based on intermolecular binding forces, expands over molecular recognition processes, receptor chemistry, carrier design, and molecular catalysis. A vast domain in this general field is the chemistry of macrocyclic and macropolycyclic metal cation complexes[24,27,35,43,229-235].



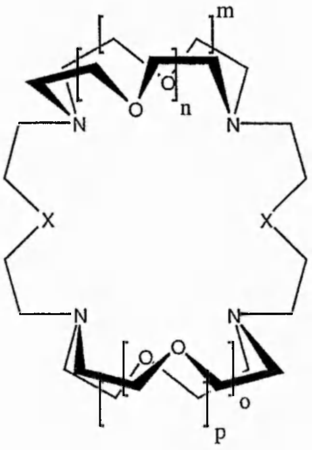
Topologically, macrocycles of type A define two-dimensional, circular cavities. Ligands of higher cyclic order contain three-dimensional cavities. Such is the case for macrobicyclic (B) and macrotricyclic (C) or spheroidal (D) topology. These ligands form inclusion complexes in which the substrate is contained inside their molecular cavity (or crypt). For this reason, such complexes are termed cryptates, the ligands themselves being cryptands[89,90,226,236-241]. Bismacrocycles of type E are obtained in the course of the synthesis of cylindrical macrotricycles C[239,240,242-244], which themselves lead to the macrotetracycles F[226,227].



m,n,p= 0,1,2

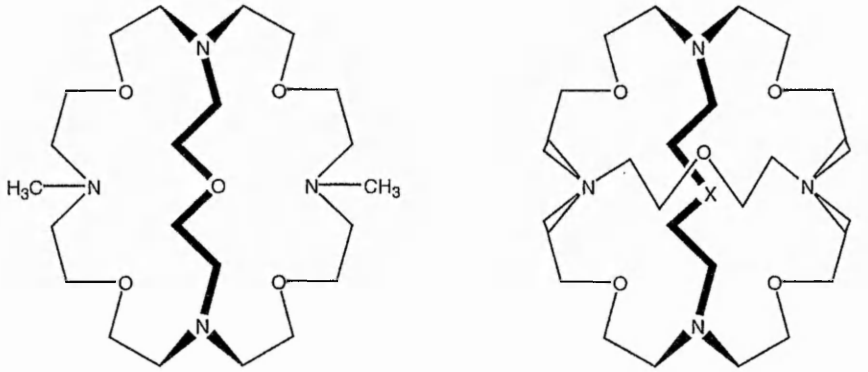
X,Y= O,S,NCH_3,NCH_2CO_2H, $NCH_2CH_2CO_2H$,CH_2

Type B



m,n,o,p= 0,1,2
X= CH_2,O,NH,C_6H_4

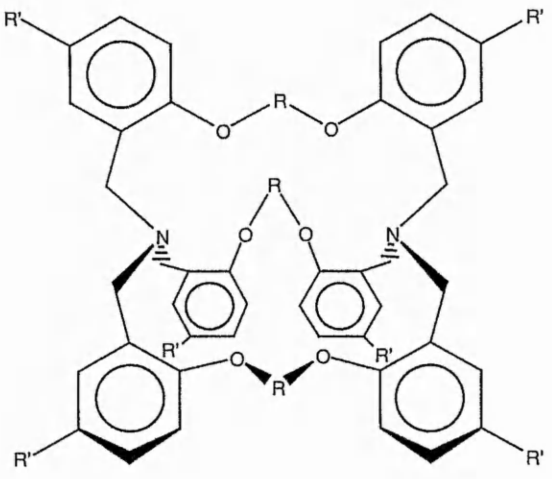
Type C



X= CH_2,O

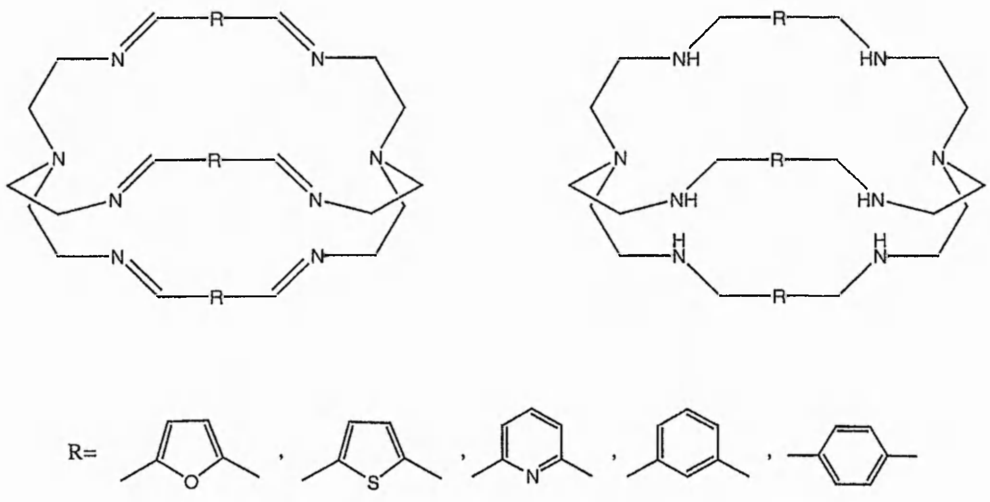
Type D

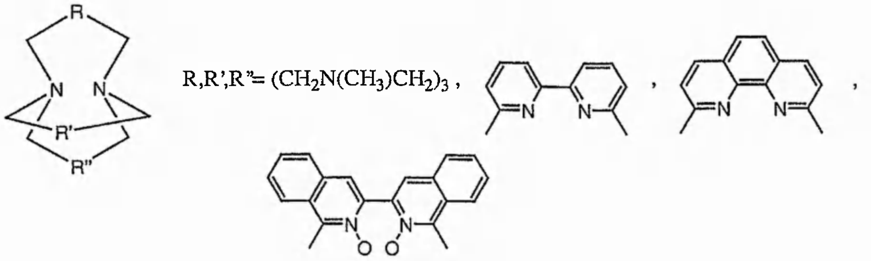
Since the classic study by Lehn et al.[245], in which a range of aza-capped polyether cages were demonstrated to show cavity size selectivity towards particular alkali and alkaline earth ions, illustrating well the use of such systems as selective receptors, different substitutions and/or inclusions have been made on those cryptands, such as the incorporation of phenoxy-ether and/or pyridine[246].

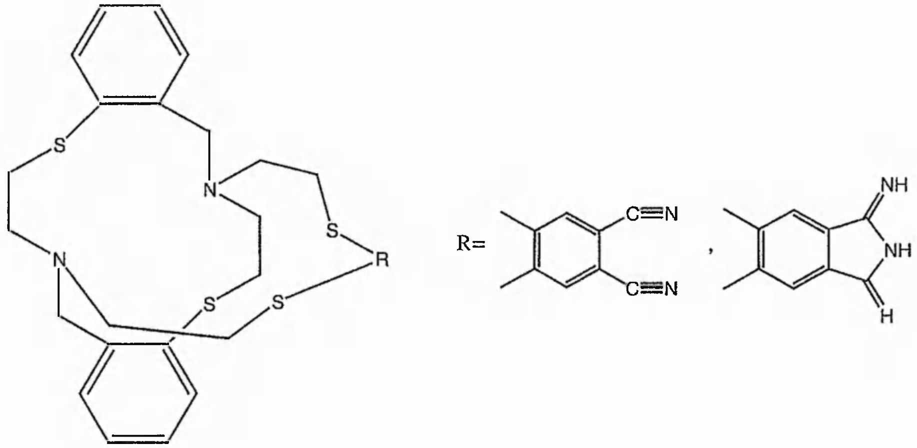


R= C_2H_4,$CH_2C_5H_3NCH_2$
R'= H,tBu

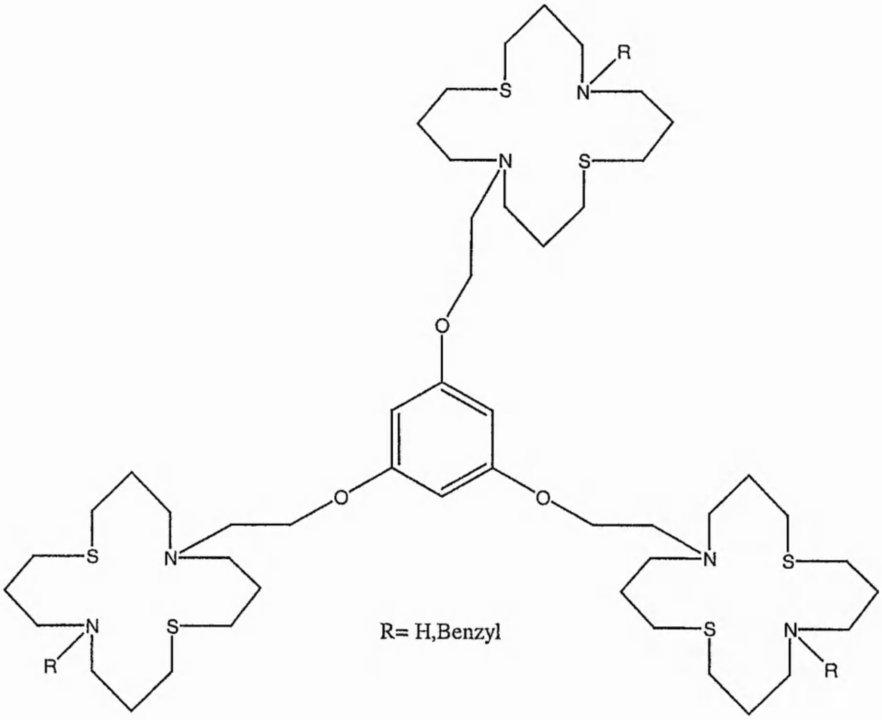
The predominance of the relatively hard ether-oxygen donors in diazapolyoxacryptands makes them excellent hosts for such hard cations, but less effective towards the softer groups 12-14 or transition cations, which are known to prefer N-donor ligands. Apart from a description of the ligating properties of the all sp^3 N-donor ligand O-bistren[247,248], the systematic study of all-aza cryptand complexation was less thoroughly pursued than that of the diazapolyoxa analogues, perhaps because of the greater difficulty of synthesis of the all-aza cryptand ligands. However, it has been noted that the stability constants of transition ion complexes with mixed N,O donor cryptands increase as each O-donor is replaced by an amino-N donor[249,250]. Hexa-Schiff-base ligands, which incorporate at least six soft sp^2 imino-N donors, might be expected to stabilize transition metal and group 12-14 cation cryptates relative to those of group 1 and 2. Schiff-base cryptands can be generated in good purity and high yield[251-257] by the [2+3] condensation of the triamine tris(2-aminoethyl)amine (tren) with the appropriate linker[258-260] or by condensation on the macrocycle itself[261,262].



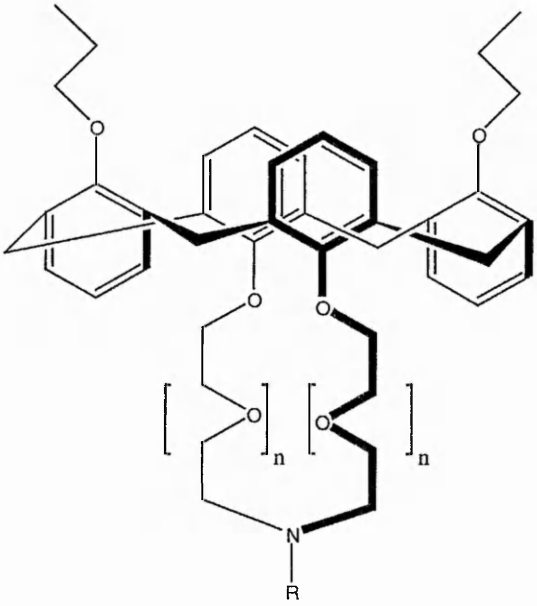




New tri-linked S_2N_2-donor macrocycles, incorporating three 16-membered rings connected by spacer groups to a phloroglucinol 'core', have been synthesized by Atkinson et al.[246], starting from the parent single rings incorporating differentially protected nitrogen donors[263]. The 'building block' approach (employing selectively protected S_2N_2-donor macrocycles) used to obtain tri-linked S_2N_2-donor macrocycles is readily extendable to the synthesis of other linked systems[262].



Calix[4]arenes have been used as 3-D molecular building blocks for the synthesis of receptors with specific properties[264-272]. They can exist in four different conformations: cone, partial cone, 1,2-alternate, and 1,3-alternate[273,274]. Recently, calix[4]crown ethers in which conventional crown ethers are incorporated into rigid calix[4]arene of the 1,3-alternate type have attracted intense interest as caesium-selective extractants[275,276].



n= 1,2
R= H,$CH_2C_5H_3N$

1.3. Ion Binding Properties

Macrocycles, cryptands, and cavitands are well known examples of molecules, which can form host-guest complexes, and because of the different sizes of their cavities, have interesting molecular recognition properties[47,245,277].

1.3.1. Cation-Coronand Complexation

1.3.1.1. Relative Cation and Ligand Cavity Sizes

Selective binding of cations in solution is a distinctive feature of the solution chemistry of macrocyclic polyethers. The design and synthesis of new macrocyclic ligands with different cavity sizes, donor atom types, ring substituents, etc. has resulted in a large number and variety of compounds. Few of these macrocycles have been studied with respect to their cation complexation properties. However, many of those which have been investigated, show unique selective cation complexation behavior. The process of ion-macrocycle association depends on several factors related to characteristic properties of the ligand, reacting ion, and solvent. The enhancement of complex stability by a close correspondence between the ionic crystal radius of the metal ion and the radius of the cavity formed by the crown ether ring has been noted[35]. Full participation of all macrocycle donor atoms with the complexed cation is expected to give the highest possible stability to the resulting complex.

The cation radii are listed in Table 1[278], which is based on X-ray structural analyses of oxides and fluorides. This set of ionic radii and others valid for nonhydrated cations have been discussed[279]. Marcus[280] has set forth arguments for the use of hydrated cation radii in correlation involving solvated cations. These radii have been calculated for more than 30 ions by using published data of the average distances between the ions and the nearest water molecules, obtained by diffraction and computer simulation methods.

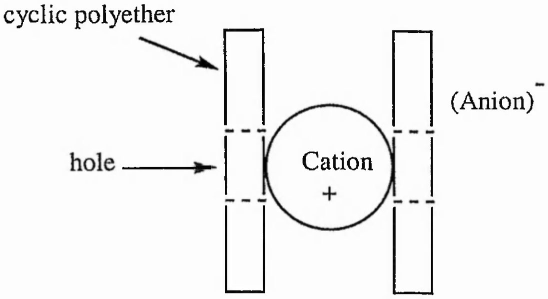
Table 1. Radii (Å) of some representative cations[278,279]

cation	radius,Å	cation	radius,Å	cation	radius,Å
Li^+	0.76	Ba^{2+}	1.35	Cu^{2+}	0.77
Na^+	1.02	Eu^{2+}	1.17	Zn^{2+}	0.74
K^+	1.38	Mn^{2+}	0.67 (L)[a]	Cd^{2+}	0.95
Rb^+	1.52		0.83 (H)[a]	Pb^{2+}	1.19
Cs^+	1.67	Fe^{2+}	0.61 (L)[a]	Hg^{2+}	1.19
Ag^+	1.15		0.78 (H)[a]	La^{3+}	1.03
Tl^+	1.50	Co^{2+}	0.65 (L)[a]	Ce^{3+}	1.01
Mg^{2+}	0.72		0.75 (H)[a]	Eu^{3+}	0.95
Ca^{2+}	1.00	Ni^{2+}	0.63 (L)[a]	Ho^{3+}	0.90
Sr^{2+}	1.18		0.69 (H)[a]	Ln^{3+}	0.86

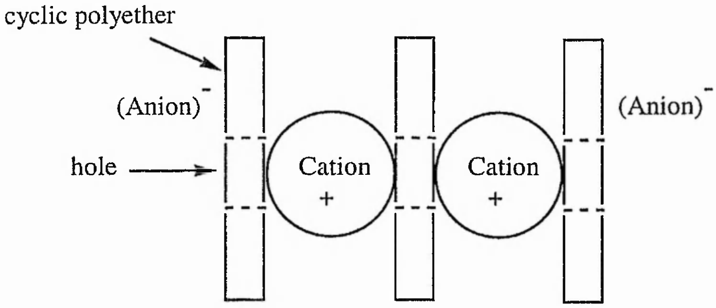
[a] L= low spin, H= high spin

When the ionic diameter for cations becomes too large for the preformed cavity, no complexation occurs. The extraction method which was used in the present work was the Pedersen method[20,21]. The stoichiometry of the crystalline complexes of sodium, potassium, ammonium, rubidium, cesium and barium salts with crown ethers was investigated in great detail by Pedersen[21]. Depending on the relative sizes of the "hole" in the cyclic polyether and of the cation, complexes with polyther: cation mole ratios of 1:1, 3:2, or 2:1 are obtained. The 2:1 complexes might possibly be "sandwich" structures and constitute a new group in the class of sandwich compounds previously reported by Taylor, Vergez, and Busch[281], and by Su and Weiher[282]. Similarly, the 3:2 complexes seem to be "club sandwich" structures (scheme 1).

Scheme 1.



"sandwich" complex



"club sandwich" complex

The "ion-in-the-hole" model has limited usefulness in predicting relative capacities of metal cations with polyethers. For example, as the number of ring atoms increases, the macrocycle flexibility increases and it becomes difficult to define the cavity diameter. Few discussions of the macrocycle hole size cation-diameter relationship can be found in the literature[283-285].

1.3.1.2. Number and Stereochemical Arrangement of Ligand Binding Sites

Even the small polyethers cannot be considered to be completely rigid molecules. Most of them are quite flexible and are capable of orienting their donor groups in space. The larger macrocycles are free to fold resulting in a smaller three-dimensional cavity, which has a closer size correspondence to the cation than does the unfolded ligand.

Binding constants depend to a great extent on the ion-dipole interaction. Any changes in number, magnitude, and direction of ligand dipoles will affect the binding energy.

For alkali and alkaline earth metal ions there are no real stereochemical requirements for complexation. However, the donor groups of the ligand should provide an electronically basic environment to replace all or part of the cation's solvation shell.

1.3.1.3. Substitution on the Macrocycle Ring

The addition of benzene groups to 18C6 alters the cation selectivity of the ligand. The change due to aromatic substituents may be attributed to some combination of ligand bulkiness leading to the isolation of the cation from the solvent, and the electron-withdrawing power of the benzo group(s) which weaken the electron donor ability of the oxygen atoms resulting in a weaker metal-ligand interaction.

The cyclohexano group has a less dramatic effect on the stability of complexes and on cation selectivity. Aliphatic substituents on this ligand do not alter the binding properties to any measurable extent.

The effect of a carbonyl group adjacent to an oxygen atom on metal ion binding has been studied for 18C6 and its pyridino derivatives[26,35,286-289], in which the carbonyl groups are not bonded to the cation.

It is known that the three-dimensional cryptands form considerably more stable complexes than do the corresponding two-dimensional coronands. Okahara[290] and Gokel[291] and their co-workers have noted enhancement of stability in the cation complexes of three dimensional N-oligoethylene glycol monoaza crown ethers. An additional factor contributing to complex stability is seen in macrocycles if cation charge neutralization occurs on complexation[292].

Coronands show pronounced cooperative effects of crown units. Binding constants per crown unit for small cations (Li^+, Na^+) do not vary between polymer and monomer, but with larger cations (K^+, Rb^+, Cs^+) preferential binding by polymers is observed. Additional polyether groups in a monomeric macrocycle show no cooperative effect[293].

Several workers[294,295] have synthesized chiral coronands. Arms added to the host provide an additional dimension for the study of host-guest interactions. Such arms may allow manipulation of the hydrophobic-lipophilic balance of the host and may provide counterions for interaction with ionic guests.

1.3.1.4. Solvent Effects

Understanding the interactions between macrocyclic ligands and ions requires the study of various parameters governing the reactions. Extensive thermodynamic and kinetic data have been collected during the past 30 years and several review articles have been published which deal with cation-macrocycle interactions. Those reviews contain compilations of equilibrium constant (K), enthalpy change (ΔH), entropy change (ΔS), rate constant (k), and activation parameter data ($\Delta X^{\neq}$). Frensdorf[296] noted that K values for the reaction of cyclic polyethers with metal cations are 10^3-10^4 larger in methanol than in water. The enhancement of stability in methanol over that in water is primarily an enthalpic effect[297,298]. On the other hand, the difference between the reaction entropies found in water and those found in methanol oppose this stability enhancement. The enthalpic stabilization is explained by the expenditure of less energy in the cation desolvation step, in the solvent of lower dielectric constant. A compensating effect (enthalpy stabilized, entropy stabilized) has been noted[299] in the variation of the enthalpy and entropy changes of complexation by B_221C7, B_224C8, and B_227C9 with Cs^+ in several solvents of low to medium donicity (nitromethane, acetonitrile, acetone, methanol, and propylene carbonate).

Both the absolute and relative values of the association constants of crown-ether complexes with cations are dependent on the type of solvent used. The parameters governing the substitution of a solvent S, for water W, for M^+-crown (Cr) interaction follow from the following thermodynamic cycle[300] (scheme 2).

Scheme 2.

$$\begin{tikzcd}
M^+_W \arrow[d, "\Delta G_{tr}"'] & + & Cr_W \arrow[d, "\Delta G_{tr}"] \arrow[r, "\Delta G_W"] & (M^+ . Cr)_W \arrow[d, "\Delta G_{tr}"] \\
M^+_S & + & Cr_S \arrow[r, "\Delta G_S"'] & (M^+ . Cr)_S
\end{tikzcd}$$

This cycle indicates that free energies of transfer ΔG, for cation, ligand, and complexed cation need to be considered in order to understand the absolute and relative values of K_w and K_s. K_w and K_s are related through the free energy of transfer terms.

$$-RT \ln(K_s / K_w) = \Delta\Delta G = \Delta G_{tr}(M^+.Cr) - \Delta G_{tr}(Cr) - \Delta G_{tr}(M^+)$$

The enthalpy of transfer (ΔΔH) is given by the following equation:

$$\Delta\Delta H = \Delta H_{tr}(M^+.Cr) - \Delta H_{tr}(Cr) - \Delta H_{tr}(M^+)$$

1.3.1.5. Cation-Polyamine Complexation

Substitution of sp^3 nitrogen for ether oxygen in the coronand ring reduces the affinity of the ligand for the alkali and alkaline earth metal ions. Most monocyclic polyamine macrocycles form metal complexes, in which four almost equivalent nitrogen atoms are coordinated in a single plane about the metal ion, and two other groups are bound in the axial sites above and below the plane. Kodama and his co-workers[301,302] report that saturated macrocyclic polyamine ligands with 5 and 6 nitrogen donor atoms and ring sizes of 15 and 18 members are particularly effective in complexing bivalent transition-metal ions.

1.3.1.6. Cation-Polythioether Complexation

Complexes of Ni^{2+} and Co^{2+} with coronands containing three, four, six and eight ring sulfur atoms have been reported[60-82,169,170,222,303-305]. The configuration of the metal ion-coronand complex is a function of the ring size and of the number of sulfur atoms in the ring.

1.3.1.7. Cation-Mixed Donor Atom Macrocycle Complexation

Numerous macrocycles containing mixtures of oxygen, nitrogen, and sulfur donor atoms have been synthesized.

1.3.1.7.1. Nitrogen-Oxygen Donor Atoms

A number of macrocycles containing both nitrogen and oxygen donor atoms have been synthesized[83-167,306-308]. Generally, the metal complexes of these macrocycles are 1:1 (metal:ligand) with the metal ion located at the center of the macrocycle. However, some coronands and cryptands can complexed as binuclear complexes M_2L^{2n+} as well as the expected mononuclear ML^{n+} complexes. The substitution of oxygen by nitrogen in coronands alters the affinity and the stability orders between cations can be a reflection of different types of bonding in the complexes.

1.3.1.7.2. Sulfur-Oxyen Donor Atoms

A number of macrocycles containing both sulfur and oxygen donor atoms have been synthesized[169,208-219]. Substitution of sulfur for oxygen in several crown-3, crown-4, crown-5, crown-6, and crown-8 macrocycles produces dramatic effects on K values for metal ion-ligand interaction[309]. In aqueous solution, little or no reaction occurs between the sulfur-containing macrocycles and either alkali or alkaline earth metal ions.

1.3.2. Cation-Cryptand Complexation

An extension of crown ether chemistry is found in the case of cryptands. These macrobicyclic ligands are capable of ion encapsulation due to their cage-like structures. Generally, their metal complexes have 1:1 metal-ligand ratios.

1.3.2.1. Relative Cation/Anion and Ligand Cavity Sizes

Generally, that metal ion, whose ionic crystal radius best matches the radius of the cavity formed by the cryptand on complexation, will form the most stable complex. The correspondence between cavity size and complex stability is more pronounced with the cryptands than with the coronands. This correspondence between K values and the match of macrocycle cavity and cation diameters is also found for alkaline earth cryptates. However, such a correspondence is not found for Cu^{2+}-cryptand complexes[310].

Cylindrical cryptands formed by two rings connected by two bridges have been synthesized. These macrocycles possess two lateral cavities, the macrocylic units, and one central cavity inside the macrotricycle. These ligands are capable of forming mononuclear and binuclear complexes of appreciable stability with alkali and alkaline earth metal cations. The stabilities and selectivities of complexation by these unusual cryptands are such that the ligand may be considered to have two almost independent macrocyclic subunits. These ligands are topologically well suited for the designed positioning of two metal cations in a binuclear inculusion complex[242,311].

1.3.2.2. Number and Stereochemical Arrangement of Ligand Binding Sites

Cryptands can assume any of three conformations according to the configuration of the two nitrogen bridgeheads-namely, in-in, in-out, or out-out. These cryptand ligands are more rigid than podands over a broader range of cavity sizes and show signs of flexibility in ion encapsulation. Lehn and Sauvage[289] concluded that rigid ligands display "peak selectivity", while flexible ligands exhibit "plateau selectivity". Rigid ligands, which are too small to accommodate the metal ion, may form 2:1 complexes.

Numerous polyoxamacrobicyclic diamines have been synthesized[289,311,312]. These ligands form metal ion complexes by encapsulating the ion in the central cavity of the macrocycle. X-ray structural determinations confirm the position of the metal ion and indicate that the two nitrogen atoms participate in bond formation along with the oxygen donors. These ligands are capable of forming very stable complexes and can selectively encapsulate ions. Since these macrocycles have a three-dimensional arrangement of binding sites, the stability constants are usually higher than those of the similar two-dimensional ligands.

1.3.2.3. Substitution on the Macrocycle Ring

Addition of benzene rings to either one or two bridges of the cryptand alters the selectivity of this ligand toward metal ions. Cox and his co-workers[312] studied the effect of substituents on the thermodynamic and kinetic stability of alkali metal cryptates in methanol. They found that alkyl ($C_{10}H_{21}$) and benzo substitution caused a reduction in the cryptate stabilities which was attributable to a cooperative action of reducing the complex formation rates and increasing the complex dissociation rates.

1.3.2.4. Solvent Effects

The stability constants for the 1:1 reaction of cryptands with cations in methanol are larger than those for the same reaction in water. The degree to which stability is enhanced for methanol over water is dependent on the cation and cryptand under consideration.

Cation selectivity by macrobicyclic ligands is affected by the nature of the solvent. In determining selectivity, the solvation of the cation has been considered to be more important than the solvation of the complex. However, for ligands, which are large enough to encapsulate the entire cation, the solvent can act only on the entire complex species and has no direct interaction with the cation[313].

1.3.3. Cation-Spherand Complexation

Spherands synthesized by Cram and his co-workers[36,104-107] are a new class of macrocycles, in which the ligating sites are fully organized during synthesis rather than during complexation, and which show remarkable selectivity toward cations. For example, when the ionic diameter for the cations becomes too large for the preformed cavity, no complexation occurs. This behavior is in contrast to that of coronand and cryptand macrocycles in which size related peak selectivity is found. The order of relative binding strengths as measured by extraction of Li^+ and Na^+ picrates in $CDCl_3$ saturated with D_2O at 25°C is spherands > cryptands > hemispherands > coronands > open-chain polyethers[104].

1.3.4. Anion Effect

The main emphasis in the work on ion encapsulation by coronands and cryptands has been on the interaction of solvated cations with ligands. The effect of the anion on the reactivity of the cation with these ligands has usually been suppressed deliberately either by using anions such as tetraphenylborate ion or, more often, by using high dilution conditions during experiments. Nevertheless, some authors have given consideration to the reaction of ion pairs with macrocycles in computing K values valid in solvents of medium to low dielectric constant. They concluded that these macrocycles have preference for the free cation over the ion pair[314] and form weaker complexes with the ion pair[315].

1.3.5. Macrocyclic Effect

Increased stability is observed for the complexes of cyclic ligands over those with an open chain of similar composition. Cabbiness and Margerum[316] termed this extra stability the "Macrocylic Effect". The macrocyclic effect on cyclic tetraamine ligands can be about ten times larger than the chelate effect. Cyclic polyethers form much more stable complexes than do their corresponding open-chain analogues. The origins of this effect depend on the system and can be either an enthalpic or an entropic origin, or both.

Another effect, especially with mixed donor atom macrocycles, has been termed by Busch and his co-workers[317] as "Multiple Juxtapositional Fixedness". This effect attributes the enhancement stabilities to the slow decomposition rates of complexes of metal ions with macrocycles compared to those with their open-chain analogues.

1.3.6. Cryptate Effect

Lehn and his co-workers[289] have noted the increase in the stability of complexes formed by the macrobicyclic ligands over those formed by macrocycles. This stability increase is more pronounced than that described as the macrocyclic effect and has been designated either as a "Cryptate Effect" or as a "Macrobicyclic Cryptate Effect". This cryptate effect is of enthalpic origin.

2. Thiophene Chemistry

2.1. Thiophene Chemistry and Binding Properties

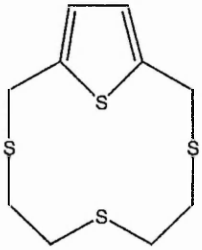
Sulfur donors are known to be good ligands for group 11 cations, particularly in their low oxidation states. However, thiophene sulfur is not considered as a strong donor ligand. In fact, the thiophene sulfur atoms are described as inert spacers[259] or only weakly donating[318]. Compared to the corresponding 5 membered heterocycle furan and pyrrole based macrocyclic systems, which have been more often reported in the literature, thiophene based macrocycles have the advantages of generally being more stable, and are able to be readily desulfurised[32].

In organometallic complexes, thiophene has been found to adopt several modes of coordination such as η^5, η^4, η^2, η^1-S, or η^1-C. The most common mode of complexation is η^5, where all five atoms of the thiophene ring are bonded to the metal center such as Ir[319] or Rh[320-322]. The η^4-mode appeared more often when the four carbons are bonded to the metal center, and the sulfur atom is bound to a metal to another metal center[321,323,324]. The η^2-mode involves two of the thiophene ring carbon atoms bound to a metal center[325]. The η^1-C mode involves one of the carbons bonded to a metal center[326,327]. Finally the least common mode, the η^1-S mode occurs when the rest of the ring is not coordinated[328]. An extremely rare example of the thiophene S atom bound to two Mo atoms and η^4-coordinated to Ir was the first example of a thiophene bound to three metal centers[324].

The weak nature of the interactions between a thiophene S atom and a transition metal makes it difficult to judge whether or not the sulfur atom is genuinely coordinated to the metal center. The S-metal bond lengths are often just less than the sum of the van der Waals radii and not significantly larger than the sum of the covalent radii (which are however often hard to determine especially for apical positions[329]). This situation is usually best assessed by considering the above coordination possibilities alongside the geometry of the ligand with respect to the usual coordination geometries of the metal center.

Drew and al.[259] have reported, for example, the X-ray structure of the di-silver (I) complex of the thiophene-spaced azacryptand hexa Schiff base $N[(CH_2)_2N{=}CHRHC{=}N(CH_2)_2]_3N$ (R= thiophene-2,5-diyl). In addition to one N(bridgehead) and three N(imine) bound to each of the silver atoms, there are long contacts between the silver atoms and the thiophene sulfur atoms ranging from 3.20(1) to 3.30(1) Å. Were these contacts to be included, the metal coordination sphere would resemble a seven-coordinate capped octahedron with the bridgehead nitrogen in the capped position, the three imine nitrogen atoms in the capped face and the three sulfur atoms in the uncapped face. The dicopper (II) complex analogue shows no major differences of coordination site geometry or cryptand conformation. The M-N (imino) distances are >0.1 Å less than in the silver structures, and the $M\text{-}N_{br}$ distances are almost identical. The M…S (thiophene) contacts are virtually identical (average 3.24 vs. 3.25 Å) to those made by Ag to sulfur, and although just less than van der Waals contact distance are 0.2-0.3 Å longer than in the analogous dicopper (I) thiophene-based macrocyclic complex[330-332]. This suggests that if any Cu…S interaction is to be proposed, it must be very weak.

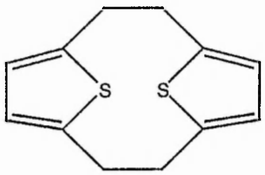
A rare example of a macrocyclic thiophene sulfur-metal interaction[329] occurs for the palladium complex of the thioether shown below. The geometry around the Pd (II) metal center appears to be approximately square pyramidal with the basal positions occupied by two of the thioether sulfur (average Pd-S= 2.279 Å) and two Br anions. The thiophene S atom is located in the apical position, Pd-S= 3.182 Å, as the sum of the van der Waals radii is 3.40 Å[333].

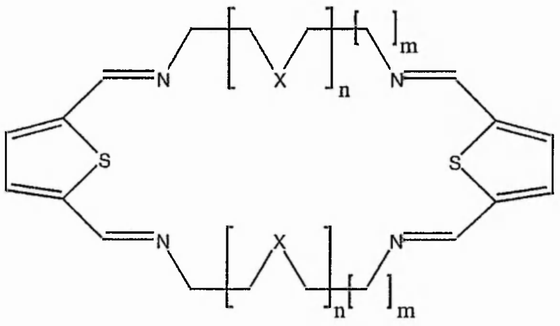


During the last 20 years, a number of macrocyclic thioether[334-336] and thiophene-based[330-332] hosts for copper and silver have been examined.

2.2. Mixed donor thiophene-based macrocycles

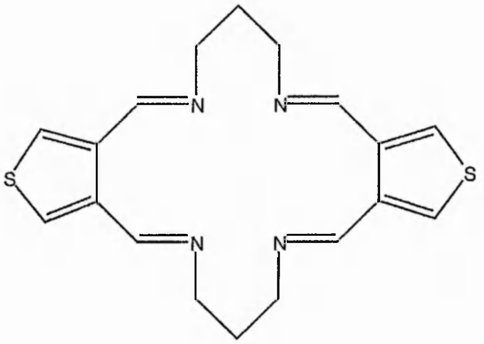
Several thiophene-based macrocycles have been synthesized and their X-ray structures investigated. Those macrocycles are classified into two groups. In the first group, the sulfur atom is part of the macrocyclic ring (endocyclic) and therefore is a potential ring donor atom[29,30,259,329].



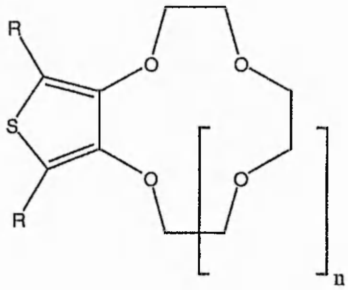


m= 1,2
n= 1,2,3...
X= O,N or S

In the other group[1-7,337], the sulfur atom is exocyclic, i.e. not part of the macrocyclic ring. The exocyclic macrocycles synthesized by Sone[32] et al. and Amer[337], cannot be considered as mixed donor macrocycle as the sulfurs are considered as non-donor.

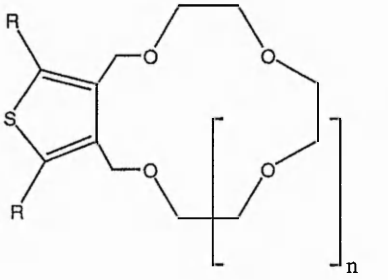


Exocyclic

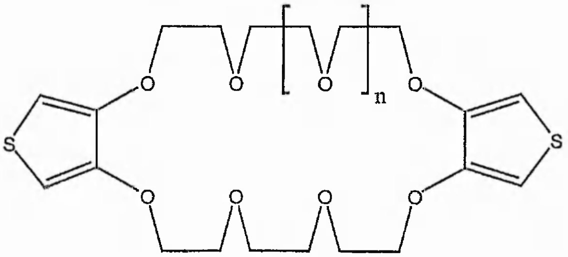


a: n= 1
b: n= 2
c: n= 3
d: n= 4

1 R= CO_2Et
2 R= H



3 R= Cl
4 R= H
5 R= Me n= 2



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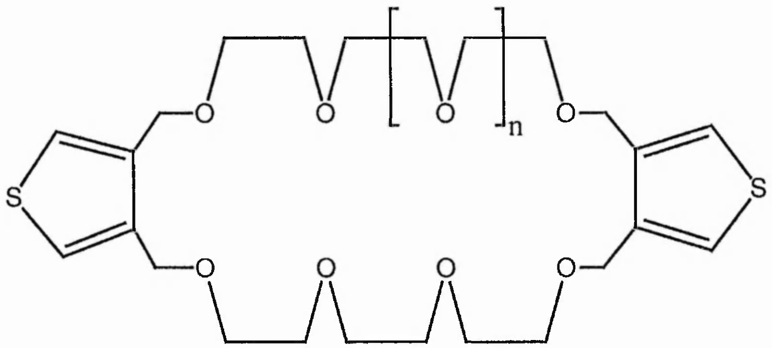

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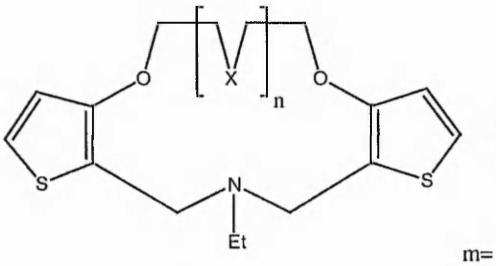
The extraction ability of those thiophene-containing crown ethers towards alkali metal cations was examined by Sone et al., via Pedersen's extraction method[20,21] (Table 2). The results show that the highest extractability is obtained by the thienocrown ethers, 2 and 6 but are a little lower than that of the corresponding benzocrown for a similar selectivity.

Table 2. Extraction of alkali metal picrates with thiophene-containing crown ethers[a,32]

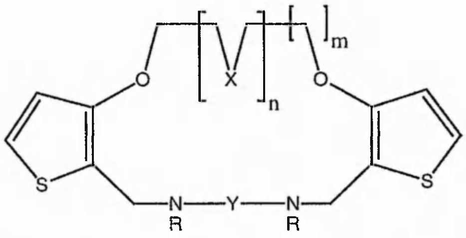
Crown compound	Extractability (%)				
	Li+	Na+	K+	Rb+	Cs+
1a	1	1	5	5	4
1b	1	4	15	8	6
1c	4	9	36	29	23
1d	5	18	55	56	52
2a	0	2	1	1	1
2b	0(2)[b]	12(25)	24(52)	14(3)	4(14)
2c	2(2)	8(21)	93(94)	83(85)	66(68)
2d	4(5)	10(17)	72(86)	93(96)	99(98)
3b	1	18	10	9	8
4a	1	0	3	2	1
4b	2	11	8	6	6
4c	2	10	36	34	31
4d	4	16	51	63	68
5	2	33	24	18	10
6a	1(1)	12(39)	33(61)	48(69)	73(78)
7a	3	12	45	47	60

a) Measured by Pedersen's method[20] at 25°C : aqueous phase : [picric acid] = $7*10^{-5}$M (1M= $1 mol.dm^{-3}$), [MNO3] = 0.1M; organic phase (CH_2Cl_2) : [crown compound] = $7*10^{-4}$M H_2O:CH_2Cl_2 = 1:1(v/v).
b) Figures in parentheses denote the values obtained for the corresponding benzo (or dibenzo) crown ether, which were prepared according to the literature[11].

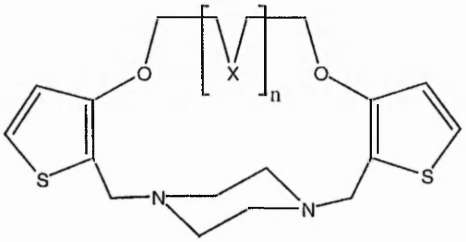
The only thiophene-based exocyclic mixed donor macrocycles reported in the literature, are those synthesized Halfpenny and co-workers[1-7]. In the macrocycles produced by this group, the thiophene sulfur atoms are exocyclic, and consequently are unlikely to be involved in the coordination of any metal ions.



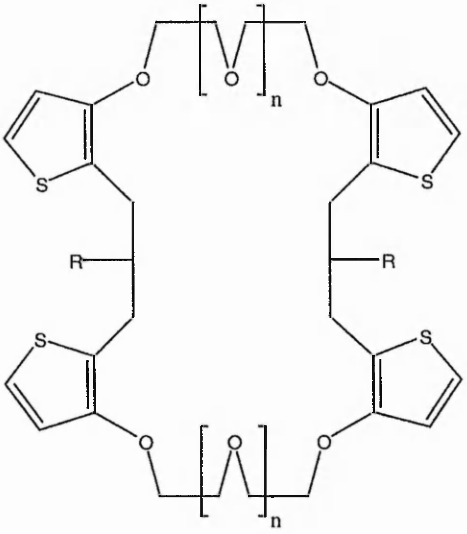
n= 0,1,2
X= O,S
10a : n= 1, X= O
10b : n= 2, X= O



m= 1,2 n= 0,1,2 X= O,S Y= $(CH_2)_2$,$(CH_2)_2O(CH_2)_2$
R= Me,$CH_2C_6H_5$,$CH_2C_6H_4Cl$,tosylate,$CH_2C_6H_5NO_2$
,$CH_2C_6H_5NH_2$...
8a : m=1, n=1, X=O, Y=$(CH_2)_2$, R=Me
8b : m=1, n=2, X=O, Y=$(CH_2)_2$, R=Me



n= 0,1,2
X= O,S
9a : n= 1, X= O
9b : n= 2, X= O



n= 1,2

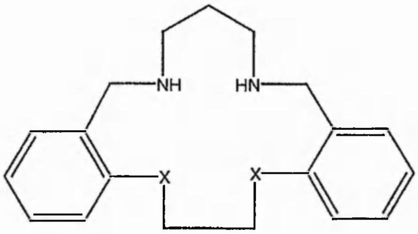
The application of the Pedersen extraction method to the azacrown ether relatives[1] (8-10) has shown (Table 3) that they form dichloromethane-soluble complexes with Li^+, Na^+, K^+, Cs^+, Ag^+, Mg^{2+}, Ca^{2+} and Sr^{2+}. A summary of the picrate extraction results is presented in Table III. In order to obtain comparisons, the greatest organic phase UV absorbance value obtained (Ca^{2+} with 9b) was taken as a reference point; the other values given, which include those for 18C6 (11), are percentages of this maximum. This table shows that these compounds are much more effective transfer agents than 18C6, but that they do not exhibit greater selectivity.

Table 3. Relative organic phase UV absorbances vs. Ca2^{+}/9b of compounds 8a,8b,9a,9b ,10a,10b and 18-crown-6 11 metal picrates[1]

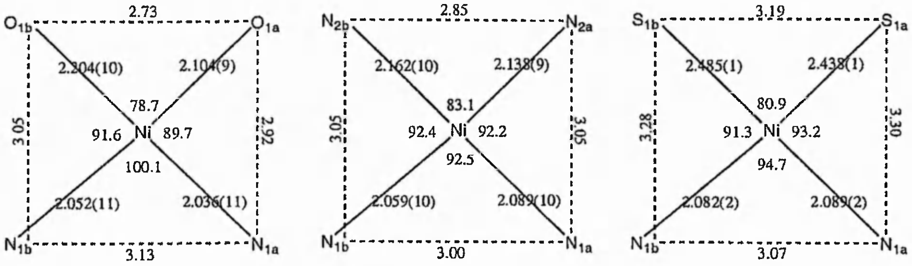
Metal	Relative absorbance						
ion	8a	8b	9a	9b	10a	10b	11
Li^+	40	30	46	13	49	9	1.2
Na^+	38	60	46	60	49	13	1.2
K^+	35	74	50	49	51	17	6.1
Cs^+	46	60	53	75	53	12	4.7
Ag^+	49	86	60	56	64	15	1.5
Mg^{2+}	41	44	43	88	51	17	0.1
Ca^{2+}	44	76	50	100	54	29	0.1
Sr^{2+}	49	88	57	80	60	11	1.3

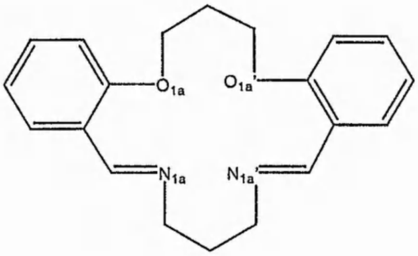
Recently, a new mixed-donor thiophene-based macrocycle has been synthesized[6]. This macrocycle contains three thiophene rings, two of them have an exocyclic sulfur atom, but the third sulfur is included in the macrocyclic ring and might be involved in coordination with metal ions. This new mixed donor thiophene-based macrocycle containing endo and exo-cyclic sulfur atoms might present interesting metal ions complexation properties.

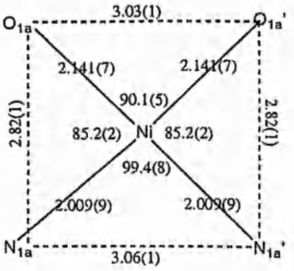
A number of macrocyclic ligand hole sizes and the X-ray structures of the nickel bromide and nickel chloride complexes have been investigated in similar work[95,96]. These macrocycles are similar in structure to the thiophene-based macrocycles, with benzene instead of thiophene[97].

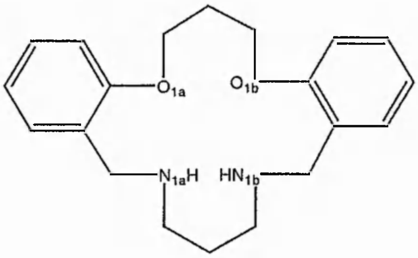


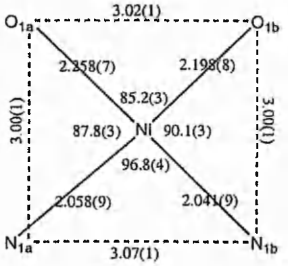
1. X= O
2. X= NH
3. X= S



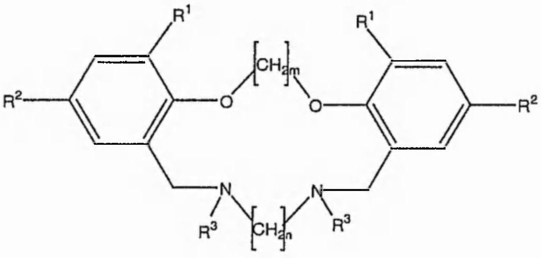




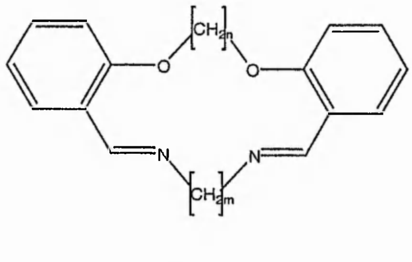




Earlier, Lindoy and co-workers determined the hole size in several free ligands[98] which had an almost ideal hole size for the Ni^{II} ion. They also considered the potential applications of mixed donor macrocycles as selective complexing agents for metal ions[97-102].



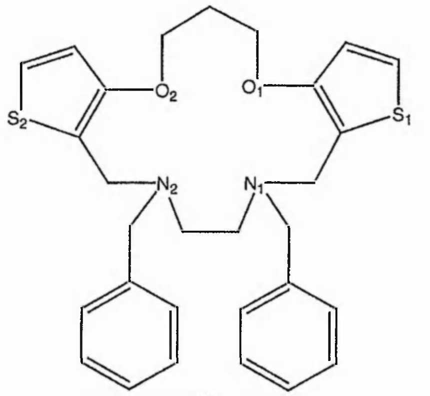
(1) a; $R^1 = R^2 = R^3 =$ H, m=n=2
b; $R^1 = R^2 = R^3 =$ H, m=2, n=3
c; $R^1 = R^2 = R^3 =$ H, m=n=3
d; $R^1 = R^2 = R^3 =$ H, m=4, n=3
(2) $R^1 = OCH_3$, $R^2 = R^3 =$ H, m=2, n=3
(3) $R^1 = R^3 =$ H, $R^2 =$ Cl, m=2, n=3
(4) $R^1 = R^2 =$ H, $R^3 = CH_3$, m=2, n=3



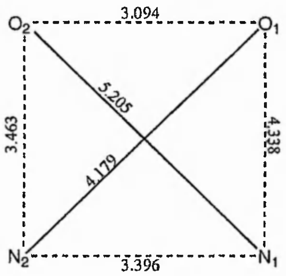
n= 2 or 3
m= 2 or 3

They concluded that, for macrocyclic ligands which have an odd number and/or a non-planar arrangement of donor atoms, a more realistic estimate of hole size is obtained, when the radius of the "hole" is calculated as the mean distance of the donor atoms from their centroid. This is instead of the conventional approach, which consists of defining the diameter of the cavity as the distance between diametrically opposed donors. The macrocyclic ligands usually encapsulate the metal ion to which they are coordinated.

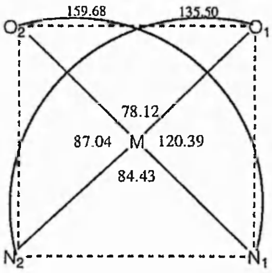
The two following thiophene-based macrocycles have been synthesised and their X-ray structures have been investigated by Halfpenny et al[4,5,7].



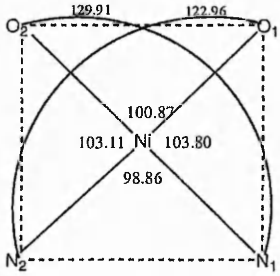
12



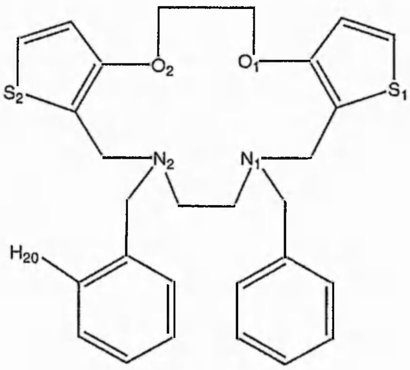
with chemdraw 3D



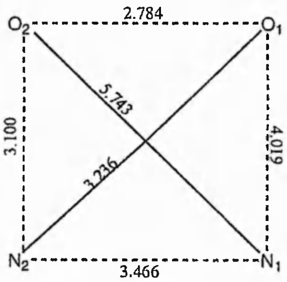
M= mass centre
srtucture A with a mass centre
calculated by platon



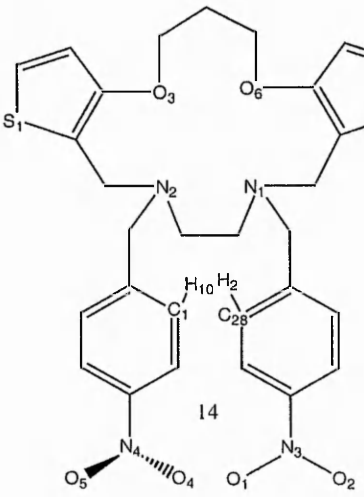
structure A with Ni(II) in the centre
calculated by platon



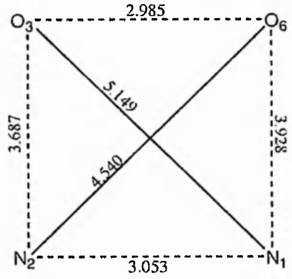
13



with chemdraw 3D



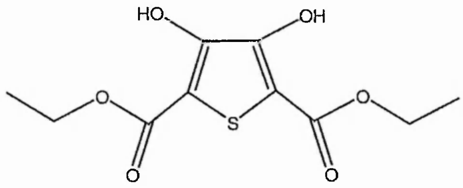
14



The cavity geometries in the free macrocycles are substantially different from those in metal complexes and geometrical calculations showed that significant conformational changes must occur to facilitate coordination to a bound metal. In some cases these would involve large torsional movements of ring atoms and indicate that forming the metal complex must confer a substantial degree of energy stabilisation[5]. Structure 12 contains a significant S...N interaction, 3.115(4) Å which is smaller than the sum of the van der Waals radii(= 3.45Å). This interaction is thought to facilitate ring formation by encouraging close approach of the reacting groups and will be discussed later in connection with the structure determinations reported in this thesis. In structure 13, which has two independent molecules in the asymmetric unit, there is a C-H...N hydrogen bond, which appears in both molecules, C28-H20...N2= 2.50(5)Å and C28-H20...N2A= 2.49(5)Å (Sum of their van der Waals radii= 2.75Å). This second interaction is in competition with the S...N interaction, so the S...N interaction is less effective in these molecules. In the structure 14, the angle between the two nitro-benzene planes is 119.53° which is 40° bigger than the angle between the two benzene in structure 12. This is due to two other interactions, which are more important. The S...N interaction S2...N1 = 3.484 Å is less effective. One of this interaction is a C-H...N interaction, C28-H2...N1 = 2.601 Å and C1-H10...N2 = 2.553 Å (Sum of their van der Waals radii = 2.75 Å), which are similar to the C-H...N interaction in structure 13. This interaction is stronger than the S...N interaction which is inexistent for S1...N2 = 3.637 Å. The second interaction appears as a N-O...N interaction, N3-O1...N4 = 4.757 Å. The C-H...N interactions confirm that the electron pairs of N1 and N2 are directed outside the cavity which is not good for a potential complexation with a metal ion because a complexation will include huge torsion in the molecule 14.

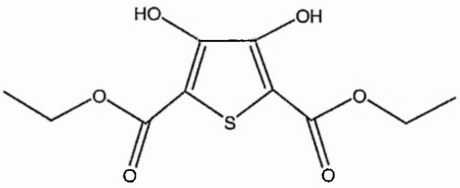
Coomber[338] thought that for successful complexation, the new design thiophene-based macrocycles should have a radius less than 1.7 Å, without large side groups, which hinder the movement in solution. Thermodynamic calculations indicated that the macrocycles that have only two thiophene groups as opposed to four seem to form more thermodynamically stable complexes in reverse to the experimentally found complexing ability in the general work. For general transition metal complexing more nitrogen donors are needed in the ring, and for group 1, 2 and 4 metals, more oxygen donors. Thiophene-based macrocycles, which contain four thiophene rings instead of two, are more flexible in solution allowing the cavity to accommodate smaller metal cations, as well as large cations.

Synthesis of diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate **15**[6]



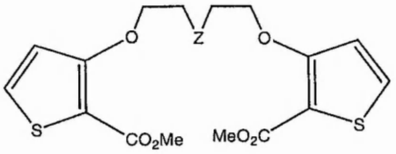
To sodium (49.91g, 2.17 moles) was added dried ethanol (500ml). When the sodium ethoxide solution had cooled, a mixture of diethyl oxalate (119.74g, 0.82 moles) and diethyl thioglycollate (140.21g, 0.68 moles) was added, with stirring. The reaction mixture was allowed to stand for 48hrs, the bright yellow disodium salt was filtered off and washed with diethyl ether. The disodium salt was dissolved in water, the solution was filtered and the filtrate was acidified with HCl (4M.). The precipitate was filtered off and recrystallised from ethanol as an off-white crystalline solid.

Recrystallisation of diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate **15**



The title compound was dissolved with stirring in a minimum of a 1:1 mixture of ethanol/dichloromethane. The stirring was stopped and, after a slow evaporation at 4°C, the compound crystallised as colourless prisms. MF: $C_{10}H_{12}O_6S$; ^1H NMR (ppm): 4.23q(CH_2), 1.24t(CH_3); ^{13}C NMR (ppm): 165.04(C=O), 152.26(C3/4), 106.48(C2/5), 97.48(C2), 61.18(CH_2), 13.86(CH_3); IR (cm^{-1}): 3333.0(OH), 3296.6(OH), 3000.3, 2979.3, 2935.4, 2906.7, 2872.3, 2816.8, 1668.0(C=O), 1557.6(Th C=C); elemental analysis: calc. C 54.54%, H 3.92%, S 10.40%, O 31.14%, exp. C 54.61%, H 3.88%, S 10.36%, O 31.15%.

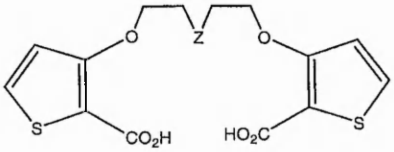
Synthesis of thiophene bisester[1,7]



Z= O or O-$(CH_2)_2$-O

A stirred solution of methyl 3-hydroxythiophene-2-carboxylate (1eq), anhydrous potassium carbonate (0.55eq) and the coupling agent $TsO(CH_2)_2Z(CH_2)_2OTs$ (0.55eq) in anhydrous dimethyl formamide (DMF) (5ml.g^{-1} of thiophene ester) was heated in an oil bath maintained at 95-100°C for 5 hours. A precipitate was obtained on quenching, which was filtered off after cooling to room temperature, washed with water and digested in hot methanol. The compound recrystallised and was filtered off. 77 to 99% yields were obtained.

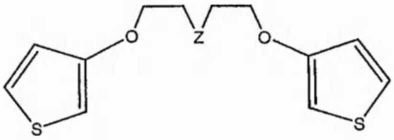
Synthesis of thiophene bisacid[1,7]



Z= O or O-$(CH_2)_2$-O

A solution of the bisester (1eq) and potassium hydroxide (4.0eq) in 80% aqueous ethanol (20ml.g^{-1} of bisester) was boiled under reflux for 1 hour. The solution was filtered off through glass wool into a stirred mixture of ice and a slight excess of hydrochloric acid. The title bisacid was filtered off, washed with water and dried under vacuum at 40°C for an extended period. 73 to 97% yields were obtained.

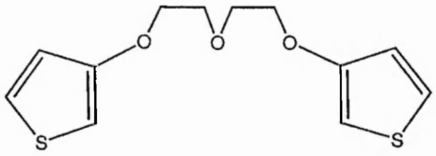
Decarboxylation[1,7]



Z= O or O-$(CH_2)_2$-O

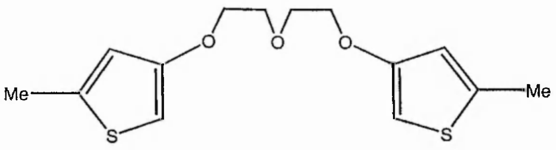
A mixture of the title bisacid (1eq) and copper (I) oxide (1.2wt eq) in pyridine (100ml.g^{-1} of bisacid) was boiled under reflux for 1 hour. The solvent was removed under reduced pressure using a cold finger, and the residue was extracted repeatedly with dichloromethane (DCM) using a Soxhlet apparatus, until no apparent colour was observed in the side arms of the apparatus. The extracts were washed with dilute hydrochloric acid, then with saturated sodium hydrogen carbonate. The acid solution was washed again with DCM. The combined organic layer were dried ($MgSO_4$) and the solvent evaporated off. Then, the compound was recrystallised from ethanol or methanol. 50 to 66% yields were obtained.

Recrystallisation of α,ω-bis-(3-oxythienyl)ethane **16**



The title compound was dissolved with stirring in a minimum of a 1:1 mixture of ethanol/dichloromethane. The stirring was stopped and, after a slow evaporation at 4°C, the compound crystallised as colourless plates. MF: $C_{12}H_{14}O_3S_2$; ^1H NMR (ppm): 7.18dd(C5), 6.79dd(C4), 6.27dd(C2), 4.15t($ThOCH_2$), 3.91t($ThOCH_2\underline{CH_2}$); ^{13}C NMR (ppm): 157.43(C3), 124.61(C5), 119.49(C4), 97.48(C2), 69.73($ThOCH_2$), 69.47($ThOCH_2\underline{CH_2}$); IR (cm^{-1}): 3172.7, 3118.7, 3109.2, 3096.3, 3089.4, 2922.0, 2881.7, 2817.0, 1542.4(Th C=C), 1190(s, C-O), 766.4(s); elemental analysis: calc. C 53.5%, H 5.2%, S 23.72%, O 17.75%, exp. C 53.2%, H 5.2%, S 23.82%, O 17.78%.

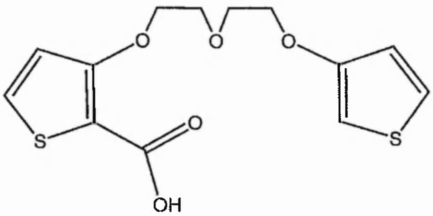
Recrystallisation of dimethyl- 5,17-dimethyl-α,ω-bis-(3-oxythienyl)-ethane **17**



The title compound was dissolved with stirring in a minimum of a 1:1 mixture of cyclohexane/dichloromethane. The solution was warmed to the boiling point. At the boiling point, a minimum of 40:60 petroleum ether was added and the solution became cloudy. Afterwards, the solution was cleared by adding dichloromethane dropwise. The stirring was stopped and, after a slow evaporation, the compound crystallised as colourless plates. MF: $C_{14}H_{18}O_3S_2$; ^1H NMR (ppm): 6.46d(C4), 5.97d(C2), 4.08q($ThOCH_2$), 3.86q($ThOCH_2\underline{CH_2}$), 2.39t(CH_3); ^{13}C NMR (ppm): 156.47(C3), 138.78(C5), 118.04(C4), 94.80(C2), 69.77($ThOCH_2$), 69.13($ThOCH_2\underline{CH_2}$), 15.87(CH_3);

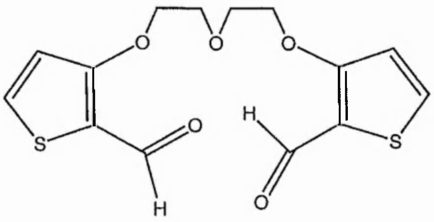
IR (cm^{-1}): 3119.5, 2911.1, 2889.3, 1567.6(Th C=C); elemental analysis: calc. C 56.35%, H 6.08%, S 21.49%, O 16.08%, exp. C 56.41%, H 6.12%, S 21.42%, O 16.05%.

Recrystallisation of 18-carboxylic-α,ω-bis-(3-oxythienyl)ethane **18**



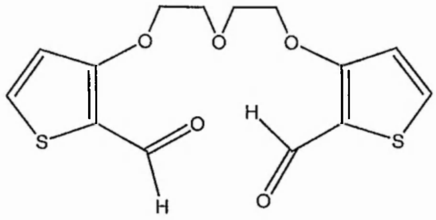
The compound **18** is an intermediate recovered from the decarboxylation step. The title compound was dissolved with stirring in a minimum of a 1:1 mixture of cyclohexane/methanol. The stirring was stopped and, after a slow evaporation at 4°C, the compound crystallised as colourless plates. MF: $C_{13}H_{14}O_5S_2$; ^1H NMR (ppm): 9.64s(OH), 7.51d(C5), 7.16dd(C10), 6.89d(C4), 6.77dd(C9), 6.27dd(C7), 4.38t($CO_2ThO\underline{CH_2}$), 4.13t($ThOCH_2$), 3.92m($CO_2ThOCH_2\underline{CH_2}$,$ThOCH_2\underline{CH_2}$); ^{13}C NMR (ppm): 163.29(C=O), 159.64(C3), 157.36(C8), 132.31(C5), 124.71(C10), 119.47(C9), 116.78(C4), 112.35(C2), 97.70(C7), 71.97($CO_2ThO\underline{CH_2}$), 69.96($ThOCH_2$), 69.49($CO_2ThOCH_2\underline{CH_2}$), 69.24($ThOCH_2\underline{CH_2}$); IR ($cm^{-1}$): 3110.8(OH), 3080.7, 2971.1, 2951.9, 2926.8, 2894.4, 2772.8, 2645.0, 2603.9, 2568.1, 2516.1, 1672.4(C=O), 1531.5(Th C=C); elemental analysis: calc. C 49.66%, H 4.49%, S 20.40%, O 25.45%, exp. C 49.65%, H 4.49%, S 20.36%, O 25.50%.

Synthesis of a thiophene bisaldehyde **19**[1,7]



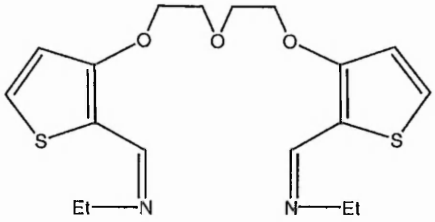
A solution of the α,ω-bis(3-oxythienyl)-ethane (1eq) in the minimum volume of anhydrous 1,2-dichloroethane was added to a stirred solution of anhydrous DMF (2.2eq) and phosphorus oxychloride ($POCl_3$) (2.2eq) in the same solvent ($10ml.g^{-1}$ of bisether). The mixture was heated at 95-100°C for 2 hours, then poured into an aqueous solution of sodium acetate (10-13%; $4g.g^{-1}$ of bisether) and stirred for a further 1 hour at ambient temperature. The aqueous layer was neutralised with dilute sodium hydroxide (4M.) solution and, after precipitation, chloroform was added to the mixture. The two phases were separated and the aqueous layer was extracted with a further portion of chloroform. The organic phases were combined, dried ($MgSO_4$) and evaporated to give the crude bisaldehyde which crystallised and was washed with ethanol. 100% yield was obtained.

Recrystallisation of α,ω-bis-(2-formyl-3-oxythienyl)ethane **19**



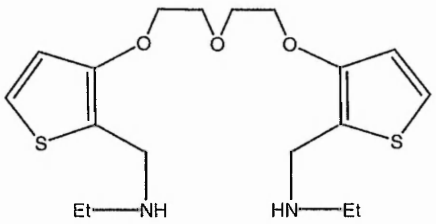
The title compound was dissolved with stirring in a minimum of a 1:1 mixture of cyclohexane/methanol. The stirring was stopped and, after a slow evaporation at 4°C, the compound crystallised as yellow needles. MF: $C_{14}H_{14}O_5S_2$; ^1H NMR (ppm): 9.99s(CHO), 7.63d(C5), 6.87d(C4), 4.34m(ThOCH$_2$), 3.94m(ThOCH$_2$$\underline{CH_2}$); ^{13}C NMR (ppm): 181.18(CHO), 163.93(C3), 135.03(C5), 121.78(C2), 116.52(C4), 71.23(ThOCH$_2$), 69.82(ThOCH$_2$$\underline{CH_2}$). IR (cm^{-1}): 3269.5, 3106.6, 3087.7, 2984.5, 2957.5, 2919.4, 2881.2, 2827.4, 2784.7, 2632.8, 2547.0, 2468.3, 1649.7(C=O), 1535.3(Th C=C), 1273.1 (m), 744.6(s); elemental analysis: calc. C 51.52%, H 4.32%, S 19.65%, O 25.45%, exp. C 51.50%, H 4.34%, S 18.75%, O 25.41%.

Synthesis of α,ω-bis-(2-propylimine-3-oxythienyl)ethane [1,7]



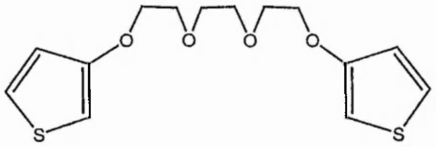
A stirred solution of the α,ω-bis(2-formyl-3-oxythienyl)-ethane **16** (1eq) and 2.5eq of (33% ethanolic solution of) n-propylamine in anhydrous ethanol (20ml.g^{-1} of bisaldehyde) was boiled under reflux for 1 hour. The mixture was cooled and the excess of solvent/reagent was removed in vacuo to give crude bisimine. 99% yield was obtained. MF: $C_{18}H_{24}O_3N_2S_2$.

Synthesis of α,ω-bis-(2-propylamine-3-oxythienyl)ethane[1,7]



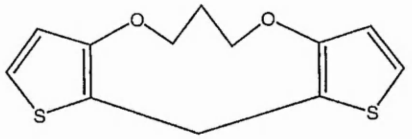
A solution of sodium borohydride (2.5eq) in anhydrous ethanol (10ml.g^{-1}) was added and the bisimine (1eq) was boiled under reflux for 1 hour. The solution was cooled and evaporated, the residue was treated with water and extracted into DCM (x4). The combined organic extracts were dried ($MgSO_4$) and evaporated to yield the crude bisamine to 70%. MF: $C_{18}H_{28}O_3N_2S_2$.

Recrystallisation of α,ω-bis-(3-ethyloxythienyl)ethane **20**



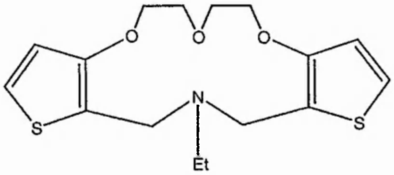
The title compound was dissolved with stirring in a minimum of a 1:1 mixture of ethanol/dichloromethane. The stirring was stopped and, after a slow evaporation at 4°C, the compound crystallised as colourless plates. MF: $C_{14}H_{18}O_4S_2$; ^{1}H NMR (ppm): 7.14dd(C5), 6.77dd(C4), 6.24dd(C2), 4.09t($ThOCH_2$), 3.83t(OCH_2CH_2O), 3.72s($ThOCH_2\underline{CH_2}$); ^{13}C NMR (ppm): 157.67(C3), 124.76(C5), 119.67(C4), 97.63(C2), 70.90($ThOCH_2$), 69.82(OCH_2CH_2O), 69.65($ThOCH_2\underline{CH_2}$); IR (cm^{-1}): 3125.8, 3097.1, 3079.2, 3061.3, 2986.1, 2930.0, 2907.3, 2872.6, 2833.2, 2809.3, 2775.9, 2710.2, 1542.2(Th C=C), 754.6(s); elemental analysis: calc. C 53.48%, H 5.77%, S 20.40%, O 20.35%, exp. C 53.49%, H 5.77%, S 20.32%, O 20.42%.

Recrystallisation of 2,6-dioxa-10,14-dithia-tricyclo[11.3.0.0]-hexadeca-1,15,7,8-tetraene **21**[339]



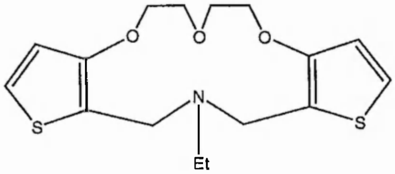
The title macrocycle was dissolved with stirring in a minimum of a 1:1:1 mixture of cyclohexane/ethanol/dichloromethane. The stirring was stopped and, after a slow evaporation, the compound crystallised as colourless plates. MF: $C_{12}H_{12}O_2S_2$; ^{1}H NMR (ppm): 6.98d(C5), 6.74d(C4), 4.32t($ThOCH_2$), 4.06s($ThCH_2Th$), 1.60m($ThOCH_2\underline{CH_2}$); ^{13}C NMR (ppm): 151.57(C3), 125.17(C5), 121.26(C2), 119.89(C4), 74.00($ThOCH_2$), 27.62($ThOCH_2\underline{CH_2}$), 21.55($ThCH_2Th$); IR (cm^{-1}): 3098.2, 2944.2, 2883.4, 1557.0(Th C=C); elemental analysis: calc. C 57.11%, H 4.79%, S 25.41%, O 12.68%, exp. C 57.03%, H 4.76%, S 25.40%, O 12.81%.

Synthesis of 15-ethyl-2,5,8-trioxa-12,18-dithia-15-azatricyclo[15.3.0.0]-tricosa-1(18),9(13),10,19-tetraene **10a**[1,7]



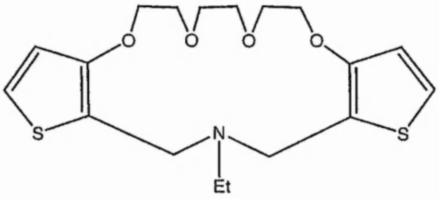
1.1eq of N-ethylamine was mixed with glacial acetic acid ($100cm^3.g^{-1}$). 2.2eq of formaldehyde (37% aq solution) was added to the solution. Finally, 1eq of α-ω-bis-(3-oxythionyl)-ethane was quickly added to the solution. After 24h, with stirring, at room temperature, the solution was neutralised with 4M NaOH, with cooling. The solution was then washed with dichloromethane (x4). The organic layer was reduced to a brown oil. The oil became, after cooling to room temperature, a little cloudy and the addition of few drops of ethanol made the macrocycle precipitate. The compound crystallised as good quality large colourless crystals. The crystals were filtered then washed with ethanol. 80% yield was obtained.

Recrystallisation of 15-ethyl-2,5,8-trioxa-12,18-dithia-15-azatricyclo[15.3.0.0]-tricosa-1(18),9(13),10,19-tetraene **10a**



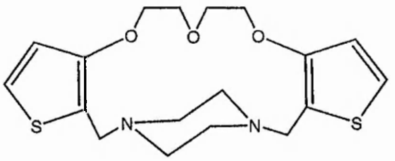
The title macrocycle was dissolved with stirring in a minimum of a 1:1 mixture of ethanol/dichloromethane. The stirring was stopped and, after a slow evaporation, the compound crystallised as colourless prisms. MF: $C_{16}H_{21}O_3NS_2$; ^{1}H NMR (ppm): 7.07d(C5), 6.76d(C4), 4.17m-4.14m($ThOCH_2$), 3.96s($ThCH_2N$), 3.67m-3.64m(CH_2OCH_2), 2.57q(NCH_2), 1.14t(CH_3); ^{13}C NMR (ppm): 153.47(C3), 122.30(C5), 121.03(C2), 117.79(C4), 70.94($ThOCH_2$), 69.2(CH_2OCH_2), 48.17($ThCH_2N$), 46.54(NCH_2), 13.00(CH_3); IR (cm^{-1}): 3106.2, 3085.7, 3074.4, 3008.3, 2967.4, 2931.6, 2880.3, 2855.5, 2839.8, 2813.5, 2781.5, 1550.4(Th C=C); elemental analysis: calc. C 56.61%, H 6.23%, N 4.13%, S 18.89%, O 14.14%, exp. C 56.61%, H 6.11%, N 4.19%, S 21.53%, O 11.56%.

Recrystallisation of 18-ethyl-2,5,8,11-tetraoxa-15,21-dithia-azatricyclo[18.3.0.0]-tricosa-1,22,12,13-tetraene **10b**[339]



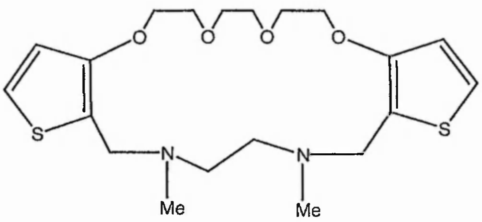
The title macrocycle was dissolved with stirring in a minimum of a 1:1 mixture of ethanol/dichloromethane. The stirring was stopped and, after a slow evaporation at 4°C, the compound crystallised as colourless plates. MF: $C_{18}H_{25}O_4NS_2$; ^{1}H NMR (ppm): 7.07d(C5), 6.74d(C4), 4.12m($ThOCH_2$), 3.80s($ThCH_2N$), 3.70m($ThOCH_2CH_2$), 3.66s(OCH_2CH_2O), 2.57q(NCH_2), 1.10t(CH_3); ^{13}C NMR (ppm): 153.44(C3), 122.50(C5), 120.74(C2), 117.21(C4), 71.20($ThOCH_2$), 70.73(OCH_2CH_2O), 69.86($ThOCH_2CH_2$), 47.94($ThCH_2N$), 46.60(NCH_2), 12.19(CH_3); IR (cm^{-1}): 3093.4, 2965.8, 2920.8, 2869.7, 2823.5, 1561.8(Th C=C); elemental analysis: calc. C 56.37%, H 6.57%, N 3.65%, S 16.72%, O 16.69%, exp. C 56.34%, H 6.61%, N 3.68%, S 16.68%, O 16.69%.

Recrystallisation of 18,11,14-trioxa-4,18-dithia-1,21-diaza-tetracyclo[18.4.4.0.0]-pentacosa-3,5,15,16-tetraene **9a**[339]



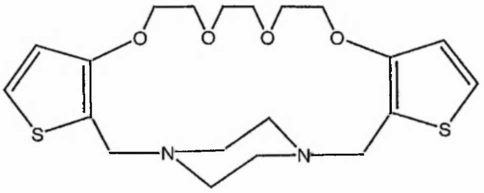
The title macrocycle was dissolved with stirring in a minimum of a 2:2:1 mixture of acetone/methanol/dichloromethane. The stirring was stopped and, after a slow evaporation at 4°C, the compound crystallised. MF: $C_{18}H_{24}O_3N_2S_2$; ^{1}H NMR (ppm): 7.11d(C5), 6.72d(C4), 4.10m(ThOCH$_2$), 3.78m(ThOCH$_2\underline{\text{CH}_2}$), 3.77s(ThCH$_2$N), 2.72s(NCH$_2CH_2$N); ^{13}C NMR (ppm): 154.71(C3), 123.18(C5), 116.34(C2), 115.04(C4), 70.13(ThOCH$_2$), 69.96(ThOCH$_2\underline{\text{CH}_2}$), 48.45(ThCH$_2$N), 44.77(NCH$_2CH_2$N); IR (cm^{-1}): 3097.0, 3077.3, 2933.8, 2892.7, 2875.7, 2847.9, 2804.6, 2762.7, 2693.9, 2655.5, 2505.0, 2429.2, 1559.6(Th C=C); elemental analysis: calc. C 56.81%, H 6.36%, N 7.36%, S 16.85%, O 12.61%, exp. C 56.81%, H 6.34%, N 7.38%, S 16.89%, O 12.58%.

Recrystallisation of 18,21-bis-(methyl)-2,5,8,11-tetraoxa-15,24-dithia-18,21-diaza-tricyclo[21.3.0.0]-hexacosa-1(26),12(16),13,25-tetraene **8b**[339]



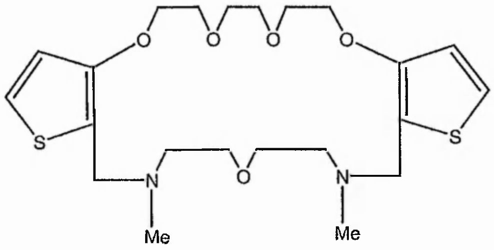
The title macrocycle was dissolved with stirring in a minimum of a 1:1 mixture of cyclohexane/methanol. The stirring was stopped and, after a slow evaporation at 4°C, the compound crystallised as colourless plates. MF: $C_{20}H_{30}O_4N_2S_2$; ^{1}H NMR (ppm): 7.11d(C5), 6.80d(C4), 4.14t(ThOCH$_2$), 3.82m(ThOCH$_2\underline{\text{CH}_2}$), 3.77s(OCH$_2CH_2$O), 3.71s(ThCH$_2$N), 2.61s(NCH$_2CH_2$N), 2.32s(CH$_3$); ^{13}C NMR (ppm): 153.07(C3), 122.62(C5), 119.07(C2), 117.10(C4), 71.53(ThOCH$_2$), 71.14(OCH$_2$CH$_2$O), 70.02(ThOCH$_2\underline{\text{CH}_2}$), 53.23(NCH$_2CH_2$N), 51.18(ThCH$_2$N), 42.79(CH$_3$); IR (cm^{-1}): 3098.2, 3053.1, 2961.6, 2943.2, 2919.8, 2878.1, 2849.7, 2834.4, 2804.4, 2774.5, 2764.5, 2692.7, 1556.3(Th C=C); elemental analysis: calc. C 55.78%, H 7.96%, N 6.51%, S 14.89%, O 14.86%, exp. C 55.75%, H 7.97%, N 6.53%, S 14.89%, O 14.86%.

Recrystallisation of 2,5,8,11-tetraoxa-15,26-dithia-18,21-diaza-tetracyclo[21.4.4.0.0]-octacosa-1(25),27,12(16),13-tetraene **9b**[339]



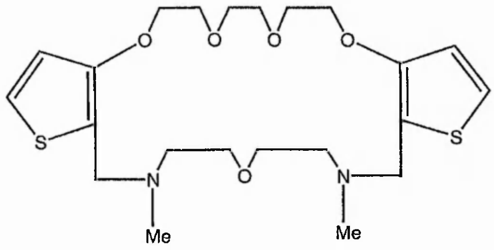
The title macrocycle was dissolved with stirring in a minimum of a 1:1 mixture of cyclohexane/methanol. The stirring was stopped and, after a slow evaporation at 4°C, the compound crystallised as colourless plates. MF: $C_{20}H_{28}O_4N_2S_2$; ^1H NMR (ppm): 7.08d(C5), 6.77d(C4), 4.16m($ThOCH_2$), 3.77m($ThOCH_2\underline{CH_2}$), 3.73s($ThCH_2N$), 3.70s(OCH_2CH_2O), 2.61s(NCH_2CH_2N); ^{13}C NMR (ppm): 154.30(C3), 122.37(C5), 116.99(C2/4), 71.03($ThOCH_2$), 70.82(OCH_2CH_2O), 70.32($ThOCH_2\underline{CH_2}$), 51.04($ThCH_2N$, NCH_2CH_2N); IR (cm^{-1}): 3095.2, 3038.0, 3010.1, 2971.5, 2949.9, 2921.6, 2909.5, 2884.1, 2846.6, 2831.4, 2802.3, 2753.5, 2701.3, 2674.0, 2653.6, 2591.1, 2567.3, 2517.3, 1557.4(Th C=C); elemental analysis: calc. C 56.58%, H 6.65%, N 6.60%, S 15.10%, O 15.07%, exp. C 56.65%, H 6.68%, N 6.61%, S 15.01%, O 15.05%.

Synthesis of 18,24-bis-(methyl)-2,5,8,11,21-pentaoxa-15,27-dithia-18,24-diaza-tricyclo[24.3.0.0]-nonacosa-1(26),12(16),13,28-tetraene **22**



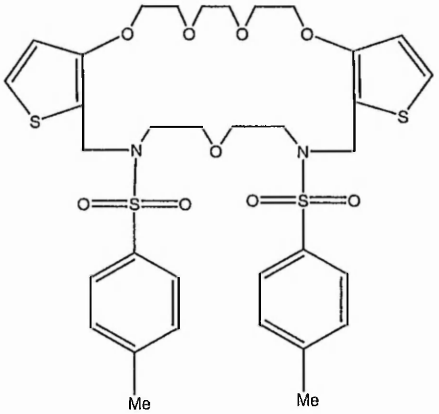
1.1eq of the diamine Me-NH-$(CH_2)_2$-O-$(CH_2)_2$-NH-Me was dissolved in glacial acetic acid ($50cm^3.g^{-1}$) and 2eq of formaldehyde (37% aq solution) with stirring. 1eq of α-ω-bis-(3-ethyloxythienyl)-ethane was quickly added to the solution. After 24h, with stirring, at room temperature, the solution was neutralised with 4M NaOH, with cooling. The solution was then washed with dichloromethane (x4). The organic layer was reduced to a orange-brown oil. 75% yield was obtained.

Recrystallisation of 18,24-bis-(methyl)-2,5,8,11,21-pentaoxa-15,27-dithia-18,24-diaza-tricyclo[24.3.0.0]-nonacosa-1(26),12(16),13,28-tetraene **22**



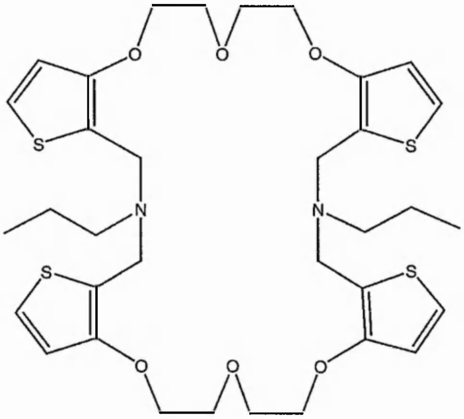
The title macrocycle was dissolved with stirring in a minimum of a 1:1 mixture of ethanol/dichloromethane. The stirring was stopped and, after a slow evaporation at 4°C, the compound precipitated, as a yellow powder. MF: $C_{22}H_{34}O_5N_2S_2$; ^1H NMR (ppm): 7.27d(C5), 6.78d(C4), 4.33s($ThCH_2N$), 4.11m($ThOCH_2$), 3.86t($NCH_2\underline{CH_2}O$), 3.70m($ThOCH_2\underline{CH_2}$), 3.59t(OCH_2CH_2O), 3.17m($N\underline{CH_2}CH_2O$), 1.97s(CH_3); ^{13}C NMR (ppm): 157.37(C3), 127.40(C5), 116.49(C2), 116.17(C4), 70.78($ThOCH_2$), 70.65(OCH_2CH_2O), 69.76($ThOCH_2\underline{CH_2}$), 65.73($NCH_2\underline{CH_2}O$), 53.40($N\underline{CH_2}CH_2O$), 48.80($ThCH_2N$), 21.51(CH_3); IR (cm^{-1}): 3088.4, 3009.1, 2934.8, 2880.4, 1562.9(Th C=C); elemental analysis: calc. C 55.67%, H 8.07%, N 5.90%, S 13.51%, O 16.85%, exp. C 55.82%, H 8.11%, N 5.88%, S 13.60%, O 16.59%.

Recrystallisation of 18,24-bis-(p-toluenesulphonamide)-2,5,8,11,21-pentaoxa-15,27-dithia-18,24-diaza-tricyclo[24.3.0.0]-nonacosa-1(26),12(16),13,28-tetraene 23[339]



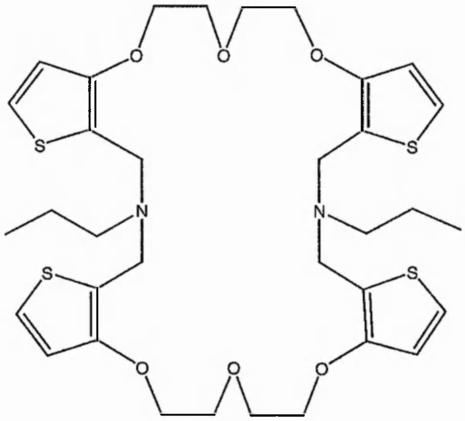
The title macrocycle was dissolved with stirring in a minimum of a 1:1 mixture of cyclohexane/methanol. The stirring was stopped and, after a slow evaporation at 4°C, the compound crystallised as colourless blocks. MF: $C_{34}H_{42}O_9N_2S_4$; ^1H NMR (ppm): 7.68d(C7/7'), 7.24d(C8/8'), 7.11d(C5), 6.70d(C4), 4.89s($ThCH_2N$), 4.05m($ThOCH_2$), 3.70m($ThOCH_2\underline{CH_2}$), 3.62s(OCH_2CH_2O), 3.39t($NCH_2\underline{CH_2}O$), 3.23t($N\underline{CH_2}CH_2O$), 2.39s(CH_3); ^{13}C NMR (ppm): 154.95(C3), 143.13(C9), 137.72(C6), 129.60(C8/8'), 127.34(C7/7'), 124.52(C5), 116.26(C2), 116.10(C4), 71.14($ThOCH_2$), 71.00(OCH_2CH_2O), 69.97($ThOCH_2\underline{CH_2}$), 68.37($NCH_2\underline{CH_2}O$), 47.75($N\underline{CH_2}CH_2O$), 42.06($ThCH_2N$), 21.59(CH_3); IR (cm^{-1}): 3105.7, 3050.4, 3026.9, 3006.8, 2983.3, 2936.3, 2928.0, 2902.8, 2881.0, 2819.0, 1596.7(Ph C=C), 1557.9(Th C=C); elemental analysis: calc. C 55.50%, H 5.95%, N 3.60%, S 16.46%, O 18.48%, exp. C 55.48%, H 5.82%, N 3.71%, S 16.57%, O 18.42%.

Synthesis of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene **24**[1,7]



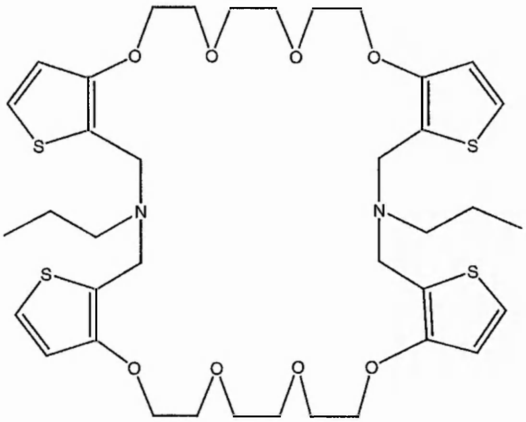
1eq of α-ω-bis-(3-oxythienyl)-ethane was added to a solution of the crude bisamine α-ω-bis-(2-propylamine-3-ethyloxythienyl)-ethane (1eq) and 2eq of formaldehyde (37% aq solution) in glacial acetic acid (50cm^3.g^{-1}). The solution was stirred at room temperature for 24 hours and, then neutralised with 4M NaOH, with cooling. The solution was then washed with dichloromethane (x4), dried ($MgSO_4$) and evaporated. The crude yield was purified on a graduated column: 1/1/2 DCM/EA/PE 60-80; 1/1 DCM/EA; 1/1 DCM/acetone, and the macrocycle finally crystallised. It was filtered and washed with ethanol. 37% yield was obtained.

Recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene **24**



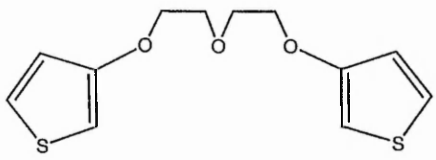
The title macrocycle was dissolved with stirring in a minimum of a 1:1:1 mixture of methanol/ether/dichloromethane. The stirring was stopped and, after a slow evaporation at 4°C, the compound crystallised as yellow needles. MF: $C_{34}H_{46}O_6N_2S_4$; ^{1}H NMR (ppm): 7.07d(C5), 6.75d(C4), 4.08t($ThOCH_2$), 3.78t($ThOCH_2\underline{CH_2}$), 3.76s($ThCH_2N$), 2.45t($N\underline{CH_2}CH_2CH_3$), 1.54q($NCH_2\,\underline{CH_2}CH_3$), 0.87t($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 153.52(C3), 122.55(C5), 121.38(C2), 117.33(C4), 71.41($ThOCH_2$), 70.21($ThOCH_2\underline{CH_2}$), 54.83($N\underline{CH_2}CH_2CH_3$), 48.42($ThCH_2N$), 20.34($NCH_2\underline{CH_2}CH_3$), 11.78($NCH_2CH_2\underline{CH_3}$); IR (cm^{-1}): 3106.5, 3073.7, 2954.4, 2930.1, 2869.4, 2814.8, 1555.5(Th C=C); elemental analysis: calc. C 58.09%, H 6.02%, N 3.98%, S 18.25%, O 13.66%, exp. C 58.04%, H 6.02%, N 3.97%, S 18.26%, O 13.71%.

Recrystallisation of 18,41-dipropyl-2,5,8,11,25,28,31,34-nonaoxa-15,21,38,44-tetrathia-18,41-diaza-pentacyclo[35.5.5.5.0.0]-hexatetraconta-1(43),12(16),13,20(24),22,35(39),36,45-octaene **25**[339]



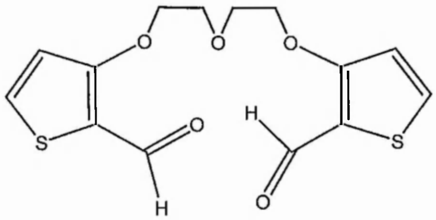
The title macrocycle was dissolved with stirring in a minimum of a 1:1:1 mixture of methanol/ether/dichloromethane. The stirring was stopped and, after a slow evaporation, the compound crystallised but no crystals suitable for diffraction were obtained. MF: $C_{38}H_{54}O_8N_2S_4$; ^{1}H NMR (ppm): 7.07d(C5), 6.76d(C4), 4.10t($ThOCH_2$), 3.73m($O\underline{CH_2CH_2}O, ThOCH_2\underline{CH_2}$), 3.69s($ThCH_2N$), 2.44t($N\underline{CH_2}CH_2CH_3$), 1.55m($NCH_2\underline{CH_2}CH_3$), 0.86t($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 159.37(C3), 124.14(C5), 115.98(C2), 111.96(C4), 71.44($ThOCH_2$), 70.44($ThOCH_2\underline{CH_2}$), 70.23($O\underline{CH_2CH_2}O$), 58.59($N\underline{CH_2}CH_2CH_3$), 50.81($ThCH_2N$), 18.22($NCH_2\underline{CH_2}CH_3$), 11.94($NCH_2CH_2\underline{CH_3}$); IR (cm^{-1}): 3095.8, 3085.2, 2960.3, 2938.2, 2892.3, 2880.4, 2832.8, 2801.2, 1561.9(Th C=C); elemental analysis: calc. C 57.40%, H 6.85%, N 3.52%, S 16.13%, O 16.10%, exp. C 57.53%, H 6.76%, N 3.48%, S 16.26%, O 15.97%.

Complexation of α,ω-bis-(3-oxythienyl)ethane with $AlCl_3$ **26**



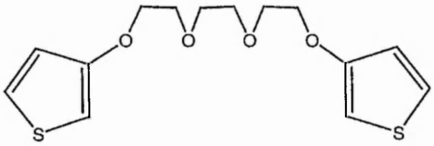
The title ligand was dissolved in a 1:1 mixture of methanol/dichloromethane (1cm^3.g^{-1}), and boiled under reflux. 1eq. of $AlCl_3.6H_2O$ was dissolved by heating in a 1:1 mixture of dichloromethane/methanol (1cm^3.g^{-1}), then was added dropwise to the stirred solution. The reflux and stirring were maintained for 1h, and then cooled to room temperature. The solution was filtered and a blue-grey solution was obtained. After solvent evaporation, blue-grey transparent plate-shaped crystals were obtained but were not suitable for X-ray crystallography. MF: $C_{12}H_{14}O_3S_2Cl_3Al$; ^1H NMR (ppm): 6.75dd(C5), 6.30dd(C4), 5.87dd(C2), 3.68t(ThOCH$_2$), 3.43t(ThOCH$_2$$\underline{CH_2}$); ^{13}C NMR (ppm): 156.35(C3), 123.70(C5), 118.35(C4), 96.57(C2), 68.55(ThOCH$_2$), 68.46(ThOCH$_2$$\underline{CH_2}$); IR (cm^{-1}): 3119.3, 3108.9, 3088.1, 2923.1, 2881.5, 1542.7(Th C=C), **1178.0**(s, C-O), **756.2**(s).

Complexation of α,ω-bis-(2-formyl-3-oxythienyl)ethane with $AlCl_3$ **27**



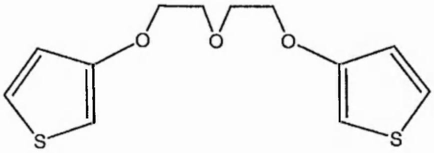
The title ligand was dissolved in a 1:1 mixture of methanol/dichloromethane (1cm^3.g^{-1}), and boiled under reflux. 1eq. of $AlCl_3.6H_2O$ was dissolved by heating in a 1:1 mixture of dichloromethane/methanol (1cm^3.g^{-1}), then was added dropwise to the stirred ligand solution. The reflux and stirring were maintained for 1h, then cooled to room temperature. The solution was filtered and a blue-grey solution was obtained. After solvent evaporation, blue-grey transparent plate-shaped crystals were obtained but were not suitable for X-ray crystallography. MF: $C_{14}H_{14}O_5S_2Cl_3Al$; ^1H NMR (ppm): 9.32s(CHO), 7.17d(C5), 6.39d(C4), 3.77t(ThOCH$_2$), 3.32t(ThOCH$_2$$\underline{CH_2}$); ^{13}C NMR (ppm): 179.33(CHO), 163.93(C3), 134.06(C5), 121.78(C2), 115.89(C4), 69.97(ThOCH$_2$), 68.20(ThOCH$_2$$\underline{CH_2}$). IR (cm^{-1}): 3271.8, 3104.1, 3086.4, 2958.8, 2925.1, 2869.4, 2854.2, 1646.6(C=O), 1537.7(Th C=C), **1261.1**(m), **802.6**(m).

Complexation of α,ω-bis-(3-ethyloxythienyl)ethane with $AlCl_3$ **28**



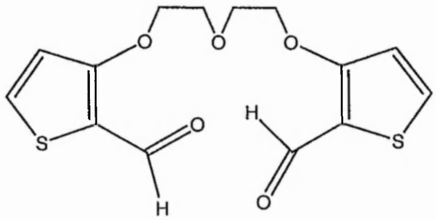
The title ligand was dissolved in a 1:1 mixture of methanol/dichloromethane ($1cm^3.g^{-1}$), and boiled under reflux. 1eq. of $AlCl_3.6H_2O$ was dissolved by heating in a 1:1 mixture of dichloromethane/methanol ($1cm^3.g^{-1}$), then was added dropwise to the stirred ligand solution. The reflux and stirring were maintained for 1h, then cooled to room temperature. The solution was filtered and a blue-grey solution was obtained. After solvent evaporation, blue-grey transparent plate-shaped crystals were obtained but were not suitable for X-ray crystallography. MF: $C_{14}H_{18}O_4S_2Cl_2Al$; ^1H NMR (ppm): 6.64dd(C5), 6.18dd(C4), 5.75dd(C2), 3.53t($ThOCH_2$), 3.25t(OCH_2CH_2O,$ThOCH_2\underline{CH_2}$); ^{13}C NMR (ppm): 156.20(C3), 123.54(C5), 118.16(C4), 96.37(C2), 69.25($ThOCH_2$), 68.26(OCH_2CH_2O), 68.23($ThOCH_2\underline{CH_2}$); IR (cm^{-1}): 2955.8, 2923.5, 2854.2, 1543.2(Th C=C), **744.5**(m).

Complexation of α,ω-bis-(3-oxythienyl)ethane with copper(II) perchlorate **29**



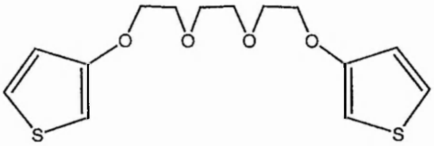
The title ligand was dissolved in a 1:1 mixture of methanol/dichloromethane ($1cm^3.g^{-1}$), and boiled under reflux. 1eq. of $Cu(ClO_4)_2.6H_2O$ was dissolved by heating in a 1:1 mixture of dichloromethane/methanol ($1cm^3.g^{-1}$), then was added dropwise to the stirred ligand solution. The reflux and stirring were maintained for 1h, and then filtered hot. A blue-green solution was obtained. After solvent evaporation the complex crystallised as blue plate-shaped crystals. MF: $C_{12}H_{14}O_{11}S_2Cl_2Cu$; ^1H NMR (ppm): 7.42m(C5), 6.88m(C4), 6.32m(C2), 4.01-4.17m($ThOCH_2\underline{CH_2}$,$ThOCH_2$); ^{13}C NMR (ppm): 168.85(C3), 122.63(C5), 118.19(C4), 90.59(C2), 71.86($ThOCH_2$), 71.72($ThOCH_2\underline{CH_2}$); IR (cm^{-1}): 3120.3, 3106.9, 3089.7, 2921.7, 2879.5, 2803.6, 1542.1(Th C=C), **628.1**(s, ClO_4^-).

Complexation of α,ω-bis-(2-formyl-3-oxythienyl)ethane with copper(II) perchlorate **30**



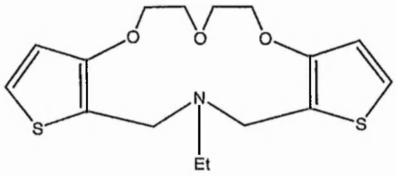
The title ligand was dissolved in a 1:1 mixture of methanol/dichloromethane ($1cm^3.g^{-1}$), and boiled under reflux. 1eq. of $Cu(ClO_4)_2.6H_2O$ was dissolved by heating in a 1:1 mixture of dichloromethane/methanol ($1cm^3.g^{-1}$), then was added dropwise to the stirred ligand solution. The reflux and stirring were maintained for 1h, then filtered hot. A yellow-brown solution was obtained. After solvent evaporation a brown powder was obtained. MF: $C_{14}H_{14}O_{13}S_2Cl_2Cu$; ^1H NMR (ppm): 10.32s(CHO), 7.77d(C5), 7.00d(C4), 4.29m($ThOCH_2$), 3.84m($ThOCH_2\underline{CH_2}$); ^{13}C NMR (ppm): 182.71(CHO), 166.96(C3), 137.35(C5), 118.54(C2/C4), 72.70($ThOCH_2$), 70.82($ThOCH_2\underline{CH_2}$); IR (cm^{-1}): 3101.2, 2980.5, 2960.6, 2926.5, 2855.4, 1646.0(C=O), 1537.5(Th C=C), **627.5**(s, ClO_4^-).

Complexation of α,ω-bis-(3-ethyloxythienyl)ethane with copper(II) perchlorate **31**



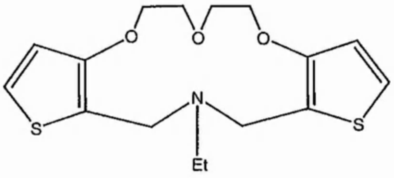
The title ligand was dissolved in a 1:1 mixture of methanol/dichloromethane ($1cm^3.g^{-1}$), and boiled under reflux. 1eq. of $Cu(ClO_4)_2.6H_2O$ was dissolved by heating in a 1:1 mixture of dichloromethane/methanol ($1cm^3.g^{-1}$), then was added dropwise to the stirred ligand solution. A blue-green precipitate (a) appeared almost immediately. The reflux and stirring were maintained for 1h, then filtered hot. A blue-green solution (b) was obtained, and the blue-green solid (a) was recovered on the filter. After solvent evaporation, blue-green plate-shaped crystals (b) were obtained which proved after spectral analysis to be the complex. MF: $C_{14}H_{18}O_{12}S_2Cl_2Cu$; ^1H NMR (ppm): 7.54s(C2), 7.39m(C5), 7.06m(C4), 4.07m($ThOCH_2$), 3.65m(OCH_2CH_2O), 3.52s($ThOCH_2\underline{CH_2}$); ^{13}C NMR (ppm): 162.87(C3), 126.33(C5), 112.18(C4), 109.65(C2), 70.83($ThOCH_2$), 70.74(OCH_2CH_2O), 70.63($ThOCH_2\underline{CH_2}$); IR (cm^{-1}): 3108.8, 3094.2, 2932.9, 2878.2, 1592.5(Th C=C), 1539.1, **625.2**(s, ClO_4^-).

Complexation of 15-ethyl-2,5,8-trioxa-12,18-dithia-15-azatricyclo[15.3.0.0]-tricosa-1(18),9(13),10,19-tetraene with nickel(II) perchlorate **32**



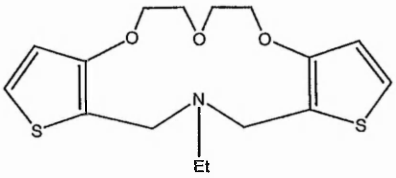
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane, and boiled under reflux. 1eq. of $Ni(ClO_4)_2.6H_2O$ was dissolved in methanol, then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot and as the solvent evaporated, a green powder was obtained. MF: $C_{16}H_{21}O_{11}NS_2Cl_2Ni$; ^1H NMR (ppm): 7.66d(C5), 7.17d(C4), 4.78s($ThCH_2N$), 4.31m-4.49m(CH_2OCH_2), 3.86t($ThOCH_2$), 3.33q(NCH_2), 1.44t(CH_3); ^{13}C NMR (ppm): 156.41(C3), 127.34(C5), 117.42(C4), 107.64(C2), 69.56($ThOCH_2$), 67.66(CH_2OCH_2), 48.37($ThCH_2N$), 46.49(NCH_2), 8.08(CH_3); IR (cm^{-1}): 3147.5, 3106.4, 2993.4, 2975.9, 2947.2, 2911.3, 2875.3, 2824.7, 2793.2, 1569.0(Th C=C), **623.2**(s, ClO_4^-); elemental analysis: calc. C 32.19%, H 3.55%, N 2.35%, Cl 11.88%, S 10.74%, O 29.48%, Ni 9.83%, exp. C 29.84%, H 4.31%, N 1.96%, Cl 12.05%, S 10.51%; (M+H)= 340.

Complexation of 15-ethyl-2,5,8-trioxa-12,18-dithia-15-azatricyclo[15.3.0.0]-tricosa-1(18),9(13),10,19-tetraene with nickel(II) chloride **33**



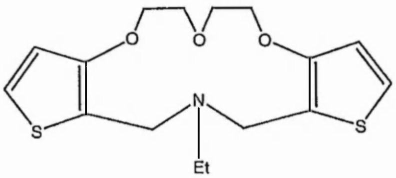
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane, and boiled under reflux. 1eq. of $NiCl_2.6H_2O$ was dissolved in methanol, then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot and as the solvent evaporated, a green powder was obtained. MF: $C_{16}H_{21}O_3NS_2Cl_2Ni$; ^1H NMR (ppm): 7.29d(C5), 6.93d(C4), 4.19t($ThOCH_2$), 4.00s($ThCH_2N$), 3.63t($ThOCH_2\underline{CH_2}$), 2.63q(NCH_2), 1.17t(CH_3); IR (cm^{-1}): 2926.7, 2880.5, 2808.6, 1555.5(Th C=C).

Complexation of 15-ethyl-2,5,8-trioxa-12,18-dithia-15-azatricyclo[15.3.0.0]-tricosa-1(18),9(13),10,19-tetraene with copper(II) perchlorate **34**



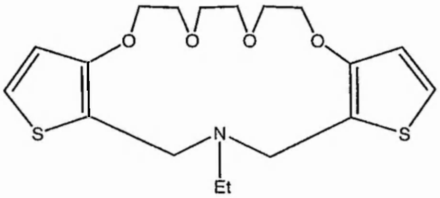
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane, and boiled under reflux. 1eq. of $Cu(ClO_4)_2.6H_2O$ was dissolved in methanol, then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot and as the solvent evaporated, a blue powder was obtained. MF: $C_{16}H_{21}O_{11}NS_2Cl_2Cu$; ^1H NMR (ppm): 7.65d(C5), 7.16d(C4), 4.75s($ThCH_2N$), 4.31m-4.51m(CH_2OCH_2), 3.86t($ThOCH_2$), 3.31q(NCH_2), 1.43t(CH_3); ^{13}C NMR (ppm): 157.14(C3), 127.99(C5), 118.04(C4), 108.23(C2), 70.21($ThOCH_2$), 68.38(CH_2OCH_2), 48.92($ThCH_2N$), 47.09(NCH_2), 8.63(CH_3); IR (cm^{-1}): 3157.8, 3101.3, 2998.6, 2952.4, 2911.3, 2875.3, 2826.4, 2794.0, 1565.8(Th C=C), **624.1**(s, ClO_4^-); ((M+H)= 340.

Complexation of 15-ethyl-2,5,8-trioxa-12,18-dithia-15-azatricyclo[15.3.0.0]-tricosa-1(18),9(13),10,19-tetraene with copper(II) chloride **35**



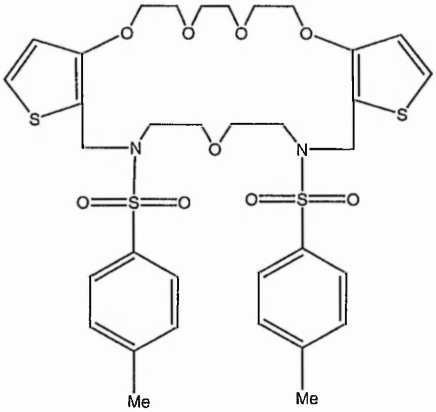
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane, and boiled under reflux. 1eq. of $CuCl_2.2H_2O$ was dissolved in methanol, then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot and as the solvent evaporated, a blue powder was obtained. MF: $C_{16}H_{21}O_3NS_2Cl_2Cu$; ^1H NMR (ppm): 7.62dd(C5), 7.13dd(C4), 4.69s($ThCH_2N$), 4.26m-4.48m(CH_2OCH_2), 3.79m($ThOCH_2$), 3.17q(NCH_2), 1.44t(CH_3); ^{13}C NMR (ppm): 156.88(C3), 129.54(C5), 117.90(C4), 109.05(C2), 71.07($ThOCH_2$), 68.73(CH_2OCH_2), 48.67($ThCH_2N$), 45.63(NCH_2), 15.07(CH_3); IR (cm^{-1}): 3152.4, 3097.8, 3075.1, 2977.9, 2931.6, 2870.0, 1555.0(Th C=C), **752.3**(m), **725.1**(m), **655.0**(m), **622.5**(w).

Complexation of 18-ethyl-2,5,8,11-tetraoxa-15,21-dithia-azatricyclo[18.3.0.0]-tricosa-1,22,12,13-tetraene with nickel(II) perchlorate **36**



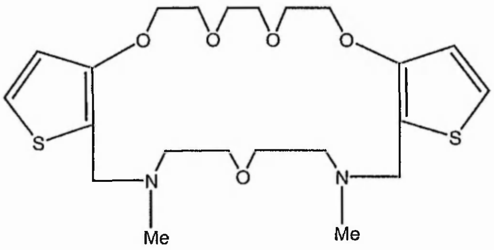
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane, and boiled under reflux. 1eq. of $Ni(ClO_4)_2.6H_2O$ was dissolved in methanol, then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot and as the solvent evaporated, a green powder was obtained. MF: $C_{18}H_{25}O_{12}NS_2Cl_2Ni$; ^1H NMR (ppm): 7.37d(C5), 6.87d(C4), 4.54m($ThOCH_2$), 4.27m($ThOCH_2CH_2$), 3.75m(OCH_2CH_2O), 3.66s($ThCH_2N$), 3.18s(NCH_2), 1.34s(CH_3); ^{13}C NMR (ppm): 157.50(C3), 127.79(C5), 116.23(C4), 105.86(C2), 70.45($ThOCH_2$), 69.90(OCH_2CH_2O), 68.80($ThOCH_2CH_2$), 47.34($ThCH_2N$), 45.40(NCH_2), 8.92(CH_3); IR (cm^{-1}): 3114.1, 3093.5, 2983.8, 2937.5, 2899.8, 2882.7, 2860.4, 2793.5, 2731.8, 2697.5, 2651.3, 1557.4(Th C=C), **625.7**(s, ClO_4^-); $[NiL]^{2+}$ ClO_4^- m/z= 540, 542 and 544.

Complexation and recrystallisation of 18,24-bis-(p-toluenesulphonamide)-2,5,8,11,21-pentaoxa-15,27-dithia-18,24-diaza-tricyclo[24.3.0.0]-nonacosa-1(26),12(16),13,28-tetraene with copper(II) perchlorate **37**



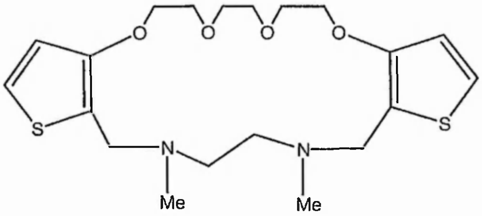
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane, and boiled under reflux. 1eq. of $Cu(ClO_4)_2.6H_2O$ was dissolved in methanol, then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot and, the solvent evaporated under vacuum. A dark blue solid film was obtained. This solid was dissolved in a 1:1:1 mixture of methanol/dichloromethane/ethyl acetate. After solvent evaporated, dark-blue plate-shaped crystals were obtained. MF: $C_{34}H_{42}O_{17}N_2S_4Cl_2Cu$; ^1H NMR (ppm): 7.76d(C7/7'), 7.32d(C8/8'), 7.02d(C5), 6.77d(C4), 4.90s($ThCH_2N$), 4.13m($ThOCH_2$), 3.80m($ThOCH_2\underline{CH_2}$), 3.50s(OCH_2CH_2O), 3.39t($NCH_2\underline{CH_2}O$), 3.08t($N\underline{CH_2}CH_2O$), 2.44s(CH_3); ^{13}C NMR (ppm): 155.52(C3), 143.53(C9), 136.93(C6), 129.75(C8/8'), 127.06(C7/7'), 124.18(C5), 121.14(C2), 113.64(C4), 73.39($ThOCH_2$,$ThOCH_2\underline{CH_2}$), 69.77($NCH_2\underline{CH_2}O$), 69.27(OCH_2CH_2O), 50.87($N\underline{CH_2}CH_2O$), 42.76($ThCH_2N$), 21.51(CH_3); IR (cm^{-1}): 2961.7, 2927.0, 2854.5, 1714.7, 1574.2(Ph C=C), 1557.3(Th C=C), **624.4**(s, ClO_4^-); elemental analysis: calc. C 40.30%, H 4.18%, N 2.76%, Cl 7.00%, S 12.66%, O 26.84%, Cu 6.27%, exp. C 42.58%, H 5.17%, N 2.29%, Cl 7.21%.

Complexation and recrystallisation of 18,24-bis-(methyl)-2,5,8,11,21-pentaoxa-15,27-dithia-18,24-diaza-tricyclo[24.3.0.0]-nonacosa-1(26),12(16),13,28-tetraene with copper(II) perchlorate **38**



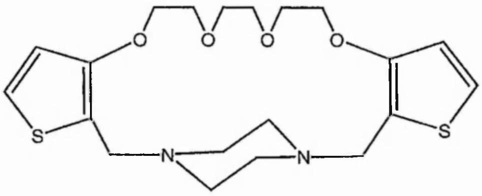
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane, and boiled under reflux. 1eq. of $Cu(ClO_4)_2.6H_2O$ was dissolved in methanol, then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot and separated in two halves. For the first half, the solvent was evaporated and a blue powder was obtained for analysis. For the second part, the solvent evaporated slowly with a slow diffusion of diethyl ether and blue plate-shaped crystals were obtained. MF: $C_{22}H_{34}O_{13}N_2S_2Cl_2Cu$; ^1H NMR (ppm): 7.31m(C5), 6.81m(C4), 4.37m($ThCH_2N$), 4.11m($ThOCH_2$), 3.95m($NCH_2\underline{CH_2}O$), 3.68m($ThOCH_2\underline{CH_2}$), 3.53t(OCH_2CH_2O), 3.39m($N\underline{CH_2}CH_2O$), 1.93s(CH_3); ^{13}C NMR (ppm): 157.65(C3), 127.91(C5), 116.06(C2), 114.93(C4), 70.44($ThOCH_2$), 70.21(OCH_2CH_2O), 69.28($ThOCH_2\underline{CH_2}$), 63.95($NCH_2\underline{CH_2}O$), 53.45($N\underline{CH_2}CH_2O$), 49.74($ThCH_2N$), 20.33(CH_3); IR (cm^{-1}): 3116.9, 2969.8, 2930.3, 2881.2, 2858.7, 1558.2(Th C=C), **624.9**(s,ClO_4^-); elemental analysis: calc. C 36.04%, H 4.67%, N 3.82%, Cl 9.67%, S 8.75%, O 28.37%, Cu 8.67%, exp. C 36.33%, H 4.66%, N 3.48%, Cl 9.58%.

Complexation of 18,21-bis-(methyl)-2,5,8,11-tetraoxa-15,24-dithia-18,21-diaza-tricyclo[21.3.0.0]-hexacosa-1(26),12(16),13,25-tetraene with copper(II) perchlorate **39**



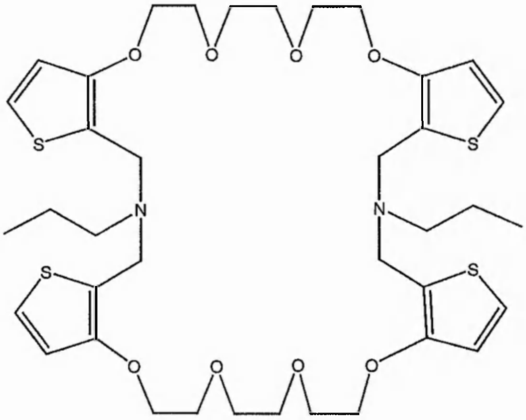
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane, and boiled under reflux. 1eq. of $Cu(ClO_4)_2.6H_2O$ was dissolved in a 1:1 mixture of methanol/dichloromethane, then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot and the solvent was slowly evaporated and a blue powder was obtained. MF: $C_{20}H_{30}O_{12}N_2S_2Cl_2Cu$; ^{1}H NMR (ppm): 6.86d(C5), 6.45d(C4), 3.72s($ThOCH_2$), 3.56m($ThOCH_2\underline{CH_2}$), 3.25m(OCH_2CH_2O), 3.16s($ThCH_2N$), 2.48s(NCH_2CH_2N), 2.13s(CH_3); ^{13}C NMR (ppm): 154.45(C3), 123.79(C5), 116.65(C4), 109.24(C2), 69.42($ThOCH_2$), 68.98(OCH_2CH_2O), 68.26($ThOCH_2\underline{CH_2}$), 53.88(NCH_2CH_2N), 51.86($ThCH_2N$), 42.60(CH_3); IR (cm^{-1}): 3100.8, 3067.8, 3047.7, 3024.0, 3001.8, 2956.5, 2924.2, 2897.7, 2869.7, 2853.9, 1556.5(Th C=C), **624.4**(s, ClO_4^-).

Complexation of 2,5,8,11-tetraoxa-15,26-dithia-18,21-diaza-tetracyclo[21.4.4.0.0]-octacosa-1(25),27,12(16),13-tetraene with copper(II) perchlorate **40**



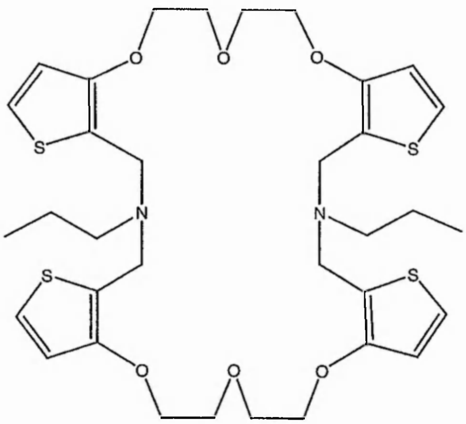
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane, and boiled under reflux. 1eq. of $Cu(ClO_4)_2.6H_2O$ was dissolved in a 1:1 mixture of methanol/dichloromethane, then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot, the solvent was slowly evaporated and a blue powder was obtained. MF: $C_{20}H_{28}O_{12}N_2S_2Cl_2Cu$; ^{1}H NMR (ppm): 7.17d(C5), 6.83d(C4), 4.09m($ThOCH_2$), 3.70s($ThCH_2N$), 3.65m($ThOCH_2\underline{CH_2}$), 3.21m(OCH_2CH_2O), 2.62s(NCH_2CH_2N); ^{13}C NMR (ppm): 156.71(C3), 124.65(C5), 117.79(C2/4), 71.95($ThOCH_2$), 71.84(OCH_2CH_2O), 71.43($ThOCH_2\underline{CH_2}$), 51.49($ThCH_2N$), 51.37(NCH_2CH_2N); IR (cm^{-1}): 2961.4, 2926.2, 2854.3, 1559.0(Th C=C), **627.2**(s, ClO_4^-); (M+H)= 425.

Complexation of 18,41-dipropyl-2,5,8,11,25,28,31,34-nonaoxa-15,21,38,44-tetrathia-18,41-diaza-pentacyclo[35.5.5.5.0.0]-hexatetraconta-1(43),12(16),13,20(24),22,35(39),36,45-octaene with copper(II) perchlorate **41**



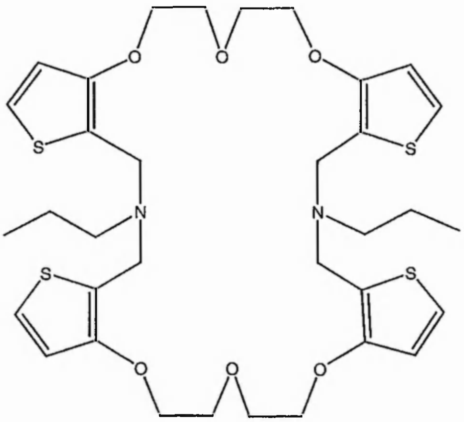
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane, and boiled under reflux. 1eq. of $Cu(ClO_4)_2.6H_2O$ was dissolved in a 1:1 mixture of methanol/dichloromethane, then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot, the solvent was slowly evaporated and blue-green crystals were obtained. MF: $C_{38}H_{54}O_{16}N_2S_4Cl_2Cu$; ^{1}H NMR (ppm): 6.99s(C5), 6.57s(C4), 3.86s($ThOCH_2\underline{CH_2}$,$ThOCH_2$), 3.42s($O\underline{CH_2}\underline{CH_2}O$), 3.28s($ThCH_2N$), 2.29s($N\underline{CH_2}CH_2CH_3$), 1.36m($NCH_2\underline{CH_2}CH_3$), 0.94s($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 154.68(C3), 132.18(C5), 126.77(C2), 116.27(C4), 70.38($ThOCH_2$), 69.76($ThOCH_2\underline{CH_2}$), 68.87($O\underline{CH_2}\underline{CH_2}O$), 53.29($N\underline{CH_2}CH_2CH_3$), 47.23($ThCH_2N$), 21.23($NCH_2\underline{CH_2}CH_3$), 14.03($NCH_2CH_2\underline{CH_3}$); IR (cm^{-1}): 3118.6, 3096.1, 2961.6, 2927.3, 2877.9, 2855.5, 2804.7, 1561.8(Th C=C), **626.4**(s, ClO_4^-).

Recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene complexed with silver (I) perchlorate[339] **42**



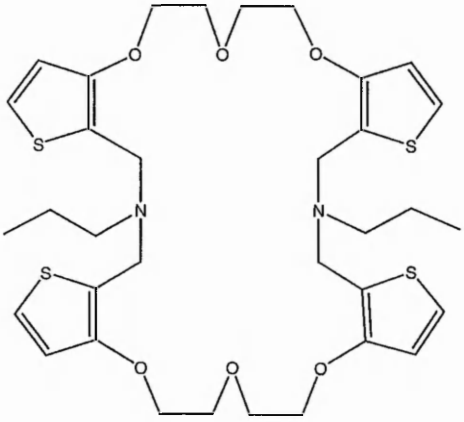
The title macrocyclic complex was dissolved with stirring in a minimum of methanol. The solution was warmed to the boiling point. At the boiling point, a minimum of 60:80 petroleum ether was added. The solution became cloudy and a further small quantity of methanol was added until cloudiness disappeared. The stirring was stopped and, after a slow evaporation at 4°C, with the flask wrapped in tinfoil (the compound was thought to be light sensitive), the compound crystallised as yellow prisms. MF: $C_{34}H_{46}O_{10}N_2S_4ClAg$; ^{1}H NMR (ppm): 7.01d(C5), 6.64m(C4), 3.88s(ThOCH$_2$), 3.68s(ThOCH$_2\underline{CH_2}$), 3.46m(ThCH$_2$N), 2.74s(N$\underline{CH_2}$CH$_2$CH$_3$), 1.36m(NCH$_2\underline{CH_2}$CH$_3$), 0.61t(NCH$_2$CH$_2\underline{CH_3}$); ^{13}C NMR (ppm): 155.16(C3), 124.50(C5), 118.03(C2), 116.11(C4), 71.29(ThOCH$_2$), 70.79(ThOCH$_2\underline{CH_2}$), 68.77(N$\underline{CH_2}$CH$_2$CH$_3$), 49.05(ThCH$_2$N), 20.75(NCH$_2\underline{CH_2}$CH$_3$), 10.89(NCH$_2$CH$_2\underline{CH_3}$); IR (cm^{-1}): 3112.6, 2956.8, 2925.3, 2907.2, 2872.0, 2861.1, 1557.8(Th C=C), **620.51**(s, ClO_4^-); elemental analysis: calc. C 44.66%, H 5.07%, N 3.06%, Cl 3.88%, S 14.03%, O 22.09%, Ag 10.64%, exp. C 44.34%, H 4.99%, N 2.63%, Cl 3.87%, S 13.19%; (M+H)= 707.

Complexation and recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with silver (I) perchlorate **43**



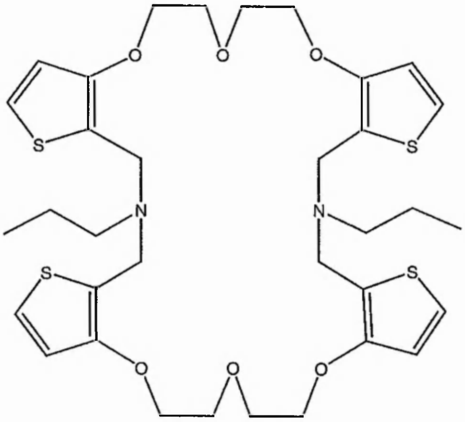
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane ($1cm^3.g^{-1}$), and boiled under reflux. 2eq. of $AgClO_4.2H_2O$ was dissolved in methanol ($1cm^3.g^{-1}$), then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, then the solution was filtered hot and when the solvent evaporated, a brown powder was obtained. The complexed macrocycle was dissolved in a minimum of a 1:1 mixture of methanol/dichloromethane. After a slow evaporation, the complex crystallised as good quality brown crystals. MF: $C_{34}H_{46}O_{14}N_2S_4Cl_2Ag_2$; ^1H NMR (ppm): 7.46d(C5), 6.86d(C4), 3.98s($ThOCH_2$), 3.65m($ThOCH_2\underline{CH_2}$), 3.21m($ThCH_2N$), 2.87m($N\underline{CH_2}CH_2CH_3$), 1.67m($NCH_2\underline{CH_2}CH_3$), 0.83t($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 159.17(C3), 128.91(C5), 117.93(C2/C4), 72.18($ThOCH_2$), 70.73($ThOCH_2\underline{CH_2}$), 54.45($N\underline{CH_2}CH_2CH_3$), 48.83($ThCH_2N$), 18.85($NCH_2\underline{CH_2}CH_3$), 11.30($NCH_2CH_2\underline{CH_3}$); IR ($cm^{-1}$): 3104.6, 3020.6, 2961.2, 2929.9, 2877.2, 2852.4, 1557.7(Th C=C), **624.4**(s, ClO_4^-); (M+H)= 707.

Complexation and recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with potassium (I) isocyanate **44**



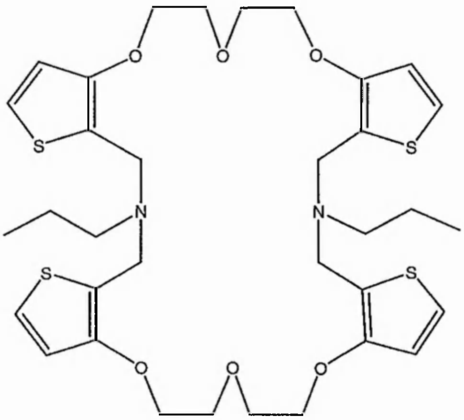
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane ($1cm^3.g^{-1}$), and boiled under reflux. 1eq. of KSCN was dissolved in methanol ($1cm^3.g^{-1}$), then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, then the solution was filtered hot and after a slow evaporation, the complexed macrocycle crystallised and a brown oil was separated. The complexed macrocycle was dissolved in a minimum of a 1:1 mixture of methanol/dichloromethane. After a slow evaporation, the complex crystallised and good quality crystals (brown needles) were obtained. MF: $C_{35}H_{46}O_6N_3S_5K$; ^{1}H NMR (ppm): 7.12d(C5), 6.76d(C4), 4.10t($ThOCH_2$), 3.79m($ThCH_2N$, $ThOCH_2\underline{CH_2}$), 2.50t($N\underline{CH_2}CH_2CH_3$), 1.58q($NCH_2\underline{CH_2}CH_3$), 0.88t($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 153.63(C3), 122.93(C5), 117.23(C2/4), 71.36($ThOCH_2$), 71.22($ThOCH_2\underline{CH_2}$), 70.15($N\underline{CH_2}CH_2CH_3$), 48.21($ThCH_2N$), 20.11($NCH_2\underline{CH_2}CH_3$), 11.71($NCH_2CH_2\underline{CH_3}$); IR ($cm^{-1}$): 3107.0, 2954.4, 2926.1, 2868.4, 2820.9, 2768.3, 2733.0, **2078.8**(s, νCN), **2051.0**(s, νCN), 1555.5(Th C=C), **755.1**(w, νCS), **470.4**(w, νNCS); elemental analysis: calc. C 52.27%, H 5.77%, N 5.23%, S 19.94%, O 11.94%, K 4.86%, exp. C 52.20%, H 5.67%, N 5.63%.

Complexation and recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with potassium (I) isocyanate **45**



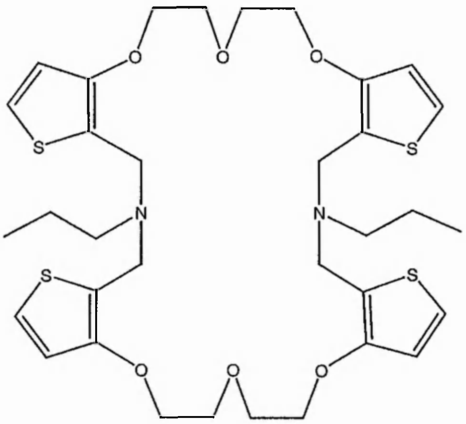
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane (1cm^3.g^{-1}), and boiled under reflux. 2eq. of KSCN was dissolved in methanol (1cm^3.g^{-1}), then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, then the solution was filtered hot and after a slow evaporation, the complexed macrocycle crystallised as brown crystals. The complexed macrocycle was dissolved in a minimum of a 1:1 mixture of methanol/dichloromethane. After a slow evaporation, the complex crystallised as brown needles. MF: $C_{35}H_{46}O_6N_3S_5K$; ^{1}H NMR (ppm): 7.10d(C5), 6.76d(C4), 4.08m($ThOCH_2$), 3.79m($ThCH_2N$, $ThOCH_2\underline{CH_2}$), 2.47m($N\underline{CH_2}CH_2CH_3$), 1.56q($NCH_2\underline{CH_2}CH_3$), 0.87t($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 153.78(C3), 122.82(C5), 117.27(C2/4), 71.37($ThOCH_2$), 71.20($ThOCH_2\underline{CH_2}$), 70.16($N\underline{CH_2}CH_2CH_3$), 48.28($ThCH_2N$), 20.14($NCH_2\underline{CH_2}CH_3$), 11.74($NCH_2CH_2\underline{CH_3}$); IR (cm^{-1}): 3106.6, 2956.4, 2920.2, 2869.5, 2853.2, 2813.4, **2054.4**(s, vCN) 1554.4(Th C=C), **748.6**(w, vCS), **470.8**(w, vNCS); elemental analysis: calc. C 47.97%, H 5.14%, N 6.22%, S 21.34%, O 10.65%, K 8.68%, exp. C 53.28%, H 5.78%, N 5.33%.

Complexation and recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with aluminium(III) sulphate **46**



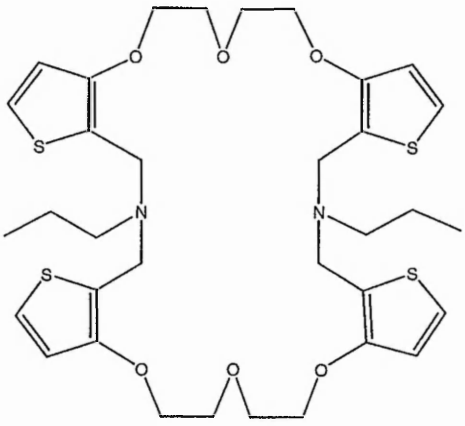
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane (1cm^3.g^{-1}), and boiled under reflux. 0.5eq. of $Al_2(SO_4)_3.18H_2O$ was added to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, then cooled to room temperature. The solution was filtered and solvent evaporated, a pale yellow powder was obtained. The complexed macrocycle was dissolved in the minimum of a 1:1 mixture of ethanol/dichloromethane. After a slow evaporation, the complex crystallised and good quality colourless crystals were obtained. MF: $C_{34}H_{46}O_{18}N_2S_7Al_2$; ^{1}H NMR (ppm): 7.55d(C5), 6.95d(C4), 4.36s($ThCH_2N$), 4.08m($ThOCH_2$), 3.75m($ThOCH_2\underline{CH_2}$), 2.88m($N\underline{CH_2}CH_2CH_3$), 1.76m($NCH_2\underline{CH_2}CH_3$), 0.93t($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 158.83(C3), 128.43(C5), 117.90(C4), 109.03(C2), 72.23($ThOCH_2$), 70.81($ThOCH_2\underline{CH_2}$), 54.09($N\underline{CH_2}CH_2CH_3$), 49.00($ThCH_2N$ hidden by methanol), 19.17($NCH_2\underline{CH_2}CH_3$), 11.46($NCH_2CH_2\underline{CH_3}$); IR (cm^{-1}): 3094.9, 3076.7, 2957.4, 2926.1, 2872.5, 2857.3, 2650.1, 1556.0(Th C=C), **820.9**(m), **740.5**(m), **722.4**(m), **604.4**(m); M+H= 1049; elemental analysis: calc. C 46.51%, H 5.28%, N 3.19%, S 20.09%, O 21.87%, Al 3.07%, exp. C 46.97%, H 5.27%, N 3.05%.

Complexation and recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with aluminium(III) chloride **47**



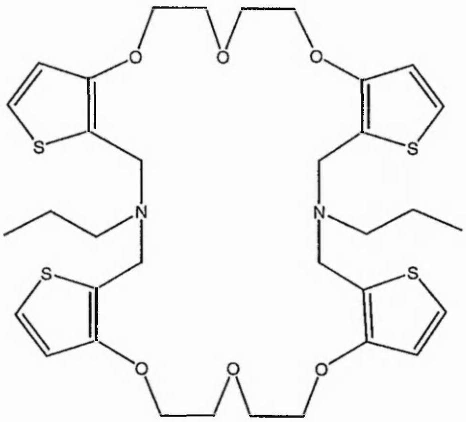
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane (1cm^3.g^{-1}), and boiled under reflux. 1eq. of $AlCl_3.6H_2O$ was dissolved by heating in a 1:1 mixture of dichloromethane/methanol (1cm^3.g^{-1}), then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, then cooled to the room temperature. The solution was filtered and when the solvent evaporated, a yellow powder was obtained. The complexed macrocycle was dissolved in a minimum of a 1:1 mixture of ethanol/dichloromethane. After a slow evaporation, the complex crystallised and good quality yellow crystals were obtained. MF: $C_{34}H_{46}O_6N_2S_4Cl_3Al$; ^{1}H NMR (ppm): 7.34d(C5), 6.71d(C4), 4.33m(ThCH$_2$N), 3.99m(ThOCH$_2$), 3.63m(ThOCH$_2\underline{CH_2}$), 2.73m(N$\underline{CH_2}$CH$_2$CH$_3$), 1.90m(NCH$_2\underline{CH_2}$CH$_3$), 0.87m(NCH$_2$CH$_2\underline{CH_3}$); ^{13}C NMR (ppm): 157.59(C3), 127.33(C5), 115.99(C4), 106.43(C2), 70.96(ThOCH$_2$), 70.55(ThOCH$_2\underline{CH_2}$), 69.62(N$\underline{CH_2}$CH$_2$CH$_3$), 46.91(ThCH$_2$N), 18.02(NCH$_2\underline{CH_2}$CH$_3$), 11.28(NCH$_2$CH$_2\underline{CH_3}$); IR (cm^{-1}): 3104.7, 2953.9, 2922.9, 2869.4, 2854.3, 1735.5, 1714.5, 1697.7, 1556.8(Th C=C), **820.0**(m), **744.7**(m), **723.2**(m).

Complexation and recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with lead (IV) ethanoate **48**



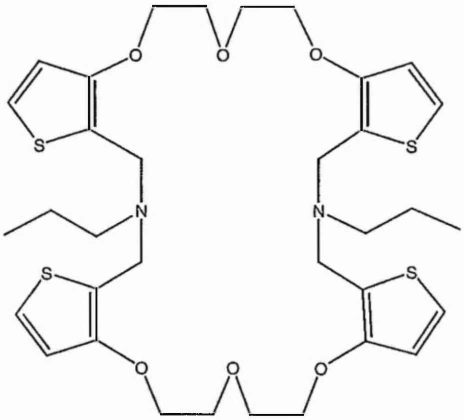
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane (1cm^3.g^{-1}), and boiled under reflux. 1eq. of Pb(IV) ethanoate was dissolved in methanol (1cm^3.g^{-1}), then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, then the solution was filtered hot and when the solvent evaporated, the complexed macrocycle crystallised and a brown oil was separated. The complexed macrocycle was dissolved in a minimum of a 1:1 mixture of methanol/dichloromethane. After a slow evaporation, the complex crystallised as good quality colourless needles. MF: $C_{42}H_{66}O_{10}N_2S_4Pb$; ^{1}H NMR (ppm): 7.22d(C5), 6.84d(C4), 4.07m($ThOCH_2$), 3.80s($ThCH_2N$), 3.73m($ThOCH_2\underline{CH_2}$), 2.44m($N\underline{CH_2}CH_2CH_3$), 1.52m($NCH_2\underline{CH_2}CH_3$), 0.84t($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 155.93(C3), 124.36(C5), 119.81(C2), 113.50(C4), 71.20($ThOCH_2$), 70.38($ThOCH_2\underline{CH_2}$), 58.38($N\underline{CH_2}CH_2CH_3$), 47.95($ThCH_2N$), 18.44($NCH_2\underline{CH_2}CH_3$), 10.80($NCH_2CH_2\underline{CH_3}$); IR (cm^{-1}): 3107.0, 3074.7, 2956.4, 2926.1, 2869.4, 2856.3, 2815.9, 2722.9, 2674.3, 2626.8, 1556.5(Th C=C).

Complexation and recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with lead(II) perchlorate **49**



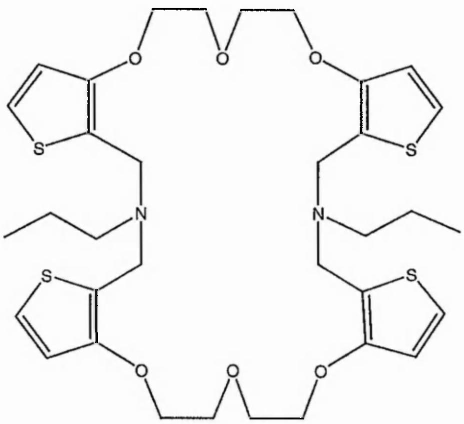
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane (1cm^3.g^{-1}), and boiled under reflux. 1eq. of $Pb(ClO_4)_2.6H_2O$ was dissolved in methanol (1cm^3.g^{-1}), then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot and, when the solvent evaporated, a brown powder was obtained. The complexed macrocycle was dissolved in a minimum of a 1:1:1 mixture of methanol/dichloromethane/cyclohexane. After a slow evaporation, the complex crystallised and good quality orange prismatic crystals were obtained. MF: $C_{34}H_{46}O_{14}N_2S_4Cl_2Pb$; ^{1}H NMR (ppm): 7.48d(C5), 6.86d(C4), 4.30s($ThCH_2N$), 3.97m($ThOCH_2$), 3.65m($ThOCH_2\underline{CH_2}$), 2.88m($N\underline{CH_2}CH_2CH_3$), 1.64m($NCH_2\underline{CH_2}CH_3$), 0.84t($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 155.45(C3), 127.98(C5), 119.91(C2), 117.91(C4), 72.19($ThOCH_2$), 70.71($ThOCH_2\underline{CH_2}$), 59.27($N\underline{CH_2}CH_2CH_3$), 47.16($ThCH_2N$), 20.26($NCH_2\underline{CH_2}CH_3$), 9.56($NCH_2CH_2\underline{CH_3}$); IR (cm^{-1}): 3109.0, 2963.4, 2934.1, 2875.2, 2783.8, 1556.0(Th C=C), **625.1**(s, ClO_4^-).

Complexation and recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with copper (II) perchlorate **50**



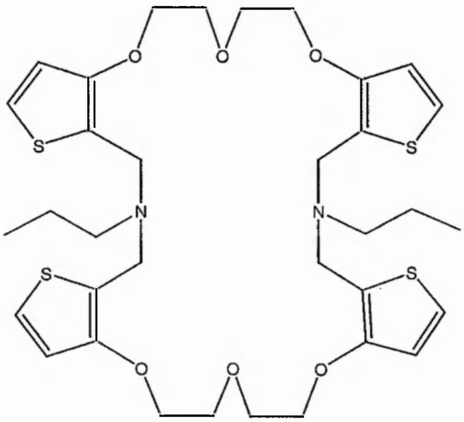
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane ($1cm^3.g^{-1}$), and was boiled under reflux. 1eq. of $Cu(ClO_4)_2.6H_2O$ was dissolved in methanol ($1cm^3.g^{-1}$), then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, then the mixture was cooled to the room temperature. The solution was filtered, then the solvent evaporated. The complexed macrocycle was dissolved in a minimum of a 1:1 mixture of methanol/dichloromethane. After a slow evaporation, the complex crystallised and good quality crystals were obtained as colourless rhomboids. MF: $C_{34}H_{46}O_{14}N_2S_4Cl_2Cu$; ^1H NMR (ppm): 7.13m(C5), 6.59d(C4), 4.01m($ThOCH_2$), 3.82s($ThOCH_2\underline{CH_2}$), 3.49s($ThCH_2N$), 2.74m($N\underline{CH_2}CH_2CH_3$), 1.40m($NCH_2\underline{CH_2}CH_3$), 1.08s($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 153.89(C3), 127.13(C5), 117.78(C2), 116.18(C4), 71.77($ThOCH_2$), 70.38($ThOCH_2\underline{CH_2}$), 55.85($N\underline{CH_2}CH_2CH_3$), 47.16($ThCH_2N$), 18.87($NCH_2\underline{CH_2}CH_3$), 10.57($NCH_2CH_2\underline{CH_3}$); IR ($cm^{-1}$): 3104.0, 3032.5, 2954.4, 2927.1, 2874.5, 2854.3, 2685.4, 1560.6(Th C=C), **621.2**(s, ClO_4^-); elemental analysis: calc. C 42.12%, H 4.78%, N 2.89%, Cl 7.31%, S 13.23%, O 23.11%, Cu 6.55%, exp. C 41.73%, H 5.25%, N 1.61%, Cl 7.83%.

Complexation and recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with copper (II) chloride **51**



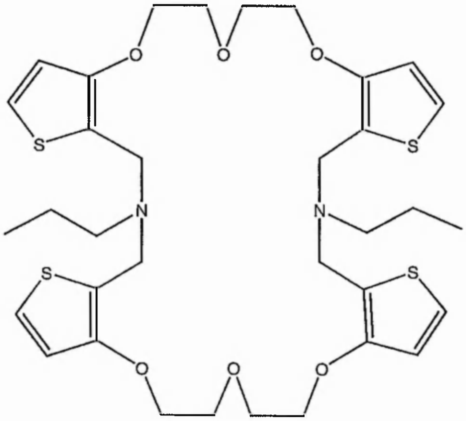
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane ($1cm^3.g^{-1}$), and was boiled under reflux. 1eq. of $CuCl_2.2H_2O$ was dissolved in a 1:1 mixture of methanol/dichloromethane ($1cm^3.g^{-1}$), then was added dropwise to the stirred macrocyclic solution. During the addition, a green precipitate appeared (**A**). The reflux and stirring were maintained for 1h, then the mixture was filtered hot and separated in two halves. The green precipitate (**A**), which was left on the filter paper, was dried in the vacuum oven and used for analysis. The first half was left for a slow evaporation of the solvents and a yellow-brown oil was obtained (**B**). The solvents of the second half were evaporated under reduced pressure (a yellow-brown oil then crystallised at 4°C and yellow needles were obtained but were not suitable for diffraction, (**C**)) and dried, then used for analysis. MF: $C_{34}H_{46}O_6N_2S_4Cl_2Cu$; **A** ^1H NMR (ppm): 7.30s(C5), 6.76s(C4), 4.22s($ThOCH_2$), 4.07s($ThOCH_2\underline{CH_2}$), 3.76s($ThCH_2N$), 2.73m($N\underline{CH_2}CH_2CH_3$), 1.87m($NCH_2\underline{CH_2}CH_3$), 0.90s($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 156.89(C3), 126.57(C5), 116.67(C2), 116.45(C4), 71.09($ThOCH_2$), 69.89($ThOCH_2\underline{CH_2}$), 51.41($N\underline{CH_2}CH_2CH_3$), 47.45($ThCH_2N$), 18.78($NCH_2\underline{CH_2}CH_3$), 11.89($NCH_2CH_2\underline{CH_3}$); **B** ^1H NMR (ppm): 7.22s(C5), 6.72s(C4), 4.09s($ThOCH_2$), 3.99s($ThOCH_2\underline{CH_2}$), 3.67s($ThCH_2N$), 2.63s($N\underline{CH_2}CH_2CH_3$), 1.70s($NCH_2\underline{CH_2}CH_3$), 0.82s($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 156.13(C3), 125.83(C5), 116.75(C2), 116.29(C4), 70.67($ThOCH_2$), 69.46($ThOCH_2\underline{CH_2}$), 52.05($N\underline{CH_2}CH_2CH_3$), 47.10($ThCH_2N$), 18.42($NCH_2\underline{CH_2}CH_3$), 11.07($NCH_2CH_2\underline{CH_3}$); **C** ^1H NMR (ppm): 7.24d(C5), 6.75d(C4), 4.12s($ThOCH_2$), 4.04s($ThOCH_2\underline{CH_2}$), 3.73s($ThCH_2N$), 2.65s($N\underline{CH_2}CH_2CH_3$), 1.75s($NCH_2\underline{CH_2}CH_3$), 0.88t($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 156.15(C3), 125.67(C5), 116.75(C2), 116.54(C4), 71.00($ThOCH_2$), 69.80($ThOCH_2\underline{CH_2}$), 53.37($N\underline{CH_2}CH_2CH_3$), 47.40($ThCH_2N$), 18.84($NCH_2\underline{CH_2}CH_3$), 11.39($NCH_2CH_2\underline{CH_3}$); **A** IR ($cm^{-1}$): 3446.6, 3351.6, 2960.3, 2923.3, 2873.8, 2854.8, 1558.2(Th C=C), **802.2**(s), **744.7**(s), **665.7**(w, sp), **593.0**(w); **B** IR (cm^{-1}): 3050.4, 2954.4, 2924.2, 2854.2, 1556.7(Th C=C), **738.7**(w, sp); **C** IR (cm^{-1}): 3110.6, 3049.7, 2964.3, 2934.4, 2878.0, 1555.1(Th C=C), **739.6**(w, sp); **A** (M+H)= 707; **B** (M+H)= 707; **C** (M+H)= 707.

Complexation and recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with nickel(II) perchlorate **52**



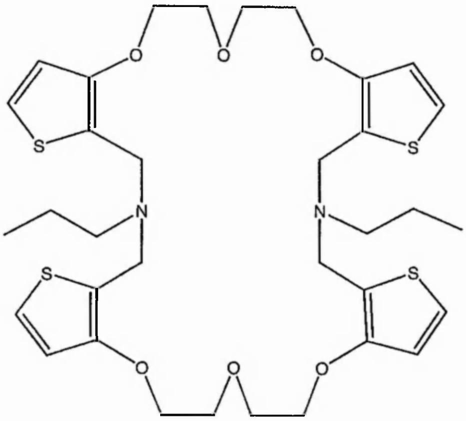
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane ($1cm^3.g^{-1}$), and boiled under reflux. 1eq. of $Ni(ClO_4)_2.6H_2O$ was dissolved in methanol ($1cm^3.g^{-1}$), then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot and, when the solvent evaporated, a green powder was obtained. The complexed macrocycle was dissolved in a minimum of a 1:1:1 mixture of methanol/dichloromethane/cyclohexane. After a slow evaporation, the complex crystallised and good quality green crystals were obtained. MF: $C_{34}H_{46}O_{14}N_2S_4Cl_2Ni$; ^1H NMR (ppm): 6.91m(C5), 6.80m(C4), 4.20m($ThOCH_2$), 3.83m($ThOCH_2\underline{CH_2}$), 3.67m($ThCH_2N$), 2.82m($N\underline{CH_2}CH_2CH_3$), 1.26m($NCH_2\underline{CH_2}CH_3$), 1.16m($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 154.13(C3), 127.62(C5), 119.46(C2), 114.89(C4), 72.22($ThOCH_2$), 69.76($ThOCH_2\underline{CH_2}$), 60.21($N\underline{CH_2}CH_2CH_3$), 47.59($ThCH_2N$), 18.84($NCH_2\underline{CH_2}CH_3$), 9.46($NCH_2CH_2\underline{CH_3}$); IR ($cm^{-1}$): 3101.9, 3032.0, 2963.9, 2933.5, 2877.9, 2806.3, 2777.6, 2684.5, 1559.3(Th C=C), **621.2**(s, ClO_4^-); elemental analysis: calc. C 42.34%, H 4.81%, N 2.90%, Cl 7.35%, S 13.30%, O 23.22%, Ni 6.08%, exp. C 43.53%, H 5.73%, N 2.51%, Cl 7.62%.

Complexation and recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with zinc(II) perchlorate **53**



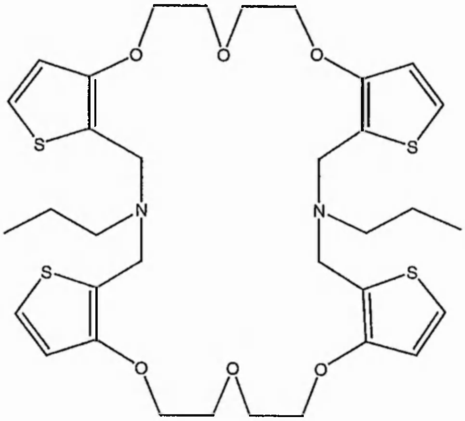
The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane (1cm^3.g^{-1}), and boiled under reflux. 1eq. of Zn(ClO$_4$)$_2$.6H$_2$O was dissolved in methanol (1cm^3.g^{-1}), then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot and, when the solvent evaporated, a white powder was obtained. The complexed macrocycle was dissolved in a minimum of a 1:1:1 mixture of methanol/dichloromethane/cyclohexane. After a slow evaporation, the complex crystallised and good quality white cubic crystals were obtained. MF: $C_{34}H_{46}O_{14}N_2S_4Cl_2Zn$; IR (cm^{-1}): 3109.0, 2962.5, 2932.1, 2878.5, 2794.6, 2665.2, 2659.9, 1558.7(C=C), **621.1**(s, ClO$_4^-$); elemental analysis: calc. C 42.04%, H 4.77%, N 2.88%, Cl 7.30%, S 13.21%, O 23.06%, Zn 6.73%, exp. C 41.90%, H 5.49%, N 2.03%, Cl 7.23%.

Complexation and recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with cobalt(II) perchlorate **54**



The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane ($1cm^3.g^{-1}$), and boiled under reflux. 1eq. of $Co(ClO_4)_2.6H_2O$ was dissolved in methanol ($1cm^3.g^{-1}$), then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot and, when the solvent evaporated, a pink-brown powder was obtained. The complexed macrocycle was dissolved in a minimum of a 1:1:1 mixture of methanol/dichloromethane/cyclohexane. After a slow evaporation, the complex crystallised and good quality pale yellow prismatic crystals were obtained. MF: $C_{34}H_{46}O_{14}N_2S_4Cl_2Co$; ^1H NMR (ppm): 6.92m(C5), 6.80m(C4), 4.23m($ThOCH_2$), 3.86m($ThCH_2N$, $ThOCH_2\underline{CH_2}$), 2.84m($N\underline{CH_2}CH_2CH_3$), 1.64m($NCH_2\underline{CH_2}CH_3$), 0.92m($NCH_2CH_2\underline{CH_3}$); ^{13}C NMR (ppm): 156.07(C3), 124.09(C5), 118.88(C2), 116.48(C4), 71.68($ThOCH_2$), 69.77($ThOCH_2\underline{CH_2}$), 57.69($N\underline{CH_2}CH_2CH_3$), 46.33($ThCH_2N$), 19.20($NCH_2\underline{CH_2}CH_3$), 8.29($NCH_2CH_2\underline{CH_3}$); IR ($cm^{-1}$): 3106.0, 3021.0, 2962.5, 2931.1, 2877.5, 2854.3, 2801.7, 2776.4, 2737.1, 2683.4, 1556.0(Th C=C), **620.9**(s, ClO_4^-).

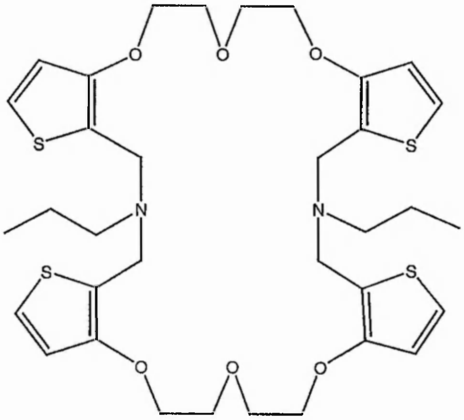
Complexation and recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with iron(II) perchlorate **55**



The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane ($1cm^3.g^{-1}$), and boiled under reflux. 1eq. of $Fe(ClO_4)_2.6H_2O$ was dissolved in methanol ($1cm^3.g^{-1}$), then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot and, when the solvent evaporated, a yellow-orange powder was obtained. The complexed macrocycle was dissolved in a minimum of a 1:1:1 mixture of methanol/dichloromethane/cyclohexane. After a slow evaporation, the complex crystallised and good quality yellow-orange cubic crystals were obtained. MF:

$C_{34}H_{46}O_{14}N_2S_4Cl_2Fe$; ^1H NMR (ppm): 6.88m(C5), 6.78m(C4), 4.18m(ThOCH$_2$), 3.81m(ThCH$_2$N, ThOCH$_2$$\underline{CH_2}$), 2.80m(N$\underline{CH_2}CH_2CH_3$), 1.68m(NCH$_2$$\underline{CH_2}CH_3$), 0.89m(NCH$_2CH_2$$\underline{CH_3}$); ^{13}C NMR (ppm): 154.77(C3), 125.45(C5), 119.45(C2), 116.77(C4), 71.09(ThOCH$_2$), 69.67(ThOCH$_2$$\underline{CH_2}$), 61.35(N$\underline{CH_2}CH_2CH_3$), 46.55(ThCH$_2$N), 22.01(NCH$_2$$\underline{CH_2}CH_3$), 10.09(NCH$_2CH_2$$\underline{CH_3}$); IR (cm^{-1}): 3108.0, 2957.4, 2925.0, 2872.5, 2854.3, 2821.9, 2664.2, 1558.9(Th C=C), **621.4**(s, ClO_4^-).

Complexation and recrystallisation of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with manganese(II) perchlorate **56**



The title macrocyclic ligand was dissolved in a 1:1 mixture of methanol/dichloromethane (1cm^3.g^{-1}), and boiled under reflux. 1eq. of $Mn(ClO_4)_2.6H_2O$ was dissolved in methanol (1cm^3.g^{-1}), then was added dropwise to the stirred macrocyclic solution. The reflux and stirring were maintained for 1h, filtered hot and, when the solvent evaporated, a yellow-orange powder was obtained. The complexed macrocycle was dissolved in a minimum of a 1:1:1 mixture of methanol/dichloromethane/cyclohexane. After a slow evaporation, the complex crystallised and good quality pink prismatic crystals were obtained. MF: $C_{34}H_{46}O_{14}N_2S_4Cl_2Mn$; ^1H NMR (ppm): 6.92m(C5), 6.46m(C4), 3.67m(ThOCH$_2$), 3.35m(ThCH$_2$N, ThOCH$_2$$\underline{CH_2}$), 2.26m(N$\underline{CH_2}CH_2CH_3$), 1.24m(NCH$_2$$\underline{CH_2}CH_3$), 0.84m(NCH$_2CH_2$$\underline{CH_3}$); ^{13}C NMR (ppm): 153.81(C3), 124.37(C5), 116.35(C4), 106.58(C2), 70.08(ThOCH$_2$), 68.72(ThOCH$_2$$\underline{CH_2}$), 61.35(N$\underline{CH_2}CH_2CH_3$), 46.93(ThCH$_2$N), 17.58(NCH$_2$$\underline{CH_2}CH_3$), 10.15(NCH$_2CH_2$$\underline{CH_3}$); IR (cm^{-1}): 3106.0, 2957.4, 2924.0, 2869.4, 2853.3, 2682.4, 1557.9(Th C=C), **621.0**(s, ClO_4^-).

Nuclear Magnetic Resonance (^{1}H and ^{13}C)

Nuclear magnetic resonance spectroscopy (NMR) was performed with a JEOL EX 270MHz machine; solvents used were deuterated chloroform or deuterated methanol or deuterated dimethyl sulfoxide.

Infrared Spectroscopy (FTIR)

The FTIR infrared spectra (IR) were obtained (KBr pellet technique: 2 mg solid per 200 mg KBr; 4000-400cm^{-1}) using a Nicolet Magna-IR^{TM} spectrometer 750 with DTGS (KBr) detector, and a KBr beam splitter operating at a resolution of 2cm^{-1} with 64 scans being accumulated for each sample.

X-ray crystallography study

The X-ray study was carried out with a RIGAKU AFC 7-R diffractometer, using a RIGAKU RU-H2R rotating anode generator. The data were analysed with the teXsan program[340].

1. Crystallographic methods

1.1. Crystal selection and mounting

Using a microscope, a good quality crystal was selected. The crystal chosen should be a reasonable size, (ideally so that the whole of the crystal is bathed in the X-ray beam) have morphology characteristic of the batch and possess smooth faces free from contamination by other crystal fragments. Once a crystal had been selected, it was then examined under a polarising microscope. Polarised light does not interact with non-cubic crystals in a uniform manner[341] and when a face of a crystal is rotated extinction may occur. If the face of the crystal fully extinguishes then a crystal axis is located in this direction. Once an axis had been located the crystal was mounted to rotate about this axis in preparation for X-ray diffraction. The crystal was mounted an adjustable goniometer head[342] by supergluing a very thin glass fibre along the crystal axis. The crystal was centered by eye. This usually involved moving the tranverse slides of the goniometer head in sequence, rotating the crystal by 90° or 180° between each movement until the crystal became exactly aligned. This was done by looking at the crystal down a cross-haired microscope mounted on the instrument. The crystal was then oriented automatically by the diffractometer using a zigzag χ-scan procedure to locate and centre strong reflections.

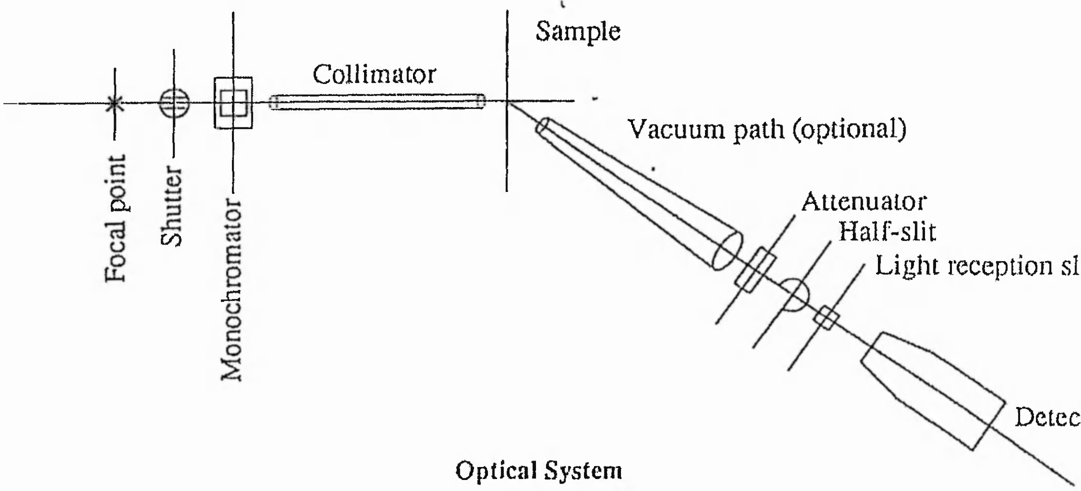
1.2. Intensity data collection

1.2.a. The 4-circle diffractometer

The RIGAKU AFC 7R diffractometer uses graphite monochromated Mo-Kα (λ= 0.71069 Å) X-ray radiation produced by a RIGAKU RU-H2R rotating anode generator. The power used can be varied if desired but for the structures reported here data were collected at 50kV and 50mA (a target loading of 2.5kW). The 4-axis goniometer is designed to be fully automatically controlled by a computer. This goniometer can be divided into the following sections:

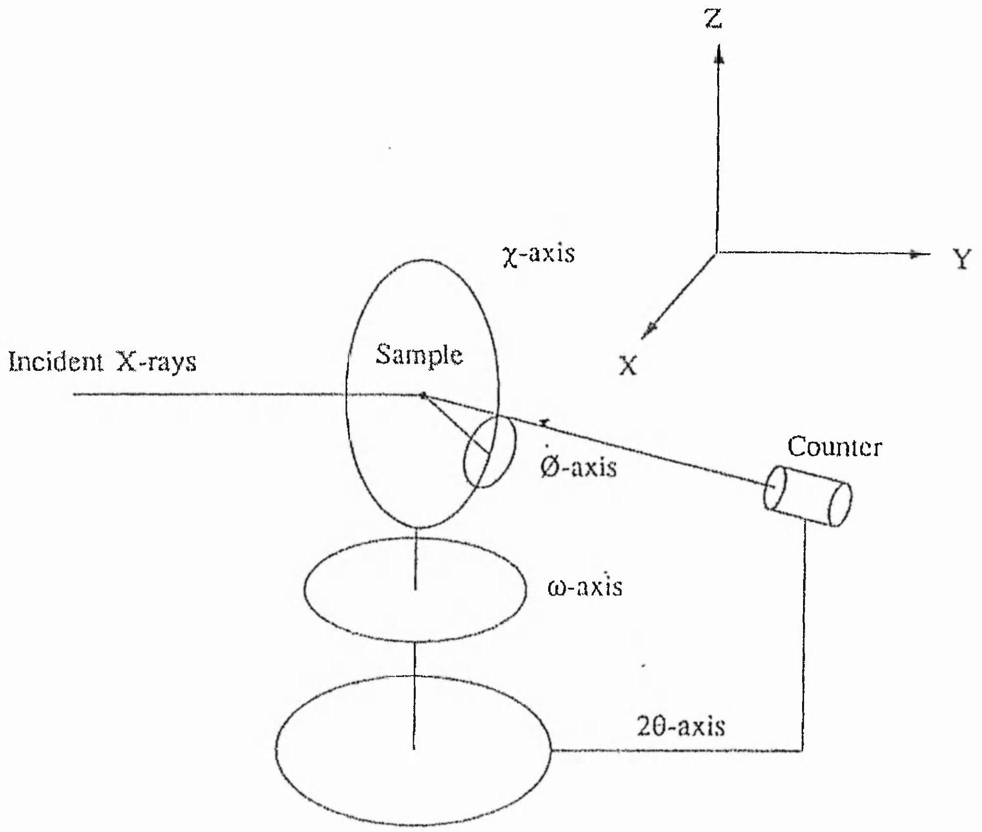
- 4-axis goniometer section
- X-ray tube section
- Monochromator/collimator section
- Sample setup/telescope section
- Attenuator (Zr foil (factor= 9.43))/light reception slit/detector section

The optical system of the goniometer is shown schematically below (scheme 3):



Optical System

The 4-axis goniometer section has the 2θ-, ω-, χ- and Ø-axes. The axis structure is shown below (scheme 4):



Axis Structure

1.2.b. Data collection

Cell constants and an orientation matrix for data collection were obtained automatically from a least-squares refinement using the setting angles of 25 carefully centered reflections. The data were collected at a temperature of 20±1°C using the ω-2θ scan technique to a maximum $2\theta \geq 50°$. Omega scans of several intense reflections, made prior to data collection, were examined to determine an average width at half-height. During the data collection the weak reflections ($I < 15.0\sigma(I)$) were rescanned (maximum of 4 scans) and the counts were accumulated to ensure good counting statistics. Data was collected in four shells to minimise any loss due to instrument failure. The ratio of peak counting time to background counting time was 2:1. The diameter of the diffractometer is 235 mm. The computer-controlled detector slits were initially set to 9.0 mm (horizontal) and 13.0 mm (vertical) and were narrowed down automatically to (usually) 3mm * 3mm by scanning though a number of strong reflections and establishing the intensity drop as the slits are narrowed.

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1.2.c. Data manipulation

1.2.c.1. Data Reduction: General method

Once the data had been collected, equivalent reflections were merged, and a decay correction applied using the intensities of three standard reflections were measured after every 200 reflections.

The data were corrected for Lorentz and polarization effects. Psi-scans of several strong reflections allowed the linear absorption coefficient, μ, to be calculated and indicated the need or not for an empirical absorption correction (transmission factors). An absorption correction was usually applied.

The input file to teXsan consisted of the intensity data headed by various factors pertaining to the specifics of the diffractometer and the console commands used during data collection. The output of the data reduction program (F^2 and $\sigma(F^2)$ placed on a common scale using decay factors determined from three standard reflections measured every 200 reflections) was copied to the input file for structure solution. A number of programs are available including SIR88, SIR97, MULTAN and SHELX97, for the structures reported here direct methods were used with the program of choice being SIR97[343]. The teXsan program also requires an instruction file, the contents varying with the task being performed.

- TeXsan[340] is an automatic solution program, which combines all of the computational elements required to solve a crystal structure given a set of post data reduction intensity data. The elements include absorption correction, direct methods routines[343], least squares refinement[344] and various Fourier syntheses[345].

1.2.c.2. Structure Solution and Refinement: General method

The structure was usually solved by direct methods[343] (Patterson methods were occasionally used) and expanded using Fourier techniques[344]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement[345] on F was based on the number of observed reflections ($I > 3.00\sigma(I)$) and the number of variable parameters and converged (largest parameter shift (times its esd)) with unweighted and weighted agreement factors of:

$$R = \Sigma \,||F_o| - |F_c|| / \Sigma \,|F_o|$$

$$R_W = [\, \Sigma\, w\, (|F_o| - |F_c|)^2 / \Sigma\, w\, F_o^2\,]^{1/2}$$

The observation of unit weight[346] showed a standard deviation or goodness of fit indicator. The weighting scheme was based on counting statistics and included a factor p to downweight the intense reflections. Plots of $\Sigma\, w\, (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices were examined for unusual trends. The final difference Fourier map gave the maximum and minimum peaks ($e^-/\text{Å}^3$).

Neutral atom scattering factors were taken from Cromer and Waber[347].The values for the mass attenuation coefficients were those of Creagh and Hubbell[348]. All calculations were performed using the teXsan[340] crystallographic software package of Molecular Structure Corporation.

Once most of the atom positions had been located from SIR97, least squares refinement followed by difference Fourier syntheses were used to locate the remainder of the atoms including all hydrogens. Bond lengths, angles and deviations from least squares planes were calculated from the "Parameter" routines and molecular drawings produced using ORTEP and Chemdraw 5.0.

Molecular modelling

The Gaussian(R) 98 program is a molecular modelling package which allows the refinement of structures built using Chem 3D[349]. The Windows NT version was used. Gaussian is capable of predicting many properties of molecules and reactions, including the following[350]:

- Molecular energies and structures
- Energies and structures of transition states
- Bond and reaction energies
- Molecular orbitals
- Multipole moments
- Atomic charges and electrostatic potentials
- Vibrational frequencies

- IR and Raman spectra
- NMR properties
- Polarizabilities and hyperpolarizabilities
- Thermochemical properties
- Reaction pathways

Computations can be carried out on systems in the gas phase or in solution, and in their ground state or in an excited state. Gaussian can serve as a powerful tool for exploring areas of chemical interest like substituent effects, reaction mechanisms, potential energy surfaces, and excitation energies.

The Gaussian program was used to optimise the molecular energy and structure. The procedure followed was – first the molecule was drawn using Chem 3D from the ChemOffice suite of programs and then optimised using:

- First MM2 (job type: minimise energy)
- MOPAC (job type: minimise energy, theory: PM3, properties: gradient norm)
- A GAUSSIAN input file was then created and used in GAUSSIAN to minimise the optimum structure.
  - Job type: minimise energy
  - Theory: method: Hartree-Fock
    - wave function: closed shell
    - basis set: 6-31G
    - diffuse: none
    - heavy atom: d
    - hydrogens: p
    - spin multiplicity: 1
  - Properties: as default setting
  - General: gas phase

1. Model chemistries

Gaussian includes many different model chemistries. Model chemistries are characterized by the combination of the theoretical procedure and basis set. Every calculation performed with Gaussian must specify the desired theoretical model chemistry in addition to specifying the molecular system to consider and which results to compute for it.

2. Method

The Gaussian program contains a hierarchy of procedures corresponding to different approximation methods (commonly referred to as different levels of theory). The ones which were used most often in this work are listed in the following table[361] (table 4):

Table 4.

Keyword	Method	Availability
HF	Hartree-Fock Self-Consistent Field	Through 2nd derivatives
B3LYP	Becke-style 3-Parameter Density Functional Theory (using the Lee-Yang-Parr correlation functional)	Through 2nd derivatives
MP2	2nd Order Møller-Plesset Perturbation Theory	Through 2nd derivatives
MP4	4th Order Møller-Plesset Perturbation Theory (including Singles, Doubles, Triples and Quadruples by default)	Energies only
QCISD(T)	Quadratic CI (Single, Doubles & Triples)	Energies only

Semi-empirical methods are characterized by their use of parameters derived from experimental data in order to simplify the approximation to the Schrödinger equation. As such, they are relatively inexpensive and can be practically applied to very, very large molecules. There are a variety of semi-empirical methods. Among the best known are AM1, PM3 and MNDO. Gaussian includes a variety of semi-empirical models, and they are also the central focus or present in many other programs including AMPAC, MOPAC, HyperChem and Spartan. Semi-empirical methods may only be used for systems where parameters have been developed for all of their component atoms. In addition to this, semi-empirical models have a number of well-known limitations. Types of problems on which they do not perform well include hydrogen bonding, transition structures, molecules containing atoms for which they are poorly parametrized, and so on.

The Hartree-Fock method provides reasonable model for a wide range of problems and molecular systems. However, Hartree-Fock theory also has limitations. They arise principally from the fact that Hartree-Fock theory does not include a full treatment of the effects of electron correlation: the energy contributions arising from electrons interacting with one another. For systems and situations where such effects are important, Hartree-Fock results may be not satisfactory. A variety of theoretical methods have been developed which include some effects of electron correlation. Traditionally, such methods are referred to as post-SCF methods because they add correlation corrections to the basic Hartree-Fock model. There are many correlation methods available in Gaussian, including the following:

- Møller-Plesset perturbation theory (MP2, MP3, MP4, MP5 and MP4SDQ)
- Quadratic CI energies (QCISD, QCISD(T) and QCISD(TQ))
- Coupled Cluster methods (CCD, CCSD and CCSD(T))
- Brueckner Doubles energies (BD, BD(T) and BD(TQ))

All these methods provide some improvement in the accurate description of molecules, but they vary quite a bit in terms of computational cost.

Hartree-Fock theory is very useful for providing initial, first-level predictions for many systems. It is also reasonably good at computing the structures and vibrational frequencies of stable molecules and some transition states. As such, it is a good basis-level theory. However, its neglect of electron correlation makes it unsuitable for some purposes. For example, it is insufficient for accurate modelling of the energetic of reactions and bond dissociation.

3. Wave function

Although not strictly part of a model chemistry, there is a third component to every Gaussian calculation improving how spin is handled: whether it is performed using an open shell model or a closed shell model; the two options are also referred to as unrestricted and restricted calculations, respectively. We chose closed shell calculations, which use doubly occupied orbitals, each containing two electrons of opposite spin. Open shell systems – for example, those with unequal numbers of spin up and spin down electrons – are usually modeled by a spin unrestricted model (which is the default for these systems in Gaussian). Restricted, closed shell calculations force each electron pair into a single spatial orbital, while open shell calculations use separate spatial orbitals for the spin up and the spin down electrons (α and β respectively).

4. Basis set

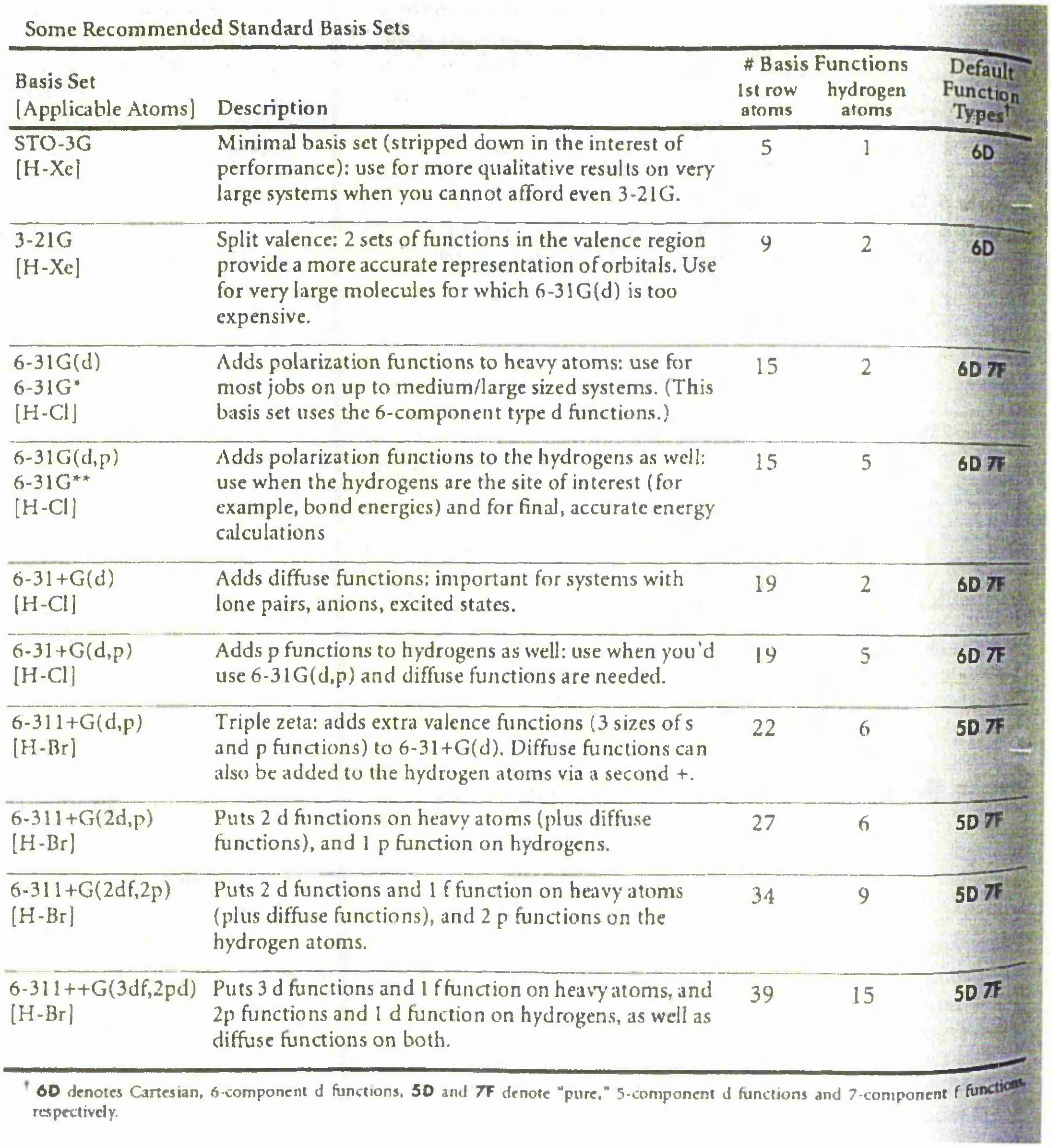
A basis set is a mathematical representation of the molecular orbitals within a molecule. The basis set can be interpreted as restricting each electron to a particular region of space. Larger basis sets impose fewer constraints on electrons and more accurately approximate exact molecular orbitals.

Minimal basis sets contain the minimum number of basis functions needed for each atom. Minimal basis sets use fixed-size atomic-type orbitals. The STO-3G basis set is a minimal basis set (although it is not the smallest possible basis set). The first way that a basis set can be made is to increase the number of basis functions per atom. Split valence basis sets, such as 3-21G and 6-31G, have two (or more) sizes of basis function for each valence orbital. For this work a 6-31G, triple split valence basis set, which uses three sizes of contracted functions for each orbital-type was used. Split valence basis sets allow orbitals to change size, but not to change shape. Polarized basis sets remove this limitation by adding orbitals with angular momentum beyond what is required for the ground state to the description of each atom. The 6-31G basis set with d functions added to heavy atoms, such as the sulphur atom, is becoming very common for calculations involving up to medium-sized systems, and is known as 6-31G(d) or 6-31G*. It was decided to use another popular polarized basis set which is 6-31G(d,p), also known as 6-31G**, which adds p functions to hydrogen atoms in addition to the d functions on heavy atoms, for the present work.

5. Diffuse functions

Diffuse functions are large-size versions of s- and p-type functions (as opposed to the standard valence-size functions). They allow orbitals to occupy a larger region of space. Basis sets with diffuse functions are important for systems where electrons are relatively far from the nucleus: molecules with lone pairs, anions and other systems with significant negative charge, systems in their excited states, systems with low ionization potentials, description of absolute acidities, and so on. This did not apply to the present work so it was decided to use non-diffuse functions.

Table 5[362].



Some Recommended Standard Basis Sets

Basis Set [Applicable Atoms]	Description	# Basis Functions 1st row atoms	 hydrogen atoms	Default Function Types†
STO-3G [H-Xe]	Minimal basis set (stripped down in the interest of performance): use for more qualitative results on very large systems when you cannot afford even 3-21G.	5	1	6D
3-21G [H-Xe]	Split valence: 2 sets of functions in the valence region provide a more accurate representation of orbitals. Use for very large molecules for which 6-31G(d) is too expensive.	9	2	6D
6-31G(d) 6-31G* [H-Cl]	Adds polarization functions to heavy atoms: use for most jobs on up to medium/large sized systems. (This basis set uses the 6-component type d functions.)	15	2	6D 7F
6-31G(d,p) 6-31G** [H-Cl]	Adds polarization functions to the hydrogens as well: use when the hydrogens are the site of interest (for example, bond energies) and for final, accurate energy calculations	15	5	6D 7F
6-31+G(d) [H-Cl]	Adds diffuse functions: important for systems with lone pairs, anions, excited states.	19	2	6D 7F
6-31+G(d,p) [H-Cl]	Adds p functions to hydrogens as well: use when you'd use 6-31G(d,p) and diffuse functions are needed.	19	5	6D 7F
6-311+G(d,p) [H-Br]	Triple zeta: adds extra valence functions (3 sizes of s and p functions) to 6-31+G(d). Diffuse functions can also be added to the hydrogen atoms via a second +.	22	6	5D 7F
6-311+G(2d,p) [H-Br]	Puts 2 d functions on heavy atoms (plus diffuse functions), and 1 p function on hydrogens.	27	6	5D 7F
6-311+G(2df,2p) [H-Br]	Puts 2 d functions and 1 f function on heavy atoms (plus diffuse functions), and 2 p functions on the hydrogen atoms.	34	9	5D 7F
6-311++G(3df,2pd) [H-Br]	Puts 3 d functions and 1 f function on heavy atoms, and 2p functions and 1 d function on hydrogens, as well as diffuse functions on both.	39	15	5D 7F

† **6D** denotes Cartesian, 6-component d functions, **5D** and **7F** denote "pure," 5-component d functions and 7-component f functions respectively.

X-ray crystallography data tables

1. Diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate **15**

Table 6. Summary of the crystal data, and structure solution and refinement parameters

A. Crystal Data

Empirical Formula	$C_8H_{12}O_6S$
Formula Weight	236.24
Crystal Color, Habit	colourless, prism
Crystal Dimensions	0.72 X 0.36 X 0.36 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (38.3 - 40.8°)
Omega Scan Peak Width at Half-height	0.22°
Lattice Parameters	a = 8.92(6) Å, b = 20.02(5) Å, c = 13.74(4) Å β = 98.2(4) Å, V = 2427(15) Å^3
Space Group	$P2_1/c$ (#14)
Z value	8
Dcalc	1.293 g/cm^3
F000	992
μ(MoKα)	2.72 cm^{-1}
Slit Aperture	3.0 mm horizontal, 3.0 mm vertical
Scan Width	(1.63 + 0.35 tan θ)°
2θmax	55.1°
No. of Reflections Measured	Total: 6105, Unique: 5751 (Rint = 0.092)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.8103 - 1.0000)

B. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma w (\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
p-factor	0.0025
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	4100
No. Variables	379
Reflection/Parameter Ratio	10.82
Residuals: R; Rw	0.055 ; 0.069
Goodness of Fit Indicator	5.86
Max Shift/Error in Final Cycle	2.5

Maximum peak in Final Diff. Map	0.30 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.41 $e^-/Å^3$

Table 7. Atomic coordinates and Biso/Beq

Estimated standard deviations (esd) are given in brackets.

Atomic coordinates and Biso/Beq[351]				
Atom	X	Y	Z	Beq
S(1)	0.78197(5)	-0.03278(2)	0.95108(3)	3.73(1)
S(2)	0.64247(5)	0.01283(2)	0.61398(3)	3.44(1)
O(1)	0.6289(2)	-0.20736(7)	1.0206(1)	6.78(5)
O(3)	0.4835(1)	-0.08042(6)	0.73143(8)	3.97(3)
O(4)	0.9186(1)	0.07062(6)	0.83508(8)	4.06(3)
O(5)	1.0164(1)	-0.00145(6)	0.73585(9)	4.67(3)
O(6)	0.7728(1)	0.13076(6)	0.53260(9)	4.53(3)
O(7)	0.8519(2)	-0.06315(7)	0.4096(1)	4.95(4)
O(8)	0.9608(2)	-0.13600(6)	0.7556(1)	4.93(4)
O(9)	0.8156(2)	-0.21958(8)	0.8745(1)	5.55(4)
O(10)	0.8715(1)	0.07971(6)	0.41049(9)	4.73(3)
O(11)	0.7199(2)	-0.16246(7)	0.5094(1)	5.94(4)
O(12)	0.5364(2)	-0.17491(6)	0.6550(1)	5.59(4)
O(13)	0.6130(2)	-0.10545(7)	1.0871(1)	6.36(4)
C(1)	0.8912(2)	-0.10987(9)	0.8284(1)	3.60(4)
C(15)	0.7745(2)	-0.04688(9)	0.4833(1)	3.43(4)
C(16)	0.7503(2)	0.01537(8)	0.5190(1)	3.17(4)
C(17)	0.8814(2)	-0.04448(9)	0.8542(1)	3.31(4)
C(18)	0.5473(2)	-0.11529(9)	0.6657(1)	3.70(4)
C(20)	0.8163(2)	-0.15305(9)	0.8883(1)	3.70(4)
C(21)	0.7514(2)	-0.11752(8)	0.9575(1)	3.62(4)
C(22)	0.7071(2)	-0.09814(8)	0.5339(1)	3.66(4)
C(23)	0.3909(2)	-0.1189(1)	0.7909(1)	4.09(5)
C(24)	0.6600(2)	-0.1488(1)	1.0245(1)	4.70(5)
C(25)	0.6324(2)	-0.07313(8)	0.6058(1)	3.28(4)
C(26)	0.8049(2)	0.07763(9)	0.4813(1)	3.62(4)
C(27)	0.9453(2)	0.01013(9)	0.8021(1)	3.44(4)
C(28)	0.3407(3)	-0.0706(1)	0.8633(2)	4.75(6)
C(29)	0.9844(3)	0.1255(1)	0.7845(2)	5.20(6)
C(30)	0.9512(3)	0.1888(1)	0.8349(2)	6.42(7)
C(31)	0.5703(5)	-0.1474(3)	1.2420(3)	11.3(1)

C(32)	0.7757(4)	0.2479(1)	0.5633(2)	6.88(8)
C(33)	0.4944(4)	-0.1299(2)	1.1483(2)	8.7(1)
C(34)	0.8281(3)	0.1948(1)	0.5016(2)	5.73(6)
H(1)	1.108(2)	0.1202(7)	0.799(1)	3.512
H(2)	0.920(2)	0.1257(8)	0.725(1)	3.512
H(3)	0.837(2)	0.1936(8)	0.810(1)	3.512
H(4)	1.008(2)	0.1873(8)	0.905(1)	3.512
H(5)	0.672(2)	0.2488(9)	0.547(1)	3.512
H(6)	0.809(2)	0.2419(8)	0.633(1)	3.512
H(7)	0.826(2)	0.2917(8)	0.548(1)	3.512
H(8)	0.938(2)	0.1927(8)	0.505(1)	3.512
H(9)	0.301(2)	-0.1364(8)	0.746(1)	3.512
H(10)	0.455(2)	-0.1484(8)	0.822(1)	3.512
H(11)	0.433(2)	-0.0547(8)	0.908(1)	3.512
H(12)	0.265(2)	-0.0919(8)	0.890(1)	3.512
H(13)	0.269(2)	-0.0333(8)	0.828(1)	3.512
H(14)	0.443(3)	-0.168(1)	1.118(2)	10.441
H(15)	0.610(4)	-0.108(2)	1.275(2)	13.593
H(16)	0.880(2)	-0.0356(9)	0.392(1)	3.512
H(17)	0.668(2)	-0.1810(9)	0.529(1)	3.512
H(18)	0.755(2)	-0.231(1)	0.893(1)	3.512
H(19)	1.015(2)	0.2206(8)	0.814(1)	3.512
H(23)	0.761(2)	0.2026(8)	0.442(1)	3.512
H(21)	0.651(4)	-0.177(2)	1.235(3)	13.593
H(25)	1.011(3)	-0.107(1)	0.715(2)	5.916
H(24)	0.423(3)	-0.095(1)	1.154(2)	10.441
H(22)	0.5012	-0.1684	1.2789	13.593

Table 8. Anisotropic displacement parameters

Anisotropic displacement parameters Uij[352]						
Atom	U11	U22	U33	U12	U13	U23
S(1)	0.0626(3)	0.0422(3)	0.0421(3)	-0.0004(2)	0.0247(2)	0.0001(2)
S(2)	0.0523(3)	0.0413(3)	0.0403(2)	0.0005(2)	0.0173(2)	-0.0016(2)
O(1)	0.123(1)	0.0473(9)	0.098(1)	-0.0118(9)	0.052(1)	0.0111(8)
O(3)	0.0629(8)	0.0457(7)	0.0490(7)	-0.0039(6)	0.0313(6)	-0.0009(6)
O(4)	0.0710(9)	0.0419(8)	0.0465(7)	-0.0025(6)	0.0254(6)	0.0029(6)
O(5)	0.0732(9)	0.0606(9)	0.0520(8)	0.0054(7)	0.0374(7)	0.0063(7)
O(6)	0.083(1)	0.0388(7)	0.0560(8)	-0.0049(7)	0.0310(7)	-0.0011(6)

O(7)	0.091(1)	0.054(1)	0.0527(9)	-0.0059(8)	0.0452(8)	-0.0018(7)
O(8)	0.085(1)	0.0525(9)	0.0578(9)	0.0087(8)	0.0386(8)	-0.0030(7)
O(9)	0.091(1)	0.0430(9)	0.086(1)	-0.0007(8)	0.0448(9)	-0.0007(8)
O(10)	0.084(1)	0.0545(8)	0.0486(8)	-0.0087(7)	0.0331(7)	0.0009(6)
O(11)	0.120(1)	0.0407(9)	0.080(1)	-0.0059(9)	0.064(1)	-0.0051(8)
O(12)	0.110(1)	0.0410(8)	0.073(1)	-0.0037(8)	0.0534(9)	0.0008(7)
O(13)	0.119(1)	0.069(1)	0.068(1)	-0.0169(9)	0.0633(9)	-0.0010(8)
C(1)	0.049(1)	0.048(1)	0.042(1)	0.0079(9)	0.0152(9)	0.0006(8)
C(15)	0.053(1)	0.046(1)	0.035(1)	0.0010(9)	0.0182(8)	0.0009(8)
C(16)	0.045(1)	0.043(1)	0.0342(9)	-0.0022(8)	0.0120(8)	0.0026(8)
C(17)	0.046(1)	0.046(1)	0.036(1)	0.0023(8)	0.0158(8)	0.0037(8)
C(18)	0.058(1)	0.043(1)	0.043(1)	0.0014(9)	0.0195(9)	0.0023(8)
C(20)	0.056(1)	0.038(1)	0.048(1)	0.0038(9)	0.0149(9)	0.0023(8)
C(21)	0.055(1)	0.040(1)	0.046(1)	0.0019(8)	0.0188(9)	0.0051(8)
C(22)	0.062(1)	0.036(1)	0.045(1)	0.0006(9)	0.0228(9)	-0.0002(8)
C(23)	0.058(1)	0.054(1)	0.047(1)	-0.004(1)	0.023(1)	0.0068(9)
C(24)	0.075(1)	0.050(1)	0.058(1)	-0.000(1)	0.026(1)	0.012(1)
C(25)	0.051(1)	0.039(1)	0.038(1)	0.0003(8)	0.0173(8)	0.0019(8)
C(26)	0.052(1)	0.044(1)	0.042(1)	-0.0023(9)	0.0077(9)	0.0009(8)
C(27)	0.044(1)	0.050(1)	0.038(1)	0.0033(9)	0.0126(8)	0.0054(8)
C(28)	0.058(1)	0.070(2)	0.059(1)	-0.000(1)	0.029(1)	-0.001(1)
C(29)	0.092(2)	0.052(1)	0.057(1)	-0.014(1)	0.021(1)	0.007(1)
C(30)	0.119(2)	0.053(2)	0.073(2)	-0.015(2)	0.016(2)	0.001(1)
C(31)	0.150(4)	0.204(5)	0.080(3)	-0.041(3)	0.032(2)	0.001(2)
C(32)	0.122(2)	0.052(1)	0.088(2)	0.005(2)	0.015(2)	0.000(1)
C(33)	0.128(3)	0.129(3)	0.085(2)	-0.032(2)	0.053(2)	0.009(2)
C(34)	0.098(2)	0.046(1)	0.078(2)	-0.010(1)	0.027(2)	0.001(1)

2. Thiophene-based open-chain compounds (compounds **16**, **17**, **18**, **19** and **20**)

Table 9. Summary of the crystal data, and structure solution and refinement parameters of compounds **16**, **17**, **18**, **19** and **20**

	16	**17**	**18**	**19**	**20**
A. Crystal Data					
Empirical Formula	$C_{12}H_{12}O_3S_2$	$C_{14}H_{18}O_3S_2$	$C_{13}H_{14}O_5S_2$	$C_{14}H_{14}O_5S_2$	$C_{14}H_{16}O_4S_2$
Formula Weight	268.35	298.41	314.37	326.38	312.4
Crystal Color, Habit	colourless, block	colourless, plate	colourless, plate	yellow, needle	colourless, plate
Crystal Dimensions	0.45 X 0.18 X 0.36 mm	0.20 X 0.10 X 0.20 mm	3.00 X 0.40 X 3.00 mm	0.90 X 0.90 X 2.00 mm	0.36 X 0.18 X 0.45 mm
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Lattice Type	Primitive	C-centered	Primitive	C-centered	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (37.4–40.8°)	25 (33.3–39.9°)	25 (20.2–22.4°)	25 (39.8–40.0°)	25 (37.4–40.8°)
Omega Scan Peak Width at Half-height	0.22°	0.20°	0.21°	0.21°	0.23°
Lattice Parameters					
a (Å)	5.38(2)	27.263(3)	8.564(2)	16.934(5)	10.44(5)
b (Å)	19.60(3)	5.070(4)	8.267(3)	9.930(7)	5.17(5)
c (Å)	12.89(3)	11.027(3)	20.682(5)	9.520(5)	14.64(4)
β (°)	100.6893	98.82(2)	101.74(2)	109.55(3)	104.8(3)
V (Å^3)	1336(5)	1506.3(9)	1433.6(7)	1508(1)	764(7)
Space Group	$P2_1/n$ (#14)	C2/c (#15)	$P2_1/n$ (#14)	C2/c (#15)	$P2_1/a$ (#14)
Z value	4	4	4	4	2
Dcalc	1.334 g/cm^3	1.316 g/cm^3	1.456 g/cm^3	1.437 g/cm^3	1.358 g/cm^3
F000	560	632	656	680	328
μ(MoKα)	3.91 cm^{-1}	3.54 cm^{-1}	3.86 cm^{-1}	3.70 cm^{-1}	3.57 cm^{-1}
Scan Width	(1.78+0.35 tan θ)°	(1.73+0.35 tan θ)°	(1.26+0.35 tan θ)°	(1.84+0.35 tan θ)°	(1.37+0.35 tan θ)°
2θmax	50.0°	50.0°	55.0°	55.0°	55.3°
No. of Reflections Measured	Total: 2693 Unique: 2425 (Rint = 0.306)	Total: 1526 Unique: 1493 (Rint = 0.120)	Total: 5535 Unique: 3516 (Rint = 0.019)	Total: 1890 Unique: 1828 (Rint = 0.063)	Total: 2041 Unique: 1941 (Rint = 0.311)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.6669 - 1.0000)	Lorentz-polarization Absorption (trans. factors: 0.8871 –1.0000)	Lorentz-polarization Absorption (trans. factors: 0.9070 –1.0000)	Lorentz-polarization Absorption (trans. factors: 0.7493 - 1.0000)	Lorentz-polarization Absorption (trans. factors: 0.3701 - 1.0000)
B. Structure Solution and Refinement					
Structure Solution	Direct Methods (SIR97)	Direct Methods (SIR97)	Direct Methods (SIR97)	Direct Methods (SIR97)	Direct Methods (SAPI91)[343]
Refinement	Full-matrix least-squares on F	Full-matrix least-squares on F	Full-matrix least-squares on F	Full-matrix least-squares on F	Full-matrix least-squares on F

Function Minimized	$\Sigma w (\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w (\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w (\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w (\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w (\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
p-factor	0.01	0.0076	0.0016	0.0024	0.0054
Anomalous Dispersion	All non-hydrogen		All non-hydrogen	All non-hydrogen	All non-hydrogen
No. Observations ($I>3.00\sigma(I)$)	1359	872	1760	1487	809
No. Variables	154	87	181	96	91
Reflection/Parameter Ratio	8.82	10.02	9.72	15.49	8.89
Residuals: R; Rw	0.076 ; 0.091	0.063 ; 0.068	0.068 ; 0.053	0.055 ; 0.056	0.310 ; 0.281
Goodness of Fit Indicator	5.67	3.05	3.49	6.71	17.51
Max Shift/Error in Final Cycle	0.09	0	0.10	4.01	0.44
Maximum peak in Final Diff. Map	0.62 e^-/Å^3	0.36 e^-/Å^3	0.52 e^-/Å^3	0.27 e^-/Å^3	1.32 e^-/Å^3
Minimum peak in Final Diff. Map	-0.51 e^-/Å^3	-0.43 e^-/Å3	-0.52 e^-/Å^3	-0.46 e^-/Å^3	-1.24 e^-/Å^3

2.1. α,ω-bis-(3-oxythienyl)ethane **16**

Table 10. Atomic coordinates and Biso/Beq

Atomic coordinates and Biso/Beq[351]				
Atom	X	Y	Z	Beq
S(1)	-0.1242(2)	0.20097(7)	0.47705(9)	6.01(3)
S(2)	0.3363(2)	0.02408(7)	1.30401(9)	5.73(3)
O(3)	0.4357(5)	0.1320(1)	0.6892(2)	4.30(7)
O(4)	0.6905(5)	0.1204(1)	1.1144(2)	4.25(7)
O(5)	0.7202(5)	0.1340(1)	0.8984(2)	4.66(7)
C(6)	0.5521(7)	0.0962(2)	1.1850(3)	3.43(9)
C(7)	0.2292(7)	0.1467(2)	0.6125(3)	3.7(1)
C(8)	0.0657(7)	0.0917(2)	0.5691(3)	4.4(1)
C(9)	0.8186(7)	0.0722(2)	1.0594(3)	4.1(1)
C(10)	0.9241(7)	0.1107(2)	0.9756(3)	4.6(1)
C(11)	0.5859(8)	0.1903(2)	0.7332(3)	5.1(1)
C(12)	-0.1330(8)	0.1152(2)	0.4956(3)	5.1(1)
C(13)	0.1518(8)	0.2090(2)	0.5705(3)	5.0(1)
C(14)	0.5309(7)	0.0286(2)	1.2137(3)	3.97(9)
C(15)	0.4156(8)	0.1401(2)	1.2366(3)	4.6(1)
C(16)	0.8019(8)	0.1655(2)	0.8114(3)	5.0(1)
C(17)	0.2897(8)	0.1114(2)	1.3019(3)	5.2(1)

H(1)	0.1334	0.1379	1.3454	4.625
H(2)	0.5898	-0.0139	1.1691	4.625
H(3)	1.0099	0.0792	0.9279	4.625
H(4)	0.6935	0.0462	1.0229	4.625
H(5)	0.9654	0.0518	1.1158	4.625
H(6)	0.8979	0.1314	0.7731	4.625
H(7)	0.6370	0.2261	0.6669	4.625
H(8)	0.4457	0.2107	0.7306	4.625
H(9)	1.0068	0.1847	0.8428	4.625
H(10)	0.2501	0.2574	0.5964	4.625
H(11)	0.3983	0.1971	1.2198	4.625
H(12)	1.0572	0.1447	1.0264	4.625
H(13)	-0.3190	0.0991	0.4788	4.625
H(14)	0.0919	0.0452	0.5888	5.298

** Note the hydrogen positions are to four decimal places with terminal zero's omitted. The hydrogen coordinates have no esd's as their positions were not refined.

Table 11. Anisotropic displacement parameters

Anisotropic Displacement Parameters[352]						
Atom	U11	U22	U33	U12	U13	U23
S(1)	0.0888(9)	0.0702(9)	0.0706(8)	0.0246(8)	0.0179(7)	0.0138(7)
S(2)	0.0654(8)	0.083(1)	0.0687(7)	-0.0146(7)	0.0104(6)	0.0177(7)
O(3)	0.074(2)	0.032(2)	0.052(2)	-0.015(1)	-0.001(1)	-0.001(1)
O(4)	0.082(2)	0.024(2)	0.059(2)	0.006(1)	0.021(1)	-0.002(1)
O(5)	0.065(2)	0.068(2)	0.045(2)	-0.010(2)	0.014(1)	-0.001(1)
C(6)	0.052(2)	0.036(2)	0.040(2)	0.001(2)	0.003(2)	0.004(2)
C(7)	0.062(3)	0.040(3)	0.043(2)	-0.004(2)	0.020(2)	-0.006(2)
C(8)	0.059(3)	0.053(3)	0.055(2)	-0.013(2)	0.006(2)	-0.004(2)
C(9)	0.064(3)	0.041(3)	0.047(2)	0.005(2)	-0.000(2)	0.003(2)
C(10)	0.059(3)	0.072(3)	0.042(2)	0.001(2)	0.007(2)	-0.001(2)
C(11)	0.079(3)	0.055(3)	0.051(2)	-0.027(2)	-0.007(2)	0.001(2)
C(12)	0.060(3)	0.064(3)	0.070(3)	-0.008(2)	0.007(2)	0.004(3)
C(13)	0.083(3)	0.050(3)	0.059(3)	0.004(2)	0.021(2)	0.007(2)
C(14)	0.060(3)	0.039(2)	0.050(2)	0.000(2)	0.004(2)	0.007(2)
C(15)	0.072(3)	0.045(3)	0.062(3)	0.021(2)	0.022(2)	0.010(2)
C(16)	0.071(3)	0.072(3)	0.051(2)	-0.035(3)	0.018(2)	-0.002(2)
C(17)	0.061(3)	0.074(3)	0.069(3)	0.019(2)	0.023(2)	0.007(3)

2.2. dimethyl α,ω-bis-(3-oxythienyl)ethane 17

Table 12. Atomic coordinates and Biso/Beq and occupancy

Atomic coordinates and Biso/Beq[351] and occupancy					
Atom	X	Y	Z	Beq	occ
S(1)	0.65329(4)	0.3078(2)	-0.05623(8)	4.99(2)	
O(2)	0.58950(7)	-0.1003(4)	0.1726(2)	3.88(5)	
O(3)	0.5	-0.2843(6)	0.25	4.46(8)	1/2
C(4)	0.6533(1)	0.2245(6)	0.1712(3)	3.59(7)	
C(5)	0.6163(1)	0.0591(6)	0.1066(3)	3.42(7)	
C(6)	0.5548(1)	-0.2739(7)	0.1019(3)	3.88(8)	
C(7)	0.5312(1)	-0.4470(7)	0.1863(3)	4.20(8)	
C(8)	0.6767(1)	0.3702(6)	0.0962(3)	4.07(8)	
C(9)	0.6113(1)	0.0799(6)	-0.0172(3)	4.05(8)	
C(10)	0.7172(1)	0.5726(7)	0.1312(3)	5.4(1)	
H(1)	0.6593	0.2273	0.2648	4.268	
H(2)	0.7351	0.5445	0.2376	4.268	
H(3)	0.5335	-0.1595	0.0558	4.268	
H(4)	0.5773	-0.4054	0.0485	4.268	
H(5)	0.4993	-0.4787	0.116	4.268	
H(6)	0.7446	0.5144	0.0805	4.268	
H(7)	0.5568	-0.559	0.2551	4.268	
H(8)	0.5889	-0.0529	-0.0868	4.268	
H(9)	0.7041	0.758	0.0852	4.268	

** Note the hydrogen positions are to four decimal places with terminal zero's omitted. The hydrogen coordinates have no esd's as their positions were not refined.

Table 13. Anisotropic displacement parameters

Anisotropic Displacement Parameters[352]						
Atom	U11	U22	U33	U12	U13	U23
S(1)	0.0744(7)	0.0682(6)	0.0537(5)	0.0046(6)	0.0309(4)	0.0088(5)
O(2)	0.050(1)	0.060(1)	0.039(1)	-0.011(1)	0.010(1)	-0.005(1)
O(3)	0.047(2)	0.043(2)	0.084(2)	0	0.024(2)	0
C(4)	0.049(2)	0.043(2)	0.046(2)	0.002(2)	0.014(1)	-0.003(2)
C(5)	0.044(2)	0.047(2)	0.041(2)	0.009(2)	0.012(1)	0.003(2)
C(6)	0.044(2)	0.054(2)	0.050(2)	0.002(2)	0.009(1)	-0.001(2)

C(7)	0.043(2)	0.055(2)	0.062(2)	0.006(2)	0.008(2)	-0.004(2)
C(8)	0.047(2)	0.042(2)	0.069(2)	0.011(2)	0.020(2)	0.001(2)
C(9)	0.061(2)	0.054(2)	0.040(2)	-0.001(2)	0.011(2)	-0.001(2)
C(10)	0.059(2)	0.060(2)	0.089(3)	-0.002(2)	0.023(2)	0.006(2)

2.3. 15-carboxylic-α,ω-bis-(3-oxythienyl)ethane **18**

Table 14. Atomic coordinates and Biso/Beq

Positional parameters and Biso/Beq[351]				
Atom	X	Y	Z	Beq
S(1)	0.8538(1)	0.0369(1)	0.90765(5)	6.64(3)
S(2)	1.0634(1)	0.0421(1)	0.39469(4)	5.96(2)
O(3)	0.9768(2)	0.3540(2)	0.43631(8)	5.06(5)
O(4)	1.1250(2)	0.3582(2)	0.53828(8)	4.87(5)
O(5)	1.0693(2)	-0.0889(2)	0.76829(8)	5.57(5)
O(6)	1.3136(2)	0.0731(3)	0.57211(9)	6.22(6)
O(7)	1.3464(2)	-0.0418(3)	0.71001(8)	5.56(5)
C(8)	1.1360(3)	0.1295(3)	0.4707(1)	4.15(7)
C(9)	1.0790(3)	0.2884(3)	0.4845(1)	4.05(7)
C(10)	0.9750(3)	-0.0406(3)	0.8108(1)	4.71(7)
C(11)	1.2289(3)	-0.1347(3)	0.7975(1)	4.53(7)
C(12)	1.0107(3)	-0.0399(3)	0.8774(1)	4.92(7)
C(13)	1.2429(3)	0.0286(4)	0.5104(1)	5.05(8)
C(14)	1.3116(3)	-0.1807(4)	0.7443(1)	5.58(8)
C(15)	1.4396(5)	-0.0680(8)	0.6620(2)	17.0(2)
C(16)	1.2638(4)	-0.1186(4)	0.4783(2)	6.6(1)
C(17)	0.7407(3)	0.0659(4)	0.8297(2)	6.7(1)
C(18)	0.8197(3)	0.0191(4)	0.7828(2)	6.38(9)
C(19)	1.4255(5)	-0.0373(7)	0.6090(2)	14.8(2)
C(20)	1.1774(4)	-0.1244(4)	0.4166(2)	7.3(1)
H(1)	1.1244	-0.1026	0.9121	5.051
H(2)	0.7537	0.0348	0.7238	5.051
H(3)	0.6171	0.1212	0.8257	5.051
H(4)	1.2062	-0.2255	0.8309	5.051
H(5)	1.2941	-0.0347	0.8282	5.051
H(6)	1.4179	-0.2412	0.7631	5.051
H(7)	1.2482	-0.2817	0.7138	5.051
H(8)	1.3729	-0.2209	0.5034	5.051

H(9)	1.1431	-0.2331	0.3754	5.051
H(10)	1.5498	-0.1002	0.6929	5.051
H(11)	0.9279	0.478	0.44	5.051
H(13)	1.3818	-0.1416	0.6564	5.051
H(14)	1.43	-0.1282	0.5874	19.462
H(15)	1.5331	0.0223	0.6122	19.462

** Note the hydrogen positions are to four decimal places with terminal zero's omitted. The hydrogen coordinates have no esd's given in brackets, as their positions were not refined.

Table 15. Anisotropic displacement parameters

Anisotropic Displacement Parameters[352]						
Atom	U11	U22	U33	U12	U13	U23
S(1)	0.0904(6)	0.0772(6)	0.0975(7)	0.0000(5)	0.0490(5)	-0.0044(6)
S(2)	0.0898(6)	0.0763(6)	0.0611(5)	-0.0155(5)	0.0169(4)	-0.0111(5)
O(3)	0.069(1)	0.063(1)	0.052(1)	0.012(1)	-0.0079(9)	0.009(1)
O(4)	0.069(1)	0.063(1)	0.046(1)	0.007(1)	-0.0030(9)	-0.002(1)
O(5)	0.060(1)	0.098(2)	0.053(1)	0.014(1)	0.009(1)	-0.003(1)
O(6)	0.076(1)	0.109(2)	0.053(1)	0.040(1)	0.016(1)	0.028(1)
O(7)	0.068(1)	0.094(2)	0.053(1)	0.022(1)	0.021(1)	0.018(1)
C(8)	0.065(2)	0.047(2)	0.048(2)	-0.007(1)	0.016(1)	0.004(1)
C(9)	0.051(2)	0.057(2)	0.045(2)	-0.009(1)	0.008(1)	0.010(1)
C(10)	0.055(2)	0.061(2)	0.066(2)	0.002(2)	0.017(1)	0.002(2)
C(11)	0.060(2)	0.060(2)	0.054(2)	0.011(2)	0.017(1)	0.010(1)
C(12)	0.068(2)	0.056(2)	0.069(2)	0.005(2)	0.028(2)	0.004(2)
C(13)	0.071(2)	0.068(2)	0.060(2)	0.015(2)	0.030(2)	0.021(2)
C(14)	0.083(2)	0.062(2)	0.071(2)	0.016(2)	0.024(2)	0.003(2)
C(15)	0.143(4)	0.416(9)	0.113(3)	0.201(5)	0.087(3)	0.147(5)
C(16)	0.104(3)	0.078(3)	0.080(2)	0.031(2)	0.044(2)	0.018(2)
C(17)	0.054(2)	0.087(3)	0.117(3)	0.014(2)	0.026(2)	0.007(2)
C(18)	0.057(2)	0.098(3)	0.085(2)	0.010(2)	0.009(2)	0.003(2)
C(19)	0.177(4)	0.324(7)	0.083(3)	0.196(5)	0.075(3)	0.101(4)
C(20)	0.130(3)	0.058(2)	0.102(3)	0.004(2)	0.057(2)	-0.004(2)

2.4. α,ω-bis-(2-formyl-3-oxythienyl)ethane **19**

Table 16. Atomic coordinates and Biso/Beq and occupancy

Positional parameters and Biso/Beq[351] and occupancy					
Atom	X	Y	Z	Beq	occ
S(1)	0.26169(2)	-0.03819(3)	0.02392(4)	4.941(9)	
O(2)	0.12104(4)	0.23565(7)	0.10271(8)	3.60(2)	
O(3)	0	0.2830(1)	0.25	3.77(2)	1/2
O(4)	0.37577(4)	0.16144(9)	0.24711(9)	5.33(2)	
C(5)	0.23759(6)	0.1064(1)	0.1024(1)	3.09(2)	
C(6)	0.15240(6)	0.1307(1)	0.0495(1)	3.01(2)	
C(7)	0.30091(7)	0.1867(1)	0.2055(1)	3.69(2)	
C(8)	0.03419(6)	0.2710(1)	0.0288(1)	3.85(3)	
C(9)	0.10765(7)	0.0320(1)	-0.0560(1)	4.21(3)	
C(10)	0.00916(6)	0.3623(1)	0.1317(1)	3.95(3)	
C(11)	0.15907(8)	-0.0622(1)	-0.0779(1)	5.04(3)	
H(1)	0.1454	-0.1399	-0.1551	3.964	
H(2)	0.0437	0.0427	-0.1052	3.964	
H(3)	0.2759	0.2812	0.2443	3.964	
H(4)	-0.008	0.1883	0.0074	3.964	
H(5)	0.0333	0.3237	-0.065	3.964	
H(6)	0.0499	0.4377	0.1702	3.964	
H(7)	-0.0471	0.4069	0.069	3.964	

** Note the hydrogen positions are to four decimal places with terminal zero's omitted. The hydrogen coordinates have no esd's as their positions were not refined.

Table 17. Anisotropic displacement parameters

Anisotropic Displacement Parameters[352]						
Atom	U11	U22	U33	U12	U13	U23
S(1)	0.0638(2)	0.0632(2)	0.0689(2)	0.0070(2)	0.0331(2)	-0.0111(2)
O(2)	0.0292(4)	0.0560(5)	0.0460(4)	0.0031(3)	0.0053(3)	-0.0069(4)
O(3)	0.0505(6)	0.0422(6)	0.0575(7)	0	0.0275(5)	0
O(4)	0.0338(4)	0.0935(7)	0.0666(6)	0.0028(4)	0.0056(4)	0.0069(5)
C(5)	0.0373(5)	0.0468(6)	0.0356(5)	0.0018(5)	0.0151(4)	0.0008(5)
C(6)	0.0389(5)	0.0458(6)	0.0306(5)	-0.0042(5)	0.0131(4)	0.0005(4)
C(7)	0.0367(6)	0.0616(7)	0.0400(6)	-0.0004(5)	0.0102(5)	0.0029(5)

C(8)	0.0283(5)	0.0656(8)	0.0491(6)	0.0036(5)	0.0086(5)	0.0082(6)
C(9)	0.0473(7)	0.0699(8)	0.0414(6)	-0.0146(6)	0.0132(5)	-0.0094(6)
C(10)	0.0355(6)	0.0496(7)	0.0650(7)	0.0060(5)	0.0168(5)	0.0126(6)
C(11)	0.0768(9)	0.0625(8)	0.0586(8)	-0.0125(7)	0.0311(7)	-0.0215(7)

2.5. α,ω-bis-(3-ethyloxythienyl)ethane **20**

Table 18. Atomic coordinates and Biso/Beq

Positional parameters and Biso/Beq[351]				
Atom	X	Y	Z	Beq
S(1)	0.6225(2)	0.0519(5)	0.4340(1)	4.37(6)
O(1)	0.7241(5)	0.036(1)	0.2000(3)	3.5(2)
O(2)	0.9181(5)	0.067(1)	0.0929(3)	3.9(2)
C(1)	0.6702(7)	-0.010(2)	0.2757(4)	2.5(2)
C(2)	0.7138(9)	0.176(2)	0.3615(5)	5.6(3)
C(3)	0.574(1)	-0.178(2)	0.2660(6)	7.2(4)
C(4)	0.8093(7)	0.249(1)	0.1997(4)	1.9(2)
C(5)	0.8529(8)	0.333(2)	0.1106(5)	6.9(3)
C(6)	0.9638(6)	0.127(1)	0.0088(5)	1.7(2)
C(7)	0.5634(8)	-0.261(3)	0.3620(6)	12.0(5)
H(1)	0.8011	0.1867	0.0893	3.291
H(2)	0.8527	0.2543	0.2565	3.291
H(3)	0.7147	0.3487	0.1694	3.291
H(4)	0.8392	0.5578	0.0891	3.291
H(5)	0.7737	0.3177	0.3711	6.706
H(6)	0.5191	-0.2377	0.2076	8.628
H(7)	0.5356	-0.4215	0.382	14.355
H(8)	1.0424	0.228	0.0265	2.072
H(10)	0.8971	0.222	-0.0346	2.072

** Note the hydrogen positions are to four decimal places with terminal zero's omitted. The hydrogen coordinates have no esd's as their positions were not refined.

Table 19. Anisotropic displacement parameters

Anisotropic Displacement Parameters[352]						
Atom	U11	U22	U33	U12	U13	U23
S(1)	0.062(2)	0.075(2)	0.030(1)	-0.015(1)	0.0151(9)	0.006(1)
O(1)	0.029(3)	0.069(5)	0.036(3)	-0.000(3)	0.010(2)	0.010(3)
O(2)	0.030(3)	0.074(5)	0.046(3)	0.039(3)	0.016(2)	0.013(3)
C(1)	0.043(5)	0.037(6)	0.012(3)	-0.026(4)	0.000(3)	0.006(3)
C(2)	0.087(8)	0.10(1)	0.049(5)	-0.057(7)	0.062(5)	-0.022(5)
C(3)	0.12(1)	0.07(1)	0.083(7)	-0.096(8)	0.013(6)	0.013(5)
C(4)	0.033(5)	0.015(5)	0.028(3)	-0.014(3)	0.012(3)	0.010(3)
C(5)	0.044(6)	0.19(1)	0.032(4)	0.081(8)	0.018(4)	0.048(6)
C(6)	-0.006(4)	-0.007(4)	0.081(5)	-0.015(3)	0.014(3)	0.001(3)
C(7)	0.021(6)	0.33(2)	0.081(6)	-0.021(9)	-0.029(5)	0.16(1)

3. Thiophene-based Macrocycles

3.1. Two donor atoms thiophene-based macrocycle: 2,6-dioxa-10,14-dithia-tricyclo[11.3.0.0]-hexadeca-1,15,7,8-tetraene **21**

Table 20. Summary of the crystal data, structure solution and refinement parameters

A. Crystal Data

Empirical Formula	$C_{13}H_{14}O_2S_2$
Formula Weight	266.37
Crystal Color, Habit	colourless, rhomboid
Crystal Dimensions	0.18 X 0.09 X 0.18 mm
Crystal System	monoclinic
Lattice Type	C-centered
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (36.6 - 39.4°)
Omega Scan Peak Width at Half-height	0.21°
Lattice Parameters	a = 47.3(2) Å, b = 8.8(2) Å, c = 8.7(3) Å β = 91.9135 Å, V = 3637(129) $Å^3$
Space Group	C2/c (#15)
Z value	8
Dcalc	0.973 g/cm^3
F000	1120
μ(MoKα)	2.83 cm^{-1}
Slit Aperture	3.0 mm horizontal, 3.0 mm vertical
Scan Width	(0.79 + 0.35 tan θ)°
2θmax	55.9°
No. of Reflections Measured	Total: 5434, Unique: 4337 (Rint = 1.406)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.9429 - 1.0000)

B. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma w (\|F_o\| - \|F_c\|)^2$
Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
p-factor	0.0019
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	1884

Structure solution was attempted using several different methods but only disordered intensity peaks were observed and it appeared that the compound had decomposed under X-rays. Data were also collected from a further three crystals with similar results.

3.2. Four donor atoms thiophene-based macrocycle: 15-ethyl-2,5,8-trioxa-12,18-dithia-15-azatricyclo[15.3.0.0]-tricosa-1(18),9(13),10,19-tetraene **10a**

Table 21. Summary of the crystal data, structure solution and refinement parameters

A. Crystal Data

Empirical Formula	$C_{16}H_{21}NO_3S_2$
Formula Weight	339.47
Crystal Color, Habit	colourless, block
Crystal Dimensions	0.27 X 0.36 X 0.36 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	24 (25.4 – 35.0°)
Omega Scan Peak Width at Half-height	0.19°
Lattice Parameters	a = 8.468(4) Å, b = 13.192(5) Å, c = 15.151(5) Å β = 93.67(4) Å, V = 1689(1) Å^3
Space Group	P21/c (#14)
Z value	4
Dcalc	1.335 g/cm^3
F000	720
μ(MoKα)	3.26 cm^{-1}
Slit Aperture	3.0 mm horizontal, 3.0 mm vertical
Scan Width	(1.57 + 0.35 tan θ)°
2θmax	56.0°
No. of Reflections Measured	Total: 4531, Unique: 4259 (Rint = 0.119)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.9616 - 1.0000)

B. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w $(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
p-factor	0.0106
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	1814

No. Variables	199
Reflection/Parameter Ratio	9.12
Residuals: R; Rw	0.068 ; 0.069
Goodness of Fit Indicator	2.37
Max Shift/Error in Final Cycle	0.04
Maximum peak in Final Diff. Map	0.55 $e^{-}/\text{Å}^{3}$
Minimum peak in Final Diff. Map	-0.38 $e^{-}/\text{Å}^{3}$

Table 22. Atomic coordinates and B_{iso}/B_{eq}

Atomic coordinates and Biso/Beq[351]				
Atom	X	Y	Z	Beq
S(1)	0.7887(1)	-0.04359(8)	0.75833(7)	3.79(2)
S(2)	0.8740(2)	0.3854(1)	0.55128(8)	5.07(3)
O(1)	0.5490(3)	0.1887(3)	0.4995(2)	5.00(9)
O(3)	0.3743(3)	0.0771(2)	0.7644(2)	3.84(7)
O(4)	0.2809(3)	0.1150(2)	0.5854(2)	4.96(8)
N(1)	0.8501(3)	0.1671(2)	0.6937(2)	3.12(8)
C(7)	0.6470(4)	0.0493(3)	0.7435(2)	2.76(8)
C(8)	0.5035(4)	0.0131(3)	0.7650(3)	2.94(9)
C(9)	0.6416(5)	0.2733(4)	0.5076(3)	3.8(1)
C(10)	0.7840(5)	0.2677(3)	0.5527(2)	3.4(1)
C(11)	0.8598(4)	0.1779(3)	0.5972(3)	3.5(1)
C(12)	0.5064(5)	-0.0894(3)	0.7945(3)	3.8(1)
C(13)	0.6825(5)	0.1566(3)	0.7172(3)	4.3(1)
C(14)	0.9362(5)	0.2474(3)	0.7419(3)	3.9(1)
C(15)	0.6521(5)	-0.1303(3)	0.7924(3)	4.5(1)
C(16)	0.2319(5)	0.0372(3)	0.7217(3)	4.5(1)
C(17)	0.2465(5)	0.0209(3)	0.6245(3)	5.0(1)
C(18)	0.6058(6)	0.3721(4)	0.4712(3)	5.4(1)
C(19)	0.3866(5)	0.1988(4)	0.4650(3)	5.3(1)
C(20)	0.9680(6)	0.2257(4)	0.8393(3)	6.3(2)
C(21)	0.7229(6)	0.4376(4)	0.4886(3)	5.5(1)
C(22)	0.2998(6)	0.1080(4)	0.4918(3)	5.7(1)
H(1)	0.6896	-0.2061	0.817	3.559
H(2)	0.3942	0.2046	0.3832	3.559
H(3)	0.361	0.2614	0.4933	3.559
H(4)	0.793	0.1143	0.5758	3.559
H(5)	0.6007	0.1772	0.6672	3.559

H(6)	0.703	0.1711	0.7565	3.559
H(7)	1.0405	0.1705	0.8504	3.559
H(9)	0.5281	0.3603	0.4418	3.559
H(10)	0.9829	0.154	0.579	3.559
H(11)	0.1658	0.1004	0.73	3.559
H(12)	0.3332	-0.0456	0.6205	3.559
H(13)	0.3966	-0.1311	0.7846	3.559
H(14)	0.1357	-0.0114	0.5864	3.559
H(15)	0.1731	0.1077	0.4591	3.559
H(16)	0.3388	0.0327	0.4937	3.559
H(17)	0.8648	0.3047	0.7308	3.559
H(18)	0.6927	0.523	0.4845	3.559
H(19)	0.212	-0.0382	0.7489	3.559
H(20)	1.0526	0.2474	0.7011	3.559
H(21)	0.8727	0.1941	0.8524	3.559
H(22)	1.0429	0.2954	0.864	3.559

** Note the hydrogen positions are to four decimal places with terminal zero's omitted. The hydrogen coordinates have no esd's as their positions were not refined.

Table 23. Anisotropic Displacement Parameters

Anisotropic Displacement Parameters[352]						
Atom	U11	U22	U33	U12	U13	U23
S(1)	0.0396(6)	0.0454(6)	0.0601(7)	0.0071(5)	0.0126(5)	0.0077(6)
S(2)	0.0793(9)	0.0592(8)	0.0561(7)	-0.0070(7)	0.0213(6)	0.0078(7)
O(1)	0.044(2)	0.077(2)	0.068(2)	0.008(2)	0.000(2)	-0.006(2)
O(3)	0.035(2)	0.044(2)	0.069(2)	0.007(1)	0.018(1)	0.002(1)
O(4)	0.065(2)	0.064(2)	0.060(2)	0.005(2)	0.013(2)	-0.000(2)
N(1)	0.029(2)	0.040(2)	0.052(2)	-0.005(1)	0.014(2)	0.004(2)
C(7)	0.032(2)	0.034(2)	0.039(2)	0.002(2)	0.006(2)	0.001(2)
C(8)	0.031(2)	0.031(2)	0.051(3)	0.001(2)	0.010(2)	0.002(2)
C(9)	0.051(3)	0.062(3)	0.035(2)	0.013(2)	0.017(2)	0.003(2)
C(10)	0.042(2)	0.053(3)	0.036(2)	0.003(2)	0.015(2)	-0.004(2)
C(11)	0.034(2)	0.051(3)	0.051(3)	0.005(2)	0.010(2)	-0.003(2)
C(12)	0.041(3)	0.037(3)	0.067(3)	-0.006(2)	0.014(2)	0.008(2)
C(13)	0.033(2)	0.054(3)	0.078(3)	-0.001(2)	0.013(2)	0.014(2)
C(14)	0.045(2)	0.057(3)	0.047(3)	-0.002(2)	0.006(2)	0.002(2)
C(15)	0.054(3)	0.036(3)	0.081(3)	-0.000(2)	0.011(2)	0.017(2)

C(16)	0.042(3)	0.049(3)	0.081(4)	0.004(2)	0.011(2)	0.015(3)
C(17)	0.052(3)	0.049(3)	0.086(4)	0.002(2)	-0.011(3)	-0.001(3)
C(18)	0.067(3)	0.099(4)	0.040(3)	0.021(3)	0.016(2)	0.012(3)
C(19)	0.058(3)	0.102(4)	0.041(3)	0.002(3)	-0.000(2)	0.003(3)
C(20)	0.079(4)	0.096(4)	0.063(3)	-0.020(3)	0.006(3)	0.002(3)
C(21)	0.089(4)	0.066(4)	0.057(3)	0.017(3)	0.027(3)	0.015(3)
C(22)	0.061(3)	0.091(4)	0.064(3)	0.002(3)	-0.010(3)	-0.005(3)

3.3. Five donor atoms thiophene-based macrocycle (4 oxygens, 1 nitrogen): 18-ethyl-2,5,8,11-tetraoxa-15,21-dithia-azatricyclo[18.3.0.0]-tricosa-1,22,12,13-tetraene **10b**

Table 24. Summary of the crystal data, structure solution and refinement parameters

A. Crystal Data

Empirical Formula	$C_{18}H_{25}S_2O_4N$
Formula Weight	383.52
Crystal Color, Habit	colourless, plate
Crystal Dimensions	0.54 X 0.80 X 0.10 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (37.0 - 39.5°)
Omega Scan Peak Width at Half-height	0.22°
Lattice Parameters	$a =$ 10.502(9) Å, $b =$ 21.445(6) Å, $c =$ 10.233(7) Å $\alpha =$ 99.49(4) Å, $\beta =$ 118.9247 Å, $\gamma =$ 94.0899 Å $V =$ 1959(2) Å^3
Space Group	P-1 (#2)
Z value	4
Dcalc	1.300 g/cm^3
F000	816
μ(MoKα)	2.93 cm^{-1}
Detector Aperture	3.0 mm horizontal, 3.0 mm vertical
Scan Width	$(0.89 + 0.35 \tan \theta)^\circ$
2θmax	50.0°
No. of Reflections Measured	Total: 7322, Unique: 6910 (Rint = 0.020)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.7879 - 1.0000)

B. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma\ w\ (|F_o| - |F_c|)^2$

Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
p-factor	0.0122
Anomalous Dispersion	All non-hydrogen atoms
No. Observations $(I>3.00\sigma(I))$	3946
No. Variables	574
Reflection/Parameter Ratio	6.87
Residuals: R; Rw	0.086 ; 0.086
Goodness of Fit Indicator	4.33
Max Shift/Error in Final Cycle	1.48
Maximum peak in Final Diff. Map	0.64 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.57 $e^-/Å^3$

Table 25. Atomic coordinates and B_{iso}/B_{eq}

Positional parameters and B(eq)[351]				
Atom	X	Y	Z	B(eq)
S(1)	-0.2736(1)	0.45282(4)	0.9715(1)	7.41(3)
S(2)	0.0378(1)	0.04591(5)	0.2116(1)	9.49(3)
S(3)	0.4812(1)	0.06016(5)	0.6219(1)	9.44(4)
S(4)	0.0611(2)	0.43936(6)	1.4331(2)	13.53(6)
O(1)	0.3562(4)	0.3596(2)	1.3880(3)	10.5(1)
O(2)	0.4342(3)	0.3792(2)	1.1748(4)	10.6(1)
O(3)	0.2119(4)	0.3323(2)	0.8651(4)	11.8(1)
O(5)	-0.0817(2)	0.3570(1)	0.7906(2)	7.07(7)
O(6)	-0.1033(2)	0.1274(1)	0.4671(3)	7.52(7)
O(7)	0.4783(3)	0.1431(1)	0.9815(3)	8.43(7)
O(10)	0.2633(3)	0.1451(1)	1.0869(3)	9.02(8)
O(11)	0.0204(3)	0.1542(1)	0.7908(3)	7.79(7)
N(1)	0.2863(3)	0.1616(1)	0.5191(3)	6.11(7)
N(2)	-0.1076(4)	0.3369(1)	1.1457(4)	6.93(9)
C(1)	0.6147(5)	0.0703(2)	0.9095(7)	9.7(2)
C(2)	-0.2055(3)	0.3878(1)	0.9221(3)	4.93(7)
C(3)	-0.1016(6)	-0.0026(2)	0.2064(6)	11.0(2)
C(4)	0.3396(7)	0.4384(3)	1.5891(5)	13.8(2)
C(5)	0.219(1)	0.4635(3)	1.586(1)	20.3(4)
C(15)	-0.1623(4)	0.4631(2)	0.8046(3)	5.87(9)
C(16)	0.0318(4)	0.1064(2)	0.3415(4)	6.47(9)
C(17)	-0.2270(3)	0.4965(2)	0.8722(4)	6.59(9)
C(19)	-0.0773(4)	0.0866(2)	0.3686(4)	6.54(9)

C(20)	-0.2074(4)	0.3277(2)	0.9799(5)	6.8(1)
C(21)	-0.1478(3)	0.4011(1)	0.8353(3)	4.95(7)
C(22)	0.5045(4)	0.1072(2)	0.8747(5)	7.3(1)
C(25)	-0.0072(5)	0.3754(2)	0.7156(4)	7.3(1)
C(26)	0.2291(6)	0.2024(2)	1.0315(5)	9.8(1)
C(27)	0.4215(4)	0.1076(2)	0.7257(5)	6.75(9)
C(28)	0.1397(6)	0.3909(2)	1.3475(4)	7.9(1)
C(29)	0.2920(4)	0.1396(2)	0.6467(4)	7.2(1)
C(30)	0.1358(4)	0.1675(2)	0.4086(5)	6.8(1)
C(31)	0.5014(7)	0.3916(4)	1.4253(8)	18.8(3)
C(32)	0.4836(5)	0.1119(2)	1.0963(5)	9.0(1)
C(33)	0.0423(5)	0.3558(2)	1.1847(4)	7.7(1)
C(34)	0.0948(6)	0.3304(2)	0.7210(6)	8.3(1)
C(35)	-0.1545(4)	0.0245(2)	0.2897(5)	8.7(1)
C(36)	0.5313(6)	0.3709(3)	1.3137(9)	12.5(2)
C(37)	-0.1165(8)	0.2779(2)	1.1955(7)	15.3(2)
C(38)	0.2828(8)	0.3939(2)	1.4404(5)	11.4(2)
C(39)	0.0621(5)	0.1952(2)	0.9325(5)	8.4(1)
C(41)	0.4621(5)	0.3634(3)	1.0644(8)	11.6(2)
C(42)	-0.1701(4)	0.0987(2)	0.5412(5)	8.5(1)
C(43)	0.3521(7)	0.3645(3)	0.9177(7)	11.4(2)
C(44)	-0.1293(4)	0.1451(2)	0.6847(6)	8.6(1)
C(45)	0.6156(6)	0.0427(2)	0.7872(9)	12.3(2)
C(46)	0.4176(6)	0.1475(2)	1.1785(5)	9.9(1)
C(47)	0.3802(9)	0.2261(3)	0.569(1)	16.3(3)
C(48)	-0.2080(7)	0.2675(2)	1.2464(7)	12.7(2)
C(50)	0.5181(8)	0.2291(4)	0.599(1)	20.1(3)
H(1)	-0.205(3)	0.306(1)	1.308(3)	15.207
H(2)	-0.182(3)	0.294(1)	0.921(3)	6.352
H(3)	0.429(3)	0.063(1)	1.044(3)	6.352
H(4)	-0.010(3)	0.152(1)	0.935(3)	6.352
H(5)	0.124(3)	0.339(1)	0.657(3)	6.352
H(6)	-0.241(3)	0.542(1)	0.878(3)	6.352
H(7)	-0.125(3)	0.059(1)	0.550(3)	6.352
H(8)	0.4757	0.3996	1.431	6.352
H(9)	0.297(3)	0.167(1)	0.707(3)	6.352
H(10)	-0.183(3)	0.139(1)	0.737(3)	6.352
H(11)	-0.125(4)	-0.028(2)	0.155(4)	6.352
H(12)	-0.221(3)	0.003(1)	0.314(3)	6.352
H(13)	0.586(3)	0.110(1)	1.156(3)	6.352
H(14)	-0.132(3)	0.475(1)	0.745(3)	6.352

H(15)	-0.082(3)	0.380(1)	0.613(3)	6.352
H(16)	0.035(3)	0.415(1)	0.758(3)	6.352
H(17)	0.149(3)	0.189(1)	0.327(3)	6.352
H(18)	0.104(3)	0.191(1)	0.454(3)	6.352
H(19)	0.201(3)	0.099(1)	0.614(3)	6.352
H(20)	0.383(4)	0.347(2)	0.849(4)	13.694
H(21)	0.621(3)	0.381(1)	1.358(3)	6.352
H(22)	0.024(3)	0.241(1)	0.903(3)	6.352
H(23)	-0.157(3)	0.190(1)	0.682(3)	6.352
H(24)	0.547(3)	0.392(1)	1.088(3)	13.893
H(25)	-0.179(3)	0.236(1)	1.306(3)	15.207
H(26)	0.265(3)	0.238(1)	1.116(3)	11.708
H(27)	-0.2565	0.1216	0.5381	6.352
H(28)	0.4056	0.4819	1.6437	6.352
H(29)	0.662(3)	0.025(1)	0.776(3)	6.352
H(30)	-0.291(3)	0.313(1)	0.950(3)	6.352
H(31)	0.546(3)	0.266(1)	0.572(3)	24.163
H(32)	0.089(3)	0.327(1)	1.165(3)	6.352
H(33)	0.040(3)	0.383(1)	1.116(3)	6.352
H(34)	0.476(3)	0.191(1)	1.217(3)	6.352
H(35)	0.680(3)	0.072(1)	1.024(3)	6.352
H(36)	0.6144	0.3913	1.5427	6.352
H(37)	0.025(3)	0.291(1)	0.687(3)	6.352
H(39)	0.393(3)	0.273(1)	0.653(3)	6.352
H(40)	0.197(3)	0.492(1)	1.623(3)	6.352
H(42)	0.5013	0.3125	1.3137	6.352
H(45)	0.412(3)	0.131(1)	1.259(3)	6.352
H(48)	-0.139(3)	0.225(1)	1.110(3)	6.352
H(50)	-0.0672	0.2945	1.3411	6.352
H(41)	0.274(3)	0.209(1)	0.972(3)	11.708
H(38)	-0.305(3)	0.253(1)	1.162(3)	15.207
H(43)	0.5262	0.1915	0.5417	24.163
H(44)	0.5812	0.2319	0.7055	24.163
H(46)	0.4829	0.321	1.0623	13.893
H(47)	0.3451	0.4082	0.9148	13.694
H(49)	0.3323	0.2481	0.489	19.5
H(51)	0.3833	0.2482	0.6588	19.5

** Note some of the hydrogen positions are to four decimal places with terminal zero's omitted. The hydrogen coordinates have no esd's as their positions were not refined.

Table 26. Anisotropic Displacement Parameters

Anisotropic Displacement Parameters[352]						
Atom	U11	U22	U33	U12	U13	U23
S(1)	0.0890(6)	0.0739(6)	0.1442(9)	0.0274(5)	0.0754(6)	0.0284(6)
S(2)	0.1053(8)	0.0968(8)	0.1057(8)	0.0489(7)	0.0160(6)	0.0001(6)
S(3)	0.1077(8)	0.1005(8)	0.184(1)	0.0275(6)	0.0990(9)	0.0295(8)
S(4)	0.381(3)	0.0830(8)	0.148(1)	0.057(1)	0.205(2)	0.0295(8)
O(1)	0.124(3)	0.152(3)	0.080(2)	-0.015(2)	0.029(2)	0.011(2)
O(2)	0.096(2)	0.182(3)	0.132(3)	0.042(2)	0.054(2)	0.055(2)
O(3)	0.137(3)	0.223(4)	0.127(3)	0.048(3)	0.085(2)	0.070(3)
O(5)	0.127(2)	0.082(2)	0.096(2)	0.027(1)	0.081(2)	0.025(1)
O(6)	0.097(2)	0.072(2)	0.114(2)	0.011(1)	0.048(2)	0.033(1)
O(7)	0.102(2)	0.076(2)	0.102(2)	0.014(1)	0.019(2)	0.030(2)
O(10)	0.112(2)	0.075(2)	0.117(2)	0.011(2)	0.029(2)	0.022(1)
O(11)	0.090(2)	0.099(2)	0.099(2)	0.027(1)	0.043(2)	0.012(1)
N(1)	0.063(2)	0.063(2)	0.099(2)	0.001(1)	0.040(2)	0.007(2)
N(2)	0.150(3)	0.068(2)	0.098(2)	0.040(2)	0.094(2)	0.037(2)
C(1)	0.090(3)	0.118(4)	0.176(5)	0.048(3)	0.061(3)	0.078(4)
C(2)	0.049(2)	0.061(2)	0.067(2)	0.007(1)	0.022(2)	0.012(2)
C(3)	0.092(3)	0.074(3)	0.142(5)	0.023(3)	-0.018(3)	0.003(3)
C(4)	0.235(6)	0.145(5)	0.060(3)	-0.128(5)	0.042(3)	-0.008(3)
C(5)	0.53(2)	0.099(5)	0.251(9)	-0.048(7)	0.31(1)	-0.028(5)
C(15)	0.070(2)	0.083(2)	0.053(2)	0.010(2)	0.017(2)	0.023(2)
C(16)	0.066(2)	0.064(2)	0.090(2)	0.024(2)	0.015(2)	0.026(2)
C(17)	0.068(2)	0.070(2)	0.100(3)	0.016(2)	0.030(2)	0.025(2)
C(19)	0.068(2)	0.055(2)	0.079(2)	0.020(2)	0.001(2)	0.018(2)
C(20)	0.078(2)	0.054(2)	0.141(4)	0.005(2)	0.072(3)	0.009(2)
C(21)	0.059(2)	0.063(2)	0.055(2)	0.010(1)	0.020(2)	0.014(2)
C(22)	0.075(2)	0.059(2)	0.129(4)	0.011(2)	0.042(3)	0.018(2)
C(25)	0.125(3)	0.098(3)	0.072(3)	0.035(3)	0.060(3)	0.027(2)
C(26)	0.142(4)	0.059(3)	0.111(3)	-0.004(3)	0.027(3)	0.000(2)
C(27)	0.059(2)	0.075(2)	0.106(3)	0.005(2)	0.032(2)	0.015(2)
C(28)	0.210(5)	0.056(2)	0.059(2)	0.028(3)	0.086(3)	0.015(2)
C(29)	0.065(2)	0.114(4)	0.080(3)	0.022(2)	0.027(2)	0.009(2)
C(30)	0.102(3)	0.067(2)	0.111(3)	0.035(2)	0.064(3)	0.034(2)
C(31)	0.088(4)	0.33(1)	0.150(6)	-0.084(5)	-0.028(4)	0.042(6)
C(32)	0.095(3)	0.089(3)	0.099(3)	0.011(3)	0.006(3)	0.014(3)
C(33)	0.126(3)	0.126(3)	0.077(3)	0.076(3)	0.067(3)	0.042(2)
C(34)	0.137(4)	0.112(3)	0.101(3)	0.015(3)	0.088(3)	0.021(3)

C(35)	0.073(3)	0.074(3)	0.131(4)	0.017(2)	0.010(3)	0.028(3)
C(36)	0.064(3)	0.163(5)	0.226(8)	0.023(4)	0.031(5)	0.126(6)
C(37)	0.416(9)	0.090(3)	0.264(6)	0.083(4)	0.294(7)	0.089(4)
C(38)	0.223(7)	0.108(4)	0.051(3)	-0.068(4)	0.043(3)	0.013(3)
C(39)	0.137(4)	0.085(3)	0.103(3)	0.046(3)	0.063(3)	0.020(3)
C(41)	0.084(3)	0.239(6)	0.158(5)	0.053(4)	0.080(4)	0.077(5)
C(42)	0.081(3)	0.108(3)	0.122(3)	0.012(2)	0.039(3)	0.042(3)
C(43)	0.132(4)	0.185(5)	0.148(6)	-0.020(4)	0.107(4)	0.019(4)
C(44)	0.073(3)	0.144(4)	0.121(4)	0.019(3)	0.051(3)	0.047(3)
C(45)	0.144(5)	0.106(4)	0.314(8)	0.082(3)	0.163(6)	0.105(5)
C(46)	0.126(4)	0.103(4)	0.090(3)	-0.012(3)	0.018(3)	0.018(3)
C(47)	0.147(6)	0.114(6)	0.38(1)	-0.027(4)	0.174(7)	-0.014(6)
C(48)	0.243(6)	0.083(3)	0.236(6)	0.026(4)	0.179(6)	0.047(3)
C(50)	0.157(6)	0.138(6)	0.42(1)	-0.050(5)	0.118(7)	0.046(7)

3.5. Six donor atoms thiophene-based macrocycle (4 oxygens, 2 nitrogens)

Table 27. Summary of the crystal data, structure solution and refinement parameters of compounds **8b** and **9b**

A. Crystal Data	8b	9b
Empirical Formula	$C_{20}H_{30}O_4N_2S_2$	$C_{18}H_{24}N_2S_2O_4$
Formula Weight	426.59	396.52
Crystal Color, Habit	colourless, plate	colourless, plate
Crystal Dimensions	0.20 X 0.04 X 0.30 mm	0.40 X 0.54 X 0.02 mm
Crystal System	monoclinic	orthorhombic
Lattice Type	Primitive	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	24 (32.2 - 36.8°)	25 (26.6 - 35.0°)
Omega Scan Peak Width at Half-height	0.22°	0.25°
Lattice Parameters	a = 8.0(3) Å, b = 6.1(2) Å c = 44.3(2) Å, β = 92(1) Å V = 2184(84) $Å^3$	a = 23.727(6) Å, b = 17.199(5) Å c = 10.463(7) Å, V = 4270(3) $Å^3$
Space Group	P21/c (#14)	Pbca (#61)
Z value	4	8
Dcalc	1.297 g/cm^3	1.234 g/cm^3
F000	912	1680
μ(MoKα)	2.71 cm^{-1}	2.72 cm^{-1}

Slit Aperture	3.0 mm horizontal, 3.0 mm vertical	3.0 mm horizontal, 3.0 mm vertical
Scan Width	$(0.94 + 0.35 \tan\theta)^\circ$	$(0.79 + 0.35 \tan\theta)^\circ$
2θmax	55.2°	55.0°
No. of Reflections Measured	Total: 5803, Unique: 5431 (Rint = 0.471)	All Unique: 5463 (Rint= 0.0)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.3702 - 1.0000)	Lorentz-polarization Absorption (trans. factors: 0.8829 - 1.0000)
B. Structure Solution and Refinement		
Structure Solution	Direct Methods (SIR97)	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F	Full-matrix least-squares on F
Function Minimized	Σ w $(\lvert F_o\rvert - \lvert F_c\rvert)^2$	Σ w $(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
p-factor	0.01	0.0099
Anomalous Dispersion	All non-hydrogen atoms	All non-hydrogen atoms
No. Observations ($I>3.00\sigma(I)$)	1668	1938
No. Variables	238	253
Reflection/Parameter Ratio	7.01	7.66
Residuals: R; Rw	0.224 ; 0.232	0.061 ; 0.058
Goodness of Fit Indicator	8.72	2.12
Max Shift/Error in Final Cycle	20.3	0.01
Maximum peak in Final Diff. Map	1.07 $e^-/Å^3$	0.28 $e^-/Å^3$
Minimum peak in Final Diff. Map	-1.08 $e^-/Å^3$	-0.34 $e^-/Å^3$

3.5.1. 18,21-bis-(methyl)-2,5,8,11-tetraoxa-15,24-dithia-18,21-diaza-tricyclo[21.3.0.0]-hexacosa-1(26),12(16),13,25-tetraene **8b**

Table 28. Atomic coordinates and B_{iso}/B_{eq}

Positional parameters and B(eq)[351]				
Atom	X	Y	Z	B(eq)
S(1)	0.7083(3)	0.3844(6)	0.23750(5)	3.43(7)
S(2)	0.9749(4)	0.2763(6)	0.04181(8)	5.33(9)
O(3)	0.504(1)	-0.500(1)	0.0812(2)	5.0(2)
O(4)	0.625(1)	-0.044(1)	0.1721(2)	3.7(2)
O(5)	0.594(1)	-0.104(2)	0.0462(2)	6.2(3)
O(6)	0.3848(8)	-0.492(1)	0.1427(1)	3.8(2)
N(1)	1.039(1)	0.240(2)	0.1844(2)	4.5(3)
N(2)	1.005(1)	0.013(2)	0.1062(2)	4.9(3)
C(1)	0.970(1)	0.195(2)	0.1533(2)	3.9(3)

C(2)	0.827(2)	0.090(2)	0.0631(3)	5(4)
C(3)	0.627(1)	0.063(3)	0.1938(3)	7.2(4)
C(4)	0.762(1)	0.219(3)	0.2130(2)	8.3(4)
C(5)	0.477(1)	0.214(2)	0.2079(2)	4.1(3)
C(6)	0.744(2)	0.084(2)	0.0074(2)	5.4(4)
C(7)	0.723(1)	0.035(2)	0.0360(4)	7.4(5)
C(8)	0.942(2)	0.089(3)	0.2051(3)	6(5)
C(9)	1.045(2)	-0.228(3)	0.0941(3)	10.6(5)
C(10)	1.001(1)	0.026(1)	0.1400(1)	1.7(2)
C(11)	0.495(1)	0.373(2)	0.2271(3)	10.8(5)
C(12)	0.836(2)	0.083(3)	0.0939(3)	8(5)
C(13)	0.488(1)	-0.182(2)	0.1702(2)	3.6(3)
C(16)	0.416(2)	-0.688(2)	0.1232(3)	4.2(3)
C(18)	0.481(2)	-0.462(1)	0.0501(1)	3.8(3)
C(19)	0.378(2)	-0.615(2)	0.0946(3)	5.5(4)
C(20)	0.527(1)	-0.303(2)	0.1444(2)	7.0(4)
C(21)	0.886(2)	0.233(2)	0.0048(3)	4.4(3)
C(23)	0.600(2)	-0.331(1)	0.0362(2)	5.6(3)
C(26)	1.059(2)	0.488(2)	0.1975(2)	5.7(4)
H(2)	1.1619	-0.2477	0.0937	12.666
H(3)	1.092	0.4507	0.1795	2.998
H(4)	1.1187	0.6177	0.2021	2.998
H(5)	0.5295	-0.7318	0.1251	5.057
H(6)	1.0345	0.4566	0.2183	2.998
H(7)	0.8805	0.0177	0.1835	2.998
H(10)	1.0064	0.3104	0.1409	4.677
H(13)	0.3659(2)	0.1816(4)	0.2011(2)	4.952
H(14)	0.6768(2)	0.0307(4)	0.0091(2)	6.494
H(15)	0.4091(2)	0.4649(4)	0.2342(1)	12.91
H(16)	0.9239(2)	0.2944(4)	0.0133(1)	5.264
H(17)	0.8518	0.2009	0.1545	4.677
H(19)	1.0048	0.0617	0.2232	7.427
H(20)	0.9208	-0.0775	0.1459	2.085
H(21)	1.1088	-0.0183	0.1473	2.085
H(22)	0.7548	-0.0172	0.1006	9.081
H(23)	0.8124	0.2237	0.1015	9.081
H(24)	0.4809	-0.2714	0.1876	4.311
H(26)	0.3462	-0.8053	0.1285	5.057
H(27)	0.481	-0.6	0.0403	4.54
H(28)	0.3754	-0.3952	0.047	4.54
H(29)	0.283	-0.5234	0.0955	6.551

H(30)	0.3518	-0.738	0.0823	6.551
H(31)	0.6354	-0.3654	0.1467	8.377
H(32)	0.5218	-0.2151	0.1268	8.377
H(34)	0.7082	-0.387	0.0411	6.72
H(1)	0.9981	-0.3323	0.1071	12.666
H(12)	0.9974	-0.2446	0.0743	12.666
H(25)	0.3865	-0.1037	0.1672	4.311
H(33)	0.5803	-0.3355	0.015	6.72

** Note the hydrogen positions are to four decimal places with terminal zero's omitted. The hydrogen coordinates have no esd's as their positions were not refined.

Table 29. Anisotropic Displacement Parameters

Anisotropic Displacement Parameters[352]						
Atom	U11	U22	U33	U12	U13	U23
S(1)	0.043(2)	0.043(2)	0.043(1)	0.000(2)	0.001(1)	0.000(2)
S(2)	0.068(2)	0.068(3)	0.068(2)	0.000(2)	0.002(2)	0.000(2)
O(3)	0.063(5)	0.063(6)	0.063(6)	0.000(5)	0.002(5)	0.000(5)
O(4)	0.047(6)	0.047(5)	0.047(5)	0.000(4)	0.002(5)	0.000(4)
O(5)	0.079(5)	0.079(9)	0.079(6)	0.000(6)	0.003(4)	0.000(6)
O(6)	0.048(4)	0.048(6)	0.048(4)	0.000(5)	0.002(3)	0.000(4)
N(1)	0.057(5)	0.057(9)	0.057(6)	0.000(6)	0.002(4)	0.000(6)
N(2)	0.062(5)	0.06(1)	0.062(6)	0.000(6)	0.002(5)	0.000(6)
C(1)	0.049(8)	0.049(9)	0.049(5)	0.000(8)	0.002(5)	0.000(5)
C(2)	0.1(3)	0.0599	0.0599	0	0.002	0
C(3)	0.091(5)	0.09(2)	0.091(8)	0.000(9)	0.003(6)	0.00(1)
C(4)	0.105(7)	0.10(2)	0.105(6)	0.00(1)	0.004(5)	0.000(9)
C(5)	0.052(8)	0.052(8)	0.052(7)	0.000(8)	0.002(6)	0.000(6)
C(6)	0.07(1)	0.07(1)	0.069(4)	0.00(1)	0.002(6)	0.000(6)
C(7)	0.093(8)	0.09(1)	0.09(2)	0.000(8)	0.00(1)	0.00(1)
C(8)	0.1(3)	0.0784	0.0784	0	0.0027	0
C(9)	0.13(1)	0.13(2)	0.134(7)	0.00(1)	0.005(8)	0.00(1)
C(10)	0.022(7)	0.022(5)	0.022(3)	0.000(5)	0.001(4)	0.000(3)
C(11)	0.136(8)	0.14(2)	0.14(1)	0.00(1)	0.005(8)	0.00(1)
C(12)	0.1(4)	0.0958	0.0958	0	0.0033	0
C(13)	0.045(7)	0.045(8)	0.045(5)	0.000(7)	0.002(5)	0.000(5)
C(16)	0.053(9)	0.053(8)	0.053(7)	0.000(7)	0.002(7)	0.000(6)
C(18)	0.05(1)	0.048(4)	0.048(4)	0.000(7)	0.002(5)	0.000(3)

C(19)	0.07(1)	0.069(8)	0.07(1)	0.000(9)	0.00(1)	0.000(8)
C(20)	0.088(8)	0.09(1)	0.088(8)	0.000(9)	0.003(7)	0.000(9)
C(21)	0.056(9)	0.056(7)	0.056(9)	0.000(8)	0.002(8)	0.000(7)
C(23)	0.07(1)	0.071(4)	0.071(7)	0.000(7)	0.002(9)	0.000(5)
C(26)	0.07(1)	0.073(9)	0.073(7)	0.00(1)	0.002(8)	0.000(6)

3.5.2. 2,5,8,11-tetraoxa-15,26-dithia-18,21-diaza-tetracyclo[21.4.4.0.0]-octacosa-1(25),27,12(16),13-tetraene **9b**

Table 30. Atomic coordinates and B_{iso}/B_{eq}

Positional parametersand B(eq)[351]				
Atom	X	Y	Z	B(eq)
S(1)	1.10657(5)	0.16475(8)	0.4687(1)	4.49(3)
S(2)	0.76371(5)	0.30195(8)	0.6321(1)	5.31(3)
O(1)	0.7524(1)	0.0801(2)	0.6692(3)	5.16(9)
O(3)	1.0541(1)	0.0263(2)	0.7333(2)	3.42(7)
O(5)	0.8240(1)	-0.0102(2)	0.8549(3)	4.88(8)
O(6)	0.9476(1)	-0.0278(2)	0.8397(3)	4.49(8)
N(1)	0.8781(1)	0.1770(2)	0.5365(3)	3.12(8)
N(7)	0.9817(1)	0.2096(2)	0.6644(3)	2.91(8)
C(9)	1.1066(2)	0.0224(2)	0.5265(4)	3.8(1)
C(10)	0.9709(2)	0.2370(2)	0.5346(4)	3.3(1)
C(11)	0.8879(2)	0.1512(2)	0.6678(4)	3.3(1)
C(12)	0.7777(2)	0.2068(3)	0.6003(4)	3.9(1)
C(13)	0.9505(2)	0.1379(2)	0.6891(3)	2.95(9)
C(14)	1.0763(1)	0.0615(2)	0.6263(4)	3.0(1)
C(15)	0.8183(2)	0.1785(3)	0.4993(4)	4.2(1)
C(16)	1.0425(2)	0.1988(2)	0.6902(4)	3.4(1)
C(17)	1.0721(1)	0.1387(2)	0.6078(4)	3.0(1)
C(18)	0.7477(2)	0.1596(3)	0.6822(4)	4.0(1)
C(19)	1.1255(2)	0.0709(3)	0.4383(4)	4.8(1)
C(20)	0.7759(2)	0.0364(3)	0.8852(4)	5.3(1)
C(21)	0.9078(2)	0.2505(2)	0.5160(4)	3.7(1)
C(22)	1.0290(2)	-0.0477(2)	0.7108(4)	4.3(1)
C(23)	0.8634(2)	-0.0073(3)	0.9574(4)	5.4(1)
C(24)	0.9121(2)	-0.0608(3)	0.9337(4)	4.9(1)
C(25)	0.7341(2)	0.0328(3)	0.7753(5)	5.8(1)

C(26)	0.9964(2)	-0.0752(2)	0.8191(4)	4.6(1)
C(27)	0.7188(2)	0.2785(3)	0.7548(5)	5.3(1)
C(28)	0.7136(2)	0.2024(3)	0.7687(4)	5.2(1)
H(1)	1.1089	-0.0283	0.5449	3.818
H(2)	1.15	0.0736	0.3562	3.818
H(3)	1.0576	0.2534	0.6762	3.818
H(4)	0.9598	0.0924	0.6295	3.818
H(5)	0.8931	0.2953	0.5619	3.818
H(6)	1.0218	-0.0725	0.9041	3.818
H(7)	1.0113	-0.0544	0.624	3.818
H(8)	0.8096	0.1323	0.4941	3.818
H(9)	0.9008	0.2784	0.4201	3.818
H(10)	0.9772	0.2	0.4722	3.818
H(11)	0.9936	0.2926	0.5088	3.818
H(12)	0.8711	0.1004	0.6792	3.818
H(13)	0.8721	0.1946	0.7265	3.818
H(14)	0.7392	-0.0176	0.7408	3.818
H(15)	0.8175	0.2051	0.4032	3.818
H(16)	0.9608	0.1256	0.7907	3.818
H(17)	1.043	0.1817	0.79	3.818
H(18)	0.7528	-0.0057	0.9727	3.818
H(19)	0.69	0.167	0.8623	3.818
H(20)	0.8772	0.0456	0.9994	3.818
H(21)	0.9327	-0.0761	1.0202	3.818
H(22)	0.8436	-0.0206	1.0468	3.818
H(23)	0.89	-0.1196	0.8993	3.818
H(24)	0.9823	-0.14	0.805	3.818
H(25)	0.7032	0.0846	0.8127	3.818
H(26)	0.6944	0.3311	0.7945	3.818
H(27)	1.0594	-0.0891	0.6528	3.818
H(28)	0.7914	0.1077	0.8943	3.818

** Note the hydrogen positions are to four decimal places with terminal zero's omitted. The hydrogen coordinates have no esd's as their positions were not refined.

Table 31. Anisotropic Displacement Parameters

Anisotropic Displacement Parameters[352]						
Atom	U11	U22	U33	U12	U13	U23
S(1)	0.0444(6)	0.0770(9)	0.0494(7)	-0.0051(6)	0.0033(6)	0.0052(7)
S(2)	0.0596(8)	0.082(1)	0.0603(8)	0.0256(7)	-0.0045(7)	0.0015(8)
O(1)	0.060(2)	0.080(3)	0.056(2)	-0.014(2)	0.006(2)	-0.001(2)
O(3)	0.043(2)	0.044(2)	0.043(2)	-0.004(1)	-0.007(1)	-0.001(2)
O(5)	0.054(2)	0.083(2)	0.049(2)	-0.000(2)	0.008(2)	-0.006(2)
O(6)	0.059(2)	0.057(2)	0.054(2)	-0.001(2)	0.006(2)	0.013(2)
N(1)	0.033(2)	0.060(2)	0.026(2)	0.005(2)	-0.001(2)	0.007(2)
N(7)	0.032(2)	0.043(2)	0.036(2)	0.003(2)	-0.007(1)	-0.002(2)
C(9)	0.036(2)	0.063(3)	0.047(3)	0.006(2)	-0.010(2)	-0.015(3)
C(10)	0.042(2)	0.038(2)	0.043(3)	-0.008(2)	-0.005(2)	0.006(2)
C(11)	0.040(2)	0.044(3)	0.040(2)	0.006(2)	-0.002(2)	0.008(2)
C(12)	0.035(2)	0.076(3)	0.037(3)	0.011(2)	-0.004(2)	0.000(3)
C(13)	0.034(2)	0.046(3)	0.032(2)	-0.002(2)	-0.002(2)	0.002(2)
C(14)	0.025(2)	0.049(3)	0.039(3)	-0.003(2)	-0.008(2)	-0.012(2)
C(15)	0.040(2)	0.086(4)	0.034(3)	-0.003(2)	-0.003(2)	-0.003(3)
C(16)	0.045(2)	0.044(2)	0.041(3)	-0.001(2)	-0.005(2)	-0.003(2)
C(17)	0.024(2)	0.051(3)	0.038(2)	-0.009(2)	-0.005(2)	-0.006(2)
C(18)	0.030(2)	0.079(4)	0.042(3)	0.001(2)	-0.007(2)	0.003(3)
C(19)	0.044(3)	0.097(4)	0.040(3)	0.003(3)	0.005(2)	0.001(3)
C(20)	0.068(3)	0.087(4)	0.048(3)	0.002(3)	0.016(3)	0.008(3)
C(21)	0.044(2)	0.049(3)	0.049(3)	0.005(2)	-0.005(2)	0.012(2)
C(22)	0.066(3)	0.045(3)	0.051(3)	-0.006(2)	0.009(3)	-0.011(2)
C(23)	0.070(4)	0.098(4)	0.038(3)	-0.011(3)	0.011(3)	-0.009(3)
C(24)	0.069(3)	0.074(4)	0.045(3)	-0.008(3)	-0.005(3)	0.009(3)
C(25)	0.065(3)	0.083(4)	0.070(4)	-0.010(3)	0.013(3)	0.003(3)
C(26)	0.063(3)	0.045(3)	0.065(3)	-0.003(2)	-0.011(3)	0.005(3)
C(27)	0.041(3)	0.104(4)	0.058(3)	0.033(3)	-0.001(2)	-0.009(4)
C(28)	0.040(3)	0.117(5)	0.042(3)	0.010(3)	0.005(2)	-0.005(3)

3.6. Seven donor atoms thiophene-based macrocycle (5 oxygens, 2 nitrogens): 18,24-bis-(p-toluenesulphonamide)-2,5,8,11,21-pentaoxa-15,27-dithia-18,24-diaza-tricyclo[24.3.0.0]-nonacosa-1(26),12(16),13,28-tetraene **23**

Table 32. Summary of the crystal data, structure solution and refinement parameters of compound **23**

A. Crystal Data

Empirical Formula	$C_{34}H_{42}N_2O_9S_4$
Formula Weight	750.95
Crystal Color, Habit	colourless, block
Crystal Dimensions	0.18 X 0.27 X 0.54 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (36.3 - 39.7°)
Omega Scan Peak Width at Half-height	0.21°
Lattice Parameters	a = 18.421(3) Å, b = 9.235(9) Å, c = 22.775(4) Å β = 105.61(1) Å, V = 3732(3) $Å^3$
Space Group	P21/c (#14)
Z value	4
Dcalc	1.337 g/cm^3
F000	1584
μ(MoKα)	3.08 cm^{-1}
Slit Aperture	3.0 mm horizontal, 3.0 mm vertical
Scan Width	(1.00 + 0.35 tan θ)°
2θmax	55.0°
No. of Reflections Measured	Total: 9346, Unique: 9075 (Rint = 0.041)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.8925 - 1.0000)

B. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma w (\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
p-factor	0.0046
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00□(I))	4185
No. Variables	568
Reflection/Parameter Ratio	7.37

Residuals: R; Rw	0.052 ; 0.043
Goodness of Fit Indicator	2.06
Max Shift/Error in Final Cycle	1.26
Maximum peak in Final Diff. Map	0.31 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.28 $e^-/Å^3$

Table 33. Atomic coordinates and B_{iso}/B_{eq}

Positional parametersand B(eq)[351]				
Atom	X	Y	Z	B(eq)
S(1)	0.58970(4)	0.15789(8)	0.61917(3)	3.71(2)
S(2)	0.90624(4)	-0.22590(9)	0.83820(4)	5.31(2)
S(3)	0.36991(5)	0.1156(1)	0.62526(4)	6.75(3)
S(4)	1.04608(5)	0.1217(1)	0.90306(5)	6.80(3)
O(1)	0.9230(1)	-0.3244(2)	0.8882(1)	7.53(7)
O(2)	0.8849(1)	0.2650(2)	0.9641(1)	6.45(6)
O(5)	0.71459(9)	0.1312(2)	0.78445(8)	4.33(5)
O(6)	0.6412(1)	0.2770(2)	0.62559(8)	4.86(5)
O(7)	0.5203(1)	0.1645(2)	0.57191(8)	5.22(5)
O(9)	0.4680(1)	0.0896(2)	0.7956(1)	5.58(6)
O(11)	0.8486(1)	-0.2602(2)	0.7834(1)	7.12(7)
O(12)	0.7258(1)	0.2808(2)	0.95243(9)	5.69(6)
O(13)	0.5588(1)	0.1792(2)	0.91321(9)	5.77(6)
N(1)	0.8809(1)	-0.0766(3)	0.8635(1)	4.64(6)
N(2)	0.5735(1)	0.1313(2)	0.68480(9)	3.36(5)
C(1)	0.5965(1)	0.2360(3)	0.7349(1)	3.60(7)
C(16)	0.6358(1)	-0.0024(3)	0.6065(1)	3.28(6)
C(17)	0.7029(2)	-0.0422(4)	0.6473(1)	4.60(8)
C(18)	0.8350(2)	0.0286(4)	0.8209(1)	4.55(8)
C(19)	0.6435(2)	0.1685(4)	0.7933(1)	4.20(7)
C(20)	0.6060(1)	-0.0867(3)	0.5560(1)	3.90(7)
C(22)	0.9906(1)	-0.1962(3)	0.8177(1)	4.05(7)
C(23)	0.5165(2)	0.0223(3)	0.6878(1)	3.91(7)
C(24)	0.4185(2)	0.1100(3)	0.7395(1)	4.61(8)
C(25)	0.6436(2)	-0.2096(3)	0.5464(1)	4.31(8)
C(26)	0.7104(2)	-0.2516(3)	0.5869(1)	4.58(8)
C(27)	0.7395(2)	-0.1662(4)	0.6369(1)	5.19(8)
C(28)	0.7599(2)	0.0515(4)	0.8332(1)	4.72(8)
C(29)	1.1228(2)	-0.1377(3)	0.7852(1)	4.70(8)

C(30)	0.9881(2)	-0.1273(4)	0.7641(1)	5.50(9)
C(31)	0.4406(2)	0.1082(4)	0.8477(2)	5.5(1)
C(32)	0.9462(2)	0.2476(4)	0.9409(1)	5.03(9)
C(33)	0.9642(2)	0.1149(4)	0.9252(1)	4.85(8)
C(34)	1.0593(2)	-0.2370(4)	0.8550(2)	5.66(9)
C(35)	0.4421(1)	0.0835(3)	0.6896(1)	4.14(7)
C(36)	0.5026(2)	0.0682(4)	0.9016(2)	5.9(1)
C(37)	0.9204(2)	-0.0219(4)	0.9251(1)	5.09(9)
C(38)	0.9967(2)	0.3568(4)	0.9347(2)	6.1(1)
C(39)	0.7792(2)	0.3896(4)	0.9763(2)	6.3(1)
C(40)	1.1241(2)	-0.2074(4)	0.8379(2)	5.85(9)
C(41)	0.3420(2)	0.1563(4)	0.7270(2)	5.8(1)
C(42)	0.8401(2)	0.3911(4)	0.9454(2)	6.1(1)
C(43)	0.6703(2)	0.2731(4)	0.9842(1)	6.5(1)
C(44)	1.0537(2)	-0.0996(4)	0.7484(1)	6.0(1)
C(45)	1.1930(2)	-0.1012(4)	0.7665(2)	7.0(1)
C(46)	1.0536(2)	0.3047(4)	0.9150(2)	7.0(1)
C(47)	0.6202(2)	0.1456(5)	0.9644(2)	6.8(1)
C(48)	0.7465(2)	-0.3998(4)	0.5781(2)	7.5(1)
C(49)	0.3104(2)	0.1602(5)	0.6670(2)	7.4(1)
H(1)	0.649(1)	0.238(3)	0.828(1)	4.352
H(2)	0.861(1)	0.115(3)	0.823(1)	4.352
H(3)	0.539(1)	-0.041(3)	0.722(1)	4.352
H(4)	0.513(1)	-0.036(3)	0.654(1)	4.352
H(5)	0.424(1)	0.218(3)	0.850(1)	4.352
H(6)	0.262(1)	0.189(3)	0.649(1)	4.352
H(7)	0.321(1)	0.175(3)	0.758(1)	4.352
H(8)	0.483(1)	0.061(3)	0.934(1)	4.352
H(9)	0.538(1)	-0.027(3)	0.902(1)	4.352
H(10)	0.816(1)	0.387(3)	0.903(1)	4.352
H(11)	0.872(1)	0.473(3)	0.957(1)	4.352
H(12)	0.697(1)	0.262(3)	1.027(1)	4.352
H(13)	0.594(1)	0.128(3)	0.995(1)	4.352
H(14)	0.399(1)	0.040(3)	0.846(1)	4.352
H(15)	1.058(1)	-0.273(3)	0.889(1)	4.352
H(16)	0.783(1)	-0.196(3)	0.666(1)	4.352
H(17)	0.626(1)	-0.262(3)	0.513(1)	4.352
H(18)	0.641(1)	0.075(3)	0.946(1)	4.352
H(19)	0.559(1)	-0.059(3)	0.533(1)	4.352
H(20)	0.832(1)	-0.003(3)	0.782(1)	4.352
H(21)	0.881(1)	-0.011(3)	0.948(1)	4.352

H(22)	0.950(1)	-0.108(3)	0.942(1)	4.352
H(23)	1.090(1)	0.353(3)	0.906(1)	4.352
H(24)	0.736(1)	-0.037(3)	0.839(1)	4.352
H(25)	0.618(1)	0.075(3)	0.806(1)	4.352
H(26)	0.945(1)	-0.102(3)	0.741(1)	4.352
H(27)	1.231(1)	-0.153(3)	0.784(1)	4.352
H(28)	0.549(1)	0.273(2)	0.744(1)	4.352
H(29)	0.625(1)	0.312(3)	0.722(1)	4.352
H(30)	0.989(1)	0.449(3)	0.940(1)	4.352
H(31)	1.050(1)	-0.050(3)	0.718(1)	4.352
H(32)	1.165(1)	-0.233(3)	0.861(1)	4.352
H(33)	0.800(1)	0.365(3)	1.019(1)	4.352
H(34)	0.762(1)	0.106(3)	0.870(1)	4.352
H(35)	0.719(1)	0.018(3)	0.678(1)	4.352
H(36)	0.755(1)	0.473(3)	0.971(1)	4.352
H(37)	1.1976	-0.1644	0.7241	4.352
H(38)	1.206(1)	-0.017(3)	0.780(1)	4.352
H(39)	0.794(1)	-0.408(3)	0.606(1)	4.352
H(40)	0.764(1)	-0.400(3)	0.542(1)	4.352
H(41)	0.7125	-0.5116	0.5582	4.352
H(42)	0.6442	0.3839	1.0053	4.352

Table 34. Anisotropic Displacement Parameters

Anisotropic Displacement Parameters[352]						
Atom	U11	U22	U33	U12	U13	U23
S(1)	0.0493(4)	0.0518(4)	0.0393(4)	0.0069(4)	0.0111(3)	0.0018(4)
S(2)	0.0529(5)	0.0550(5)	0.0949(7)	-0.0032(4)	0.0220(5)	0.0005(5)
S(3)	0.0512(5)	0.1141(8)	0.0848(6)	0.0059(5)	0.0076(4)	-0.0075(6)
S(4)	0.0626(5)	0.0928(8)	0.1042(7)	-0.0068(5)	0.0245(5)	-0.0260(6)
O(1)	0.096(2)	0.064(2)	0.139(2)	0.007(1)	0.054(2)	0.031(2)
O(2)	0.087(2)	0.075(2)	0.087(2)	0.028(1)	0.030(1)	0.022(1)
O(5)	0.036(1)	0.080(1)	0.047(1)	0.010(1)	0.0079(8)	0.009(1)
O(6)	0.076(1)	0.054(1)	0.063(1)	-0.010(1)	0.031(1)	0.002(1)
O(7)	0.064(1)	0.078(1)	0.045(1)	0.025(1)	-0.0057(9)	-0.004(1)
O(9)	0.063(1)	0.091(2)	0.070(1)	-0.001(1)	0.039(1)	-0.014(1)
O(11)	0.054(1)	0.094(2)	0.116(2)	-0.023(1)	0.011(1)	-0.039(2)
O(12)	0.078(1)	0.080(2)	0.060(1)	-0.001(1)	0.023(1)	-0.016(1)
O(13)	0.090(2)	0.073(2)	0.061(1)	-0.012(1)	0.028(1)	0.002(1)

N(1)	0.050(1)	0.064(2)	0.056(2)	0.014(1)	0.004(1)	0.005(1)
N(2)	0.041(1)	0.046(1)	0.043(1)	-0.003(1)	0.015(1)	-0.006(1)
C(1)	0.041(2)	0.050(2)	0.047(2)	0.003(1)	0.014(1)	-0.008(1)
C(16)	0.039(1)	0.053(2)	0.033(1)	0.003(1)	0.009(1)	-0.001(1)
C(17)	0.048(2)	0.074(2)	0.048(2)	0.007(2)	0.004(1)	-0.016(2)
C(18)	0.046(2)	0.071(2)	0.051(2)	0.010(2)	0.007(2)	0.007(2)
C(19)	0.042(2)	0.074(2)	0.043(2)	0.006(2)	0.012(1)	-0.002(2)
C(20)	0.044(2)	0.056(2)	0.045(2)	0.005(2)	0.006(1)	0.002(2)
C(22)	0.046(2)	0.043(2)	0.061(2)	0.003(1)	0.009(1)	-0.004(1)
C(23)	0.048(2)	0.050(2)	0.055(2)	-0.002(1)	0.021(2)	-0.005(1)
C(24)	0.052(2)	0.053(2)	0.075(2)	-0.011(2)	0.025(2)	-0.014(2)
C(25)	0.055(2)	0.059(2)	0.049(2)	-0.001(2)	0.012(2)	-0.010(2)
C(26)	0.045(2)	0.070(2)	0.065(2)	0.007(2)	0.025(2)	-0.009(2)
C(27)	0.042(2)	0.085(2)	0.063(2)	0.018(2)	0.002(1)	-0.005(2)
C(28)	0.050(2)	0.071(2)	0.057(2)	0.009(2)	0.013(2)	0.010(2)
C(29)	0.052(2)	0.052(2)	0.076(2)	0.006(2)	0.021(2)	-0.006(2)
C(30)	0.043(2)	0.089(3)	0.069(2)	0.010(2)	0.001(2)	0.005(2)
C(31)	0.080(2)	0.059(2)	0.087(3)	-0.019(2)	0.054(2)	-0.014(2)
C(32)	0.060(2)	0.077(3)	0.049(2)	0.012(2)	0.005(2)	0.010(2)
C(33)	0.051(2)	0.074(2)	0.050(2)	0.011(2)	-0.002(1)	0.000(2)
C(34)	0.065(2)	0.067(2)	0.080(3)	0.014(2)	0.015(2)	0.029(2)
C(35)	0.044(2)	0.050(2)	0.066(2)	-0.004(1)	0.020(1)	-0.009(2)
C(36)	0.090(3)	0.073(3)	0.076(3)	-0.015(2)	0.046(2)	0.008(2)
C(37)	0.061(2)	0.072(2)	0.054(2)	0.015(2)	0.006(2)	0.014(2)
C(38)	0.084(3)	0.072(3)	0.071(2)	0.004(2)	0.012(2)	-0.003(2)
C(39)	0.080(3)	0.078(3)	0.077(2)	0.021(2)	0.012(2)	-0.007(2)
C(40)	0.040(2)	0.074(2)	0.099(3)	0.016(2)	0.004(2)	0.016(2)
C(41)	0.055(2)	0.074(2)	0.102(3)	-0.003(2)	0.041(2)	-0.020(2)
C(42)	0.065(2)	0.072(3)	0.088(3)	0.002(2)	0.010(2)	0.006(2)
C(43)	0.100(3)	0.101(3)	0.053(2)	-0.016(2)	0.036(2)	-0.026(2)
C(44)	0.069(2)	0.093(3)	0.065(2)	0.007(2)	0.018(2)	0.014(2)
C(45)	0.065(2)	0.077(3)	0.133(4)	0.010(2)	0.042(3)	-0.020(3)
C(46)	0.072(3)	0.101(3)	0.093(3)	-0.016(2)	0.023(2)	-0.018(2)
C(47)	0.096(3)	0.116(4)	0.056(2)	-0.003(3)	0.037(2)	0.006(2)
C(48)	0.090(3)	0.089(3)	0.106(3)	0.043(2)	0.026(2)	-0.008(3)
C(49)	0.047(2)	0.106(3)	0.122(3)	0.012(2)	0.013(2)	-0.017(3)

3.7. Eight donor atoms thiophene-based macrocycle (6 oxygens, 2 nitrogens): 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene **24**

Table 35. Summary of the crystal data, structure solution and refinement parameters of compound **24**

A. Crystal Data

Empirical Formula	$C_{34}H_{46}N_2O_6S_4$
Formula Weight	706.99
Crystal Color, Habit	yellow, needle
Crystal Dimensions	0.20 X 0.20 X 1.00 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	24 (39.7 - 40.0°)
Omega Scan Peak Width at Half-height	0.21°
Lattice Parameters	a = 9.528(3) Å, b = 14.004(6) Å, c = 6.874(4) Å α = 92.70(5) Å, β = 98.70(4) Å, γ = 106.01(3) Å, V = 867.7(7) $Å^3$
Space Group	P-1 (#2)
Z value	1
Dcalc	1.353 g/cm^3
F000	376
μ(MoKα)	3.20 cm^{-1}
Slit Aperture	3.0 mm horizontal, 3.0 mm vertical
Scan Width	(1.31 + 0.35 tan θ)°
2θmax	55.0°
No. of Reflections Measured	Total: 4216, Unique: 3979 (Rint = 0.079)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.9461 - 1.0000)

B. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR88)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma w (\|F_o\| - \|F_c\|)^2$
Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
p-factor	0.0192
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00□(I))	2572
No. Variables	208
Reflection/Parameter Ratio	12.37

Residuals: R; Rw	0.066 ; 0.079
Goodness of Fit Indicator	3.23
Max Shift/Error in Final Cycle	0
Maximum peak in Final Diff. Map	0.69 $e^{-}/\text{Å}^{3}$
Minimum peak in Final Diff. Map	-0.33 $e^{-}/\text{Å}^{3}$

Table 36. Atomic coordinates and B_{iso}/B_{eq}

Positional parameters and B(eq)[351]				
Atom	X	Y	Z	B(eq)
S(1)	-0.01067(8)	0.24285(6)	0.1805(1)	3.63(2)
S(2)	0.39326(8)	0.41483(5)	0.2636(1)	3.25(2)
O(1)	0.4689(2)	0.2553(1)	-0.1587(2)	3.33(4)
O(2)	-0.1465(2)	0.0466(1)	-0.2686(2)	3.61(4)
O(3)	-0.3570(2)	-0.0616(1)	-0.6092(3)	4.63(5)
N(1)	0.1254(2)	0.3529(1)	-0.1569(3)	2.42(4)
C(1)	-0.1372(3)	0.1385(2)	0.2342(4)	3.85(7)
C(2)	-0.1831(3)	0.0677(2)	0.0806(4)	3.63(6)
C(3)	-0.1182(3)	0.0991(2)	-0.0866(3)	2.66(5)
C(4)	-0.0203(3)	0.1927(2)	-0.0553(3)	2.41(5)
C(5)	0.3786(3)	0.3668(2)	0.0222(3)	2.50(5)
C(6)	0.4659(3)	0.3040(2)	0.0184(3)	2.55(5)
C(7)	0.5477(3)	0.2963(2)	0.2065(4)	3.32(6)
C(8)	0.5172(3)	0.3527(2)	0.3542(4)	3.55(6)
C(9)	0.5442(3)	0.1786(2)	-0.1477(4)	3.20(6)
C(10)	0.5081(3)	0.1232(2)	-0.3524(4)	3.72(7)
C(11)	-0.2247(3)	-0.0572(2)	-0.2789(4)	3.54(6)
C(12)	-0.2533(3)	-0.0987(2)	-0.4907(4)	4.05(7)
C(13)	0.0833(3)	0.2429(2)	-0.1878(4)	2.74(5)
C(14)	0.2872(3)	0.3956(2)	-0.1491(4)	2.73(5)
C(15)	0.0498(3)	0.3965(2)	-0.3156(4)	3.38(6)
C(16)	-0.1181(3)	0.3682(2)	-0.3303(4)	4.08(7)
C(17)	-0.1672(3)	0.4144(2)	-0.1586(5)	4.59(8)
H(1)	-0.1586	0.2889	-0.3357	2.988
H(2)	-0.1625	0.3993	-0.4469	2.988
H(3)	-0.1247	0.493	-0.1296	2.988
H(4)	-0.1323	0.3829	-0.0277	2.988
H(5)	0.0968	0.4791	-0.2868	2.988
H(6)	0.072	0.3769	-0.4587	2.988

H(7)	0.3085	0.4716	-0.159	2.988
H(8)	-0.1586	-0.1024	-0.1958	2.988
H(9)	-0.3375	-0.0633	-0.2365	2.988
H(10)	0.1738	0.2139	-0.1705	2.988
H(11)	0.0379	0.216	-0.3218	2.988
H(12)	-0.2632	0.0123	0.0885	2.988
H(13)	-0.1446	0.1292	0.3838	2.988
H(14)	-0.1483	-0.0711	-0.5412	2.988
H(15)	-0.2933	-0.1703	-0.4933	2.988
H(16)	-0.2832	0.4211	-0.1984	2.988

** Note the hydrogen positions are to four decimal places with terminal zero's omitted. The hydrogen coordinates have no esd's as their positions were not refined.

Table 37. Anisotropic Displacement Parameters

Anisotropic Displacement Parameters[352]						
Atom	U11	U22	U33	U12	U13	U23
S(1)	0.0542(5)	0.0446(4)	0.0335(4)	0.0066(3)	0.0083(3)	-0.0081(3)
S(2)	0.0400(4)	0.0482(4)	0.0345(4)	0.0134(3)	0.0061(3)	-0.0074(3)
O(1)	0.046(1)	0.050(1)	0.034(1)	0.0239(9)	0.0001(8)	-0.0069(8)
O(2)	0.053(1)	0.036(1)	0.034(1)	-0.0078(9)	0.0080(9)	-0.0063(8)
O(3)	0.070(1)	0.042(1)	0.046(1)	-0.004(1)	-0.006(1)	0.0008(9)
N(1)	0.025(1)	0.033(1)	0.032(1)	0.0058(9)	0.0050(8)	-0.0019(9)
C(1)	0.055(2)	0.056(2)	0.033(1)	0.012(2)	0.010(1)	0.006(1)
C(2)	0.043(2)	0.047(2)	0.039(1)	-0.002(1)	0.007(1)	0.012(1)
C(3)	0.034(1)	0.034(1)	0.030(1)	0.007(1)	0.001(1)	0.002(1)
C(4)	0.031(1)	0.033(1)	0.027(1)	0.011(1)	0.001(1)	-0.001(1)
C(5)	0.026(1)	0.034(1)	0.032(1)	0.004(1)	0.005(1)	-0.001(1)
C(6)	0.027(1)	0.033(1)	0.034(1)	0.007(1)	0.004(1)	-0.004(1)
C(7)	0.040(2)	0.043(2)	0.036(1)	0.006(1)	-0.000(1)	-0.004(1)
C(8)	0.041(2)	0.050(2)	0.040(2)	0.009(1)	0.003(1)	-0.001(1)
C(9)	0.042(2)	0.038(2)	0.043(2)	0.020(1)	0.000(1)	-0.012(1)
C(10)	0.047(2)	0.045(2)	0.047(2)	0.009(1)	0.009(1)	-0.013(1)
C(11)	0.050(2)	0.033(2)	0.046(2)	0.008(1)	-0.000(1)	-0.000(1)
C(12)	0.054(2)	0.036(2)	0.055(2)	0.003(1)	0.007(1)	-0.011(1)
C(13)	0.030(1)	0.035(1)	0.035(1)	0.004(1)	0.007(1)	-0.006(1)
C(14)	0.024(1)	0.034(1)	0.043(1)	0.002(1)	0.006(1)	0.006(1)
C(15)	0.037(2)	0.053(2)	0.037(1)	0.013(1)	0.001(1)	0.006(1)

C(16)	0.038(2)	0.064(2)	0.049(2)	0.016(1)	-0.007(1)	0.001(1)
C(17)	0.044(2)	0.055(2)	0.076(2)	0.019(2)	0.004(2)	-0.000(2)

4. Thiophene-based ligands complexed with metal ions

4.1. 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with copper (II) perchlorate **50**

Table 38. Summaries of the crystal data, structure solution and refinement parameters

A. Crystal Data

Empirical Formula	$C_{34}H_{46}N_2O_{14}S_4Cl_2Cu$
Formula Weight	969.43
Crystal Color, Habit	colourless, rhomboid
Crystal Dimensions	0.18 X 0.18 X 0.09 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (24.0 - 27.7°)
Omega Scan Peak Width at Half-height	0.24°
Lattice Parameters	a = 16.80(1) Å, b = 12.819(7) Å, c = 21.508(6) Å β = 109.83(3) Å, V = 4356(4) $Å^3$
Space Group	P21/c (#14)
Z value	4
Dcalc	1.478 g/cm^3
F000	2012
μ(MoKα)	8.79 cm^{-1}
Slit Aperture	3.0 mm horizontal, 3.0 mm vertical
Scan Width	(1.78 + 0.35 tan θ)°
2θmax	50.0°
No. of Reflections Measured	Total: 6429, Unique: 6193 (Rint = 0.037)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.9189 - 1.0000)

B. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma w (\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$

p-factor	0.011
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00□(I))	2069
No. Variables	514
Reflection/Parameter Ratio	4.03
Residuals: R; Rw	0.134 ; 0.132
Goodness of Fit Indicator	5.52
Max Shift/Error in Final Cycle	0.77
Maximum peak in Final Diff. Map	2.52 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.66 $e^-/Å^3$

Table 39. Atomic coordinates and B_{iso}/B_{eq}

Positional parameters and B(eq)[351]				
Atom	X	Y	Z	B(eq)
Cu(2)	0.265(1)	0.237(1)	0.9393(8)	93(1)
Cl(1)	0.8720(3)	0.3270(3)	1.0604(2)	6.9(1)
Cl(2)	0.6494(3)	0.2695(4)	1.2487(2)	7.5(1)
S(1)	0.1095(3)	0.0630(3)	1.0933(2)	6.8(1)
S(4)	0.6048(2)	0.1809(3)	1.0100(2)	8.0(1)
S(5)	0.4128(3)	0.4426(4)	1.1576(2)	9.4(2)
S(6)	-0.1092(3)	0.2824(3)	0.8287(2)	8.9(1)
O(1)	0.7946(7)	0.2778(8)	1.0543(5)	11.4(4)
O(2)	0.879(1)	0.4098(9)	1.0978(7)	18.5(7)
O(3)	0.8823(7)	0.364(1)	1.0016(6)	13.5(5)
O(4)	0.7027(8)	0.280(1)	1.3095(7)	19.1(6)
O(5)	0.5766(8)	0.319(1)	1.2410(6)	16.6(5)
O(6)	0.6347(9)	0.167(1)	1.2324(9)	18.8(7)
O(7)	0.680(1)	0.307(2)	1.202(1)	30(1)
O(8)	0.3828(7)	0.0922(7)	0.8936(5)	6.6(3)
O(11)	0.2078(6)	0.0808(6)	0.8221(4)	6.4(3)
O(12)	0.1288(5)	0.0585(6)	0.9232(4)	5.8(3)
O(13)	0.9394(6)	0.2547(7)	1.0895(5)	8.5(3)
O(14)	0.3714(6)	0.4253(7)	0.9721(5)	7.8(3)
O(15)	0.1107(7)	0.3399(9)	0.8211(4)	9.4(3)
O(16)	0.2876(8)	0.3861(7)	0.8394(5)	7.7(3)
N(1)	0.0908(5)	0.2833(7)	0.9700(4)	3.8(3)
N(2)	0.4136(6)	0.2012(8)	1.0541(5)	5.2(3)
C(1)	-0.017(1)	0.270(2)	0.753(1)	10.3(7)

C(2)	0.464(1)	0.132(1)	0.9216(9)	6.5(5)
C(3)	0.1284(8)	-0.0243(9)	0.8770(7)	6.5(4)
C(4)	0.1343(7)	0.0352(9)	0.9858(6)	3.3(3)
C(5)	0.1708(8)	-0.0456(9)	1.0260(8)	5.7(4)
C(6)	0.0333(8)	0.3675(8)	0.9275(7)	5.4(4)
C(7)	0.4176(8)	0.3911(9)	1.0863(7)	4.8(4)
C(24)	0.3751(8)	0.449(1)	1.0316(8)	5.5(5)
C(25)	0.4652(8)	0.296(1)	1.0796(6)	6.3(4)
C(26)	0.1497(7)	0.335(1)	1.0354(7)	6.7(4)
C(27)	0.0919(8)	0.1022(9)	1.0156(6)	4.7(4)
C(28)	0.515(1)	0.157(1)	0.8866(7)	6.4(5)
C(29)	0.4671(8)	0.1125(9)	1.0396(6)	5.2(4)
C(30)	0.3616(8)	0.164(1)	1.0965(6)	6.4(4)
C(32)	0.5038(9)	0.140(1)	0.990(1)	6.5(5)
C(34)	0.0386(7)	0.1933(9)	0.9838(5)	4.3(3)
C(35)	0.028(1)	0.313(1)	0.8140(9)	7.5(5)
C(36)	0.274(1)	0.012(1)	0.8165(6)	7.9(5)
C(37)	0.1267(9)	0.0257(9)	0.8146(6)	6.2(4)
C(39)	-0.010(1)	0.327(1)	0.8608(9)	7.2(5)
C(40)	0.163(1)	-0.042(1)	1.0836(7)	8.7(5)
C(41)	0.362(1)	0.508(1)	0.9251(8)	9.2(6)
C(43)	-0.091(1)	0.245(1)	0.7547(7)	10.0(6)
C(45)	0.348(1)	0.079(1)	0.8259(8)	8.0(5)
C(46)	0.342(1)	0.540(2)	1.0504(9)	10.6(7)
C(47)	0.105(1)	0.394(1)	1.0735(8)	8.4(5)
C(48)	0.3549(9)	0.542(1)	1.116(1)	9.2(6)
C(50)	0.594(1)	0.185(1)	0.9295(9)	7.8(5)
C(51)	0.143(1)	0.366(1)	0.7663(6)	9.0(6)
C(54)	0.164(1)	0.420(1)	1.1416(8)	11.6(6)
C(55)	0.411(1)	0.112(1)	1.1593(7)	9.6(5)
C(56)	0.215(1)	0.438(1)	0.7942(8)	10.3(7)
C(57)	0.354(1)	0.113(2)	1.2021(8)	15.3(8)
C(60)	0.361(1)	0.449(1)	0.8666(9)	10.6(6)
H(1)	0.3148	0.5913	1.0004	4.791
H(2)	0.4833	0.3276	1.04	4.791
H(3)	0.1793	-0.051	0.9022	4.791
H(4)	0.4158	0.0576	1.029	4.791
H(5)	0.0938	0.3818	0.9312	4.791
H(6)	0.1062	0.3216	1.1067	4.791
H(7)	0.3728	0.0306	0.8053	4.791
H(8)	0.2037	0.2756	1.0687	4.791

H(9)	0.1986	0.3763	1.0259	4.791
H(10)	0.2037	-0.0889	1.1289	4.791
H(11)	0.3042	0.1206	1.0577	4.791
H(12)	0.3802	0.0577	1.2379	4.791
H(13)	0.017	0.1614	0.9389	4.791
H(14)	0.4846	0.1376	0.829	4.791
H(15)	0.0473	0.4162	1.0564	9.706
H(16)	0.6447	0.2044	0.9157	8.912
H(17)	0.3841	0.2278	1.1426	4.791
H(18)	0.0011	0.2582	0.7122	12.348
H(19)	-0.135	0.2096	0.7179	10.91
H(20)	0.3331	0.5964	1.1405	9.978
H(21)	0.2025	-0.1014	1.0111	6.425
H(22)	0.4403	0.1603	1.2083	4.791
H(23)	0.5244	0.2611	1.1229	4.791

** Note the hydrogen positions are to four decimal places with terminal zero's omitted. Those hydrogen coordinates have no esd's as their positions were not refined.

Table 40. Anisotropic Displacement Parameters

Anisotropic Displacement Parameters[352]						
Atom	U11	U22	U33	U12	U13	U23
Cu(2)	1.82(5)	0.89(3)	1.17(3)	-0.29(3)	0.99(3)	-0.36(2)
Cl(1)	0.109(4)	0.060(3)	0.117(4)	-0.000(3)	0.071(3)	0.004(3)
Cl(2)	0.069(3)	0.101(4)	0.100(3)	0.008(3)	0.012(3)	0.010(3)
S(1)	0.126(3)	0.081(3)	0.053(2)	-0.006(3)	0.031(2)	0.012(2)
S(4)	0.083(3)	0.098(3)	0.140(4)	-0.015(3)	0.061(3)	-0.021(3)
S(5)	0.154(4)	0.104(4)	0.107(4)	-0.002(3)	0.053(3)	-0.035(3)
S(6)	0.078(3)	0.112(4)	0.126(4)	-0.024(3)	0.003(3)	0.051(3)
O(1)	0.12(1)	0.109(9)	0.22(1)	-0.001(8)	0.077(9)	0.033(9)
O(2)	0.37(2)	0.09(1)	0.31(2)	-0.02(1)	0.21(2)	-0.08(1)
O(3)	0.14(1)	0.26(2)	0.13(1)	0.08(1)	0.070(9)	0.09(1)
O(4)	0.12(1)	0.34(2)	0.21(2)	-0.04(1)	-0.01(1)	-0.07(2)
O(5)	0.10(1)	0.34(2)	0.15(1)	0.05(1)	-0.012(8)	-0.07(1)
O(6)	0.24(2)	0.10(1)	0.37(2)	0.00(1)	0.10(2)	-0.08(1)
O(7)	0.45(3)	0.38(3)	0.48(3)	0.19(2)	0.40(3)	0.27(2)
O(8)	0.091(8)	0.104(8)	0.075(8)	0.012(7)	0.053(7)	-0.001(6)
O(11)	0.113(8)	0.068(6)	0.067(6)	0.002(7)	0.039(6)	-0.018(5)

O(12)	0.123(8)	0.033(5)	0.077(7)	-0.002(5)	0.051(6)	-0.007(5)
O(13)	0.113(8)	0.088(8)	0.141(8)	0.028(7)	0.067(7)	0.020(6)
O(14)	0.124(9)	0.067(7)	0.084(8)	-0.024(6)	0.008(7)	-0.028(7)
O(15)	0.067(8)	0.19(1)	0.067(7)	0.032(8)	-0.022(6)	0.009(7)
O(16)	0.15(1)	0.088(8)	0.078(7)	0.002(8)	0.071(7)	0.024(6)
N(1)	0.051(6)	0.051(7)	0.048(6)	-0.001(6)	0.023(5)	-0.004(6)
N(2)	0.076(8)	0.054(8)	0.057(7)	0.001(7)	0.008(6)	0.014(6)
C(1)	0.13(2)	0.08(1)	0.13(2)	0.01(1)	-0.02(2)	0.04(1)
C(2)	0.09(1)	0.08(1)	0.11(2)	-0.00(1)	0.07(1)	-0.02(1)
C(3)	0.13(1)	0.043(9)	0.09(1)	0.004(8)	0.05(1)	-0.005(9)
C(4)	0.047(9)	0.045(9)	0.028(8)	-0.008(7)	0.006(7)	0.009(7)
C(5)	0.09(1)	0.020(8)	0.09(1)	0.015(7)	0.014(9)	0.008(9)
C(6)	0.08(1)	0.038(8)	0.065(9)	-0.014(8)	-0.004(8)	0.007(8)
C(7)	0.08(1)	0.036(9)	0.07(1)	0.013(8)	0.028(9)	-0.005(8)
C(24)	0.07(1)	0.05(1)	0.08(1)	-0.005(8)	0.01(1)	-0.02(1)
C(25)	0.07(1)	0.08(1)	0.067(9)	-0.007(9)	-0.011(8)	0.015(9)
C(26)	0.045(9)	0.10(1)	0.10(1)	-0.021(8)	0.011(8)	0.011(9)
C(27)	0.08(1)	0.039(8)	0.058(9)	0.011(7)	0.022(8)	0.019(7)
C(28)	0.11(1)	0.06(1)	0.10(1)	0.00(1)	0.07(1)	-0.022(9)
C(29)	0.07(1)	0.044(9)	0.09(1)	0.022(8)	0.039(9)	-0.022(8)
C(30)	0.08(1)	0.11(1)	0.059(9)	0.008(9)	0.027(8)	0.007(9)
C(32)	0.07(1)	0.06(1)	0.14(2)	-0.009(8)	0.06(1)	-0.02(1)
C(34)	0.067(9)	0.061(9)	0.036(7)	-0.013(8)	0.016(6)	-0.012(7)
*C(35)	0.06(1)	0.07(1)	0.08(1)	-0.03(1)	-0.07(1)	0.02(1)
C(36)	0.12(2)	0.10(1)	0.10(1)	0.07(1)	0.06(1)	-0.03(1)
C(37)	0.12(1)	0.07(1)	0.051(9)	-0.039(9)	0.025(9)	-0.005(8)
C(39)	0.11(2)	0.08(1)	0.09(1)	0.01(1)	0.03(1)	-0.00(1)
C(40)	0.20(2)	0.07(1)	0.06(1)	0.01(1)	0.05(1)	0.009(9)
C(41)	0.21(2)	0.06(1)	0.08(1)	-0.04(1)	0.05(1)	0.02(1)
C(43)	0.26(2)	0.05(1)	0.021(9)	-0.04(1)	-0.02(1)	-0.007(7)
C(45)	0.09(1)	0.16(2)	0.07(1)	-0.01(1)	0.04(1)	-0.03(1)
C(46)	0.23(2)	0.09(2)	0.10(1)	0.01(1)	0.07(2)	0.02(1)
C(47)	0.16(2)	0.07(1)	0.13(1)	0.04(1)	0.10(1)	-0.03(1)
C(48)	0.08(1)	0.04(1)	0.22(2)	0.007(8)	0.05(1)	-0.04(1)
C(50)	0.09(1)	0.09(1)	0.14(2)	-0.03(1)	0.08(1)	-0.02(1)
C(51)	0.12(2)	0.20(2)	0.031(9)	0.02(1)	0.05(1)	0.05(1)
C(54)	0.23(2)	0.14(2)	0.10(1)	-0.05(1)	0.09(1)	-0.07(1)
C(55)	0.17(2)	0.10(1)	0.07(1)	0.04(1)	0.01(1)	0.06(1)
C(56)	0.11(2)	0.17(2)	0.11(2)	0.01(1)	0.04(1)	0.07(1)
C(57)	0.30(3)	0.22(2)	0.09(1)	-0.01(2)	0.11(2)	0.06(1)
C(60)	0.12(1)	0.12(2)	0.16(2)	-0.09(1)	0.05(1)	-0.01(1)

4.2. 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with cobalt (II) perchlorate **54**

Table 41. Summaries of the crystal data, structure solution and refinement parameters

A. Crystal Data	
Empirical Formula	$C_{34}H_{46}N_2O_{14}S_4Cl_2Co$
Formula Weight	964.82
Crystal Color, Habit	paleyellow, prism
Crystal Dimensions	0.27 X 0.18 X 0.18 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (22.5 - 27.7°)
Omega Scan Peak Width at Half-height	0.22°
Lattice Parameters	a = 16.82(2) Å, b = 12.818(9) Å, c = 21.545(7) Å β = 109.90(4) Å, V = 4367(5) Å^3
Space Group	P21/c (#14)
Z value	4
Dcalc	1.467 g/cm^3
F000	2004
μ(MoKα)	7.70 cm-1
Detector Aperture	3.0 mm horizontal, 3.0 mm vertical
Scan Width	(1.63 + 0.35 tan θ)°
2θmax	50.0°
No. of Reflections Measured	Total: 7843, Unique: 7596 (Rint = 0.124)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.9328 - 1.0000)
B. Structure Solution and Refinement	
Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma w (\|F_o\| - \|F_c\|)^2$
Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
p-factor	0.0103
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	2121
No. Variables	652
Reflection/Parameter Ratio	3.25
Residuals: R; Rw	0.133 ; 0.134
Goodness of Fit Indicator	5.2

Max Shift/Error in Final Cycle	9.78
Maximum peak in Final Diff. Map	1.84 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.74 $e^-/Å^3$

Table 42. Atomic coordinates and B_{iso}/B_{eq}

Positional parametersand B(eq)[351]

Atom	X	Y	Z	B(eq)
Co(2)	0.2406(6)	0.2630(7)	0.0606(4)	47.0(5)
Cl(1)	0.3731(3)	-0.1744(3)	0.0607(2)	6.5(1)
Cl(2)	0.1483(3)	-0.2292(4)	0.2485(2)	7.0(1)
S(1)	0.3903(3)	0.4366(3)	-0.0930(2)	6.6(1)
S(2)	-0.1054(3)	0.3206(3)	-0.0103(2)	7.8(1)
S(5)	0.0880(3)	0.0569(3)	-0.1576(2)	8.8(1)
S(6)	0.6102(3)	0.2173(3)	0.1722(2)	9.1(1)
O(1)	0.3709(5)	0.4425(6)	0.0770(4)	5.9(3)
O(2)	0.2932(7)	0.4221(6)	0.1776(4)	6.3(3)
O(3)	0.3842(7)	-0.141(1)	0.0029(6)	13.2(5)
O(4)	0.2949(8)	-0.2221(8)	0.0555(6)	11.3(4)
O(5)	0.1120(8)	0.4057(8)	0.1019(5)	6.8(3)
O(6)	0.166(2)	-0.205(2)	0.190(2)	49(2)
O(7)	0.130(1)	-0.321(1)	0.2280(9)	19.9(8)
O(8)	0.2001(8)	-0.222(1)	0.3083(7)	17.7(6)
O(13)	0.1299(6)	0.0763(7)	0.0244(5)	7.3(3)
O(14)	0.4399(6)	-0.2468(7)	0.0878(5)	7.5(3)
O(15)	0.2129(9)	0.1150(8)	0.1606(5)	7.9(4)
O(16)	0.3894(7)	0.1640(9)	0.1771(4)	9.0(4)
O(22)	0.0733(8)	-0.189(1)	0.2424(6)	13.9(5)
O(25)	0.3769(9)	-0.0911(9)	0.1006(6)	14.9(6)
N(1)	0.4079(6)	0.2158(7)	0.0297(4)	3.5(3)
N(2)	0.0863(6)	0.2973(7)	-0.0533(5)	4.8(3)
C(1)	0.508(1)	0.173(1)	0.1430(8)	6.5(5)
C(3)	0.4677(8)	0.1333(9)	0.0735(7)	5.1(4)
C(4)	0.4594(7)	0.3083(9)	0.0197(5)	4.0(3)
C(5)	0.4090(7)	0.3954(9)	-0.0139(5)	4.0(4)
C(6)	0.3474(7)	0.164(1)	-0.0323(6)	5.0(4)
C(7)	0.3693(8)	0.4586(9)	0.0153(6)	4.2(4)
C(8)	0.3315(9)	0.540(1)	-0.0215(8)	6.3(5)
C(10)	0.3676(8)	0.5266(9)	0.1224(6)	5.4(4)

C(11)	0.0277(8)	0.2067(9)	-0.0831(6)	5.8(4)
C(13)	0.0313(8)	0.389(1)	-0.0407(7)	6.1(4)
C(30)	0.118(1)	0.051(1)	-0.0386(8)	6.1(5)
C(31)	0.379(1)	0.4762(9)	0.1864(7)	6.9(5)
C(32)	0.036(1)	0.364(1)	0.078(1)	6.7(6)
C(33)	0.1333(8)	0.338(1)	-0.0985(7)	6.1(4)
C(34)	-0.0008(9)	0.361(1)	0.0119(9)	5.6(5)
C(36)	0.0808(9)	0.108(1)	-0.0899(6)	4.7(4)
C(38)	0.471(1)	0.193(1)	0.1882(7)	5.6(5)
C(39)	0.584(2)	0.255(1)	0.2456(6)	12.3(7)
C(41)	0.121(2)	-0.009(2)	0.0658(9)	16.5(9)
C(42)	-0.011(1)	0.349(1)	0.1139(8)	7.1(5)
C(43)	0.396(1)	0.108(1)	-0.0700(6)	7.4(5)
C(44)	0.143(1)	-0.041(1)	-0.119(1)	11.0(6)
C(45)	0.292(2)	0.071(2)	0.210(1)	12.6(9)
C(46)	0.150(1)	0.428(1)	0.171(1)	8.3(6)
C(47)	0.334(1)	0.539(1)	-0.0811(8)	7.5(5)
C(48)	0.089(1)	0.391(1)	-0.1603(8)	12.4(7)
C(49)	-0.089(1)	0.322(1)	0.0747(9)	8.5(6)
C(50)	0.228(1)	0.488(1)	0.1864(8)	9.4(7)
C(51)	0.156(1)	-0.040(1)	-0.0523(8)	8.0(5)
C(52)	0.137(1)	0.046(2)	0.123(1)	12.2(7)
C(53)	0.512(1)	0.226(2)	0.249(1)	13.4(9)
C(54)	0.368(1)	0.136(1)	0.2370(8)	9.5(7)
C(57)	0.153(1)	0.406(2)	-0.1984(9)	15.2(9)
C(58)	0.333(1)	0.086(1)	-0.1427(7)	10.0(6)
H(1)	0.0429	0.3494	-0.1859	14.903
H(2)	0.0983	0.3734	-0.2304	4.67
H(3)	0.3558	0.197	0.2576	11.379
H(4)	0.3145	0.5613	0.1065	6.44
H(5)	0.3932	0.1648	-0.1077	4.67
H(6)	0.4045	0.1124	0.0708	4.67
H(7)	0.082	0.4066	-0.0226	4.67
H(8)	0.0203	0.1878	-0.0328	4.67
H(9)	0.2193	0.5467	0.1577	11.321
H(10)	0.1839	-0.0765	-0.0073	4.67
H(12)	0.1602	0.3285	-0.2075	4.67
H(13)	0.1405	-0.1072	-0.1393	4.67
H(14)	0.3273	0.1471	-0.1686	11.958
H(15)	0.3911	0.5267	0.2206	8.242
H(16)	0.1355	-0.0052	0.1548	14.691

H(17)	0.3123	0.2154	-0.0599	5.962
H(18)	0.4928	0.2854	-0.0054	4.758
H(19)	0.3139	0.0335	-0.1069	4.67
H(20)	0.305	0.5937	-0.0055	7.549
H(21)	0.6219	0.2949	0.28	14.815
H(22)	0.307	0.5891	-0.1139	8.988
H(23)	0.4934	0.2276	0.2859	16.067
H(24)	0.0074	0.3553	0.1606	8.473
H(25)	-0.133	0.305	0.0918	10.207
H(26)	0.1746	0.386	-0.0727	7.37
H(27)	0.1607	0.2797	-0.1092	7.37
H(28)	0.2774	0.047	0.2461	15.177
H(29)	0.3081	0.0133	0.1889	15.177
H(30)	0.1114	0.466	0.1849	9.912
H(31)	0.1631	0.3635	0.194	9.912
H(32)	0.4953	0.3314	0.0618	4.758
H(33)	0.4117	0.5755	0.1269	6.44
H(34)	0.0694	0.4566	-0.1517	14.903
H(35)	0.4125	0.0985	0.2679	11.379
H(36)	-0.0098	0.2261	-0.1256	6.925
H(37)	0.423	0.4262	0.1965	8.242
H(38)	0.3132	0.1147	-0.0197	5.962
H(39)	0.417	0.0435	-0.0487	8.862
H(40)	0.2451	0.5115	0.2308	11.321
H(41)	0.0897	0.0909	0.1146	14.691
H(42)	0.5107	0.1172	0.0557	6.07
H(44)	0.0664	-0.039	0.0507	19.783
H(45)	0.1622	-0.0626	0.0697	19.783
H(47)	-0.0149	0.4029	-0.08	7.32
H(51)	0.3554	0.0312	-0.1619	11.958
H(52)	0.1871	0.4656	-0.1815	18.22

** Note the hydrogen positions are to four decimal places with terminal zero's omitted. Those hydrogen coordinates have no esd's as their positions were not refined.

Table 43. Anisotropic Displacement Parameters

Anisotropic Displacement Parameters352						
Atom	U11	U22	U33	U12	U13	U23
Co(2)	0.70(2)	0.49(1)	0.56(1)	-0.02(1)	0.16(1)	-0.06(1)
Cl(1)	0.101(4)	0.065(3)	0.103(3)	-0.005(3)	0.062(3)	-0.002(3)
Cl(2)	0.064(3)	0.089(4)	0.097(4)	0.004(3)	0.008(3)	0.005(3)
S(1)	0.120(4)	0.072(3)	0.060(3)	0.005(3)	0.033(2)	0.015(2)
S(2)	0.094(4)	0.077(3)	0.140(4)	-0.013(3)	0.059(3)	-0.016(3)
S(5)	0.162(5)	0.084(3)	0.087(3)	0.014(3)	0.042(3)	-0.026(3)
S(6)	0.087(4)	0.108(4)	0.132(4)	-0.020(3)	0.014(3)	0.052(3)
O(1)	0.123(9)	0.032(5)	0.084(7)	-0.005(5)	0.054(6)	-0.010(5)
O(2)	0.116(8)	0.072(7)	0.052(6)	0.031(7)	0.028(6)	0.002(5)
O(3)	0.13(1)	0.26(2)	0.13(1)	0.07(1)	0.073(9)	0.09(1)
O(4)	0.15(1)	0.094(9)	0.21(1)	0.007(8)	0.10(1)	0.023(9)
O(5)	0.11(1)	0.107(8)	0.068(8)	0.016(7)	0.064(8)	-0.003(6)
O(6)	1.03(6)	0.37(3)	0.91(5)	0.41(3)	0.91(6)	0.46(3)
O(7)	0.28(2)	0.10(1)	0.38(3)	-0.05(1)	0.12(2)	-0.12(1)
O(8)	0.12(1)	0.33(2)	0.18(1)	-0.00(1)	-0.01(1)	-0.08(2)
O(13)	0.129(9)	0.045(6)	0.088(8)	-0.003(6)	0.017(7)	0.007(6)
O(14)	0.085(8)	0.073(7)	0.137(8)	0.040(6)	0.051(6)	0.027(6)
O(15)	0.15(1)	0.096(9)	0.078(8)	0.008(9)	0.079(8)	0.019(7)
O(16)	0.070(8)	0.21(1)	0.056(7)	0.033(9)	0.015(7)	0.013(7)
O(22)	0.09(1)	0.24(2)	0.18(1)	0.06(1)	0.024(9)	-0.02(1)
O(25)	0.28(2)	0.11(1)	0.22(1)	-0.03(1)	0.14(1)	-0.07(1)
N(1)	0.054(7)	0.039(6)	0.052(7)	-0.011(6)	0.034(6)	-0.000(6)
N(2)	0.076(9)	0.049(7)	0.072(8)	0.000(7)	0.042(7)	0.001(6)
C(1)	0.09(1)	0.07(1)	0.08(1)	-0.004(9)	0.01(1)	-0.019(9)
C(3)	0.08(1)	0.048(9)	0.07(1)	0.000(8)	0.036(9)	0.001(8)
C(4)	0.039(8)	0.07(1)	0.050(8)	0.035(8)	0.024(7)	0.006(7)
C(5)	0.07(1)	0.047(8)	0.050(8)	0.032(8)	0.038(8)	0.013(7)
C(6)	0.049(9)	0.09(1)	0.044(8)	0.018(8)	0.003(7)	-0.016(8)
C(7)	0.08(1)	0.027(9)	0.05(1)	0.012(8)	0.022(9)	0.042(8)
C(8)	0.11(1)	0.06(1)	0.07(1)	-0.00(1)	0.04(1)	-0.03(1)
C(10)	0.10(1)	0.047(9)	0.07(1)	-0.029(8)	0.051(9)	-0.014(8)
C(11)	0.08(1)	0.027(8)	0.10(1)	-0.010(8)	0.025(9)	-0.032(8)
C(13)	0.06(1)	0.06(1)	0.10(1)	0.015(8)	0.03(1)	-0.028(9)
C(30)	0.08(1)	0.10(1)	0.06(1)	-0.04(1)	0.03(1)	-0.04(1)
C(31)	0.14(2)	0.06(1)	0.09(1)	-0.07(1)	0.08(1)	-0.044(9)
C(32)	0.03(1)	0.11(1)	0.13(2)	-0.01(1)	0.06(1)	0.00(1)

C(33)	0.05(1)	0.07(1)	0.11(1)	0.012(8)	0.02(1)	-0.011(9)
C(34)	0.06(1)	0.049(9)	0.13(1)	-0.017(8)	0.06(1)	-0.02(1)
C(36)	0.08(1)	0.07(1)	0.042(9)	-0.000(9)	0.031(9)	0.017(8)
C(38)	0.04(1)	0.09(1)	0.04(1)	-0.01(1)	-0.042(9)	0.013(9)
C(39)	0.39(4)	0.019(9)	-0.003(7)	-0.04(2)	-0.01(1)	-0.001(6)
C(41)	0.45(4)	0.13(2)	0.08(1)	-0.10(2)	0.13(2)	-0.02(1)
C(42)	0.07(1)	0.07(1)	0.14(2)	-0.04(1)	0.05(1)	-0.05(1)
C(43)	0.15(2)	0.08(1)	0.08(1)	-0.05(1)	0.07(1)	-0.059(9)
C(44)	0.17(2)	0.03(1)	0.17(2)	0.04(1)	-0.00(2)	-0.07(1)
C(45)	0.25(3)	0.17(2)	0.11(2)	0.06(2)	0.11(2)	0.06(2)
C(46)	0.12(2)	0.11(1)	0.13(2)	0.01(1)	0.09(1)	0.00(1)
C(47)	0.12(1)	0.06(1)	0.12(1)	0.02(1)	0.04(1)	0.03(1)
C(48)	0.12(2)	0.18(2)	0.10(1)	-0.01(1)	-0.06(1)	0.10(1)
C(49)	0.16(2)	0.05(1)	0.18(2)	0.01(1)	0.16(2)	0.01(1)
C(50)	0.17(2)	0.10(1)	0.14(2)	0.09(1)	0.11(2)	0.03(1)
C(51)	0.17(2)	0.05(1)	0.08(1)	0.02(1)	0.04(1)	-0.01(1)
C(52)	0.13(2)	0.18(2)	0.14(2)	-0.11(2)	0.02(2)	0.09(2)
C(53)	0.14(2)	0.12(2)	0.19(2)	0.00(2)	-0.01(2)	0.08(2)
C(54)	0.14(2)	0.14(2)	0.07(1)	-0.02(1)	0.04(1)	0.02(1)
C(57)	0.30(3)	0.19(2)	0.14(2)	0.09(2)	0.14(2)	0.08(2)
C(58)	0.24(2)	0.08(1)	0.10(1)	-0.01(1)	0.11(1)	-0.02(1)

4.3. 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with silver (I) perchlorate **42**

Table 44. Summaries of the crystal data, structure solution and refinement parameters

A. Crystal Data

Empirical Formula	$C_{34}H_{46}O_{10}N_2S_4AgCl$
Formula Weight	914.31
Crystal Color, Habit	yellow, block
Crystal Dimensions	0.10 X 0.05 X 0.10 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (20.1 - 26.4°)
Omega Scan Peak Width at Half-height	0.21°
Lattice Parameters	a = 17.90(1) Å, b = 11.019(7) Å, c = 20.363(8) Å

	β = 91.33(4) Å, V = 4015(3) Å^3
Space Group	P21/c (#14)
Z value	4
Dcalc	1.512 g/cm^3
F000	1888
μ(MoKα)	8.30 cm^{-1}
Slit Aperture	3.0 mm horizontal, 3.0 mm vertical
Scan Width	(0.73 + 0.35 tan θ)°
2θmax	55.0°
No. of Reflections Measured	Total: 9998, Unique: 9697 (Rint = 0.047)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.9343 - 1.0000)

B. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w $(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
p-factor	0.0161
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	3206
No. Variables	607
Reflection/Parameter Ratio	5.28
Residuals: R; Rw	0.048 ; 0.045
Goodness of Fit Indicator	1.44
Max Shift/Error in Final Cycle	0.41
Maximum peak in Final Diff. Map	0.00 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.45 e$^-$/Å^3

Table 45. Atomic coordinates and B_{iso}/B_{eq}

Positional parameters and B(eq)[351]				
Atom	X	Y	Z	B(eq)
Ag(1)	0.25469(3)	-0.61197(5)	0.82054(3)	4.33(1)
Cl(1)	0.2450(1)	0.1871(2)	0.1556(1)	5.65(6)
S(3)	0.1206(1)	-0.4399(2)	0.7876(1)	5.17(6)
S(4)	0.3753(1)	0.2071(2)	0.8093(1)	4.74(5)
S(5)	0.5061(1)	-0.3047(2)	0.8519(1)	5.30(6)
S(6)	0.0103(1)	0.1207(2)	0.9146(1)	6.35(6)
O(1)	0.2719(4)	0.0881(6)	0.1941(3)	9.8(2)
O(2)	0.1912(4)	0.1485(7)	0.1142(4)	14.0(3)

O(3)	0.2232(6)	0.2790(7)	0.1937(4)	15.2(3)
O(4)	0.3004(4)	0.2296(8)	0.1153(4)	12.8(3)
O(7)	0.3684(3)	-0.2000(4)	0.7162(2)	4.1(1)
O(8)	0.1844(2)	-0.2199(4)	0.9239(2)	4.3(1)
O(9)	0.2177(3)	-0.1178(5)	0.7061(2)	5.5(1)
O(10)	0.2781(3)	-0.1826(5)	1.0339(2)	5.1(1)
O(11)	0.0893(3)	-0.0058(4)	0.7556(2)	4.5(1)
O(12)	0.3286(3)	0.0398(5)	0.9686(2)	5.0(1)
N(1)	0.3131(3)	-0.4291(4)	0.8347(2)	3.0(1)
N(2)	0.1932(3)	0.2243(4)	0.8626(2)	3.0(1)
C(1)	0.4290(4)	-0.3147(6)	0.8001(3)	3.5(2)
C(2)	0.4208(4)	-0.2105(6)	0.7646(4)	3.8(2)
C(3)	0.2605(4)	-0.3320(7)	0.8107(4)	3.5(2)
C(5)	0.3303(4)	-0.4107(6)	0.9056(3)	3.3(2)
C(19)	0.1828(4)	-0.3508(5)	0.8328(3)	3.1(2)
C(20)	0.0031(4)	-0.0609(8)	0.8404(5)	4.9(2)
C(21)	0.1479(3)	-0.3011(6)	0.8840(3)	3.2(2)
C(22)	0.2381(4)	0.1127(7)	0.8498(3)	3.4(2)
C(23)	0.3193(3)	0.1320(5)	0.8639(3)	3.1(2)
C(24)	0.3819(4)	-0.4281(6)	0.7942(4)	3.3(2)
C(25)	0.1862(4)	0.2450(7)	0.9339(4)	4.0(2)
C(26)	0.0533(4)	0.0133(6)	0.8133(4)	3.7(2)
C(27)	0.0675(3)	0.1156(7)	0.8478(3)	3.6(2)
C(28)	0.1486(5)	0.3621(8)	0.9504(4)	5.5(3)
C(29)	0.0717(4)	-0.3364(8)	0.8893(4)	4.9(2)
C(30)	0.3604(4)	0.0991(7)	0.9174(4)	4.2(2)
C(31)	0.1186(4)	0.2159(7)	0.8286(4)	3.9(2)
C(32)	0.4749(5)	-0.1207(8)	0.7820(4)	5.0(2)
C(33)	0.2731(6)	-0.0887(7)	0.6602(4)	5.1(2)
C(34)	0.0906(5)	-0.1256(8)	0.7299(4)	4.8(2)
C(35)	0.3441(6)	-0.0806(7)	0.6966(4)	5.3(3)
C(36)	0.3739(5)	-0.5128(9)	0.9372(4)	5.2(2)
C(37)	0.3324(6)	-0.1003(9)	1.0578(4)	6.2(3)
C(38)	0.4373(4)	0.1369(9)	0.9145(5)	5.9(3)
C(39)	0.1456(6)	-0.1271(9)	0.6779(4)	5.9(3)
C(40)	0.3765(5)	-0.0381(9)	1.0065(4)	5.9(3)
C(41)	0.4508(4)	0.1956(8)	0.8595(5)	5.4(2)
C(42)	0.0295(5)	-0.0147(9)	0.8945(5)	6.3(3)
C(43)	0.2077(5)	-0.1276(9)	1.0260(4)	5.6(3)
C(44)	0.0512(4)	-0.4125(8)	0.8411(5)	6.2(3)
C(45)	0.1583(5)	-0.204(1)	0.9885(5)	6.1(3)

C(46)	0.5241(5)	-0.1605(9)	0.8269(5)	6.4(3)
C(50)	0.3858(6)	-0.486(2)	1.0091(6)	10.3(4)
C(53)	0.1444(7)	0.390(1)	1.0232(6)	9.3(4)
H(1)	0.421(3)	-0.524(6)	0.920(3)	4.046
H(2)	0.379(3)	-0.047(6)	0.670(3)	4.046
H(3)	0.474(4)	-0.053(6)	0.762(3)	4.046
H(4)	0.361(3)	-0.332(6)	0.913(3)	4.046
H(5)	0.286(3)	-0.395(6)	0.926(3)	4.046
H(6)	0.061(3)	-0.043(6)	0.917(3)	4.046
H(7)	0.015(3)	-0.142(5)	0.819(3)	4.046
H(8)	0.132(3)	0.202(5)	0.782(3)	4.046
H(9)	0.095(3)	0.287(5)	0.839(3)	4.046
H(10)	0.465(4)	0.135(6)	0.945(3)	4.046
H(11)	0.233(3)	0.242(5)	0.953(3)	4.046
H(12)	0.165(3)	0.186(6)	0.952(3)	4.046
H(13)	0.092(3)	0.364(6)	0.940(3)	4.046
H(14)	0.100(3)	-0.178(5)	0.767(3)	4.046
H(15)	0.363(3)	-0.434(5)	0.747(3)	4.046
H(16)	0.266(3)	-0.331(6)	0.766(3)	4.046
H(17)	0.277(3)	-0.249(6)	0.825(3)	4.046
H(18)	0.262(3)	-0.007(6)	0.653(3)	4.046
H(19)	0.226(3)	0.089(5)	0.803(3)	4.046
H(20)	0.223(3)	0.051(5)	0.875(3)	4.046
H(21)	0.044(3)	-0.311(6)	0.923(3)	4.046
H(22)	0.494(3)	0.226(6)	0.848(3)	4.046
H(23)	0.040(3)	-0.142(5)	0.717(3)	4.046
H(24)	0.140(3)	-0.068(5)	0.645(3)	4.046
H(25)	0.265(3)	-0.146(6)	0.626(3)	4.046
H(26)	0.343(4)	-0.033(6)	0.731(3)	4.046
H(27)	0.116(3)	0.326(6)	1.048(3)	4.046
H(28)	0.427(3)	-0.438(6)	1.022(3)	4.046
H(29)	0.409(4)	-0.542(6)	1.026(3)	4.046
H(30)	0.011(3)	-0.427(6)	0.831(3)	4.046
H(31)	0.152(3)	-0.286(6)	1.008(3)	4.046
H(32)	0.347(3)	-0.596(5)	0.928(3)	4.046
H(33)	0.187(3)	-0.107(6)	1.066(3)	4.046
H(34)	0.115(3)	-0.191(7)	0.986(3)	4.046
H(35)	0.166(4)	0.421(6)	0.930(3)	4.046
H(36)	0.187(3)	0.428(6)	1.010(3)	4.046
H(37)	0.366(3)	-0.140(6)	1.083(3)	4.046
H(38)	0.338(3)	-0.515(6)	1.018(3)	4.046

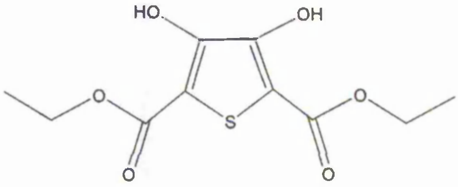
H(39)	0.552(4)	-0.124(6)	0.845(3)	4.046
H(40)	0.390(3)	-0.099(6)	0.974(3)	4.046
H(41)	0.412(3)	0.015(5)	1.029(3)	4.046
H(42)	0.143(4)	-0.192(6)	0.654(3)	4.046
H(43)	0.218(3)	-0.040(5)	1.009(3)	4.046
H(44)	0.314(4)	-0.049(6)	1.088(3)	4.046
H(45)	0.410(3)	-0.488(5)	0.813(3)	4.046
H(46)	0.098(3)	0.427(6)	1.019(3)	4.046

Table 46. Anisotropic Displacement Parameters

Anisotropic Displacement Parameters352						
Atom	U11	U22	U33	U12	U13	U23
Ag(1)	0.0619(4)	0.0382(3)	0.0647(4)	-0.0052(3)	0.0057(3)	0.0041(3)
Cl(1)	0.084(2)	0.073(2)	0.057(1)	-0.001(1)	-0.005(1)	-0.003(1)
S(3)	0.064(1)	0.048(1)	0.083(2)	-0.005(1)	-0.023(1)	-0.005(1)
S(4)	0.059(1)	0.050(1)	0.072(1)	0.002(1)	0.023(1)	0.008(1)
S(5)	0.045(1)	0.080(2)	0.076(2)	-0.001(1)	-0.004(1)	-0.005(1)
S(6)	0.064(1)	0.086(2)	0.092(2)	-0.007(1)	0.035(1)	-0.005(1)
O(1)	0.197(7)	0.105(6)	0.067(4)	0.028(5)	-0.021(4)	0.021(4)
O(2)	0.150(7)	0.132(7)	0.243(9)	-0.051(6)	-0.133(7)	0.057(6)
O(3)	0.34(1)	0.123(7)	0.114(6)	0.077(8)	0.085(7)	-0.032(5)
O(4)	0.123(7)	0.202(9)	0.163(8)	0.010(6)	0.042(6)	0.066(7)
O(7)	0.059(3)	0.041(3)	0.054(3)	0.002(3)	0.009(3)	0.003(3)
O(8)	0.041(3)	0.075(4)	0.048(3)	-0.010(3)	0.015(3)	-0.019(3)
O(9)	0.059(3)	0.098(4)	0.051(3)	0.020(3)	0.011(3)	0.020(3)
O(10)	0.061(4)	0.065(4)	0.067(4)	0.008(3)	-0.013(3)	0.002(3)
O(11)	0.070(4)	0.043(3)	0.057(4)	-0.007(3)	0.004(3)	0.006(3)
O(12)	0.048(3)	0.076(4)	0.064(3)	0.009(3)	-0.001(3)	0.026(3)
N(1)	0.043(3)	0.031(3)	0.038(3)	-0.000(3)	0.005(3)	0.001(2)
N(2)	0.037(3)	0.037(3)	0.040(4)	0.006(3)	0.011(3)	0.004(3)
C(1)	0.043(5)	0.050(5)	0.040(4)	-0.002(4)	0.010(3)	-0.005(4)
C(2)	0.033(4)	0.054(5)	0.056(5)	-0.007(4)	0.022(4)	-0.009(4)
C(3)	0.049(5)	0.043(4)	0.042(5)	0.010(4)	0.008(4)	0.009(4)
C(5)	0.034(4)	0.053(5)	0.039(4)	0.012(4)	0.001(3)	0.001(4)
C(19)	0.037(4)	0.032(4)	0.048(4)	-0.001(3)	-0.002(4)	0.003(3)
C(20)	0.044(5)	0.053(5)	0.090(7)	-0.011(4)	-0.001(5)	0.017(5)
C(21)	0.030(4)	0.043(4)	0.047(4)	-0.003(4)	-0.002(3)	0.003(4)
C(22)	0.049(5)	0.035(4)	0.045(4)	-0.003(4)	0.006(4)	0.003(4)

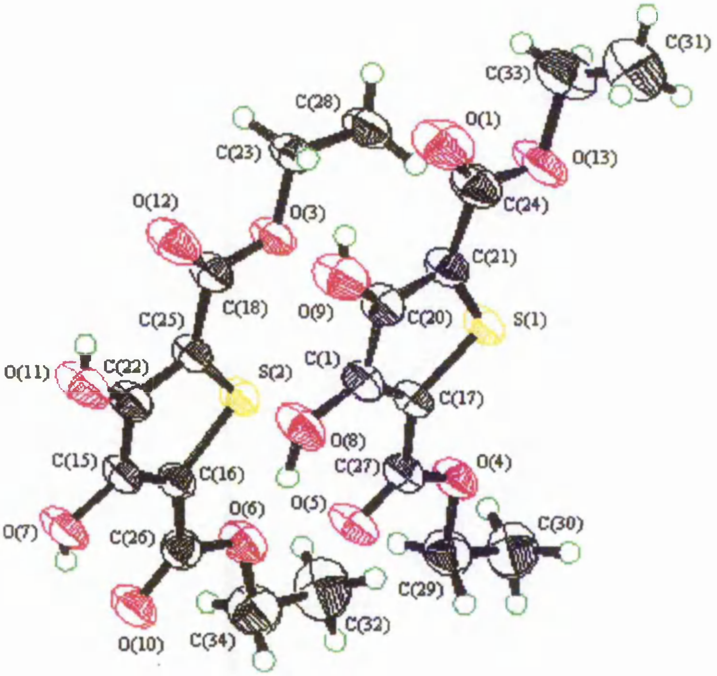
C(23)	0.039(4)	0.034(4)	0.047(4)	0.006(3)	0.010(4)	0.004(3)
C(24)	0.041(5)	0.049(5)	0.036(4)	-0.001(4)	0.005(4)	-0.003(3)
C(25)	0.042(5)	0.045(5)	0.064(6)	0.012(4)	0.010(4)	-0.000(4)
C(26)	0.035(4)	0.047(5)	0.060(5)	0.000(4)	0.002(4)	0.015(4)
C(27)	0.030(4)	0.049(4)	0.057(4)	-0.005(4)	0.007(3)	0.006(4)
C(28)	0.085(7)	0.063(7)	0.062(7)	0.009(6)	0.028(5)	-0.006(5)
C(29)	0.035(5)	0.070(6)	0.081(7)	-0.000(4)	-0.001(4)	0.009(5)
C(30)	0.043(5)	0.055(5)	0.061(5)	0.011(4)	0.006(4)	0.010(4)
C(31)	0.038(5)	0.054(5)	0.055(5)	0.007(4)	0.001(4)	-0.003(4)
C(32)	0.053(5)	0.063(6)	0.077(7)	-0.007(6)	0.016(5)	-0.001(5)
C(33)	0.098(7)	0.044(6)	0.052(6)	0.011(5)	-0.003(6)	0.004(4)
C(34)	0.058(5)	0.062(6)	0.061(6)	-0.000(5)	-0.007(5)	0.010(5)
C(35)	0.099(8)	0.045(6)	0.056(6)	-0.001(5)	0.016(6)	0.008(4)
C(36)	0.060(6)	0.091(7)	0.046(5)	0.015(5)	-0.008(4)	0.012(5)
C(37)	0.095(8)	0.080(7)	0.059(6)	0.010(6)	-0.026(6)	-0.003(5)
C(38)	0.038(6)	0.089(7)	0.097(8)	0.008(5)	-0.007(5)	0.007(6)
C(39)	0.090(7)	0.082(7)	0.052(6)	0.014(7)	-0.012(6)	-0.005(5)
C(40)	0.075(7)	0.088(7)	0.059(6)	-0.011(6)	-0.015(5)	0.025(5)
C(41)	0.040(5)	0.073(6)	0.095(7)	-0.003(5)	0.027(5)	0.017(5)
C(42)	0.046(6)	0.082(7)	0.111(9)	-0.012(5)	0.029(5)	0.029(6)
C(43)	0.088(7)	0.066(6)	0.059(6)	-0.012(6)	0.026(5)	-0.020(5)
C(44)	0.037(5)	0.061(6)	0.136(9)	-0.009(5)	-0.026(6)	0.007(6)
C(45)	0.061(6)	0.078(7)	0.093(8)	-0.009(6)	0.011(6)	-0.025(6)
C(46)	0.057(7)	0.086(7)	0.100(8)	-0.034(5)	0.014(6)	-0.028(6)
C(50)	0.082(8)	0.23(2)	0.075(8)	0.04(1)	-0.040(7)	0.013(9)
C(53)	0.15(1)	0.10(1)	0.103(9)	0.029(9)	0.046(9)	0.018(8)

1. Diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate **15**



1.1. Discussion of the structure derived data (tables 6 to 8)

Two different conformations of the molecule, A and B, were present in the cell. For both conformations, the thermal ellipsoids of the oxygens were larger than the other atoms, although these are, except the sulfur atoms, the heaviest atoms. This could be due to the fact that the oxygens are on the outer edges of the thiophene rings, which are the central rings of these molecules **15A** and **15B**, and the rings could be moving (wagging) with thermal motion. The position displacement parameters in the molecules (table 8, p89) are best visualized in the "ortep style" drawing[353] below. The larger displacement parameters occur at the extremities of the molecules. The oxygen atoms have the greater displacement, and also the outermost carbon atoms (**15A**: C23, C28, C32, C34; **15B**: C29, C30, C31, C33) which are bonded to those oxygens.



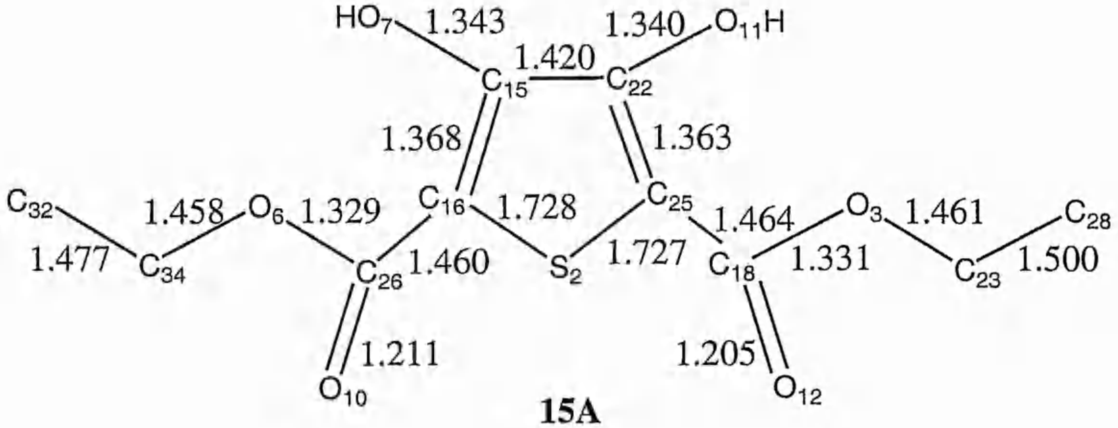
1.2. Discussion of the structural geometry

Table 47. Bond lengths (Å)

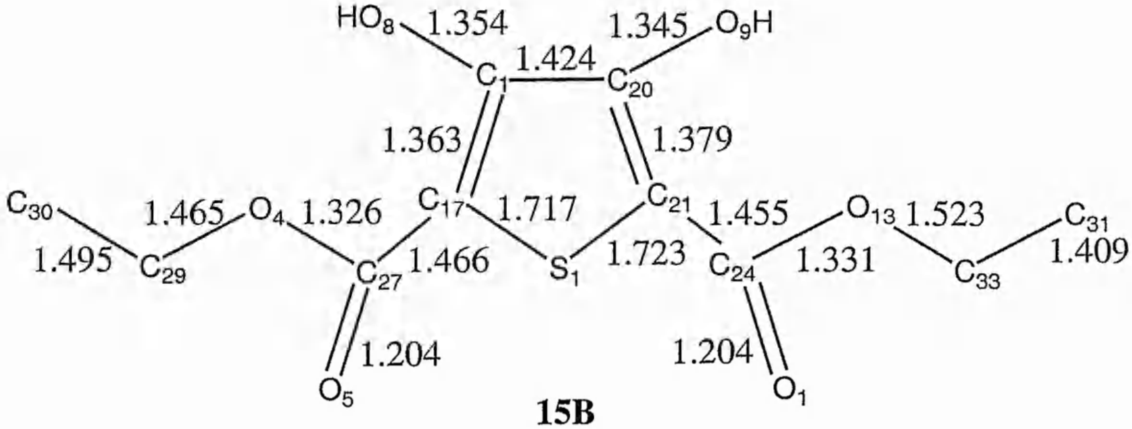
Bond Lengths (Å)					
Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
S(1) -C(17)	1.717(8)	O(12) -C(18)	1.205(6)	C(29) -H(2)	0.93(4)
S(1) -C(21)	1.723(6)	O(13) -C(24)	1.331(6)	C(30) -H(3)	1.03(4)
S(2) -C(16)	1.728(8)	O(13) -C(33)	1.523(9)	C(30) -H(4)	1.02(4)
S(2) -C(25)	1.727(6)	C(1) -C(17)	1.363(6)	C(30) -H(19)	0.93(4)
O(1) -C(24)	1.204(6)	C(1) -C(20)	1.424(7)	C(31) -C(33)	1.41(1)
O(3) -C(18)	1.331(6)	C(15) -C(16)	1.368(6)	C(31) -H(15)	1.02(7)
O(3) -C(23)	1.461(7)	C(15) -C(22)	1.420(6)	C(31) -H(20)	1.28(9)
O(4) -C(27)	1.326(6)	C(16) -C(26)	1.460(6)	C(31) -H(21)	0.96(7)
O(4) -C(29)	1.465(6)	C(17) -C(27)	1.466(6)	C(32) -C(34)	1.477(9)
O(5) -C(27)	1.204(6)	C(18) -C(25)	1.464(7)	C(32) -H(5)	0.92(4)
O(6) -C(26)	1.329(5)	C(20) -C(21)	1.379(7)	C(32) -H(6)	0.97(4)
O(6) -C(34)	1.458(7)	C(21) -C(24)	1.455(7)	C(32) -H(7)	1.02(4)
O(7) -C(15)	1.343(7)	C(22) -C(25)	1.363(7)	C(33) -H(14)	1.12(6)
O(7) -H(16)	0.66(4)	C(23) -C(28)	1.500(7)	C(33) -H(20)	1.13(8)
O(8) -C(1)	1.354(7)	C(23) -H(9)	1.01(4)	C(33) -H(24)	1.06(6)
O(8) -H(25)	0.68(4)	C(23) -H(10)	0.89(4)	C(34) -H(8)	0.98(4)
O(9) -C(20)	1.345(6)	C(28) -H(11)	1.00(4)	C(34) -H(23)	0.96(4)
O(9) -H(18)	0.67(4)	C(28) -H(12)	0.91(4)		
O(10) -C(26)	1.211(6)	C(28) -H(13)	1.06(4)		
O(11) -C(22)	1.340(6)	C(29) -C(30)	1.495(8)		
O(11) -H(17)	0.68(4)	C(29) -H(1)	1.10(4)		

Chemically, it would be expected that the molecules would be symmetrical (the compound is chemically mirrored between C15 and C22 and through S2, and between C1 and C20 and through S1) and that the bond lengths and bond angles would be the same in each half molecule and in both the independent molecules. This is not the case. In the crystal, the molecule does not have a plane of symmetry. To the contrary, the compound exists in two different conformations, which are both non-symmetric. The differing geometries are reflected in the bond lengths and bond angles.

For ease of description the bond lengths (to 3 decimal places) of **15A** and **15B** are shown on a schematic drawing next page.



15A



15B

The S2 thiophene ring has fairly similar bond lengths either side of the sulphur atom. This confirms the aromatic character of the thiophene ring. The C15-C22= 1.420 Å, C15-C16= 1.368 Å and C22-C25= 1.363 Å bond lengths are similar to those in unsubstituted thiophene[354], but the S2-C16= 1.728 Å and S2-C25= 1.727 Å bond lengths are slightly longer than S-C= 1.714 Å of unsubstituted thiophene. The bond lengths of structure **15A** are fairly symmetric as the bond length differences vary from 0.001 Å to 0.006 Å and for the terminal C-C bonds = 0.023 Å, which do not exceed the esd's. However, the differences between the terminal O-C (O4-C29= 1.465 Å and O13-C33= 1.523 Å) and C-C (C29-C30= 1.495 Å and C31-C33= 1.41 Å) bond lengths are significant in the structure **15B**.

In structure **15B**, the thiophene bond lengths are less symmetric than for **15A**, S1-C17= 1.717 Å, C1-C17= 1.363 Å, C1-C20= 1.424 Å, S1-C17= 1.723 Å and C20-C21= 1.379 Å, but they are still close to the corresponding unsubstituted thiophene bond lengths. The distortions between the other bond lengths in structure **15B** vary from 0.000Å to 0.086Å, and are especially important on the outermost bonds.

Table 48. Bond angles (°)

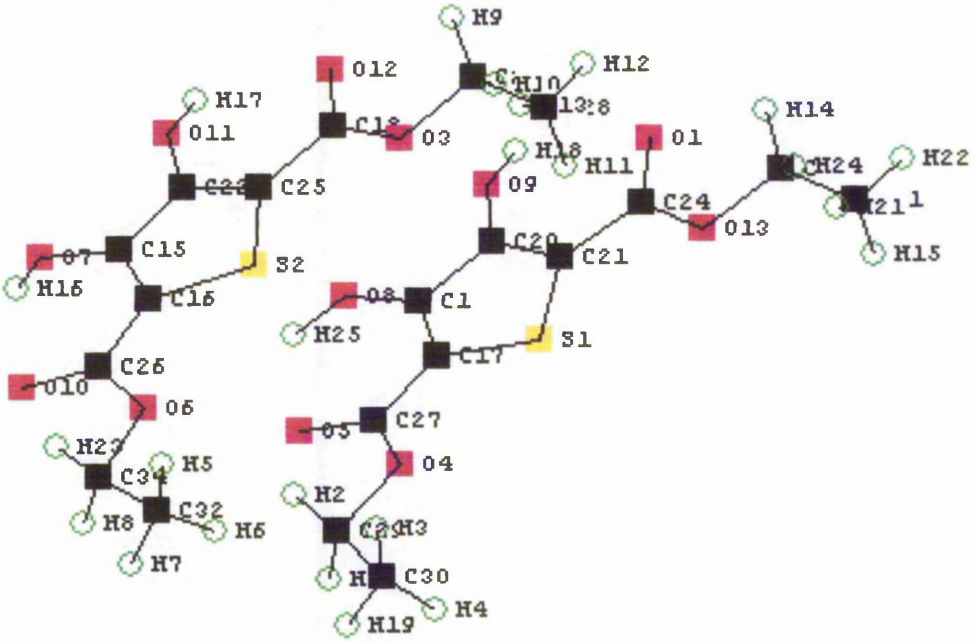
Bond Angles (°)			
Bond	Angle (°)	Bond	Angle (°)
C(17) -S(1) -C(21)	90.5(2)	O(9) -C(20) -C(21)	127.9(4)
C(16) -S(2) -C(25)	90.5(2)	C(1) -C(20) -C(21)	111.3(5)
C(18) -O(3) -C(23)	115.6(4)	S(1) -C(21) -C(20)	112.8(4)
C(27) -O(4) -C(29)	114.8(4)	S(1) -C(21) -C(24)	124.3(3)
C(26) -O(6) -C(34)	116.2(4)	C(20) -C(21) -C(24)	122.8(5)
C(15) -O(7) -H(16)	109(4)	O(11) -C(22) -C(15)	121.0(4)
C(1) -O(8) -H(25)	99(5)	O(11) -C(22) -C(25)	127.1(4)
C(20) -O(9) -H(18)	105(4)	C(15) -C(22) -C(25)	111.9(4)
C(22) -O(11) -H(17)	110(4)	O(3) -C(23) -C(28)	106.0(5)
C(24) -O(13) -C(33)	117.0(5)	O(3) -C(23) -H(9)	108(2)
O(8) -C(1) -C(17)	128.1(4)	O(3) -C(23) -H(10)	104(3)
O(8) -C(1) -C(20)	119.6(5)	C(28) -C(23) -H(9)	110(2)
C(17) -C(1) -C(20)	112.3(4)	C(28) -C(23) -H(10)	110(3)
O(7) -C(15) -C(16)	128.0(4)	H(9) -C(23) -H(10)	118(4)
O(7) -C(15) -C(22)	119.4(4)	O(1) -C(24) -O(13)	124.9(5)
C(16) -C(15) -C(22)	112.6(4)	O(1) -C(24) -C(21)	122.5(5)
S(2) -C(16) -C(15)	112.2(3)	O(13) -C(24) -C(21)	112.6(5)
S(2) -C(16) -C(26)	122.9(3)	S(2) -C(25) -C(18)	124.4(3)
C(15) -C(16) -C(26)	125.0(4)	S(2) -C(25) -C(22)	112.8(3)
S(1) -C(17) -C(1)	113.1(3)	C(18) -C(25) -C(22)	122.8(4)
S(1) -C(17) -C(27)	123.8(4)	O(6) -C(26) -O(10)	124.4(4)
C(1) -C(17) -C(27)	123.1(4)	O(6) -C(26) -C(16)	112.8(4)
O(3) -C(18) -O(12)	124.6(4)	O(10) -C(26) -C(16)	122.8(4)
O(3) -C(18) -C(25)	112.6(4)	O(4) -C(27) -O(5)	125.0(4)
O(12) -C(18) -C(25)	122.8(4)	O(4) -C(27) -C(17)	114.4(4)
O(9) -C(20) -C(1)	120.9(4)	O(5) -C(27) -C(17)	120.6(4)
C(23) -C(28) -H(11)	108(2)	C(34) -C(32) -H(7)	108(2)
C(23) -C(28) -H(12)	106(3)	H(5) -C(32) -H(6)	114(4)
C(23) -C(28) -H(13)	112(2)	H(5) -C(32) -H(7)	113(4)
H(11) -C(28) -H(12)	119(3)	H(6) -C(32) -H(7)	103(3)
H(11) -C(28) -H(13)	116(3)	O(13) -C(33) -C(31)	107.6(8)
H(12) -C(28) -H(13)	95(3)	O(13) -C(33) -H(14)	117(4)
O(4) -C(29) -C(30)	107.3(5)	O(13) -C(33) -H(20)	165(5)
O(4) -C(29) -H(1)	108(2)	O(13) -C(33) -H(24)	112(4)
O(4) -C(29) -H(2)	101(2)	C(31) -C(33) -H(14)	110(4)
C(30) -C(29) -H(1)	105(2)	C(31) -C(33) -H(20)	59(5)

C(30) -C(29) -H(2)	105(3)	C(31) -C(33) -H(24)	99(4)
H(1) -C(29) -H(2)	129(3)	H(14) -C(33) -H(20)	76(5)
C(29) -C(30) -H(3)	100(2)	H(14) -C(33) -H(24)	110(5)
C(29) -C(30) -H(4)	108(2)	H(20) -C(33) -H(24)	66(5)
C(29) -C(30) -H(19)	106(3)	O(6) -C(34) -C(32)	108.5(5)
H(3) -C(30) -H(4)	131(3)	O(6) -C(34) -H(8)	109(2)
H(3) -C(30) -H(19)	117(4)	O(6) -C(34) -H(23)	101(2)
H(4) -C(30) -H(19)	94(3)	C(32) -C(34) -H(8)	114(2)
C(33) -C(31) -H(15)	113(5)	C(32) -C(34) -H(23)	99(2)
C(33) -C(31) -H(21)	88(6)	H(20) -C(31) -H(21)	131(7)
H(15) -C(31) -H(20)	129(7)	C(34) -C(32) -H(5)	105(3)
H(15) -C(31) -H(21)	84(6)	C(34) -C(32) -H(6)	113(2)

In the structure **15A**, the S-C-C and C-C-C bond angles for the thiophene rings are close to those in unsubstituted thiophene[354], S2-C16-C15= 112.2(3)°, S2-C25-C22= 112.8(3)°, C16-C15-C22= 112.6(4)° and C15-C22-C25= 111.9(4)°, while the C16-S2-C25= 90.5(2)° angle is smaller than its counterpart. This distortion on the C16-S2-C25 bond angle could be due to two weak S...O interactions which are S2...O3= 2.958 Å and S2...O6= 2.923 Å (sum of their van der Waals radii= 3.35 Å). Those S...O interactions also have an effect on both carbonyls C=O. The C-C-O angles are from 2.8° to 4.6° bigger and the O-C-O angles are from 7.2° to 7.4° smaller than the expected 120° angles for a trihedral conformation. The distortions on the carbonyls are also due to an O-H...O hydrogen bond on each C=O, O7-H16...O10= 2.325 Å and O11-H17...O12= 2.230 Å (sum of their van der Waals radii= 2.75 Å). The etheroxides bonded to the C=O groups have two small angles C18-O3-C23= 115.6(4)°, C26-O6-C34= 116.2(4)°, O3-C23-C28= 106.0(5)° and O6-C34-C32= 108.5(5)°. These small angles are due to C-H...O contacts which are C23-H9...O12= 2.702 Å, C23-H10...O12= 2.559 Å, C34-H23...O10= 2.708 Å, C34-H8...O10= 2.632 Å, C28-H13...O3= 2.650 Å, C28-H11...O3= 2.579 Å, C32-H5...O6= 2.547 Å and C32-H6...O6= 2.612 Å.

In the structure **15B**, the distortion of the angles in the thiophene rings is greater than for structure **15A**, with C17-S1-C21= 90.5(2)°, S1-C17-C1= 113.1(3)°, S1-C21-C20= 112.8(4)°, C17-C1-C20= 112.3(4)° and C1-C20-C21= 111.3(5)°. These distortions are due to similar interactions to those in structure **15A**; there are two S...O interactions, S1...O4= 2.977 Å and S1...O13= 2.946 Å. The differences in the distortions are due to apparently stronger O-H...O and C-H...O contact bonds: C27=O5, O8-H25...O5= 2.141 Å, C29-H1...O5= 2.672 Å and C29-H2...O5= 2.683 Å. On the carbonyl C24=O1, there is a hydrogen bond from O9-H18...O1= 2.262 Å and there is only one C-H...O bond, C33-H14...O1= 2.403 Å. Both of these are again stronger than in structure **15A**. These interactions also have an effect on the trihedral conformation of the carbonyls, O1-C24-O13= 124.9(5)°, O1-C24-C21= 122.5(5)°, O13-C24-C21= 122.6(5)°, O5-C27-O4= 125.0(4)°, O5-C27-C17= 120.6(4)° and O4-C27-C17= 114.4(4)°. The bond angles in the etheroxide chains are C27-O4-C29= 114.8(4)°, O4-C29-C30= 107.3(5)°, C24-O13-C33= 117.0(5)° and O13-C33-C31= 107.6(8)°. On the O4-C29-C30 etheroxide chain, there are four C-H...O bonds which are C29-H1...O5 and C29-H2...O5, C30-H3...O4= 2.577 Å and C30-H4...O4= 2.608 Å. On the O13-C33-C31 etheroxide chain, there are only three C-H...O contact bonds, C33-H14...O1, C31-H15...O13= 2.589 Å and C31-H21...O13= 2.470 Å.

Intermolecular contacts between **15A** and **15B** have an effect on the O6-C34-C32 and O4-C29-C30 etheroxide chains. These intermolecular bonds and interactions are S2...O5= 3.523 Å, C29-H2...O6= 2.777 Å, C29-H2...H6-C32= 2.762 Å and C30-H3...H6-C32= 2.594 Å (H...H sum of van der Waals= 2.40Å). The H...H interactions are fairly close contacts despite being longer than the sum of the van der Waals radii. Another possible intermolecular bond appears between the O3-C23-C28 and O13-C33-C31 etheroxide chains as C28-H11...O13= 2.924 Å.



The thiophene rings of structures **15A** and **15B** are planar and almost lie in two parallel planes as the angle between them is only 1.57°. The structure **15A** appears to be fairly planar as the maximum deviations from the S2 thiophene plane are O2= 0.1151 Å, C23= 0.1543 Å, C32= 0.1507 Å and C34= 0.1203 Å. In structure **15B**, the atoms of the etheroxide chains are more clearly outside the S1 thiophene plane, the deviations are O4= 0.1017 Å, O1= 0.2132 Å, C29= 0.1216 Å, C30= 0.1012 Å, C31= 0.8759 Å and C33= 0.3483 Å. The full deviations from the least squares planes of these regions for both structures are given below.

Table 49. Least-squares planes

Plane number 1

Atoms defining plane	Distance
S(2)	-.0003(11)
C(15)	-.0055(42)
C(16)	.0054(39)
C(22)	.0012(45)
C(25)	.0024(41)
Additional atoms	**Distance**
O(7)	-.0151
O(11)	.0019
O(10)	-.0957
O(6)	.0810
O(3)	-.0400
O(12)	-.1151
C(18)	-.0530
C(23)	-.1543
C(26)	-.0073
C(28)	-.0220
C(32)	.1507
C(34)	.1203

Mean deviation from plane is .0030 Ångstroms.

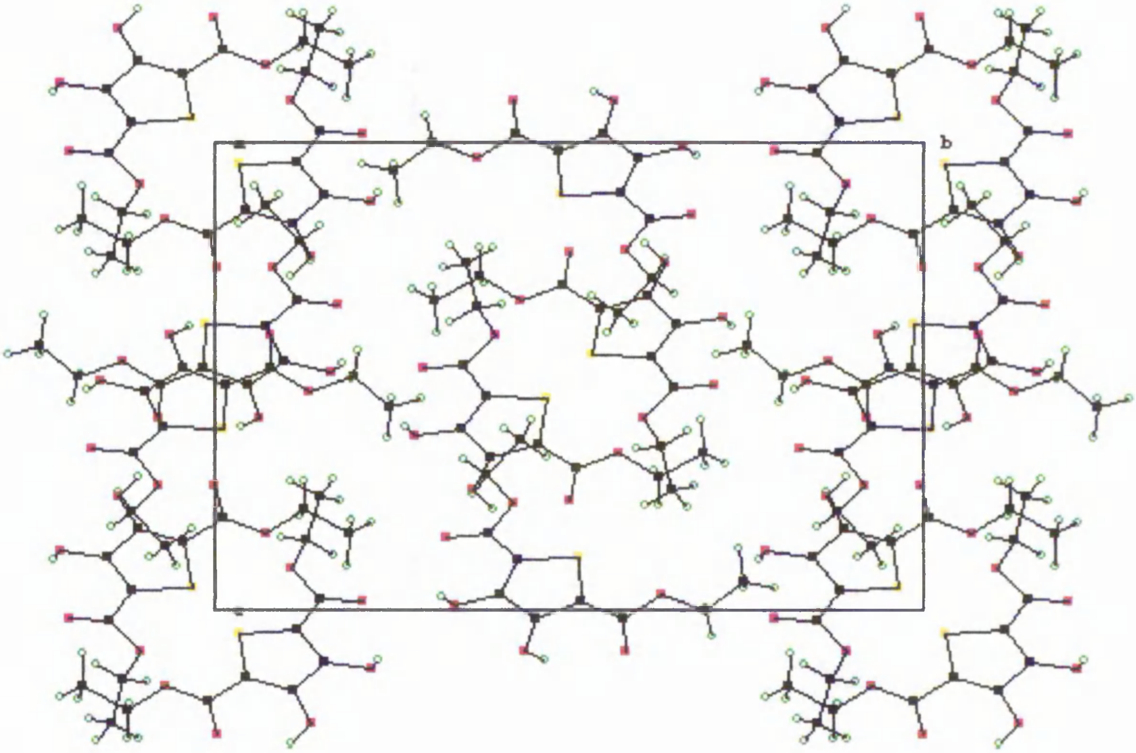
Plane number 2

Atoms defining plane	Distance
S(1)	.0002(12)
C(1)	-.0002(42)
C(17)	-.0017(40)
C(20)	.0031(44)
C(21)	-.0038(43)
Additional atoms	Distance
O(8)	-.0049
O(9)	.0225
O(5)	-.0193
O(4)	-.1017
O(1)	-.2132
O(13)	-.0300
C(27)	-.0454
C(29)	-.1216
C(30)	-.1012
C(31)	.8759
C(33)	-.3484
C(24)	-.0822

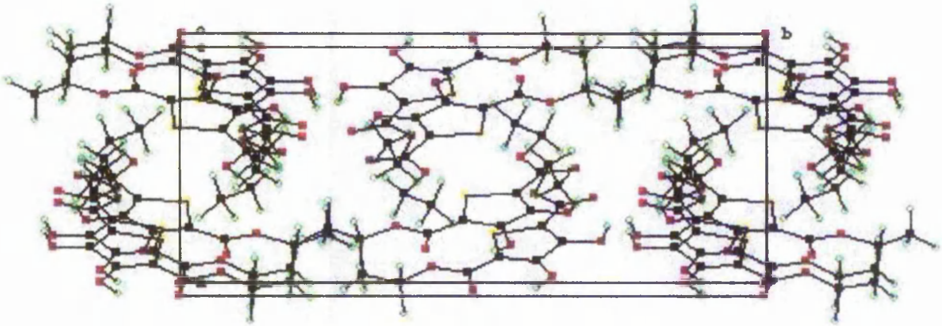
Mean deviation from plane is .0018 Ångstroms.

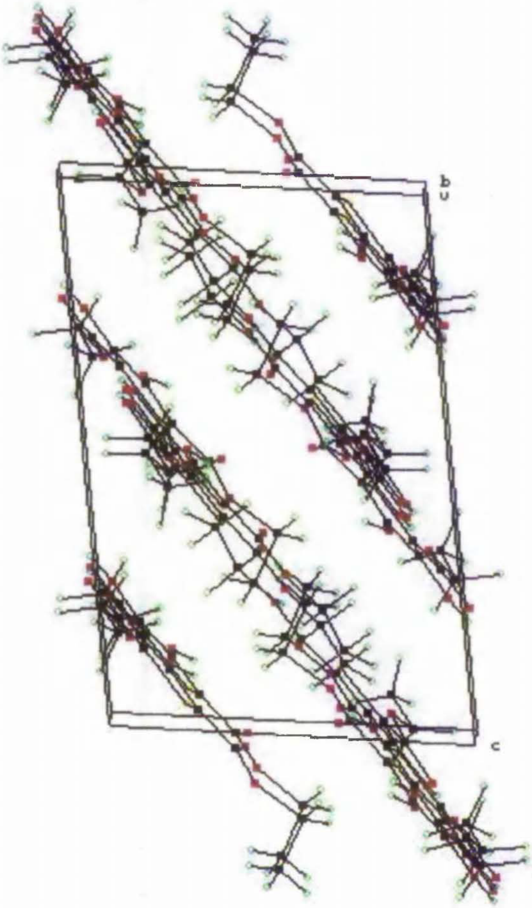
Dihedral angles between least-squares planes 2 and 1 = 1.57°.

In the crystal, there may be intermolecular H...H interactions, H4(x, y, z)...H7(x, ½-y, ½+z)= 2.750 Å. This is a fairly close contact, despite being longer than the sum of the van der Waals radii (2.40 Å). The more important intermolecular interactions in the unit cell are the C-H...O and O-H...O hydrogen bonds, O7(x, y, z)...H15-C31(x, y, z)= 2.781 Å, O1(-x, ½+y, ½-z)...H5-C32(x, y, z)= 2.848 Å, O12(x, y, z)...H23-C34(-x, -y, -z)= 2.844 Å, O4(x, y, z)...H24-C33(-x, -y, -z)= 3.110 Å, O1(x, ½-y, ½+z)...H17-O11(x, y, z)= 2.262 Å and O11(x, y, z)...H18-O9(x, ½-y, ½+z)= 2.718 Å. The literature[333] contact distance for the C-H...O bond is 2.72 Å. The formation of C-H...O hydrogen bonds is now an accepted interaction[355]. The ability of a C-H group to act as a proton donor depends on the carbon hybridisation C(sp)-H>C(sp^2)-H>C(sp^3)-H.



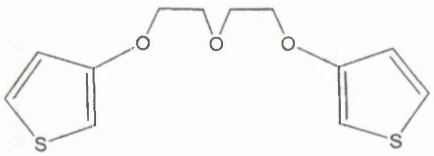
On the preceding view of the cell, it appears that the molecules (x, y, z) and (-x, -y, -z) are arranged along a 2_1 axis parallel to the c-axis. On two other views (following), it appears that the molecules are arranged along an ac-plane, and the molecules (x, y, z) and (x, ½-y, ½+z) are arranged parallel to the b-axis.




b
c
c

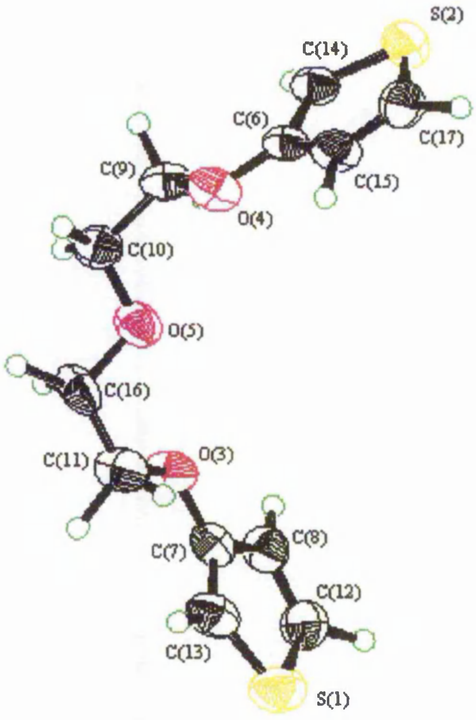
2. Thiophene-based open-chain compounds (compounds **16**, **17**, **18**, **19** and **20**) (table 9)

2.1. α,ω-bis-(3-oxythienyl)ethane **16**



2.1.1. Discussion of the structure derived data (tables 9 to 11)

Four molecules appear in the unit cell and the space group is $P2_1/n$ or a variation of n°14, so that there is one molecule per asymmetric unit. The thermal ellipsoids of the sulphurs are larger than the other atoms, although these are the heaviest atoms. This could be due to the fact that the thiophene rings are on the outer edges of the molecules and the rings could be moving (wagging) with thermal motion. The positions and displacement parameters of the atoms in the molecule are best visualised in the "ortep style" drawing[353] below.



The larger displacement parameters occur at the extremities of the molecule. The thiophene rings have the largest displacement in the sulphur, and the outermost carbon atoms (C12, C13, C17). The oxygens O3, O4 and O5 also have significant displacements.

2.1.2. Discussion of structural geometry

Table 50. Bond lengths (Å)

Bond Lengths (Å)			
Bond	Lengths (Å)	Bond	Lengths (Å)
S(1) -C(12)	1.70(1)	C(9) -H(4)	0.904
S(1) -C(13)	1.74(1)	C(9) -H(5)	1.048
S(2) -C(14)	1.706(9)	C(10) -H(3)	1.038
S(2) -C(17)	1.73(1)	C(10) -H(12)	1.101
O(3) -C(7)	1.37(1)	C(11) -C(16)	1.47(1)
O(3) -C(11)	1.45(1)	C(11) -H(7)	1.177
O(4) -C(6)	1.363(9)	C(11) -H(8)	0.849
O(4) -C(9)	1.43(1)	C(12) -H(13)	1.033
O(5) -C(10)	1.41(1)	C(13) -H(10)	1.107
O(5) -C(16)	1.42(1)	C(14) -H(2)	1.092
C(6) -C(14)	1.39(1)	C(15) -C(17)	1.30(1)
C(6) -C(15)	1.38(1)	C(15) -H(11)	1.138
C(7) -C(8)	1.44(1)	C(16) -H(6)	1.026
C(7) -C(13)	1.37(1)	C(16) -H(9)	1.164
C(8) -C(12)	1.37(1)	C(17) -H(1)	1.211
C(9) -C(10)	1.51(1)		

** Note the hydrogen bond lengths are to two decimal places with terminal zero's omitted and have no esd's as the hydrogen positions were not refined.

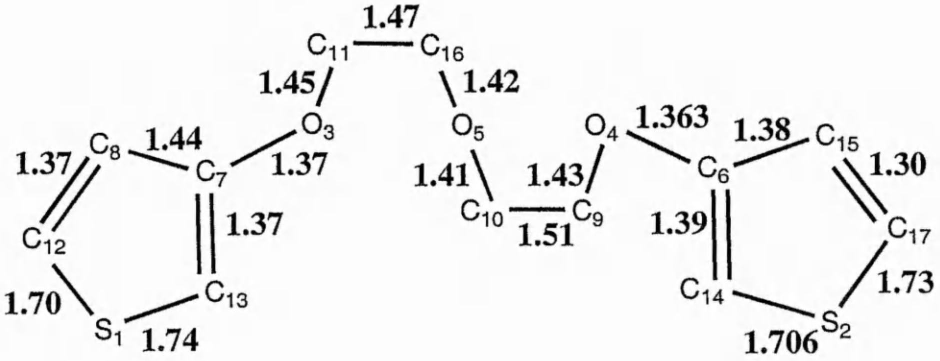
It would be expected chemically that the two halves of this molecule (the compound is chemically mirrored through O5) would have the same bond lengths and bond angles. This is not the case. In the crystal structure, the compound does not have a mirror plane and the two halves of the molecule have differing geometries, which are reflected in the bond lengths and bond angles.

Table 51. Bond angles (°)

Bond Angles (°)			
Bond	Angle (°)	Bond	Bond
C(12) -S(1) -C(13)	92.0(5)	O(3) -C(11) -H(8)	85.92
C(14) -S(2) -C(17)	92.5(4)	C(16) -C(11) -H(7)	115.64
C(7) -O(3) -C(11)	115.7(7)	C(16) -C(11) -H(8)	139.9
C(6) -O(4) -C(9)	118.3(7)	H(7) -C(11) -H(8)	90.93
C(10) -O(5) -C(16)	112.6(7)	S(1) -C(12) -C(8)	113.0(8)
O(4) -C(6) -C(14)	126.3(8)	S(1) -C(12) -H(13)	108.84
O(4) -C(6) -C(15)	120.8(8)	C(8) -C(12) -H(13)	130.08
C(14) -C(6) -C(15)	112.9(8)	S(1) -C(13) -C(7)	110.6(8)
O(3) -C(7) -C(8)	118.5(8)	S(1) -C(13) -H(10)	125.88
O(3) -C(7) -C(13)	128.1(9)	C(7) -C(13) -H(10)	123.46
C(8) -C(7) -C(13)	113.3(9)	S(2) -C(14) -C(6)	108.8(7)
C(7) -C(8) -C(12)	111.1(9)	S(2) -C(14) -H(2)	126.44
O(4) -C(9) -C(10)	107.7(7)	C(6) -C(14) -H(2)	122.87
O(4) -C(9) -H(4)	104.43	C(6) -C(15) -C(17)	115.5(9)
O(4) -C(9) -H(5)	106.1	C(6) -C(15) -H(11)	123.49
C(10) -C(9) -H(4)	104.58	C(17) -C(15) -H(11)	120.84
C(10) -C(9) -H(5)	110.53	O(5) -C(16) -C(11)	111.4(8)
H(4) -C(9) -H(5)	122.65	O(5) -C(16) -H(6)	110.73
O(5) -C(10) -C(9)	108.6(7)	O(5) -C(16) -H(9)	106.13
O(5) -C(10) -H(3)	98.42	C(11) -C(16) -H(6)	106.77
O(5) -C(10) -H(12)	123.83	C(11) -C(16) -H(9)	135.07
C(9) -C(10) -H(3)	113.24	H(6) -C(16) -H(9)	81.3
C(9) -C(10) -H(12)	99.62	S(2) -C(17) -C(15)	110.3(7)
H(3) -C(10) -H(12)	113.62	S(2) -C(17) -H(1)	121.86
O(3) -C(11) -C(16)	108.6(8)	C(15) -C(17) -H(1)	127.15
O(3) -C(11) -H(7)	111.95		

** Note the bond angles including hydrogen atoms are to two decimal places with terminal zero omitted and have no esd's as the hydrogen atoms positions were not refined.

For ease of description the bond lengths (to 2 decimal places) are shown on a schematic drawing next page.



However, the bond lengths in the ether bridge are fairly symmetric around O5. The ether bridge respectively makes, via the aromatic C-O, a large angle with the double bond of the thiophene rings (O3-C7-C13= 128.1(9)° and O4-C6-C14= 126.3(8)°), and a smaller angle with the single bond (O3-C7-C8= 118.5(8)° and O4-C6-C15= 120.8(8)°). The aromatic C6-O4= 1.363 Å and C7-O3= 1.37 Å are smaller than the lengths of aliphatic C-O bonds as determined for typical phenolic compounds[363]. The C-O-C bond angle with the central oxygen O5 is from 3.1° to 5.7° smaller than the aromatic C-O-C angles. Also, the O-C-C bond angles in the ether bridge are smaller than the O-C-C angles with the corresponding aromatic C-O, O3-C11-C16= 108.6(8)°, O4-C9-C10= 107.7(7)°, O5-C16-C11= 111.4(8)° and O5-C10-C9= 108.6(7)°, O3-C7-C8= 118.5(8)°, O3-C7-C13= 128.1(9)°, O4-C6-C15= 120.8(8)° and O4-C6-C14= 126.3(8)°. The other C-O bond lengths are C9-O4= 1.43 Å, C10-O5= 1.41 Å, C16-O5= 1.42 Å and C11-O3= 1.45 Å. The C-C bond lengths are C9-C10= 1.51 Å and C11-C16= 1.47 Å. The torsion angles between the two halves of the ether bridge are fairly similar with O3-C11-C16-O5= -64(1)° and O4-C9-C10-O5= -67.7(9)°.

Table 52. Least-Squares Planes

Plane number 1

Atoms defining plane	Distance
S(2)	-.0002(27)
C(6)	-.0029(79)
C(14)	.0027(82)
C(15)	.0025(96)
C(17)	-.0001(99)

Additional atoms	Distance
O(4)	-.0066
C(9)	-.0780
C(10)	-.2714

Mean deviation from plane is .0017 Ångstroms

Plane number 2

Atoms defining plane	Distance
S(1)	.0003(27)
C(7)	-.0010(75)
C(8)	.0040(87)
C(12)	-.0048(93)
C(13)	-.0012(88)

Additional atoms	Distance
O(3)	-.0207
C(11)	-.0895
C(16)	-.0637

Mean deviation from plane is .0023 Ångstroms.

Dihedral angle between least-squares planes 2 and 1 = 94.99°.

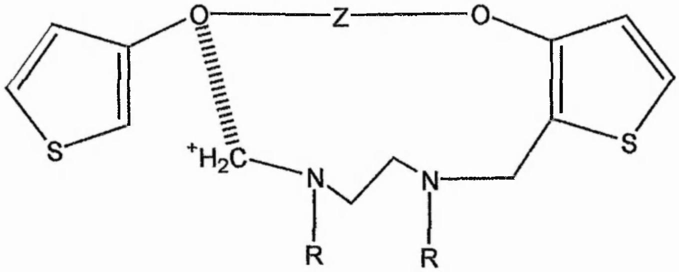
In contrast to the ether bridge which has the expected geometry, the thiophene rings present significant distortions compared to unsubstituted thiophene[354]. The thiophene rings are planar. The angle between these two planes is 94.99°. The molecule is almost separated by O5 into two planes as the O3, C11 and C16 atoms lie in the same plane as the S1 thiophene rings, and O4, C9 lie in the S2 thiophene ring plane. Only C10 is slightly out of the S2 thiophene ring plane with a deviation of 0.2714 Å. The deviation of C10 from the S2 thiophene plane might be due to H...H interactions and an O...H hydrogen bond, C16-H6...H3-C10= 2.224 Å, C16-H9...H3...C10= 2.339 Å and C10-H12...O4= 2.498 Å. The thiophene ring bond lengths are differently distorted and in both cases are not symmetric, especially in the S2 thiophene ring. The exceptions are the C-S-C angles, C12-S1-C13= 92.0(5)° and C14-S2-C17= 92.5(4)°, which are fairly similar to the C-S-C angle of unsubstituted thiophene. Those distortions in the S2 thiophene ring probably lessen its aromatic character.

In the S1 thiophene ring, the S-C bond lengths differ by 0.04 Å, S1-C12= 1.70 Å and S1-C13= 1.74 Å. The rest of the S1 ring bond lengths are symmetric with C7-C13= 1.37 Å, C8-C12= 1.37 Å and C7-C8= 1.44 Å. But, the bond angles are different. The S1-C13-C7 angle is 2.4° smaller than the S1-C12-C8 angle. This could be due to the two H...H interactions, which are C11-H7...H10-C13= 2.198 Å and C11-H8...H10-C13= 2.064 Å., and the two C-H...O hydrogen bonds, C8-H14...O3= 2.666 Å and C16-H6...O3= 2.521 Å. The C8-H14...O3 bond, H7...H10 and H8...H10 interactions added to the substitution on C7, also affect the thiophene C-C-C bond angles as C12-C8-C7= 111.1(9)° and C8-C7-C13= 113.3(9)°.

In the S2 thiophene ring, the difference between the S-C bonds, S2-C14= 1.706 Å and S2-C17= 1.73 Å, is reversed when compared to the S1 thiophene. This time, the shorter S-C bond is the closer to the ether bridge-thiophene bonding. This might be due to the C14-H2...H4-C9= 2.376 Å, C14-H2...H5-C9= 2.595 Å interactions and O4...H2-C14= 2.804 Å contact bond, which associated with the O4...H11-C15= 2.714 Å and O4...H12-C10= 2.498 Å bonds, explains the angular differences from the other thiophene ring. The S2 thiophene ring bond angles are S2-C14-C6= 108.8(7)°, S2-C17-C15= 110.3(7)°, C14-C6-C15= 112.9(8)° and C6-C15-C17= 115.5(9)°.

The distance between S1 and S2 is 11.047 Å and between C13 and C14 is 8.897 Å. The distance between C13 and C14 is important because the macrocyclisation with an amine or diamine will occur on these carbons. As reported by Halfpenny and co-workers[6], one method of ring closure avoids all problems of formation of higher oligomers or polymers, low yields and purification difficulties, via its self-templating mechanism. The reaction used was a Mannich reaction, which involves electrophilic substitution at the 2-position of the thiophene ring by reaction of the mildly electrophilic condensate of formaldehyde and a secondary amine[356]. The formation of oligomers/polymers was limited, presumably due to an electrostatic interaction between one of the ether oxygens and the electropositive methylene carbon of the reaction intermediate. This has the effect of bringing the reactive electrophilic arm proximate to the thiophene ring of the same molecule where reaction takes place (scheme 5). Also the fact that high yields of the [1+1] macrocycles are obtained at normal dilution and that there is no oligomeric or a polymeric byproduct suggests that intermolecular electrostatic interactions are minimal.

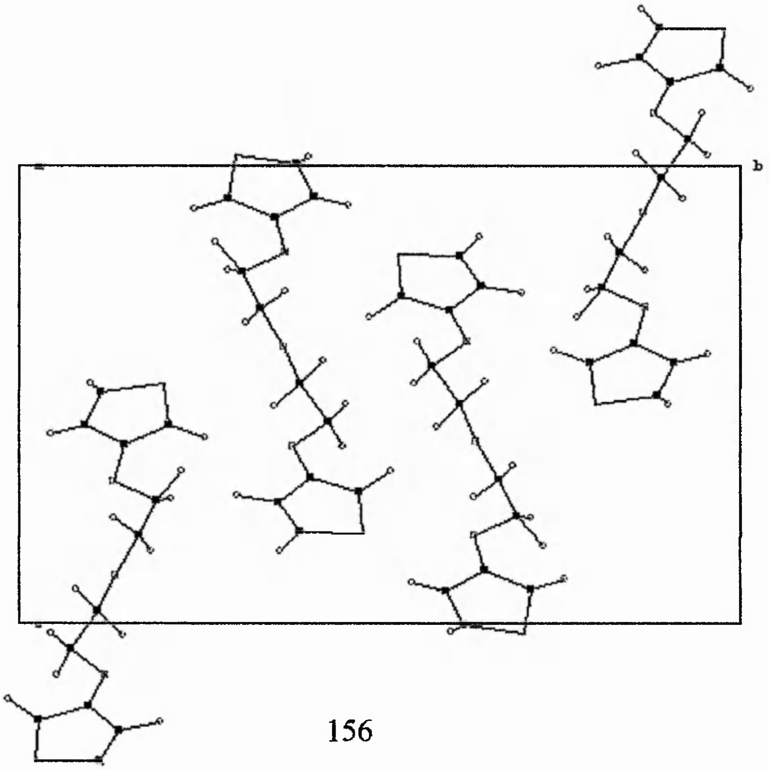
Scheme 5.



In the present compound, the carbon C14 is freer of steric effect than C13. The macrocyclisation reaction might first occur on C14. Then, because the free lone pairs of O3 are directed towards C14, there might be an interaction between NCH_2^+ and O3 that will facilitate the macrocyclisation on C13 instead of a polymerisation (scheme 5).

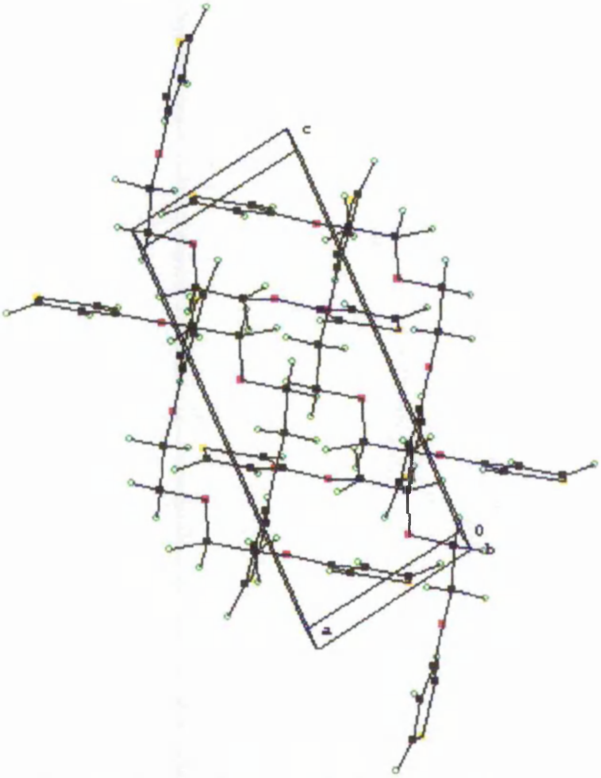
The thiophene-based ether chain of **16**, which is widely flexible, contains three oxygen donors on the ether bridge. This flexibility and the presence of donor atoms allow this ligand to complex with a metal ion.

In the crystal, there may be some H...H interactions, H7(x, y, z)...H11(½+x, ½ -y, ½+z)= 2.087 Å, H12(x, y, z)...H10(½+x, ½ -y, ½+z)= 2.789 Å, H2(½-x, ½+y, ½-y)...H4(½+x, ½ -y, ½+z)= 2.729 Å, H3(½-x, ½+y, ½-y)...H5(½+x, ½ -y, ½+z)= 2.638 Å and H4(½-x, ½+y, ½-y)...H4(½+x, ½ -y, ½+z)= 2.739 Å, these are fairly close contacts in the unit cell, despite only one being smaller than the sum of the van der Waals radii (2.40 Å). The unit cell may also contain a C-H...O hydrogen bond, O4(½+x, ½ -y, ½+z)...H10(x, y, z)= 2.435 Å, which is situated within the usual range C-H...O= 2.4-2.8 Å[353].

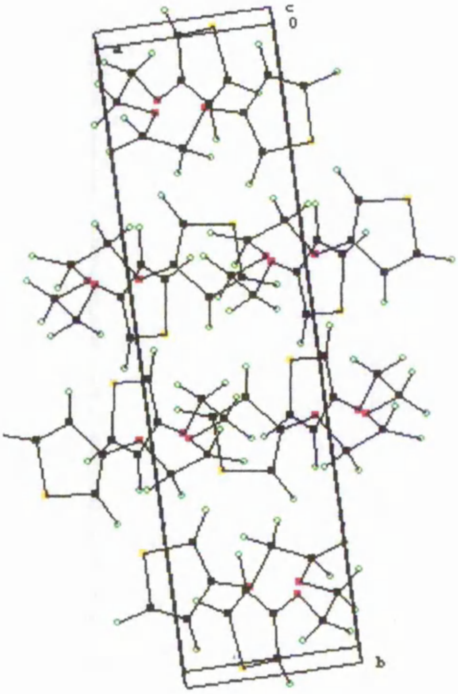


On the previous view of the unit cell, it appears that the molecules (½-x, ½+y, ½-z) and (½+x, ½-y, ½+z) are arranged along a 2_1 helicoidal axis.

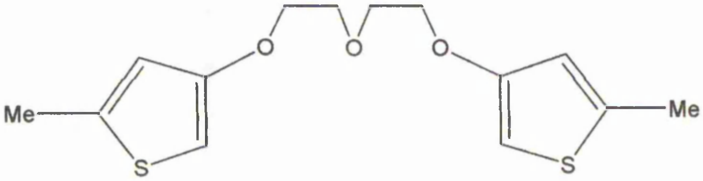
The following view of the unit cell shows that the molecules are arranged along an n translation plane perpendicular to the b axis.



In another view of the unit cell (below), it appears that the molecules are arranged in a layer perpendicular to the b axis.



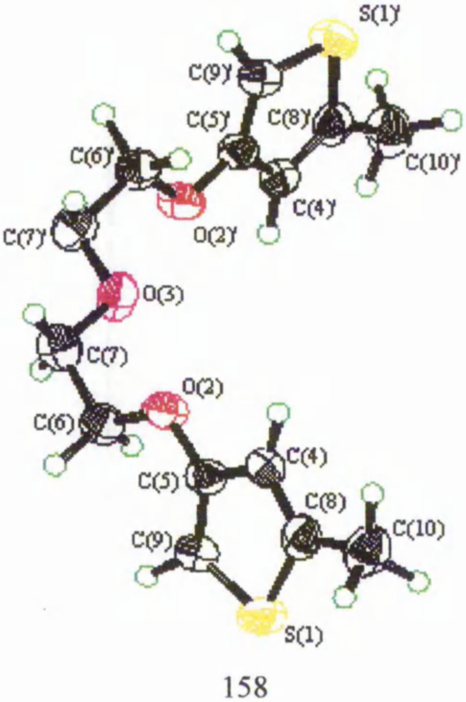
2.2. dimethyl α,ω-bis-(3-oxythienyl)ethane **17**



The compound dimethyl α-ω-bis-(3-oxythionyl)-propane was hoped to be a macrocycle with the same nitrogen bridge as ethyl-trioxa-azatricyclo-tricosa-tetraene. In fact, after the study by X-ray crystallography and verification by NMR ^{1}H, ^{13}C and Infra-Red spectroscopy, it was concluded that it was the starting material for the last stage of the synthesis of this macrocycle, which clearly had not proceeded to completion.

2.2.1. Discussion of the structure derived data (tables 9, 12 and 13)

Just half of the molecule is unique (due to the existence of a C2 axis centered on O3) and after refinement and all atoms had been found, it was expanded to obtain the entire molecule. The thermal ellipsoids of the sulfurs are large, although these are the heaviest atoms. This could be due to the fact that the thiophene rings are on the outer edges of the molecule and the rings could be moving (wagging) with thermal motion. The positions and displacement parameters of the atoms in the molecule are best visualised in the "ortep style" drawing[353] below.



The larger displacement parameters occur at the extremities of the molecule. The thiophene rings have greater displacements for the sulfur, and the outermost carbon atoms (C8, C9, C10). The oxygens O2 and O3 also have significant displacements.

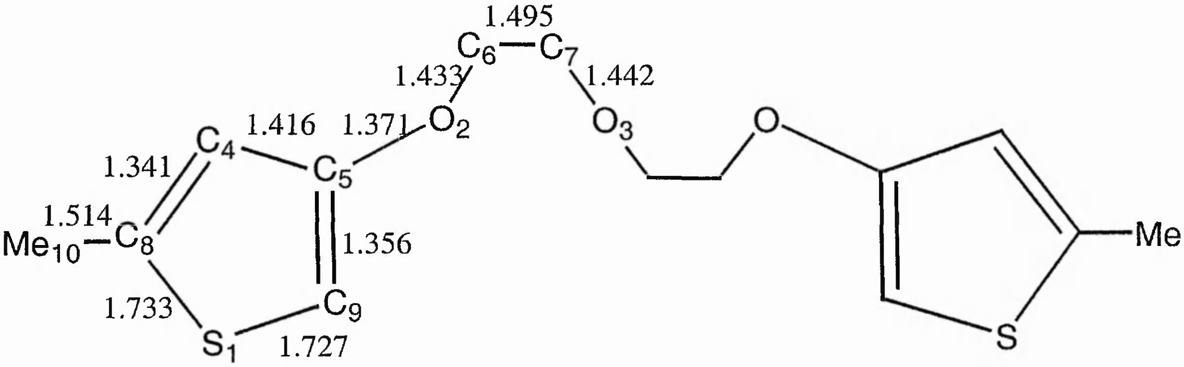
2.2.2. Discussion of structural geometry

Table 53. Bond lengths (Å)

Bond Lengths(Å)			
Bond	Length(Å)	Bond	Length(Å)
S1 - C8	1.733(6)	C6 - C7	1.495(8)
S1 - C9	1.727(6)	C6 - H3	0.917
02 - C5	1.371(6)	C6 - H4	1.131
02 - C6	1.433(6)	C7 - H5	1.085
03 - C7	1.442(6)	C7 - H7	1.106
03 - C7	1.442(6)	C8 - C10	1.514(8)
C4 - C5	1.416(7)	C9 - H8	1.127
C4 - C8	1.341(7)	C10 - H2	1.208
C4 - H1	1.021	C10 - H6	1.043
C5 - C9	1.356(7)	C10 - H9	1.102

** Note the hydrogen bond lengths are to three decimal places with terminal zero's omitted and have no esd's as the hydrogen positions were not refined.

For ease of description the bond lengths (to 3 decimal places) are shown on a schematic drawing below.



The molecules **16** and **17** are different only in the substitution of the hydrogen by a methyl C10 on the C8 thiophene. This extra atom lies in the plane formed by the thiophene ring. The molecule has a C2 axis centered on O3, so the halves of the compound have the same bond lengths.

The two thiophene rings do not lie in the same plane. The molecule has two planes, each containing half the molecule except for atom O3 where the C2 axis is situated, which has the maximum deviation from the least squares planes defined by all the non-hydrogen atoms of the thiophenes (-1.1063 Å). The angle between the plane of each thiophene ring is 110.2°. So, the geometry of the compound has two approximately planar regions joined by the ether bridge. Deviations from the least squares planes of these regions are given below.

Table 54. Least-Squares Plane

Atoms Defining Plane	Distance
S1	-.0004
C4	-.0019
C5	.0015
C8	.0014
C9	-.0006

Additional Atoms	Distance
O2	-.0025
O3	-1.1063
C6	.0821
C7	.1634
C10	-.0327

Mean deviation from plane is .0012 Ångstroms

The S1 thiophene ring has fairly similar bond lengths either side of the sulfur atom, which was not the case for compound **16**. This confirms the aromatic character of the thiophene ring in compound **17**. The C-CH_3 bond length, C8-C10= 1.514 Å, is fairly close to the expected bond length for a carbon 5-substituted thiophene[357]. Also, the thiophene bond lengths, C4-C5= 1.416 Å, S1-C8= 1.733 Å, S1-C9= 1.727 Å, C4-C8= 1.341 Å and C5-C9= 1.356 Å, agree with those in unsubstituted thiophene[354].

In the ether bridge, the aromatic C5-O2= 1.371 Å is similar to those in compound **16**, and consequently is smaller than the aliphatic C-O bonds as determined for typical phenolic compounds. The other C-O bond lengths are C6-O2= 1.433 Å and C7-O3= 1.442 Å, whereas the similar C-O bonds in structure **16** were varying between 1.41 Å and 1.45 Å. The C6-C7 bond length is 1.495 Å.

Table 55. Bond angles (°)

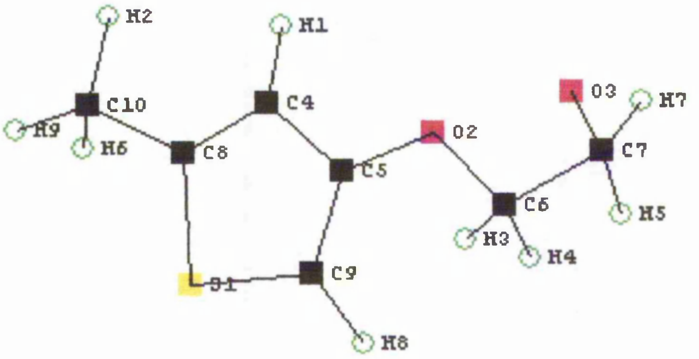
Bond Angles(°)			
Bond	Angle(°)	Bond	Angle(°)
C8 - S1 - C9	92.3(3)	O3 - C7 - H7	108.53
C5 - O2 - C6	115.7(4)	C6 - C7 - H5	90.87
C7 - O3 - C7	110.2(6)	C6 - C7 - H7	116.2
C5 - C4 - C8	112.7(5)	H5 - C7 - H7	140.11
C5 - C4 - H1	120.61	S1 - C8 - C4	111.0(4)
C8 - C4 - H1	126.68	S1 - C8 - C10	121.1(4)
O2 - C5 - C4	118.6(4)	C4 - C8 - C10	127.9(6)
O2 - C5 - C9	127.0(5)	S1 - C9 - C5	109.6(4)
C4 - C5 - C9	114.4(5)	S1 - C9 - H8	122.69
O2 - C6 - C7	109.4(4)	C5 - C9 - H8	126.84
O2 - C6 - H3	102.8	C8 - C10 - H2	109.79
O2 - C6 - H4	106.27	C8 - C10 - H6	103.1
C7 - C6 - H3	114.93	C8 - C10 - H9	106.76
C7 - C6 - H4	107.33	H2 - C10 - H6	105.66
H3 - C6 - H4	115.55	H2 - C10 - H9	127.09
O3 - C7 - C6	108.0(5)	H6 - C10 - H9	101.71
O3 - C7 - H5	88.01		

** Note the bond angles including hydrogen atoms are to one decimal place with terminal zeros omitted and have no esd's as the hydrogen atoms positions were not refined.

The bond angles in the thiophene rings are fairly similar to those in unsubstituted thiophene[354] with C8-S1-C9= 92.3(3)°, S1-C8-C4= 111.1(4)° and C5-C4-C8= 112.5(5)°, S1-C9-C5= 109.7(4)°; C4-C5-C9= 114.4(5)° is larger. The methyl bonded to the thiophene makes angles, S1-C8-C10= 121.2(4)° and C4-C8-C10= 127.7(5)°. The ether bridge is bonded to the thiophene via the O2 and has two angles, O2-C5-C4= 118.3(4)°

and O2-C5-C9= 127.3(5)°, which are fairly close to those in compound **16**. This bridge has two large angles (>109.47°) C5-O2-C6= 115.5(4)° and C7-O3-C7= 111.2(6)°. The ether bridge contains two other angles, O2-C6-C7= 109.7(4)° directly bonded to the thiophene (108.6° and 107.7° in **16**), and O3-C7-C7= 109.2(5)° (108.6° and 111.4° in **16**).

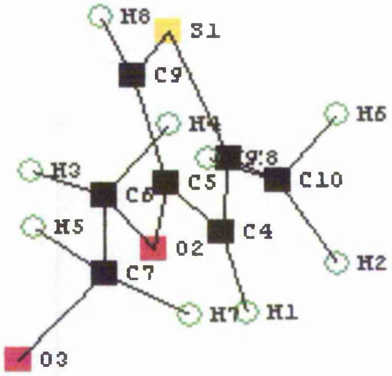
Those differences from the structure **16** might be due to the different bonding created by the presence of the substituted methyl C10 on the thiophene. Indeed, three S...H hydrogen bonds appear in the molecule, S1...H8-C9= 2.520 Å, S1...H9-C10= 2.983 Å and S1...H6-C10= 2.902 Å (sum of their van der Waals radii= 3.00 Å). There is also a C...H interaction between the atoms H9 (methyl) and C5 (thiophene), C10-H9...C5= 2.876 Å, which is lower than the sum of their van der Waals radii (2.90 Å). Other hydrogen contacts appear between the bridge and the thiophene. These contacts are C-H...C, C-H...O and C-H...S bonds, C6-H4...C9= 2.767 Å, C4-H1...O2= 2.612 Å and C6-H4...S1= 2.9113 Å. The C4-H1...O2 bond and the C-H...O and H...H hydrogen contacts within the ether bridge are similar to those in the structure **16**, C7-H7...O2= 2.697 Å, C6-H3...O3= 2.534 Å, H3...H5= 2.030 Å, H4...H5= 2.386 Å and H4...H8= 2.380 Å.



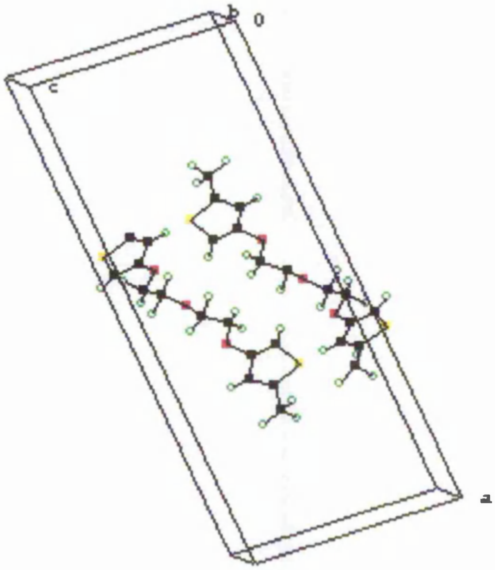
The distance between S1 and S1A is 11.523 Å and between C9 and C9A is 9.084 Å, those distances are respectively 0.476 Å and 0.187 Å larger than in the structure **16**. In that case, the carbon C9 and C9A are identically free of steric effect and also the lone pairs of O2 and O2A are respectively and symmetrically pointing at C9A and C9. The intended Mannich reaction should have occurred firstly on C9 or C9A with no distinction, then an interaction between NCH_2^+ and O2 or O2A would have facilitated the ring closure. The longer distances between C9 and C9A added to the direction of the O2's lone pairs and the presence of a substituted methyl on the thiophenes might be the reason why the macrocyclisation reaction did not work on the thiophene open-chain compound.

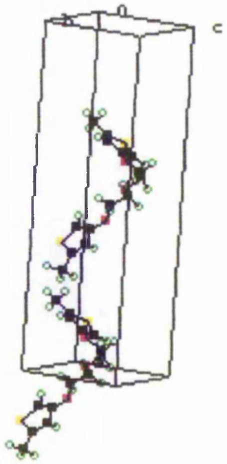
The ether chain **17** has similar properties to compound **16**. The great flexibility and the three oxygen donors present in the ligand should allow an eventual complexation.

As can be seen above, the oxygens directly bound to the thiophenes are in the same plane. For both planes, the three methylene carbons C10, C6 and C7 are fairly close to the plane (maximum deviation= 1.1 Å) formed by the thiophene rings.

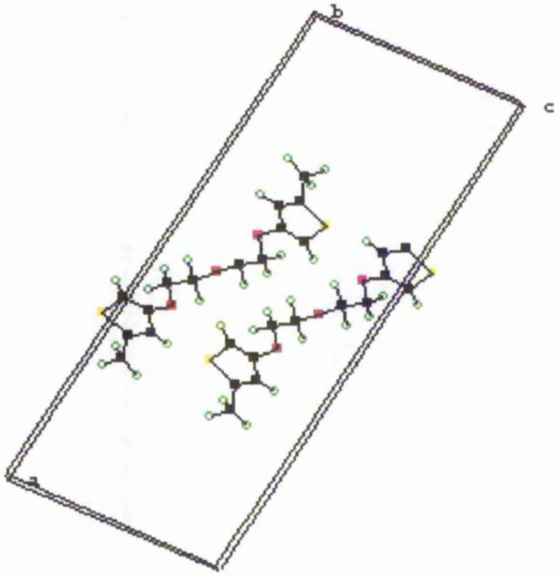


In the crystal, there may be some intermolecular H...H interactions, H2(x, y, z)...H2(½+x, ½+y, z)= 2.663 Å, H2(x, y, z)...H9(½+x, ½+y, z)= 2.7724 Å, H3(x, y, z)...H3(x, -y, ½+z)= 2.605 and H5(x, -y, ½+z)...H8(x, y, z)= 2.602 Å, these are all fairly close contacts, despite being bigger than their sum of the van der Waals radii (2.40 Å).

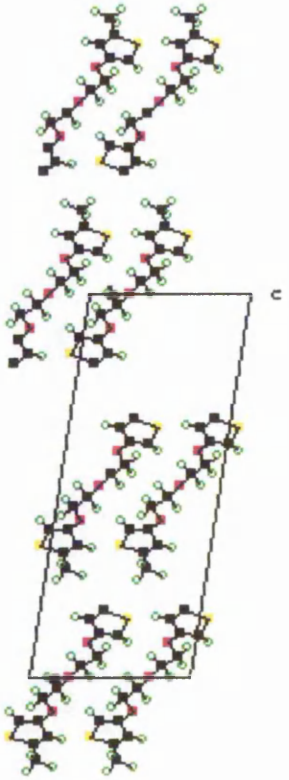


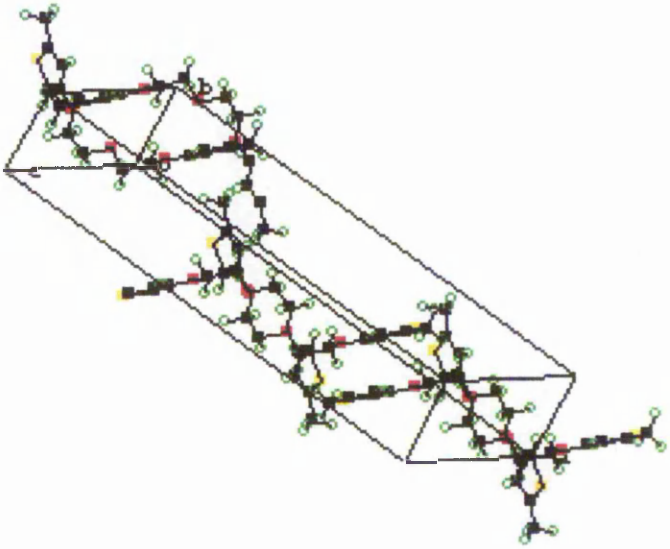


The unit cell may also contain a C-H...O hydrogen bond between O2(x, -y, ½+z) and H8(x, y, z)= 2.767 Å which is situated within the usual range C-H...O= 2.4-2.8 Å. It should be noted that the hydrogen atoms were placed in calculated positions with C-H distances of 1.13 Å, hence the “real” distance may be rather shorter than that quoted here.

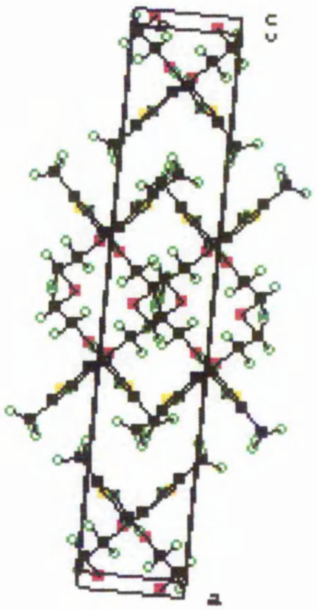


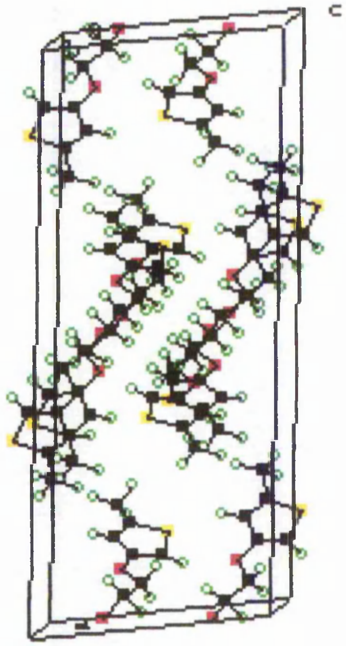
In another view of the cell (above) it appears that the molecules (x, y, z) and the molecules (x, -y, ½+z) are arranged along a C2 axis.



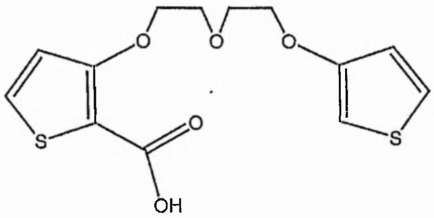


This is a recognisable repeating pattern in the full cell. And, it can also be noted that each molecule is bound to another in the successive layer of molecules along the a-axis by two hydrogen bonds, and that there is a similar layer along the b-axis.





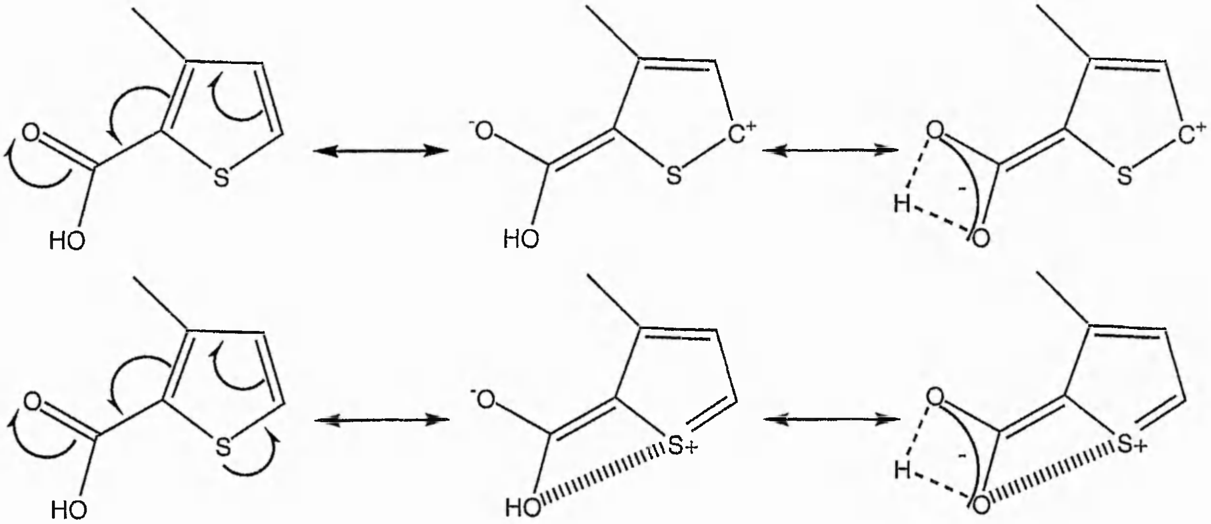
2.3. 15-carboxylic-α,ω-bis-(3-oxythienyl)ethane **18**



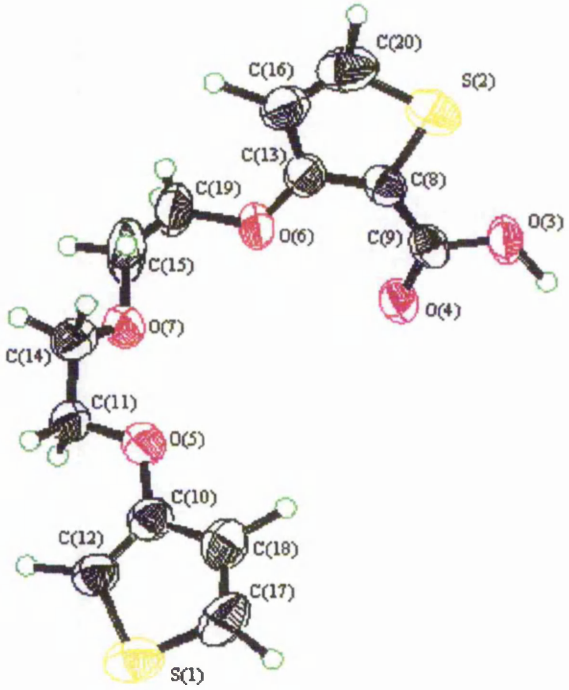
2.3.1. Discussion of the structure derived data (tables 9, 14 and 15)

Four molecules appear in the unit cell and the space group is $P2_1/n$ or a variation of n°14. The displacement parameters divide the molecule in two halves by O7. As with compounds **16** and **17**, the thermal ellipsoid for the sulphur S1 is bigger than those of most of the other atoms. This is due to the same reasons. However, S2 shows less thermal motion, and the carbons C8 (thiophene) and C9 (carboxylic), which are on the outer edge of the molecule, have a smaller displacement than the other outer carbons. Also, the oxygens O5, O6 and O7 in the ether bridge have a bigger displacement than the oxygens O3 and O4 of the carboxylic acid group. This could be due to an electron delocalisation on the thiophene and the carboxylic acid group (scheme 6). The carbons C15 and C19 in the bridge have the biggest displacement in the molecule. This also might be due to the presence of the carboxylic acid group and the delocalisation effect.

Scheme 6.



The positions and displacement parameters of the atoms in the molecule are best visualised in the "ortep style" drawing[353] below.



2.3.2. Discussion of structural geometry

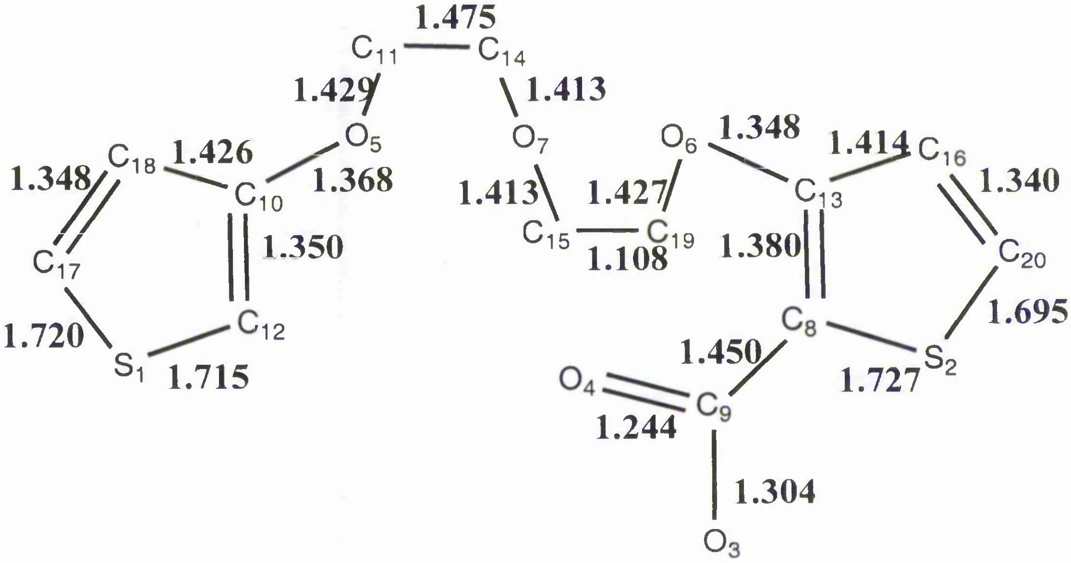
Table 56. Bond lengths (Å)

Bond Lengths (Å)			
Bond	Length(Å)	Bond	Length(Å)
S(1) -C(12)	1.715(5)	C(11) -H(4)	1.065
S(1) -C(17)	1.720(6)	C(11) -H(5)	1.12
S(2) -C(8)	1.727(5)	C(12) -H(1)	1.203
S(2) -C(20)	1.695(6)	C(13) -C(16)	1.414(8)
O(3) -C(9)	1.304(5)	C(14) -H(6)	1.041
O(3) -H(11)	1.116	C(14) -H(7)	1.118
O(4) -C(9)	1.244(5)	C(15) -C(19)	1.108(8)
O(5) -C(10)	1.368(5)	C(15) -H(10)	1.06
O(5) -C(11)	1.429(5)	C(15) -H(13)	0.778
O(6) -C(13)	1.348(6)	C(16) -C(20)	1.340(8)
O(6) -C(19)	1.427(7)	C(16) -H(8)	1.288
O(7) -C(14)	1.413(6)	C(17) -C(18)	1.348(7)
O(7) -C(15)	1.411(7)	C(17) -H(3)	1.141

C(8) -C(9)	1.450(7)	C(18) -H(2)	1.243
C(8) -C(13)	1.380(6)	C(19) -H(14)	0.879
C(10) -C(12)	1.350(6)	C(19) -H(15)	1.035
C(10) -C(18)	1.426(7)	C(20) -H(9)	1.233
C(11) -C(14)	1.475(6)		

** Note the hydrogen bond lengths are to three decimal places with terminal zero's omitted and have no esd's as the hydrogen positions were not refined.

For ease of description the bond lengths (to 3 decimal places) are shown on a schematic drawing below.



Molecule **18** is divided in to two halves by O7, differing by the substitution of a hydrogen on the thiophene ring by a carboxylic acid group. The effects of the carboxylic acid group are reflected in the bond lengths and the bond angles. The two thiophene ring planes form an angle of 44.58°. The table of deviations from least-squares planes is given below (table 58).

Table 57. Bond angles (°)

Bond Angles (°)			
Bond	Angle(°)	Bond	Angle(°)
C(12) -S(1) -C(17)	92.5(3)	C(8) -C(13) -C(16)	111.9(5)
C(8) -S(2) -C(20)	90.9(3)	O(7) -C(14) -C(11)	110.3(4)
C(9) -O(3) -H(11)	122.17	O(7) -C(14) -H(6)	108.65

C(10) -O(5) -C(11)	116.4(4)	O(7) -C(14) -H(7)	116.82
C(13) -O(6) -C(19)	117.1(6)	C(11) -C(14) -H(6)	111.16
C(14) -O(7) -C(15)	115.8(6)	C(11) -C(14) -H(7)	111.21
S(2) -C(8) -C(9)	119.1(4)	H(6) -C(14) -H(7)	98.05
S(2) -C(8) -C(13)	111.2(4)	O(7) -C(15) -C(19)	134.3(7)
C(9) -C(8) -C(13)	129.7(5)	O(7) -C(15) -H(10)	100.13
O(3) -C(9) -O(4)	122.1(5)	O(7) -C(15) -H(13)	77.9
O(3) -C(9) -C(8)	115.2(4)	C(19) -C(15) -H(10)	123.9
O(4) -C(9) -C(8)	122.6(5)	C(19) -C(15) -H(13)	95.42
O(5) -C(10) -C(12)	128.1(5)	H(10) -C(15) -H(13)	110.72
O(5) -C(10) -C(18)	117.6(5)	C(13) -C(16) -C(20)	112.3(6)
C(12) -C(10) -C(18)	114.3(5)	C(13) -C(16) -H(8)	121.81
O(5) -C(11) -C(14)	108.4(4)	C(20) -C(16) -H(8)	125.04
O(5) -C(11) -H(4)	100.13	S(1) -C(17) -C(18)	111.4(4)
O(5) -C(11) -H(5)	111.62	S(1) -C(17) -H(3)	117.44
C(14) -C(11) -H(4)	118.78	C(18) -C(17) -H(3)	131.12
C(14) -C(11) -H(5)	110.71	C(10) -C(18) -C(17)	111.7(5)
H(4) -C(11) -H(5)	106.74	C(10) -C(18) -H(2)	129.42
S(1) -C(12) -C(10)	110.0(4)	C(17) -C(18) -H(2)	118.84
S(1) -C(12) -H(1)	122.79	O(6) -C(19) -C(15)	126.9(7)
C(10) -C(12) -H(1)	126.5	O(6) -C(19) -H(14)	111.68
O(6) -C(13) -C(8)	121.0(5)	O(6) -C(19) -H(15)	102.85
O(6) -C(13) -C(16)	127.1(5)	C(15) -C(19) -H(14)	107.45
C(15) -C(19) -H(15)	97.43	S(2) -C(20) -H(9)	111.33
H(14) -C(19) -H(15)	108.05	C(16) -C(20) -H(9)	133.86
S(2) -C(20) -C(16)	113.7(5)		

** Note the bond angles including hydrogen atoms are to two decimal places with terminal zeros omitted and have no esd's as the hydrogen atoms positions were not refined.

Table 58. Least-Squares Planes

Plane number 1

Atoms Defining Plane	Distance
S(2)	-.0007(15)
C(8)	.0039(45)

C(13)	-.0002(49)
C(16)	-.0100(60)
C(20)	.0135(61)

Additional Atoms	Distance
C(9)	-.0104
O(3)	-.0024
O(4)	-.0180
O(6)	-.0033
C(19)	.0272
C(15)	-.5462
O(7)	-1.6403

Mean deviation from plane is .0057 Ångstroms

Chi-squared: 7.6

Plane number 2

Atoms Defining Plane	Distance
S(1)	.0003(17)
C(10)	.0041(53)
C(17)	-.0009(61)
C(18)	-.0021(63)
C(12)	-.0039(52)

Additional Atoms	Distance
O(5)	.0326
C(11)	.1568
C(14)	.1858
O(7)	1.4271

Mean deviation from plane is .0023 Ångstroms

Chi-squared: 1.1

The S1 thiophene is only substituted on C10 by the oxygen O5 of the ether bridge. The bond lengths and bond angles in the S1 thiophene ring are fairly symmetric and close to the values in unsubstituted thiophene[354]. The bond lengths and bond angles are S1-C12= 1.715 Å, S1-C17= 1.720 Å, C10-C12= 1.350 Å, C17-C18= 1.348 Å, C10-C18= 1.426 Å, C12-S1-C17= 92.5(3)°, S1-C12-C10= 110.0(4)°, S1-C17-C18=

111.4(4)°, C10-C18-C17= 111.7(5)° and C12-C10-C18= 114.3(5)°. The bond lengths and bond angles between the thiophene and the ether bridge on C10 are similar to those in structures **16** and **17**, C10-O5= 1.368 Å, a large angle with the thiophene double bond C12-C10-O5= 128.1(5)° and a smaller angle with the single bond O5-C10-C18= 117.6(5)°.

The S2 thiophene is substituted on C13 by the ether bridge and on C8 by a carboxylic acid group, which is lying in the plane formed by the thiophene rings. The electron delocalisation created by the carboxylic group (scheme 6) affects the bond lengths, the bond angles and torsion angles in this half of the molecule. Indeed, on the thiophene, the bond lengths and bond angles are not symmetric. The delocalisation effects appear as S2-C20= 1.695 Å, S2-C8= 1.727 Å and C8-S2-C20= 90.9(3)°, S2-C20 has more double bond character than S2-C8. The same effect appears on C16-C20= 1.340 Å and C8-C13= 1.380 Å, S2-C8-C13= 111.2(4)°, S2-C20-C16= 113.7(5)°, C8-C13-C16= 111.9(5)° and C13-C16-C20= 112.3(6)°. Also, the bond length C8-C9= 1.450 Å, which is 0.07 Å shorter than the expected 1.52 Å single bond[357], indicates that the bond character is between a single and a double bond. This indicates a possible conjugation with the adjacent thiophene ring and the carboxylic group. The angles between the thiophene and the carboxylic group are C9-C8-C13= 129.7(5)° and S2-C8-C9= 119.1(4)°. On the carboxylic group, the C=O bond length is C9-O3= 1.244 Å, and the C-O bond length is C9-O3= 1.304 Å. The angles C8-C9-O4= 122.6(5)°, C8-C9-O3= 115.2(4)° and O3-C9-O4= 122.1(5)° are fairly close to the expected 120° for a trigonal conformation. The atoms S2 and O3 are in interaction, S2...O3= 2.864 Å (sum of the van der Waals radii= 3.35 Å), and form a torsion angle of S2-C8-C9-O3= -1.1(6)° whereas S2 and O4 form a torsion angle of S2-C8-C9-O4= 179.7(4)°.

The electron delocalisation also affects the ether bridge as O6-C13= 1.348 Å which is around 0.02 Å shorter than usual and the angles O6-C13-C18= 121.0(5)° and O6-C13-C16= 127.1(5)° are reversed compared to their counterparts with the S1 thiophene ring. A few intramolecular contacts appear, such as O4...O6= 2.863 Å, O6...H8-C16= 2.912 Å, C16-H8...H14-C19= 1.871 Å and C16-H8...C19= 2.622 Å. The interaction O4...O6 is reflected in the torsion angles O4-C9-C8-C13= -180.0(5)° and O3-C9-C8-C13= 0.6(8)°. The delocalisation and the interactions O4...O6, H8...H14 and H8...C19 might explain the very short bond length C15-C19= 1.108 Å. The electron delocalisation may create a large electron movement on the ether bridge, which is appearing in the displacement parameters of C15 and C19.

The atoms O6, C15 and C19 also lie in the S2 thiophene ring plane. The oxygen

O7 is the only atom that is out of both thiophene planes, its deviation from plane 1= 1.6403 Å and from plane 2= 1.4271 Å. The aliphatic C-O bond lengths in the ether bridge vary from 1.413 Å to 1.429 Å. The C11-C14= 1.475 Å bond length is similar to those in structures **16** and **17**. However, the electron delocalisation and the different hydrogen bonds affect the O-C-C and C-O-C bond angles. The angle C14-O7-C15= 115.8(6)° is 4.6° and 3.2° respectively larger than in compound **16** and **17**. The torsion angles differ as O5-C11-C14-O7= 73.3(5)° whereas O6-C19-C15-O7= 14(3)°. In the half of the molecule containing the carboxylic group, C13-O6-C19= 117.1(6)°, O6-C19-C15= 126.9(7)° and O7-C15-C19= 134.3(7)°, the O-C-C and C-O-C bond angles are respectively 0.7°, 18.5° and 24.0° larger than in the other half of the ether bridge. This could be due to the delocalisation and the different intramolecular contacts O4...O6, H8...C19, H8...H14, O6...H8, O6...H13-C15= 2.473 Å, O7...H14-C19= 2.862 Å and O7...H15-C19= 2.871 Å. In the other half there are fewer and weaker contacts, O7...H5-C11= 2.574 Å, O5...H7-C14= 2.619 Å, O5...H2-C18= 2.861 Å and O5...H1-C12= 2.918 Å.

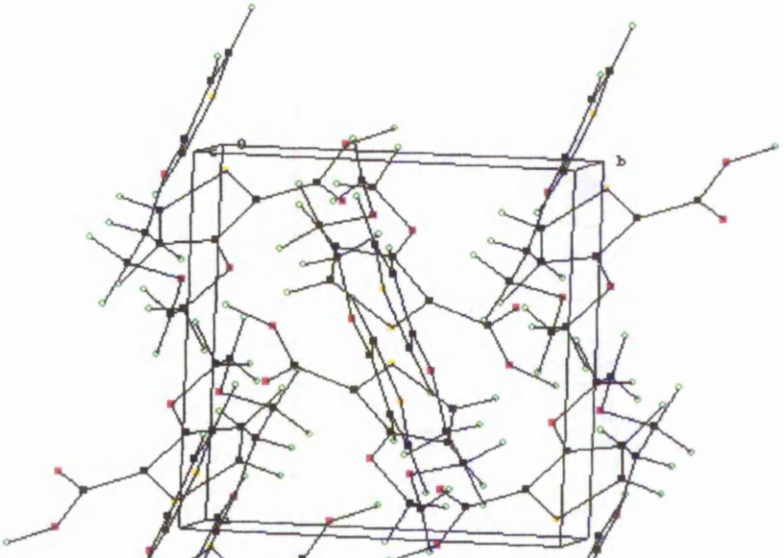
Table 59. Torsion angles (°)

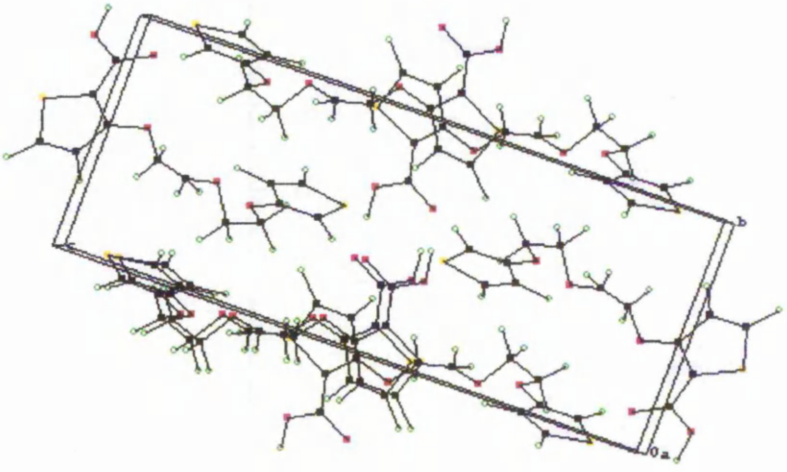
Torsion or Conformation Angles (°)			
Bond	Angle(°)	Bond	Angle(°)
S(1)-C(12)-C(10)-O(5)	178.5(4)	C(8)-C(13)-O(6)-C(19)	-178.4(6)
S(1)-C(12)-C(10)-C(18)	-0.7(7)	C(8)-C(13)-C(16)-C(20)	1.2(8)
S(1)-C(17)-C(18)-C(10)	-0.3(7)	C(9)-C(8)-S(2)-C(20)	-179.7(4)
S(2)-C(8)-C(9)-O(3)	-1.1(6)	C(9)-C(8)-C(13)-C(16)	178.8(5)
S(2)-C(8)-C(9)-O(4)	179.5(4)	C(10)-O(5)-C(11)-C(14)	-179.3(4)
S(2)-C(8)-C(13)-O(6)	-179.7(4)	C(10)-C(12)-S(1)-C(17)	0.5(5)
S(2)-C(8)-C(13)-C(16)	-0.1(6)	C(11)-O(5)-C(10)-C(12)	-4.5(8)
S(2)-C(20)-C(16)-C(13)	-1.8(8)	C(11)-O(5)-C(10)-C(18)	174.7(5)
O(3)-C(9)-C(8)-C(13)	-180.0(5)	C(11)-C(14)-O(7)-C(15)	174.0(6)
O(4)-C(9)-C(8)-C(13)	0.6(8)	C(12)-S(1)-C(17)-C(18)	-0.1(5)
O(5)-C(10)-C(18)-C(17)	-178.6(5)	C(12)-C(10)-C(18)-C(17)	0.6(8)
O(5)-C(11)-C(14)-O(7)	73.3(5)	C(13)-O(6)-C(19)-C(15)	-139(2)
O(6)-C(13)-C(8)-C(9)	-0.8(8)	C(13)-C(8)-S(2)-C(20)	-0.7(4)
O(6)-C(13)-C(16)-C(20)	-179.2(5)	C(14)-O(7)-C(15)-C(19)	127(2)
O(6)-C(19)-C(15)-O(7)	14(3)	C(16)-C(13)-O(6)-C(19)	2.0(9)
C(8)-S(2)-C(20)-C(16)	1.5(5)		

The thiophene-based chain molecule **18** contains five oxygen donors. Despite the rigidity created by the carboxylic group, the molecule and especially the ether bridge are still flexible enough in solution for metal complexation. The flexibility of the structure **18** associated with the presence of the carboxylic group, which is a good electron-donor will facilitate an eventual complexation. This molecule is more likely to complex than the compounds **16** and **17**. Any complex formed would also be more stable.

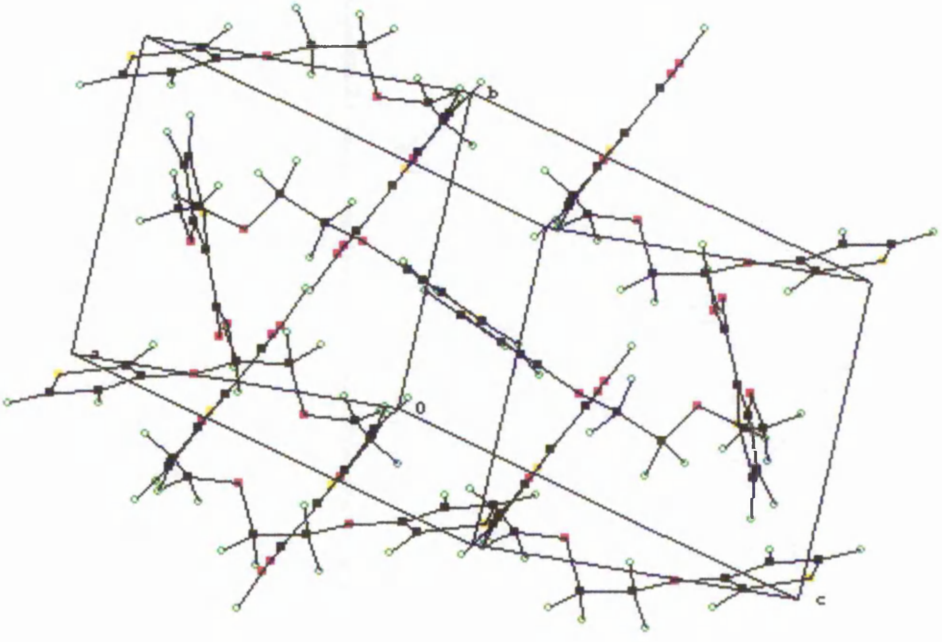
In the unit cell, there are a few O…H intermolecular hydrogen bonds: C12-H1(+x, +y, +z)…O4(½-x, ½+y, ½-z)= 2.206 Å, C11-H4(+x, +y, +z)…O6(½-x, ½+y, ½-z)= 2.638 Å, C11-H4(+x, +y, +z)…O7(½-x, ½+y, ½-z)= 2.758 Å and C14-H7(+x, +y, +z)…O7(½-x, ½+y, ½-z)= 2.878 Å. The short O…H bond C12-H1(+x, +y, +z)…O4(½-x, ½+y, ½-z)= 2.206 Å is due to the strong electronegativity of the oxygen atom O4, which is part of the carboxylic group. An extremely short O…H hydrogen bond appears between O3-H11(x, y, z)…O4(-x, -y, -z)= 1.524 Å, but also an O…O interaction O4(x, y, z)…O3(-x, -y, -z)= 2.623 Å. Finally, two intermolecular contacts appear between C11-H5(x, y, z)…O3(½+x, ½-y, ½+z)= 2.873 Å and C11-H5(x, y, z)…H11(½+x, ½-y, ½+z)-O3= 2.409 Å.

On the two views of the unit cell below, it appears that all the molecules are arranged along the c-axis.

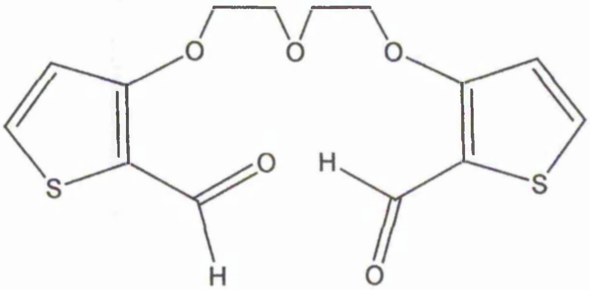




Another view of the unit cell shows that the S1 thiophene ring planes (x, y, z) and (-x, -y, -z) are parallel in the cell. The S1 thiophene (½-x, ½+y, ½-z) and (½+x, ½-y, ½+z) ring planes are also parallel in the cell but directed in the opposite way to the corresponding (x, y, z) and (-x, -y, -z) planes. The S2 thiophene ring plane forms an angle of 44.58° with the S1 thiophene ring plane in each molecule. So, the S2 thiophene ring planes (x, y, z) and (-x, -y, -z) are also parallel in the cell, as well as (½-x, ½+y, ½-z) and (½+x, ½-y, ½+z) in the opposite direction. Moreover, the S1 thiophene rings planes (x, y, z) and (-x, -y, -z) are orthogonal to the S2 thiophene rings plane (½-x, ½+y, ½-z) and (½+x, ½-y, ½+z).



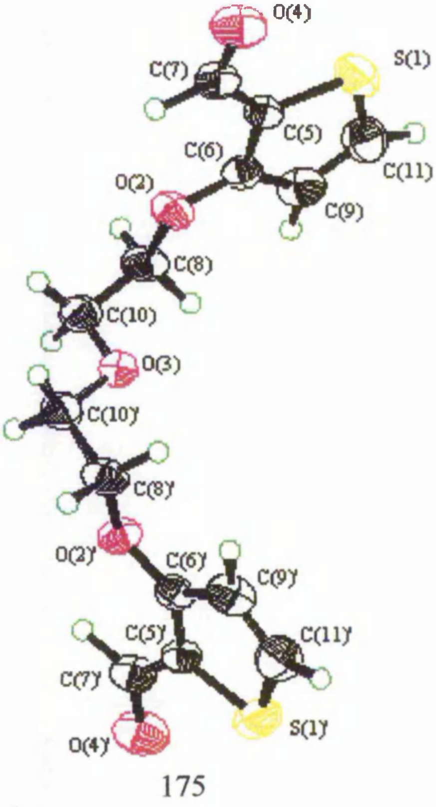
2.4. α,ω-bis-(2-formyl-3-oxythienyl)ethane **19**



2.4.1. Discussion of the structure derived data (tables 9, 16 and 17)

Just half of the molecule is present in the asymmetric unit (due to the existence of a C2 axis centered on O3) and after refinement, it was expanded to obtain the entire molecule. Four molecules are present in the unit cell and the space group is C2/c or a variation of n°15.

The anisotropic displacement parameters of the sulfurs are similarly to compounds **16**, **17** and **18** quite large. The positions and displacement parameters of the atoms in the molecule are best visualised in the "ortep style" drawing[353] below. The larger displacement parameters occur at the extremities of the molecule. Indeed, the oxygen atom O4 of the aldehyde group has a larger thermal ellipsoid than the other oxygen atoms of the ether bridge.



2.4.2. Discussion of structural geometry

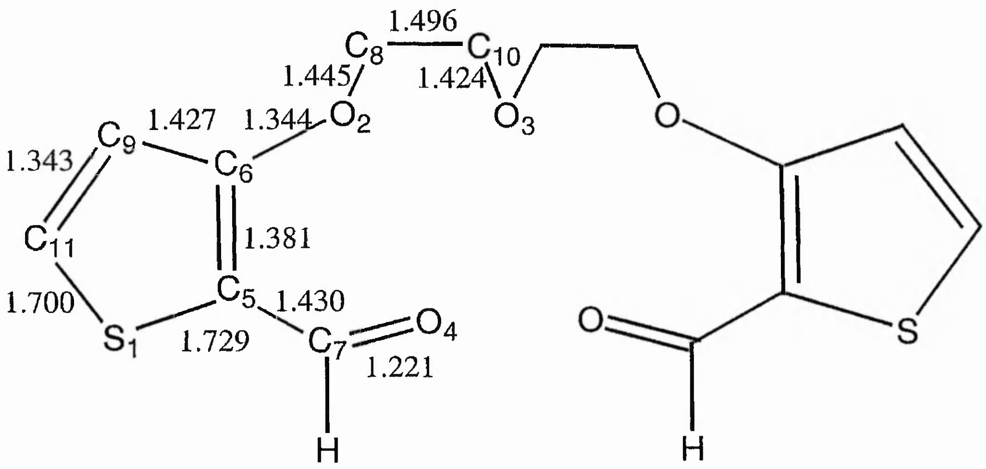
Table 60. Bond lengths (Å)

Bond Lengths(Å)			
Bond	Length(Å)	Bond	Length(Å)
S(1) -C(5)	1.729(3)	C(7) -H(3)	1.14
S(1) -C(11)	1.700(4)	C(8) -C(10)	1.496(4)
O(2) -C(6)	1.344(3)	C(8) -H(4)	1.063
O(2) -C(8)	1.445(3)	C(8) -H(5)	1.03
O(3) -C(10)	1.424(3)	C(9) -C(11)	1.341(4)
O(3) -C(10)*	1.424(3)	C(9) -H(2)	1.031
O(4) -C(7)	1.221(3)	C(10) -H(6)	1.002
C(5) -C(6)	1.381(3)	C(10) -H(7)	1.039
C(5) -C(7)	1.430(4)	C(11) -H(1)	1.037
C(6) -C(9)	1.427(4)		

* At (–x, +y, ½+z)

** Note the hydrogen bond lengths are to three decimal places with terminal zero's omitted and have no esd's as the hydrogen positions were not refined.

The esd's for the bond lengths are reasonable. For ease of description the bond lengths (to 3 decimal places) are shown on a schematic drawing below.



The molecule **19** has the hydrogen on C5 substituted by an aldehyde group, which lies in the plane formed by the thiophene ring. The molecule has a C2 axis centered on O3, so the two halves of the compound have the same bond lengths.

The two thiophene rings do not lie in the same plane. The molecule has two planar zones each containing half the molecule except for atom O3, where the C2 axis is situated which has the maximum deviation from the planes of -1.7619 Å. The angle between the planes of the two thiophene rings is 112.9°. So, the compound has two approximately planar regions joined by the ether bridge. Deviations from the least squares plane are given below.

Table 61. Least-Squares Plane

Atoms Defining Plane	Distance
S(1)	-.0003(9)
C(5)	.0047(25)
C(6)	-.0043(24)
C(9)	.0023(29)
C(11)	.0017(33)

Additional Atoms	Distance
O(4)	.0645
C(7)	.0394
O(2)	-.0614
C(8)	.1452
C(10)	-.3377
O(3)	-1.7619

Mean deviation from plane is .0026 Ångstroms

Chi-squared: 7.4

As in the structure **18**, an electron delocalisation appears on the thiophene rings but this time this is due to the aldehyde group (scheme 7). The delocalisation is again created by the C=O carbonyl, C7=O4 = 1.221 Å. The effects of this delocalisation on the bond lengths and bond angles are similar to those in the compound **18**, especially in the thiophene rings.

Scheme 7.

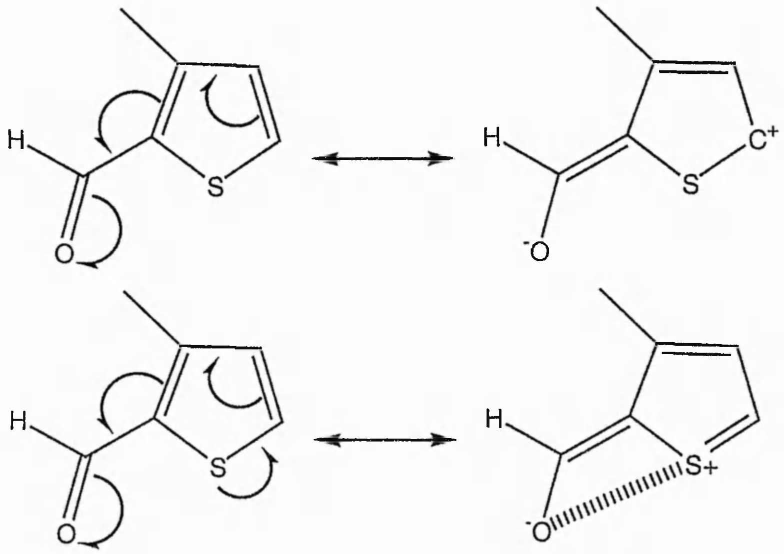


Table 62. Bond angles (°)

Bond Angles(°)			
Bond	Angle(°)	Bond	Angle(°)
C(5) -S(1) -C(11)	91.1(1)	C(10) -C(8) -H(4)	105.92
C(6) -O(2) -C(8)	118.1(2)	C(10) -C(8) -H(5)	109.57
C(10) -O(3) -C(10)	112.9(3)	H(4) -C(8) -H(5)	114.33
S(1) -C(5) -C(6)	110.9(2)	C(6) -C(9) -C(11)	111.7(3)
S(1) -C(5) -C(7)	121.9(2)	C(6) -C(9) -H(2)	118.58
C(6) -C(5) -C(7)	127.2(2)	C(11) -C(9) -H(2)	129.73
O(2) -C(6) -C(5)	119.7(2)	O(3) -C(10) -C(8)	108.2(2)
O(2) -C(6) -C(9)	127.9(2)	O(3) -C(10) -H(6)	111.61
C(5) -C(6) -C(9)	112.4(2)	O(3) -C(10) -H(7)	111.63
O(4) -C(7) -C(5)	124.5(3)	C(8) -C(10) -H(6)	112.39
O(4) -C(7) -H(3)	121.47	C(8) -C(10) -H(7)	106.75
C(5) -C(7) -H(3)	114.01	H(6) -C(10) -H(7)	106.17
O(2) -C(8) -C(10)	107.1(2)	S(1) -C(11) -C(9)	114.0(2)
O(2) -C(8) -H(4)	114.47	S(1) -C(11) -H(1)	116.88
O(2) -C(8) -H(5)	105.23	C(9) -C(11) -H(1)	128.79

** Note the bond angles including hydrogen atoms are to two decimal place with terminal zeros omitted and have no esd's as the hydrogen atom positions were not refined.

The bond lengths and bond angles in the thiophene rings are similar to those in the S2 thiophene rings of structure **18**. In the thiophene rings, S1-C11= 1.700 Å is more double bonded than S1-C5= 1.729 Å (1.695 Å and 1.727 Å for the compound **18**) and, the angle C5-S1-C11= 91.1(1)°. The C6-C9= 1.427 Å is similar to the corresponding C-C bond length in the S2 thiophene of compound **18**. The C5-C6= 1.381 Å has more single bond character than C9-C11= 1.341 Å. The delocalisation effect also appears on the bond angles S1-C5-C6= 110.9(2)° and C6-C9-C11= 111.7(3)°, which are smaller than S1-C11-C9= 114.0(2)° and C5-C6-C9= 112.4(2)°. The aldehyde group bond angles with the S1 thiophene rings S1-C5-C7= 121.9(2)° and C6-C5-C7= 127.2(2)° are respectively 2.8° bigger and 2.5° smaller than the corresponding angles in compound **18** between the carboxylic group and the S2 thiophene. The C-C bond length between the aldehyde and the thiophene rings, C5-C7= 1.430 Å, is 0.09 Å smaller than the expected 1.52 Å for a single bond[357]. This could be due to an eventual conjugation with the thiophene ring. The oxygen of the C7=O4 carbonyl is in interaction with the S1 thiophene, S1...O4= 3.071 Å, which is similar to the S...O interactions in structures **15A**, **15B** and **18**. This interaction agrees with the electron delocalisation, which was also the case with the carboxylic group of the compound **18**. The S1...O4 interaction is weaker than the O4...O6 interaction in structure **18**, as the C7=O4 carbonyl bond length is 0.023 Å smaller than the corresponding carbonyl on the carboxylic group in **18**. The resulting torsion angles formed by the atoms S1 and O4, and between the atoms O4 and C6 are S1-C5-C7-O4= -0.2(4)° and O4-C7-C5-C6= 178.9(3)°.

The electron delocalisation created by the aldehyde group may increase the strength of the conjugation between the ether bridge and the adjacent thiophene ring. Indeed, the aromatic C-O bond length is shorter than expected, C6-O2= 1.344 Å. The aliphatic C-O bond lengths in the bridge are C8-O2= 1.445 Å and C10-O8= 1.424 Å. An hydrogen bond appears between O2 and the aldehyde's hydrogen H3, C7-H3...O2= 2.556 Å. This contact bond results in the bond angles O2-C6-C5= 119.7(2)° and O2-C6-C9= 127.9(2)°, which are respectively 1.3° bigger and 0.8° smaller than the corresponding angles in the structure **18**. In the ether bridge, the C-O-C bond angles between the thiophene and the bridge are 5.2° longer than those in the bridge, C6-O2-C8= 118.1(2)° and C10-O3-C10A= 112.9(3)°. This could be due to the short H...H interactions that appear in the ether bridge. For the C-O-C bond between the thiophene and the ether bridge there is only one short contact, C8-H4...H2-C9= 2.153 Å, whereas in the C-O-C bond in the bridge three H...H interactions appear, C10-H6...H7A-C10A= 2.518 Å, C10-H7...H6A-C10A= 2.518 Å, and C10-H6...H6A-C10A= 2.624 Å. The O-

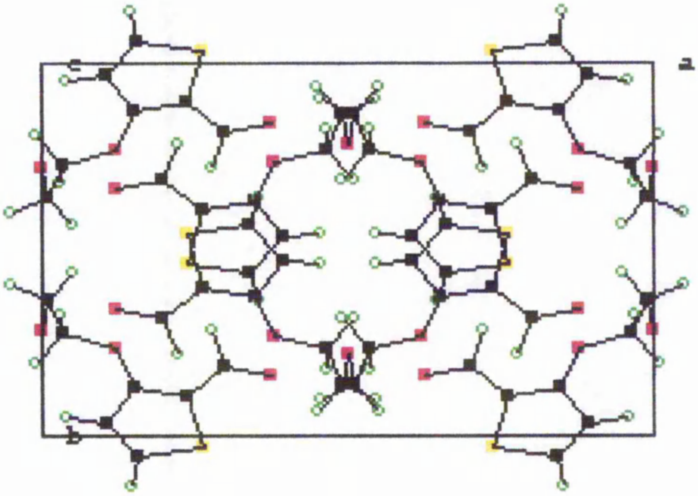
C-C bond angles are shorter than the C-O-C bond angles, O2-C8-C10= 107.1(2)° and O3-C10-C8= 108.2(2)° (C8-C10= 1.496 Å). This could be due to the strong O...H hydrogen bonds are C10-H6...O2= 2.531 Å and C8-H4...O3= 2.455 Å. The resulting O-O torsion angle in the bridge is O2-C8-C10-O3= -74.1(2)°.

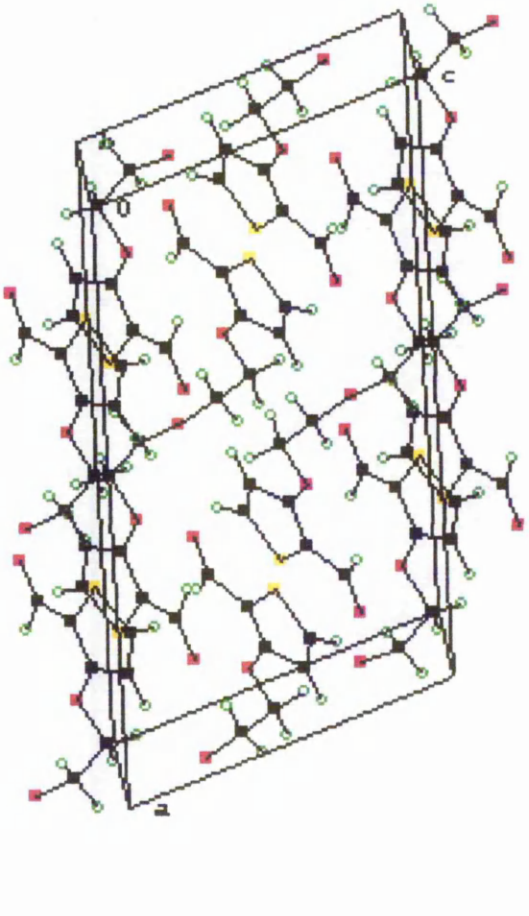
Table 63. Torsion angles (°)

Torsion or Conformation Angles(°)			
Bond	Angle(°)	Bond	Angle(°)
S(1)-C(5)-C(6)-O(2)	177.1(2)	C(5)-C(6)-O(2)-C(8)	170.3(2)
S(1)-C(5)-C(6)-C(9)	-0.8(3)	C(5)-C(6)-C(9)-C(11)	0.6(4)
S(1)-C(5)-C(7)-O(4)	-0.2(4)	C(6)-O(2)-C(8)-C(10)	164.5(2)
S(1)-C(11)-C(9)-C(6)	-0.2(4)	C(6)-C(5)-S(1)-C(11)	0.5(2)
O(2)-C(6)-C(5)-C(7)	-4.1(4)	C(7)-C(5)-S(1)-C(11)	-178.4(2)
O(2)-C(6)-C(9)-C(11)	-177.0(3)	C(7)-C(5)-C(6)-C(9)	178.1(3)
O(2)-C(8)-C(10)-O(3)	-74.1(2)	C(8)-O(2)-C(6)-C(9)	-12.2(4)
O(4)-C(7)-C(5)-C(6)	-178.9(3)	C(8)-C(10)-O(3)-C(10)	169.5(2)
C(5)-S(1)-C(11)-C(9)	-0.2(3)		

Despite the rigidity imposed by the delocalisation and so by the aldehyde groups in the molecule, the flexibility of the molecule in solution is still important. The flexibility and the presence of five oxygen donors in the molecule, especially the oxygen donors of the aldehyde groups, give the ability to this ether thiophene-based chain to react as a ligand and to complex with a metal ion. The resulting complexes should be more stable than those with the ligands **16**, **17** and **18**.

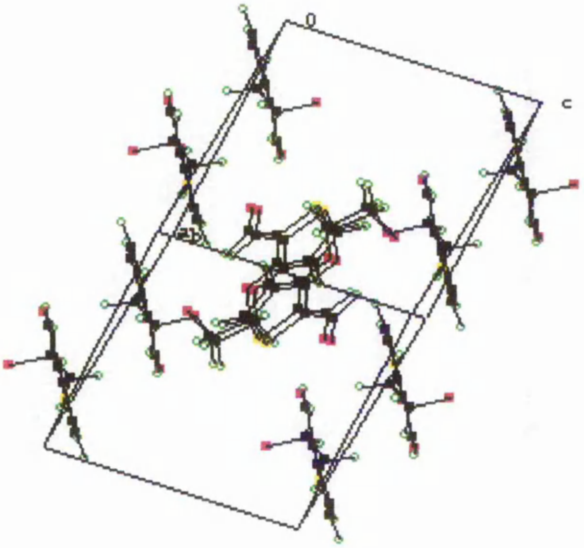
In the crystal, few intermolecular contacts appear. These hydrogen contacts are essentially H...H and O...H intermolecular contacts such as C10-H6(x, y, z)...H6A(-x, y, ½-z)= 2.624 Å, C10-H6(x, y, z)...H7A-C10A(-x, y, ½-z)= 2.518 Å. The unit cell contains two O...H bonds, C11-H1(x, -y, ½+z)...O3(x, y, z)= 2.722 Å and C11-H1(x, -y, ½+z)...O2(x, y, z)= 2.399 Å. Another O...H hydrogen bond appears between the molecules at (x, y, z) and (½-x, ½+y, ½-z), C10-H6(x, y, z)...O4(½-x, ½+y, ½-z)= 2.545 Å, as well as between (x, y, z) and (½-x, ½-y, -z), C8-H5(x, y, z)...O4(x, -y, ½+z)= 2.681 Å, and between (-x, y, ½-z) and (½-x, ½-y, -z), C8-H4(½-x, ½-y, -z)...O4(-x, y, ½-z)= 2.997 Å. Finally, a H...H interaction appears between (½+x, ½+y, +z) and (½-x, ½-y, -z), C9-H2(½+x, ½+y, +z)...H4-C8(½-x, ½-y, -z)= 2.621 Å.

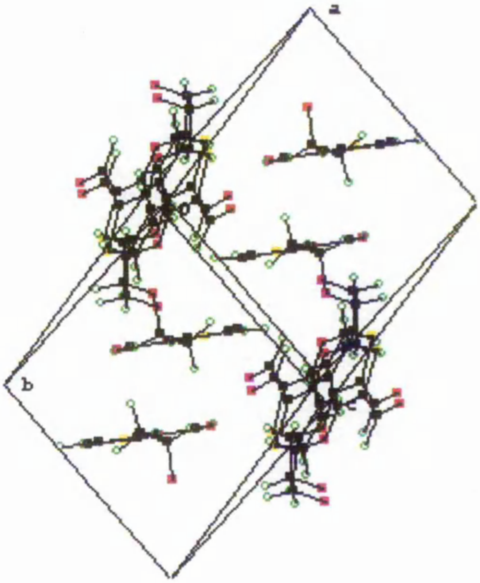




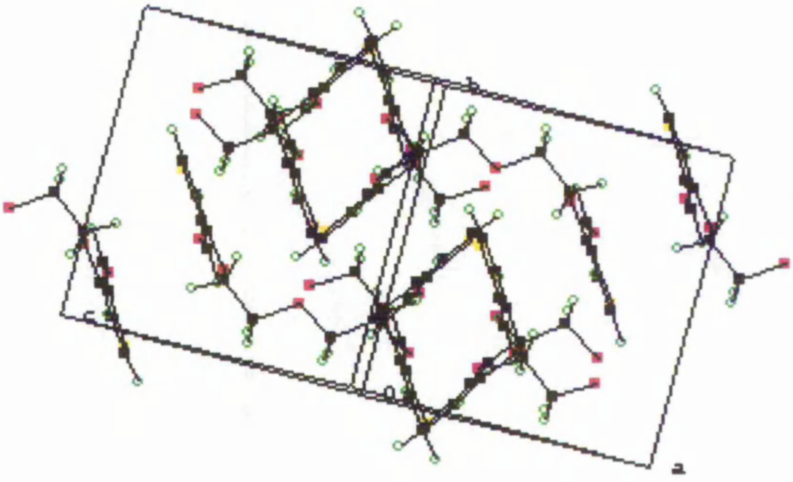
On the view of the unit cell on the right above, it appears that the molecules (x, y, z) and (½-x, ½-y, -z) are arranged along the a axis.

The view of the unit cell (below), on the left, shows that the S1 thiophene ring planes in molecules (x, y, z) and (½+x, ½+y, z) are parallel, those in the molecules (-x, -y, -z) and (½+x, ½+y, z) are also parallel but at 90° to the first two rings. The other view, on the right, shows the same thing for the S1 thiophene ring planes (-x, -y, -z) and (½-x, ½+y, ½-z) which are parallel, and the rings in the molecules (-x, -y, -z) and (½+x, ½-y, ½+z) are also parallel to each other but at 90° to the others.

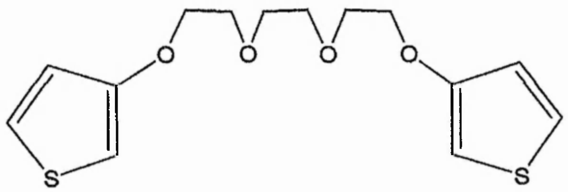




Finally, the following view of the cell shows that the S1 thiophene ring planes (x, y, z) and (-x, y, ½-z) form an angle of 112.9°.



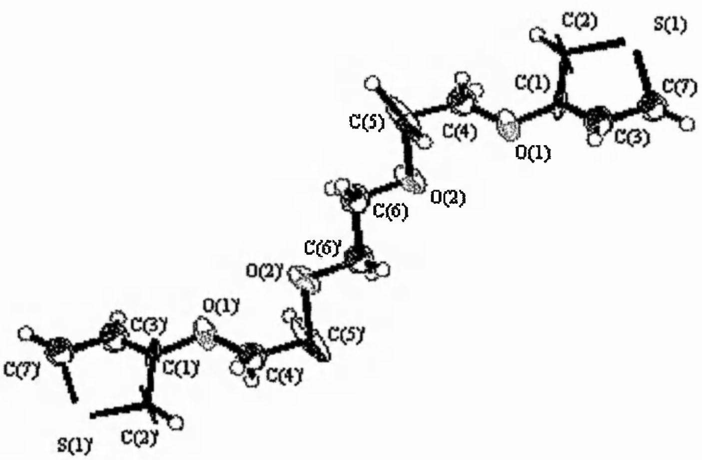
2.5. α,ω-bis-(3-ethyloxythienyl)ethane **20**



2.5.1. Discussion of the structure derived data (tables 9, 18 and 19)

Just half of the molecule appeared in the asymmetric unit (due to the existence of a C2 axis through the bond C6-C6') and after refinement and all atoms had been found, it was expanded to obtain the entire molecule. Two molecules are present in the unit cell and the space group is $P2_1/a$ or a variation of n°14. The structure solution refinement used was the direct methods program SAPI91 instead of SIR97 as for the previous structures. This was used as SIR97 did not produce a clear e-map. The residuals were R= 0.310 and Rw= 0.281, and the goodness of fit indicator was 17.51. These factors are not very good and the structure refinement is therefore much less accurate than for those structures discussed earlier.

The lower accuracy of this structure **20** is reflected in the thermal parameters of the atoms and so affects the bond lengths and bond angles. The C1, C2, C5 and S1 atoms Uij's are particularly affected. The positions and displacement parameters of the atoms in the molecule are best visualised in the "ortep style" drawing[353] below.



2.5.2. Discussion of structural geometry

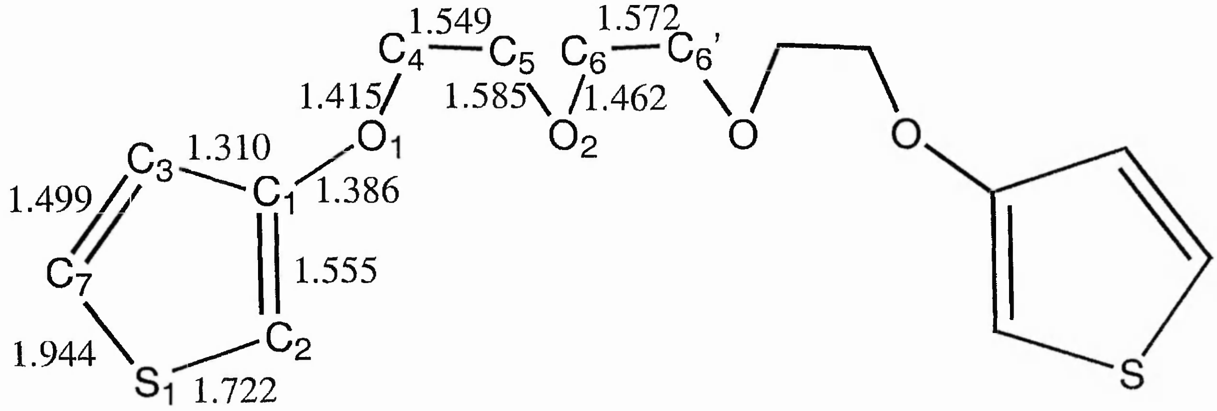
Table 64. Bond lengths (Å)

Bond Lengths(Å)			
Bond	Length(Å)	Bond	Length(Å)
S(1) -C(2)	1.72(3)	C(3) -H(6)	0.939
S(1) -C(7)	1.94(7)	C(4) -C(5)	1.55(3)
O(1) -C(1)	1.39(3)	C(4) -H(2)	0.84
O(1) -C(4)	1.42(4)	C(4) -H(3)	1.101
O(2) -C(5)	1.59(5)	C(5) -H(1)	0.935
O(2) -C(6)	1.46(3)	C(5) -H(4)	1.205
C(1) -C(2)	1.55(4)	C(6) -C(6)'*	1.57(5)
C(1) -C(3)	1.31(4)	C(6) -H(8)	0.961
C(2) -H(5)	0.959	C(7) -H(7)	0.921
C(3) -C(7)	1.50(4)		

* (-x, -y, -z)

** Note the hydrogen bond lengths are to three decimal places with terminal zero's omitted and have no esd's as the hydrogen positions were not refined.

For ease of description the bond lengths (to 3 decimal places) are shown on a schematic drawing below.



The molecule has a C2 axis through the bond C6-C6' [C6' is at position –x, -y, -z compared to C6], so the halves of the compound have the same bond lengths and bond angles.

The molecule has two distinct planes formed by the thiophene rings. Each contains half the molecule except for atoms O2 and C6, which have the maximum deviations from the least squares plane defined by all the non-hydrogen atoms of the thiophenes with 1.1176 Å and 1.0270 Å. So, the geometry of the compound shows two approximately planar regions joined by the ether bridge. The two planes formed by the thiophene rings are parallel. Deviations from the least squares planes of these regions are given below.

Table 38. Least-Squares Plane

Atoms Defining Plane	Distance
S(1)	-.0129(109)
C(2)	.0923(4460
C(1)	.0370(328)
C(3)	-.2346(524)
C(7)	.2231(473)

Additional Atoms	Distance
O(1)	.0748
C(4)	.1004
C(5)	-.0873
O(2)	1.1176
C(6)	1.0270

Mean deviation from plane is .1200 Ångstroms

Chi-squared: 50.8

In the S1 thiophene ring, the distortions of the bond lengths and bond angles are due to the poor quality of the crystal data and the large displacement parameters of the thiophene atoms. The bond lengths in the thiophene ring are S1-C2= 1.722 Å, S1-C7= 1.944 Å, C1-C2= 1.555 Å, C3-C7= 1.499 Å and C1-C3= 1.310 Å. The thiophene ring bond angles are also strongly affected, C2-S1-C7= 97(2)°, S1-C2-C1= 100(2)°, S1-C7-C3= 100(3)°, C1-C3-C7= 109(3)° and C2-C1-C3= 124(3)°.

The bond angles between the thiophene and the ether bridge are affected as well, O1-C1-C2= 116(3)° and O1-C1-C3= 119(3)°. Also, the aromatic C-O bond length C1-O1= 1.386 Å is longer than expected and longer than the corresponding aromatic C-O bond length in the structures **16, 17** and **18**. However, the esd on this bond length is quite considerable. In the bridge, the resulting C-O-C and O-C-C bond angles with the thiophene, O1-C4-C5= 123(3)°, C1-O1-C4= 121(2)°, are larger than the corresponding angles in the bridge, O2-C5-C4= 97(3)°, O2-C6-C6'= 103(3)°, C5-O2-C6= 101(2)°. The aliphatic C-O and C-C bond lengths are affected by the large displacement parameters of C5, C4-O1= 1.415 Å, C6-O2= 1.462 Å, C5-O2= 1.585 Å, C4-C5= 1.549 Å and C6-C6'= 1.572 Å. The O-C-C-O torsion angles are O1-C4-C5-O2= -58(3)° and O2-C6-C6'-O2'= -180°. Some H...H and O...H intramolecular hydrogen contacts appear in the bridge and between the bridge and the thiophene rings. The O...H bonds are C3-H6...O1= 2.592 Å, C5-H1...O1= 2.131 Å, C4-H2...O2= 2.825 Å, C6-H10...O2'= 2.741 Å and C6-H8...O2'= 2.431 Å. One H...H close approach occurs between the thiophene ring and the ether bridge, C2-H5...H2-C4= 2.075 Å. All of those intramolecular contacts may be fictitious, due to the bad quality of the structure.

Table 66. Bond angles (°)

Bond Angles(°)			
Bond	Angle(°)	Bond	Angle(°)
C(2) -S(1) -C(7)	97(2)	C(5) -C(4) -H(2)	128.66
C(1) -O(1) -C(4)	121(2)	C(5) -C(4) -H(3)	87.44
C(5) -O(2) -C(6)	101(2)	H(2) -C(4) -H(3)	125.94
O(1) -C(1) -C(2)	116(3)	O(2) -C(5) -C(4)	97(3)
O(1) -C(1) -C(3)	119(3)	O(2) -C(5) -H(1)	58.72
C(2) -C(1) -C(3)	124(3)	O(2) -C(5) -H(4)	145.42
S(1) -C(2) -C(1)	100(2)	C(4) -C(5) -H(1)	77.66
S(1) -C(2) -H(5)	129.02	C(4) -C(5) -H(4)	116.61
C(1) -C(2) -H(5)	130.96	H(1) -C(5) -H(4)	132.31
C(1) -C(3) -C(7)	109(3)	O(2) -C(6) -C(6)'	103(3)
C(1) -C(3) -H(6)	127.78	O(2) -C(6) -H(8)	109.32
C(7) -C(3) -H(6)	123.19	C(6)' -C(6) -H(8)	94.27
O(1) -C(4) -C(5)	123(3)	S(1) -C(7) -C(3)	100(3)
O(1) -C(4) -H(2)	101.67	S(1) -C(7) -H(7)	123.2
O(1) -C(4) -H(3)	82.3	C(3) -C(7) -H(7)	135.66

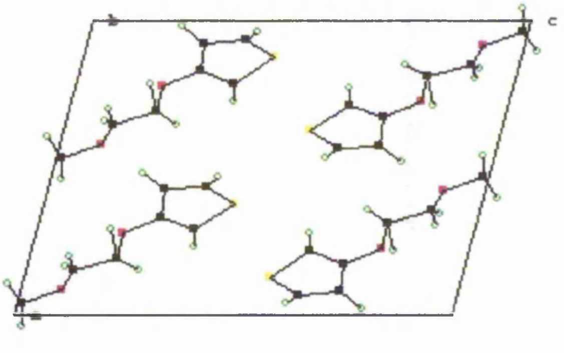
** Note the bond angles including hydrogen atoms are to two decimal places with terminal zeros omitted and have no esd's as the hydrogen atoms positions were not refined.

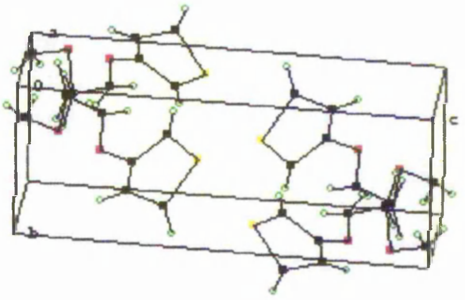
The distances between the sulfurs S1 and S1' and especially between the carbons C2 and C2' are 16.581 Å and 13.537 Å. The carbons C2 and C2', due to the symmetry of the molecule, have the same steric effect. So, the macrocyclisation reaction might first occur on either C2 or C2' without any distinction. Then, because the free lone pairs of O1' or O1 are pointing at C2 or C2', there might be an interaction between NCH_2^+ and O1' or O1 that would facilitate the macrocyclisation on C2' or C2 instead of a polymerisation (scheme 5, p156).

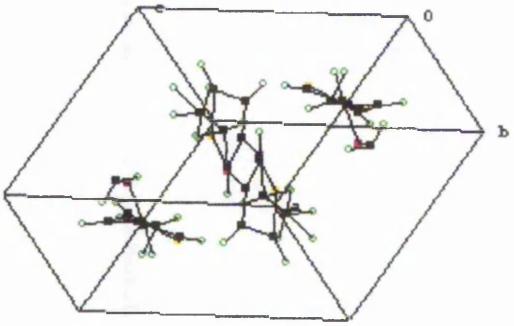
This thiophene-based ether chain **20**, which is widely flexible, contains four oxygen donors on the ether bridge. This flexibility and the presence of four donor atoms should allow this ligand to complex with a metal ion.

A few H...H interactions appear between molecules in the unit cell, C10-H8(x, y, z)...H8-C10(½+x, ½-y, z)= 2.418 Å, C3-H6(x, y, z)...H4-C5(½+x, ½-y, z)= 2.395 Å and C5-H1(x, y, z)...H8-C10(½+x, ½-y, z)= 2.657 Å. An S...H and an O...H intermolecular bond also appear, C2-H5(x, y, z)...S1(½-x, ½+y, -z)= 3.034 Å and C10-H8(½+x, ½-y, z)...O1(x, y, z)= 3.013 Å. Again, these intermolecular contacts could be fictitious due to the poor quality of the data.

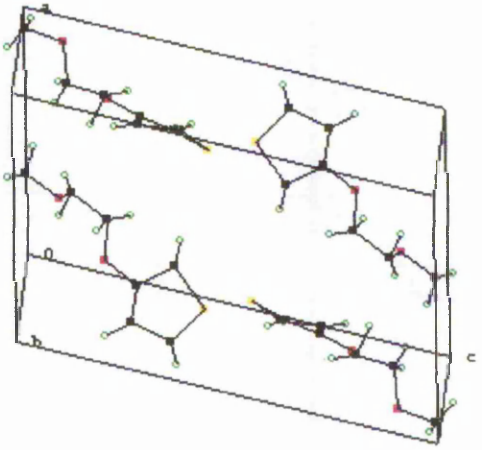
The different views of the unit cell below, shows that the molecules (x, y, z) and (½-x, ½+y, -z) are arranged along the c axis, whereas the molecules (x, y, z) and (½+x, ½-y, z) are arranged along the a axis, and also the molecules (x, y, z) and (-x, -y, -z) are arranged in the ac plane.

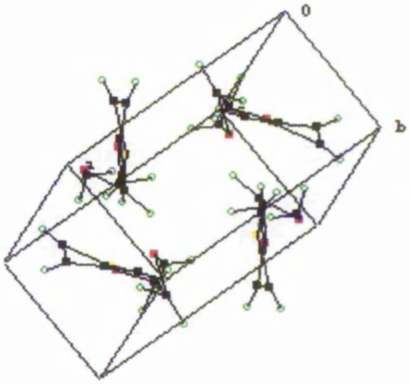






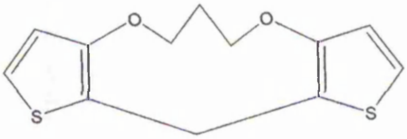
The following views of the cell show that the S1 thiophene ring planes (x, y, z) and (-x, -y, -z) are parallel but directed in the opposite way in the ac plane. The views also show that, the thiophene rings planes (x, y, z) and (½+x, ½-y, z) are orthogonal along the a axis. The thiophene rings planes (½-x, ½+y, -z) are also orthogonal to (x, y, z) but directed in the opposite way along the c axis.





3. Thiophene-based Macrocycles

3.1. Two donor atoms thiophene-based macrocycle: 2,6-dioxa-10,14-dithia-tricyclo[11.3.0.0]-hexadeca-1,15,7,8-tetraene **21**



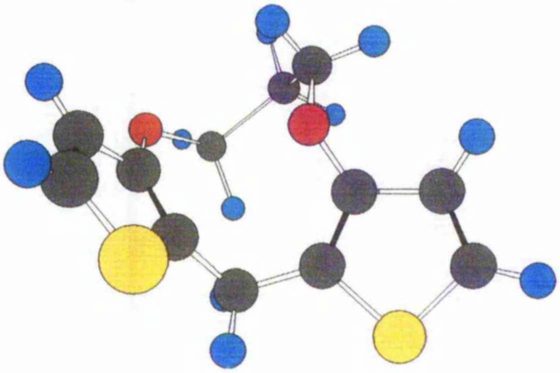
3.1.1. X-ray Crystallography (table 20)

The crystals were decomposed by the X-rays and no useful X-ray crystallography data were obtained. The structure data obtained couldn't be refined. However, important information obtained included the crystal system (monoclinic), the lattice type (C-centered), the unit cell parameters (a= 47.3(2) Å, b= 8.8(2) Å, c= 8.7(3) Å, β= 91.9135 Å, V= 3637(129) Å^3), the Z value (8) and the space group (C2/c or no.15). This information could be used to model the macrocycle in the unit cell.

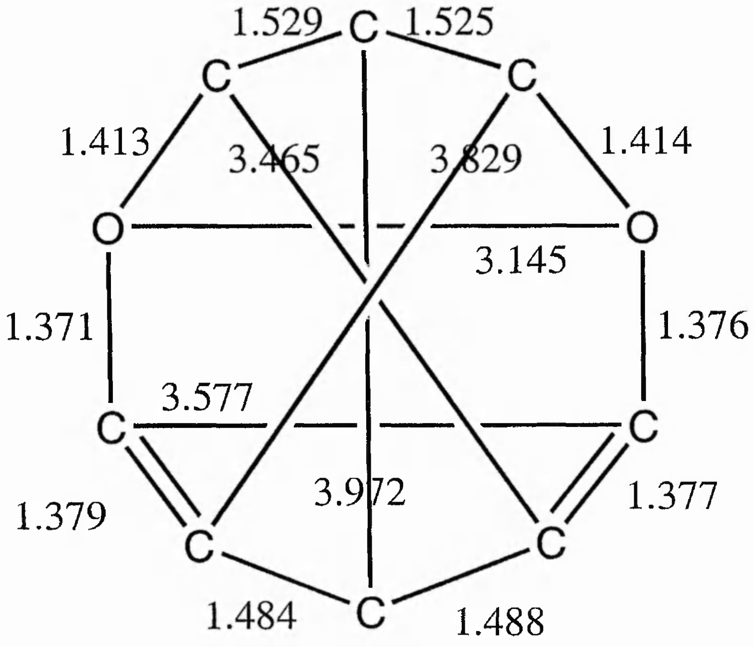
The reason for the crystal decomposition could be due to the C-C-C bond between the thiophene rings which could be too short and strained and therefore too fragile to resist the X-rays. Also, the lattice parameter a= 47.3(2) Å is very long and is close to the limit of measurement of the diffractometer which is situated between 45 and 50 Å.

3.1.2. Molecular modelling

This macrocycle **21** was modelled by minimization of its energy via the programs MM2 (steric energy) then MOPAC (heat of conformation).

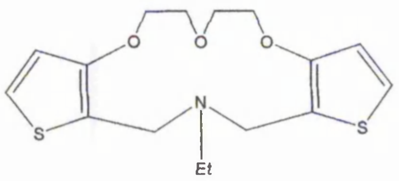


The distances between the atom donors and the resulting cavity are shown schematically below.



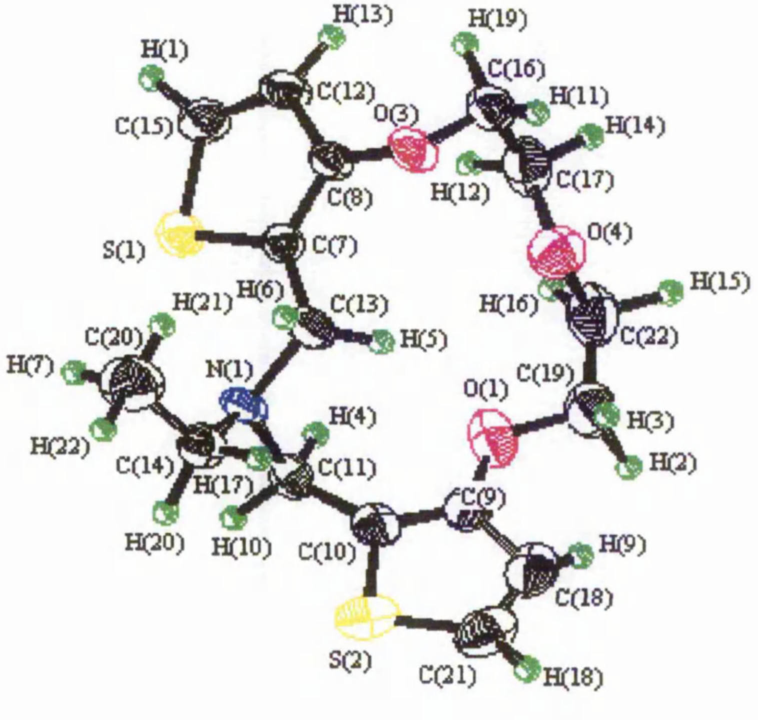
The cavity contains only two oxygen donor atoms. The distances between the atoms of the cavity are fairly symmetric but are not planar. The size of the cavity is too small to include a metal ion such as Nickel(II). Also, the C-C-C bond between the thiophene rings is too short and too rigid in solution for an eventual complexation.

3.2 Four donor atoms thiophene-based macrocycle: 15-ethyl-2,5,8-trioxa-12,18-dithia-15-azatricyclo[15.3.0.0]-tricosa-1(18),9(13),10,19-tetraene **10a**



3.2.1. X-ray Crystallography

3.2.1.1. Discussion of the structure derived data (tables 21 to 23)



The greatest displacement occurs at the extremities of the molecule. In the diagram, the distance between C15 and C21 is 8.832 Å and C20 and O4 is 6.924 Å. The two thiophene rings have greater displacements in their outermost atoms, but this is largest in the S2 thiophene ring. Greater displacement is expected for atoms at the outer regions of the molecule. On the other hand, the more tightly bound (i.e. attached to more atoms) an atom is, the lower its displacement is expected to be. This is shown in the nitrogen atoms N1 (bound to three carbons), in the carbons C7 and C10 (bound to three carbons) and in the carbons C8 and C9 (each bound to one oxygen and two carbons) having the smallest displacement in the molecule.

3.2.1.2. Discussion of the structural geometry

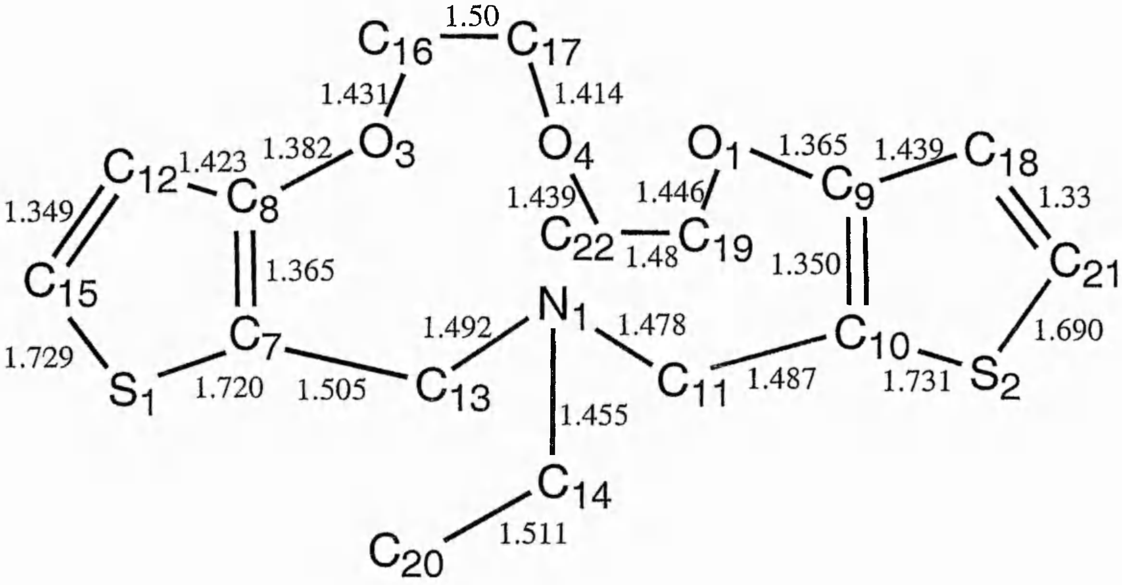
Table 67. Bond Lengths(Å)

Bond Lengths(Å)			
Bond	Length(Å)	Bond	Length(Å)
S1 - C7	1.720(6)	C13 - H5	1.029
S1 - C15	1.729(6)	C13 - H6	0.639
S2 - C10	1.731(6)	C14 - C20	1.511(9)
S2 - C21	1.690(8)	C14 - H17	0.976
O1 - C9	1.365(8)	C14 - H20	1.196
O1 - C19	1.446(7)	C15 - H1	1.107
O3 - C8	1.382(6)	C16 - C17	1.50(1)
O3 - C16	1.432(7)	C16 - H11	1.016
O4 - C17	1.414(8)	C16 - H19	1.095
O4 - C22	1.439(8)	C17 - H12	1.147
N1 - C11	1.478(7)	C17 - H14	1.151
N1 - C13	1.492(7)	C18 - C21	1.33(1)
N1 - C14	1.455(7)	C18 - H9	0.786
C7 - C8	1.366(7)	C19 - C22	1.48(1)
C7 - C13	1.505(8)	C19 - H2	1.248
C8 - C12	1.423(8)	C19 - H3	0.962
C9 - C10	1.350(8)	C20 - H7	0.96
C9 - C18	1.44(1)	C20 - H21	0.94
C10 - C11	1.487(8)	C20 - H22	1.165
C11 - H4	1.051	C21 - H18	1.156
C11 - H10	1.139	C22 - H15	1.152
C12 - C15	1.349(8)	C22 - H16	1.046
C12 - H13	1.082		

** Note the hydrogen bond lengths are to two decimal places with terminal zero's omitted and have no esd's as the hydrogen positions were not refined.

It would be expected that the halves of the macrocycle (the molecule is chemically mirrored through O4, N1 (C14 and C20)) would have the same bond lengths. This is not the case. In the crystal, the macrocycle is not mirrored and the two halves of the molecules have differing geometries reflected in the bond lengths.

For ease of description the bond lengths (to 3 decimal places) are shown on a schematic drawing below.



In the S1 thiophene, the bond lengths C8-C12= 1.423 Å, S1-C15= 1.729 Å, S1-C7= 1.720 Å, C12-C15= 1.349 Å and C7-C8= 1.365 Å are close to the unsubstituted thiophene bond lengths[354]. In the S2 thiophene the S2-C10= 1.731 Å and S2-C21= 1.690 Å bonds are more distorted from ideal compared to the S1 thiophene ring. Also, the C9-C18= 1.439 Å single bond length is slightly longer than in unsubstituted thiophene. The C-C double bonds are fairly symmetric C10-C9= 1.350 Å and C18-C21= 1.33 Å. This could indicate that the S1 thiophene ring has a greater aromatic character than the other thiophene.

The bond lengths of the other C-C bonds vary in the range 1.48-1.51 Å. The aromatic C-O, C8-O3= 1.382 Å and C9-O1= 1.365 Å, are 0.032 to 0.074 Å shorter than the aliphatic C-O bonds. The C-N bonds vary from 1.455 to 1.492 Å. The C7-C13 (1.505 Å) and more significantly C10-C11 (1.487 Å) are shorter than the 1.52 Å[356], which could be expected. This may indicate a π delocalisation due to the neighbouring thiophene rings.

Table 68. Bond Angles(°)

Bond Angles(°)			
Bond	Angle(°)	Bond	Angle(°)
C7 - S1 - C15	92.1(3)	C8 - C12 - C15	111.7(5)
C10 - S2 - C21	93.1(4)	C8 - C12 - H13	116.22

C9 - O1 - C19	119.1(6)	C15 - C12 - H13	124.9
C8 - O3 - C16	115.0(5)	N1 - C13 - C7	111.1(5)
C17 - O4 - C22	113.3(6)	N1 - C13 - H5	113.99
C11 - N1 - C13	111.0(5)	N1 - C13 - H6	89.31
C11 - N1 - C14	111.6(5)	C7 - C13 - H5	107.84
C13 - N1 - C14	113.7(5)	C7 - C13 - H6	94.73
S1 - C7 - C8	110.1(4)	H5 - C13 - H6	137.35
S1 - C7 - C13	123.7(4)	N1 - C14 - C20	113.8(6)
C8 - C7 - C13	126.1(5)	N1 - C14 - H17	101.12
O3 - C8 - C7	120.1(5)	N1 - C14 - H20	98.27
O3 - C8 - C12	125.5(5)	C20 - C14 - H17	112.61
C7 - C8 - C12	114.2(5)	C20 - C14 - H20	113.8
O1 - C9 - C10	119.3(6)	H17 - C14 - H20	115.67
O1 - C9 - C18	126.8(6)	S1 - C15 - C12	111.9(5)
C10 - C9 - C18	113.8(7)	S1 - C15 - H1	121.04
S2 - C10 - C9	108.9(5)	C12 - C15 - H1	126.57
S2 - C10 - C11	122.8(5)	O3 - C16 - C17	112.1(5)
C9 - C10 - C11	128.2(6)	O3 - C16 - H11	95.61
N1 - C11 - C10	118.4(5)	O3 - C16 - H19	108
N1 - C11 - H4	99.46	C17 - C16 - H11	108.67
N1 - C11 - H10	108.81	C17 - C16 - H19	105.23
C10 - C11 - H4	106.73	H11 - C16 - H19	126.87
C10 - C11 - H10	119.07	O4 - C17 - C16	108.5(6)
H4 - C11 - H10	100.78	O4 - C17 - H12	119.94
O4 - C17 - H14	107.28	C19 - C22 - H16	127.98
C16 - C17 - H12	104.75	H15 - C22 - H16	107.03
C16 - C17 - H14	115.44	C14 - C20 - H21	100.88
H12 - C17 - H14	101.26	C14 - C20 - H22	102.9
C9 - C18 - C21	112.1(7)	H7 - C20 - H21	100.09
C9 - C18 - H9	100.82	H7 - C20 - H22	102.3
C21 - C18 - H9	145.83	H21 - C20 - H22	137.63
O1 - C19 - C22	107.8(6)	S2 - C21 - C18	112.1(6)
O1 - C19 - H2	104.82	S2 - C21 - H18	125.75
O1 - C19 - H3	98.8	C18 - C21 - H18	117.61
C22 - C19 - H2	112.48	O4 - C22 - C19	107.9(6)
C22 - C19 - H3	116.36	O4 - C22 - H15	105.33
H2 - C19 - H3	114.68	O4 - C22 - H16	95.11
C14 - C20 - H7	112.73	C19 - C22 - H15	110.49

** Note the bond angles including hydrogen atoms are to one decimal places with terminal zeros omitted and have no esd's as the hydrogen atom positions were not refined.

The bond angles in the thiophene rings are similarly distorted from ideal. The S1 thiophene ring angles are closest to those in unsubstituted thiophene[354]: C7-S1-C15= 92.1(3)°, C8-C12-C15= 111.7(5)°, S1-C7-C8= 110.1(4)°, C7-C8-C12= 114.2(5)° and S1-C15-C12= 111.9(5)°. The C-S-C bond angle in the S2 thiophene (C10-S2-C21= 93.1(4)°) is slightly larger than in the S1 thiophene ring and in unsubstituted thiophene. The unsubstituted S2-C21-C18 angle is 3.2° larger than the substituted S2-C10-C9. The C10-C9-C18= 113.8(7)° bond angle substituted with the ether bridge on C9 and amine bridge on C10 is 1.7° larger than the C9-C18-C21 unsubstituted angle. This may be due to the oxygen O1 directly bound to C9, and the conjugation with the adjacent thiophene ring. It has the same effect on C8 bound to O3. The ether bridge has four large angles (>109.47° tetrahedral angle) C8-O3-C16= 115.0(5)°, O3-C16-C17= 112.1(5)°, C17-O4-C22= 113.3(6)° and C9-O1-C19= 119.1(6)°, and may contain six C-H...O hydrogen close contacts within he bridge, C22-H16...O1= 2.719 Å, C18-H9...O1= 2.429 Å, C12-H13...O3= 2.769 Å, C17-H12...O3= 2.719 Å, C16-H11...O4= 2.461 Å and C19-H3...O4= 2.501 Å. The bridge may also contain three H...H hydrogen interactions, H3...H9= 2.112 Å, H14...H16= 2.362 Å, H12...H16= 2.185 Å. These close contacts are due to the strained geometry of the bridge. The macrocycle contains two other C-H...O hydrogen bonds, C11-H4...O1= 2.503 Å and C11-H5...O1= 2.555 Å. In the amine bridge the C11-N1-C13= 111.0(5)°, C11-N1-C14= 111.6(5)° and C13-N1-C14= 113.7(5)° are arranged for a trigonal conformation of the nitrogen. Around the nitrogen are three other large angles, N1-C11-C10= 118.4(5)°, N1-C13-C7= 111.1(5)° and N1-C14-C20= 113.8(6)° which are larger than the 109.47° tetrahedral angle. There are two C-H...S and two C-H...N hydrogen bonds in the bridge, C14-H17...S2= 2.926 Å, C13-H6...S1= 2.924 Å, C20-H21...N1= 2.426 Å and C20-H7...N1= 2.783 Å. These close contacts may also be due to the geometry of the bridge and the interactions between sulphur and nitrogen. This S...N interaction could be due to a similar effect to the S...O interaction in the compound **18** and **19**.

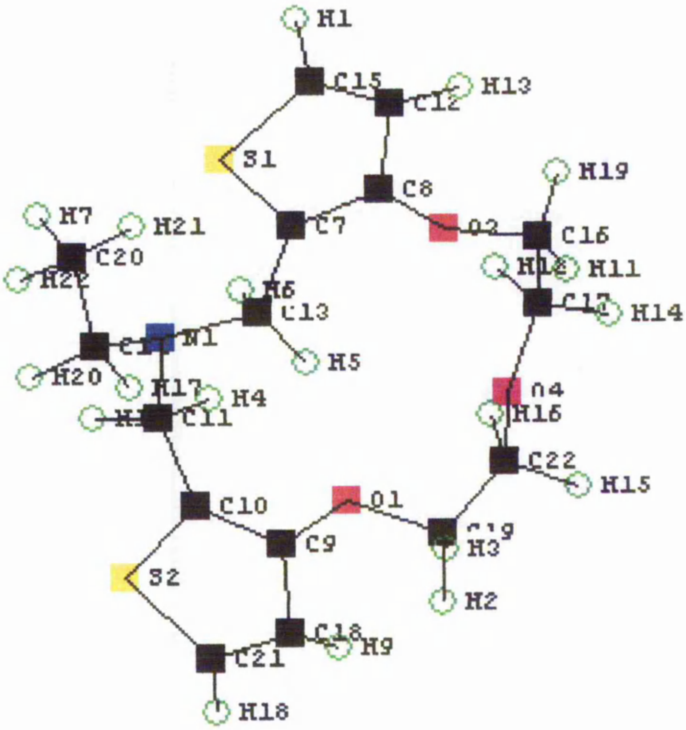


Table 69. Least-Squares Planes

Plane number 1

Atoms defining plane	Distance
S1	0.001(2)
C7	-0.002(5)
C8	-0.003(6)
C12	0.012(7)
C15	-0.015(7)

Additional Atoms	Distance
N1	-0.011
C13	0.089
O3	0.094

Plane number 2

Atoms defining plane	Distance
S2	-0.002(2)
C10	0.010(5)

C9	-0.004(6)
C18	-0.010(7)
C21	0.020(7)

Additional Atoms	Distance
C22	-0.643
C19	-0.243
O1	0.008
C11	0.044
N1	-1.224

Summary

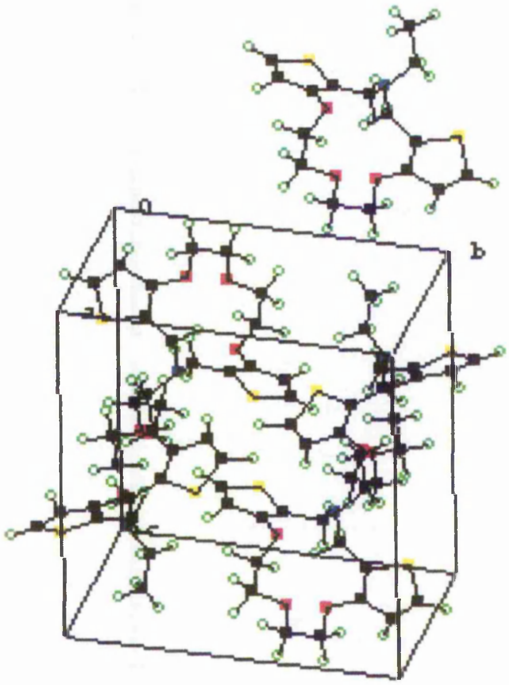
plane	mean deviation	χ^2
1	0.0067	7.9
2	0.0093	15.2

Dihedral angles between planes= 143.25°

The two thiophene rings do not lie in the same plane. O3, C13 and N1 lie in the plane of the S1 thiophene ring, while C22, C19, O1 and C11 lie in the S2 thiophene ring plane. The angle between the plane of each thiophene ring is 143.25°. The macrocycle has two approximately planar regions, so the cavity is best viewed looking approximately in the plane of the thiophene rings.

The oxygen atoms bound to the thiophenes are completely in the thiophene ring plane in each case. For the plane including the S2 thiophene ring the three methylene carbons C19, C22 and C10 are almost in the plane (deviation= 0.04-0.7 Å) with the nitrogen N1 considerably out of the plane (deviation= 1.224 Å). The plane containing the S1 thiophene ring has only the C13 methylene carbon (between the thiophene ring and N1) nearly planar (deviation= 0.089 Å) and the N1 atom is in the plane (deviation= 0.011 Å). The distance between S2 and N1= 3.612 Å (Sum of van der Waals radii= 3.45 Å[333]). The distance between S1 and N1= 3.004 Å. This is significantly lower than the sum of their van der Waals radii 3.45 Å (contact radii= 3.35 Å). In appropriately 2-substituted thiophenes the short S...N contact is a common feature[358], which varies between 2.927 Å and 3.094 Å.

There are several H...H interactions between the molecules in the crystal. As can be seen in the diagram each macrocycle has close contacts with two others, H9(x, y, z)...H18(-x, -y, -z)= 2.7172 Å and H18(x, y, z)...H9(-x, -y, -z)= 2.7172 Å, H17(x, y, z)...H13(-x, ½+y, ½-z)= 2.3677 Å and H17(x, y, z)...H19(-x, ½+y, ½-z)= 2.1989 Å and H22(-x, -y, -z)...H15(-x, ½+y, ½-z)= 2.1736 Å (Sum of van der Waals radii= 2.40 Å).



The macrocycle contains six potential donor atoms (2S, 1N and 3O) and the orientation of their lone pairs of electrons is important not only for donation in possible metal complexes but also for possible hydrogen bonds, dipole interactions etc, which influence the observed geometry. The nitrogen and the three oxygens, which form the donor atoms of the cavity, lie in the same plane.

Table 70. Least-Squares Planes

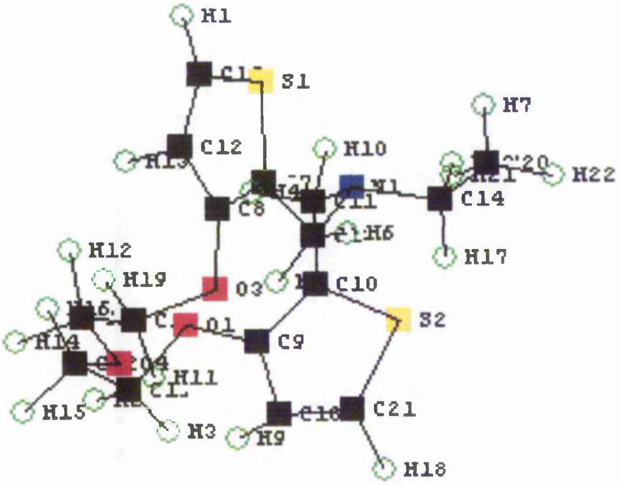
Atoms Defining Plane	Distance
O1	-.0377(49)
O3	-.0221(40)
O4	.0419(47)
N1	.0211(48)

Additional Atoms	Distance
C7	.9128
C8	1.0122
C9	-.9504
C10	-.7941
C11	.2875
C13	-.2519
C16	.3781
C17	.9942
C19	-.3277
C22	.5347

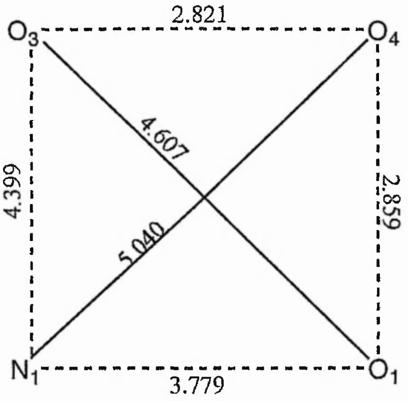
Mean deviation from plane is .0307 Ångstroms

Chi-squared: 190.1

The lone pairs of the oxygens are directed to the macrocyclic cavity. This appears for the oxygen O1 which has two C-H...O hydrogen bonds within the macrocyclic cavity, C11-H4...O1= 2.503 Å and C13-H5...O1= 2.555 Å. On the contrary, the nitrogen lone pair is directed away from the cavity, which is shown by the S...N interaction.



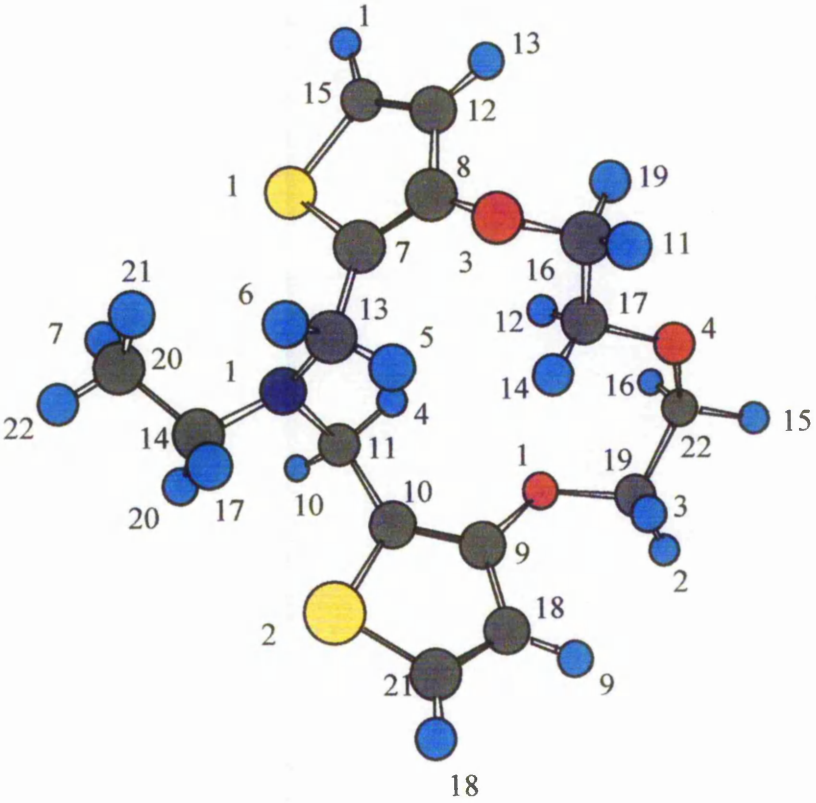
The cavity is drawn schematically below.



The cavity size is quite close to the size of cavities in the macrocycles previously studied by this research group[1,6] and the similar macrocycles found in the literature[95-98] which are close to ideal for complexation to nickel(II). It appears, that the oxygens O1 and O4 are close together (2.859 Å) and also O3 and O4 (2.821 Å) (Sum of van der Waals radii 2.80 Å). This will certainly change when the macrocycle complexes with a metal. The planarity of the donor atoms could presume a square planar arrangement of those atoms around the metal ion.

Before the X-ray crystal structure was obtained, molecular modelling of this macrocycle was performed to evaluate the size of the cavity and so to evaluate the ability of the macrocycle to complex with a transition metal ion such as Cu(II). This molecular modelling aimed to facilitate macrocyclic molecular design.

3.2.2. Molecular Modelling



24 iterations were carried out find the energy of the system, computed at the Hartree-Fock level, which is about $-7.3770294169691483*10^{-15}$ Joules or -1692.076945 Hartrees.

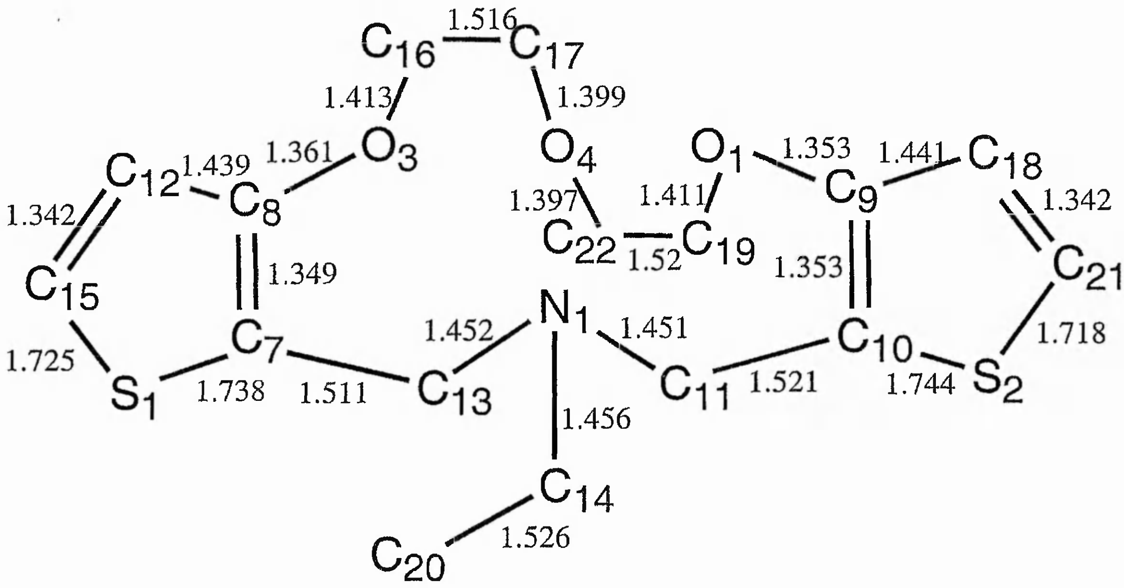
Table 71. Bond Lengths(Å) from molecular modelling

Bond Lengths(Å)		
Bond	Actual Length(Å) (modelled)	Optimal Length(Å) (literature)
C(9) -C(18)	1.441	1.503
C(9) -O(1)	1.353	1.355
C(9) -C(10)	1.353	1.337
C(9),H(3)	2.552	
C(18) -C(21)	1.342	1.337
C(18) -H(9)	1.072	1.1

O(1) -C(19)	1.411	1.402
C(10) -C(11)	1.521	1.497
C(10) -S(2)	1.744	1.856
C(21) -S(2)	1.718	1.856
C(21) -H(18)	1.071	1.1
C(11) -N(1)	1.451	1.438
C(11) -H(10)	1.085	1.113
C(11) -H(4)	1.082	1.113
C(11),H(20)	2.5	
N(1) -C(13)	1.452	1.438
N(1) -C(14)	1.456	1.438
N(1),S(1)	3.088	
C(13) -C(7)	1.511	1.497
C(13) -H(6)	1.083	1.113
C(13) -H(5)	1.086	1.113
C(14) -C(20)	1.526	1.523
C(14),H(6)	2.453	
C(14) -H(20)	1.084	1.113
C(14) -H(17)	1.09	1.113
C(7) -S(1)	1.738	1.856
C(7) -C(8)	1.349	1.337
C(20) -H(22)	1.086	1.113
C(20) -H(7)	1.084	1.113
C(20) -H(21)	1.085	1.113
S(1) -C(15)	1.725	1.856
C(19) -C(22)	1.52	1.505
C(19) -H(2)	1.086	1.111
C(19) -H(3)	1.084	1.111
C(22) -O(4)	1.397	1.402
C(22) -H(15)	1.083	1.111
C(22) -H(16)	1.088	1.111
C(22),H(12)	2.53	
O(4) -C(17)	1.399	1.402
C(17) -C(16)	1.516	1.505
C(17) -H(12)	1.083	1.111
C(17) -H(14)	1.083	1.111
C(16) -O(3)	1.413	1.402
C(16) -H(11)	1.08	1.111
C(16) -H(19)	1.085	1.111
O(3) -C(8)	1.361	1.355

C(8) -C(12)	1.439	1.503
C(12) -C(15)	1.342	1.337
C(12) -H(13)	1.073	1.1
C(15) -H(1)	1.071	1.1

The macrocycle seems to be in a higher energy conformation when modelled than when in the crystalline state. For ease, the bond lengths from the molecular modelling are shown below (compare page 193 for the crystallographic bond lengths).



The least differences between the experimental crystal structure and the modeled thiophene-based macrocycle appear in the thiophenes, especially in the S1 thiophene ring, where the bond lengths vary from –1.19% to +1.05% compared to the X-ray structure. In the S2 thiophene ring the bond lengths are a little longer (+0.07 to +1.66%) but the distortions are similar. In the macrocyclic cavity, the modelled bond lengths seem to be more symmetric.

The C-C bond lengths vary in the range 1.511-1.521 Å, close to the 1.52 Å[358] expected. In the ether bridge, the C-C bonds are +1.07% and +2.70% larger than in the real structure. In the amine bridge, the C-C bonds are closer to the experimental, except for C10-C11 which is +2.29% larger. The C-N bonds vary from 1.451 Å to 1.456 Å, respectively 0.04 Å and 0.027 Å smaller than in the X-ray structure. The aromatic C-O distances vary between 1.353 and 1.361 Å, which are respectively 0.021 Å and 0.012 Å shorter than the corresponding bonds from the crystal structure and are shorter than the aliphatic C-O bonds (1.397-1.413 Å, -1.07% to -3.01% shorter than the experimental).

Table 72. Bond Angles(°)

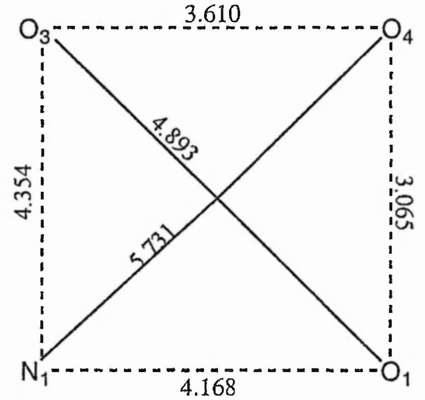
Bond Angles(°)		
Bond	Actual Angle(°) (modelled)	Optimal Angle(°) (literature)
C(18)-C(9)-O(1)	124.041	124.3
C(18)-C(9)-C(10)	114.032	120
O(1)-C(9)-C(10)	121.886	124.3
C(9)-C(18)-C(21)	112.049	120
C(9)-C(18)-H(9)	124.289	120
H(9)-C(18)-C(21)	123.661	120
C(9)-O(1)-C(19)	119.421	110.8
C(9)-C(10)-C(11)	127.212	121.4
C(9)-C(10)-S(2)	109.593	119
C(11)-C(10)-S(2)	122.789	120
C(18)-C(21)-S(2)	112.054	119
C(18)-C(21)-H(18)	127.324	120
H(18)-C(21)-S(2)	120.619	120
C(10)-C(11)-N(1)	118.91	110.74
C(10)-C(11)-H(1-)	108.531	109.41
C(10)-C(11)-H(4)	106.971	109.41
N(1)-C(11)-H(4)	108.166	108.8
H(10)-C(11)-N(1)	107.3	108.8
H(10)-C(11)-H(4)	106.316	109.4
C(10)-S(2)-C(21)	92.268	98.5
C(11)-N(1)-C(13)	115.408	107.7
C(11)-N(1)-C(14)	116.62	107.7
C(13)-N(1)-C(14)	115.504	107.7
N(1)-C(13)-C(7)	112.742	110.74
N(1)-C(13)-H(6)	108.383	108.8
N(1)-C(13)-H(5)	112.252	108.8
C(7)-C(13)-H(5)	109.008	109.41
H(6)-C(13)-C(7)	108.216	109.41
H(6)-C(13)-H(5)	105.936	109.4
N(1)-C(14)-C(20)	112.586	109.5
N(1)-C(14)-H(17)	107.692	108.8
N(1)-C(14)-H(20)	112.011	108.8
C(20)-C(14)-H(20)	108.169	109.41
C(20)-C(14)-H(17)	109.572	109.41
H(20)-C(14)-H(17)	106.538	109.4

C(13)-C(7)-S(1)	120.968	120
C(13)-C(7)-C(8)	128.62	121.4
S(1)-C(7)-C(8)	110.266	119
C(14)-C(20)-H(22)	110.152	110
C(14)-C(20)-H(7)	110.427	110
C(14)-C(20)-H(21)	112.06	110
H(22)-C(20)-H(7)	108.615	109
H(22)-C(20)-H(21)	107.578	109
H(7)-C(20)-H(21)	107.891	109
C(7)-S(1)-C(15)	91.801	98.5
O(1)-C(19)-C(22)	109.078	107.4
O(1)-C(19)-H(2)	109.288	106.7
O(1)-C(19)-H(3)	110.904	106.7
H(2)-C(19)-C(22)	109.692	109.41
H(2)-C(19)-H(3)	108.678	109.4
H(3)-C(19)-C(22)	109.183	109.41
C(19)-C(22)-O(4)	113.913	107.4
C(19)-C(22)-H(15)	108.856	109.41
C(19)-C(22)-H(16)	108.937	109.41
O(4)-C(22)-H(16)	110.729	106.7
H(15)-C(22)-O(4)	105.851	106.7
H(15)-C(22)-H(16)	108.372	109.4
C(22)-O(4)-C(17)	115.226	106.8
O(4)-C(17)-C(16)	109.103	107.4
O(4)-C(17)-H(12)	110.339	106.7
O(4)-C(17)-H(14)	110.799	106.7
C(16)-C(17)-H(12)	110.217	109.41
C(16)-C(17)-H(14)	108.449	109.41
H(12)-C(17)-H(14)	107.909	109.4
C(17)-C(16)-O(3)	109.972	107.4
C(17)-C(16)-H(11)	110.42	109.41
C(17)-C(16)-H(19)	110.794	109.41
H(11)-C(16)-O(3)	106.064	106.7
H(11)-C(16)-H(19)	108.444	109.4
H(19)-C(16)-O(3)	111.037	106.7
C(16)-O(3)-C(8)	116.324	110.8
C(7)-C(8)-O(3)	123.675	124.3
C(7)-C(8)-C(12)	113.878	120
O(3)-C(8)-C(12)	122.421	124.3
C(8)-C(12)-C(15)	111.955	120

C(8)-C(12)-H(13)	123.394	120
H(13)-C(12)-C(15)	124.647	120
S(1)-C(15)-C(12)	112.1	119
S(1)-C(15)-H(1)	120.414	120
C(12)-C(15)-H(1)	127.487	120

In the two thiophenes, both C-S-C angles are close to the 92.1° [354] expected in non-substituted thiophene. On the other hand, in the thiophene ring, the modelled angles are close to the experimental results. The ether bridge has four large angles (>109.47°) but these are not the same as the experimental, C8-O3-C16= 116.3°, C17-O4-C22= 115.2°, C9-O1-C19= 119.4° and O4-C22-C19= 113.9°. The ether bridge contains two C...H hydrogen interactions, C19-H3...C9= 2.552 Å and C17-H12...C22= 2.53 Å. In the amine bridge, the C-N-C are arranged to give a trigonal conformation. The bridge also contains three N-C-C large angles (>109.47° tetrahedral angle). Two C...H intramolecular interactions appear in this bridge, C13-H6...C14= 2.453 Å, C17-H12...C22= 2.530 Å and C14-H20...C11= 2.5 Å.

In the model, the short contact between S1 and N1 observed experimentally also appears, at 3.088 Å significantly lower than the sum of the van der Waals radii (3.45 Å)[333]. The nitrogen and the three oxygens form the cavity drawn below.

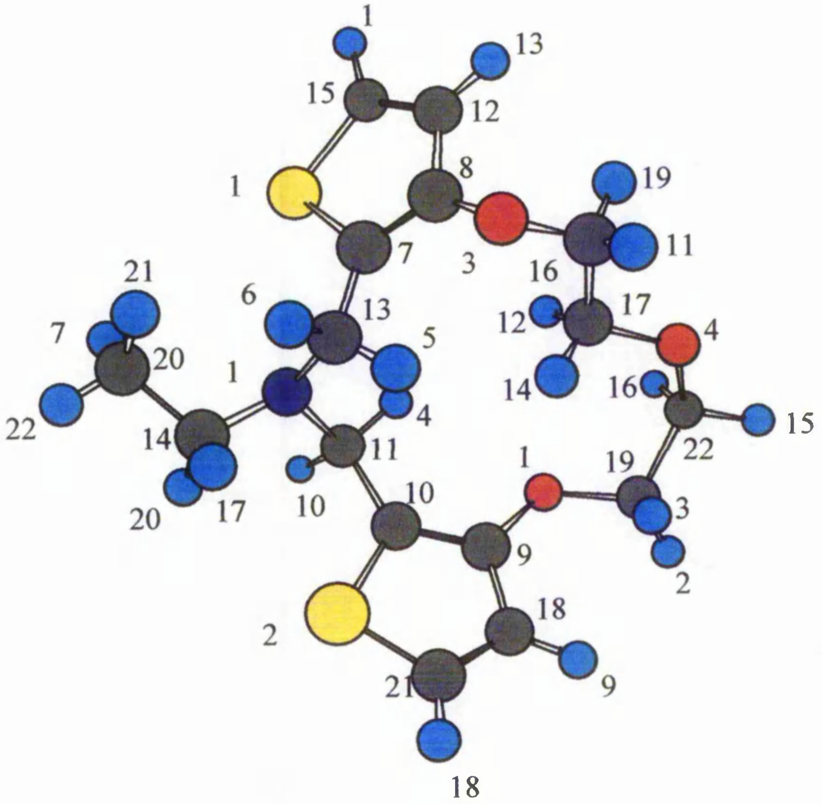


optimisation with Gaussian 98 via chemdraw 3 D

The cavity size is similar to the experimental (page 200) except for the short contact between O1...O4 and O3...O4.

In a publication concerning "the structures of the thienopyridine isomers and their isosteres", studied by the same modelling program, J.S.Webber and R.G.Woolley[359] compared five different basis sets[360]. These basis sets are namely, 3-21G*, 6-31G, 6-31G*, 6-31G** and a non-standard basis, 6-31GM, which is a modification of the 6-31G basis set. The number of Gaussian primitives, which differ between 6-31G and 3-21G, has a marked effect on the total electronic energy. But otherwise, it was observed that the 3-21G* and 6-31GM basis sets are fairly comparable in performance for sulphur containing heterocycles. Finally, for the modelling of the thiophene itself, both the 3-21G* and 6-31GM basis sets were seen to perform reasonably well within the SCF context and since they are considerably smaller than the fully polarized 6-31G*, 6-31G** basis sets (which offer no real improvement). For the thionopyridine isomers, it was difficult to choose between the 3-21G* and 6-31GM. So, to be sure that the 6-31G** basis set used for the modelling of this macrocycle was efficient, the modelling was repeated starting from the X-ray crystal structure parameters, using the same Gaussian basis set.

3.2.3. Molecular Modelling starting from the X-ray Crystal structure parameters



20 iterations were carried out to find the energy of the system, computed at the Hartree-Fock level, which is about $-7.3771976491887906*10^{-15}$ Joules or -1692.115533 Hartrees. The new system is closer to the X-ray structure and has an energy which is

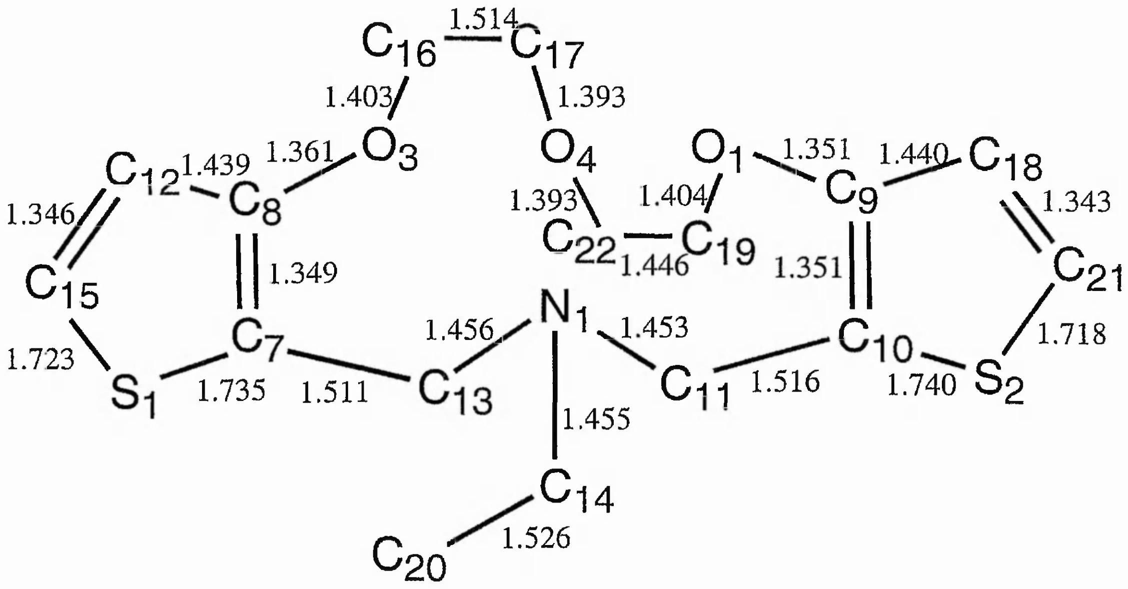
$3.85876*10^{-2}$ Hartrees or $1.6823221964232*10^{-19}$ Joules smaller than the previous model. This shows that the order of the molecular modelling programs or the programs themselves may not pass all the energy levels.

Table 73. Bond Lengths(Å)

Bond Lengths(Å)		
Bond	Actual Length(Å) (modelled)	Optimal Length(Å) (literature)
C(9) -C(18)	1.440	1.503
C(9) -O(1)	1.351	1.355
C(9) -C(10)	1.351	1.337
C(9),H(3)	2.593	
C(18) -C(21)	1.343	1.337
C(18) -H(9)	1.073	1.1
O(1) -C(19)	1.404	1.402
C(10) -C(11)	1.516	1.497
C(10) -S(2)	1.740	1.856
C(21) -S(2)	1.718	1.856
C(21) -H(18)	1.071	1.1
C(11) -N(1)	1.453	1.438
C(11) -H(10)	1.085	1.113
C(11) -H(4)	1.082	1.113
C(11),H(20)	2.505	
N(1) -C(13)	1.456	1.438
N(1) -C(14)	1.455	1.438
N(1),S(1)	3.003	
C(13) -C(7)	1.511	1.497
C(13) -H(6)	1.084	1.113
C(13) -H(5)	1.085	1.113
C(14) -C(20)	1.526	1.523
C(14),H(6)	2.458	
C(14) -H(20)	1.085	1.113
C(14) -H(17)	1.093	1.113
C(7) -S(1)	1.735	1.856
C(7) -C(8)	1.347	1.337
C(20) -H(22)	1.085	1.113
C(20) -H(7)	1.084	1.113

C(20) -H(21)	1.085	1.113
S(1) -C(15)	1.723	1.856
C(19) -C(22)	1.446	1.505
C(19) -H(2)	1.087	1.111
C(19) -H(3)	1.085	1.111
C(22) -O(4)	1.393	1.402
C(22) -H(15)	1.226	1.111
C(22) -H(16)	1.097	1.111
C(22),H(12)	2.680	
O(4) -C(17)	1.393	1.402
C(17) -C(16)	1.514	1.505
C(17) -H(12)	1.098	1.111
C(17) -H(14)	1.088	1.111
C(16) -O(3)	1.403	1.402
C(16) -H(11)	1.081	1.111
C(16) -H(19)	1.088	1.111
O(3) -C(8)	1.361	1.355
C(8) -C(12)	1.439	1.503
C(12) -C(15)	1.346	1.337
C(12) -H(13)	1.074	1.1
C(15) -H(1)	1.071	1.1

The macrocycle is in a lower energy conformation than the previous model but still seems to be in a higher energy conformation than the experimental. For ease, the macrocycle is drawn below (compare p193 and p203).



The conformational difference between the two modelled structures is very small. In the thiophene rings the bond lengths vary from –1.17% to +1.12% compared to the X-ray structure and from –0.23% to +0.30% compared to the previous model. As for the previous model, the smallest differences between the experimental crystal structures and the modeled thiophene-based macrocycles are in the thiophenes, especially in the S1 thiophene ring. In the S2 thiophene ring the bond lengths are 0.001 Å to 0.028 Å bigger than the X-ray structure but the distortions are similar. In the macrocyclic cavity, the bond lengths seem to be more symmetric.

The C-C bond lengths vary in the range 1.511-1.526 Å, close to the 1.52 Å[357] expected, except for C19-C22= 1.446 Å. The bond lengths are closer to the X-ray structure than those in the previous model, from -2.30% smaller and +1.95% larger than the experimental values. The C-N bond lengths are similar to the other model. Indeed, the C-N bonds vary from 1.453 Å to 1.456 Å, which except the N1-C14 bond length are between -1.69 % and -2.41 % smaller than the real structure. The aromatic C-O distances vary between 1.351 and 1.361 Å, which are respectively -1.03% and -1.52% shorter then their corresponding lengths in the experimental work and are shorter than the aliphatic C-O bonds (1.393-1.404 Å, -1.49 to -3.20% smaller than experimental).

Table 74. Bond Angles(°)

Bond Angles(°)		
Bond	Actual Angle(°) (modelled)	Optimal Angle(°) (literature)
C(18)-C(9)-O(1)	124.904	124.3
C(18)-C(9)-C(10)	114.044	120
O(1)-C(9)-C(10)	121.016	124.3
C(9)-C(18)-C(21)	111.097	120
C(9)-C(18)-H(9)	124.523	120
H(9)-C(18)-C(21)	123.577	120
C(9)-O(1)-C(19)	119.456	110.8
C(9)-C(10)-C(11)	127.233	121.4
C(9)-C(10)-S(2)	109.802	119
C(11)-C(10)-S(2)	122.857	120
C(18)-C(21)-S(2)	112.093	119
C(18)-C(21)-H(18)	127.249	120
H(18)-C(21)-S(2)	120.657	120

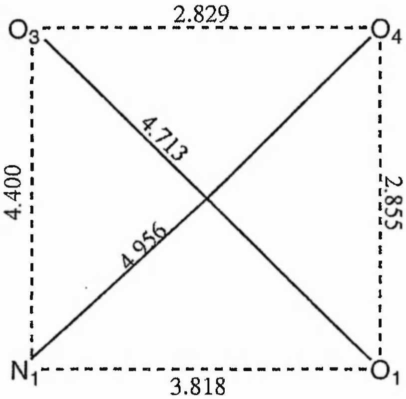
C(10)-C(11)-N(1)	117.823	110.74
C(10)-C(11)-H(1-)	107.181	109.41
C(10)-C(11)-H(4)	109.026	109.41
N(1)-C(11)-H(4)	107.860	108.8
H(10)-C(11)-N(1)	107.739	108.8
H(10)-C(11)-H(4)	106.695	109.4
C(10)-S(2)-C(21)	92.156	98.5
C(11)-N(1)-C(13)	114.312	107.7
C(11)-N(1)-C(14)	115.396	107.7
C(13)-N(1)-C(14)	115.572	107.7
N(1)-C(13)-C(7)	111.911	110.74
N(1)-C(13)-H(6)	108.965	108.8
N(1)-C(13)-H(5)	111.773	108.8
C(7)-C(13)-H(5)	113.397	109.41
H(6)-C(13)-C(7)	104.522	109.41
H(6)-C(13)-H(5)	106.099	109.4
N(1)-C(14)-C(20)	112.603	109.5
N(1)-C(14)-H(17)	111.813	108.8
N(1)-C(14)-H(20)	107.645	108.8
C(20)-C(14)-H(20)	109.885	109.41
C(20)-C(14)-H(17)	108.124	109.41
H(20)-C(14)-H(17)	106.494	109.4
C(13)-C(7)-S(1)	121.024	120
C(13)-C(7)-C(8)	124.201	121.4
S(1)-C(7)-C(8)	111.154	119
C(14)-C(20)-H(22)	110.124	110
C(14)-C(20)-H(7)	110.428	110
C(14)-C(20)-H(21)	112.110	110
H(22)-C(20)-H(7)	108.654	109
H(22)-C(20)-H(21)	107.587	109
H(7)-C(20)-H(21)	107.818	109
C(7)-S(1)-C(15)	91.376	98.5
O(1)-C(19)-C(22)	109.544	107.4
O(1)-C(19)-H(2)	110.262	106.7
O(1)-C(19)-H(3)	110.878	106.7
H(2)-C(19)-C(22)	110.206	109.41
H(2)-C(19)-H(3)	108.902	109.4
H(3)-C(19)-C(22)	106.992	109.41
C(19)-C(22)-O(4)	112.418	107.4
C(19)-C(22)-H(15)	133.056	109.41

C(19)-C(22)-H(16)	131.453	109.41
O(4)-C(22)-H(16)	83.632	106.7
H(15)-C(22)-O(4)	94.921	106.7
H(15)-C(22)-H(16)	87.196	109.4
C(22)-O(4)-C(17)	118.090	106.8
O(4)-C(17)-C(16)	109.024	107.4
O(4)-C(17)-H(12)	110.497	106.7
O(4)-C(17)-H(14)	111.156	106.7
C(16)-C(17)-H(12)	111.327	109.41
C(16)-C(17)-H(14)	107.097	109.41
H(12)-C(17)-H(14)	107.694	109.4
C(17)-C(16)-O(3)	113.158	107.4
C(17)-C(16)-H(11)	109.998	109.41
C(17)-C(16)-H(19)	109.197	109.41
H(11)-C(16)-O(3)	104.947	106.7
H(11)-C(16)-H(19)	108.113	109.4
H(19)-C(16)-O(3)	111.250	106.7
C(16)-O(3)-C(8)	119.809	110.8
C(7)-C(8)-O(3)	124.355	124.3
C(7)-C(8)-C(12)	112.163	120
O(3)-C(8)-C(12)	123.373	124.3
C(8)-C(12)-C(15)	112.881	120
C(8)-C(12)-H(13)	124.196	120
H(13)-C(12)-C(15)	122.920	120
S(1)-C(15)-C(12)	111.469	119
S(1)-C(15)-H(1)	120.245	120
C(12)-C(15)-H(1)	128.284	120

In the two thiophenes, the C-S-C angles are still close to the 92.1°[354] expected in unsubstituted thiophene and to the X-ray structure. On the other hand, in the thiophene ring, the modelled angles deviate from the experimental more than those in the previous model. Here, the ether bridge has five large angles (>109.47°) but contrary to the previous model these are almost the same as the experimental, C9-O1-C19= 119.456°, O3-C16-C17= 113.158°, C8-O3-C16= 119.809°. However, the O1-C19-C22= 109.544° bond angle is slightly superior to 109.47° and is only 1.744° bigger than the experimental. The fifth large bond angle is O4-C22-C19= 112.418°. The ether bridge contains two C...H hydrogen interactions, C19-H3...C9= 2.552 Å and C17-H12...C22= 2.53 Å. In the amine bridge, the C-N-C are arranged to give a trigonal conformation. The bridge also contains three N-C-C large angles (>109.47° tetrahedral angle). Three C...H intramolecular contacts appear in this bridge, C13-H6...C14= 2.458 Å, C17-H12...C22= 2.680 Å and C14-H20...C11= 2.505 Å, which are similar to the previous model.

In the new model, the short contact between S1 and N1 also appears at 3.003 Å, which is closer to the experimental and significantly lower than the sum of the van der Waals radii (3.45 Å)[333]. The nitrogen and the three oxygens form the cavity drawn below.

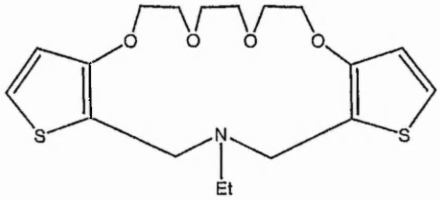
The cavity size is closer to the experimental than the other model due to closer approximation of bond angles and bond lengths in the cavity to the crystal structure.



optimisation with Gaussian 98 via chemdraw 3 D from the X-ray crystallography structure

The two model structures obtained above show some differences, but both of the conformations are close to the X-ray structure. Despite the apparent deviations from the X-ray structure, both models give a correct the estimation of the cavity size, which is the most important thing here because it gives an idea of the ability of the macrocycle to include a metal ion inside the cavity. This work has shown that it is possible to use molecular modelling to design macrocycles using the 6-31G** basis set.

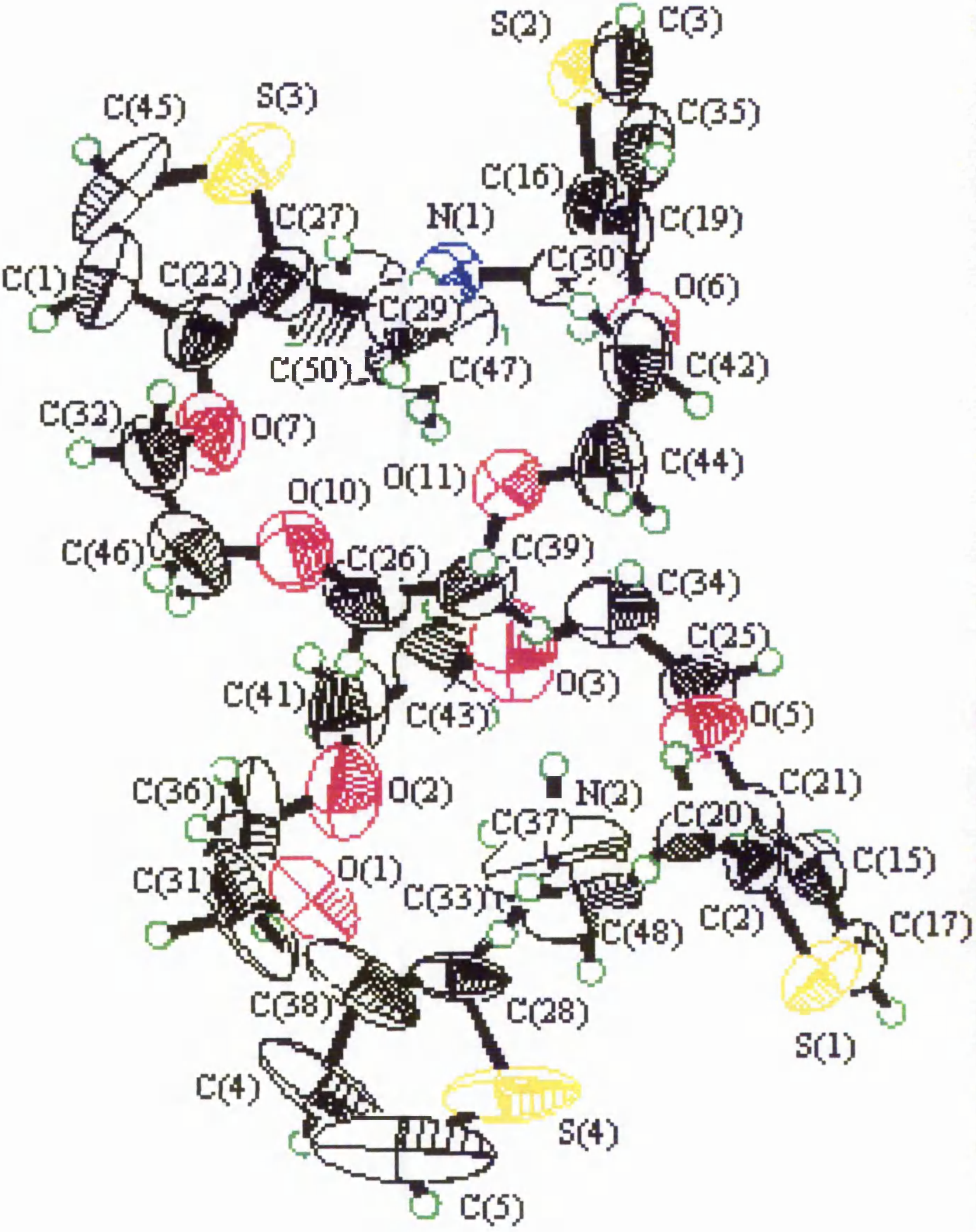
3.3. Five donor atoms thiophene-based macrocycle (4 oxygens, 1 nitrogen): 18-ethyl-2,5,8,11-tetraoxa-15,21-dithia-azatricyclo[18.3.0.0]-tricosa-1,22,12,13-tetraene **10b**



3.3.1. Discussion of the structure derived data (table 24 to 26)

There are two independent molecules A and B in each asymmetric unit, therefore this structure allows comparison of two forms of the molecule which are stable in the solid state. The positions and anisotropic displacement parameters of the atoms in the two different macrocycles are best-visualized in the "ortep style" drawing on the next page[353].

In both conformations, the displacement parameters are significant and may affect accuracy of the bond lengths and bond angles. The greatest displacement occurs on both molecules at the extremities of the molecules. The thiophene rings have greater displacements in their outermost atoms, but this is larger in the S3 and S4 thiophene rings. The ethyl carbons bonded to the nitrogen atoms have a great flexibility that is reflected in their Uij's. The nitrogen atoms N1 and N2, which form two tertiary amines and so are more tightly bound than the other atoms, have the smallest displacement parameters of the two macrocycles. The carbons C2, C28, C16 and C27 (bound to three carbons) and the carbons C21, C38, C19 and C22 (each bound to one oxygen and two carbons) also have lower displacements. The relative flexibility of the ether bridges is reflected in the large thermal ellipsoids of the atoms, and especially in the S1, S4 thiophene macrocycle.


S(2)
C(3)
C(45)
S(3)
C(35)
C(16)
C(27)
N(1)
C(19)
C(1)
C(22)
C(30)
O(6)
C(29)
C(50)
C(47)
C(42)
C(32)
O(7)
O(11)
C(44)
O(10)
C(39)
C(46)
C(26)
C(34)
C(25)
C(41)
O(3)
C(43)
O(5)
C(36)
O(2)
C(21)
N(2)
C(20)
C(37)
C(15)
O(1)
C(31)
C(33)
C(2)
C(17)
C(48)
C(38)
C(28)
S(1)
C(4)
S(4)
C(5)

3.3.2. Discussion of the structural geometry

Table 75. Bond Lengths(Å)

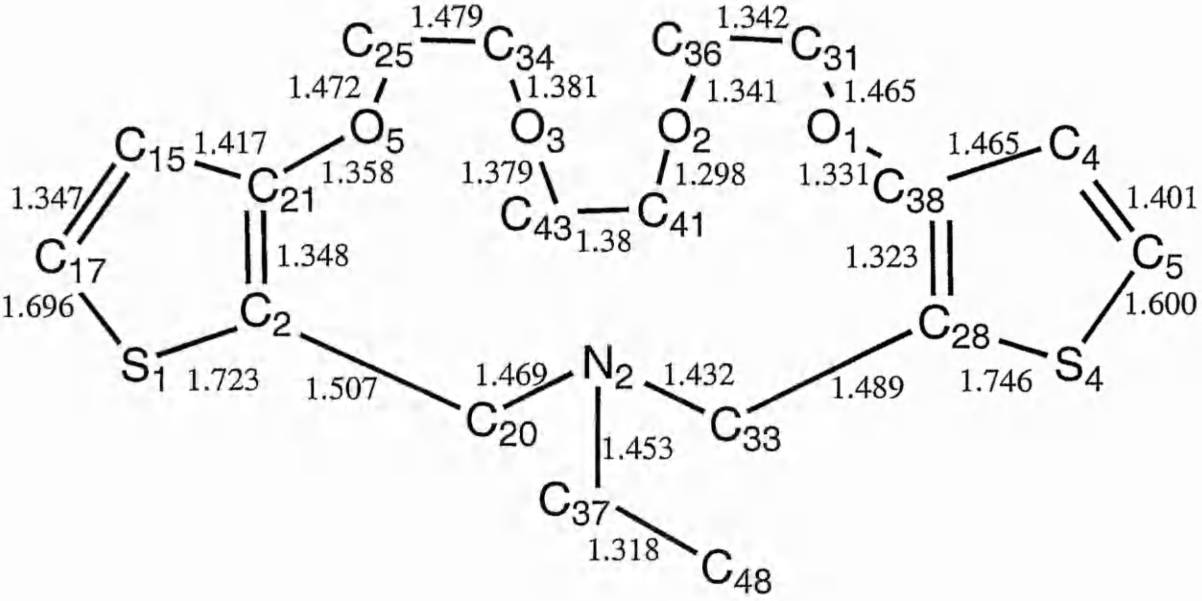
Bond Lengths(Å)			
Bond	Length(Å)	Bond	Length(Å)
S(1) -C(2)	1.723(6)	N(1) -C(30)	1.463(9)
S(1) -C(17)	1.696(7)	N(1) -C(47)	1.50(2)
S(2) -C(3)	1.71(1)	N(2) -C(20)	1.469(9)
S(2) -C(16)	1.725(7)	N(2) -C(33)	1.43(1)
S(3) -C(27)	1.713(7)	N(2) -C(37)	1.453(9)
S(3) -C(45)	1.72(1)	C(1) -C(22)	1.38(1)
S(4) -C(5)	1.60(2)	C(1) -C(45)	1.30(1)
S(4) -C(28)	1.746(8)	C(1) -H(35)	1.03(5)
O(1) -C(31)	1.46(1)	C(2) -C(20)	1.507(9)
O(1) -C(38)	1.33(1)	C(2) -C(21)	1.348(7)
O(2) -C(36)	1.34(1)	C(3) -C(35)	1.31(1)
O(2) -C(41)	1.30(1)	C(3) -H(11)	0.63(6)
O(3) -C(34)	1.38(1)	C(4) -C(5)	1.40(2)
O(3) -C(43)	1.38(1)	C(4) -C(38)	1.46(1)
O(3) -H(43)	1.15(6)	C(4) -H(28)	1.012
O(5) -C(21)	1.358(6)	C(5) -H(40)	0.78(6)
O(5) -C(25)	1.412(8)	C(15) -C(17)	1.347(9)
O(6) -C(19)	1.367(8)	C(15) -C(21)	1.417(8)
O(6) -C(42)	1.433(9)	C(15) -H(14)	0.87(5)
O(7) -C(22)	1.382(8)	C(16) -C(19)	1.359(9)
O(7) -C(32)	1.43(1)	C(16) -C(30)	1.47(1)
O(10) -C(26)	1.43(1)	C(17) -H(6)	0.99(5)
O(10) -C(46)	1.42(1)	C(19) -C(35)	1.39(1)
O(11) -C(39)	1.406(9)	C(20) -H(2)	0.99(5)
O(11) -C(44)	1.387(9)	C(20) -H(30)	0.80(5)
N(1) -C(29)	1.44(1)	C(22) -C(27)	1.343(9)
C(25) -C(34)	1.48(1)	C(37) -C(48)	1.32(1)
C(25) -H(15)	0.99(5)	C(37) -H(47)	1.212
C(25) -H(16)	0.87(5)	C(37) -H(48)	1.23(5)
C(26) -C(39)	1.52(1)	C(37) -H(50)	1.291
C(26) -H(26)	0.91(5)	C(39) -H(4)	1.17(5)
C(26) -H(46)	1.01(6)	C(39) -H(22)	1.12(5)
C(27) -C(29)	1.49(1)	C(39) -H(46)	1.16(8)

C(28) -C(33)	1.49(1)	C(41) -C(43)	1.39(1)
C(28) -C(38)	1.32(1)	C(41) -H(24)	0.80(6)
C(29) -H(9)	0.76(6)	C(42) -C(44)	1.48(1)
C(29) -H(19)	1.13(5)	C(42) -H(7)	1.00(5)
C(30) -H(17)	1.08(5)	C(42) -H(27)	1.052
C(30) -H(18)	0.83(5)	C(43) -H(20)	0.70(6)
C(31) -C(36)	1.34(2)	C(43) -H(43)	1.25(6)
C(31) -H(8)	0.353	C(44) -H(10)	0.96(5)
C(31) -H(36)	1.216	C(44) -H(23)	1.03(5)
C(32) -C(46)	1.48(1)	C(45) -H(29)	0.68(6)
C(32) -H(3)	1.08(5)	C(46) -H(34)	0.99(6)
C(32) -H(13)	0.95(5)	C(46) -H(45)	0.97(5)
C(33) -H(32)	0.87(5)	C(47) -C(50)	1.32(2)
C(33) -H(33)	0.97(5)	C(47) -H(38)	0.60(8)
C(34) -H(5)	0.89(5)	C(47) -H(39)	1.16(5)
C(34) -H(37)	0.98(5)	C(47) -H(41)	1.16(8)
C(35) -H(12)	0.96(5)	C(48) -H(1)	1.11(5)
C(36) -H(21)	0.81(6)	C(48) -H(25)	0.86(6)
C(36) -H(42)	1.269	C(48) -H(47)	0.981
C(50) -H(31)	0.87(6)		
C(50) -H(38)	1.1(1)		
C(50) -H(41)	1.05(7)		

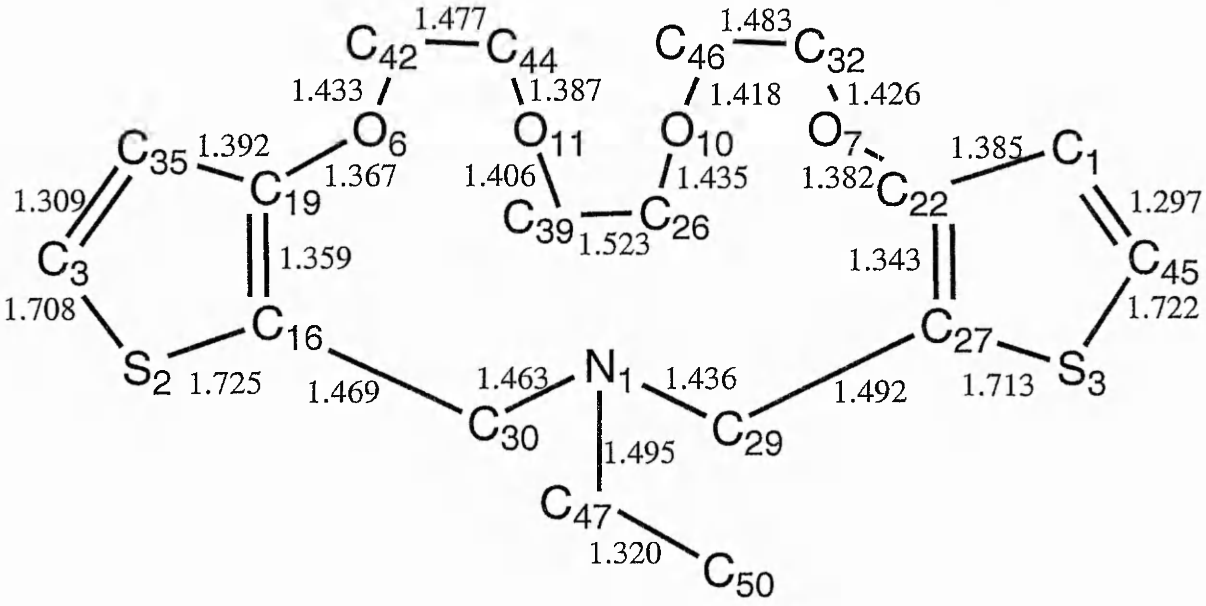
** Note some of the hydrogen bond lengths are to three decimal places with terminal zero's omitted and have no esd's as those hydrogen positions were not refined.

It would be expected that in both conformations the halves of the macrocycle **10bA** and **10bB** (the molecule is chemically mirrored respectively through C41-C43 and N2, and through C26-C39 and N1) would have the same bond lengths. This is not the case. In the crystal structure, the two halves of the molecules have differing geometries reflected in the bond lengths. However, the bond lengths and bond angles seem more symmetric in the S2, S3 thiophene macrocycle. The molecular distortions are also reflected in the bond angles that are shown in the following table (table 76).

For ease of description the bond lengths (to 3 decimal places) of the two conformations **10bA** and **10bB** are shown on the schematic drawings on the next page.



10bA



10bB

Table 76. Bond Angles(°)

Bond Angles(°)			
Bond	Angle(°)	Bond	Angle(°)
C(2) -S(1) -C(17)	92.5(3)	S(2) -C(3) -C(35)	114.4(7)
C(3) -S(2) -C(16)	90.4(5)	S(2) -C(3) -H(11)	112(8)
C(27) -S(3) -C(45)	90.4(5)	C(35) -C(3) -H(11)	132(8)

C(5) -S(4) -C(28)	90.5(7)	C(5) -C(4) -C(38)	107(1)
C(31) -O(1) -C(38)	116(1)	C(5) -C(4) -H(28)	91.15
C(36) -O(2) -C(41)	118(1)	C(38) -C(4) -H(28)	136.49
C(34) -O(3) -C(43)	122.5(9)	S(4) -C(5) -C(4)	118(1)
C(34) -O(3) -H(43)	89(3)	S(4) -C(5) -H(40)	97(6)
C(43) -O(3) -H(43)	59(3)	C(4) -C(5) -H(40)	144(6)
C(21) -O(5) -C(25)	117.9(5)	C(17) -C(15) -C(21)	112.9(6)
C(19) -O(6) -C(42)	116.8(6)	C(17) -C(15) -H(14)	128(4)
C(22) -O(7) -C(32)	115.1(7)	C(21) -C(15) -H(14)	119(4)
C(26) -O(10) -C(46)	112.2(7)	S(2) -C(16) -C(19)	109.2(6)
C(39) -O(11) -C(44)	113.9(7)	S(2) -C(16) -C(30)	121.8(6)
C(29) -N(1) -C(30)	111.5(6)	C(19) -C(16) -C(30)	129.0(7)
C(29) -N(1) -C(47)	112(1)	S(1) -C(17) -C(15)	111.3(5)
C(30) -N(1) -C(47)	106.9(9)	S(1) -C(17) -H(6)	119(3)
C(20) -N(2) -C(33)	110.4(5)	C(15) -C(17) -H(6)	129(3)
C(20) -N(2) -C(37)	111.1(7)	O(6) -C(19) -C(16)	119.3(6)
C(33) -N(2) C(37)	107.7(8)	O(6) -C(19) -C(35)	125.6(9)
C(22) -C(1) -C(45)	111(1)	C(16) -C(19) -C(35)	115.1(8)
C(22) -C(1) -H(35)	114(4)	N(2) -C(20) -C(2)	113.5(6)
C(45) -C(1) -H(35)	134(4)	N(2) -C(20) -H(2)	111(3)
S(1) -C(2) -C(20)	121.8(5)	N(2) -C(20) -H(30)	115(5)
S(1) -C(2) -C(21)	110.3(5)	C(2) -C(20) -H(2)	107(3)
C(20) -C(2) -C(21)	127.9(6)	C(2) -C(20) -H(30)	108(5)
H(2) -C(20) -H(30)	101(5)	N(1) -C(29) -H(9)	112(5)
O(5) -C(21) -C(2)	119.4(5)	N(1) -C(29) -H(19)	115(3)
O(5) -C(21) -C(15)	127.5(6)	C(27) -C(29) -H(9)	107(5)
C(2) -C(21) -C(15)	113.0(6)	C(27) -C(29) -H(19)	99(3)
O(7) -C(22) -C(1)	124.6(9)	H(9) -C(29) -H(19)	111(6)
O(7) -C(22) -C(27)	119.7(7)	N(1) -C(30) -C(16)	113.2(5)
C(1) -C(22) -C(27)	115.7(9)	N(1) -C(30) -H(17)	104(3)
O(5) -C(25) -C(34)	109.4(6)	N(1) -C(30) -H(18)	109(4)
O(5) -C(25) -H(15)	108(3)	C(16) -C(30) -H(17)	115(3)
O(5) -C(25) -H(16)	108(4)	C(16) -C(30) -H(18)	105(4)
C(34) -C(25) -H(15)	116(3)	H(17) -C(30) -H(18)	111(5)
C(34) -C(25) -H(16)	114(4)	O(1) -C(31) -C(36)	111(1)
H(15) -C(25) -H(16)	100(5)	O(1) -C(31) -H(8)	56.08
O(10) -C(26) -C(39)	108.6(8)	O(1) -C(31) -H(36)	122.81
O(10) -C(26) -H(26)	114(4)	C(36) -C(31) -H(8)	139.9
O(10) -C(26) -H(46)	61(5)	C(36) -C(31) -H(36)	104.17
C(39) -C(26) -H(26)	116(4)	H(8) -C(31) -H(36)	114.33

C(39) -C(26) -H(46)	50(5)	O(7) -C(32) -C(46)	109.9(8)
H(26) -C(26) -H(46)	124(6)	O(7) -C(32) -H(3)	109(3)
S(3) -C(27) -C(22)	109.3(6)	O(7) -C(32) -H(13)	103(4)
S(3) -C(27) -C(29)	120.3(6)	C(46) -C(32) -H(3)	113(3)
C(22) -C(27) -C(29)	130.4(7)	C(46) -C(32) -H(13)	116(4)
S(4) -C(28) -C(33)	117.6(8)	H(3) -C(32) -H(13)	105(5)
S(4) -C(28) -C(38)	112.4(8)	N(2) -C(33) -C(28)	113.2(7)
C(33) -C(28) -C(38)	130.0(9)	N(2) -C(33) -H(32)	119(4)
N(1) -C(29) -C(27)	113.1(6)	N(2) -C(33) -H(33)	107(3)
C(28) -C(33) -H(32)	107(4)	H(47) -C(37) -H(50)	92.14
C(28) -C(33) -H(33)	111(4)	H(48) -C(37) -H(50)	131.58
H(32) -C(33) -H(33)	99(5)	O(1) -C(38) -C(4)	129(1)
O(3) -C(34) -C(25)	115.5(7)	O(1) -C(38) -C(28)	118.3(9)
O(3) -C(34) -H(5)	113(4)	C(4) -C(38) -C(28)	113(1)
O(3) -C(34) -H(37)	109(4)	O(11) -C(39) -C(26)	107.1(7)
C(25) -C(34) -H(5)	105(4)	O(11) -C(39) -H(4)	80(3)
C(25) -C(34) -H(37)	97(4)	O(11) -C(39) -H(22)	105(3)
H(5) -C(34) -H(37)	117(5)	O(11) -C(39) -H(46)	104(3)
C(3) -C(35) -C(19)	111(1)	C(26) -C(39) -H(4)	117(3)
C(3) -C(35) -H(12)	126(4)	C(26) -C(39) -H(22)	113(3)
C(19) -C(35) -H(12)	122(4)	C(26) -C(39) -H(46)	41(3)
O(2) -C(36) -C(31)	115(1)	H(4) -C(39) -H(22)	125(4)
O(2) -C(36) -H(21)	127(5)	H(4) -C(39) -H(46)	76(4)
O(2) -C(36) -H(42)	107.03	H(22) -C(39) -H(46)	147(4)
C(31) -C(36) -H(21)	102(5)	O(2) -C(41) -C(43)	117.2(9)
C(31) -C(36) -H(42)	92.25	O(2) -C(41) -H(24)	114(5)
H(21) -C(36) -H(42)	107.16	C(43) -C(41) -H(24)	120(5)
N(2) -C(37) -C(48)	119(1)	O(6) -C(42) -C(44)	107.4(7)
N(2) -C(37) -H(47)	144.66	O(6) -C(42) -H(7)	98(3)
N(2) -C(37) -H(48)	120(2)	O(6) -C(42) -H(27)	111.45
N(2) -C(37) -H(50)	106.43	C(44) -C(42) -H(7)	118(3)
C(48) -C(37) -H(47)	45.39	C(44) -C(42) -H(27)	65.64
C(48) -C(37) -H(48)	102(3)	H(7) -C(42) -H(27)	147.86
C(48) -C(37) -H(50)	61.25	O(3) -C(43) -C(41)	118(1)
H(47) -C(37) -H(48)	56.88	O(3) -C(43) -H(20)	116(6)
O(3) -C(43) -H(43)	52(3)	H(38) -C(47) -H(39)	133(11)
C(41) -C(43) -H(20)	119(6)	H(38) -C(47) -H(41)	83(12)
C(41) -C(43) -H(43)	125(3)	H(39) -C(47) -H(41)	111(5)
H(20) -C(43) -H(43)	110(7)	C(37) -C(48) -H(1)	125(3)
O(11) -C(44) -C(42)	112.3(7)	C(37) -C(48) -H(25)	123(5)

O(11) -C(44) -H(10)	108(4)	C(37) -C(48) -H(47)	61.54
O(11) -C(44) -H(23)	106(3)	H(1) -C(48) -H(25)	98(5)
C(42) -C(44) -H(10)	119(4)	H(1) -C(48) -H(47)	172.68
C(42) -C(44) -H(23)	120(3)	H(25) -C(48) -H(47)	79.88
H(10) -C(44) -H(23)	88(4)	C(47) -C(50) -H(31)	112(5)
S(3) -C(45) -C(1)	113.4(7)	C(47) -C(50) -H(38)	27(4)
S(3) -C(45) -H(29)	113(6)	C(47) -C(50) -H(41)	57(5)
C(1) -C(45) -H(29)	133(6)	H(31) -C(50) -H(38)	138(7)
O(10) -C(46) -C(32)	113.9(8)	H(31) -C(50) -H(41)	79(7)
O(10) -C(46) -H(34)	114(3)	H(38) -C(50) -H(41)	71(7)
O(10) -C(46) -H(45)	96(4)	N(1) -C(47) -H(39)	131(3)
C(32) -C(46) -H(34)	104(3)	N(1) -C(47) -H(41)	116(5)
C(32) -C(46) -H(45)	118(4)	C(50) -C(47) -H(38)	55(13)
H(34) -C(46) -H(45)	112(5)	C(50) -C(47) -H(39)	100(3)
N(1) -C(47) -C(50)	119(1)	C(50) -C(47) -H(41)	49(3)
N(1) -C(47) -H(38)	65(13)		

** Note some of the bond angles including hydrogen atoms are to two decimal places with terminal zeros omitted and have no esd's as those hydrogen atom positions were not refined.

In the macrocycle **10bA**, the bond lengths and bond angles of the S4 thiophene ring are asymmetric either side of the S4 sulphur atom. However, the S4 thiophene ring atoms have significant thermal ellipsoids which are the greatest in the macrocycle. The two thiophene rings are planar and include in their planes the oxygen and carbon atoms directly bonded to them. These two thiophene ring planes form an angle of 86.52°. In the S1 thiophene, the bond length C15-C21= 1.417 Å is close to the 1.419 Å in unsubstituted thiophene[354]. Also, the C=C bonds have a strong double character, C2-C21= 1.348 Å and C15-C17= 1.347 Å. The bond angles in the S1 thiophene ring are also fairly symmetric either side of the sulphur atom and are close to those in unsubstituted thiophene, C2-S1-C17= 92.5(3)°, S1-C2-C21= 110.3(5)°, S1-C17-C15= 111.3(5)°, C2-C21-C15= 113.0(6)° and C17-C15-C21= 112.9(6)°. The S-C bond lengths are S1-C17= 1.696 Å and S1-C2= 1.723 Å. A weak S…N interaction, S1…N2= 3.388 Å (sum of the van der Waals radii= 3.45 Å), appears on this half of the molecule which could be fictitious due to the significant displacement parameters of the S1 atom. In the S4 thiophene ring, the distortions are greater as the bond lengths and bond angles are not close to those in unsubstituted thiophene any more. Indeed, the C-C bond length is longer than in the S1 thiophene ring, C4-C38= 1.465 Å. The C28-C38= 1.323 Å bond length has a more strongly double bond character than C4-C5= 1.401 Å. The S-C bond length distortions from ideal in this ring are even larger than in the S1 thiophene. The S4-C5= 1.600 Å bond length is clearly more double bonded in character than S4-C28= 1.746 Å. These stronger distortions could be due to the fact that the S...N interaction S4...N2= 2.982 Å is significantly shorter than the S1...N2 interaction and might create an electron withdrawing effect. The distortion is also reflected in the S4 thiophene bond angles, C5-S4-C28= 90.5(7)°, S4-C5-C4= 118(1)°, S4-C28-C38= 112.4(8)°, C5-C4-C38= 107(1)° and C4-C38-C28= 113(1)°.

In the ether chain of the macrocycle **10bA**, the distortions from ideal are also quite significant but these could due to the large displacement parameters and so the low accuracy of the bond lengths and bond angles. The C-O aromatic bond lengths which are lowered by conjugation with the adjacent thiophene ring, vary between 1.331 Å and 1.358 Å, and the aliphatic C-O bond lengths vary between 1.298 Å and 1.472 Å. The C-C bond lengths in this ether bridge also vary between 1.342 and 1.479 Å, which is lower than the expected 1.52 Å[358]. The O-C-C and C-O-C bond angles between the ether bridge and the thiophene rings are respectively O1-C38-C4= 129(1)°, O1-C38-C28= 118.3(9)°, C31-O1-C38= 116(1)°, O5-C21-C2= 119.4(5)°, O5-C21-C15= 127.5(6)° and C21-O5-C25= 117.9(5)°. These bond angles are similarly distorted in both halves of the macrocycle. In the S1 thiophene half, some H...H, O...H and O...C contacts appear, which could be fictitious. These intramolecular contacts are C15-H14...H15-C25= 2.490 Å, C15-H14...H16-C25= 2.207 Å, O5...H14-C15= 2.680 Å, O5...C15= 2.489 Å and also contact bonds involving the amine bridge O5...H33-C33= 2.861 Å, O5...H2-C20= 2.539 Å, and finally O5...C20= 2.940 Å. In the other half of the molecule, the interactions observed are weaker and fewer. Only two O...H hydrogen bonds appear and one of them is with the amine bridge, O1...H28-C4= 3.198 Å and O1...H32-C33= 2.564 Å. Two other intramolecular contacts appear as O1...C4= 2.522 Å and C31-H8...C4= 2.704 Å. The other O-C-C and C-O-C bond angles are O1-C31-C36= 111(1)°, C36-O2-C41= 118(1)°, O2-C36-C31= 115(1)°, O2-C43-C41= 117.2(9)°, C43-O3-C34= 122.5(9)°, O3-C43-C41= 118(1)°, O3-C34-C25= 115.5(7)° and finally O5-C25-C34= 109.4(6)°. These bond angles are fairly symmetric and have similar hydrogen contacts, C36-H21...H24-C41= 2.545 Å, C36-H21...H46-C41= 2.666 Å, C36-H42...H46-C41= 2.522 Å, C34-H5...H47-C43= 2.620 Å, O2...H8-C31= 2.397 Å, O2...H20-C41= 3.058 Å, O3...H16-C25= 2.635 Å and O3...H46-C43= 2.633 Å. In the amine bridge, the distortions are weaker. It seems that the S...N interactions are the reasons for these distortions, S1...N2= 3.388 Å and S4...N2= 2.982 Å. The S4...N2 interaction is stronger and seems to affect more significantly the bond lengths and bond angles in the amine bridge. Indeed, the C-C bond length C28-C33= 1.489 Å shortened by a conjugation effect with the adjacent thiophene ring, is 0.031 Å smaller than the expected 1.52 Å[357], whereas C2-C20= 1.507 Å is not significantly smaller than 1.52 Å. The C-N bond lengths are similarly affected as C33-N2= 1.432 Å, C20-N2= 1.469 Å and C37-N2= 1.453 Å. The C-N-C bond angles are C20-N2-C33= 110.4(5)°, C20-N2-C37= 111.1(7)° and C33-N2-C37= 107.7(8)°. The N-C-C bond angles with the thiophenes, N2-C20-C2= 113.5(6)° and N2-C33-C28= 113.2(7)°, are shorter than the N2-C37-C48= 119(1)° bond angle in the ethyl group. This could be due to the S...H and N...H hydrogen bonds, S1...H30-C20= 2.954 Å, S4...H33-C33= 3.170 Å, N2...H38-C48= 2.739 Å and N2...H1-C48= 2.486 Å. The short bond length C37-C48= 1.318 Å is probably due to errors in the atomic positions. Two last hydrogen interactions appear as C20-H2...H48-C37= 2.517 Å and C20-H30...H38-C48= 2.756 Å. The bond angles between the amine bridge and the thiophene rings are S1-C2-C20= 121.8(5)°, C20-C2-C21= 127.9(6)°, S4-C28-C33= 117.6(8)° and C33-C28-C38= 130.0(9)°.

In the case of the macrocycle **10bB**, the distortions in the thiophene rings are different from the other conformation. Indeed, the distortions that are reflected in the thiophene bond lengths and bond angles seem fairly symmetric in the molecule. The two thiophene rings are planar and include in their planes the oxygen and the carbon atoms directly bonded to them. Those two thiophene rings form an angle of 96.27°. In the S2 thiophene, the C19-C35 and C3=C35 bond lengths are clearly distorted, and are shorter than their corresponding lengths in the non-substituted thiophene[354], e.g. C19-C35= 1.392 Å, C16-C19= 1.359 Å and C3-C35= 1.309 Å. Also, these distortions could be due to the fact that the carbon atoms C3 and C35 that are unsubstituted, are on the outer edge of the thiophene ring and consequently have large displacement parameters. The S C bond lengths are similar to those in the previous conformation, S2-C3= 1.708 Å and S2-C16= 1.725 Å. The distortions are also quite significant in the S2 thiophene bond angles, C3-S2-C16= 90.4(5)°, S2-C3-C35= 114.4(7)°, S2-C16-C19= 109.2(6)°, C3-C35-C19= 111(1)° and C16-C19-C35= 115.1(8)°. Indeed, the C-C-C bond angle substituted by the ether bridge on C19 is 4° larger than its unsubstituted counterpart, while the substituted S-C-C bond angle is 5.2° smaller than the non-substituted S-C-C angle. In this conformation of the macrocycle **10bB**, the distortions could also be due to the S...N interactions between the lone pair of the nitrogen amine atom and the sulphur thiophene atoms, in addition to the errors in the structure. These interactions, S2...N1= 3.380 Å and S3...N1= 3.056 Å, are fairly similar to those in the conformation **10bA**, but as for the previous conformation the S2...N1 interaction could be fictitious. The S3...N1 interaction is the strongest of the two in **10bB** as in the structure **10bA**, but the effect on the S3 thiophene ring is different as the S-C bond lengths, S3-C27= 1.713 Å and S3-C45= 1.722 Å, are close to the corresponding bond lengths in the unsubstituted thiophene[354]. Moreover, the rest of the bond lengths and the bond angles are fairly close to those in the S2 thiophene ring.

In the ether bridge of the structure **10bB**, the bond lengths and bond angles are less distorted from ideal than in the conformation **10bA**. The C-O and C-C bond lengths in the ether bridge seem fairly symmetric either side of the molecule and less distorted than in compound **10bA**. The C-O aromatic bond lengths are C19-O6= 1.367 Å and C22-O7= 1.382 Å, and are shorter than the aliphatic C-O bond lengths, which vary between 1.387 Å and 1.433 Å. The C-C bond lengths in the ether chain vary from 1.477 Å to 1.523 Å, which are closer to the expected 1.52 Å[357] for a single C-C bond than in structure **10bA**. The O-C-C and C-O-C bond angles in the ether bridge are also symmetrically distorted. In the S2 half of the molecule, the O-C-C and C-O-C bond angles between the thiophene and the chain are O6-C19-C16= 119.3(6)°, O6-C19-C35= 125.6(9)° and C19-O6-C42= 116.8(6)°. The hydrogen contacts between the thiophene and the ether chain are O6...H12-C35= 2.715 Å and C35-H12...H7-C42= 2.191 Å. Another O...H hydrogen bond with the amine bridge, which is O6...H18-C30= 2.559 Å, might also affect the C19-O6-C42 bond angle. The O-C-C and C-O-C bond angles with the S3 thiophene ring are O7-C22-C1= 124.6(9)°, O7-C22-C27= 119.7(7)° and C22-O7-C32= 115.1(7)°. Similar hydrogen contacts between the S3 thiophene ring and the ether bridge as for the S2 thiophene ring appear, which could also be fictitious. These intramolecular contacts are O7...H35-C1= 2.601 Å, C1-H35...H13-C32= 2.118 Å and C1-H35...H3-C32= 2.736 Å. And finally, there is also an O...H bond with the amine bridge, O7...H9-C29= 2.687 Å. The other O-C-C and C-O-C bond angles are O6-C42-C44= 107.4(7)°, O11-C44-C42= 112.3(7)°, C44-O11-C39= 113.9(7)°, O11-C39-C26= 107.1(7)°, O10-C26-C39= 108.6(8)°, C26-O10-C46= 112.2(7)°, O10-C46-C32= 113.9(8)° and O7-C32-C46= 109.9(8)°. Some hydrogen bonds and some secondary interactions appear on the O-C-C and C-O-C bond angles: O6...H23-C44= 2.700 Å, O6...C44= 2.345 Å, O7...H34-C46= 2.476 Å, O7...C46= 2.381 Å, O6...H18-C30, O7...H9-C29, O11...H27-C42= 2.734 Å, O11...H7-C42= 2.610 Å, O11...C42= 2.379 Å, O10...H3-C32= 2.698 Å, O10...C32= 2.432 Å, C39-H22...H23-C44= 2.156 Å, C39-H22...H10-C44= 1.915 Å, C39-H4...H10-C44= 1.910 Å, C26-H41...H34-C46= 2.489

Å and C26-H26...H34-C46= 2.232 Å, O11...H41-C26= 2.441 Å, O11...C26= 2.357 Å, O10...H4-C39= 2.549 Å and O10...C39= 2.402 Å. In the amine bridge, the S...N interactions are similar to those in the conformation **10bA**, but their effects are different as more competitive interactions appear. The S2...N1 interaction is in competition with hydrogen bonds such as S2...H17-C30= 3.025 Å and O6...H18-C30=2.559 Å which are also close to their counterparts in the structure **10bA**. So, these interactions are almost the same as in the conformation **10bA** as are the resulting bond angles, N1-C30= 1.463 Å, S2-C16-C30= 121.8(6)° and N1-C30-C16= 113.2(5)°. However, the C16-C30= 1.469 Å bond length is 0.038 Å smaller than its corresponding C2-C20 bond length while the C19-C16-C30= 129.0(7)° bond angle is fairly close to its counterpart C21-C2-C20. The sulphur S3 atom is in interaction with the N1 nitrogen's lone pair, but S3 also form hydrogen bonds with H19 and H43, S3...H19-C29= 3.081 Å and S3...H43-C50= 3.128 Å. Those close approaches, together with the other hydrogen interactions within the amine and especially the nitrogen N1, probably weaken the S3...N1 which is 0.074 Å weaker than its counterpart S4...N2. The following bond angles and bond lengths are similar to those in the structure **10bA**, C27-C29= 1.492 Å, N1-C29= 1.436 Å, C22-C27-C29= 130.4(7)°, N1-C29-C27= 113.1(6)°, only S3-C27-C29= 120.3(6)° is significantly different and larger than its counterpart. In the ethyl group, the bond lengths and bond angles are the N1-C47= 1.495 Å, C47-C50= 1.320 Å and N1-C47-C50= 119(1)°. The short C47-C50 bond length is probably due, similarly to the other conformation, to the flexibility of the ethyl group which increases the thermal ellipsoids of the ethyl carbon atoms and lowers the bond length accuracy. Numerous hydrogen bonds and interactions appear on the amine, N1...H43-C50= 2.441 Å, N1...H44-C50= 2.859 Å, C30-H17...H49-C47= 1.980 Å and C29-H9...H39-C47= 2.661 Å. These hydrogen contacts affect the C29-N1-C30= 111.5(6)°, C29-N1-C47= 112(1)° and C30-N1-C47= 106.9(9)° bond angles, which are respectively 1.1° and 4.3° larger, and 4.2° smaller than the corresponding angles in compound **10bA**. Again, these differences have to be affected by the low accuracy.

The two conformations **10bA** and **10bB** are linked together by a few intermolecular hydrogen bonds and interactions such as O1...H49-C47= 2.798 Å, O3...H41-C26= 3.028 Å, O5...H22-C39= 2.976 Å, O6...H25-C48= 3.007 Å, C20-H2...H22-C39= 2.591 Å, C26-H26...H42-C36= 2.510 Å, C33-H32...H22-C29= 2.737 Å, C34-H37...H22-C39= 2.606 Å and C43-H20...H39-C50= 2.387 Å.

Table 77. Least-Squares Planes through thiophene rings

Plane number 1

Atoms Defining Plane	Distance
S(1)	.0006(20)
C(2)	-.0090(52)
C(21)	.0101(54)
C(15)	-.0068(62)
C(17)	-.0010(65)

Additional Atoms	Distance
N(2)	1.3035
C(20)	.0303
O(5)	.0722
O(3)	1.9816
C(25)	.2517
C(34)	.7205
C(43)	3.0975

Mean deviation from plane is .0055 Ångstroms

Chi-squared: 7.0

Plane number 2

Atoms Defining Plane	Distance
S(4)	-.0008(24)
C(4)	.0015(97)
C(5)	.0082(150)
C(28)	.0091(66)
C(38)	-.0132(84)

Additional Atoms	Distance
O(1)	.0077
O(2)	2.0824
N(2)	-.5469
C(31)	.8836
C(33)	.1023

C(36)	1.3753
C(41)	2.6472

Mean deviation from plane is .0066 Ångstroms

Chi-squared: 4.1

Dihedral angles between least-squares planes 1 and 2= 86.52°

Plane number 3

Atoms Defining Plane	Distance
S(2)	-.0012(20)
C(3)	.0285(103)
C(16)	.0087(58)
C(19)	-.0047(57)
C(35)	-.0102(79)

Additional Atoms	Distance
O(6)	-.0178
O(11)	2.0443
N(1)	1.3571
C(30)	.0580
C(39)	2.5430
C(42)	.5166
C(44)	.9565

Mean deviation from plane is .0107 Ångstroms

Chi-squared: 11.4

Dihedral angles between least-squares planes 1 and 3= 44.09°

Dihedral angles between least-squares planes 2 and 3= 127.40°

Plane number 4

Atoms Defining Plane	Distance
S(3)	-.0001(22)
C(1)	-.0010(93)
C(22)	-.0005(66)
C(27)	.0007(63)
C(45)	.0021(107)

Additional Atoms	Distance
O(7)	.0225
O(10)	-1.6959
N(1)	.7177
C(26)	-.8126
C(29)	-.0441
C(32)	-.8421
C(46)	-.9928

Mean deviation from plane is .0009 Ångstroms

Chi-squared: .1

Dihedral angles between least-squares planes 1 and 4= 54.71°

Dihedral angles between least-squares planes 2 and 4= 31.88°

Dihedral angles between least-squares planes 3 and 4= 96.27°

The atom donors O1, O2, O5 and N2 of the conformation **10bA** form a plane, which does not include the atom O3 (deviation= -0.9190 Å). In the molecule **10bB**, the plane is composed by the donor atoms O7, O10, O11 and N1, and does not include the atom O6 (deviation= -0.7955 Å). The two cavity planes form an angle of only 10.58° (table 78).

Table 78. Least-Squares Planes through donor atoms

Plane number 1

Atoms Defining Plane	Distance
O(1)	-.0234(71)
O(2)	.0189(67)
O(5)	-.0053(42)
N(2)	.087(51)

Additional Atoms	Distance
O(3)	-.9190

Mean deviation from plane is .0141 Ångstroms

Chi-squared: 22.6

Plane number 2

Atoms Defining Plane	Distance
O(7)	-.0265(49)
O(10)	.0321(49)
O(11)	-.0224(49)
N(1)	.0178(50)

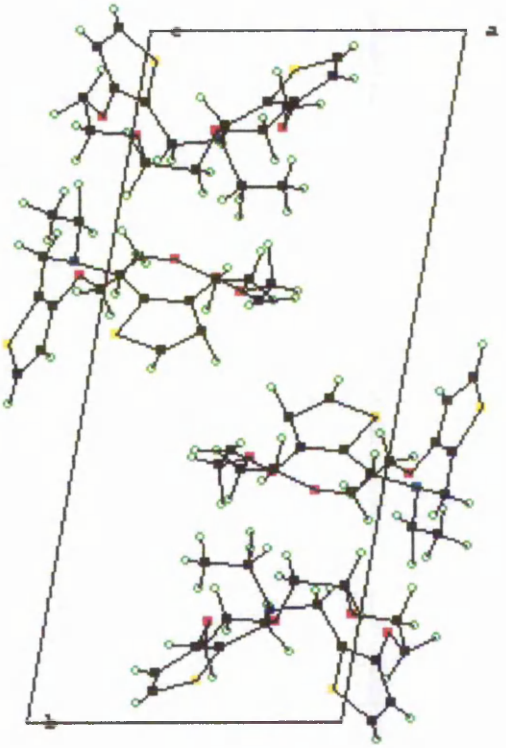
Additional Atoms	Distance
O(6)	-.7955

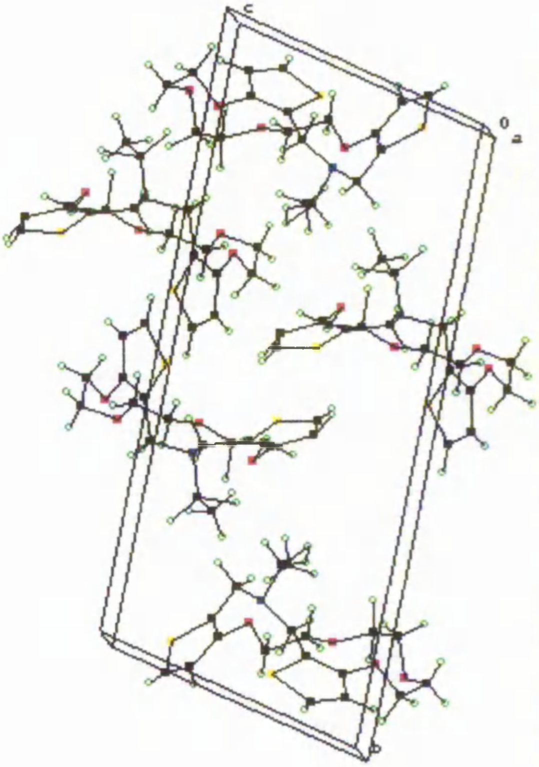
Mean deviation from plane is .0247 Ångstroms

Chi-squared: 104.2

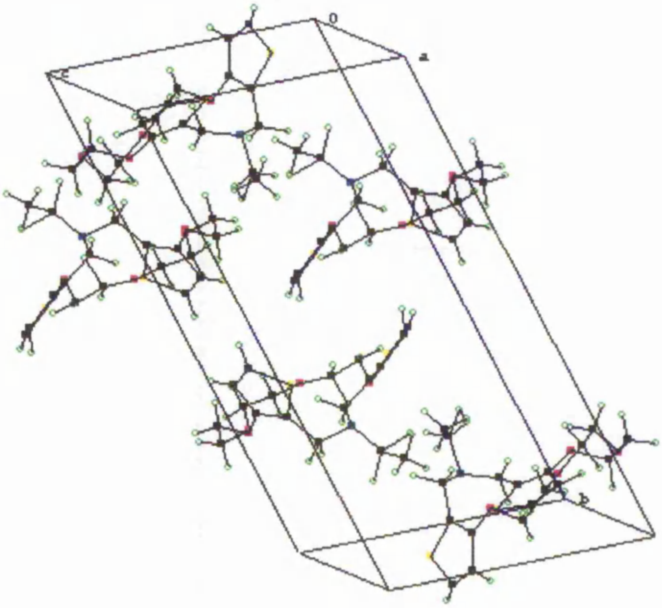
Dihedral angles between least-squares planes 1 and 2= 10.58°

The unit cell contains four molecules, two of each conformation **10bA** and **10bB**. Only two close contacts appear between the molecules **10bA**(x, y, z) and **10bA**(-x, -y, -z) and between the molecules **10bB**(x, y, z) and **10bB**(-x, -y, -z), O2(x, y, z)...H28-C4(-x, -y, -z)= 3.098 Å and S2(x, y, z)...S2(-x, -y, -z)= 4.111 Å. The following views of the cell shows that the four molecules **10bA** (x, y, z), **10bA** (-x, -y, -z), **10bB** (x, y, z) and **10bB** (-x, -y, -z) are arranged along the b axis.

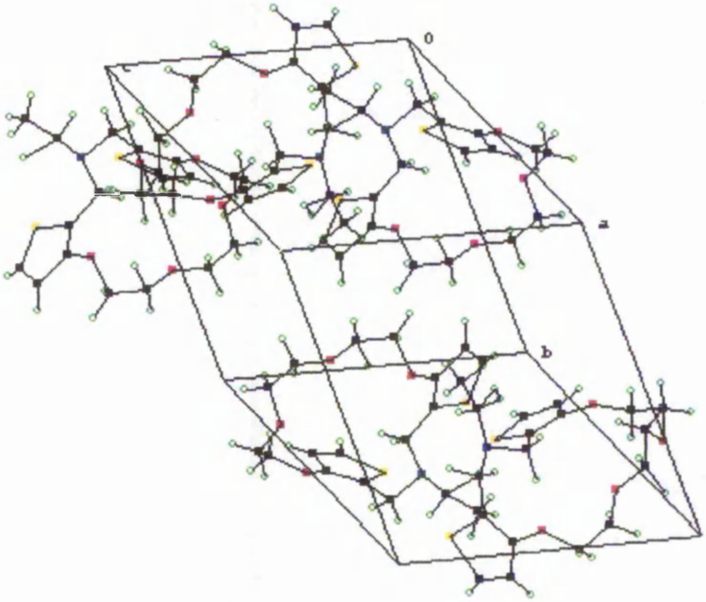




Another view of the cell, below, shows that the S1, S2, S3, and S4 thiophene rings (x, y, z) and (-x, -y, -z) are respectively parallel.

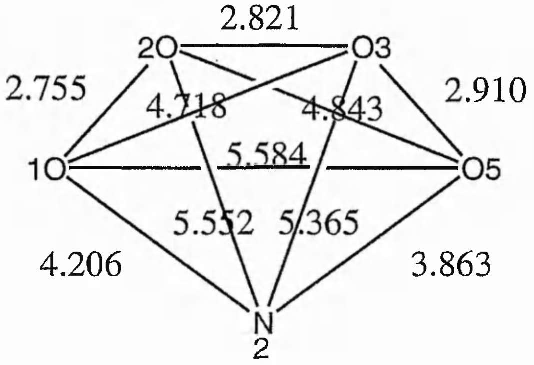


Finally, the following view of the cell shows that the atom donors that form the cavities are almost parallel and arranged in layers.

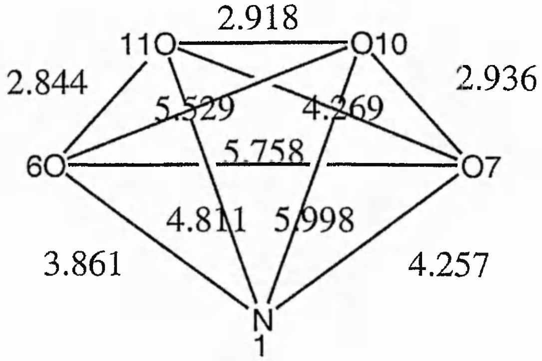


The lone pairs of the oxygens are directed to the macrocyclic cavities. On the contrary, the nitrogen's lone pairs are directed away from the cavity. This is also shown by the S...N interactions.

The two cavities are drawn schematically below.



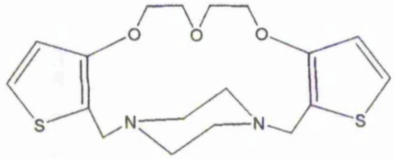
10bA



10bB

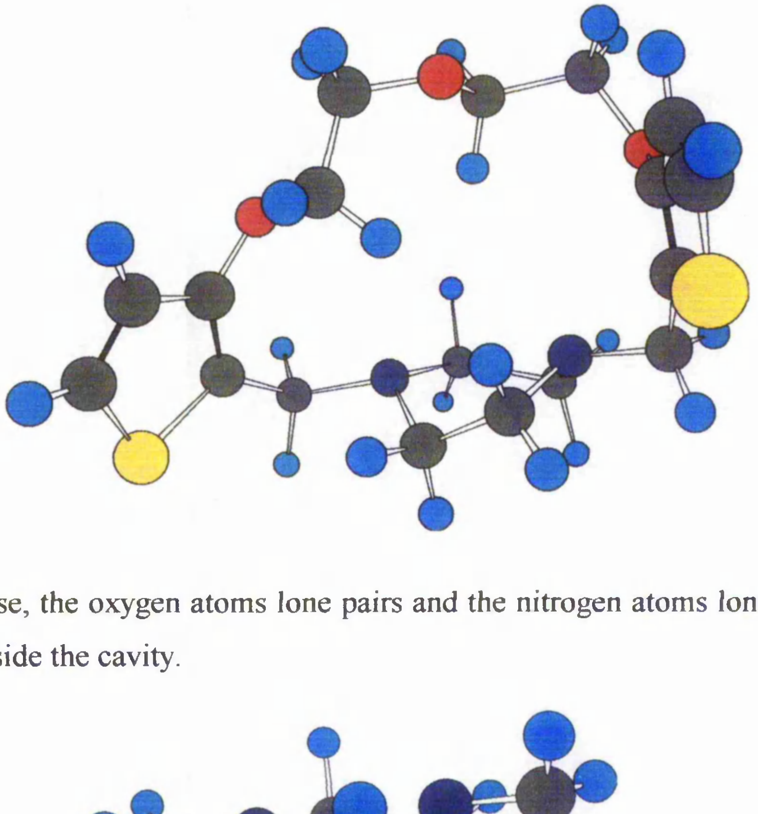
The cavity sizes obtained are larger than the cavity size of the compound **10a**, also larger than the size of cavities in of the macrocycles previously studied by this research group[1,6] and the similar macrocycles found in the literature[95-98]. Indeed, the cavity radius found in the crystal structure of macrocycle **10a** is 0.924 Å, while for the molecules **10bA** and **10bB** it is respectively 0.986 Å and 1.263 Å. Consequently, these macrocycles **10bA** and **10bB** might be able to include a wider range of metal ions (table 1, p23) in their cavity. The addition of an extra OCH_2CH_2 in the macrocyclic ring between the molecules **10a** and **10b** did increase the cavity radii by 0.062 Å and 0.339 Å. It appears that the **10bA**'s cavity is more symmetric than that of **10bB**. In the structure **10bA**, the N2-O2= 5.552 Å, N2-O3= 5.365 Å and O1-O5= 5.584 Å cross-ring distances are clearly longer than those in the compound **10a** (4.607 Å and 5.040 Å). In the molecule **10bB**, the corresponding cross-ring distances have a larger disparity, N1-O11= 4.811 Å, N1-O10= 5.998 Å and O6-O7= 5.758 Å. The nitrogen lone pairs are in both conformations directed to the outside of the cavity as for compound **10a**. However, the great flexibility of these macrocycles **10bA** and **10bB**, which is even larger than for the structure **10a**, should allow them to include a metal ion in their cavities. As is shown in table 78, the donor atoms O1, O2, O5, N2 of conformation **10bA** and the donor atoms O7, O10, O11 and N1 of conformation **10bB** respectively form a plane, which does not include the atoms O3 and O6. Despite this fact, the four oxygen donors of both molecules are nearly planar and could be expected to have a square planar arrangement around a metal cation even if the nitrogen atom is not involved in the bonding.

3.4. Five donor atoms thiophene-based macrocycle (3 oxygens, 2 nitrogens): 18,11,14-trioxa-4,18-dithia-1,21-diaza-tetracyclo[18.4.4.0.0]-pentacosa-3,5,15,16-tetraene **9a**

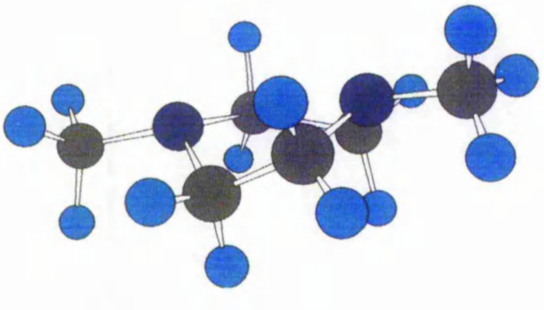


This macrocycle **9a** was modelled by minimization of its energy via the programs MM2 (steric energy) then MOPAC (heat of conformation). This macrocycle contains five donor atoms, as for the compound **10b**. But, instead of 4 oxygen atoms and 1 nitrogen atom, it contains 3 oxygen and 2 nitrogen atoms. It is also more than rigid than the previous compound due to the presence of the cyclodiamine, and so should be a more selective macrocycle in terms of possible coordination to other species.

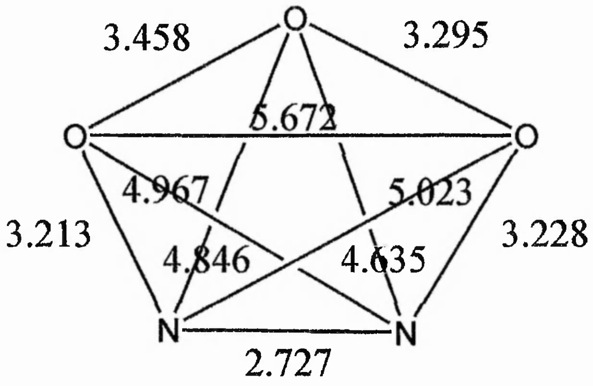
In the first model, the conformation adopted for the piperazine was the boat conformation.



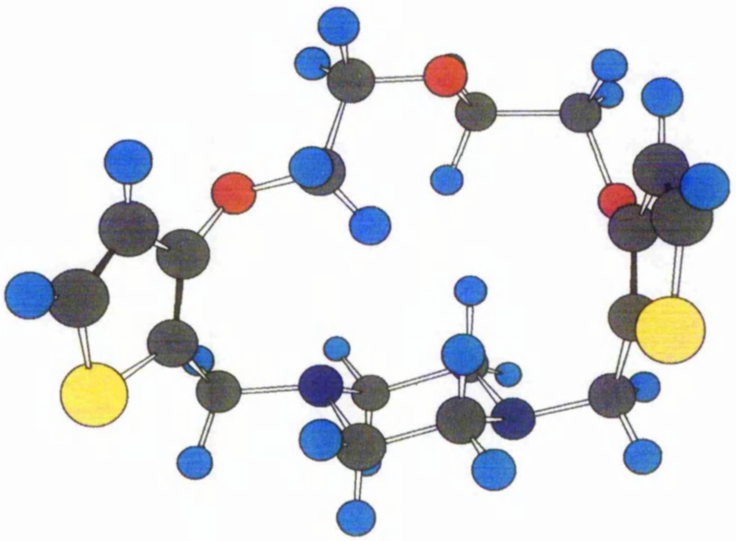
In that case, the oxygen atoms lone pairs and the nitrogen atoms lone pairs were found to point inside the cavity.

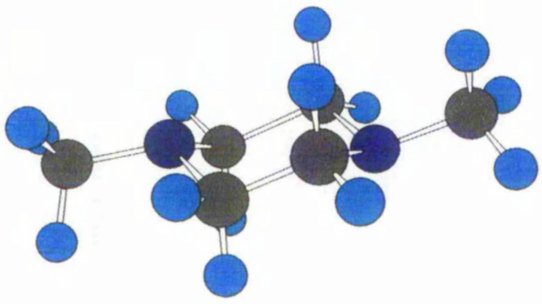


The resulting cavity is schematically drawn below. The radius of this cavity is 0.898Å, which is smaller than for the molecules **10bA** and **10bB** and even than for the macrocyle **10a**. The inclusion of a cyclodiamine in the boat conformation instead of an ethylamine in the macrocycle **9a** compared to the compound **10a** did not increase the size of the cavity. However, the cavity size is still near the ideal size to include a metal ion like Nickel(II). The distances between the donor atoms in the cavity are fairly similar due to the rigidity imposed by the cyclodiamine. The shape of this cavity is similar to those in the molecule **10b**, and especially to the conformation **10bA**. However, the N-O cross-rings in this cavity are from 9.7% to 16.5% shorter and the O-O cross ring is 1.0% longer than in compound **10bA**. Also, the atom donor's lone pairs including the nitrogen's lone pairs are pointing inside the cavity. This added to the flexibility of the macrocycle in solution should allow it to complex and include a metal ion in its cavity.

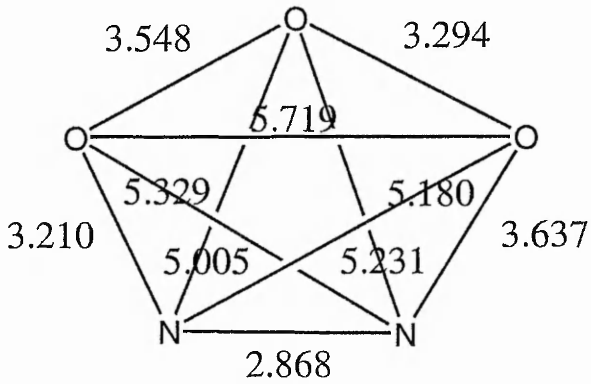


In the second model, the conformation adopted for the piperazine was the chair conformation. In this case, the nitrogen atom lone pairs are not pointing inside the cavity and are directed in opposite direction to each other, so this configuration is less favourable for metal ion coordination. Indeed, Chenevert and Plante[366] studies of *molecular models of macrocyclic polyethers possessing the piperazine subunit indicate* that cyclic compound of this type must be in the boat conformation otherwise there would be a very unfavourable interaction between a metal ion and the lone pairs on the nitrogen atoms.



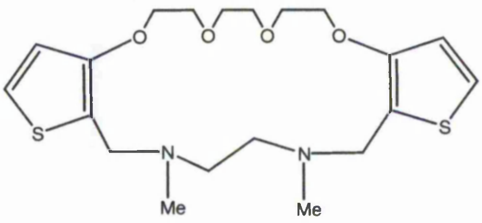


The resulting cavity is schematically drawn on the next page. The distances between the donor atoms in the cavity are again fairly similar due to the rigidity imposed by the cyclodiamine. The nitrogen atoms in the boat conformation are more distant than in the boat conformation: N-N= 2.868 Å instead of 2.727 Å. However, the cross-ring lengths are from 0.047 Å to 0.596 Å longer than in the boat conformation and are closer to those of the molecule **10bA**. This cavity size is larger than for the boat conformation with a cavity radius of 1.083Å. Indeed, the chair conformation gives a larger cavity that could allow bigger metal ions to enter in the cavity and complex with them than the previous conformation. However, only the oxygen atom lone pairs are pointing inside the cavity, while the nitrogen atom lone pairs are pointed away from it. This arrangement of the nitrogen lone pairs is not favorable for a metal ion inclusion inside the cavity. So, if the macrocycle **9a** is in this conformation, the ability to include a metal ion in the cavity could be significantly reduced due to the distortions that would occur on the piperazine if it were required to coordinate to the metal via the nitrogen atoms. However, the macrocycle should still have a relative flexibility in solution, which might allow it to complex and include a metal ion in its cavity, perhaps coordinated to the oxygens only. Both conformations of this macrocycle **9a** should be more selective than the macrocycles **10a** and **10b**.



3.5. Six donor atoms thiophene-based macrocycle (4 oxygens, 2 nitrogens)

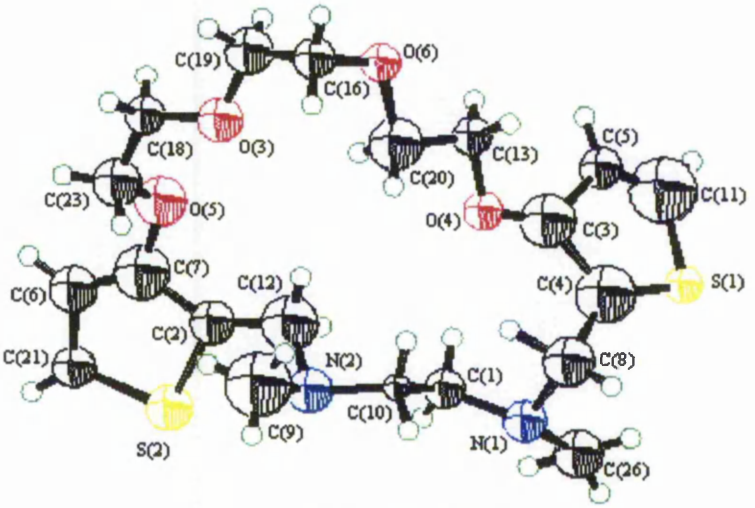
3.5.1. 18,21-bis-(methyl)-2,5,8,11-tetraoxa-15,24-dithia-18,21-diaza-tricyclo[21.3.0.0]-hexacosa-1(26),12(16),13,25-tetraene **8b**



3.5.1.1. Discussion of the structure derived data (tables 27, 28 and 29)

After refinement of this structure, the residuals were R= 0.224 and Rw= 0.232, and the goodness of fit indicator was 8.72. These factors are not very good and the structure refinement was therefore less accurate than for most of the structures discussed earlier. This was due to the poor quality of the data.

The positions and isotropic displacement parameters of the atoms in the macrocycle are best visualized in the "ortep style" drawing below[353].



The more tightly bound (i.e. attached to more atoms) an atom is, the lower its thermal displacement is expected to be. This is however not the case in the carbons C2 and C4 (bound to three carbons) and in the carbons C3 and C7 (each bound to one oxygen and two carbons). This could be due to the fact that these carbon atoms are part of the thiophene rings, which are on the outer-edge of the molecule. The methyl carbons C9 and C26 bonded to the nitrogen atoms are fairly free to vibrate and this is reflected in their large displacement parameters. In the ether and diamine bridges, the displacement parameters are also significant especially for the atoms O5, C19, C20 and C23 for the ether bridge, and the atoms C8 and C12 for the diamine bridge. This is due to the great flexibility of the ether bridges. Indeed, the flexibility of the whole molecule is increased similarly to the molecules **10bA** and **10bB** by the inclusion of an extra OCH_2CH_2 in the ether chain and by the substitution of the ethylamine by a dimethyldiamine.

3.5.1.2. Discussion of the structural geometry

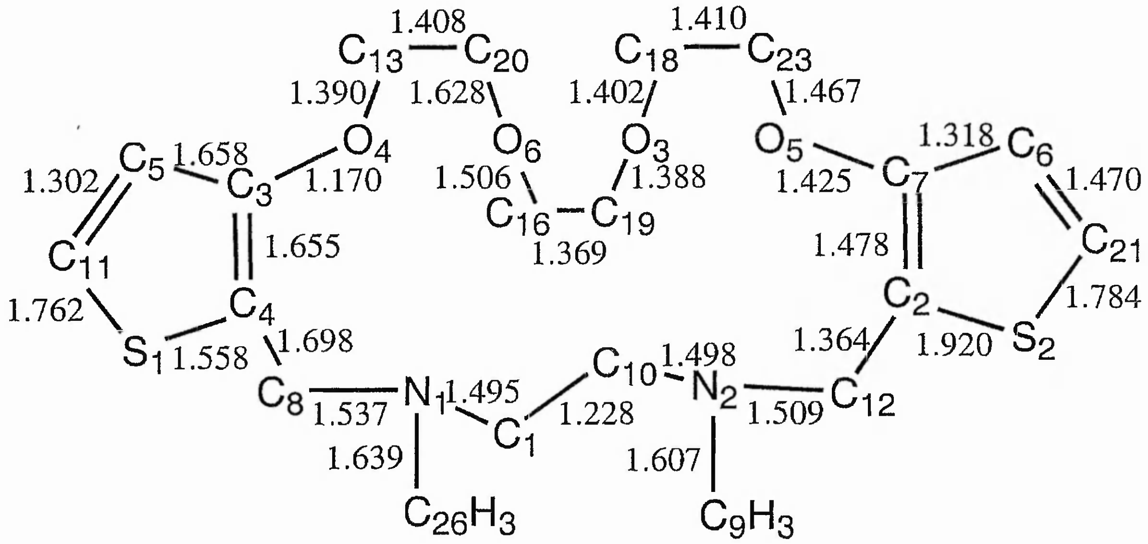
Table 79. Bond Lengths(Å)

Bond Lengths(Å)			
Bond	Length(Å)	Bond	Length(Å)
S(1) -C(4)	1.56(5)	C(2) -C(7)	1.48(5)
S(1) -C(11)	1.76(8)	C(2) -C(12)	1.36(5)
S(2) -C(2)	1.92(5)	C(3) -C(4)	1.66(7)
S(2) -C(21)	1.78(4)	C(3) -C(5)	1.66(7)
O(3) -C(18)	1.40(3)	C(4) -C(8)	1.70(7)
O(3) -C(19)	1.39(5)	C(5) -C(11)	1.30(4)
O(4) -C(3)	1.17(5)	C(6) -C(7)	1.32(6)
O(4) -C(13)	1.39(5)	C(6) -C(21)	1.47(7)
O(5) -C(7)	1.43(6)	C(9) -H(2)	0.887
O(5) -C(23)	1.47(5)	C(13) -C(20)	1.41(3)
O(6) -C(16)	1.51(5)	C(13) -H(8)	0.707
O(6) -C(20)	1.63(6)	C(16) -C(19)	1.37(5)
N(1) -C(1)	1.50(4)	C(16) -H(5)	1.11
N(1) -C(8)	1.54(5)	C(18) -C(23)	1.41(5)
N(1) -C(26)	1.64(6)	C(19) -H(1)	1.216
N(2) -C(9)	1.61(7)	C(23) -H(11)	1.162
N(2) -C(10)	1.50(3)	C(26) -H(3)	0.88
N(2) -C(12)	1.51(7)	C(26) -H(4)	0.947
C(1) -C(10)	1.23(5)	C(26) -H(6)	0.967
C(1) -H(10)	0.951		

** Note the hydrogen bond lengths are to three decimal places with terminal zero's omitted and have no esd's as the hydrogen positions were not refined.

In this structure **8b**, the thermal parameters are all large and so affect the accuracy of the bond lengths and bond angles. This is due to the poor quality of the data obtained.

For ease of description the bond lengths (to 3 decimal places) are shown on a schematic drawing below.



It would be expected that the halves of the macrocycle **8b** (the molecule is chemically mirrored respectively through C16-C19 and C1-C10) would have the same bond lengths. As with other structures discussed earlier, this is not the case as in the crystal, the two halves of the molecule are crystallographically independent and have differing geometries reflected in the bond lengths. The bond lengths and angles are distorted by the low accuracy of the structure as can be seen in the tables.

Table 80. Bond Angles(°)

Bond Angles(°)			
Bond	Angle(°)	Bond	Angle(°)
C(4) -S(1) -C(11)	95(2)	O(5) -C(7) -C(2)	106(4)
C(2) -S(2) -C(21)	97(2)	O(5) -C(7) -C(6)	124(4)
C(18) -O(3) -C(19)	115(3)	C(2) -C(7) -C(6)	130(5)
C(3) -O(4) -C(13)	112(3)	N(1) -C(8) -C(4)	107(4)
C(7) -O(5) -C(23)	116(3)	N(2) -C(9) -H(2)	108.23

C(16) -O(6) -C(20)	118(3)	N(2) -C(10) -C(1)	122(3)
C(1) -N(1) -C(8)	105(3)	S(1) -C(11) -C(5)	107(3)
C(1) -N(1) -C(26)	122(2)	N(2) -C(12) -C(2)	113(4)
C(8) -N(1) -C(26)	113(3)	O(4) -C(13) -C(20)	100(3)
C(9) -N(2) -C(10)	113(2)	O(4) -C(13) -H(8)	85.46
C(9) -N(2) -C(12)	109(3)	C(20) -C(13) -H(8)	165.1
C(10) -N(2) -C(12)	107(3)	O(6) -C(16) -C(19)	104(3)
N(1) -C(1) -C(10)	122(3)	O(6) -C(16) -H(5)	117.83
N(1) -C(1) -H(10)	105.48	C(19) -C(16) -H(5)	93.59
C(10) -C(1) -H(10)	95.13	O(3) -C(18) -C(23)	117(3)
S(2) -C(2) -C(7)	95(3)	O(3) -C(19) -C(16)	115(4)
S(2) -C(2) -C(12)	120(3)	O(3) -C(19) -H(1)	88.14
C(7) -C(2) -C(12)	144(4)	C(16) -C(19) -H(1)	105.72
O(4) -C(3) -C(4)	138(3)	O(6) -C(20) -C(13)	104(3)
O(4) -C(3) -C(5)	130(3)	S(2) -C(21) -C(6)	108(3)
C(4) -C(3) -C(5)	87(4)	O(5) -C(23) -C(18)	113(3)
S(1) -C(4) -C(3)	123(3)	O(5) -C(23) -H(11)	141.12
S(1) -C(4) -C(8)	135(3)	C(18) -C(23) -H(11)	105.51
C(3) -C(4) -C(8)	100(4)	N(1) -C(26) -H(3)	57.54
C(3) -C(5) -C(11)	127(4)	N(1) -C(26) -H(4)	154.41
C(7) -C(6) -C(21)	110(4)	N(1) -C(26) -H(6)	97.31
H(3) -C(26) -H(4)	104.62	H(4) -C(26) -H(6)	94.69
H(3) -C(26) -H(6)	152.42		

** Note the bond angles including hydrogen atoms are to two decimal places with terminal zeros omitted and have no esd's as the hydrogen atom positions were not refined.

Each thiophene ring forms a plane. Those planes are at an angle of 112°. The S2 thiophene plane includes the atoms O5 and C12, which are directly bonded to the S2 thiophene ring. The S2 sulphur atom is in interaction with the N2 nitrogen lone pair, S2…N2= 3.283 Å. This S…N interaction might create an electron withdrawing and/or a π delocalisation. The distortions in the S2 thiophene ring bond lengths and bond angles are however more due to the thermal displacements than to a conjugation, S2-C2= 1.920 Å, S2-C6= 1.470 Å, C2-C7= 1.478 Å, C6-C21= 1.470 Å, C6-C7= 1.318 Å, C2-S2-C21= 97(2)°, S2-C2-C7= 95(3)°, S2-C21-C6= 108(3)°, C2-C7-C6= 130(5)° and C7-C6-C21= 110(4)°. The bond lengths and bond angles between the S2 thiophene and the bridges are also affected as C2-C12= 1.364 Å, O5-C7= 1.425 Å, S2-C2-C12= 120(3)°, C7-C2-C12=

144(4)°, C2-C7-O5= 106(4)° and O5-C7-C6= 124(4)°. A few intramolecular close contacts appear, which could be fictitious, such as the S2...N2 interaction but also the S2...C12= 2.856 Å, S2...H23-C12= 3.003 Å, O5...H22-C12= 2.747 Å and O5...H14-C6= 2.689 Å. The S1 thiophene ring plane includes the atoms O4 and C8, which are directly bonded to the S1 thiophene, but also the carbon atom C20 which is part of the ether bridge. The distortions observed for the S1 thiophene ring are different and the S1 sulphur atom is not close enough to interact with the N1 nitrogen lone pair, S1...N1= 3.711 Å (sum of the van der Waals radii= 3.45 Å). However, the S1 sulphur atom may interact with other atoms of the amine bridge, S1...C8= 3.007 Å and S1...H6-C26= 2.816 Å. The resulting bond lengths and bond angles in the S1 thiophene ring are S1-C4= 1.558 Å, S1-C11= 1.762 Å, C3-C4= 1.655 Å, C5-C11= 1.302 Å, C3-C5= 1.658 Å, C4-S1-C11= 95(2)°, S1-C4-C3= 123(3)°, S1-C11-C5= 107(3)°, C3-C5-C11= 127(4)° and C4-C3-C5= 87(4)°. The bond lengths and bond angles between the S1 thiophene and the bridges are also affected and strongly distorted C4-C8= 1.698 Å, O4-C3= 1.170 Å, S1-C4-C8= 135(3)°, C3-C4-C8= 100(4)°, O4-C3-C4= 138(3)° and O4-C3-C5= 130(3)°. Some hydrogen bonds between the S1 thiophene ring and the ether bridge may occur O4...H7-C8= 2.136 Å, O4...H17-C1= 2.507 Å, O4...H20-C1= 2.684 Å and O4...H13-C5= 2.843 Å.

In the ether chain, the C-O and C-C bond lengths are widely distorted and respectively vary from 1.388 Å to 1.638 Å and from 1.369 Å to 1.410 Å (expected C-C single bond length = 1.52 Å[357]), as well as the O-C-C and C-O-C bond angles, C3-O4-C13= 112(3)°, O4-C13-C20= 100(3)°, O6-C20-C13= 104(3)°, C16-O6-C20= 118(3)°, O6-C16-C19= 104(3)°, O3-C19-C16= 115(4)°, C18-O3-C19= 115(3)°, O3-C18-C23= 117(3)°, O5-C23-C18= 113(3)° and C7-O5-C23= 116(3)°, compared to the macrocycle **10b**. There may be some hydrogen close contacts appearing in the ether bridge, which are C5-H13...H25-C13= 2.319 Å, O4...H31-C20= 2.275 Å, O4...H32-C20= 2.386 Å, O6...H25-C13= 2.621 Å, O6...H24-C13= 2.505 Å, O3...H5-C16= 2.415 Å, O3...H34-C23= 2.553 Å, C19-H30...H27-C18= 2.321 Å and O5...H28-C18= 2.509 Å.

In the diamine bridge, the resulting bond lengths are symmetric. Indeed, the bond lengths are N1-C8= 1.537 Å, N2-C12= 1.509 Å, N1-C26= 1.639 Å, N2-C9= 1.607 Å, N1-C1= 1.495 Å, N2-C10= 1.498 Å and C1-C10= 1.228 Å. On the S2 thiophene edge of the diamine chain, only three close contacts seem to appear O5...H22-C12, S2...H23-C12, S2...C12, and the strongest which is S2...N2. The S1 thiophene does not have an S...N interaction, but there could be other close approaches: S1...C8, S1...H19-C8, S1...H6-C26, S1...H21-C10, O4...H7-C8, O4...H17-C1 and O4...H20-C10. However, the bond angles are different in the two halves of the diamine. The very short C1-C10 bond length might be explained by the poor quality of the data. The effect of the S2...N2 interaction increases the angle N2-C12-C2= 113(4)° (6° larger than its counterpart N1-C8-C4= 107(4)°), and the respective torsion angles are S2-C2-C12-N2= -59(6)° and S1-C4-C8-N1= -88(5)°. The C1-N1-C8= 105(3)° is fairly similar to its counterpart C10-N2-C12= 107(4)°. The other C-N-C bond angles are C1-N1-C26= 122(2)° and C8-N1-C26= 113(3)°, which are respectively 9° and 4° larger than their counterparts C9-N2-C10= 113(2)° and C9-N2-C12= 109(3)°, due to the secondary interactions which are different in each amine. The remaining bond angles are N1-C1-C10= 122(3)° and N2-C10-C1= 122(3)°, and the torsion angle between N1 and N2 is N1-C1-C10-N2= -151(3)°.

Table 81. Least-Squares Planes

Plane number 1

Atoms Defining Plane	Distance
S(1)	-.0073(92)
C(4)	.129(44)
C(3)	-.043(30)
C(5)	.003(34)
C(11)	.073(54)

Additional Atoms	Distance
C(8)	.005
C(26)	2.044
C(1)	2.136
N(1)	1.396
O(4)	.199
O(6)	-.981
C(13)	-.453
C(20)	-.104
C(16)	-1.152

Mean deviation from plane is .0509 Ångstroms
Chi-squared: 11.9

Plane number 2

Atoms Defining Plane	Distance
S(2)	-.002(11)
C(2)	.040(38)
C(6)	.017(37)
C(7)	-.033(33)
C(21)	.011(31)

Additional Atoms	Distance
C(19)	1.048
C(18)	1.098
C(23)	1.133
C(12)	-.079
C(9)	2.435
C(10)	.710
N(2)	1.005
O(3)	1.191
O(5)	-.058

Mean deviation from plane is .0206 Ångstroms

Chi-squared: 2.3

Dihedral angles between least-squares planes 1 and 2= 112°

Plane number 3

Atoms Defining Plane	Distance
O(3)	.527(22)
O(4)	-.602(23)
O(5)	-1.039(28)
O(6)	.160(22)
N(1)	.213(29)
N(2)	.765(31)

Additional Atoms	Distance
S(1)	-1.906
S(2)	-.915

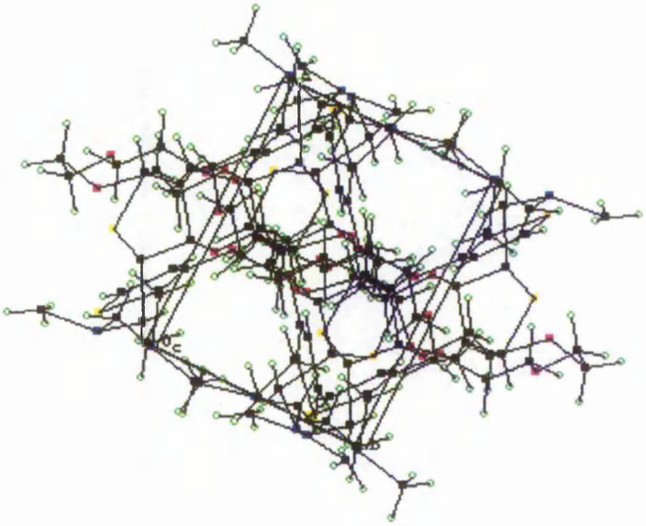
Mean deviation from plane is .5509 Ångstroms

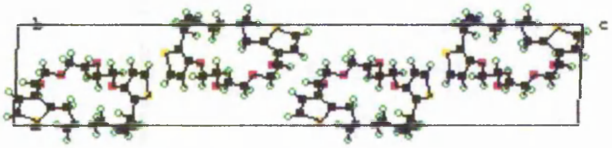
Chi-squared: 3315.6

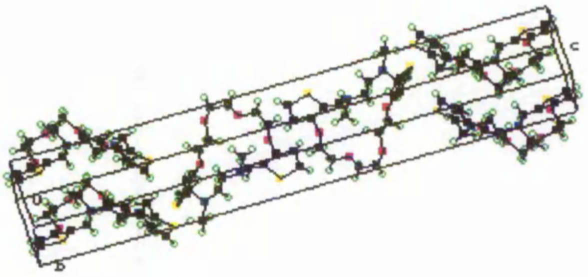
Dihedral angles between least-squares planes 1 and 3= 122°

Dihedral angles between least-squares planes 2 and 3= 14°

Three intermolecular O...H and S...H bonds appear in the unit cell: S1(x, y, z)...H15-C11(-x, ½+y, ½-z)= 3.031Å, S1(x, ½-y, ½+z)...H15-C11(-x, -y, -z)= 3.031Å, O5(-x, ½+y, ½-z)...H14-C6(x, ½-y, ½+z)= 2.716 Å. The following views of the unit cell show that the molecules are all arranged along the c axis.

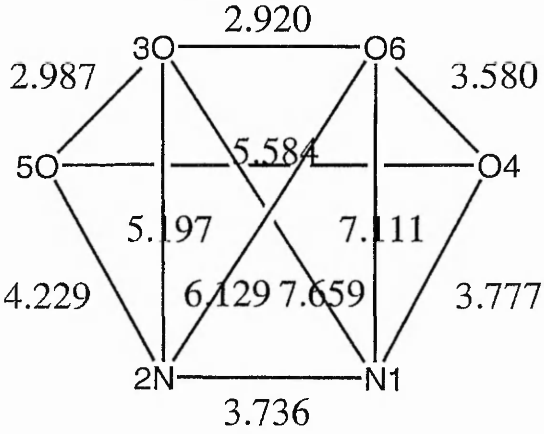






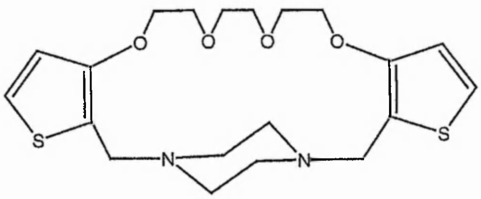
The donor atoms that form the cavity are not at all planar as is shown in the table of least squares above (table 81). The lone pairs of the oxygens are directed to the macrocyclic cavity. The nitrogen lone pairs are, as for the macrocycles **10a** and **10b**, directed away from the cavity, but in opposite directions as the N1's lone pair is directed above the cavity and the N2's lone pair is directed below the cavity, which is shown by the S2...N2 interaction.

The cavity is drawn schematically below.



The cross-ring distances as well as the entire cavity are not symmetric. Indeed, the cross-ring lengths are N1-O3= 7.659 Å, N2-O6= 6.129 Å and O4-O5= 5.584 Å, and considerably longer than the cross-ring distances in the preceding molecules. Also, the distance between the nitrogen atoms of the flexible dimethyldiamine chain N1-N2= 3.736 Å is significantly longer than in the modelled macrocycle **9a** in either the boat or the chair conformation of the rigid piperazine unit. The resulting cavity radius= 1 Å was assimilated as the mean distance of the donor atoms from their centroid as determined by Lindoy and co-workers[98-102], while the cavity radius obtained by the conventional approach is 0.773 Å, which consists of defining the diameter of the cavity as the distance between diametrically opposed donors. The general method gives a cavity size which is smaller than for the preceding molecules and so lowers the range of metal ions which can complex in the cavity (see table 1 p23), while the other approach gives a cavity that is again quite close to cavity size of the compounds **10a** and **10b**, but it is especially close to the modelled chair conformation of compound **9a**. Despite the close cavity radii between **9a** and **8b**, the macrocycle **8b** should be less selective due to its wide flexibility compared to **9a**, and both will be less selective than the macrocycles **10a** and **10b**. The nitrogen lone pairs are both directed to the outside of the cavity as for compounds **10a**, **10b** and the chair conformation of molecule **9a**. However, the great flexibility of this macrocycle and the presence of six donor atoms, which is ideal for complexation to a transition metal ion, should allow this macrocycle to include a metal ion in the macrocyclic cavity.

3.5.2. 2,5,8,11-tetraoxa-15,26-dithia-18,21-diaza-tetracyclo[21.4.4.0.0]-octacosa-1(25),27,12(16),13-tetraene **9b**

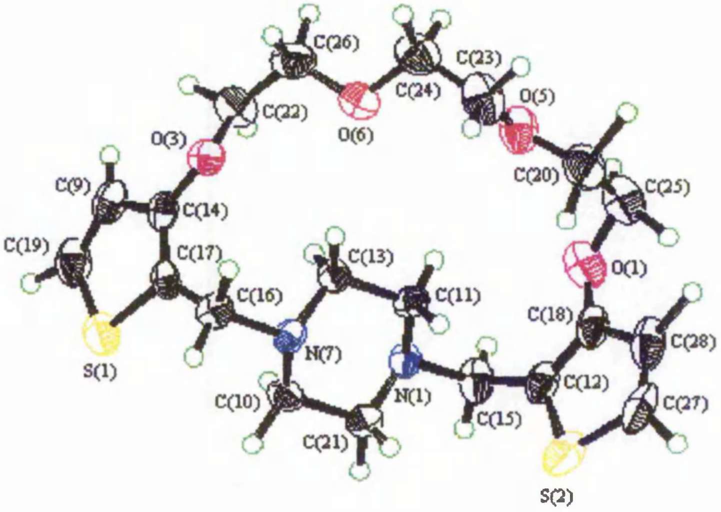


3.5.2.1. Discussion of the structure derived data (tables 27, 30 and 31)

Eight molecules are present in the unit cell and the space group is Pbca or n°61. The crystal system is orthorhombic.

The greatest displacement occurs at the extremities of the molecules. Greater displacement is expected for atoms at the outer regions of the molecule such as the atoms S1, S2, C9, C19, C27 and C28. The sulphur atoms S1 and S2 are not only on the outer regions of the molecule, they are also the heaviest atoms. On the other hand, the more tightly bound (i.e. attached to more atoms) an atom is, the lower its displacement is expected to be. This is shown in the nitrogen atoms N1 and N7 (bound to three carbons), and also in the carbons C12 and C17 (bound to three carbons) and in the carbons C14 and C18 (each bound to one oxygen and two carbons). This could be due to the fact that those carbon atoms are part of the thiophene rings, which are on the outer-edge of the molecule. The nitrogen N1 and N7 have smaller thermal ellipsoids than their counterpart in the macrocycle **8b**. This is due to the rigidity of the cyclodiamine compared to the dimethyldiamine in compound **8b**. This rigidity is also reflected on the thermal parameters of the carbon atoms of the diamine. Indeed, the carbon atoms C10, C11, C13 and C21 have smaller displacement parameters than their counterparts in compound **8b**. In the ether bridge, the displacement parameters are also significant due to the flexibility.

The positions and anisotropic displacement parameters of the atoms in the macrocycle are best-visualized in the "ortep style" drawing below[353].



3.5.3.2. Discussion of the structural geometry

Table 82. Bond Lengths(Å)

Bond Lengths(Å)			
Bond	Length(Å)	Bond	Length(Å)
S(1) -C(17)	1.728(6)	C(11) -H(13)	1.038
S(1) -C(19)	1.705(7)	C(12) -C(15)	1.510(8)
S(2) -C(12)	1.703(6)	C(12) -C(18)	1.379(8)
S(2) -C(27)	1.717(8)	C(13) -H(4)	1.024
O(1) -C(18)	1.379(7)	C(13) -H(16)	1.111
O(1) -C(25)	1.443(7)	C(14) -C(17)	1.346(7)
O(3) -C(14)	1.379(7)	C(15) -H(8)	0.822
O(3) -C(22)	1.424(6)	C(15) -H(15)	1.105
O(5) -C(20)	1.430(7)	C(16) -C(17)	1.519(7)
O(5) -C(23)	1.423(7)	C(16) -H(3)	1.015
O(6) -C(24)	1.412(7)	C(16) -H(17)	1.086
O(6) -C(26)	1.433(7)	C(18) -C(28)	1.420(9)
N(1) -C(11)	1.463(6)	C(19) -H(2)	1.038
N(1) -C(15)	1.472(7)	C(20) -C(25)	1.521(9)
N(1) -C(21)	1.464(7)	C(20) -H(18)	1.29
N(7) -C(10)	1.460(7)	C(20) -H(28)	1.283
N(7) -C(13)	1.463(6)	C(21) -H(5)	0.972
N(7) -C(16)	1.479(6)	C(21) -H(9)	1.124

C(9) -C(14)	1.435(8)	C(22) -C(26)	1.452(8)
C(9) -C(19)	1.323(8)	C(22) -H(7)	1.006
C(9) -H(1)	0.894	C(22) -H(27)	1.181
C(10) -C(21)	1.528(7)	C(23) -C(24)	1.499(9)
C(10) -H(10)	0.924	C(23) -H(20)	1.061
C(10) -H(11)	1.13	C(23) -H(22)	1.071
C(11) -C(13)	1.517(7)	C(24) -H(21)	1.062
C(11) -H(12)	0.968	C(24) -H(23)	1.194
C(25) -H(14)	0.948	C(27) -C(28)	1.322(9)
C(25) -H(25)	1.219	C(27) -H(26)	1.151
C(26) -H(6)	1.076	C(28) -H(19)	1.281
C(26) -H(24)	1.172		

** Note the hydrogen bond lengths are to three decimal places with terminal zero's omitted and have no esd's as the hydrogen positions were not refined.

The bond lengths and bond angles in both halves of the molecule are fairly symmetric, especially in the ether and diamine bridges. The distortions are reflected in the bond angles that are shown in the following table (table 83). This close symmetry may be due to the cyclodiamine rigidity.

For ease of description the bond lengths (to 3 decimal places) are shown on a schematic drawing below.

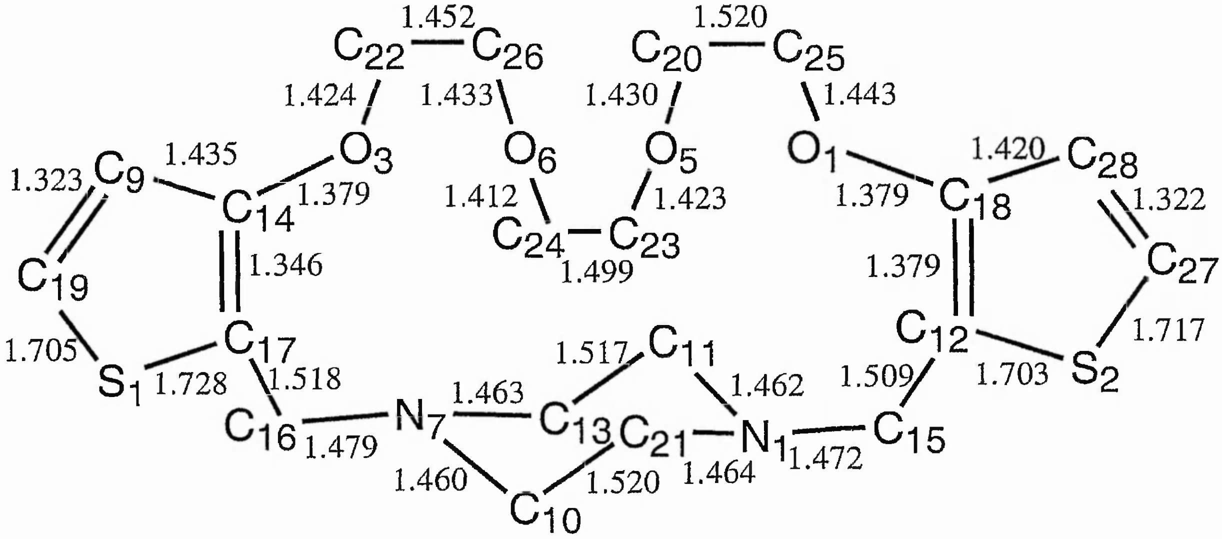


Table 83. Bond Angles(°)

Bond Angles(°)			
Bond	Angle(°)	Bond	Angle(°)
C(17) -S(1) -C(19)	92.1(3)	H(12) -C(11) -H(13)	115.19
C(12) -S(2) -C(27)	92.4(3)	S(2) -C(12) -C(15)	124.8(5)
C(18) -O(1) -C(25)	117.2(5)	S(2) -C(12) -C(18)	110.1(5)
C(14) -O(3) -C(22)	114.7(4)	C(15) -C(12) -C(18)	125.1(6)
C(20) -O(5) -C(23)	109.7(5)	N(7) -C(13) -C(11)	110.0(4)
C(24) -O(6) -C(26)	110.9(5)	N(7) -C(13) -H(4)	115.27
C(11) -N(1) -C(15)	114.0(4)	N(7) -C(13) -H(16)	102.53
C(11) -N(1) -C(21)	108.8(4)	C(11) -C(13) -H(4)	103.8
C(15) -N(1) -C(21)	114.3(4)	C(11) -C(13) -H(16)	112.65
C(10) -N(7) -C(13)	110.4(4)	H(4) -C(13) -H(16)	112.89
C(10) -N(7) -C(16)	112.4(4)	O(3) -C(14) -C(9)	125.3(6)
C(13) -N(7) -C(16)	110.8(4)	O(3) -C(14) -C(17)	121.5(5)
C(14) -C(9) -C(19)	112.4(6)	C(9) -C(14) -C(17)	113.3(6)
C(14) -C(9) -H(1)	109.3	N(1) -C(15) -C(12)	115.8(5)
C(19) -C(9) -H(1)	138.15	N(1) -C(15) -H(8)	104.1
N(7) -C(10) -C(21)	109.8(5)	N(1) -C(15) -H(15)	105.34
N(7) -C(10) -H(10)	113.94	C(12) -C(15) -H(8)	101.4
N(7) -C(10) -H(11)	114.32	C(12) -C(15) -H(15)	119.48
C(21) -C(10) -H(10)	99.96	H(8) -C(15) -H(15)	109.59
C(21) -C(10) -H(11)	107.92	N(7) -C(16) -C(17)	115.7(4)
H(10) -C(10) -H(11)	109.8	N(7) -C(16) -H(3)	101.66
N(1) -C(11) -C(13)	109.9(4)	N(7) -C(16) -H(17)	102.76
N(1) -C(11) -H(12)	108.87	C(17) -C(16) -H(3)	112.58
N(1) -C(11) -H(13)	106.25	C(17) -C(16) -H(17)	110.85
C(13) -C(11) -H(12)	104.48	H(3) -C(16) -H(17)	112.7
C(13) -C(11) -H(13)	112.15	S(1) -C(17) -C(14)	110.0(5)
S(1) -C(17) -C(16)	121.4(4)	O(5) -C(23) -C(24)	111.1(5)
C(14) -C(17) -C(16)	128.6(5)	O(5) -C(23) -H(20)	122.97
O(1) -C(18) -C(12)	118.7(6)	O(5) -C(23) -H(22)	111.34
O(1) -C(18) -C(28)	128.6(6)	C(24) -C(23) -H(20)	110.92
C(12) -C(18) -C(28)	112.7(7)	C(24) -C(23) -H(22)	110.56
S(1) -C(19) -C(9)	112.2(5)	H(20) -C(23) -H(22)	87.47
S(1) -C(19) -H(2)	105.12	O(6) -C(24) -C(23)	109.1(6)
C(9) -C(19) -H(2)	142.59	O(6) -C(24) -H(21)	114.79
O(5) -C(20) -C(25)	109.3(6)	O(6) -C(24) -H(23)	113.1

O(5) -C(20) -H(18)	100.51	C(23) -C(24) -H(21)	111.47
O(5) -C(20) -H(28)	108.94	C(23) -C(24) -H(23)	103.31
C(25) -C(20) -H(18)	103.66	H(21) -C(24) -H(23)	104.42
C(25) -C(20) -H(28)	106.29	O(1) -C(25) -C(20)	111.3(5)
H(18) -C(20) -H(28)	127.27	O(1) -C(25) -H(14)	100.57
N(1) -C(21) -C(10)	108.8(4)	O(1) -C(25) -H(25)	90.95
N(1) -C(21) -H(5)	115.96	C(20) -C(25) -H(14)	103.92
N(1) -C(21) -H(9)	115.33	C(20) -C(25) -H(25)	96.98
C(10) -C(21) -H(5)	114.23	H(14) -C(25) -H(25)	150.36
C(10) -C(21) -H(9)	108.88	O(6) -C(26) -C(22)	111.3(5)
H(5) -C(21) -H(9)	92.86	O(6) -C(26) -H(6)	107.77
O(3) -C(22) -C(26)	112.6(5)	O(6) -C(26) -H(24)	109.26
O(3) -C(22) -H(7)	115.17	C(22) -C(26) -H(6)	109.37
O(3) -C(22) -H(27)	111.56	C(22) -C(26) -H(24)	111.29
C(26) -C(22) -H(7)	116.47	H(6) -C(26) -H(24)	107.77
C(26) -C(22) -H(27)	122.04	S(2) -C(27) -C(28)	111.9(6)
H(7) -C(22) -H(27)	73.86	S(2) -C(27) -H(26)	113.37
C(28) -C(27) -H(26)	133.75	C(18) -C(28) -H(19)	119.29
C(18) -C(28) -C(27)	113.0(7)	C(27) -C(28) -H(19)	126.46

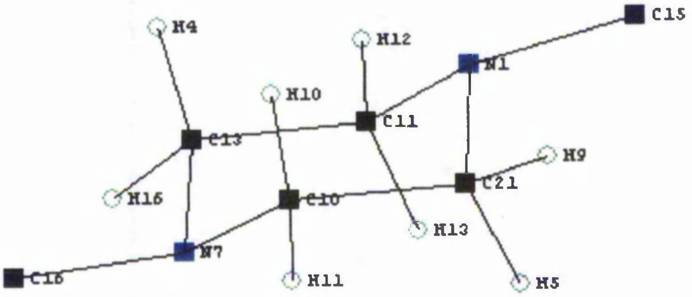
** Note the bond angles including hydrogen atoms are to two decimal places with terminal zeros omitted and have no esd's as the hydrogen atom positions were not refined.

The thiophene rings are both planar and include in their planes the oxygen and the carbon atoms directly bonded to them. Those two planes form an angle of 12.28°. The thiophene's bond lengths and bond angles are fairly close to each other and they are similar to those in unsubstituted thiophene[354]. The S1 thiophene ring bond lengths and bond angles are S1-C19= 1.705 Å, S1-C17= 1.728 Å, C9-C19= 1.323 Å, C14-C17= 1.346 Å, C9-C14= 1.435 Å, C17-S1-C19= 92.1(3)°, S1-C17-C14= 110.0(5)°, S1-C19-C9= 112.2(5)°, C9-C14-C17= 113.3(6)° and C14-C9-C19= 112.4(6)°. However, the non-substituted C=C bond length is shorter than its counterpart in unsubstituted thiophene. But, this unsubstituted C-C double bond is situated on the outer edge of the S1 thiophene ring, so this bond could be wagging with thermal motion as shown on the diagram and this could lower the bond length accuracy. In the S2 thiophene ring, the S-C bond lengths are reversed compare to the S1 thiophene ring, S2-C27= 1.717 Å, S2-C12= 1.703 Å. The C27-C28= 1.322 Å bond length is almost the same as its counterpart in thiophene S1 and its shortness could be due to similar reasons, but the C12-C18= 1.379 Å is more significantly longer C27-C28 while keeping a double bond character. Whereas the C18-C28= 1.420 Å bond length is similar to the C-C bond length in the non-substituted thiophene. The S2 thiophene bond angles are C12-S2-C27= 92.4(3)°, S2-C12-C18= 110.1(5)°, S2-C27-C28= 111.9(6)°, C12-C18-C28= 112.7(7)° and C18-C28-C27= 113.0(7)°. Those differences between the thiophene rings are not significant. In this macrocycle, the sulphur atoms do not interact with the nitrogen's lone pairs, due to the rigidity imposed by the cyclodiamine.

In the ether bridge, the C-O aromatic bond lengths, C14-O3= 1.379 Å and C18-O1= 1.379 Å, are similar to those in typical phenolic compounds, and are smaller than the aliphatic C-O bond lengths in the ether bridge, C22-O3= 1.424 Å, C26-O6= 1.433 Å, C24-O6= 1.412 Å, C23-O5= 1.423 Å, C20-O5= 1.430 Å and C25-O1= 1.443 Å. The C-C bond lengths in ether bridge are C22-C26= 1.452 Å, C23-C24= 1.499 Å and C20-C25= 1.520 Å. Those differences between the C-C bond lengths could be due to the different interactions that appear in the bridge and to the thermal displacements. The O-C-C bond angles with the thiophene rings are different as O1-C18-C12= 118.7(6)° and O1-C18-C28= 128.6(5)° are respectively 2.8° smaller and 3.3° larger than their counterparts O3-C14-C17= 121.5(5)° and O3-C14-C9= 125.3(6)°. This could be due to the O...H bonds that appear on O3 and O1. Indeed, the oxygen atom O1 has only three hydrogen bonds within the macrocycle, O1...H28-C20= 2.574 Å, O1...H8-C15= 2.450 Å and O1...H12-C11= 2.839 Å, whereas the oxygen atom O3 has five hydrogen bonds, O3...H1-C9= 2.542 Å, O3...H6-C26= 2.581 Å, O3...H17-C16= 2.750 Å, O3...H4-C13= 2.733 Å and O3...H16-C13= 2.859 Å. The C-O-C bond angles with the thiophene rings, C18-O1-C25= 117.2(5)° and C14-O3-C22= 114.7(4)°, are similarly distorted from ideal due to the previous hydrogen contacts with O1 and O3 but also due to the H...H interactions, C25-H25...H19-C28= 1.541 Å, C9-H1...H7-C22= 2.499 Å and C9-H1...H27-C22= 1.936 Å. The O-C-C bond angles in the ether bridge, O1-C25-C20= 111.3(5)°, O3-C22-C26= 112.6(5)°, O5-C20-C25= 109.3(6)°, O6-C26-C22= 111.3(5)°, O5-C23-C24= 111.1(5)° and O6-C24-C23= 109.1(6)°, are fairly symmetrical. Different O...H bonds affect them, O1...H28-C20= 2.574 Å, O3...H6-C26= 2.581 Å, O5...H14-C25= 2.342 Å, O6...H7-C22= 2.755 Å, O5...H23-C24= 2.491 Å and O6...H20-C23= 2.679 Å. The other C-O-C bond angles are C20-O5-C23= 109.7(5)° and C24-O6-C26= 110.9(5)°. The C20-O5-C23 bond angle contains only one H...H interaction, C23-H22...H18-C20= 2.304 Å, but this interaction is stronger than the two hydrogen close contacts for the C24-O6-C26 bond angle, C26-H6...H21-C24= 2.440 Å and C26-

H24...H23-C24= 2.428 Å.

In the amine bridge, a rigidity is created by the presence of the cyclodiamine, piperazine. This piperazine is in the chair conformation, which is stabilized by the hydrogen bonds that appear on the cyclodiamine within the molecule. This chair conformation is shown in the following view.



Indeed, the hydrogen atoms H4 and H16 are in close contact with oxygen atom O3 of the ether bridge, O3...H4-C13= 2.733 Å and O3...H16-C13= 2.859 Å. A similar bond appears with the oxygen atom O1, O1...H12-C11= 2.839 Å. Two other hydrogen bonds appear between the ether chain and the amine bridge, O3...H17-C16= 2.750 Å and O1...H8-C15= 2.450 Å. There are also a few hydrogen bonds within the cyclodiamine between the nitrogen atoms N1 and N7 and the axial hydrogen atoms, N1...H10-C10= 2.477 Å, N1...H4-C13= 2.613 Å, N7...H13-C11= 2.694 Å and N7...H5-C21= 2.782 Å (sum of the van der Waals radii= 2.75 Å). The atoms N1, N7, form a plane with the atoms C13 and C21 and another plane with the atoms C10 and C11. The bond lengths in the piperazine and in the rest of the bridge are symmetric, C12-C15= 1.509 Å, C16-C17= 1.518 Å, N1-C15= 1.472 Å, N7-C16= 1.479 Å, N1-C11= 1.462 Å, N1-C21= 1.464 Å, N7-C10= 1.460 Å, N7-C13= 1.463 Å, C10-C21= 1.528 Å and C11-C13= 1.517 Å. The N-C-C bond angles in the cyclodiamine are N1-C11-C13= 109.9(4)°, N1-C21-C10= 108.8(4)°, N7-C10-C21= 109.8(5)° and N7-C13-C11= 110.0(4)°. However, the tetrahedral bond angles on the nitrogen atoms are not symmetrically distributed, C11-N1-C15= 114.0(4)°, C11-N1-C21= 10.8(4)°, C15-N1-C21= 114.3(4)° for N1, and C10-N7-C13= 110.4(4)°, C10-N7-C16= 112.4(4)° and C13-N7-C16= 110.8(4)°. This could be due to the different hydrogen bonds and interactions. The nitrogen's lone pairs are, as for compound **8b**, pointing outside the cavity in the opposite direction from that required for coordination to an included species. However, for **9b**, the diamine is more rigid so it would be expected that the nitrogen's lone pairs are less likely to point inside the donor atom cavity. This rigidity imposed by the cyclodiamine in the chair conformation also prevents the lone pairs of the nitrogens from interacting with the S1 and S2 sulphur atoms. The S1 sulphur atom is in interaction with a hydrogen atom, S1...H13-C16= 2.896 Å (sum of the van der Waals radii= 3.05 Å). The effect of this hydrogen bond is that the bond angles between the S1 thiophene ring and the amine bridge are S1-C17-C16= 121.4(4)° and C14-C17-C16= 128.6(6)°, and are respectively 3.4° smaller and 3.5° larger than their counterpart with the S2 thiophene, which contains no interactions with the S2 sulphur atom. The last two bond angles are similar, N1-C15-C12= 115.8(5)° and N7-C16-C17= 115.7(4)°.

Table 84. Least-Squares Planes

Plane number 1

Atoms Defining Plane	Distance
S(1)	.0047(16)
O(3)	.0212(36)
C(9)	-.0309(54)
C(14)	-.0152(49)
C(16)	-.0241(55)
C(17)	-.0117(49)
C(19)	-.0036(62)

Mean deviation from plane is .0159 Ångstroms

Chi-squared: 114.8

Plane number 2

Atoms Defining Plane	Distance
S(2)	-.0037(18)
O(1)	-.0168(42)
C(12)	.0014(53)
C(15)	.0257(56)
C(18)	.0118(54)
C(27)	.0269(67)
C(28)	.0066(66)

Mean deviation from plane is .0133 Ångstroms

Chi-squared: 68.5

Dihedral angles between least-squares planes 1 and 2= 12.28°

Plane number 3

Atoms Defining Plane	Distance
N(1)	.0118(43)
N(7)	.0111(42)
C(13)	-.0173(53)
C(21)	-.0235(61)

Additional Atoms	Distance
C(10)	.6889
C(11)	-.7003

Mean deviation from plane is .0159 Ångstroms

Chi-squared: 38.0

Dihedral angles between least-squares planes 1 and 3= 90.69°

Dihedral angles between least-squares planes 2 and 3= 96.62°

Plane number 4

Atoms Defining Plane	Distance
N(1)	.0076(45)
N(7)	.0069(42)
C(10)	-.0115(56)
C(11)	-.0109(55)

Additional Atoms	Distance
C(13)	.6794
C(21)	-.7197

Mean deviation from plane is .0092 Ångstroms

Chi-squared: 12.8

Dihedral angles between least-squares planes 1 and 4= 88.38°

Dihedral angles between least-squares planes 2 and 4= 87.43°

Dihedral angles between least-squares planes 3 and 4= 33.85°

Plane number 5

Atoms Defining Plane	Distance
C(13)	.0050(54)
C(11)	-.0053(56)
C(10)	-.0054(57)
C(21)	.0069(64)

Mean deviation from plane is .0057 Ångstroms

Chi-squared: 3.5

Dihedral angles between least-squares planes 1 and 5= 61.94°

Dihedral angles between least-squares planes 2 and 5= 60.48°

Dihedral angles between least-squares planes 3 and 5= 147.13°

Dihedral angles between least-squares planes 4 and 5= 147.10°

Plane number 6

Atoms Defining Plane	Distance
O(1)	-.0299(46)
O(5)	.0896(43)
O(3)	.0284(37)
O(6)	-.1033(42)

Additional Atoms	Distance
N(1)	.5169
N(7)	1.9178

Mean deviation from plane is .0628 Ångstroms

Chi-squared: 1074.7

Dihedral angles between least-squares planes 1 and 6= 61.78°

Dihedral angles between least-squares planes 2 and 6= 62.20°

Dihedral angles between least-squares planes 3 and 6= 141.72°

Dihedral angles between least-squares planes 4 and 6= 149.61°

Dihedral angles between least-squares planes 5 and 6= 7.76°

Plane number 7

Atoms Defining Plane	Distance
N(1)	.0000
N(7)	.0000
C(24)	.0000

Additional Atoms	Distance
C(23)	1.2560

Mean deviation from plane is .0000 Ångstroms; Chi-squared: .0

Dihedral angles between least-squares planes 1 and 7= 89.97°

Dihedral angles between least-squares planes 2 and 7= 85.83°

Dihedral angles between least-squares planes 3 and 7= 170.69°

Dihedral angles between least-squares planes 4 and 7= 155.46°

Dihedral angles between least-squares planes 5 and 7= 29.54°

Dihedral angles between least-squares planes 6 and 7= 33.31°

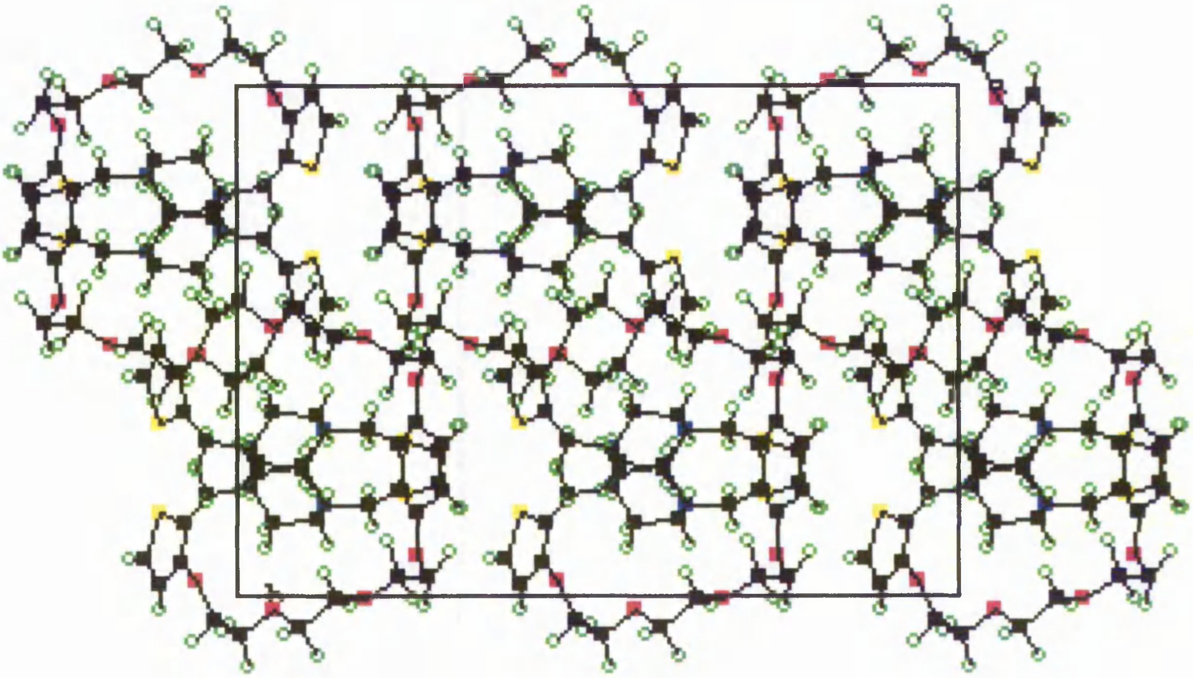
Numerous hydrogen close approaches appear between the molecules in the unit cell. For ease, those hydrogen interactions are reported in the following table (table 85).

Table 85. Hydrogen interactions between molecules of the unit cell

Hydrogen interactions			
Bond	Length(Å)	Bond	Length(Å)
C27-H26(a)...H2-C19(b)	2.507	O1(b)...H18-C20(c)	2.424
C10-H11(a)...H24-C26(c)	2.337	O1(b)...H22-C23(c)	2.807
C16-H3(a)...H24-C26(c)	2.073	C26-H24(b)...N7(d)	2.742
C27-H26(a)...H23-C24(f)	2.436	C26-H6(b)...H11-C10(d)	2.519
C27-H26(a)...O5(f)	2.835	C9-H1(b)...N1(f)	2.714
C11-H13(a)...H9-C21(g)	2.187	O5(b)...H2-C19(f)	2.539
C13-H16(a)...H9-C21(g)	2.566	S1(b)...H19-C28(g)	2.655
S2(a)...H15-C15(g)	3.112	C24-H21(c)...O3(g)	2.735
C28-H19(a)...S1(h)	2.655		

(a)= (x, y, z)
(b)= (½+x, ½-y, -z)
(c)= (-x, ½+y, ½-z)
(d)= (½-x, -y, ½+z)
(e)= (-x, -y, -z)
(f)= (½-x, ½+y, z)
(g)= (x, ½-y, ½+z)
(h)= (½+x, +y, ½-z)

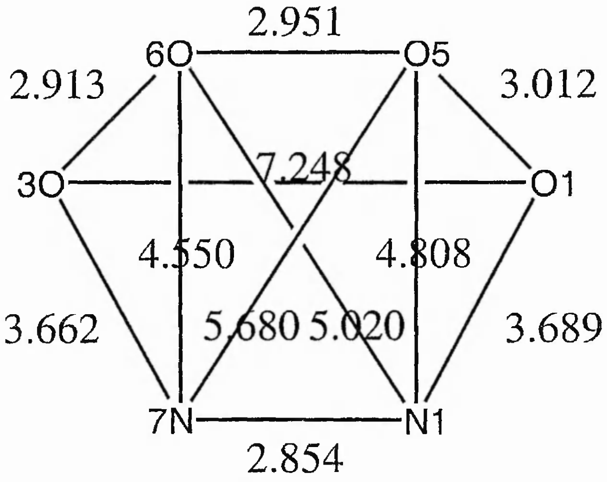
The following view of the cell shows that all the molecules in the unit cell are arranged along the a-axis.



The donor atoms that form the cavity are not planar, as shown in the table of least squares (table 84). The oxygen donor atoms however form a plane almost parallel to the plane formed by the carbon atoms C10, C11, C13 and C21 of the piperazine. The lone pairs of the oxygens are directed into the macrocyclic cavities. The distance between the nitrogen atoms N1-N7= 2.854 Å is fairly similar to its counterpart in the modelled chair conformation of compound **9a**, and is significantly shorter than the N-N distance for compound **8b** which contains a flexible dimethyldiamine instead of a rigid piperazine unit. The distances between the donor atoms in the cavity, which include the cross-ring distances, are more symmetric than in **8b** due to the rigidity of the cyclodiamine. Also, N1-O6= 5.020 Å and N7-O5= 5.680 Å are respectively 34.5% and 7.4% shorter than the similar distances in macrocycle **8b**, while O1-O3= 7.248 Å is 29.8% longer than its counterpart. The inclusion of an extra OCH_2CH_2 in the ether chain compared to macrocycle **9a** has significantly increased the O-O cross-ring distance while the N-O cross-ring distances are pretty much the same. The resulting cavity radius calculated by the conventional approach (0.855 Å) is shorter than in compound **8b** calculated by the alternative method that is more appropriate in the case of **8b**, while this second method also gives a larger radius for **9b** (1.029 Å). The classic approach that is more appropriate to **9b**, despite the fact that the donor atoms are not very planar, gives a radius of cavity smaller than for compounds **9a**, **10a** and **10b** calculated by the same method.

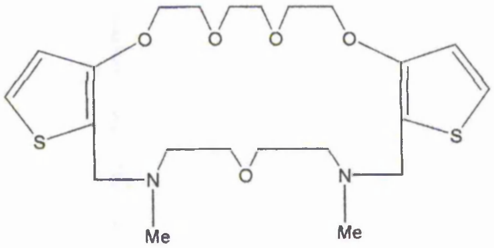
Despite the rigidity imposed by the cyclodiamine and the fact that the nitrogen's lone pairs are directed outside the cavity, the macrocycle **9b** has still a reasonable flexibility in solution. Also, the presence of six donor atoms is ideal for complexation to a transition metal ion, and should allow this macrocycle to include a metal ion in the cavity. As concluded for the compound **9a**, the chair conformation of the piperazine will make this macrocycle more selective than the previous macrocycle and especially the compound **8b**. This chair conformation of the piperazine contradicts Chenevert and Plante[366] who concluded after studies of molecular models of macrocyclic polyethers possessing the piperazine unit that this cyclodiamine must be more likely in the boat conformation. The interaction between the lone pairs on the nitrogen atoms must be more important than expected.

The cavity is drawn schematically below.

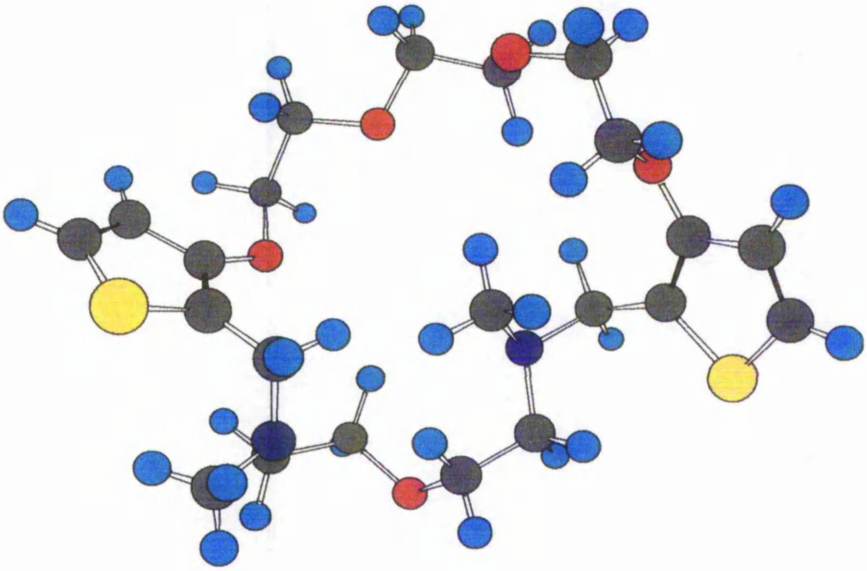


3.6. Seven donor atoms thiophene-based macrocycle (5 oxygens, 2 nitrogens)

3.6.1. 18,24-bis-(methyl)-2,5,8,11,21-pentaoxa-15,27-dithia-18,24-diaza-tricyclo[24.3.0.0]-nonacosa-1(26),12(16),13,28-tetraene **22**

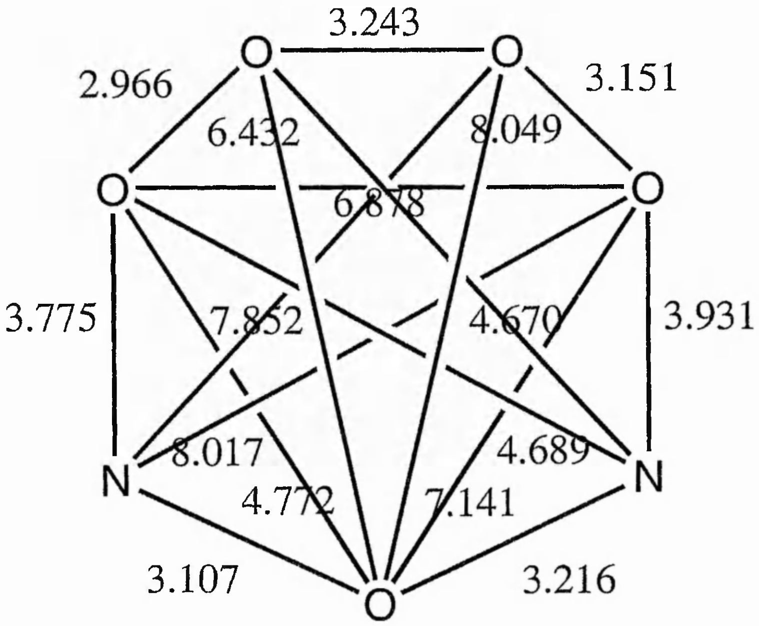


This macrocycle was modelled by minimization of its energy via the programs MM2 (steric energy) then MOPAC (heat of formation). Macrocycle **22** contains seven donor atoms, 5 oxygen atoms and 2 nitrogen atoms. One of the oxygens is placed between the nitrogen atoms in the diamine bridge. This might provide better complexation possibilities for metals, which prefer to coordinate with oxygen, rather than nitrogen, e.g. aluminium, sodium, and potassium.



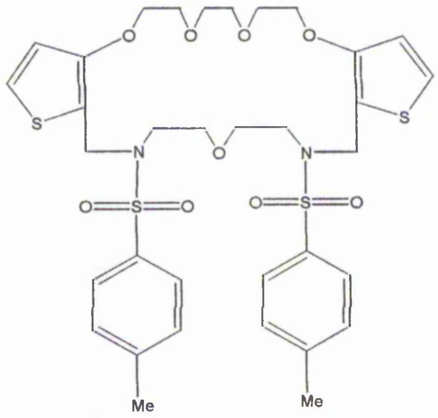
The donor atom lone pairs are not especially oriented towards the inside of the cavity. This is due to the large flexibility of both the ether and the diamine bridges. Also, the donor atoms do not form a planar arrangement as in compounds **10a** and **10b** but instead the five oxygens are arranged approximately as a square pyramid shape, or perhaps as the geometry could be better considered as a distorted octahedron with 4 oxygens and the 2 nitrogens, or even a distorted pentagonal bipyramidal shape involving all 7 donor atoms around the centre of the cavity.

The distances between the atom donors and the resulting cavity are shown schematically below.



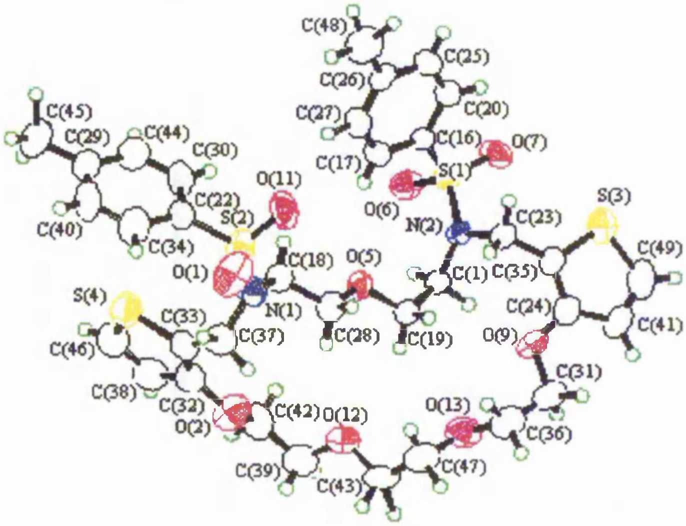
The distances between the seven donor atoms are not symmetric. The substitution of the diamine chain by an even larger diaminoether chain has greatly increased the flexibility and the size of the cavity compared to all the preceding macrocycles in this work. Indeed, the resulting cavity radius= 1.836 Å has nearly doubled compared to the other molecules. This macrocycle **22** could include in its cavity a metal ion as large as Cs^+, which has a ionic radius of 1.67 Å. Also, the fact that the donor atom lone pairs are not especially oriented towards the cavity in this structure is not a problem for an eventual complexation as the macrocycle is very flexible in solution. On the other hand, this macrocycle will not be very selective as the cavity is large and there are many different coordination possibilities to some or all the donor atoms.

3.6.2. 18,24-bis-(p-toluenesulphonamide)-2,5,8,11,21-pentaoxa-15,27-dithia-18,24-diaza-tricyclo[24.3.0.0]-nonacosa-1(26),12(16),13,28-tetraene **23**



3.6.2.1. Discussion of the structure derived data (tables 32 to 34)

Four molecules are present in the unit cell and the space group is $P2_1/c$ or n°14. The positions and anisotropic displacement parameters of the atoms in the macrocycle are best-visualized in the "ortep style" drawing below[353].



The greatest displacement occurs at the extremities of the molecules, S3, C49, O9, S4, C46, O2, C48. However, the thermal ellipsoids are relatively small, due to the rigidity and steric effect created by the presence of the tosylate groups in substitution of the methyl on the nitrogen atoms in compound **22**.

3.6.2.2. Discussion of the structural geometry

Table 86. Bond Lengths(Å)

Bond Lengths(Å)			
Bond	Length(Å)	Bond	Length(Å)
S(1) -O(6)	1.436(3)	C(1) -C(19)	1.512(5)
S(1) -O(7)	1.435(2)	C(1) -H(28)	0.99(3)
S(1) -N(2)	1.619(3)	C(1) -H(29)	0.98(3)
S(1) -C(16)	1.769(4)	C(16) -C(17)	1.382(5)
S(2) -O(1)	1.426(3)	C(16) -C(20)	1.372(5)
S(2) -O(11)	1.440(3)	C(17) -C(27)	1.377(6)
S(2) -N(1)	1.611(3)	C(17) -H(35)	0.88(3)
S(2) -C(22)	1.760(4)	C(18) -C(28)	1.497(5)
S(3) -C(35)	1.720(4)	C(18) -H(2)	0.95(3)
S(3) -C(49)	1.687(5)	C(18) -H(20)	0.90(3)
S(4) -C(33)	1.714(4)	C(19) -H(1)	0.98(3)
S(4) -C(46)	1.708(6)	C(19) -H(25)	1.06(3)
O(2) -C(32)	1.378(5)	C(20) -C(25)	1.377(5)
O(2) -C(42)	1.424(5)	C(20) -H(19)	0.90(3)
O(5) -C(19)	1.418(4)	C(22) -C(30)	1.367(5)
O(5) -C(28)	1.405(4)	C(22) -C(34)	1.372(5)
O(9) -C(24)	1.367(4)	C(23) -C(35)	1.493(5)
O(9) -C(31)	1.421(5)	C(23) -H(3)	0.96(3)
O(12) -C(39)	1.409(6)	C(23) -H(4)	0.91(3)
O(12) -C(43)	1.399(5)	C(24) -C(35)	1.344(5)
O(13) -C(36)	1.431(5)	C(24) -C(41)	1.426(5)
O(13) -C(47)	1.421(6)	C(25) -C(26)	1.382(5)
N(1) -C(18)	1.472(5)	C(25) -H(17)	0.86(3)
N(1) -C(37)	1.485(5)	C(26) -C(27)	1.373(5)
N(2) -C(1)	1.467(4)	C(26) -C(48)	1.503(6)
N(2) -C(23)	1.473(4)	C(27) -H(16)	0.90(3)
C(28) -H(24)	0.93(3)	C(41) -H(7)	0.88(3)
C(28) -H(34)	0.98(3)	C(42) -H(10)	0.98(3)
C(29) -C(40)	1.355(6)	C(42) -H(11)	0.93(3)
C(29) -C(44)	1.368(6)	C(43) -C(47)	1.490(7)
C(29) -C(45)	1.499(6)	C(43) -H(12)	1.01(3)
C(30) -C(44)	1.376(6)	C(43) -H(42)	0.95(3)
C(30) -H(26)	0.83(3)	C(44) -H(31)	0.82(3)

C(31) -C(36)	1.478(7)	C(45) -H(27)	0.89(3)
C(31) -H(5)	1.06(3)	C(45) -H(37)	0.84(3)
C(31) -H(14)	0.98(3)	C(45) -H(38)	0.89(3)
C(32) -C(33)	1.346(6)	C(46) -H(23)	0.89(3)
C(32) -C(38)	1.406(6)	C(47) -H(13)	0.98(3)
C(33) -C(37)	1.497(6)	C(47) -H(18)	0.95(3)
C(34) -C(40)	1.378(6)	C(48) -H(39)	0.95(3)
C(34) -H(15)	0.84(3)	C(48) -H(40)	0.97(3)
C(36) -H(8)	0.92(3)	C(48) -H(41)	0.86(3)
C(36) -H(9)	1.10(3)	C(49) -H(6)	0.94(3)
C(37) -H(21)	1.00(3)	C(39) -H(33)	1.00(3)
C(37) -H(22)	0.97(3)	C(39) -H(36)	0.90(3)
C(38) -C(46)	1.339(6)	C(40) -H(32)	0.84(3)
C(38) -H(30)	0.88(3)	C(41) -C(49)	1.331(6)
C(39) -C(42)	1.478(7)		

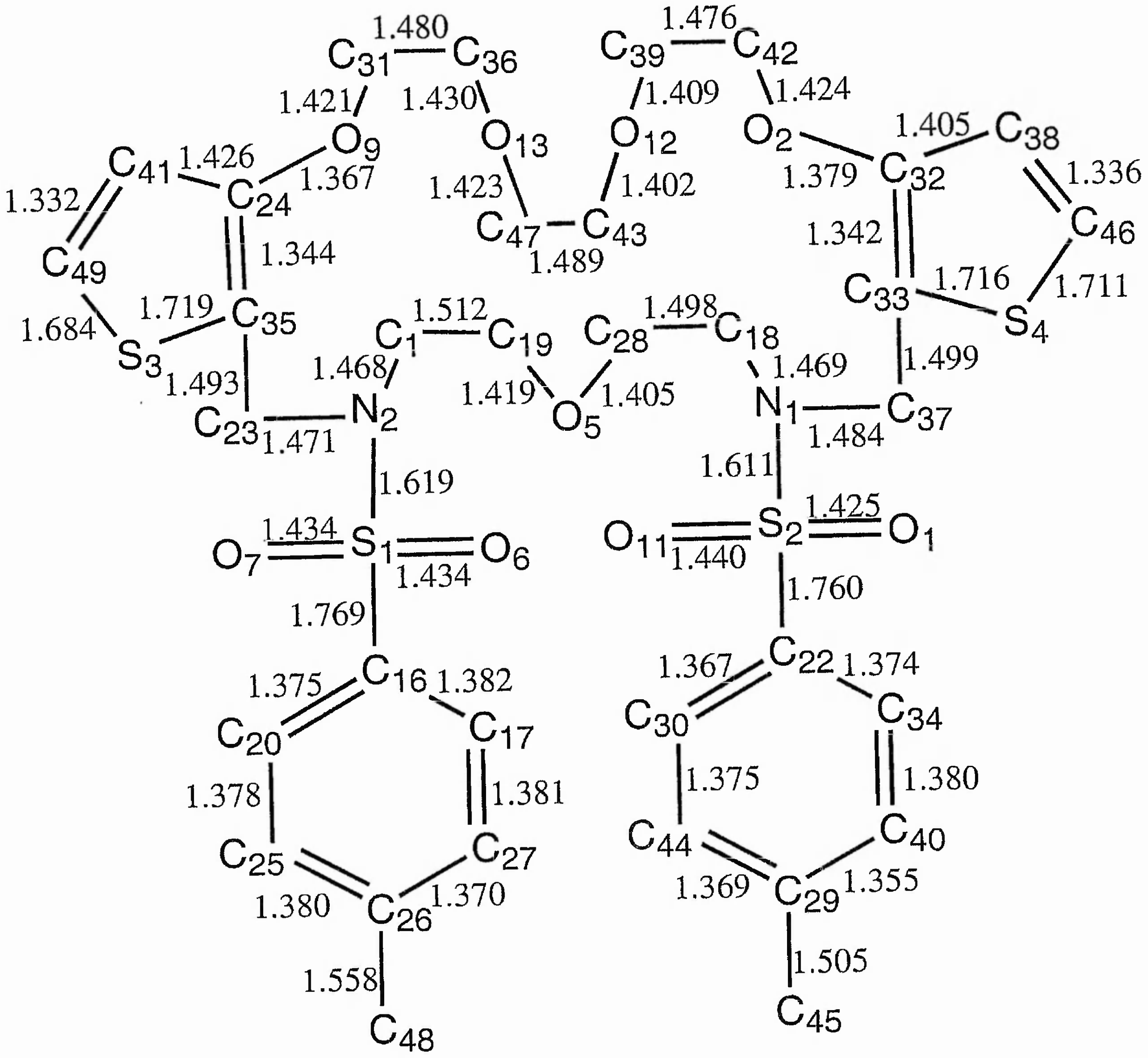
Table 87. Bond Angles(°)

Bond Angles(°)			
Bond	Angle(°)	Bond	Angle(°)
O(6) -S(1) -O(7)	118.4(2)	N(2) -C(1) -H(28)	108(2)
O(6) -S(1) -N(2)	107.6(1)	N(2) -C(1) -H(29)	107(2)
O(6) -S(1) -C(16)	109.0(2)	C(19) -C(1) -H(28)	107(2)
O(7) -S(1) -N(2)	110.5(2)	C(19) -C(1) -H(29)	109(2)
O(7) -S(1) -C(16)	106.4(2)	H(28) -C(1) -H(29)	113(3)
N(2) -S(1) -C(16)	104.0(2)	S(1) -C(16) -C(17)	119.7(3)
O(1) -S(2) -O(11)	120.2(2)	S(1) -C(16) -C(20)	120.7(3)
O(1) -S(2) -N(1)	106.3(2)	C(17) -C(16) -C(20)	119.5(3)
O(1) -S(2) -C(22)	107.1(2)	C(16) -C(17) -C(27)	119.7(4)
O(11) -S(2) -N(1)	106.3(2)	C(16) -C(17) -H(35)	115(2)
O(11) -S(2) -C(22)	107.6(2)	C(27) -C(17) -H(35)	125(2)
N(1) -S(2) -C(22)	108.9(2)	N(1) -C(18) -C(28)	111.4(3)
C(35) -S(3) -C(49)	91.9(2)	N(1) -C(18) -H(2)	110(2)
C(33) -S(4) -C(46)	91.9(2)	N(1) -C(18) -H(20)	107(2)
C(32) -O(2) -C(42)	116.8(4)	C(28) -C(18) -H(2)	110(2)
C(19) -O(5) -C(28)	113.1(3)	C(28) -C(18) -H(20)	113(2)
C(24) -O(9) -C(31)	117.9(3)	H(2) -C(18) -H(20)	105(3)
C(39) -O(12) -C(43)	111.7(4)	O(5) -C(19) -C(1)	108.0(3)

C(36) -O(13) -C(47)	111.4(4)	O(5) -C(19) -H(1)	112(2)
S(2) -N(1) -C(18)	120.0(3)	O(5) -C(19) -H(25)	109(2)
S(2) -N(1) -C(37)	120.8(3)	C(1) -C(19) -H(1)	111(2)
C(18) -N(1) -C(37)	116.7(3)	C(1) -C(19) -H(25)	114(2)
S(1) -N(2) -C(1)	122.1(2)	H(1) -C(19) -H(25)	103(2)
S(1) -N(2) -C(23)	117.3(2)	C(16) -C(20) -C(25)	119.8(3)
C(1) -N(2) -C(23)	118.3(3)	C(16) -C(20) -H(19)	116(2)
N(2) -C(1) -C(19)	113.0(3)	C(25) -C(20) -H(19)	124(2)
S(2) -C(22) -C(30)	119.3(3)	H(24) -C(28) -H(34)	103(3)
S(2) -C(22) -C(34)	121.8(3)	C(40) -C(29) -C(44)	117.4(4)
C(30) -C(22) -C(34)	118.9(4)	C(40) -C(29) -C(45)	122.8(4)
N(2) -C(23) -C(35)	114.5(3)	C(44) -C(29) -C(45)	119.8(5)
N(2) -C(23) -H(3)	107(2)	C(22) -C(30) -C(44)	119.9(4)
N(2) -C(23) -H(4)	104(2)	C(22) -C(30) -H(26)	119(2)
C(35) -C(23) -H(3)	113(2)	C(44) -C(30) -H(26)	121(2)
C(35) -C(23) -H(4)	112(2)	O(9) -C(31) -C(36)	107.1(4)
H(3) -C(23) -H(4)	105(3)	O(9) -C(31) -H(5)	110(2)
O(9) -C(24) -C(35)	118.5(4)	O(9) -C(31) -H(14)	110(2)
O(9) -C(24) -C(41)	127.3(4)	C(36) -C(31) -H(5)	112(2)
C(35) -C(24) -C(41)	114.2(4)	C(36) -C(31) -H(14)	107(2)
C(20) -C(25) -C(26)	121.6(4)	H(5) -C(31) -H(14)	111(3)
C(20) -C(25) -H(17)	122(2)	O(2) -C(32) -C(33)	119.7(4)
C(26) -C(25) -H(17)	117(2)	O(2) -C(32) -C(38)	126.0(4)
C(25) -C(26) -C(27)	117.7(4)	C(33) -C(32) -C(38)	114.2(4)
C(25) -C(26) -C(48)	120.9(4)	S(4) -C(33) -C(32)	110.0(3)
C(27) -C(26) -C(48)	121.4(4)	S(4) -C(33) -C(37)	123.3(3)
C(17) -C(27) -C(26)	121.7(4)	C(32) -C(33) -C(37)	126.7(4)
C(17) -C(27) -H(16)	120(2)	C(22) -C(34) -C(40)	119.8(4)
C(26) -C(27) -H(16)	118(2)	C(22) -C(34) -H(15)	116(3)
O(5) -C(28) -C(18)	107.9(3)	C(40) -C(34) -H(15)	124(3)
O(5) -C(28) -H(24)	111(2)	S(3) -C(35) -C(23)	123.2(3)
O(5) -C(28) -H(34)	108(2)	S(3) -C(35) -C(24)	109.8(3)
C(18) -C(28) -H(24)	112(2)	C(23) -C(35) -C(24)	126.8(4)
C(18) -C(28) -H(34)	114(2)	O(13) -C(36) -C(31)	109.4(4)
O(13) -C(36) -H(8)	109(2)	O(2) -C(42) -C(39)	107.7(4)
O(13) -C(36) -H(9)	101(2)	O(2) -C(42) -H(10)	109(2)
C(31) -C(36) -H(8)	108(2)	O(2) -C(42) -H(11)	108(2)
C(31) -C(36) -H(9)	122(2)	C(39) -C(42) -H(10)	108(2)
H(8) -C(36) -H(9)	106(3)	C(39) -C(42) -H(11)	111(2)
N(1) -C(37) -C(33)	114.4(3)	H(10) -C(42) -H(11)	113(3)

N(1) -C(37) -H(21)	107(2)	O(12) -C(43) -C(47)	112.0(4)
N(1) -C(37) -H(22)	100(2)	O(12) -C(43) -H(12)	110(2)
C(33) -C(37) -H(21)	111(2)	O(12) -C(43) -H(42)	113(2)
C(33) -C(37) -H(22)	114(2)	C(47) -C(43) -H(12)	111(2)
H(21) -C(37) -H(22)	109(3)	C(47) -C(43) -H(42)	110(2)
C(32) -C(38) -C(46)	112.0(5)	H(12) -C(43) -H(42)	100(3)
C(32) -C(38) -H(30)	124(3)	C(29) -C(44) -C(30)	121.8(4)
C(46) -C(38) -H(30)	124(3)	C(29) -C(44) -H(31)	121(3)
O(12) -C(39) -C(42)	111.0(4)	C(30) -C(44) -H(31)	117(3)
O(12) -C(39) -H(33)	105(2)	C(29) -C(45) -H(27)	114(3)
O(12) -C(39) -H(36)	108(2)	C(29) -C(45) -H(37)	114(3)
C(42) -C(39) -H(33)	111(2)	C(29) -C(45) -H(38)	108(2)
C(42) -C(39) -H(36)	110(2)	H(27) -C(45) -H(37)	83(3)
H(33) -C(39) -H(36)	112(3)	H(27) -C(45) -H(38)	102(3)
C(29) -C(40) -C(34)	122.1(4)	H(37) -C(45) -H(38)	132(4)
C(29) -C(40) -H(32)	118(2)	S(4) -C(46) -C(38)	111.8(4)
C(34) -C(40) -H(32)	119(2)	S(4) -C(46) -H(23)	121(2)
C(24) -C(41) -C(49)	110.7(4)	C(38) -C(46) -H(23)	127(2)
C(24) -C(41) -H(7)	121(2)	O(13) -C(47) -C(43)	112.4(5)
C(49) -C(41) -H(7)	129(2)	O(13) -C(47) -H(13)	102(2)
O(13) -C(47) -H(18)	97(2)	H(39) -C(48) -H(40)	97(3)
C(43) -C(47) -H(13)	108(2)	H(39) -C(48) -H(41)	109(4)
C(43) -C(47) -H(18)	115(2)	H(40) -C(48) -H(41)	108(4)
H(13) -C(47) -H(18)	122(3)	S(3) -C(49) -C(41)	113.4(4)
C(26) -C(48) -H(39)	114(2)	S(3) -C(49) -H(6)	121(2)
C(26) -C(48) -H(40)	109(2)	C(41) -C(49) -H(6)	125(2)
C(26) -C(48) -H(41)	117(3)		

The two halves of the molecule have fairly symmetric geometries. For ease of description the bond lengths (to 3 decimal places) are shown on a schematic drawing on the next page.



The bond angle distortions from ideal in the thiophene rings are similar compared to those in unsubstituted thiophene[354]. In this macrocycle, no S…N interaction occurs on the thiophene rings due to other competitive interactions. The thiophene rings form two planes with an angle of 92.11°. The S3 thiophene ring includes the atoms O9, C31, C36 and C23 in its plane, whereas the S4 thiophene ring only includes the atoms O2 and C37 in its plane. Those atoms that are lying in the thiophene ring planes are directly bonded to the thiophene rings.

The bond angles between the ether bridge and the thiophene rings as well as the other O-C-C bond angles are fairly symmetric: O9-C24-C41= 127.3(4)°, O9-C24-C35= 118.5(4)°, O2-C32-C38= 126.0(4)°, O2-C32-C33= 119.7(4)°, O9-C31-C36= 107.1(4)°, O13-C36-C31= 109.4(4)°, O13-C47-C43= 112.4(5)°, O12-C43-C47= 112.0(4)°, O12-C39-C42= 111.0(4)°, O2-C42-C39= 107.7(4)°, and in the amine bridge O5-C19-C1= 108.0(3)° and O5-C28-C18= 107.9(3)°. Furthermore, similar hydrogen bonds occur on the oxygen atoms, O9...H9-C36= 2.651 Å, O13...H15-C31= 2.538 Å, O12...H18-C47= 2.442 Å, O12...H10-C42= 2.458 Å, O5...H20-C18= 2.504 Å, O5...H2-C18= 2.608 Å and O5...H29-C1= 2.506 Å. On the S4 thiophene ring half of the molecule, the oxygen atom O2 forms two hydrogen bonds, O2...H30-C38= 2.572 Å and O2...H21-C37= 2.572 Å, and an H...H interaction also appears between the ether bridge and the thiophene, C38-H30...H11-C42= 2.315 Å. On the S3 thiophene ring, more intramolecular contacts appear, O9...H7-C41= 2.731 Å, C31-H14...H7-C41= 2.476 Å, C31-H5...H7-C41= 2.456 Å, O9...H3-C23= 2.677 Å, O9...H28-C1= 2.719 Å and O9...H25-C19= 2.716 Å. The hydrogen bonds O9...H3, O9...H28 and O9...H25 between the ether bridge and the diamine bridge, compared with the contact bonds O2...H21 and O12...H34-C28= 2.689 Å on the other half of the molecule, shows that in the S3 thiophene ring half the ether chain and the diamine chain are closer together. The C-O bond lengths involving the thiophene ring carbons are C24-O9= 1.367 Å and C32-O2= 1.379 Å. Those bond lengths are shorter than the other C-O bond lengths in the macrocycle, C31-O9= 1.421 Å, C36-O13= 1.430 Å, C47-O13= 1.423 Å, C43-O12= 1.402 Å, C39-O12= 1.409 Å, C42-O2= 1.424 Å, C19-O5= 1.419 Å and C28-O5= 1.405 Å, due to a possible conjugation with the adjacent thiophene ring, and so are close to their counterparts in the phenol molecule[363]. The C-O-C bond angles between the ether bridge and the thiophene rings, C24-O9-C31= 117.9(3)° and C32-O2-C42= 116.8(4)°, are larger than the other C-O-C bond angles, C36-O13-C47= 111.4(4)°, C39-O12-C43= 111.7(4)° and C19-O5-C28= 113.1(3)°. The C36-O13-C47 and C39-O12-C43 bond angles are similar and also present similar H...H interactions, C47-H18...H9-C36= 2.121 Å, C47-H13...H8-C36= 2.222 Å and C39-H33...H12-C43= 2.174 Å. In the amine bridge, the C19-O5-C28 bond angle also has two hydrogen close approaches, C28-H34...H1-C19= 2.386 Å and C28-H24...H25-C19= 2.340 Å. The C-C bond lengths in the molecule are close to the expected 1.52 Å[357] considering the esd's. Indeed, the C-C bond lengths in the ether bridge vary from 1.476 Å to 1.489 Å. In the diamine bridge the C-C bond lengths are C1-C19= 1.512 Å, C18-C28= 1.498 Å, C23-C35= 1.493 Å and C33-C37= 1.499 Å. Compared to the C-O bond lengths with the thiophene rings, the C23-C35 and C33-C37 bond lengths are not affected by a conjugation with the adjacent thiophenes.

In the amine bridge, the bond angles between the thiophene rings and the diamine are fairly similar, S3-C35-C23= 123.2(3)°, C23-C35-C24= 126.8(4)°, S4-C33-C37= 123.3(3)° and C32-C33-C37= 126.7(4)°, and they have similar hydrogen close approaches with the sulphur atoms, S3...H4-C23= 2.904 Å and S4...H22-C37= 3.035 Å (sum of the van der Waals radii= 3.05 Å). The presence of the tosylate on the nitrogen atoms creates a steric effect which induces a rigidity compared to compound **22**. The tosylates form two planes at an angle of 78.65°, which do not include the oxygen atoms. The tosylate groups are fairly close to each other as shown by O11...H16-C27= 2.695 Å. The S3 sulphur atom might have a very weak interaction with the O7 oxygen atom of the adjacent tosylate group, S3...07= 3.341 Å (sum of the van der Waals radii= 3.35 Å). The C1-N2= 1.468 Å, C23-N2= 1.471 Å, C18-N1= 1.469 Å and C37-N1= 1.484 Å bond lengths are typical of a C-N single bond[363]. However, the S-N bond lengths, S1-N2= 1.619 Å and S2-N1= 1.611 Å, are shorter than the usual S-N single bond length[363], which could be due to a conjugation with the tosylate groups. The N1-C37-C33= 114.4(3)° and N2-C23-C35= 114.5(3)° bond angles are similar. On the other hand, the N-C-C bond angles N1-C18-C28= 111.4(3)° and N2-C1-C18= 113.0(3)° are different, due to the numerous hydrogen bonds that occur with the ether chain, which is also closer to the N2 half of the amine bridge, O9...H3, O9...H28, O9...H25, O12...H34 and O12...H21. The S=O bond lengths are S1-O7= 1.434 Å, S1-O6= 1.434 Å, S2-O11= 1.440 Å and S2-O1= 1.425 Å. Several close approaches of the S=O bond oxygen atoms to neighbouring hydrogens occur, for example O6...H29-C1= 2.304 Å, O6...H35-C17= 2.877 Å, O11...H20-C18= 2.393 Å, O11...H26-C30= 2.680 Å and O11...H16-C27= 2.695 Å. The oxygen atoms O1 and O7 each have two similar hydrogen bonds, O1...H15-C34= 2.528 Å, O1...H22-C37= 2.322 Å, O7...H19-C20= 2.433 Å and O7...H4-C23= 2.656 Å. However, the oxygen O7 could be in interaction with the S3 sulphur atom thiophene ring contrary to the O1 oxygen atom with the S4 sulphur atom thiophene ring. The steric effect induced by the tosylate units is reflected in the C-N-C and S-N-C bond angles. The S2-N1-C37= 120.8(3)°, S2-N1-C18= 120.0(3)° and C18-N1-C37= 116.7(3)° are respectively 3.6° larger, 2.1° smaller and 1.7° smaller than their counterpart on N1. The O6-S1-O7= 118.4(2)° is closer to the ideal tetrahedral value, whereas the O1-S2-O11= 120.2(2)° is widened probably due to the repulsive interaction between the short S=O bonds. The other bond angles within the S1O$_2$ group are respectively O6-S1-N2= 107.6(1)°, O7-S1-N2= 110.5(2)°, O6-S1-C16= 109.0(2)°, O7-S1-C16= 106.4(2)° and N2-S1-C16= 104.0(2)°. Those bond angles are less symmetric than their counterparts on S2, O1-S2-N1= 106.3(2)°, O11-S2-N1= 106.3(2)°, O1-S2-C22= 107.1(2)°, O11-S2-

C22= 107.6(2)° and N1-S2-C22= 108.9(2)°. The S2-C22= 1.760 Å and S1-C16= 1.769 Å bond lengths between the SO_2 groups and the phenyls are fairly close to the values reported in the International Tables for X-ray Crystallography (1.758 Å)[363]. The bond lengths in the S1 phenyl vary from 1.370 to 1.382 Å which is close to the 1.380 Å expected for a phenyl[363], and confirms the aromatic character of this group. The bond angles with and inside this phenyl group are fairly symmetric, S1-C16-C17= 119.7(3)°, S1-C16-C20= 120.7(3)°, C25-C26-C48= 120.9(4)°, C27-C26-C48= 121.4(4)°, C17-C16-C20= 119.5(3)°, C25-C26-C27= 117.7(4)°, C16-C17-C27= 119.7(4)°, C16-C20-C25= 119.8(3)°, C17-C27-C26= 121.7(4)° and C20-C25-C26= 121.6(4)°. The CH_3-Caromatic bond length C48-C26= 1.558 Å is longer than the usual average[363]. On the other phenyl group, the C-C bond lengths are slightly shorter. Especially, the C-C bond length adjacent to the substitutent groups has a stronger double bond character as C22-C30= 1.367 Å, C22-C34= 1.374 Å, C29-C40= 1.355 Å and C29-C44= 1.369 Å, compared to C30-C44= 1.375 Å and C34-C40= 1.380 Å bond lengths. However, the CH_3-Caromatic bond length C45-C29= 1.505 Å is in accordance with the International Tables for X-ray Crystallography[363]. The bond angles on this substituted phenyl group are less symmetrically distributed, S2-C22-C30= 119.3(3)°, S2-C22-C34= 121.8(3)°, C40-C29-C45= 122.8(4)° and C44-C29-C45= 119.8(5)°, although the C-C-C bond angles within the phenyl group are still symmetric, C20-C22-C34= 118.9(4)°, C40-C29-C44= 117.4(4)°, C22-C30-C44= 119.9(4)°, C22-C34-C40= 119.8(4)°, C29-C44-C30= 121.8(4)° and C29-C40-C34= 122.1(4)°. These differences between the phenyl groups could be due to a weak d...d interaction of the S2 phenyl group with the S4 sulphur atom thiophene ring as the distances between the S4 atom and the phenyl group vary from 3.518 Å to 4.120 Å, and the distances between the S1 phenyl group and the S3 sulphur atom thiophene ring vary from 5.147 Å to 7.386 Å.

Table 88. Least-Squares Planes

Plane number 1

Atoms Defining Plane	Distance
S(4)	.0097(13)
O(2)	.0374(28)
C(32)	-.0323(38)
C(33)	-.0141(36)

C(38)	-.0487(48)
C(46)	-.0205(52)
C(37)	-.0336(40)

Additional Atoms	Distance
N(1)	-1.3179
O(11)	-2.6989
O(1)	-.2206
O(5)	-4.0505
C(18)	-2.5419
C(28)	-2.7576

Mean deviation from plane is .0280 Ångstroms

Chi-squared: 503.6

Plane number 2

Atoms Defining Plane	Distance
S(3)	.0057(14)
O(9)	.0107(29)
C(23)	-.0505(39)
C(24)	.0080(38)
C(35)	.0279(36)
C(41)	-.0255(48)
C(49)	-.0565(56)

Additional Atoms	Distance
N(2)	1.2551
O(5)	1.8970
O(6)	3.0620
O(7)	1.4592
S(1)	1.7228
C(1)	2.2005
C(19)	1.7758

Mean deviation from plane is .0264 Ångstroms

Chi-squared: 413.7

Dihedral angles between least-squares planes 1 and 2= 94.13°

Plane number 3

Atoms Defining Plane	Distance
S(2)	.0033(12)
C(22)	-.0263(35)
C(30)	-.0176(49)
C(34)	-.0179(50)
C(40)	.0005(49)
C(44)	.0016(52)
C(29)	.0239(38)

Additional Atoms	Distance
C(45)	.0968
O(1)	-.2929
O(11)	-.8076
N(1)	1.5044

Mean deviation from plane is .0130 Ångstroms

Chi-squared: 134.1

Dihedral angles between least-squares planes 1 and 3= 74.44°

Dihedral angles between least-squares planes 2 and 3= 34.80°

Plane number 4

Atoms Defining Plane	Distance
S(1)	.0010(9)
C(16)	-.0114(32)
C(17)	-.0065(42)
C(20)	-.0087(37)
C(25)	.0064(39)
C(26)	.0072(38)
C(27)	.0026(45)

Additional Atoms	Distance
C(48)	-.0356
O(6)	1.1200
O(7)	-.0941
N(2)	-1.3455

Mean deviation from plane is .0062 Ångstroms

Chi-squared: 29.2

Dihedral angles between least-squares planes 1 and 4= 112.29°

Dihedral angles between least-squares planes 2 and 4= 43.76°

Dihedral angles between least-squares planes 3 and 4= 78.40°

Plane number 5

Atoms Defining Plane	Distance
O(2)	.1082(29)
O(12)	-.2553(30)
O(13)	.1685(29)
O(9)	-.0474(30)

Additional Atoms	Distance
O(5)	-.2783
N(1)	2.2608
N(2)	-1.1724

Mean deviation from plane is .1449 Ångstroms

Chi-squared: 12411.5

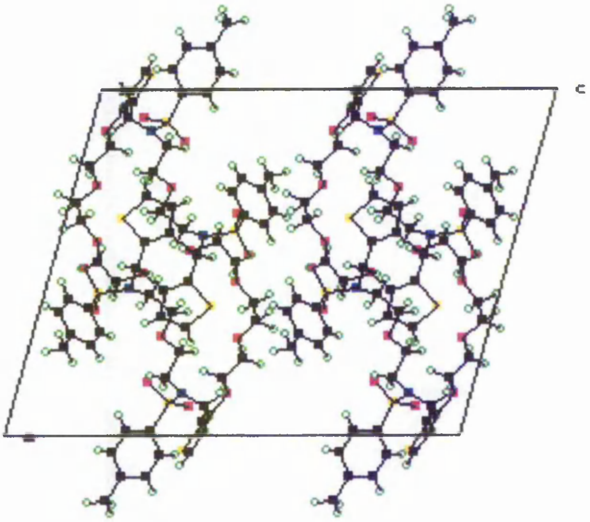
Dihedral angles between least-squares planes 1 and 5= 58.68°

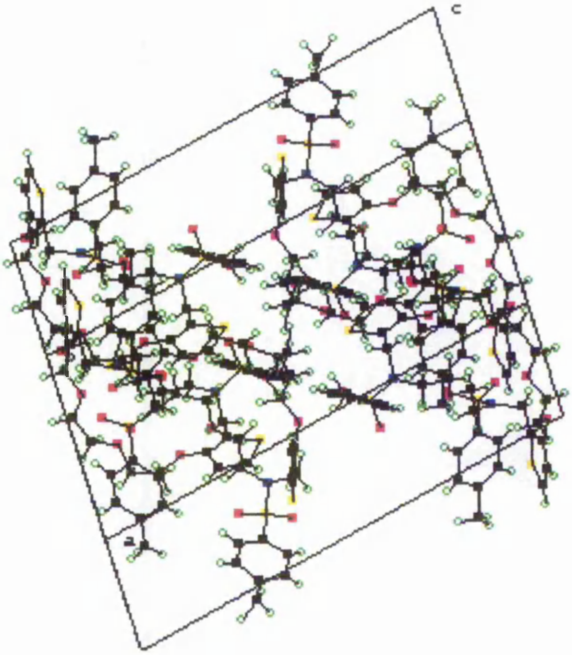
Dihedral angles between least-squares planes 2 and 5= 149.77°

Dihedral angles between least-squares planes 3 and 5= 130.98°

Dihedral angles between least-squares planes 4 and 5= 130.41°

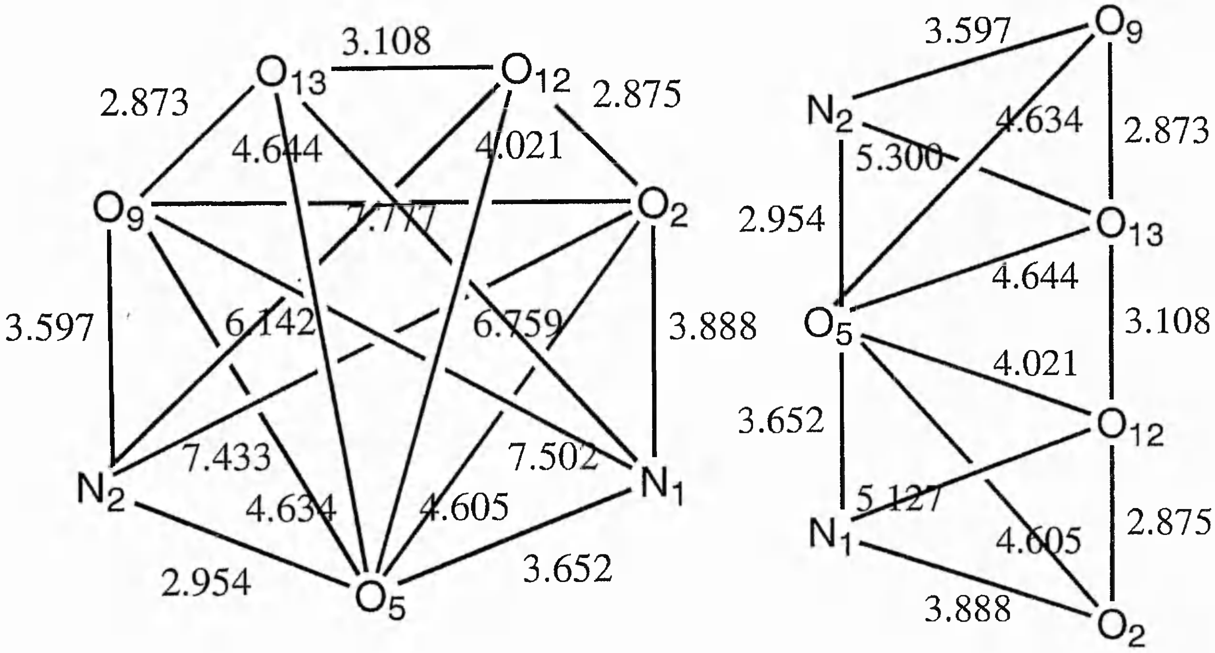
Some hydrogen contacts appear between the molecules in the unit cell, notably between the molecule (x, y, z) and (x, 1+y, z), C38-H30(x, y, z)...O1(x, 1+y, z)= 2.545 Å, C42-H11(x, y, z)...O1(x, 1+y, z)= 2.765 Å and O6(x, y, z)...H41-C48(x, 1+y, z)= 2.995 Å. Hydrogen close approaches also appear between the molecules (x, y, z) and (-x, ½+y, ½-z), C49-H6(x, y, z)...O11(-x, ½+y, ½-z)= 2.904 Å and C39-H36(x, y, z)...S2(-x, ½+y, ½-z)= 3.016 Å. There are also two hydrogen bonds between the molecules (x, y, z) and (-x, -y, -z), O7(x, y, z)...H7-C41(-x, -y, -z)= 2.996 Å and O7(x, y, z)...H19-C20(-x, -y, -z)= 2.617 Å. Finally, four hydrogen close approaches appear between the molecules (x, y, z) and (x, ½-y, ½+z), C43-H42(x, y, z)...S1(x, ½-y, ½+z)= 3.048 Å, C47-H13(x, y, z)...O6(x, ½-y, ½+z)= 3.004 Å, C43-H12(x, y, z)...O6(x, ½-y, ½+z)= 2.731 Å and C43-H42(x, y, z)...H19-C20(x, ½-y, ½+z)= 2.456 Å.





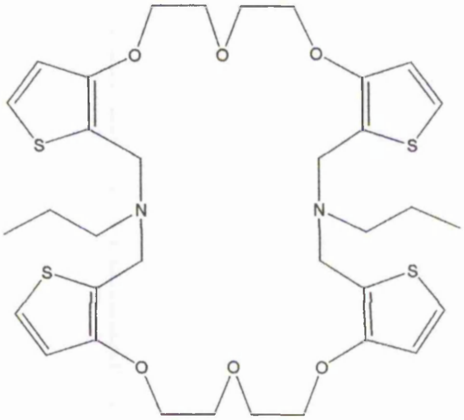
The lone pairs of the donor atoms O2, O12, O13 and O9 of the ether bridge which are almost planar with the atom O5, are oriented inside the cavity, whereas the lone pairs of the atoms O5, N1 and N2 of the diamine bridge are pointing outside the cavity.

The distances between the atom donors and the resulting cavity are shown schematically below.



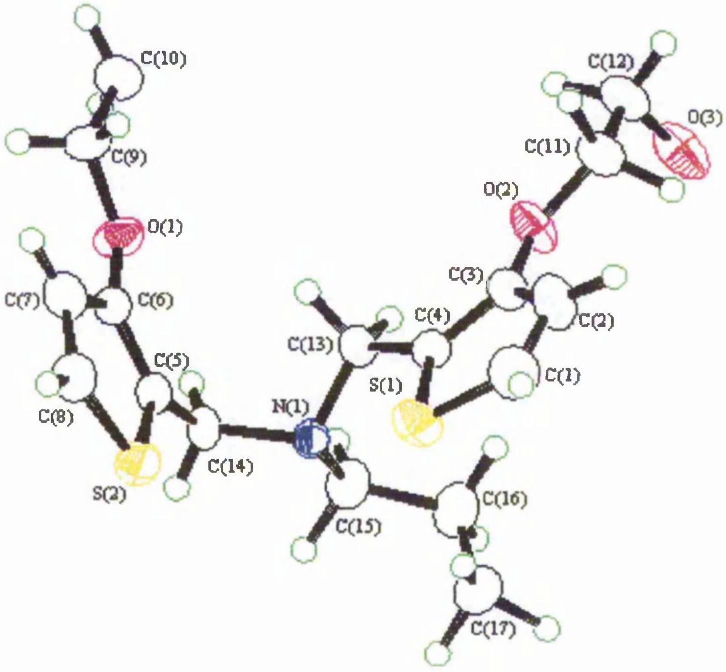
The cross-ring distances between the seven donor atoms are fairly symmetric compared to the macrocycle **22**. The substitution of the methyl groups in compound **22** by tosyl units has induced rigidity in the macrocycle and especially in the diamine chain which has reduced the size of the cavity. Indeed, the resulting radius of the cavity has been reduced to 0.923 Å, which is similar to the radius of the macrocycle **10a**. However, this macrocycle should still be more flexible in solution and should still be less selective than **9a**, **9b**, **10a** and **10b**. The tosyl groups create a steric effect, which should affect the ability of the macrocycle **23** to complex with a metal ion and will probably make it be more selective than the macrocycle **22**. Moreover, the cavity can be divided into two sections, each distorted between square planar and tetrahedral geometries, which have radii of 0.9025 Å and 0.917 Å respectively and could each integrate a range of metal ions similar to macrocycles **9a** and **10a**. Also, the SO_2 groups that are part of the tosylate could enter in competition with the donor atoms of the cavity for an eventual complexation. This macrocyclic cavity is still flexible and big enough to include a large range of metal ions and has many different coordination possibilities to some or all of the donor atoms.

3.7. Eight donor atoms thiophene-based macrocycle (6 oxygens, 2 nitrogens): 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene **24**



3.7.1. Discussion of the structure derived data (tables 35 to 37)

The crystal system is triclinic. One molecule is present in the unit cell and the space group is P-1 or n°2. The positions and anisotropic displacement parameters of the atoms in the macrocycle are best-visualized in the "ortep style" drawing of half the molecule below[353].



Just half of the molecule is unique (due to the existence of a centre of symmetry at the center of the molecule) and after all atom positions had been found and refined, it was expanded to obtain the entire molecule. The thermal parameters of the atoms in the molecule are fairly low.

3.7.2. Discussion of the structural geometry

Table 89. Bond Lengths(Å)

Bond Lengths(Å)			
Bond	Length(Å)	Bond	Length(Å)
S(1) -C(1)	1.714(5)	C(6) -C(7)	1.430(6)
S(1) -C(4)	1.715(4)	C(7) -C(8)	1.370(6)
S(2) -C(5)	1.732(4)	C(9) -C(10)	1.518(6)
S(2) -C(8)	1.714(5)	C(11) -C(12)	1.498(7)
O(1) -C(6)	1.375(5)	C(11) -H(8)	1.126
O(1) -C(9)	1.446(5)	C(11) -H(9)	1.137
O(2) -C(3)	1.372(5)	C(12) -H(14)	1.084
O(2) -C(11)	1.432(6)	C(12) -H(15)	0.967
O(3) -C(10)*	1.437(6)	C(13) -H(10)	1.044
O(3) -C(12)	1.411(6)	C(13) -H(11)	0.967
N(1) -C(13)	1.476(5)	C(14) -H(7)	1.034
N(1) -C(14)	1.484(5)	C(15) -C(16)	1.525(7)
N(1) -C(15)	1.466(6)	C(15) -H(5)	1.115
C(1) -C(2)	1.346(7)	C(15) -H(6)	1.076
C(1) -H(13)	1.053	C(16) -C(17)	1.514(8)
C(2) -C(3)	1.417(6)	C(16) -H(1)	1.066
C(2) -H(12)	0.937	C(16) -H(2)	1.022
C(3) -C(4)	1.369(6)	C(17) -H(3)	1.06
C(4) -C(13)	1.500(6)	C(17) -H(4)	1.069
C(5) -C(6)	1.370(6)	C(17) -H(16)	1.128
C(5) -C(14)	1.495(6)		

* At (–x, -y, -z)

** Note the hydrogen bond lengths are to three decimal places with terminal zero's omitted and have no esd's as the hydrogen positions were not refined.

For ease of description the bond lengths (to 3 decimal places) are shown on a schematic drawing below.

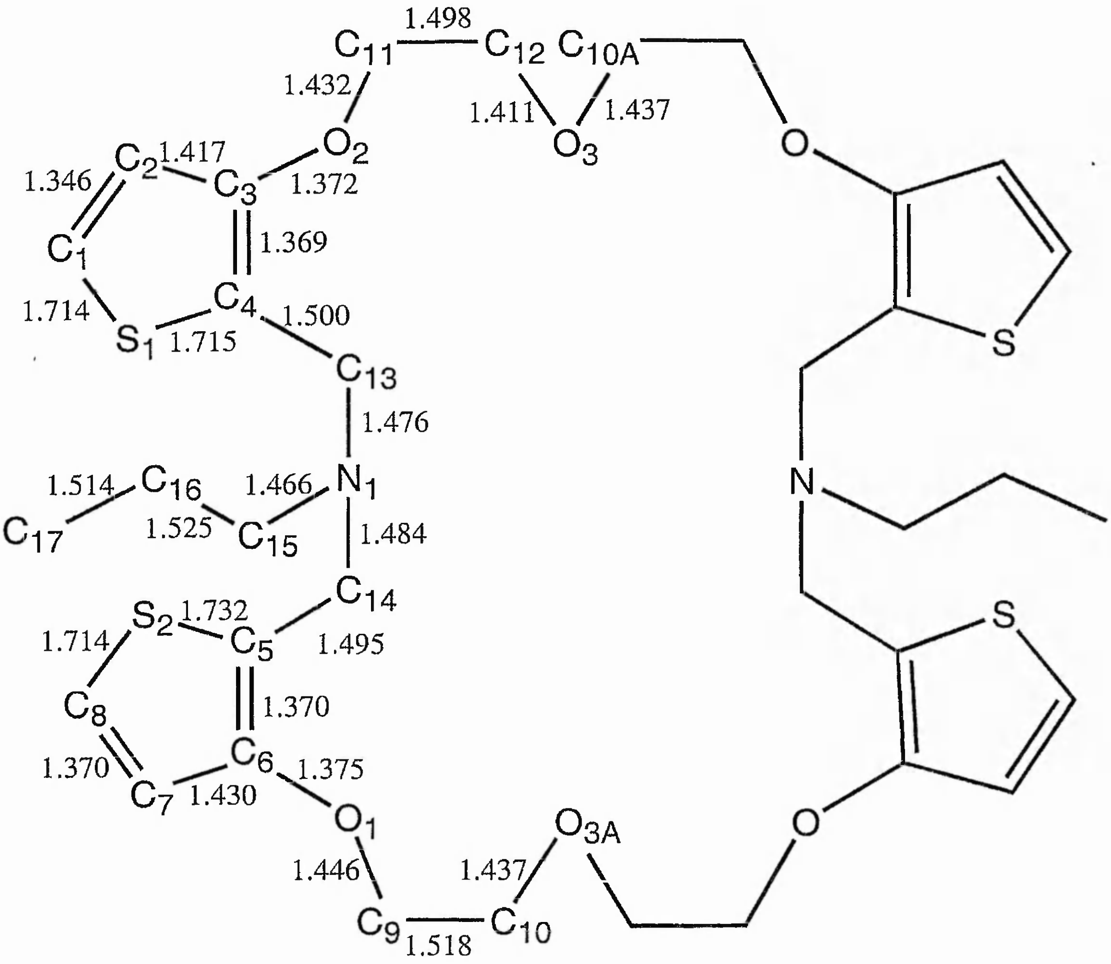


Table 90. Bond Angles(°)

Bond Angles(°)			
Bond	Angles(°)	Bond	Angles(°)
C(1) -S(1) -C(4)	92.4(2)	C(6) -C(7) -C(8)	111.5(4)
C(5) -S(2) -C(8)	93.2(2)	S(2) -C(8) -C(7)	111.5(4)
C(6) -O(1) -C(9)	116.1(3)	O(1) -C(9) -C(10)	106.4(4)
C(3) -O(2) -C(11)	116.2(4)	O(3) -C(10) -C(9)	110.4(4)
C(10) -O(3) -C(12)	116.9(4)	O(2) -C(11) -C(12)	107.7(4)
C(13) -N(1) -C(14)	110.5(3)	O(2) -C(11) -H(8)	113.36
C(13) -N(1) -C(15)	112.3(3)	O(2) -C(11) -H(9)	107.81
C(14) -N(1) -C(15)	107.5(3)	C(12) -C(11) -H(8)	105.38
S(1) -C(1) -C(2)	111.8(4)	C(12) -C(11) -H(9)	106.5
S(1) -C(1) -H(13)	118	H(8) -C(11) -H(9)	115.59
C(2) -C(1) -H(13)	127.51	O(3) -C(12) -C(11)	112.1(4)

C(1) -C(2) -C(3)	112.2(4)	O(3) -C(12) -H(14)	107.07
C(1) -C(2) -H(12)	117.8	O(3) -C(12) -H(15)	108.59
C(3) -C(2) -H(12)	128.83	C(11) -C(12) -H(14)	105.05
O(2) -C(3) -C(2)	126.7(4)	C(11) -C(12) -H(15)	106.91
O(2) -C(3) -C(4)	119.6(4)	H(14) -C(12) -H(15)	117.17
C(2) -C(3) -C(4)	113.6(4)	N(1) -C(13) -C(4)	113.2(3)
S(1) -C(4) -C(3)	110.0(3)	N(1) -C(13) -H(10)	113.57
S(1) -C(4) -C(13)	121.8(3)	N(1) -C(13) -H(11)	114.17
C(3) -C(4) -C(13)	127.7(4)	C(4) -C(13) -H(10)	107.84
S(2) -C(5) -C(6)	109.1(3)	C(4) -C(13) -H(11)	107.07
S(2) -C(5) -C(14)	123.0(3)	H(10) -C(13) -H(11)	100.01
C(6) -C(5) -C(14)	127.8(4)	N(1) -C(14) -C(5)	113.3(4)
O(1) -C(6) -C(5)	119.2(4)	N(1) -C(14) -H(7)	107.97
O(1) -C(6) -C(7)	126.1(4)	C(5) -C(14) -H(7)	115
C(5) -C(6) -C(7)	114.7(4)	N(1) -C(15) -C(16)	114.3(4)
N(1) -C(15) -H(5)	106.79	C(17) -C(16) -H(2)	101.72
N(1) -C(15) -H(6)	112.58	H(1) -C(16) -H(2)	115.23
C(16) -C(15) -H(5)	109.67	C(16) -C(17) -H(3)	115.97
C(16) -C(15) -H(6)	107.09	C(16) -C(17) -H(4)	108.15
H(5) -C(15) -H(6)	106.15	C(16) -C(17) -H(16)	112.19
C(15) -C(16) -C(17)	113.2(4)	H(3) -C(17) -H(4)	107.02
C(15) -C(16) -H(1)	108.24	H(3) -C(17) -H(16)	90.53
C(15) -C(16) -H(2)	109.38	H(4) -C(17) -H(16)	122.24
C(17) -C(16) -H(1)	109.07		

** Note the bond angles including hydrogen atoms are to two decimal places with terminal zeros omitted and have no esd's as the hydrogen atom positions were not refined.

The S1 and S2 thiophene rings form two planes with an angle of 82.42° and are respectively parallel to the S1A and S2A thiophene ring planes. In the S1 thiophene ring, the bond lengths, S1-C1= 1.714 Å, S1-C4= 1.715 Å, C3-C4= 1.369 Å, C1-C2= 1.346Å and C2-C3= 1.417 Å, are fairly similar to those in unsubstituted thiophene[354]. The C1-S1-C4= 92.4(2)°, S1-C1-C2= 111.8(4)° and C1-C2-C3= 112.2(4)° bond angles are also fairly close to their counterparts in unsubstituted thiophene. The S1-C4-C3= 110.0(3)° and C2-C3-C4= 113.6(4)° angles of the substituted C3 and C4 carbon atoms are respectively 1.4° smaller and 2.2° larger than those in unsubstituted thiophene. In the S2 thiophene ring, the S2-C8= 1.714 Å, S2-C5= 1.732 Å, C6-C7= 1.430 Å, C5-C6= 1.370

Å and C7-C8= 1.370 Å bond lengths are also similar to their counterpart in the non-substituted thiophene. The C5-S2-C8= 93.2(8)°, S2-C8-C7= 111.5(4)°, C6-C7-C8= 111.5(4)°, S2-C5-C6= 109.1(3)° and C5-C6-C7= 114.7(4)° bond angle distortions are similar to those in the S1 thiophene ring. The unsubstituted S-C-C and C-C-C angles are respectively 2.4° larger and 3.2° smaller than the on the substituted C5 and C6 carbon atoms. The differences between the thiophene rings appear on the S1 sulphur atom that has an interaction with the nitrogen N1 lone pair, S1...N1= 3.095 Å, whereas the S2 sulphur atom interacts only weakly and even insignificantly with the nitrogen N1, S2...N1= 3.454 Å (sum of the van der Waals radii= 3.45 Å).

Table 91. Least-Squares Planes

Plane number 1

Atoms Defining Plane	Distance
S(1)	.0003(14)
C(1)	-.0090(53)
C(2)	.0107(52)
C(3)	-.0054(43)
C(4)	.0010(41)

Additional Atoms	Distance
O(2)	-.0503
C(11)	.2255
C(12)	.0336
C(13)	.1847
N(1)	-.4066

Mean deviation from plane is .0053 Ångstroms

Chi-squared: 8.3

Plane number 2

Atoms Defining Plane	Distance
S(2)	-.0005(13)
C(5)	.0090(41)
C(6)	-.0104(43)

C(7)	.0063(48)
C(8)	.0010(50)

Additional Atoms	Distance
O(1)	-.0373
C(9)	-.2710
C(10)	-.5200
C(14)	.0804
N(1)	-1.1806

Mean deviation from plane is .0054 Ångstroms

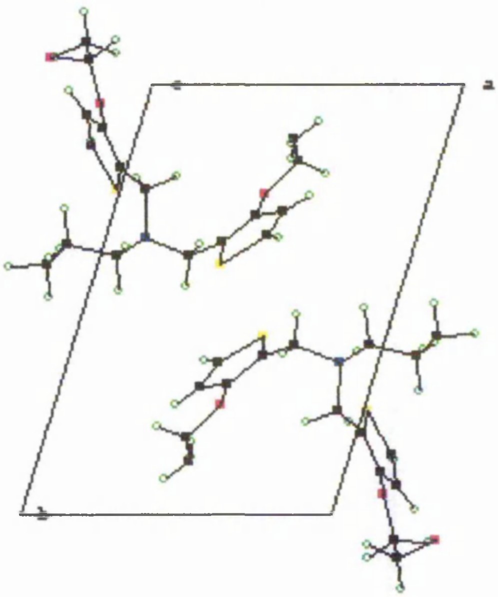
Chi-squared: 12.8

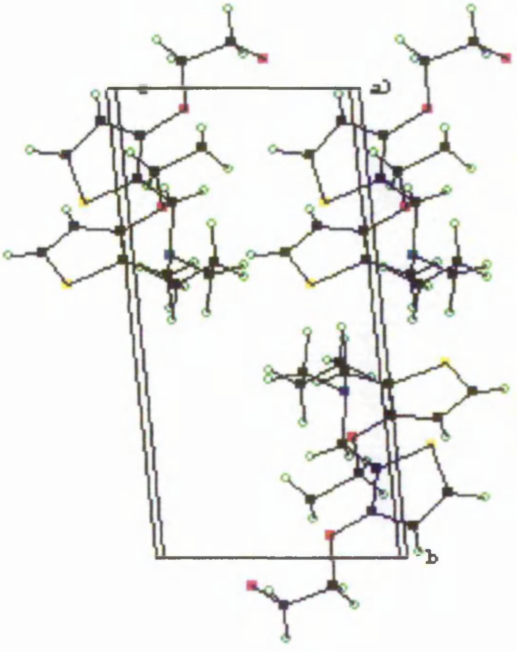
Dihedral angle between least-squares planes 1 and 2= 82.42°

In the ether bridge, the C(thiophene)-O bond lengths, C3-O2= 1.372 Å and C6-O1= 1.375 Å, are shortened compared to the other C-O bond lengths in the chain, which vary from 1.411 Å to 1.446 Å. This could be due to a conjugation with the adjacent thiophene ring. The C9-C10= 1.518 Å and C11-C12= 1.498 Å bond lengths are close to the usual 1.52 Å[357,363]. The O-C-C bond angles between the ether bridge and the thiophene rings are similar, O1-C6-C5= 119.2(4)°, O1-C6-C7= 126.1(4)°, O2-C3-C4= 119.6(4)° and O2-C3-C2= 126.7(4)°. There are also similar hydrogen contacts such as O1...H17-C7= 2.794 Å, O1...H23-C14= 2.573 Å, O2...H12-C2= 2.853 Å and O2...H11-C13= 2.613 Å, although the oxygen atom O1 has one more hydrogen interaction with the amine bridge, O1...H10-C13= 2.697 Å, that shows how close the two ether bridges are. The other O-C-C bonds form two small and two large angles (>109.47°), O1-C9-C10= 106.4(4)°, O2-C11-C12= 107.7(4)°, O3A-C10-C9= 110.4(4)° and O3-C12-C11= 112.1(4)°. Those O-C-C bond angles are affected by some hydrogen bonds, O1...H22-C10= 2.460 Å, O2...H14-C12= 2.431 Å, O3...H9-C11- 2.542 Å and O3...H36A-C9A= 2.543 Å. The C3-O2-C11= 116.2(4)° and C6-O1-C9= 116.1(3)° angles are similar but have different H...H interactions. Indeed, on the C3-O2-C11 bond angle only one hydrogen interaction appears, C2-H12...H9-C11= 2.345 Å, but this is a closer approach than the two hydrogen interactions on the C6-O1-C9 bond angle, C7-H17...H19-C9= 2.483 Å and C7-H17...H20-C9= 2.413 Å. Finally, the C10A-O3-C12= 116.9(4)° bond angle also has a very short H...H interaction C10A-H38A...H15-C12= 2.157 Å.

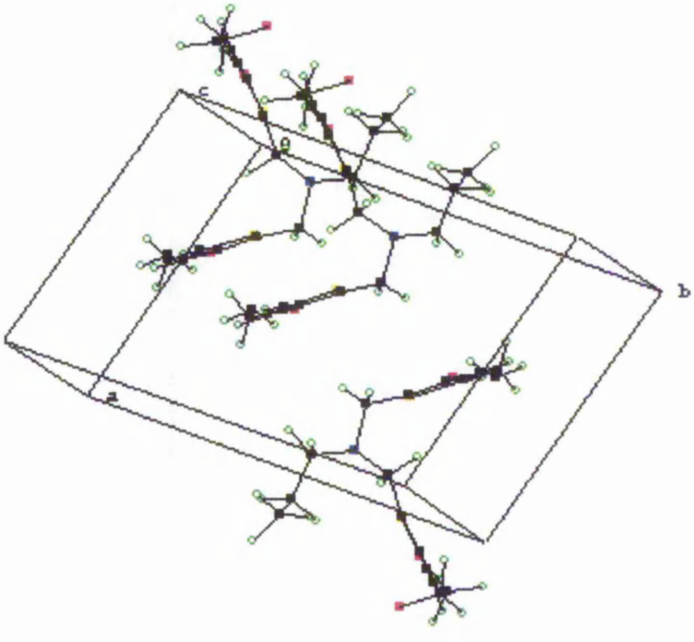
In the amine bridge, the C4-C13= 1.500 Å and C5-C14= 1.495 Å bond lengths are slightly shorter than the C15-C16= 1.525 Å and C16-C17= 1.514 Å bond lengths. This could be due to a conjugation with the adjacent thiophene ring, that is more pronounced on the C(thiophene)-O bond lengths of the ether bridge. The C-C=C bond angles between the amine bridge and the thiophene rings, C3-C4-C13= 127.7(4)° and C6-C5-C14= 127.8(4)°, are similarly larger than the S-C-C bond angles, S1-C4-C13= 121.8(3)° and S2-C5-C14= 123.0(3)°. The N1-C13-C4= 113.2(3)° and N1-C14-C5= 113.3(4)° bond angles are fairly close to each other, while the N-C-C bond angle with the propyl substituent is N1-C15-C16= 114.3(4)°. The C-C-C bond angle on the propyl group is C15-C16-C17= 113.2(4)°. The S...H close approach between the S1 thiophene ring and the propyl group, S1...H4-C17= 2.873 Å, shows that the propyl group is closer to the S1 thiophene ring than the S2 thiophene ring. The N1-C13= 1.476 Å and N1-C14= 1.484 Å bond lengths and the N1-C15= 1.466 Å bond length with the propyl group are close to a typical C-N single bond[363]. The C13-N1-C14= 110.5(3)°, C13-N1-C15= 112.3(3)° and C14-N1-C15= 107.5(3)° bond angles deviate from the ideal tetrahedral conformation. This is due to the S...N interaction, which shows that the N1 nitrogen lone pair is pointing outside the cavity.

Two hydrogen interactions appear between the adjacent molecules, O3(556001: x, y, z)...H12-C2(555001: x, y, z)= 2.538 Å and O2(556001: x, y, z)...H13-C1(555001: x, y, z)= 2.704 Å. The two following views of the unit cell show that the molecules are arranged parallel to the ab plane.

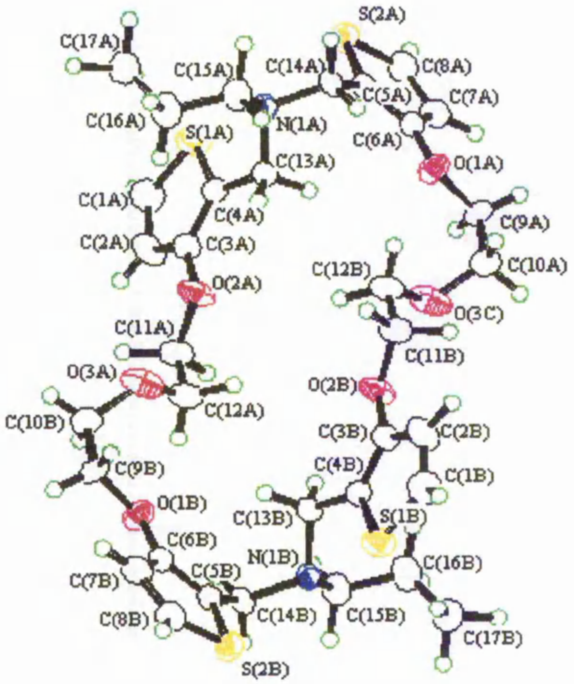




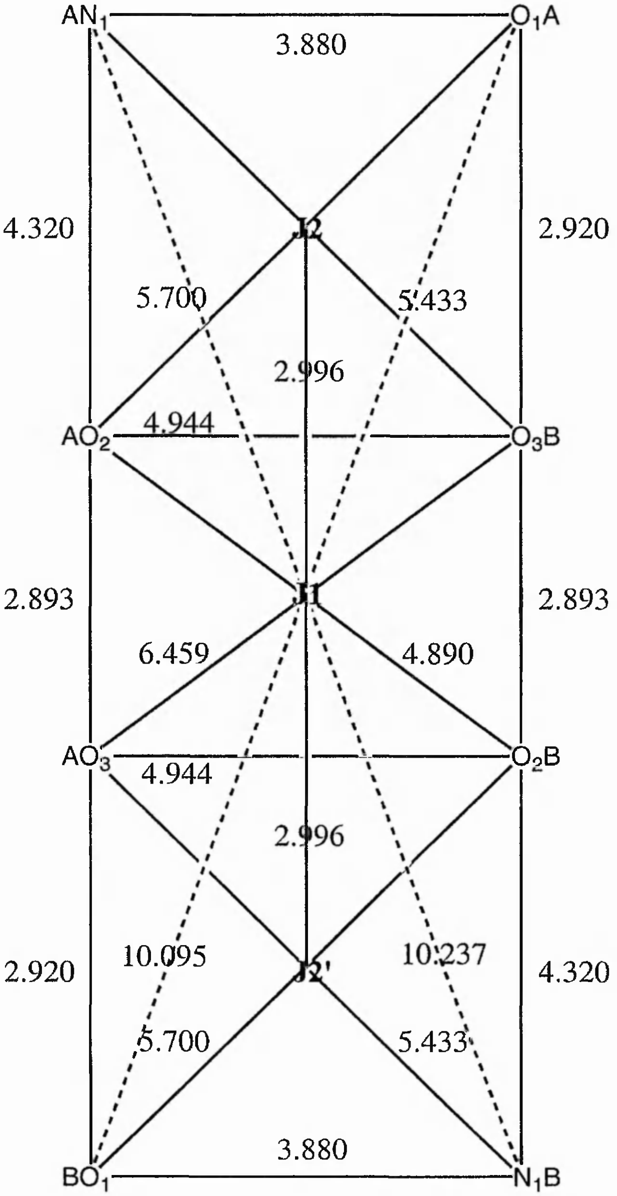
The last view, below, shows that the S1 thiophene ring and the S2 thiophene ring planes are parallel to their counterparts in the neighbouring molecules.



The lone pairs of the oxygen donor atoms are oriented inside the cavity, whereas the lone pairs of the atoms N1 and N1A of the amine bridge are pointing outside the cavity.

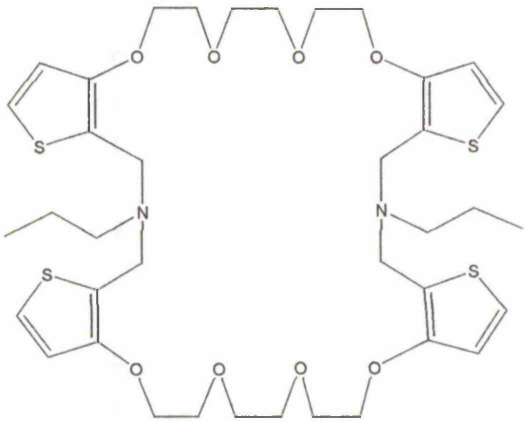


The distances between the atom donors and the resulting cross cavity distances are shown schematically below.

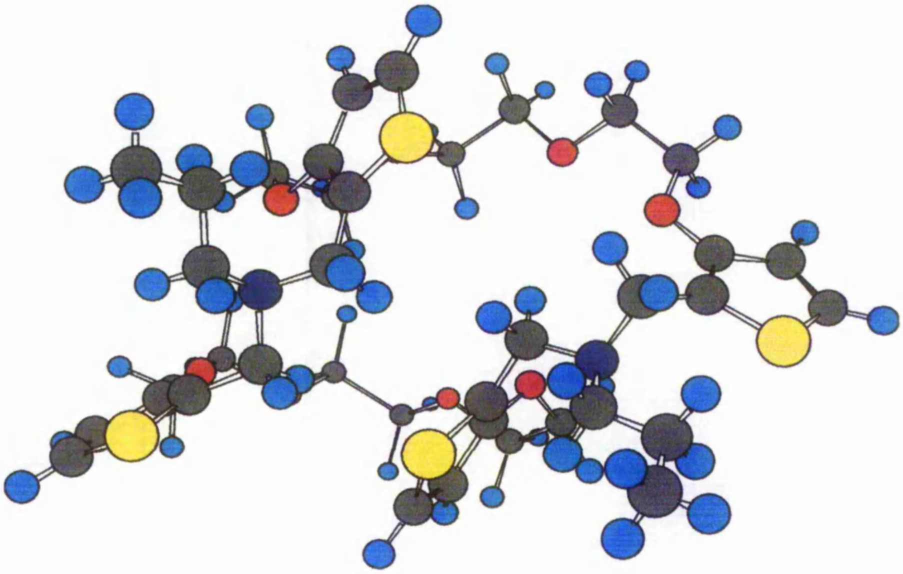


The distances between the seven donor atoms are fairly symmetric. The donor atoms as well as the entire molecule lie almost in a plane. The cavity formed by the donor atoms has all approximately rectangular shape and is clearly much longer in one direction than the other. This cavity can be divided in to three other cavities. The central cavity **24a** is approximately square planer with a radius of 0.995 Å, while the others **24b** and **24b'**, which are symmetric through the centre of symmetry at the center of the molecule, are intermediate between a square plane and a tetrahedral geometry and have a radius of 1.267 Å. The centroid positions J1 and J2 of the cavity **23a** and **23b** have been calculated and give a cavity radius of 1.045 Å for **24a** and 1.044 Å for **24b**. These centroids J1 and J2 are distant by 2.996 Å. Both calculations of the cavity radii give cavity sizes similar to the previous macrocycles discussed such as **9a**, **9b**, **10a**, **10b** and **23**. The ether bridges have a very high flexibility, which should enable the macrocycle to easily include between one and three metal ions such as copper(II) or a larger ion like lead(II). This macrocycle should be able to form up to three square planar coordinations with metal ions, or to literally form a cage and encapsulate single metal ion on complexation. This macrocycle would be predicted overall to have a high ability to complex a metal ion but should be less selective than all the previous macrocycles discussed.

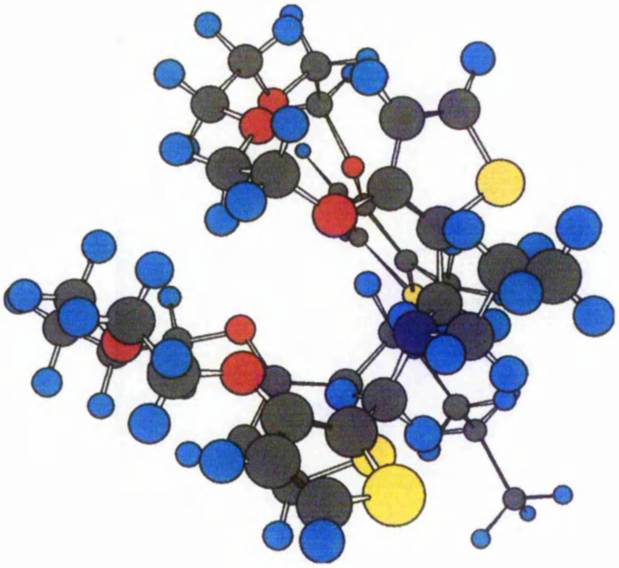
3.8. Ten donor atoms thiophene-based macrocycle (8 oxygens, 2 nitrogens): 18,41-dipropyl-2,5,8,11,25,28,31,34-nonaoxa-15,21,38,44-tetrathia-18,41-diaza-pentacyclo[35.5.5.5.0.0]-hexatetraconta-1(43),12(16),13,20(24),22,35(39),36,45-octaene **25**

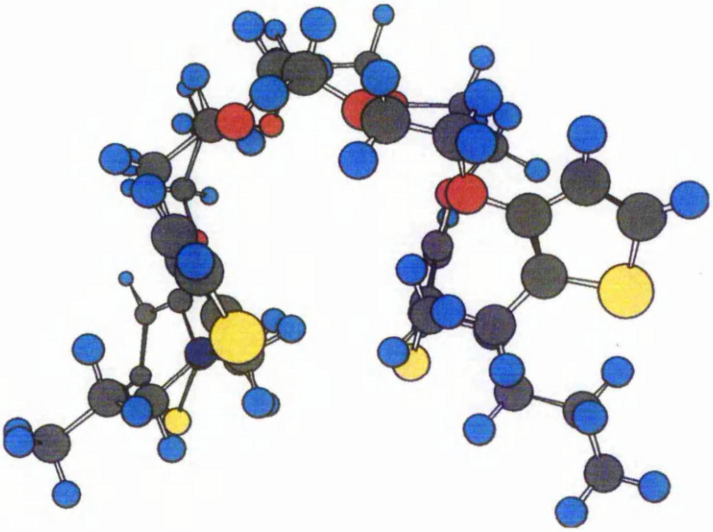


Macrocycle **25** was modelled by minimization of its energy via the programs MM2 (steric energy) then MOPAC (heat of formation). This macrocycle is similar to compound **24** but it contains ten donor atoms instead of eight, 8 oxygen atoms in the ether bridge and 2 nitrogen atoms in the amine bridge.

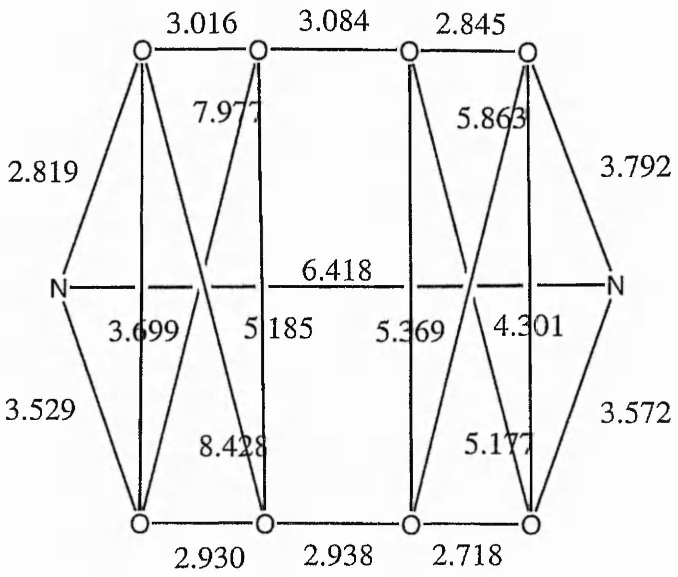


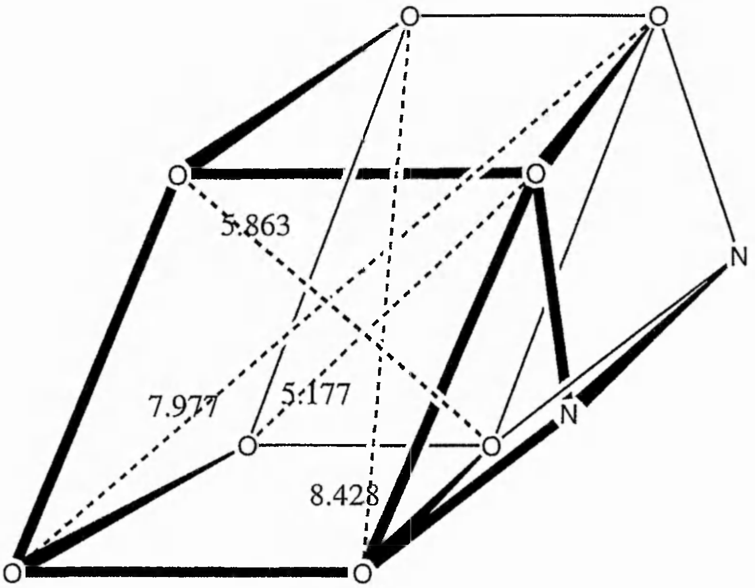
The most stable macrocycle conformation seems to exist as a cryptand cage that could readily integrate a metal ion, perhaps more than one. The four oxygen atoms of each ether bridge form two planes, which are parallel to each other. Those donor atoms have their lone pairs pointing inside the cavity.





The distances between the atom donors and the resulting cavity geometry are shown schematically on the next page.





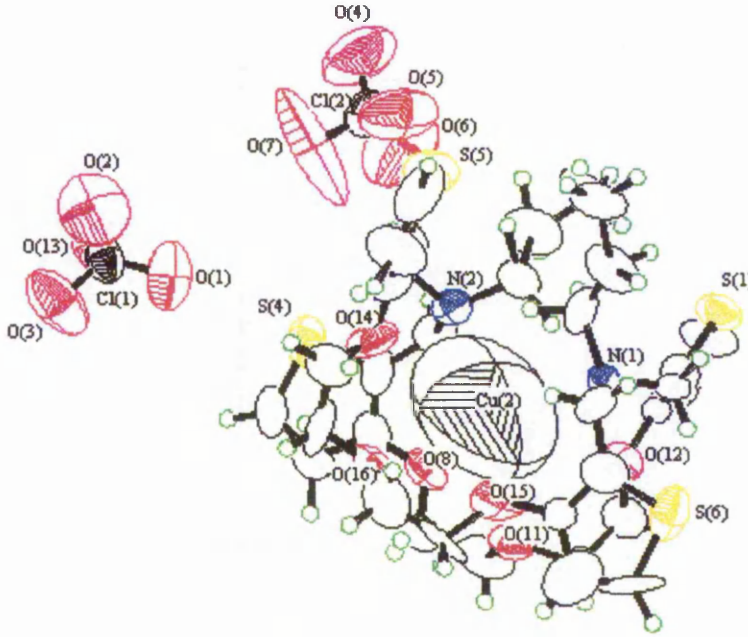
The cavity radius obtained is 1.189 Å, which is larger than for the macrocycles **8b**, **9a**, **9b**, **10a**, **10bA**, **21** and **23**. The ether bridges have an even greater flexibility than those in macrocycle **24**. So as for macrocycle **24**, this macrocycle can literally form a cage and could encapsulate the metal ion during complexation. Similarly to compound **24**, this macrocycle should be able to complex one or more metal ions. The implication of the ten donor atoms in the complexation with a metal ion would create a very uncommon high coordination. The bonding would be predominantly ionic and the metal cation would need a charge high enough to attract the large number of donor atoms. This macrocycle should overall have a higher ability to complex a metal ion but should be less selective than all the previous macrocycles. Also, the complex stability would be considerably lower.

4. Thiophene-based ligands complexed with metal ions

4.1. The complex of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with copper (II) perchlorate **50**

4.1.1. Discussion of the structure derived data (tables 38 to 40)

The crystal system of this macrocyclic complex is triclinic. One molecule is present in the unit cell and the space group is $P2_1/c$ or n°14. The positions and anisotropic displacement parameters of the atoms in the complex are best visualized in the "ortep style" drawing below[353].



The thermal parameters of the atoms in the macrocyclic ligand are all fairly large, but O8, O11, O12, O14, O15, O16, N1 and N2 have smaller thermal ellipsoids than the other atoms around the ring. This could be due to their interaction with the metal ion. The propyl group carbon atoms and the perchlorate counterion oxygen atoms have very large thermal ellipsoids and the esd's of the atomic positions are large also. Finally, the copper(II) ion has the greatest displacement parameters due to the fact that it is not strongly bonded to any of the six donor atoms and instead is moving around in the cavity. The copper ion must be moving between different possible donor atom coordination sites. The distances between the metal ion and the donor atoms are unusually long, which lowers the stability of this complex. This macrocyclic complex is, as described by Cram[364], a capsular complex. (Please see note on page 303).

4.1.2. Discussion of the structural geometry

Table 92. Bond Lengths(Å)

Bond Lengths(Å)			
Bond	Length(Å)	Bond	Length(Å)
Cl(1) -O(1)	1.41(2)	O(16) -C(56)	1.44(4)
Cl(1) -O(2)	1.31(3)	O(16) -C(60)	1.42(3)
Cl(1) -O(3)	1.41(2)	N(1) -C(6)	1.53(3)
Cl(1) -O(13)	1.43(2)	N(1) -C(26)	1.57(3)
Cl(2) -O(4)	1.32(3)	N(1) -C(34)	1.54(3)
Cl(2) -O(5)	1.34(3)	N(2) -C(25)	1.49(3)
Cl(2) -O(6)	1.36(3)	N(2) -C(29)	1.55(3)
Cl(2) -O(7)	1.38(3)	N(2) -C(30)	1.54(3)
S(1) -C(27)	1.67(3)	C(1) -C(35)	1.39(5)
S(1) -C(40)	1.67(4)	C(1) -C(43)	1.30(5)
S(4) -C(32)	1.68(3)	C(1) -H(18)	1.032
S(4) -C(50)	1.68(4)	C(2) -C(28)	1.35(4)
S(5) -C(7)	1.70(3)	C(2) -C(32)	1.39(4)
S(5) -C(48)	1.67(4)	C(3) -C(37)	1.48(3)
S(6) -C(39)	1.67(4)	C(3) -H(3)	0.91
S(6) -C(43)	1.78(4)	C(4) -C(5)	1.35(3)
O(8) -C(2)	1.39(4)	C(4) -C(27)	1.40(3)
O(8) -C(45)	1.38(3)	C(5) -C(40)	1.29(4)
O(11) -C(36)	1.46(3)	C(5) -H(21)	1.007
O(11) -C(37)	1.49(3)	C(6) -C(39)	1.47(4)
O(12) -C(3)	1.45(3)	C(6) -H(5)	1.01
O(12) -C(4)	1.35(3)	C(7) -C(24)	1.37(4)
O(14) -C(24)	1.30(3)	C(7) -C(25)	1.49(4)
O(14) -C(41)	1.44(3)	C(24) -C(46)	1.40(5)
O(15) -C(35)	1.39(4)	C(25) -H(2)	1.073
O(15) -C(51)	1.49(3)	C(25) -H(23)	1.197
C(26) -C(47)	1.49(4)	C(55) -C(57)	1.53(5)
C(26) -H(8)	1.213	C(55) -H(22)	1.174

C(26) -H(9)	1.055	C(57) -H(12)	1.028
C(27) -C(34)	1.49(3)	C(41) -C(60)	1.46(4)
C(28) -C(50)	1.39(4)	C(43) -H(19)	0.992
C(28) -H(14)	1.194	C(45) -H(7)	0.941
C(29) -C(32)	1.45(4)	C(46) -C(48)	1.35(5)
C(29) -H(4)	1.075	C(46) -H(1)	1.213
C(30) -C(55)	1.48(4)	C(47) -C(54)	1.50(4)
C(30) -H(11)	1.176	C(47) -H(6)	1.171
C(30) -H(17)	1.245	C(47) -H(15)	0.955
C(34) -H(13)	0.998	C(48) -H(20)	1.016
C(35) -C(39)	1.37(5)	C(50) -H(16)	1.019
C(36) -C(45)	1.47(4)	C(51) -C(56)	1.47(5)
C(40) -H(10)	1.152		

** Note the hydrogen bond lengths are to three decimal places with terminal zero's omitted and have no esd's as the hydrogen positions were not refined.

Table 93. Contact bonds(Å)

Contact bonds(Å)					
Bond	Length(Å)	ADC(*)	Bond	Length(Å)	ADC(*)
Cu(2) -N(2)	2.88(5)	1	S(4) -O(1)	3.25(3)	1
Cu(2) -O(14)	2.94(4)	1	S(5) -O(5)	3.15(3)	1
Cu(2) -O(16)	3.00(4)	1	S(6) -O(4)	3.15(3)	45404
Cu(2) -H(9)	3.058	1	O(1) -H(1)	2.471	66703
Cu(2) -O(8)	3.10(4)	1	O(1) -H(21)	2.672	65703
Cu(2) -O(11)	3.10(3)	1	O(2) -H(5)	2.816	66703
Cu(2) -O(12)	3.17(4)	1	O(3) -H(15)	2.701	65501
Cu(2) -O(15)	3.24(5)	1	O(13) -H(18)	2.493	65504
Cu(2) -N(1)	3.27(4)	1	O(13) -H(6)	2.83	65501
Cl(2) -H(23)	2.809	1	O(13) -H(15)	2.991	65501
O(4) -H(10)	2.372	65702	O(5) -H(22)	2.963	1
O(4) -H(20)	2.74	64702	O(6) -H(7)	2.654	65703
O(4) -H(16)	2.777	4	O(6) -H(23)	2.732	1
O(5) -H(23)	2.503	1	O(6) -H(20)	2.754	64702
O(5) -H(14)	2.873	4	O(7) -H(23)	2.658	1

* The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number shown in the table is a composite of three one digit numbers and one two digit number: TA(1st digit) + TB(2nd digit) + TC(3rd digit) + SN(4th and 5th digit). TA, TB, & TC are the crystal lattice translation

digits along cell edges a, b, and c. A translation digit of 5 indicates the origin unit cell. If TA=4, this indicates a translation of one unit cell length along the a axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus (+/-)4 lattice translations from the origin (TA=5,TB=5,TC=5) can be represented. The SN or symmetry operator number refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of the symmetry operators relevant to this structure are given below. For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell (TA=5,TB=5,TC=5) and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always ADC=55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of that atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis. An ADC of 1 indicates an intermolecular contact between two fragments (i.e. cation and anion) that reside in the same asymmetric unit.

Symmetry Operators:

(1) +X, +Y, +Z (2) -X, 1/2+Y, 1/2-Z
(3) -X, -Y, -Z (4) +X, 1/2-Y, 1/2+Z

The macrocyclic ligand **24** (pages 274-283) is encapsulating the copper(II) metal ion to form the macrocyclic-capsular complex **50**. The interactions between the copper ion and the donor atoms create distortions throughout the macrocyclic ligand that are reflected in the bond lengths and bond angles. The Cu-O and Cu-N interactions are not exactly the same strength, and this is reflected in the changes to the other bond lengths and angles in the ligand.

For ease of description the bond lengths in the ligand (to 2 decimal places) are shown on a schematic drawing on the next page. Compare with those of compound 24 (page 276).

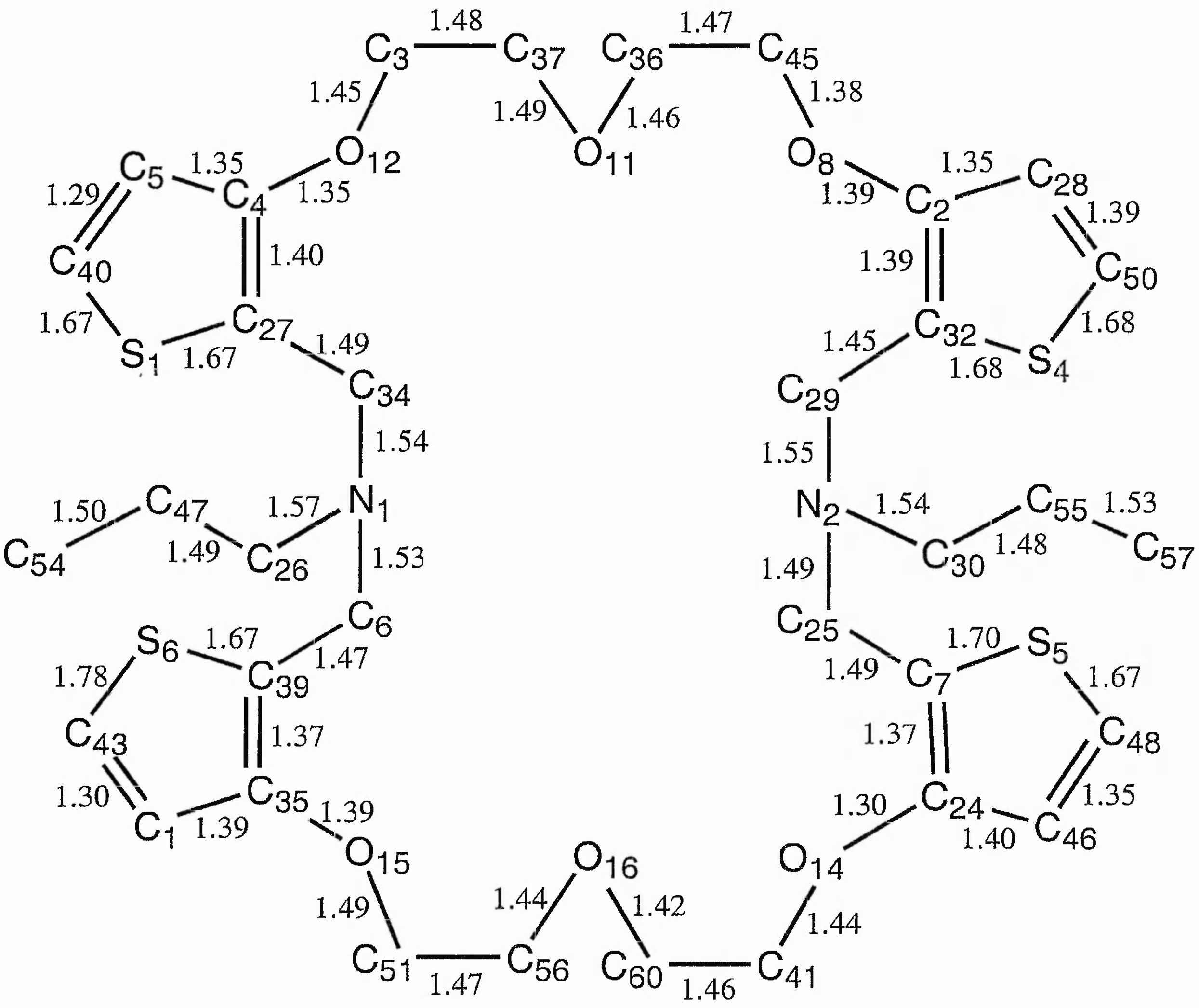


Table 94. Bond Angles(°)

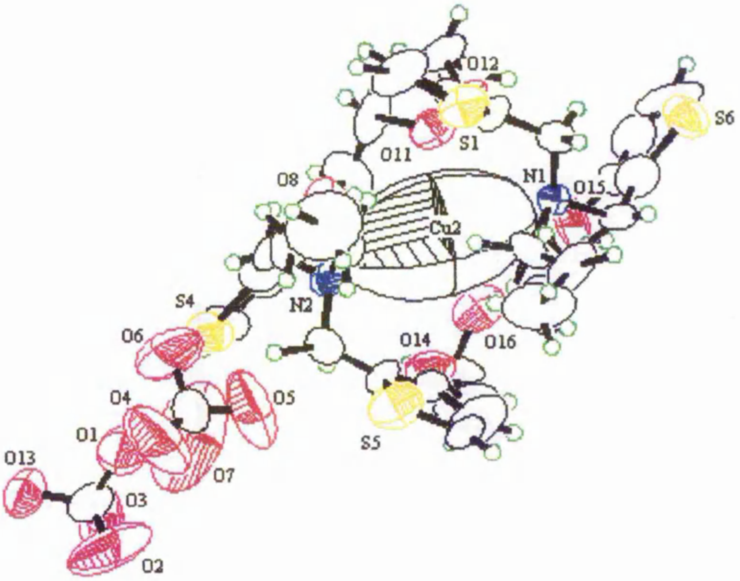
Bond Angles(°)			
Bond	Angle(°)	Bond	Angle(°)
O(1) -Cl(1) -O(2)	108(2)	C(25) -N(2) -C(30)	115(2)
O(1) -Cl(1) -O(3)	117(2)	C(29) -N(2) -C(30)	112(2)
O(1) -Cl(1) -O(13)	109(1)	C(35) -C(1) -C(43)	107(5)
O(2) -Cl(1) -O(3)	105(2)	C(35) -C(1) -H(18)	129.44
O(2) -Cl(1) -O(13)	111(2)	C(43) -C(1) -H(18)	123.85
O(3) -Cl(1) -O(13)	107(1)	O(8) -C(2) -C(28)	124(4)
O(4) -Cl(2) -O(5)	111(2)	O(8) -C(2) -C(32)	122(3)
O(4) -Cl(2) -O(6)	111(2)	C(28) -C(2) -C(32)	114(4)

O(4) -Cl(2) -O(7)	113(3)	O(12) -C(3) -C(37)	107(2)
O(5) -Cl(2) -O(6)	110(2)	O(12) -C(3) -H(3)	94.68
O(5) -Cl(2) -O(7)	107(2)	C(37) -C(3) -H(3)	115.4
O(6) -Cl(2) -O(7)	103(3)	O(12) -C(4) -C(5)	132(3)
C(27) -S(1) -C(40)	92(2)	O(12) -C(4) -C(27)	116(2)
C(32) -S(4) -C(50)	90(2)	C(5) -C(4) -C(27)	112(3)
C(7) -S(5) -C(48)	90(2)	C(4) -C(5) -C(40)	114(3)
C(39) -S(6) -C(43)	91(2)	C(4) -C(5) -H(21)	120.93
C(2) -O(8) -C(45)	120(3)	C(40) -C(5) -H(21)	124.63
C(36) -O(11) -C(37)	113(2)	N(1) -C(6) -C(39)	110(2)
C(3) -O(12) -C(4)	120(2)	N(1) -C(6) -H(5)	70.5
C(24) -O(14) -C(41)	118(3)	C(39) -C(6) -H(5)	106.95
C(35) -O(15) -C(51)	126(3)	S(5) -C(7) -C(24)	113(2)
C(56) -O(16) -C(60)	116(3)	S(5) -C(7) -C(25)	127(3)
C(6) -N(1) -C(26)	109(2)	C(24) -C(7) -C(25)	120(3)
C(6) -N(1) -C(34)	111(2)	O(14) -C(24) -C(7)	124(3)
C(26) -N(1) -C(34)	112(2)	O(14) -C(24) -C(46)	126(4)
C(25) -N(2) -C(29)	112(2)	C(7) -C(24) -C(46)	110(3)
N(2) -C(25) -C(7)	116(2)	H(11) -C(30) -H(17)	146.11
N(2) -C(25) -H(2)	107.42	S(4) -C(32) -C(2)	112(3)
N(2) -C(25) -H(23)	101.72	S(4) -C(32) -C(29)	122(3)
C(7) -C(25) -H(2)	94.5	C(2) -C(32) -C(29)	126(3)
C(7) -C(25) -H(23)	124.4	N(1) -C(34) -C(27)	113(2)
H(2) -C(25) -H(23)	112	N(1) -C(34) -H(13)	99.4
N(1) -C(26) -C(47)	115(3)	C(27) -C(34) -H(13)	95.06
N(1) -C(26) -H(8)	112.55	O(15) -C(35) -C(1)	114(5)
N(1) -C(26) -H(9)	109.56	O(15) -C(35) -C(39)	126(3)
C(47) -C(26) -H(8)	114.24	C(1) -C(35) -C(39)	120(4)
C(47) -C(26) -H(9)	114.74	O(11) -C(36) -C(45)	105(3)
H(8) -C(26) -H(9)	87.3	O(11) -C(37) -C(3)	112(2)
S(1) -C(27) -C(4)	109(2)	S(6) -C(39) -C(6)	128(3)
S(1) -C(27) -C(34)	125(2)	S(6) -C(39) -C(35)	107(3)
C(4) -C(27) -C(34)	126(2)	C(6) -C(39) -C(35)	125(3)
C(2) -C(28) -C(50)	109(3)	S(1) -C(40) -C(5)	113(3)
C(2) -C(28) -H(14)	113.69	S(1) -C(40) -H(10)	120.19
C(50) -C(28) -H(14)	136.06	C(5) -C(40) -H(10)	125.07
N(2) -C(29) -C(32)	113(2)	O(14) -C(41) -C(60)	101(3)
N(2) -C(29) -H(4)	92.57	S(6) -C(43) -C(1)	115(3)
C(32) -C(29) -H(4)	121.11	S(6) -C(43) -H(19)	122.31
N(2) -C(30) -C(55)	115(3)	C(1) -C(43) -H(19)	123.03

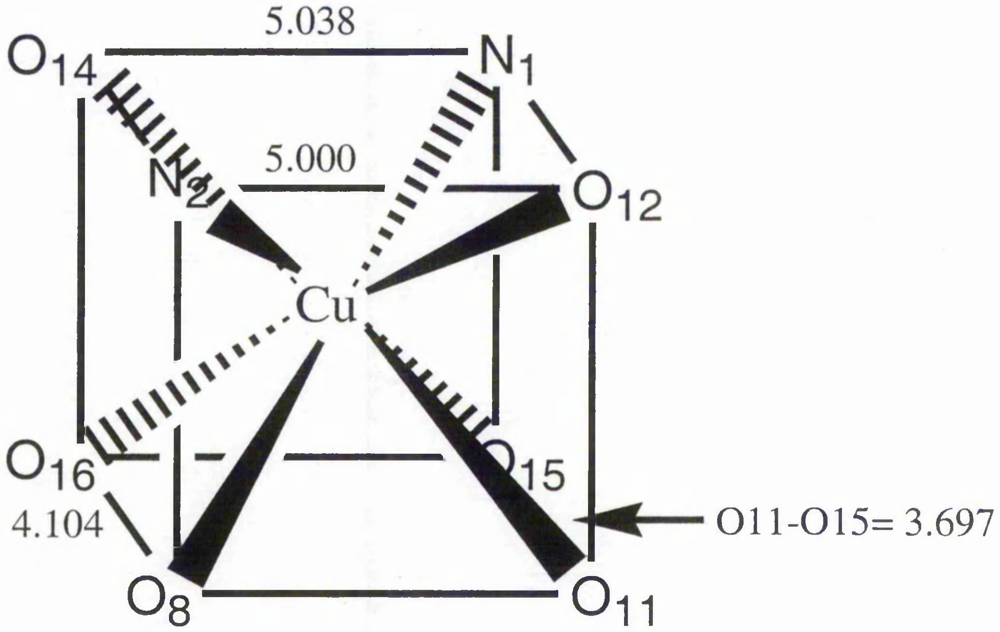
N(2) -C(30) -H(11)	102.6	O(8) -C(45) -C(36)	105(3)
N(2) -C(30) -H(17)	100.67	O(8) -C(45) -H(7)	118.5
C(55) -C(30) -H(11)	120.67	C(36) -C(45) -H(7)	92.31
C(55) -C(30) -H(17)	69.01	C(24) -C(46) -C(48)	113(4)
C(24) -C(46) -H(1)	105.22	S(4) -C(50) -C(28)	115(3)
C(48) -C(46) -H(1)	142.12	S(4) -C(50) -H(16)	120.1
C(26) -C(47) -C(54)	111(3)	C(28) -C(50) -H(16)	125.03
C(26) -C(47) -H(6)	91.23	O(15) -C(51) -C(56)	107(3)
C(26) -C(47) -H(15)	124.88	C(30) -C(55) -C(57)	106(3)
C(54) -C(47) -H(6)	73.02	C(30) -C(55) -H(22)	121.38
C(54) -C(47) -H(15)	123.77	C(57) -C(55) -H(22)	67.45
H(6) -C(47) -H(15)	105.81	O(16) -C(56) -C(51)	113(4)
S(5) -C(48) -C(46)	114(3)	C(55) -C(57) -H(12)	104.76
S(5) -C(48) -H(20)	118.92	O(16) -C(60) -C(41)	114(3)
C(46) -C(48) -H(20)	127.54		

** Note the bond angles including hydrogen atoms are to two decimal places with terminal zeros omitted and have no esd's as the hydrogen atom positions were not refined.

The following view shows that the metal-ligand complex without the perchlorate counterions has an approximate two-fold axis centered on Cu. The thiophene rings form an helixoïd.



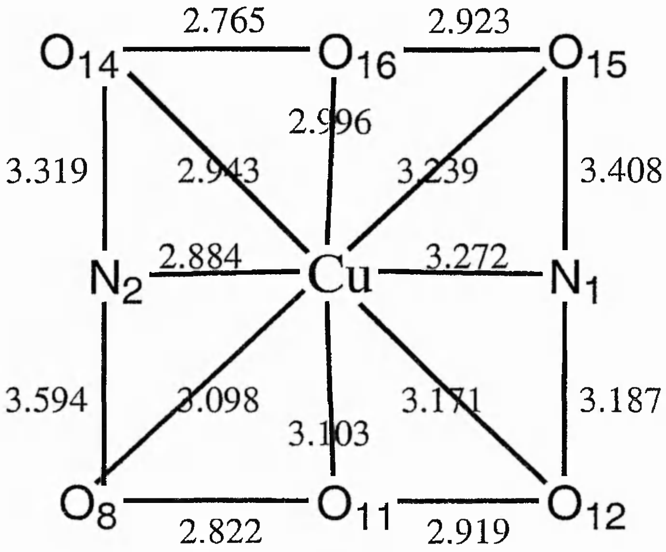
The donor atoms form a slightly distorted octahedral cage which is encapsulating the copper(II) ion. This macrocyclic cage is fairly symmetric and is schematically drawn below.



* Note the other donor atom distances are indicated on the following diagram page 295.

The oxygen atoms O8, O11 and O12 form a plane that has an angle of 167.25° with the plane formed by the oxygen atoms O14, O15 and O16. The distances of the Cu ion from those planes are fairly similar, 2.09Å and 1.97Å.

The following scheme shows the distances between the donor atoms and the copper(II) ion. These contacts between the oxygen and nitrogen atoms and the copper ion are unusually long as they vary from 2.884 to 3.272Å which is much longer than the sum of the van der Waals radii between Cu and O and between Cu and N, Cu-O= 2.17Å and Cu-N= 2.27Å. Despite these very long contacts, the effect on the macrocycle bond lengths and bond angles is significant. It seems that the copper ion is closer to the O8, O14, O16 and N2 atoms, 2.884-3.098Å, than the O11, O12, O15 and N1 atoms, 3.103-3.272Å. This closer contact with the copper ion could be due to the presence of the perchlorate counterions (especially the Cl2 perchlorate ion) near the S4 and S5 thiophene rings (table 93). The negative perchlorate ions could weakly attract the metal ion towards this side of the ring. The weak interactions with the perchlorate ions may be reflected in the Cl-O bond lengths. The Cl2 perchlorate is closer to the ligand and its bond lengths vary from 1.32Å to 1.38Å while the Cl1 perchlorate bond lengths are longer and vary from 1.41Å to 1.43Å, except Cl1-O2= 1.31Å which is directed away from the macrocycle.



In the thiophene rings, the bond lengths and bond angles are strongly distorted compared to unsubstituted thiophene[354] and to the free ligand **24**. Moreover, the effect of the interactions with the copper(II) ion is different on the S4 and S5 thiophene rings compared to their counterpart S1 and S6 thiophene rings. This could be due to the presence of the perchlorate counterions near the S4 and S5 thiophenes and closer to the copper(II) cation than the other perchlorates in the unit cell, S4...O1-Cl1= 3.25 Å and S5...O5-Cl2= 3.15 Å (sum of the van der Waals radii= 3.25 Å), Cl1-O1(x, y, z)...H1-C46(-x, -y, -z)= 2.471 Å. The S-C bond lengths, in the S1 and S4 thiophene rings are symmetrically distorted, S1-C10 and S1-C27= 1.67Å and S4-C32 and S4-C50= 1.68Å. In the S4 and S6 rings, the S-C bonds are unsymmetrically distorted. S5-C7= 1.70Å and S5-C48= 1.67Å are fairly symmetric and are as short as for the S1 and S4 thiophenes, whereas S6-C39= 1.67Å is similar to the preceding bond lengths and S6-C43= 1.78Å is longer. This could be due to the contacts that occur between the perchlorate ions and the thiophene rings in the unit cell that are less weakened by the copper(II) ion compared to the S4 and S5 thiophenes. Indeed, the S1 thiophene ring (-x, ½+y, ½-z) has a strong hydrogen bond with the Cl2(x, y, z) perchlorate ion, Cl2-O4(x, y, z)...H10-C40(-x, ½+y, ½-z)= 2.372 Å, while the S6 thiophene (+x, ½-y, ½+z) is bonded to the Cl1(x, y, z) perchlorate ion by a similar hydrogen bond, Cl1-O13(x, y, z)...H18-C1(+x, ½-y, ½+z)= 2.493 Å, and the S6 thiophene (x, y, z) interacts with the Cl2(+x, ½-y, ½+z) perchlorate, S6(x, y, z)...O4-Cl2(+x, ½-y, ½+z)= 3.15 Å. This is also observed in the C=C bond lengths as, in the S4 and S5 thiophenes, the C2-C32 and C28-C50= 1.39Å, C7-C24=

1.37Å and C46-C48= 1.35Å bond lengths are fairly symmetric while in the S1 and S6 thiophene rings the C5-C40= 1.29Å and C1-C43= 1.30Å bond lengths have a stronger double bond character than the C4-C27= 1.40Å and C35-C39= 1.37Å bond lengths. Finally on the thiophenes, the single C-C bond lengths are C2-C28= 1.35Å, C4-C5= 1.35Å, C1-C35= 1.39Å and C24-C46= 1.40Å. The different distortions between the thiophene rings are also reflected in the bond angles. Indeed, the bond angles differ in each thiophene. The C32-S4-C50, C7-S5-C48= 90°, C27-S1-C40= 92° and C39-S6-C43= 91° angles are similar to their counterparts in unsubstituted thiophene. The other bond angles in the thiophene rings are, as for the bond lengths, differently and unsymmetrically distorted. In the S1 thiophene ring, S1-C40-C5= 113° and C4-C5-C40= 114° are larger than those substituted by the ether bridge and the amine bridge, S1-C27-C4= 109° and C5-C4-C27= 112°. In the S6 thiophene ring, the bond angles are completely different as S6-C43-C1= 115° and C35-C1-C43= 107°, both unsubstituted, are respectively larger and smaller than their substituted counterparts, S6-C39-C35= 107° and C1-C35-C39= 120°. In the S4 thiophene, the bond angles are similarly distorted to those in the S6 thiophene, S4-C50-C28= 115°, C2-C28-C50= 109°, S4-C32-C2= 112° and C28-C2-C32= 114°. In the S5 thiophene ring, the bond angle distortions are similar to those in the S1 thiophene. The unsubstituted S5-C48-C46= 114° and C24-C46-C48= 113° angles are larger than their substituted counterpart S5-C7-C24= 113° and C7-C24-C46= 110°.

The thiophene rings form four planes, which each respectively include the ether bridge oxygen atom and the amine bridge carbon atom directly bonded to them. However, the C(th)-O and C(th)-C bond lengths and especially the bond angles are different for each thiophene. The C4-O12= 1.35Å, C2-O8= 1.39Å and C35-O15= 1.39Å bond lengths are close to the expected length in the phenol molecule[363]. C24-O14= 1.30Å is shorter than the others and has a character between a single and a double bond. This could be due to a more important conjugation with the adjacent thiophene ring and to the fact that O14 is the oxygen atom that interacts most strongly with the copper (II) ion. The bond angles between the thiophene rings and the ether bridges are also affected. The O-C=C bond angles O8-C2-C32= 122° and O14-C24-C7= 124° are not significantly smaller than the O-C-C bond angles O8-C2-C28= 124° and O14-C24-C46= 126°, compared to the free ligand **24**. Also, these differences compared to the free ligand could be due to the twisting of this same ligand during complexation. A few hydrogen bonds and close contacts appear between the ether bridges and the S4 and S5 thiophene rings, O8...H4-C29= 2.700Å, O8...H14-C28= 2.609Å, C28-H14...H7-C45= 1.942Å, O14...H2-C25= 2.317Å, O14...H1-C46= 2.490Å and C46-H1...H29-C41= 1.851Å (sum of the van der Waals radii= 2.4Å). O14...H2, O14...H1, H14...H7 and H1...H29 are very close approaches, which could be induced by the torsion imposed in the ligand during complexation to get the O8 and O14 oxygen donors closer to the copper(II) ion. The O-C=C angle with the S1 thiophene ring O12-C4-C27= 116° is clearly smaller than the O12-C4-C5= 132° bond angle. Two hydrogen bonds also appear O12...H13-C34= 2.781Å and O12...H21-C5= 2.780Å, but those interactions are weaker than the preceding ones for the S4 and S5 thiophenes (sum of the van der Waals radii= 2.8Å). In the case of the S6 thiophene, the geometry is reversed as the O15-C35=C39= 126° bond angle is larger than the O15-C35-C1= 114° angle. Three hydrogen bonds appear O15...H18-C1= 2.574Å, O15...H5-C6= 2.536Å and a weak H...H contact C1-H18...H32-C51= 2.361Å. In the ether bridges, the C-O bond lengths vary from 1.38Å to 1.49Å. The C45-O8= 1.38Å is shorter than a normal single bond. This could be due to the conjugation between the oxygen atom O8 and the adjacent thiophene ring and the closer contact of the donor atom to the metal ion. This is also observed for the atoms O14 and O16 as C41-O14= 1.44Å, C56-O16= 1.44Å and C60-O16= 1.42Å are shorter than their counterparts C51-O15= 1.49Å, C3-O2= 1.45Å, C36-O11= 1.46Å and C37-O11= 1.49Å. The C-C bond lengths in the ether chains vary from 1.46Å to 1.48Å and are shorter than usual[363]. The ether chains form a large C-O-C bond angle with the thiophene rings, C3-O12-C4= 120°, C2-O8-C45= 120°, C24-O14-C41= 118° and C35-O15-C51= 126°. The other C-O-C angles are also large, C36-O11-C37= 113° and C56-O16-C60= 116° despite being smaller than the C(th)-O-C angles. H...H interactions appear which may affect these two bond angles, C36-H39...H41-C37= 2.395Å and C56-H34...H36-C60= 2.304Å. The O12-C3-C37= 107°, O8-C45-C36= 105°, O11-C36-C45= 105°, O14-C41-C60= 101° and O15-C51-C56= 107° bond angles are smaller than O11-C37-C3= 112°, O16-C60-C41= 114° and O16-C56-C51= 113°. This could be due to the fact that those smaller bond angles have associated O...H bonds that are stronger than for the other angles, O12...H40-C37= 2.474Å, O8...H38-C36= 2.325Å, O11...H42-C45= 2.368Å, O15...H33-C56= 2.463Å, O16...H29-C41=2.596Å and O16...H31-C51= 2.557Å.

The C(th)-C bond lengths between the amine bridges and the thiophene rings vary from 1.45Å to 1.49Å, and are shorter than the usual 1.52Å for a C(ar)-C bond length[363]. This could be due (as for the C(th)-O bond lengths) to a conjugation with the adjacent thiophene. The resulting angles between the S1 and S4 thiophene rings and their respective amine bridges, S1-C27-C34= 125°, C4-C27-C34= 126°, S4-C32-C24= 122°

and C2-C32-C24= 126°, are similar and they also have similar hydrogen contacts, O12...H13-C34= 2.781Å, S1...H45-C34= 2.790Å (sum of the van der Waals radii= 3.05Å), O8...H4-C29= 2.700Å and S4...H46-C29= 2.731Å. Contrary to the preceding bond angles, the S-C-C angles with the amine bridges, S5-C7-C25= 127° and S6-C39-C6= 128°, are larger than the C-C-C bond angles, C24-C7-C25= 120° and C6-C39-C35= 125°. This could be due to the differences of strength of the hydrogen contacts and due to the stretching imposed in the ligand. Indeed, S6...H43-C6= 2.870Å is weaker than its counterpart with the S1 and S4 atoms and there is no S5...H contact. Also, the O...H bonds between the ether bridge and the amine bridges are stronger than their counterparts, O15...H5-C6= 2.536Å and O14...H2-C25= 2.317Å. The N-C bond lengths are all longer than the usual N(sp^3: pyramidal)-C(sp^3)= 1.469Å, N1-C6= 1.53Å, N1-C26= 1.57Å, N1-C34= 1.54Å, N2-C25= 1.49Å, N2-C29= 1.55Å and N2-C30= 1.54Å. This could be due to the interaction of the nitrogen lone pairs with the copper (II) cation and the electron withdrawing effect that could be created. The N2 nitrogen atom is 0.388Å closer to the cation than the N1 nitrogen atom. Despite this contact bond difference, the N-C bond lengths on both sides of the molecule are similar. This could be due to interactions with the perchlorate anions that are closer to the N2 atom and therefore weaken the effect of the copper (II) ion. Indeed, three O...H close contacts appear between the C25 carbon atom and the Cl2 perchlorate's oxygen atoms, Cl2-O5...H23-C25= 2.503Å, Cl2-O7...H23-C25= 2.658Å, Cl2-O6...H23-C25= 2.732Å, and a Cl...H hydrogen contact Cl2...H23-C25= 2.809Å (sum of the van der Waals radii= 3.00Å). Also, the C25-N2-C29= 112° and C29-N2-C30= 112° bond angles on N2 are close to their counterparts on N1, C6-N1-C34= 111° and C26-N1-C34= 112° while the C25-N2-C30= 115° angle is 6° larger than its counterpart C6-N1-C26= 109°. This is also reflected on the N-C-C bond angles as the N1-C6-C39= 110° is 6° smaller than the corresponding angle on N2, N2-C25-C7= 116°, whereas the other angles are respectively similar, N1-C26-C47= 115°, N1-C34-C27= 113°, N2-C30-C55= 115° and N2-C29-C32= 113°. The C-C bond lengths in the propyl groups are C26-C47= 1.49Å, C30-C55= 1.48Å, C47-C54= 1.50Å and C55-C57= 1.53Å. The C26-C47 and C30-C55 bond lengths are shorter than the usual C-C= 1.52Å, while the C47-C54 and C55-C57 bond lengths are closer. However, the C55-C57 bond length, which is in contact with the Cl2 perchlorate (Cl2-O5...H22-C55= 2.963Å), is 0.03Å longer than the C47-C54 bond lengths. This difference is reflected in the C-C-C angles as C26-C47-C54= 111° is larger than C30-C55-C57= 106°.

Table 95. Least-Squares Planes

Plane number 1

Atoms Defining Plane	Distance
S(1)	.003(9)
C(4)	.03(2)
C(5)	-.01(3)
C(27)	-.03(3)
C(40)	-.02 (4)

Additional Atoms	Distance
O(12)	.05
C(34)	-.14
N(1)	1.15
Cu(2)	3.08

Mean deviation from plane is .0195 Ångstroms

Chi-squared: 3.5

Plane number 2

Atoms Defining Plane	Distance
S(6)	-.001(9)
C(1)	-.03(4)
C(35)	.002(31)
C(39)	.004(35)
C(43)	.03(4)

Additional Atoms	Distance
O(15)	-.00
C(6)	.08
N(1)	1.54
Cu(2)	2.43

Mean deviation from plane is .0139 Ångstroms

Chi-squared: .9

Dihedral angles between least-squares planes 1 and 2= 102.25°

Plane number 3

Atoms Defining Plane	Distance
S(4)	-.001(9)
C(2)	-.004(32)
C(28)	-.002(29)
C(32)	.005(29)
C(50)	.005(33)

Additional Atoms	Distance
O(8)	.10
C(29)	.09
N(2)	-1.28
Cu(2)	-2.32

Mean deviation from plane is .0034 Ångstroms

Chi-squared: .1

Dihedral angles between least-squares planes 1 and 3= 105.01°

Dihedral angles between least-squares planes 2 and 3= 20.23°

Plane number 4

Atoms Defining Plane	Distance
S(5)	.0000(107)
C(7)	.01(2)
C(24)	-.01(3)
C(46)	.03(4)
C(48)	-.017(35)

Additional Atoms	Distance
O(14)	.01
C(25)	.09
N(2)	-1.17
Cu(2)	-2.62

Mean deviation from plane is .0139 Ångstroms

Chi-squared: .8

Dihedral angles between least-squares planes 1 and 4= 12.97°

Dihedral angles between least-squares planes 2 and 4= 104.62°

Dihedral angles between least-squares planes 3 and 4= 102.70°

Plane number 5

Atoms Defining Plane	Distance
O(8)	.0000
O(11)	.0000
O(12)	.0000

Additional Atoms	Distance
Cu(2)	-2.09

Mean deviation from plane is .0000 Ångstroms

Chi-squared: .0

Dihedral angles between least-squares planes 1 and 5= 118.67°

Dihedral angles between least-squares planes 2 and 5= 25.68°

Dihedral angles between least-squares planes 3 and 5= 13.67°

Dihedral angles between least-squares planes 4 and 5= 115.85°

Plane number 6

Atoms Defining Plane	Distance
O(14)	.0000
O(15)	.0000
O(16)	.0000

Additional Atoms	Distance
Cu(2)	-1.97

Mean deviation from plane is .0000 Ångstroms

Chi-squared: .0

Dihedral angles between least-squares planes 1 and 6= 70.83°

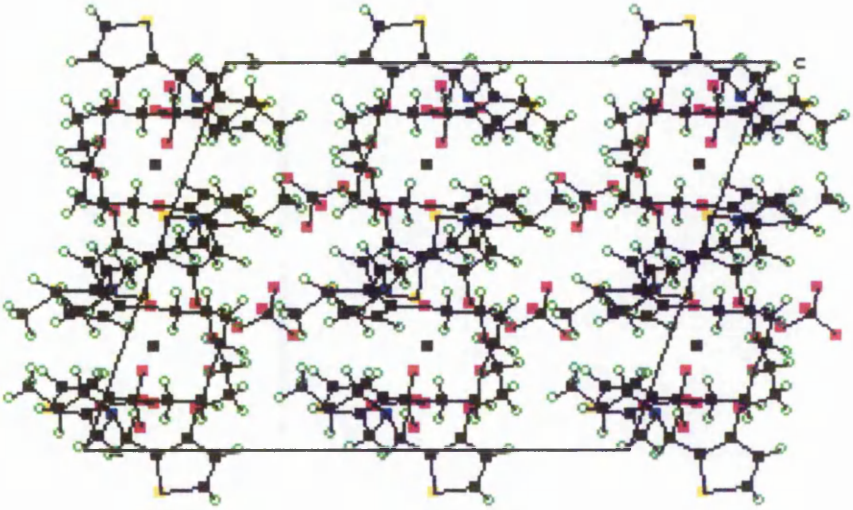
Dihedral angles between least-squares planes 2 and 6= 166.65°

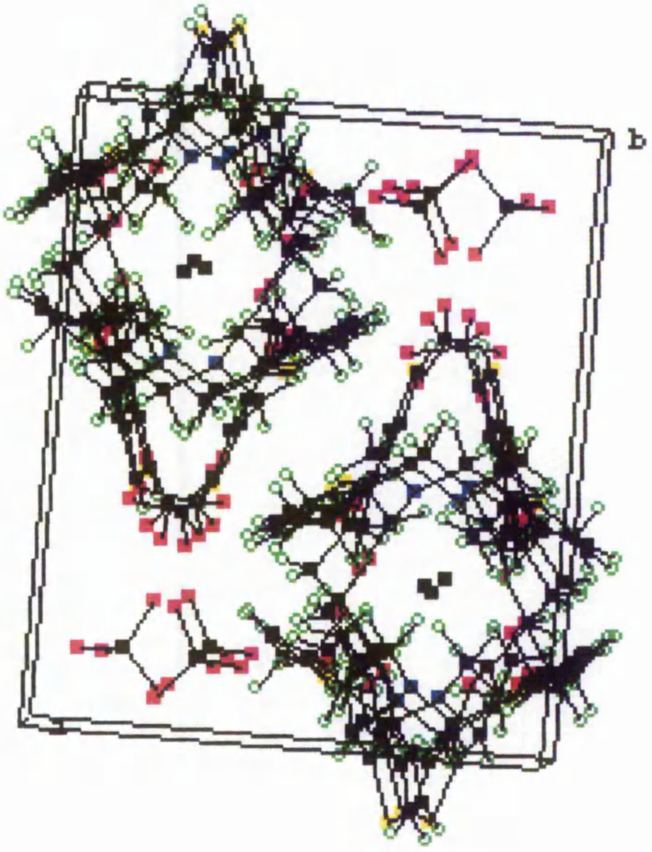
Dihedral angles between least-squares planes 3 and 6= 170.66°

Dihedral angles between least-squares planes 4 and 6= 71.31°

Dihedral angles between least-squares planes 5 and 6= 167.25°

The following views of the unit cell show that the complexes, which include the ligand and the Cu cation, the Cl2 and the Cl1 perchlorate anions are respectively arranged along the a-axis and also along the c-axis. The complexes (x, y, z) and (x, ½-y, ½+z), and the complexes (-x, ½+y, ½-z) and (-x, -y, -z) are respectively arranged along the c-axis, whereas the complexes (x, y, z) and (-x, -y, -z), and the complexes (-x, ½+y, ½-z) and (x, ½-y, ½+z) are respectively arranged along the a-axis.





The copper ions are stacked in the c direction as can be seen on the previous page. The distances between the copper(II) ions in the unit cell are Cu(x, y, z)...Cu(x, ½-y, ½+z) and Cu(-x, ½+y, ½-z)...Cu(-x, -y, -z) along the c-axis= 10.759Å, Cu(x, y, z)...Cu(-x, -y, -z)= 10.027Å and Cu(-x, ½+y, ½-z)...Cu(x, ½-y, ½+z)= 9.577Å along the a-axis.

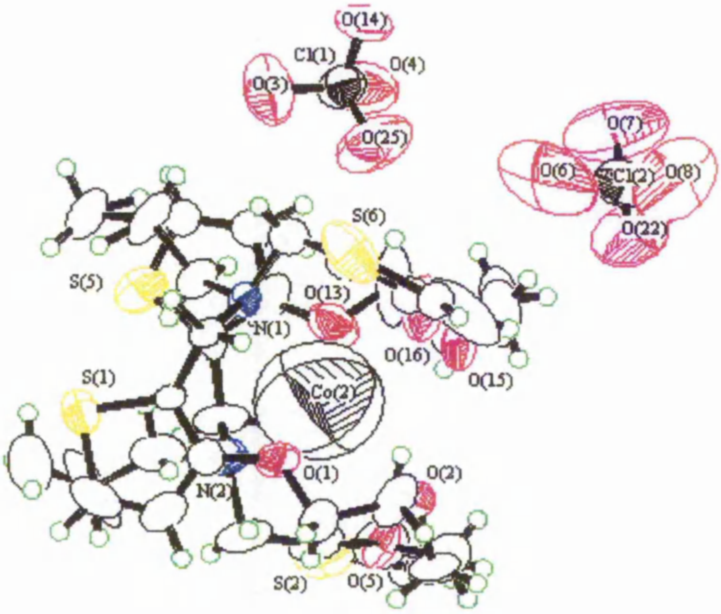
Some O...H intermolecular hydrogen contacts are present in the unit cell between the ligand and the perchlorate anions. The following interactions, Cl2-O6(x, y, z)...H7-C45(-x, -y, -z)= 2.654Å, Cl2-O5(x, y, z)...H14-C28(x, ½-y, ½+z)= 2.873Å and Cl2-O4(x, y, z)...H16-C50(x, ½-y, ½+z)= 2.777Å may be strong enough to have some effect on the bond lengths O8-C45, O8-C2, C2-C28, C2-C32, C28-C50 and S4-C50. A similar effect appears on the S5 thiophene ring as Cl2-O6(x, y, z)...H20-C48(-x, ½+y, ½-z)= 2.754Å, Cl2-O4(x, y, z)...H20-C48(-x, ½+y, ½-z)= 2.74Å and Cl1-O1(x, y, z)...H1-C46 (-x, -y, -z)= 2.471Å. Other weak interactions appear between Cl1(x, y, z) and the ligand(1+x, y, z), Cl1-O13(x, y, z)...H6-C47(1+x, y, z)= 2.83Å, Cl1-O3(x, y, z)...H15-C45(1+x, y, z)= 2.701Å, between Cl1(x, y, z) and the ligand(-x, -y, -z), Cl1-O2(x, y, z)...H5-C6(-x, -y, -z)= 2.816Å, Cl1-O1(x, y, z)...H21-C5(-x, -y, -z)= 2.672Å, between Cl1(x, y, z) and the ligand(x, ½-y, ½+z), Cl1-O13(x, y, z)...H18-C1(x, ½-y, ½+z)= 2.493Å, and between the ligand(x, y, z) and Cl2(x, ½-y, ½+z), S6(x, y, z)...O4-Cl2(x, ½-y, ½+z).

Note - As the copper atom proved to have such a large temperature factor, the possibility was later considered that the large singular electron density peak initially observed within the macrocycle ring could be due to another species e.g. water or solvent molecules, perhaps disordered. Replacing the copper by an oxygen atom localised on the peak reduced the R value by about 5%. However if copper is not present in the molecule there are a number of unexplained factors about the structure, in particular the question of what is balancing the charge on the two negative perchlorate ions. If the macrocycle ring is doubly protonated the most likely sites are the nitrogen atoms. The relevant bond distances and angles do not however provide any particular evidence for this and difference maps did not enable location of hydrogen atoms at these sites (residual 0.3 e/Å^3) although all other H atoms in the molecule were easily so located. The NMR spectra did not indicate protonated N and the calculated chemical analysis also agrees better with the experimental % C, H, N, Cl if copper is assumed to be present. Due to lack of time this work could not be taken further and the foregoing discussion assumes that copper is present.

4.2. The complex of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with cobalt(II) perchlorate **54**

4.2.1. Discussion of the structure derived data (tables 41 to 43)

The crystal structure of this cobalt(II) complex 54 is fairly similar to the preceding macrocyclic complex **50** which had a copper(II) complexed to the same ligand **24**. The crystal system is triclinic. The space group is P2$_1$/c or n°14. Again, the positions and anisotropic displacement parameters of the atoms in the complex are best visualized in the "ortep style" drawing below[353].



Similarly to the complex **50**, the thermal parameters of the atoms in the macrocyclic ligand are all fairly large, but O1, O2, O5, O13, O15, O16, N1 and N2 have smaller thermal ellipsoids than the other atoms around the ring. The propyl group carbon atoms and the perchlorate counterion oxygen atoms again have very large thermal ellipsoids due to the flexibility of these groups and the low accuracy of the atomic positions. Finally, the cobalt(II) ion has the greatest displacement parameters as in a similar way to the copper(II) ion of complex **50**, it is moving fairly freely within the cavity and is not strongly attached to any of the donor atoms. The movement seems to be less than for the copper ion in the complex **50**. However, the interactions between the metal ion and the donor atoms are still unusually long and this will lower the stability of this complex. This macrocyclic complex is, as described by Cram[364], a capsular complex.

4.2.2. Discussion of the structural geometry

Table 96. Bond Lengths(Å)

Bond Lengths(Å)			
Bond	Length(Å)	Bond	Length(Å)
Cl(1) -O(3)	1.39(2)	O(15) -C(52)	1.48(7)
Cl(1) -O(4)	1.41(2)	O(16) -C(38)	1.35(3)
Cl(1) -O(14)	1.42(2)	O(16) -C(54)	1.47(4)
Cl(1) -O(25)	1.34(2)	N(1) -C(3)	1.51(3)
Cl(2) -O(6)	1.41(4)	N(1) -C(4)	1.50(3)
Cl(2) -O(7)	1.27(2)	N(1) -C(6)	1.52(3)
Cl(2) -O(8)	1.29(3)	N(2) -C(11)	1.51(3)
Cl(2) -O(22)	1.33(2)	N(2) -C(13)	1.55(3)
S(1) -C(5)	1.68(2)	N(2) -C(33)	1.50(3)
S(1) -C(47)	1.70(3)	C(1) -C(3)	1.50(4)
S(2) -C(34)	1.76(3)	C(1) -C(38)	1.32(4)
S(2) -C(49)	1.76(4)	C(3) -H(6)	0.9(2)
S(5) -C(36)	1.64(3)	C(3) -H(42)	1.1(2)
S(5) -C(44)	1.59(7)	C(4) -C(5)	1.46(3)
S(6) -C(1)	1.74(3)	C(4) -H(18)	0.7(2)
S(6) -C(39)	1.84(5)	C(4) -H(32)	1.1(2)
O(1) -C(7)	1.35(2)	C(5) -C(7)	1.34(3)
O(1) -C(10)	1.42(7)	C(6) -C(43)	1.53(4)
O(2) -C(31)	1.51(3)	C(6) -H(17)	1.0(2)
O(2) -C(50)	1.50(3)	C(6) -H(38)	1.2(2)
O(5) -C(32)	1.34(4)	C(7) -C(8)	1.33(3)
O(5) -C(46)	1.51(5)	C(8) -C(47)	1.35(4)
O(5) -H(30)	0.8(5)	C(8) -H(20)	0.9(2)
O(13) -C(30)	1.36(3)	C(10) -C(31)	1.46(7)
O(13) -C(41)	1.44(4)	C(10) -H(33)	0.4(6)
O(15) -C(45)	1.39(5)	C(11) -C(36)	1.52(3)
C(11) -H(8)	1.1(2)	C(46) -C(50)	1.40(6)
C(11) -H(36)	1.1(2)	C(46) -H(30)	1.0(5)
C(13) -C(34)	1.50(4)	C(48) -C(57)	1.64(7)

C(13) -H(7)	1.3(2)	C(48) -H(1)	1.0(7)
C(13) -H(47)	0.9(3)	C(48) -H(26)	1.2(4)
C(30) -C(36)	1.32(4)	C(49) -H(25)	1.1(3)
C(30) -C(51)	1.42(4)	C(51) -H(10)	0.7(2)
C(31) -H(15)	1.1(2)	C(52) -H(16)	1.3(6)
C(32) -C(34)	1.33(4)	C(54) -H(35)	1.1(3)
C(32) -C(42)	1.35(4)	C(57) -H(1)	0.8(5)
C(33) -C(48)	1.60(5)	C(57) -H(2)	1.0(2)
C(33) -H(26)	1.2(5)	C(57) -H(12)	0.9(2)
C(33) -H(27)	0.9(2)	C(57) -H(52)	1.1(4)
C(34) -H(47)	1.0(3)	C(58) -H(14)	0.8(3)
C(38) -C(53)	1.33(6)	C(58) -H(51)	0.5(6)
C(39) -C(53)	1.35(8)	C(43) -H(39)	0.9(3)
C(39) -H(21)	0.6(4)	C(44) -C(51)	1.3(1)
C(41) -C(52)	1.35(8)	C(44) -H(13)	0.9(4)
C(42) -C(49)	1.38(5)	C(45) -C(54)	1.51(7)
C(42) -H(24)	1.0(2)	C(45) -H(28)	1.1(4)
C(43) -C(58)	1.54(6)		

Table 97. Contact bonds(Å)

Contact bonds(Å)					
Bond	Length(Å)	ADC(*)	Bond	Length(Å)	ADC(*)
Co(2) -N(2)	2.90(3)	1	S(2) -H(45)	2.8(5)	3
Co(2) -O(13)	2.95(3)	1	S(2) -H(7)	3.0(2)	56503
Co(2) -O(15)	3.01(3)	1	S(2) -O(4)	3.26(3)	3
Co(2) -O(1)	3.07(2)	1	S(5) -O(22)	3.19(3)	3
Co(2) -O(2)	3.11(2)	1	S(6) -O(8)	3.19(3)	65502
Co(2) -N(1)	3.14(3)	1	O(3) -H(42)	2.6(2)	65503
Co(2) -O(16)	3.15(3)	1	O(3) -H(18)	2.9(2)	65503
Co(2) -O(5)	3.18(3)	1	O(4) -H(4)	2.6(2)	54501
Cl(2) -H(36)	2.8(2)	3	O(4) -H(10)	2.9(2)	1
S(1) -H(35)	2.7(3)	55404	O(14) -H(18)	2.7(2)	65503
S(2) -H(9)	2.5(3)	56503	O(14) -H(23)	2.8(4)	64502
O(4) -H(45)	2.9(5)	1	O(15) -H(52)	2.9(4)	4
O(6) -H(36)	2.5(2)	3	O(22) -H(36)	2.4(2)	3
O(7) -H(36)	2.6(2)	3	C(42) -H(34)	2.6(3)	56503
O(7) -H(13)	2.9(5)	54504	C(45) -H(52)	2.7(4)	4
O(7) -H(40)	2.9(3)	54501	C(49) -H(34)	2.7(3)	56503

O(8) -H(13)	2.9(3)	54504	H(25) -H(34)	1.7(3)	56503
O(13) -H(44)	2.8(4)	3	H(29) -H(52)	2.2(5)	4
C(30) -H(44)	2.6(4)	3	H(44) -H(44)	1.9(6)	3
C(32) -H(34)	2.8(3)	56503	H(3) -H(14)	2.4(3)	4
C(36) -H(44)	2.8(4)	3	H(7) -H(25)	2.0(3)	56503
H(3) -H(5)	2.3(3)	4	H(8) -H(44)	2.2(4)	3

*see note(*) in table 88 (p.149)

Symmetry Operators:

(1) +X, +Y, +Z   (2) -X, 1/2+Y, 1/2-Z
(3) -X, -Y, -Z   (4) +X, 1/2-Y, 1/2+Z

The macrocyclic ligand **24** is encapsulating the cobalt(II) metal ion in the same way as it encapsulated the copper ion in compound **50**, and forms a macrocyclic-capsular complex **54**. Similarly to the copper complex, the interactions between the cobalt ion and the donor atoms create distortions in the macrocyclic ligand that are reflected in the bond lengths and bond angles when compared to the free macrocycle. The Co-O and Co-N interactions are not exactly symmetric in strength although they are better distributed than for the copper(II) ion in complex **50** and this may be why the motion of the cobalt ion is less. Note that the Co^{2+} radius at high spin= 0.75Å is almost equal to the radius of Cu^{2+}=0.77Å (Table 1, p.23).

Note - As the cobalt atom proved to have a very large temperature factor, (though considerably smaller than that for the copper in complex 50), in a similar manner to that described for complex 50 on p.303 the possibility was later considered that the large singular electron density peak initially observed within the macrocycle ring could be due to another species e.g. water or solvent molecules, perhaps disordered. Replacing the cobalt by an oxygen atom localised on the peak reduced the R value by about 5%. However if cobalt is not present in the molecule there are a number of unexplained factors about the structure, in particular the question of what is balancing the charge on the two negative perchlorate ions. If the macrocycle ring is doubly protonated the most likely sites are the nitrogen atoms. The relevant bond distances and angles do not however provide any particular evidence for this and difference maps did not enable location of hydrogen atoms at these sites (residual 0.4 e/Å^3) although all other H atoms in the molecule were easily so located. The NMR spectra did not indicate protonated N. Due to lack of time this work could not be taken further and the following discussion assumes that cobalt is present.

For ease of description the bond lengths (to 2 decimal places) are shown on a schematic drawing on the next page.

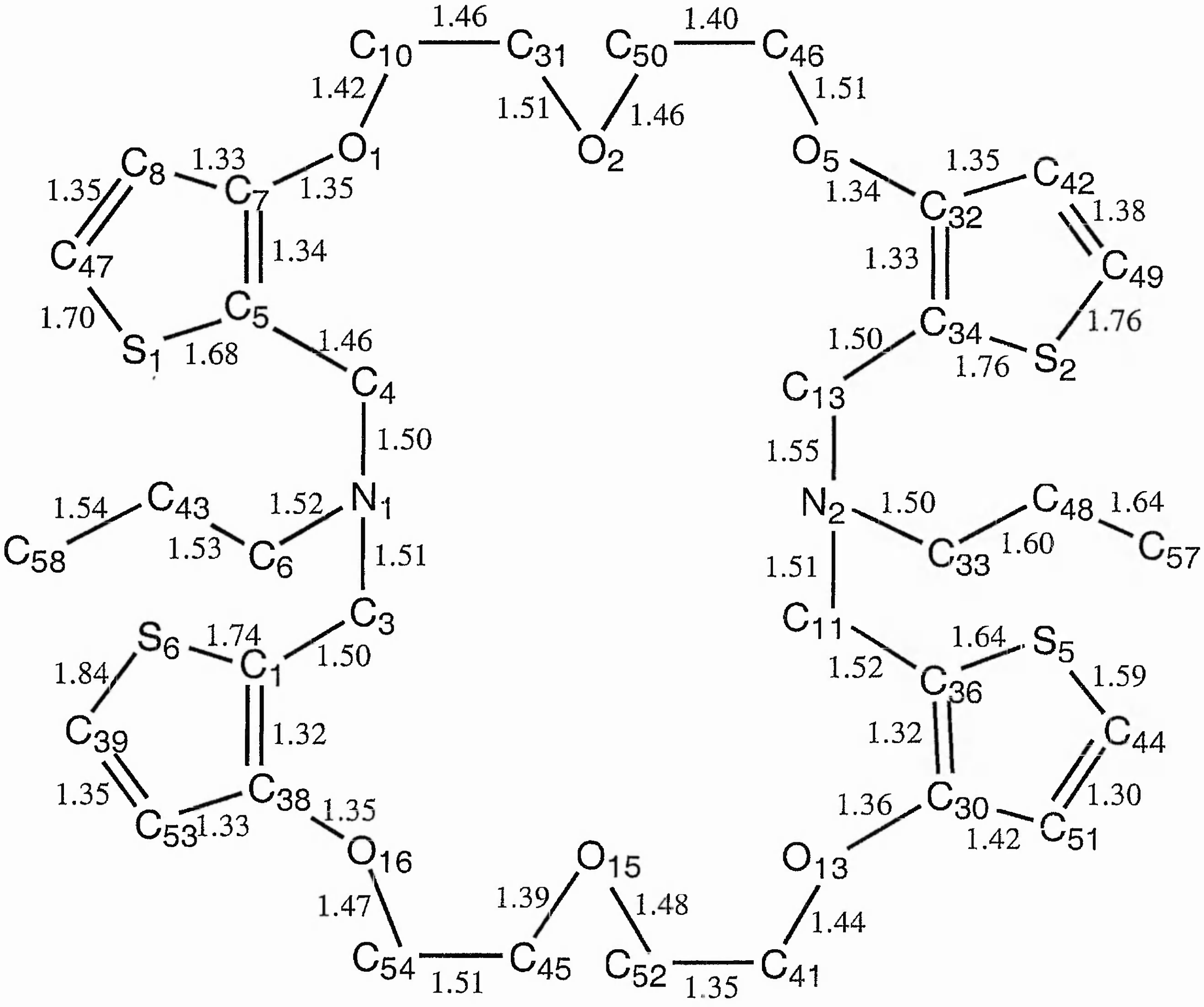


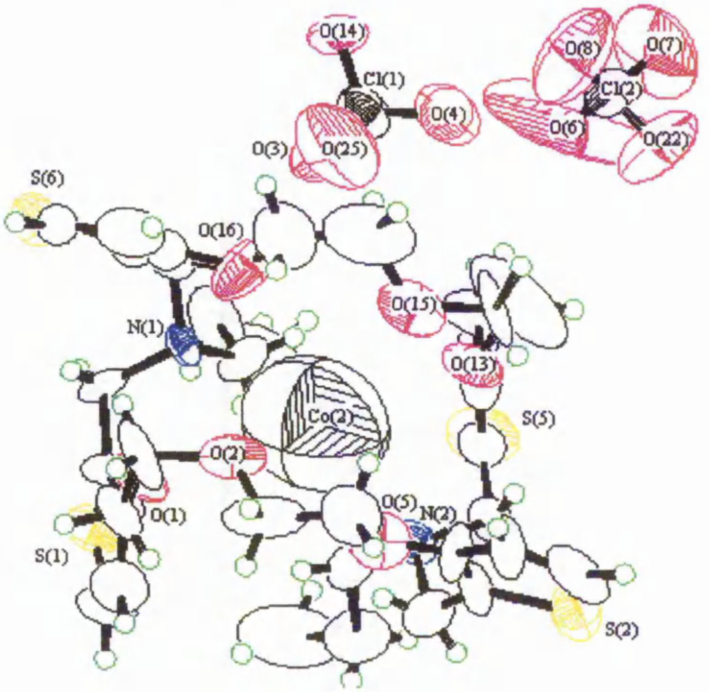
Table 98. Bond Angles(°)

Bond Angles(°)			
Bond	Angle(°)	Bond	Angle(°)
O(3) -Cl(1) -O(4)	118(2)	C(4) -N(1) -C(6)	115(2)
O(3) -Cl(1) -O(14)	104(1)	C(11) -N(2) -C(13)	110(2)
O(3) -Cl(1) -O(25)	109(2)	C(11) -N(2) -C(33)	114(2)
O(4) -Cl(1) -O(14)	109(1)	C(13) -N(2) -C(33)	109(2)
O(4) -Cl(1) -O(25)	101(2)	S(6) -C(1) -C(3)	121(3)
O(14) -Cl(1) -O(25)	116(2)	S(6) -C(1) -C(38)	109(3)
O(6) -Cl(2) -O(7)	93(3)	C(3) -C(1) -C(38)	129(3)
O(6) -Cl(2) -O(8)	124(4)	N(1) -C(3) -C(1)	113(2)

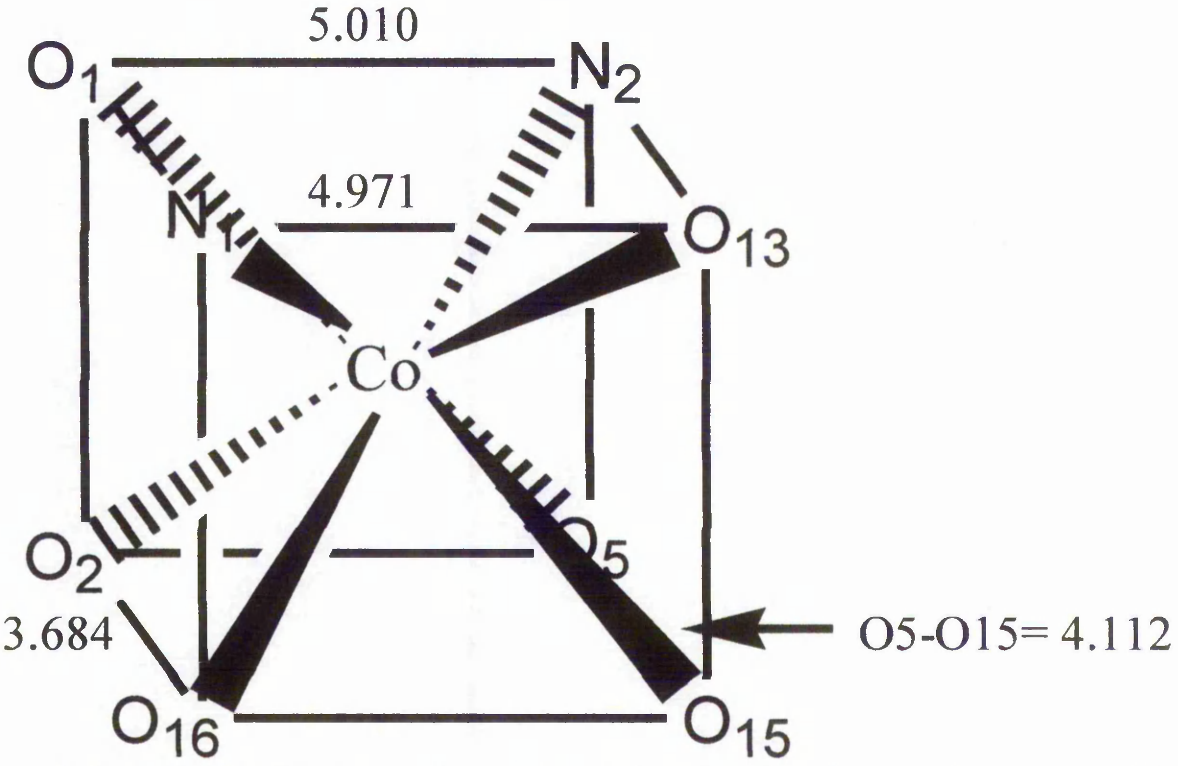
O(6) -Cl(2) -O(22)	108(3)	N(1) -C(3) -H(6)	107(16)
O(7) -Cl(2) -O(8)	116(3)	N(1) -C(3) -H(42)	88(12)
O(7) -Cl(2) -O(22)	103(2)	C(1) -C(3) -H(6)	102(15)
O(8) -Cl(2) -O(22)	110(2)	C(1) -C(3) -H(42)	141(12)
C(5) -S(1) -C(47)	92(1)	H(6) -C(3) -H(42)	102(17)
C(34) -S(2) -C(49)	86(2)	N(1) -C(4) -C(5)	115(2)
C(36) -S(5) -C(44)	91(3)	N(1) -C(4) -H(18)	115(19)
C(1) -S(6) -C(39)	85(2)	N(1) -C(4) -H(32)	113(10)
C(7) -O(1) -C(10)	123(3)	C(5) -C(4) -H(18)	113(20)
C(31) -O(2) -C(50)	116(3)	C(5) -C(4) -H(32)	85(11)
C(32) -O(5) -C(46)	117(3)	H(18) -C(4) -H(32)	111(23)
C(32) -O(5) -H(30)	108(38)	S(1) -C(5) -C(4)	127(2)
C(46) -O(5) -H(30)	35(33)	S(1) -C(5) -C(7)	111(2)
C(30) -O(13) -C(41)	120(3)	C(4) -C(5) -C(7)	122(2)
C(45) -O(15) -C(52)	117(4)	N(1) -C(6) -C(43)	112(2)
C(38) -O(16) -C(54)	118(3)	N(1) -C(6) -H(17)	124(15)
C(3) -N(1) -C(4)	111(2)	N(1) -C(6) -H(38)	115(10)
C(3) -N(1) -C(6)	111(2)	C(43) -C(6) -H(17)	83(14)
C(43) -C(6) -H(38)	98(10)	O(2) -C(31) -C(10)	108(4)
H(17) -C(6) -H(38)	116(18)	O(2) -C(31) -H(15)	91(14)
O(1) -C(7) -C(5)	122(2)	C(10) -C(31) -H(15)	126(13)
O(1) -C(7) -C(8)	125(3)	O(5) -C(32) -C(34)	117(3)
C(5) -C(7) -C(8)	113(3)	O(5) -C(32) -C(42)	124(4)
C(7) -C(8) -C(47)	116(3)	C(34) -C(32) -C(42)	118(4)
C(7) -C(8) -H(20)	113(16)	N(2) -C(33) -C(48)	112(2)
C(47) -C(8) -H(20)	114(17)	N(2) -C(33) -H(26)	137(20)
O(1) -C(10) -C(31)	109(4)	N(2) -C(33) -H(27)	86(17)
O(1) -C(10) -H(33)	163(78)	C(48) -C(33) -H(26)	48(22)
C(31) -C(10) -H(33)	79(71)	C(48) -C(33) -H(27)	68(18)
N(2) -C(11) -C(36)	114(2)	H(26) -C(33) -H(27)	110(28)
N(2) -C(11) -H(8)	108(11)	S(2) -C(34) -C(13)	118(3)
N(2) -C(11) -H(36)	108(12)	S(2) -C(34) -C(32)	112(3)
C(36) -C(11) -H(8)	103(11)	S(2) -C(34) -H(47)	85(20)
C(36) -C(11) -H(36)	114(12)	C(13) -C(34) -C(32)	130(3)
H(8) -C(11) -H(36)	109(18)	C(13) -C(34) -H(47)	34(19)
N(2) -C(13) -C(34)	111(2)	C(32) -C(34) -H(47)	159(19)
N(2) -C(13) -H(7)	96(8)	S(5) -C(36) -C(11)	131(2)
N(2) -C(13) -H(47)	124(20)	S(5) -C(36) -C(30)	111(2)
C(34) -C(13) -H(7)	121(9)	C(11) -C(36) -C(30)	119(3)
C(34) -C(13) -H(47)	38(19)	O(16) -C(38) -C(1)	119(3)

H(7) -C(13) -H(47)	139(22)	O(16) -C(38) -C(53)	114(4)
O(13) -C(30) -C(36)	126(3)	C(1) -C(38) -C(53)	126(4)
O(13) -C(30) -C(51)	119(4)	S(6) -C(39) -C(53)	117(4)
C(36) -C(30) -C(51)	115(3)	S(6) -C(39) -H(21)	111(40)
C(53) -C(39) -H(21)	78(46)	C(42) -C(49) -H(25)	77(18)
O(13) -C(41) -C(52)	106(3)	O(2) -C(50) -C(46)	110(4)
C(32) -C(42) -C(49)	108(4)	C(30) -C(51) -C(44)	104(4)
C(32) -C(42) -H(24)	113(15)	C(30) -C(51) -H(10)	104(20)
C(49) -C(42) -H(24)	139(16)	C(44) -C(51) -H(10)	148(21)
C(6) -C(43) -C(58)	110(3)	O(15) -C(52) -C(41)	118(4)
C(6) -C(43) -H(39)	103(24)	O(15) -C(52) -H(16)	100(34)
C(58) -C(43) -H(39)	138(24)	C(41) -C(52) -H(16)	125(38)
S(5) -C(44) -C(51)	119(4)	C(38) -C(53) -C(39)	102(5)
S(5) -C(44) -H(13)	106(34)	O(16) -C(54) -C(45)	103(3)
C(51) -C(44) -H(13)	135(34)	O(16) -C(54) -H(35)	134(16)
O(15) -C(45) -C(54)	115(5)	C(45) -C(54) -H(35)	108(17)
O(15) -C(45) -H(28)	179(24)	C(48) -C(57) -H(1)	31(53)
C(54) -C(45) -H(28)	65(29)	C(48) -C(57) -H(2)	56(14)
O(5) -C(46) -C(50)	102(4)	C(48) -C(57) -H(12)	110(17)
O(5) -C(46) -H(30)	27(30)	C(48) -C(57) -H(52)	156(19)
C(50) -C(46) -H(30)	100(35)	H(1) -C(57) -H(2)	87(56)
S(1) -C(47) -C(8)	108(3)	H(1) -C(57) -H(12)	127(49)
C(33) -C(48) -C(57)	103(4)	H(1) -C(57) -H(52)	127(54)
C(33) -C(48) -H(1)	91(40)	H(2) -C(57) -H(12)	71(19)
C(33) -C(48) -H(26)	46(22)	H(2) -C(57) -H(52)	141(25)
C(57) -C(48) -H(1)	26(36)	H(12) -C(57) -H(52)	73(28)
C(57) -C(48) -H(26)	74(20)	C(43) -C(58) -H(14)	93(20)
H(1) -C(48) -H(26)	52(44)	C(43) -C(58) -H(51)	132(62)
S(2) -C(49) -C(42)	116(3)	H(14) -C(58) -H(51)	122(71)
S(2) -C(49) -H(25)	76(17)		

The following view shows that, similar to compound **50**, the metal-ligand complex without the perchlorate counterions has an approximate two-fold axis centered on Co. The thiophene rings again form an helixoïd.

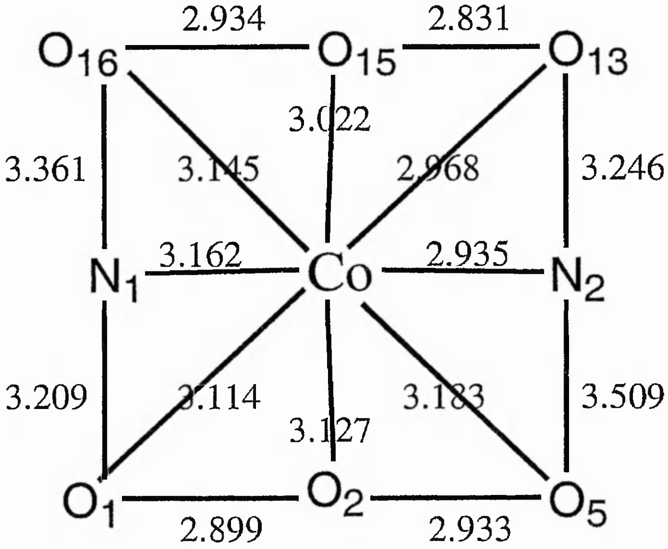


The donor atoms form a cage which is encapsulating the cobalt(II) metal ion. This macrocyclic cage is fairly symmetric and is schematically drawn below. The size and the shape of this donor atom's cage is fairly similar to the copper(II) metal ion cage **50**.



* Note the other donor atom distances are indicated on the following diagram page 312.

The oxygen atoms O1, O2 and O5 form a plane that has an angle of 167.96° with the plane formed by the oxygen atoms O13, O15 and O16. The distances of the Co ion from these planes are fairly close, 2.08Å and 1.90Å.



The scheme above shows the distances between the donor atoms and the cobalt(II) ion. The contacts between the oxygen and nitrogen atoms and the cobalt atom are similar to those in complex **50** with the copper ion, unusually long: they vary from 2.935 to 3.183Å which is much longer than the sum of the van der Waals radii between Co(high spin) and O and between Co(high spin) and N, Co-O= 2.15Å and Cu-N= 2.25Å. Despite being very long contacts, the effects on the bond lengths and bond angles of the macrocycle are again significant. Similarly to the copper ion in complex **50**, the cobalt ion is closer to the O13, O15, O16 and N2 atoms, 2.935-3.145Å, than to the O1, O2, O5 and N1 atoms, 3.114-3.183Å. These closer contacts are less significantly different than in compound **50**, but the difference could again be due to the perchlorate counterions that are near the S5 and S6 thiophene rings. However the perchlorate ions are more distant from the ligand than in complex **50**, and this may explain why the differences in bond lengths are not so great. Only two weak O...H hydrogen contacts appear between the perchlorate and the ligand, Cl1-O4...H45-C41= 2.9Å and Cl1-O4...H10-C51= 2.9Å. The interactions or non-interactions with the perchlorate ions are reflected in the Cl-O bond lengths. The Cl1 perchlorate is closer to the ligand and its bond lengths vary from 1.39Å to 1.42Å, except for the Cl1-O25= 1.34Å bond length, while the Cl2 perchlorate bond lengths are shorter and vary from 1.27Å to 1.33Å, except for the oxygen O6 bond length Cl2-O6= 1.41Å. The shorter Cl1-O25 and the longer Cl2-O6 bond lengths could be due to the fact that the oxygen atoms O25 and O6 respectively have very large thermal parameters and their positions could not be determined very accurately.

Table 99. Least-Squares Planes

Plane number 1

Atoms Defining Plane	Distance
S(1)	.00(1)
C(5)	.02(2)
C(7)	-.02(2)
C(8)	.03(3)
C(47)	-.02(4)

Additional Atoms	Distance
O(1)	-.09
C(4)	.08
N(1)	-1.17
Co(2)	-3.00

Mean deviation from plane is .0191 Ångstroms

Chi-squared: 2.7

Plane number 2

Atoms Defining Plane	Distance
S(6)	.00(1)
C(1)	.01(3)
C(38)	-.03(3)
C(39)	-.03(3)
C(53)	.06(4)

Additional Atoms	Distance
O(16)	-.02
C(3)	-.10
N(1)	-1.49
Co(2)	-2.37

Mean deviation from plane is .0283 Ångstroms

Chi-squared: 2.8

Dihedral angles between least-squares planes 1 and 2= 102.96°

Plane number 3

Atoms Defining Plane	Distance
S(2)	.00(1)
C(32)	.03(3)
C(34)	-.02(3)
C(42)	-.01(3)
C(49)	.00(3)

Additional Atoms	Distance
O(5)	-.16
C(13)	-.14
N(2)	1.24
Co(2)	2.23

Mean deviation from plane is .0122 Ångstroms

Chi-squared: 1.1

Dihedral angles between least-squares planes 1 and 3= 106.41°

Dihedral angles between least-squares planes 2 and 3= 19.77°

Plane number 4

Atoms Defining Plane	Distance
S(5)	.00(1)
C(30)	-.00(3)
C(36)	-.00(2)
C(44)	-.04(9)
C(51)	.01(4)

Additional Atoms	Distance
O(13)	.11
C(11)	-.07
N(2)	1.23
Co(2)	2.78

Mean deviation from plane is .0098 Ångstroms

Chi-squared: .2

Dihedral angles between least-squares planes 1 and 4= 11.79°

Dihedral angles between least-squares planes 2 and 4= 105.53°

Dihedral angles between least-squares planes 3 and 4= 104.82°

Plane number 5

Atoms Defining Plane	Distance
O(1)	.0000
O(2)	.0000
O(5)	.0000

Additional Atoms	Distance
Co(2)	-2.08

Mean deviation from plane is .0000 Ångstroms

Chi-squared: .0

Dihedral angles between least-squares planes 1 and 5= 61.80°

Dihedral angles between least-squares planes 2 and 5= 155.31°

Dihedral angles between least-squares planes 3 and 5= 168.19°

Dihedral angles between least-squares planes 4 and 5= 63.82°

Plane number 6

Atoms Defining Plane	Distance
O(13)	.0000
O(15)	.0000
O(16)	.0000

Additional Atoms	Distance
Co(2)	-1.90

Mean deviation from plane is .0000 Ångstroms

Chi-squared: .0

Dihedral angles between least-squares planes 1 and 6= 108.63°

Dihedral angles between least-squares planes 2 and 6= 13.62°

Dihedral angles between least-squares planes 3 and 6= 7.26°

Dihedral angles between least-squares planes 4 and 6= 108.45°

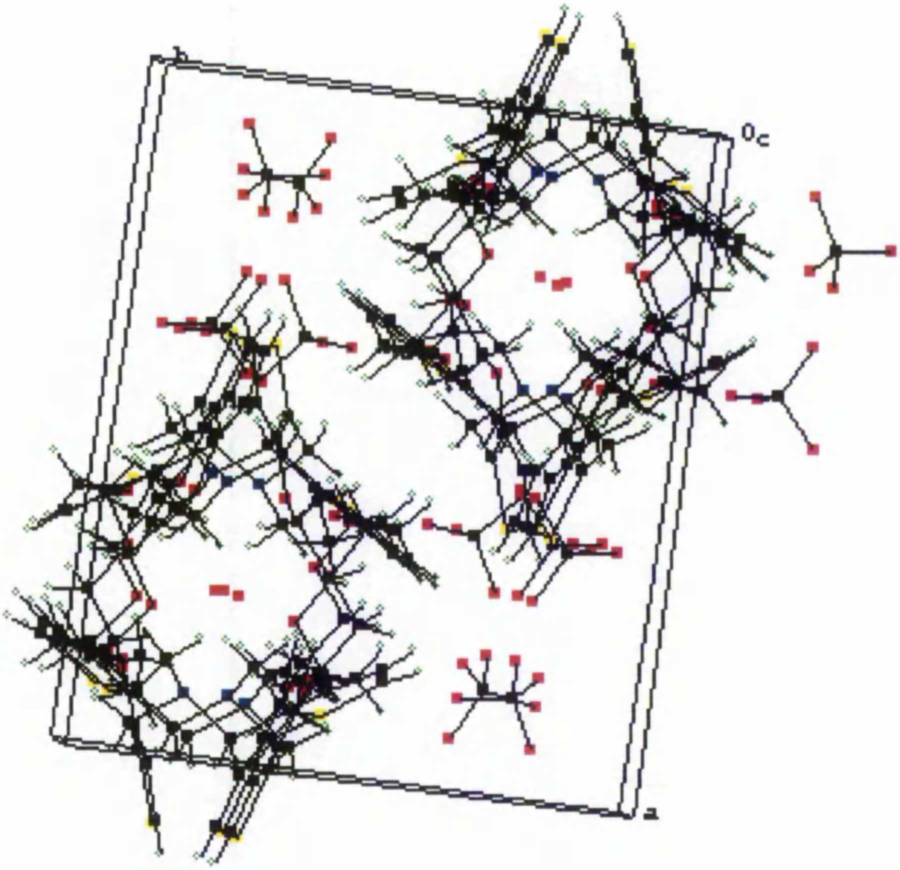
Dihedral angles between least-squares planes 5 and 6= 167.96°

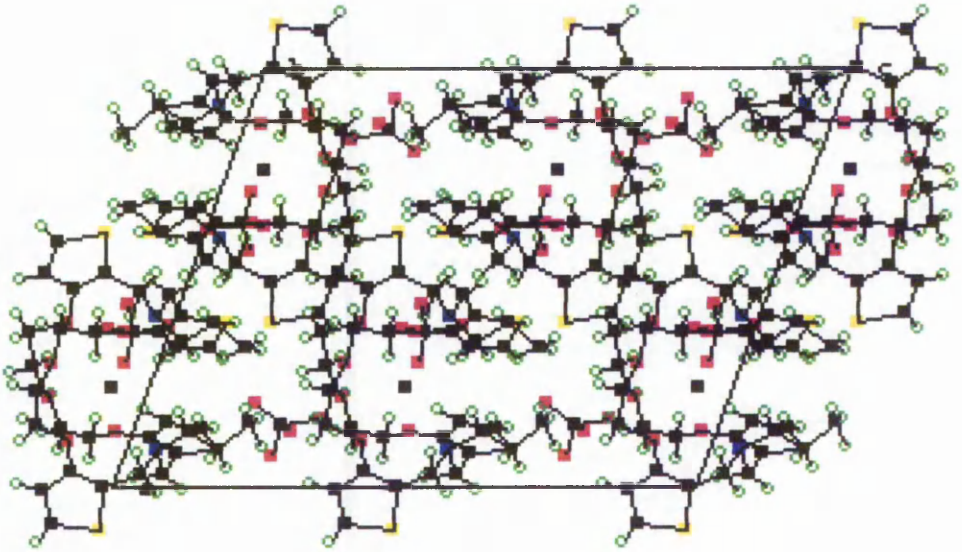
Similarly to the copper(II) metal ion in the complex **50**, the cobalt(II) ion in the present complex has created distortions in the bond lengths and bond angles of the original ligand **24**. However, the distortions observed for the present compound are different to those in the ligand of complex **50**. The bond lengths and bond angles in the thiophenes are again strongly distorted compared to unsubstituted thiophene[354]. Moreover, the effect is different for the S2 and S5 thiophene rings compared to their counterpart S1 and S6 thiophene rings. This could be due, as in compound **50**, to the presence of the perchlorate counterions near the S2 and S5 thiophenes, despite the fact that in the present compound these anions are more distant from both the ligand and the metal cation. On the other hand, the bond lengths and bond angles are distorted differently from ideal in every thiophene ring. In the S1 and S5 thiophenes, the S1-C5= 1.68Å, S1-C47= 1.70Å, S5-C36= 1.64Å and S5-C44= 1.59Å bond lengths are asymmetric and are shorter than the S-C single bond= 1.714Å in unsubstituted thiophene. Those bonds and especially the S5-C36 and S5-C44 bonds have a greater double bond character. In the S1 thiophene ring, the three carbon-carbon bonds have a double bond character, C8-C47= 1.35Å, C5-C7= 1.34Å and C8-C7= 1.33Å. This could be due to an electron delocalisation in the thiophene, and to an O...H interaction (O14-Cl2(x, y, z)...H18-C4(-x, -y, -z)= 2.7Å), that is also reflected in the bond lengths with the ether and amine bridges, C7-O1= 1.35Å and C5-C4= 1.46Å. The resulting bond angles are C5-S1-C47= 92°, S1-C47-C8= 108°, S1-C5-C7= 111°, C47-C8-C7= 116° and C5-C7-C8= 113°. In the case of the S5 thiophene ring, the C30-C51= 1.42Å bond length is close to its counterpart in unsubstituted thiophene[354]. The C=C bond lengths, C30-C36= 1.32Å and C44-C51= 1.30Å, have an even stronger double bond character than in the S1 thiophene. This could also be due to a delocalisation around the thiophene ring that also affects the C30-O13= 1.36Å bond length with the ether bridge but this does not extend to the C11-C36= 1.52Å bond length with the amine bridge. Furthermore, a few O...H bonds appear on the S5 thiophene such as Cl1-O4...H10-C51= 2.9Å, Cl2-O6(x, y, z)...H36-C11(-x, -y, -z)= 2.5Å, Cl2-O7(x, y, z)...H36-C11(-x, -y, -z)= 2.6Å, Cl2-O22(x, y, z)...H13-C11(-x, -y, -z)= 2.4Å, Cl2-O8(x, y, z)...H13-C44(-x, -y, -z)= 2.8Å, Cl2-O7(x, y, z)...H13-C11(x, ½-y, ½+z)= 2.9Å and S5(x, y, z)...O22-Cl2(-x, -y, -z)= 3.19Å. These close contacts could explain the differences in angles from the S1 thiophene and the shorter C44-C51 bond. Indeed, the S5-C44-C51= 119° angle is larger than the C30-

C51-C44= 104° angle whereas this is reversed in the S1 thiophene ring. The other bond angles are C36-S5-C44= 91°, S5-C36-C30= 111° and C36-C30-C51= 115°. In the S2 and S6 rings, the S-C bonds are considerably longer than in unsubstituted thiophene[354], S2-C34 and S2-C49= 1.76Å, S6-C1= 1.74Å and S6-C39= 1.84Å. The S2 atom is probably interacting with Cl1 perchlorate ion (-x, -y, -z), S2...O4-Cl1(-x, -y, -z)= 3.26Å (sum of the van der Waals radii= 3.25Å), while in the case of the S6 thiophene ring three close contacts appear between the ligand and the Cl2 perchlorate ion (-x, -y, -z), S6(x, y, z)...O8-Cl2(-x, ½+y, ½-z)= 3.19Å, between the ligand (-x, -y, -z) and the Cl1 perchlorate ion, Cl1-O3(x, y, z)...H42-C3(-x, -y, -z)= 2.6Å, and between the ligand (-x, -y, -z) and the Cl2 perchlorate ion, Cl2-O14(x, y, z)...H23-C53(-x, ½+y, ½-z)= 2.8Å. These interactions added to the possible electron delocalisation could explain the double bond character of the three C-C bond lengths in the S2 and S6 thiophenes, C32-34= 1.33Å, C42-C49= 1.38Å, C32-C42= 1.35Å, C1-C38= 1.32Å, C39-C53= 1.35Å and C38-C53= 1.33Å. The delocalisation effect is also reflected in the C32-O5= 1.34Å and C38-O16= 1.35Å bond lengths with the ether bridges, whereas this is not the case with the amine bridges (C13-C34= 1.50Å and C1-C3= 1.50Å). The long S-C bond lengths in the S2 and S6 thiophene result in smaller C-S-C bond angles (C32-S2-C49= 86° and C1-S6-C39= 85°). The other bond angles in these thiophenes are also distorted from ideal. Indeed, the substituted and non-substituted bond angles are reversibly distorted. The differences between the S-C-C and C-C-C angles are larger in the S6 ring (S2-C49-C42= 116°, C32-C42-C49= 108°, S2-C34-C32= 112°, C34-C32-C42= 118°, S6-C39-C53= 117°, C38-C53-C39= 102°, S6-C1-C38= 109° and C1-C38-C53= 126°).

The thiophene rings form four planes which respectively include the ether bridge oxygen atom and the amine bridge carbon atom directly bonded to them. The O-C=C bond angles between the S1 and S2 thiophene rings and the ether bridge are smaller than the O-C-C bond angles; this is contrary to those between the S5 and S6 thiophene rings and in the corresponding ether bridge. This could be due to the weaker hydrogen contacts: O1-C7=C5= 122°, O1-C7-C8= 125°, O5-C32=C34= 117° and O5-C32-C42= 124° compared to O13-C30=C36= 126°, O13-C30-C51= 119°, O16-C38=C1= 119° and O16-C38-C53= 114° could be due to the twisting of the ether bridges to get the oxygen atoms closer to cobalt(II). The intramolecular contacts are respectively O1...H32-C4= 2.643Å, O1...H20-C8= 2.608Å, C8-H20...H4-C10= 2.399Å, O5...H24-C42= 2.574Å, O5...H7-C13= 2.556Å, C46-H30...H24-C42= 2.173Å, O13...H8-C11= 2.326Å, O13...H10-C51= 2.356Å, C51-H10...H45-C41= 1.823Å, O16...H6-C3= 2.479Å, C54-H3...H23-C53= 2.217Å and C54-H35...H23-C53= 2.094Å. H30...H24, H10...H45, H3...H23 and H35...H23 are quite strong repulsions. These interactions may be forced, similarly to complex **50**, by the twisting of the molecule to get the O5, O13 and O16 donor atoms near to the metal ion. The C-O-C bond angles with the thiophene rings (C7-O1-C10= 123°, C32-O5-C46= 117°, C30-O13-C41= 120° and C38-O16-C54= 118°) are larger than the other C-O-C angles in the ether chains (C31-O2-C50= 116° and C45-O15-C52= 117°). The O2-C31-C10= 108° and O2-C50-C46= 110° bond angles are smaller than their counterparts O15-C45-C54= 115° and O15-C52-C41= 118°. This could be due to the fact that only a weak hydrogen bond occurs on O15, O15...H3-C54= 2.798Å, while two stronger O...H bonds appear on O2, O2...H4-C10= 2.456Å and O2...H31-C46= 2.449Å, and to the stronger Co...O attraction between O15 and Co (Co...O2= 3.127Å and Co...O15= 3.022Å). The other O-C-C bond angles are smaller, O1-C10-C31= 109°, O5-C46-C50= 102°, O13-C41-C52= 106° and O16-C54-C45= 103°, and also have hydrogen contacts, O1...H37-C31= 2.430Å, O5...H9-C50= 2.547Å, O13...H41-C52= 2.272Å and O16...H29-C45= 2.429Å. O13...H41 is a very short hydrogen bond and may be due, similarly to the H10...H45 interaction, to the torsion of the ligand to get the O13 donor atom near the cobalt(II) ion. The O-C and C-C bond lengths in the ether bridges are strongly distorted from ideal and respectively vary from 1.39Å to 1.51Å and from 1.35Å to 1.51Å. This could be explained by the significant movements of these atoms, shown by their large thermal ellipsoids, and by the interaction between the oxygen donors and cobalt(II).

The angles between the S1 and S5 thiophene rings and their respective amine bridges, S1-C5-C4= 127°, C7-C5-C4= 122°, S5-C36-C11= 131° and C30-C36-C11= 119°, are similar and there are similar hydrogen contacts, O1...H32-C4= 2.643Å, S1...H18-C4= 2.841Å, O13...H8-C11= 2.326Å and S5...H36-C11= 2.9431Å. Contrary to those bond angles, the S-C-C angles with the amine bridges and the S2 and S6 thiophenes, S2-C34-C13= 118° and S6-C1-C3= 121°, are smaller than the C-C-C bond angles, C32-C34-C13= 130° and C38-C1-C3= 129°. This could be due to the different strengths of the hydrogen contacts and could be due, as for the ether bridges, to the torsion of the molecule to get the nitrogen donors near the metal ion. Indeed, S2...H47-C13= 2.690Å and S6...H42-C3= 2.809 Å indicate closer approaches than occur for the S1 and S5 atoms. O...H bonds also appear between the ether bridges and the amine bridges bonded to the thiophene rings, O5...H7-C13= 2.556Å and O16...H6-C3= 2.479Å. Similarly to complex **50**, the N-C bond lengths are longer than the usual N(sp^3: pyramidal)-C(sp^3)= 1.469Å, N1-C3= 1.51Å, N1-C4= 1.50Å, N1-C6= 1.52Å, N2-C11= 1.51Å, N2-C13= 1.55Å and N2-C33= 1.50Å. However, the N-C bond lengths are generally shorter than in complex **50**. Also, the C-N-C bond angles on the nitrogen atoms N1 and N2 are similar. C3-N1-C6= 111° and C13-N2-C33= 109° are smaller than their respective counterparts C4-N1-C6= 115° and C11-N2-C33= 114°. Despite being larger than the sum of the van der Waals radii (3.45Å), these bond angle differences could be due to the S2...N2= 3.658Å and S6...N1= 3.727Å interactions, which are stronger than the S1...N1= 3.814Å and S5...N2= 3.820Å interactions. The other C-N-C angles are fairly close to each other, C3-N1-C4= 111° and C11-N2-C13= 110°. The C-C bond lengths in the N1 propyl group (C6-C43= 1.53Å and C43-C58= 1.54Å) are fairly close to the usual Csp^3-Csp^3 bond length[363]. This is not the case for the N2 propyl group as the C33-C48= 1.60Å and C48-C57= 1.64Å bond lengths are significantly longer. Those long carbon-carbon bonds could be explained by the large thermal parameters of the C48 and C57 carbon atoms and the lack of precision in determining their positions, which also affects the C-C-C bond angles, C6-C43-C58= 110° and C33-C48-C57= 103°.





The views of the unit cell above show that the complexes, which include the ligand and the Co metal ion, the Cl2 and the Cl1 perchlorate anions are arranged similarly to compound **50** along the a-axis and also along the c-axis. The molecules (x, y, z) and (x, ½-y, ½+z), and the molecules (-x, ½+y, ½-z) and (-x, -y, -z) are respectively arranged along the c-axis, whereas the molecules (x, y, z) and (-x, -y, -z), and the molecules (-x, ½+y, ½-z) and (x, ½-y, ½+z) are respectively arranged along the a-axis.

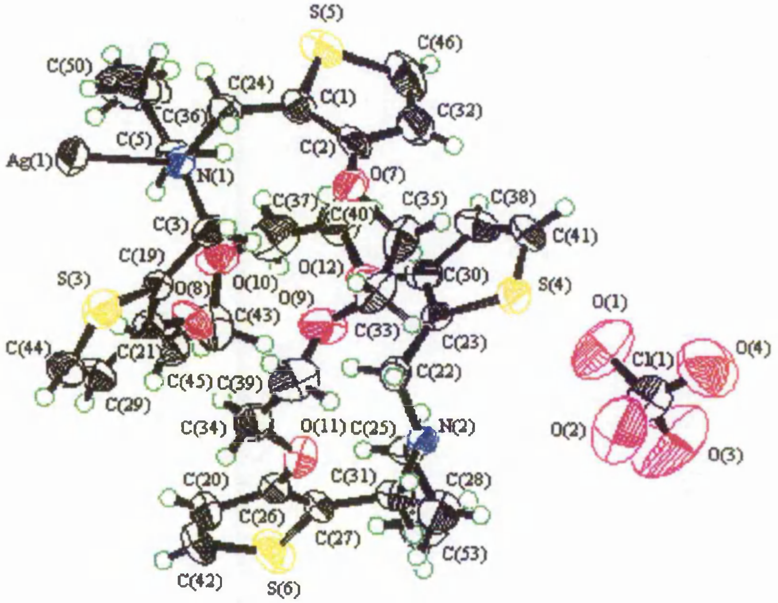
In the unit cell, the distances between the cobalt(II) metal ions Co(x, y, z)…Co(x, ½-y, ½+z) and Co(-x, ½+y, ½-z)…Co(-x, -y, -z) along the c-axis= 10.777Å are similar to the distances between the corresponding copper(II) metal ions in complex **50**, whereas the Co(x, y, z)…Co(-x, -y, -z)= 11.637Å and Co(-x, ½+y, ½-z)…Co(x, ½-y, ½+z)= 11.997Å along the a-axis are longer than their counterparts.

Some hydrogen contacts appear between molecules in the unit cell and are summarised in Table 97. The perchlorate ions and the ligands in the unit cell are linked by the following contacts, Cl1-O4(x, y, z)…H4-C10(x, 1-y, z)= 2.6 Å, Cl2-O7(x, y, z)…H40-C50(x, 1-y, z)= 2.9 Å, S6(x, y, z)…O8-Cl2(-x, ½+y, ½-z)= 3.19 Å, Cl1-O14(x, y, z)…H23-C53(-x, ½+y, ½-z)= 2.8 Å, Cl2(x, y, z)…H36-C11(-x, -y, -z)= 2.8 Å, S2(x, y, z)…O4-Cl1(-x, -y, -z)= 3.26 Å, S5(x, y, z)…O22-Cl2(-x, -y, -z)= 3.19 Å, Cl2-O6(x, y, z)…H36-C11(-x, -y, -z)= 2.5 Å, Cl2-O7(x, y, z)…H36-C11(-x, -y, -z)= 2.6 Å, Cl2-O22(x, y, z)…H36-C11(-x, -y, -z)= 2.4 Å, Cl1-O3(x, y, z)…H42-C3(-x, -y, -z)= 2.6 Å, Cl1-O3(x, y, z)…H18-C4(x, ½-y, ½+z)= 2.9 Å, Cl1-O14(x, y, z)…H18-C4(-x, -y, -z)= 2.7 Å and Cl2-O8(x, y, z)…H13-C11(x, ½-y, ½+z)= 2.9 Å.

4.3. Complex of 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetrathia-15,35-diaza-pentacyclo[29.5.5.5.0.0]-tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene with silver (I) perchlorate **42**

4.3.1. Discussion of the structure derived data (tables 44 to 46)

The space group of the complex **42** containing a silver(I) ion was the same as previously determined for the complex **50** and **54**, $P2_1/c$ or n°14. Although the structure would therefore be expected to be similar, the silver(I) metal ion was found to have complexed with the ligand **24** in a completely different way. Indeed, instead of being encapsulated by the ligand the silver(I) ion is bonded by the nitrogen atoms to two ligands and forms a chain in the cell. As usual the positions and anisotropic displacement parameters of the atoms in the complex are best visualized in the "ortep style" drawing below[353].



Compared to the complexes **50** and **54**, the thermal ellipsoids of the atoms in the ligand and of the silver ion are significantly smaller and there was a greater accuracy in determining the atomic positions. The silver(I) ion is strongly bonded to the nitrogen atoms, while the copper(II) and cobalt(II) metal ions in complexes **50** and **54** were only in weak contact with the oxygen and nitrogen donors of ligand **24**. The N1 and N2 atoms are each bonded to four other atoms which include the silver(I) ion. Consequently these nitrogen atoms have the smallest thermal ellipsoids of all the ligand atoms. The propyl group carbon atoms C28, C36, C50 and C53 have large thermal parameters due to the flexibility of these groups. However, compared to the free ligand **24** and the compounds **50** and **54** this flexibility is decreased by the presence of the silver(I) ion bonded to the nitrogen atoms of the amine bridges. The perchlorate counterion oxygen atoms have the greatest thermal ellipsoids of the whole complex and their positions are therefore less accurately defined.

4.3.2. Discussion of the structural geometry

Table 100. Bond Lengths(Å)

Bond Lengths(Å)			
Bond	Length(Å)	Bond	Length(Å)
Ag(1) -N(1)	2.286(6)	N(1) -C(3)	1.50(1)
Ag(1) -N(2A)*	2.290(6)	N(1) -C(5)	1.48(1)
Cl(1) -O(1)	1.421(7)	N(1) -C(24)	1.50(1)
Cl(1) -O(2)	1.334(8)	N(2) -C(22)	1.50(1)
Cl(1) -O(3)	1.340(8)	N(2) -C(25)	1.48(1)
Cl(1) -O(4)	1.383(9)	N(2) -C(31)	1.49(1)
S(3) -C(19)	1.733(7)	C(1) -C(2)	1.36(1)
S(3) -C(44)	1.70(1)	C(1) -C(24)	1.51(1)
S(4) -C(23)	1.726(8)	C(2) -C(32)	1.42(1)
S(4) -C(41)	1.68(1)	C(3) -C(19)	1.49(1)
S(5) -C(1)	1.721(8)	C(3) -H(16)	0.92(7)
S(5) -C(46)	1.70(1)	C(3) -H(17)	1.00(7)
S(6) -C(27)	1.723(8)	C(5) -C(36)	1.51(1)
S(6) -C(42)	1.70(1)	C(5) -H(4)	1.03(7)
O(7) -C(2)	1.348(9)	C(5) -H(5)	0.92(7)
O(7) -C(35)	1.44(1)	C(19) -C(21)	1.35(1)
O(8) -C(21)	1.365(9)	C(20) -C(26)	1.42(1)
O(8) -C(45)	1.42(1)	C(20) -C(42)	1.31(1)
O(9) -C(33)	1.42(1)	C(20) -H(7)	1.02(7)
O(9) -C(39)	1.40(1)	C(21) -C(29)	1.42(1)
O(10) -C(37)	1.41(1)	C(22) -C(23)	1.49(1)
O(10) -C(43)	1.40(1)	C(22) -H(19)	1.01(7)
O(11) -C(26)	1.369(9)	C(22) -H(20)	0.91(7)
O(11) -C(34)	1.42(1)	C(23) -C(30)	1.35(1)
O(12) -C(30)	1.366(9)	C(24) -H(15)	1.02(7)
O(12) -C(40)	1.43(1)	C(24) -H(45)	0.91(7)
C(25) -C(28)	1.50(1)	C(37) -C(40)	1.49(1)

C(25) -H(11)	0.92(7)	C(37) -H(37)	0.90(7)
C(25) -H(12)	0.85(7)	C(37) -H(44)	0.90(7)
C(26) -C(27)	1.35(1)	C(38) -C(41)	1.32(1)
C(27) -C(31)	1.49(1)	C(38) -H(10)	0.79(7)
C(28) -C(53)	1.52(2)	C(39) -H(24)	0.93(7)
C(28) -H(13)	1.03(7)	C(39) -H(42)	0.87(7)
C(28) -H(35)	0.84(7)	C(40) -H(40)	0.98(7)
C(29) -C(44)	1.34(1)	C(40) -H(41)	0.97(7)
C(29) -H(21)	0.90(7)	C(41) -H(22)	0.88(7)
C(30) -C(38)	1.44(1)	C(42) -H(6)	0.80(7)
C(31) -H(8)	0.99(7)	C(43) -C(45)	1.43(1)
C(31) -H(9)	0.92(7)	C(43) -H(33)	0.93(7)
C(32) -C(46)	1.33(1)	C(43) -H(43)	1.04(7)
C(32) -H(3)	0.85(7)	C(44) -H(30)	0.76(7)
C(33) -C(35)	1.46(1)	C(45) -H(31)	1.00(7)
C(33) -H(18)	0.94(7)	C(45) -H(34)	0.78(7)
C(33) -H(25)	0.95(7)	C(46) -H(39)	0.73(7)
C(34) -C(39)	1.46(1)	C(50) -H(28)	0.95(7)
C(34) -H(14)	0.96(7)	C(50) -H(29)	0.81(7)
C(34) -H(23)	0.95(7)	C(50) -H(38)	0.93(7)
C(35) -H(2)	0.91(7)	C(53) -H(27)	1.01(7)
C(35) -H(26)	0.87(7)	C(53) -H(36)	0.92(7)
C(36) -C(50)	1.50(2)	C(53) -H(46)	0.93(7)
C(36) -H(1)	0.92(7)	C(36) -H(32)	1.06(7)

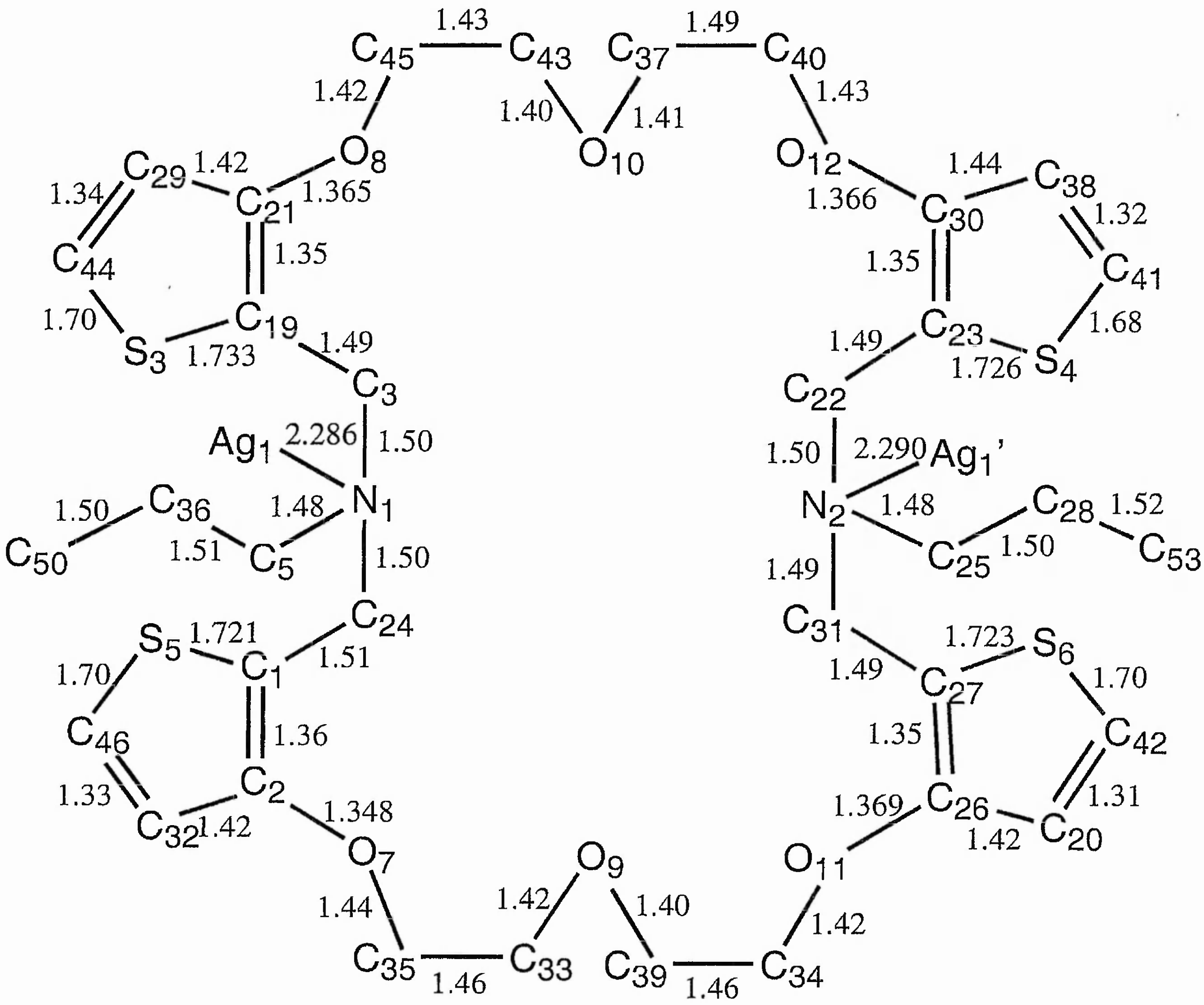
*At (x, -1+y, z)

Table 101. Contact bonds(Å)

Contact bonds(Å)					
Bond	Length(Å)	ADC(*)	Bond	Length(Å)	ADC(*)
Ag(1) -S(3)	3.118(3)	1	O(3) -H(8)	2.47(7)	55404
Ag(1) -S(4)	2.958(1)	54501	O(3) -H(19)	2.65(7)	55404
Ag(1) -O(1)	2.613(7)	54504	O(3) -H(18)	2.74(7)	55404
Ag(1) -O(3)	3.21(1)	54504	O(10) -H(25)	2.67(7)	54504
Ag(1) -Cl(1)	3.459(3)	54504	O(2) -H(6)	2.67(7)	55603
O(1) -H(15)	2.57(7)	54404	O(2) -H(27)	2.71(7)	55401
O(1) -H(44)	2.76(8)	55401	O(11) -H(30)	2.64(8)	55602

*see note (*) table 93 (p.289)

For ease of description the bond lengths (to 2 decimal places) are shown on a schematic drawing below.



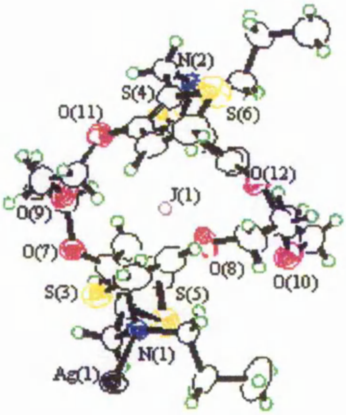
In complex **42**, the silver(I) metal ion is bonded to two thiophene-based macrocycles and constitutes a new "sandwich" or "club sandwich" structure as named by Taylor, Vergez, and Busch[281], and by Su and Weiher[282] (Scheme 1, page 24). The resulting effects on the bond lengths and bond angles of ligand **24** are fairly symmetric.

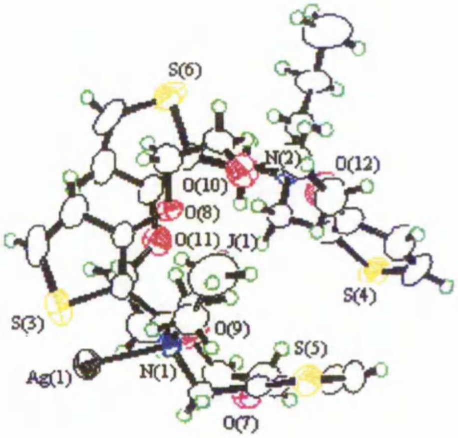
Table 102. Bond Angles(°)

Bond Angles(°)			
Bond	Angles(°)	Bond	Angles(°)
N(1) -Ag(1) -N(2)	150.5(2)	C(22) -N(2) -C(25)	110.9(6)
O(1) -Cl(1) -O(2)	109.5(5)	C(22) -N(2) -C(31)	110.3(6)
O(1) -Cl(1) -O(3)	111.1(5)	C(25) -N(2) -C(31)	111.8(7)
O(1) -Cl(1) -O(4)	110.4(6)	S(5) -C(1) -C(2)	110.3(6)
O(2) -Cl(1) -O(3)	113.1(7)	S(5) -C(1) -C(24)	122.7(6)
O(2) -Cl(1) -O(4)	104.5(7)	C(2) -C(1) -C(24)	126.9(7)
O(3) -Cl(1) -O(4)	108.1(7)	O(7) -C(2) -C(1)	121.6(8)
C(19) -S(3) -C(44)	91.7(5)	O(7) -C(2) -C(32)	125.4(9)
C(23) -S(4) -C(41)	92.4(5)	C(1) -C(2) -C(32)	112.9(9)
C(1) -S(5) -C(46)	91.8(5)	N(1) -C(3) -C(19)	112.8(7)
C(27) -S(6) -C(42)	91.9(5)	N(1) -C(3) -H(16)	105(5)
C(2) -O(7) -C(35)	118.8(7)	N(1) -C(3) -H(17)	112(4)
C(21) -O(8) -C(45)	118.0(7)	C(19) -C(3) -H(16)	115(4)
C(33) -O(9) -C(39)	113.5(8)	C(19) -C(3) -H(17)	108(4)
C(37) -O(10) -C(43)	111.8(8)	H(16) -C(3) -H(17)	104(6)
C(26) -O(11) -C(34)	118.1(7)	N(1) -C(5) -C(36)	114.0(7)
C(30) -O(12) -C(40)	116.4(7)	N(1) -C(5) -H(4)	110(4)
Ag(1) -N(1) -C(3)	107.8(5)	N(1) -C(5) -H(5)	108(4)
Ag(1) -N(1) -C(5)	109.1(5)	C(36) -C(5) -H(4)	108(4)
Ag(1) -N(1) -C(24)	108.5(4)	C(36) -C(5) -H(5)	113(5)
C(3) -N(1) -C(5)	109.5(6)	H(4) -C(5) -H(5)	104(6)
C(3) -N(1) -C(24)	109.5(6)	S(3) -C(19) -C(3)	120.8(6)
C(5) -N(1) -C(24)	112.4(6)	S(3) -C(19) -C(21)	109.8(6)
Ag(1) -N(2) -C(22)	108.5(4)	C(3) -C(19) -C(21)	129.3(7)
Ag(1) -N(2) -C(25)	107.4(5)	C(26) -C(20) -C(42)	112(1)
Ag(1) -N(2) -C(31)	107.9(5)	C(26) -C(20) -H(7)	119(4)
C(42) -C(20) -H(7)	129(4)	O(11) -C(26) -C(27)	119.2(8)
O(8) -C(21) -C(19)	120.3(7)	C(20) -C(26) -C(27)	114.0(9)
O(8) -C(21) -C(29)	125.5(8)	S(6) -C(27) -C(26)	109.3(7)
C(19) -C(21) -C(29)	114.2(8)	S(6) -C(27) -C(31)	124.1(7)
N(2) -C(22) -C(23)	112.0(7)	C(26) -C(27) -C(31)	126.3(8)
N(2) -C(22) -H(19)	106(4)	C(25) -C(28) -C(53)	115(1)
N(2) -C(22) -H(20)	111(5)	C(25) -C(28) -H(13)	114(4)
C(23) -C(22) -H(19)	114(4)	C(25) -C(28) -H(35)	113(6)
C(23) -C(22) -H(20)	107(5)	C(53) -C(28) -H(13)	98(4)

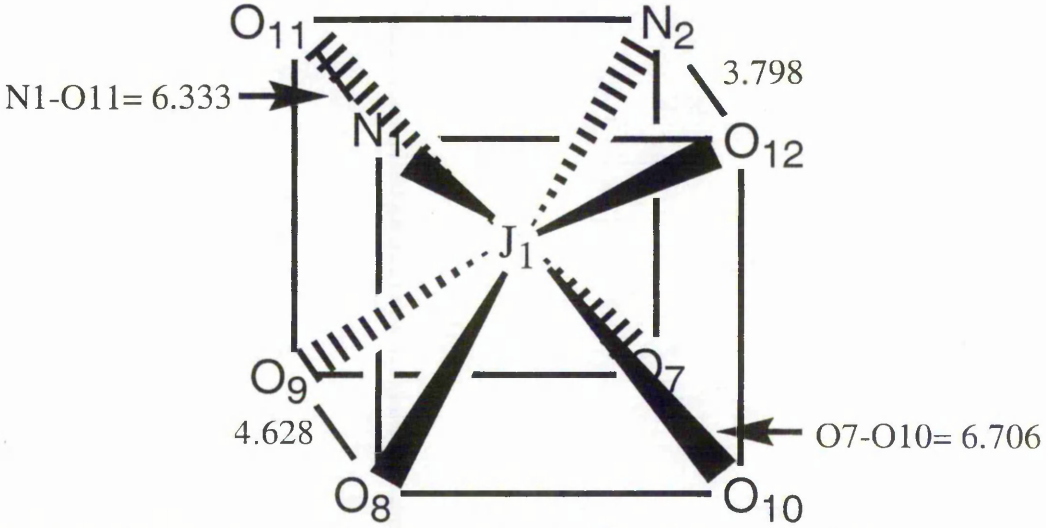
H(19) -C(22) -H(20)	107(6)	C(53) -C(28) -H(35)	111(6)
S(4) -C(23) -C(22)	121.4(6)	H(13) -C(28) -H(35)	105(7)
S(4) -C(23) -C(30)	109.6(6)	C(21) -C(29) -C(44)	111.3(9)
C(22) -C(23) -C(30)	128.9(7)	C(21) -C(29) -H(21)	121(5)
N(1) -C(24) -C(1)	115.2(7)	C(44) -C(29) -H(21)	128(5)
N(1) -C(24) -H(15)	105(4)	O(12) -C(30) -C(23)	121.1(8)
N(1) -C(24) -H(45)	102(5)	O(12) -C(30) -C(38)	125.8(8)
C(1) -C(24) -H(15)	107(4)	C(23) -C(30) -C(38)	113.1(9)
C(1) -C(24) -H(45)	105(5)	N(2) -C(31) -C(27)	118.1(7)
H(15) -C(24) -H(45)	122(6)	N(2) -C(31) -H(8)	103(4)
N(2) -C(25) -C(28)	113.7(8)	N(2) -C(31) -H(9)	105(5)
N(2) -C(25) -H(11)	108(5)	C(27) -C(31) -H(8)	107(4)
N(2) -C(25) -H(12)	111(5)	C(27) -C(31) -H(9)	106(5)
C(28) -C(25) -H(11)	110(5)	H(8) -C(31) -H(9)	118(7)
C(28) -C(25) -H(12)	111(5)	C(2) -C(32) -C(46)	112(1)
H(11) -C(25) -H(12)	102(7)	C(2) -C(32) -H(3)	119(6)
O(11) -C(26) -C(20)	126.7(9)	C(46) -C(32) -H(3)	128(6)
O(9) -C(33) -C(35)	107.1(8)	O(10) -C(37) -H(44)	112(5)
O(9) -C(33) -H(18)	100(5)	C(40) -C(37) -H(37)	105(5)
O(9) -C(33) -H(25)	104(5)	C(40) -C(37) -H(44)	114(5)
C(35) -C(33) -H(18)	102(5)	H(37) -C(37) -H(44)	100(7)
C(35) -C(33) -H(25)	122(5)	C(30) -C(38) -C(41)	111.8(9)
H(18) -C(33) -H(25)	119(6)	C(30) -C(38) -H(10)	122(6)
O(11) -C(34) -C(39)	107.2(9)	C(41) -C(38) -H(10)	125(7)
O(11) -C(34) -H(14)	106(4)	O(9) -C(39) -C(34)	109.3(8)
O(11) -C(34) -H(23)	105(5)	O(9) -C(39) -H(24)	108(5)
C(39) -C(34) -H(14)	117(5)	O(9) -C(39) -H(42)	109(6)
C(39) -C(34) -H(23)	117(4)	C(34) -C(39) -H(24)	116(5)
H(14) -C(34) -H(23)	104(6)	C(34) -C(39) -H(42)	113(6)
O(7) -C(35) -C(33)	109.9(8)	H(24) -C(39) -H(42)	100(7)
O(7) -C(35) -H(2)	109(5)	O(12) -C(40) -C(37)	109.6(9)
O(7) -C(35) -H(26)	110(5)	O(12) -C(40) -H(40)	101(4)
C(33) -C(35) -H(2)	109(5)	O(12) -C(40) -H(41)	106(5)
C(33) -C(35) -H(26)	114(5)	C(37) -C(40) -H(40)	108(5)
H(2) -C(35) -H(26)	105(7)	C(37) -C(40) -H(41)	107(5)
C(5) -C(36) -C(50)	109(1)	H(40) -C(40) -H(41)	125(7)
C(5) -C(36) -H(1)	114(5)	S(4) -C(41) -C(38)	113.1(8)
C(5) -C(36) -H(32)	110(4)	S(4) -C(41) -H(22)	121(5)
C(50) -C(36) -H(1)	106(5)	C(38) -C(41) -H(22)	126(5)
C(50) -C(36) -H(32)	114(4)	S(6) -C(42) -C(20)	112.7(8)

H(1) -C(36) -H(32)	104(7)	S(6) -C(42) -H(6)	120(6)
O(10) -C(37) -C(40)	115.2(9)	C(20) -C(42) -H(6)	127(6)
O(10) -C(37) -H(37)	110(5)	O(10) -C(43) -C(45)	110.4(9)
O(10) -C(43) -H(33)	112(5)	H(27) -C(53) -H(36)	154(7)
O(10) -C(43) -H(43)	106(4)	H(27) -C(53) -H(46)	84(7)
C(45) -C(43) -H(33)	111(5)	H(36) -C(53) -H(46)	122(8)
C(45) -C(43) -H(43)	119(4)	S(5) -C(46) -H(39)	120(7)
H(33) -C(43) -H(43)	98(6)	C(32) -C(46) -H(39)	126(7)
S(3) -C(44) -C(29)	113.0(8)	C(36) -C(50) -H(28)	118(6)
S(3) -C(44) -H(30)	120(7)	C(36) -C(50) -H(29)	109(7)
C(29) -C(44) -H(30)	124(7)	C(36) -C(50) -H(38)	90(5)
O(8) -C(45) -C(43)	110.8(9)	H(28) -C(50) -H(29)	85(7)
O(8) -C(45) -H(31)	108(4)	H(28) -C(50) -H(38)	149(8)
O(8) -C(45) -H(34)	108(7)	H(29) -C(50) -H(38)	96(10)
C(43) -C(45) -H(31)	113(4)	C(28) -C(53) -H(27)	113(5)
C(43) -C(45) -H(34)	121(7)	C(28) -C(53) -H(36)	75(5)
H(31) -C(45) -H(34)	94(8)	C(28) -C(53) -H(46)	94(5)
S(5) -C(46) -C(32)	112.7(8)		



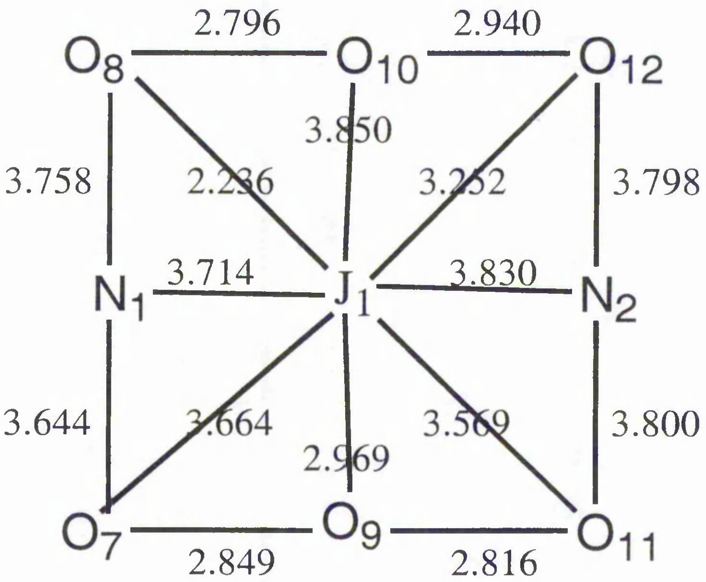


The preceding views of the macrocyclic complex **42** show that in addition to the two silver atoms bonded to the ligand, the macrocyclic ligand forms a similar cage to those obtained for the compounds **50** and **54**, which is schematically drawn below. This cavity, centered at point J1, has a radius of 0.856Å and so is able to include a metal ion such as copper(II) or cobalt(II). However, the nitrogen lone pairs are used to bond to the silver ions and so are pointed outside the macrocyclic cavity.

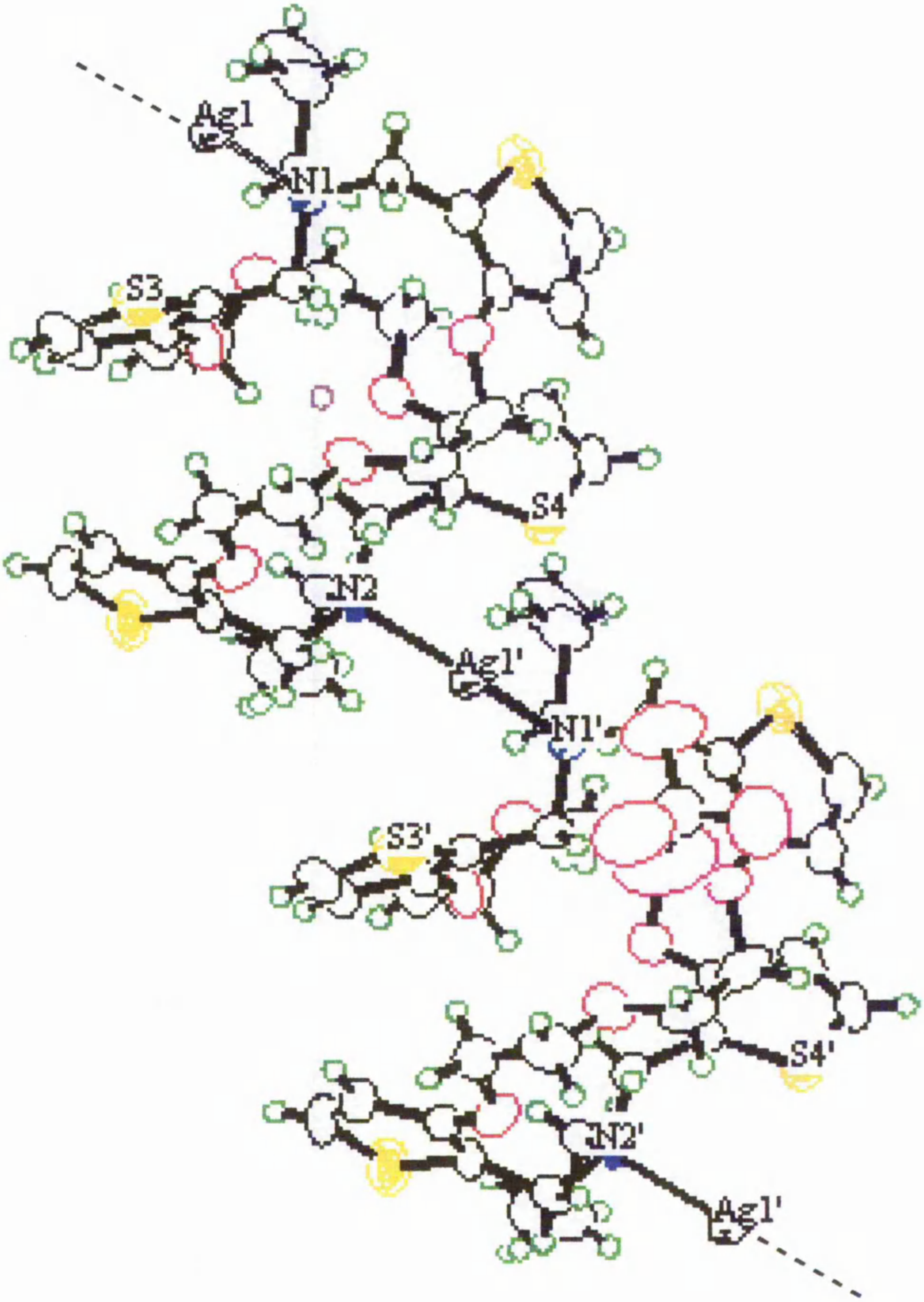


* Note the other donor atom distances are indicated on the following diagram.

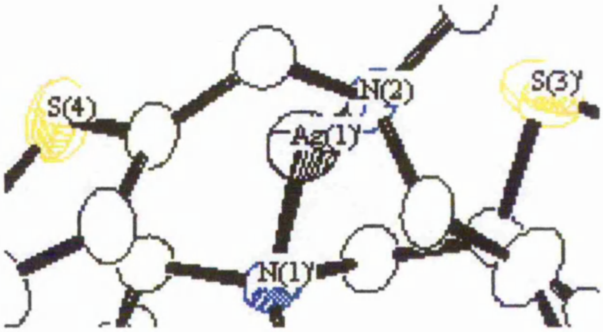
The centroid J1 of the macrocycle cavity has been calculated by the teXsan program and the distances between J1 and the donor atoms of the ligand are shown below. The distances to the centroid J1 are not symmetrically distributed. The shortest distance is O8-J1= 2.236Å, while O9-J1= 2.969Å and O12-J1= 3.252Å are similar to the contact bonds found in complex **50** and **54** between the copper(II) and cobalt(II) ions and the donor atoms of the cavity. The other donor atom-centroid distances are much longer, O7-J1= 3.664Å, O10-J1= 3.850Å, O11-J1= 3.569Å, N1-J1= 3.714Å and N2-J1= 3.830Å. The long distances N1-J1 and N2-J1 are due to effect of the Ag-N bonds.



The silver atom Ag1 is bonded to two macrocycles. After refinement and all atoms had been found, the structure was expanded to obtain the following view, which shows the silver coordination and the formation of a chain of macrocycles along the b direction in the unit cell.



The Ag1-N1= 2.286(6)Å and Ag1'-N2= 2.290(6)Å bonds are slightly shorter than the usual Ag-N= 2.372Å bond length with a tertiary amine[365], and form an angle N1'-Ag1'-N2 of 150.5°, which is a long way from the expected linear 180°. This could be due to the Ag...S(thiophene) η^1-S long contacts that appear on the silver ion, Ag1'...S4= 2.951Å and Ag1'...S3'= 3.118Å (sum of the van der Waals radii= 3.00 Å), and which are shorter than those observed by Drew in a thiophene-linked azacryptand complex with two silver(I) ions[259]. Were these contacts to be included, the metal coordination sphere would resemble a tetrahedron. This is shown in the following partial views of the molecule below.



Furthermore, the silver(I) ion has a long contact with the perchlorate anion (x, ½-y, ½+z), Ag1'(x, y, z)...O1-Cl1(x, ½-y, ½+z)= 2.613Å. This contact between the perchlorate oxygen O1 and the silver ion is reflected in the Cl-O bond lengths as the Cl1-O1= 1.421Å bond length is longer than the other Cl-O bonds, C1-O2= 1.334Å, Cl1-O3= 1.340Å and Cl1-O4= 1.383Å. *This shows that the contact of the silver atom with the* perchlorate could be a η^1 or η^2-ClO_4 contact bond[365].

The thiophene ring bond lengths and bond angles are all distorted from ideal in a similar fashion. The thiophene rings each form a plane, which includes the oxygen and carbon atoms directly bonded to them. In each thiophene, the outermost S-C and C=C bond lengths are shorter than their counterparts, S3-C19= 1.70Å, S3-C19= 1.733Å, C29-C44= 1.34Å, C19-C21= 1.35Å, S4-C41= 1.68Å, S4-C23= 1.726Å, C38-C41= 1.32Å, C23-C30= 1.35Å, S5-C46= 1.70Å, S5-C1= 1.721Å, C32-C46= 1.33Å, C1-C2= 1.36Å, S6-C42= 1.70Å, S6-C27= 1.723Å, C20-C42= 1.31Å and C26-C27= 1.35Å. The single *C-C bond lengths in the thiophene rings vary from 1.42 to 1.44Å and are fairly close to* the S-C= 1.419Å of unsubstituted thiophene[354]. The C-S-C bond angles, C19-S3-C44= 91.7(5)°, C23-S4-C41= 92.4(5)°, C1-S5-C46= 91.8(5)° and C27-S6-C42= 91.9(5)°, are also fairly similar and close to their counterparts in unsubstituted thiophene. The thiophene rings' bond angles are also all similarly distorted from ideal as the outermost S-C-C (vary from 112.7(8)° to 113.1(8)°) and C-C-C (vary from 111.3(9)° to 112(1)°) angles are respectively larger and smaller than their substituted counterparts (S-C-C vary from 109.3(7)° to 110.3(6)° and C-C-C vary from 112.9(9)° to 114.2(8)°).

The conjugation that appears between the oxygen atoms O7, O8, O11 and O12 of the ether bridges and their respective adjacent thiophene rings has a shortening effect on the C(thiophene)-O(ether bridge) bond length (1.348-1.365Å). Consequently, the C-O bond lengths are shorter than the other C-O bonds in the ether bridges, and are close to the C(aromatic)-O bond length in the phenol molecule[363]. The aliphatic C-O bond lengths vary from 1.40Å to 1.44Å and are in accordance with values in the International Tables for Crystallography[363], while the C-C bond lengths vary from 1.43Å to 1.49Å and are shorter than the Csp^3-Csp^3= 1.52Å bond length[363]. The O-C(thiophene)-C(thiophene) bond angles vary from 125.4(9)° to 126.7(9)° and are larger than the O-C(thiophene)=C(thiophene) angles, which vary from 119.2(8)° to 121.6(8)°. The O11-C26-C20 and O11-C26-C27 angles are respectively slightly larger and smaller than their counterparts. This could be due to the secondary interactions, which differ for the four thiophenes. The oxygen atom O11 has a weak O…H bond to its adjacent thiophene ring, O11…H7-C20= 2.744Å, and a stronger bond with the amine bridge bonded to the same thiophene ring, O11…H8-C31= 2.467Å, than the corresponding oxygen atoms O7, O8 and O12 (O7…H3-C32= 2.644Å, O7…H15-C24= 2.649Å, O8…H21-C29= 2.704Å, O8…H17-C3= 2.656Å, O12…H10-C38= 2.702Å and O12…H20-C22= 2.649Å). The O-C-C bond angles in the ether bridges are not symmetrical. Indeed, the O10-C37-C40= 115.2(9)° angle is much larger than O10-C43-C45= 110.1(9)°, O8-C45-C43= 110.8(9)°, O12-C40-C37= 109.6(9)°, O7-C35-C33= 109.9(8)°, O9-C33-C35= 107.1(8)°, O9-C39-C34= 109.3(8)° and O11-C34-C39= 107.2(9)°. Some O…H hydrogen bonds appear to affect the O-C-C bond angles: O7…H25-C33= 2.651Å, O9…H26-C35= 2.475Å, O9…H14-C34= 2.552Å, O10…H40-C40= 2.541Å and O12…H44-C37= 2.636Å. Finally, the C(thiophene)-O-C bond lengths, C2-O7-C35= 118.8(7)°, C21-O8-C45= 118.0(7)°, C26-O11-C34= 118.1(7)° and C30-O12-C40= 116.4(7)°, are larger than those in the ether bridges, C33-O9-C39= 113.5(8)° and C37-O10-C43= 111.8(8)°. Again H…H close approaches appear on the C-O-C bond angles, C43-H43…H44-C37= 2.318Å, C43-H33…H44-C37= 2.386Å, C33-H18…H24-C39= 2.275Å and C33-H25…H42-C39= 2.322Å, C45-H34…H21-C29= 2.225Å, C38-H10…H41-C40= 2.375Å, C34-H14…H7-C20= 2.380Å and C34-H23…H7-C20= 2.320Å. H18…H24 and H34…H21 are quite strong repulsions which could be due to the twisting that occurs in the molecule.

The C(thiophene)-C(amine bridge) bond lengths, which vary from 1.49 to 1.51Å, seem not to be affected by possible conjugation with the adjacent thiophene ring. The S-

C-C bond angles between the S3 and S4 thiophene rings and their corresponding amine bridge are significantly smaller than the C=C-C bond angles (S3-C19-C3= 120.8(6)°, C3-C19-C21= 129.3(7)°, S4-C23-C22= 121.1(6)° and C22-C23-C30= 128.9(7)°), while the differences between the corresponding angles with the S5 and S6 thiophene are less (S5-C1-C24= 122.7(6)°, C2-C1-C24= 126.9(7)°, S6-C27-C31= 124.1(7)° and C26-C27-C31= 126.3(8)°). This could be due to the contact bonds between S3 and Ag1 and between S4 and Ag1', which could explain the lower S3...H16-C3= 2.910Å and S4...H19-C22= 2.967Å contacts compared to S5...H45-C24= 2.755Å and S6...H9-C31= 2.848Å. Those S...Ag bonds could also explain the smaller N1-C3-C19= 112.8(7)° and N2-C22-C23= 112.0(7)° bond angles compared to N1-C24-C1= 115.2(7)° and N2-C31-C27= 118.1(7)°. The N-C-C bond angles with the propyl groups are N1-C5-C36= 114.0(7)° and N2-C25-C28= 113.7(8)°. The N-C bond lengths vary from 1.48Å to 1.50Å. The nitrogen atoms N1 and N2 are in a tetrahedral conformation as the Ag-N-C and C-N-C bond angles vary from 107.8(5)° to 112.4(6)° for N1, and from 107.4(5)° to 111.8(7)° for N2. The C-C bond lengths in the propyl groups vary from 1.50Å to 1.52Å. The C5-C36-C50= 109(1)° bond angle is much smaller than its counterpart C25-C28-C53= 115(1)°. This could perhaps be due to the Ag1(x, y, z)...H32-C36(-x, ½+y, ½-z)= 2.707Å close approach.

Table 103. Least-Squares Planes

Plane number 1

Atoms Defining Plane	Distance
S(3)	-.003(2)
C(19)	.016(7)
C(21)	-.013(7)
C(29)	-.006(10)
C(44)	.026(10)

Additional Atoms	Distance
O(8)	-.105
C(3)	-.027
N(1)	1.334
Ag(1)	2.496

Mean deviation from plane is .0124 Ångstroms

Chi-squared: 14.5

Plane number 2

Atoms Defining Plane	Distance
S(5)	.001(2)
C(1)	-.015(8)
C(2)	.017(8)
C(32)	-.015(10)
C(46)	.000(1)

Additional Atoms	Distance
O(7)	.135
C(24)	.014
N(1)	-1.322
Ag(1)	-1.020

Mean deviation from plane is .0096 Ångstroms

Chi-squared: 10.6

Dihedral angles between least-squares planes 1 and 2= 87.52°

Plane number 3

Atoms Defining Plane	Distance
S(4)	.001(2)
C(23)	-.008(7)
C(30)	.008(8)
C(38)	.003(12)
C(41)	-.012(11)

Additional Atoms	Distance
O(12)	-.017
C(22)	-.047
N(2)	-1.424

Mean deviation from plane is .0064 Ångstroms

Chi-squared: 3.5

Dihedral angles between least-squares planes 1 and 3= 59.16°

Dihedral angles between least-squares planes 2 and 3= 40.23°

Plane number 4

Atoms Defining Plane	Distance
S(6)	-.001(3)
C(20)	-.006(9)
C(26)	-.001(7)
C(27)	.004(8)
C(42)	.012(11)

Additional Atoms	Distance
O(11)	-.085
C(31)	-.110
N(2)	1.127

Mean deviation from plane is .0047 Ångstroms

Chi-squared: 1.7

Dihedral angles between least-squares planes 1 and 4= 30.32°

Dihedral angles between least-squares planes 2 and 4= 79.19°

Dihedral angles between least-squares planes 3 and 4= 69.76°

Plane number 5

Atoms Defining Plane	Distance
O(7)	.0000
O(9)	.0000
O(11)	.0000

Mean deviation from plane is .0000 Ångstroms

Chi-squared: .0

Dihedral angles between least-squares planes 1 and 5= 36.80°

Dihedral angles between least-squares planes 2 and 5= 96.95°

Dihedral angles between least-squares planes 3 and 5= 56.99°

Dihedral angles between least-squares planes 4 and 5= 67.11°

Plane number 6

Atoms Defining Plane	Distance
O(8)	.0000
O(10)	.0000
O(12)	.0000

Mean deviation from plane is .0000 Ångstroms

Chi-squared: .0

Dihedral angles between least-squares planes 1 and 6= 68.82°

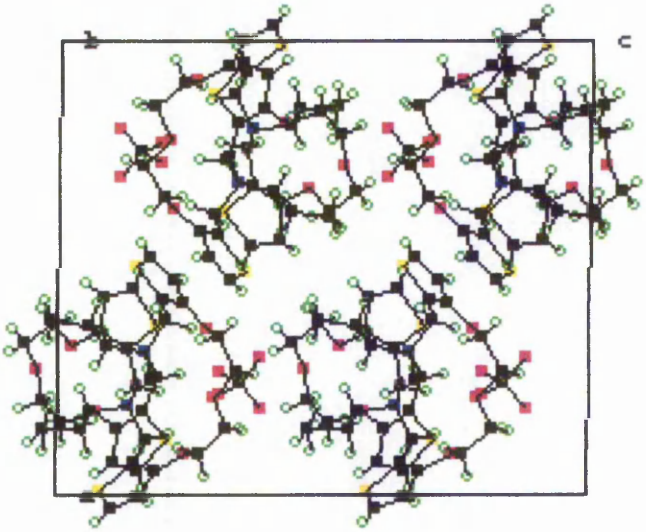
Dihedral angles between least-squares planes 2 and 6= 20.18°

Dihedral angles between least-squares planes 3 and 6= 35.30°

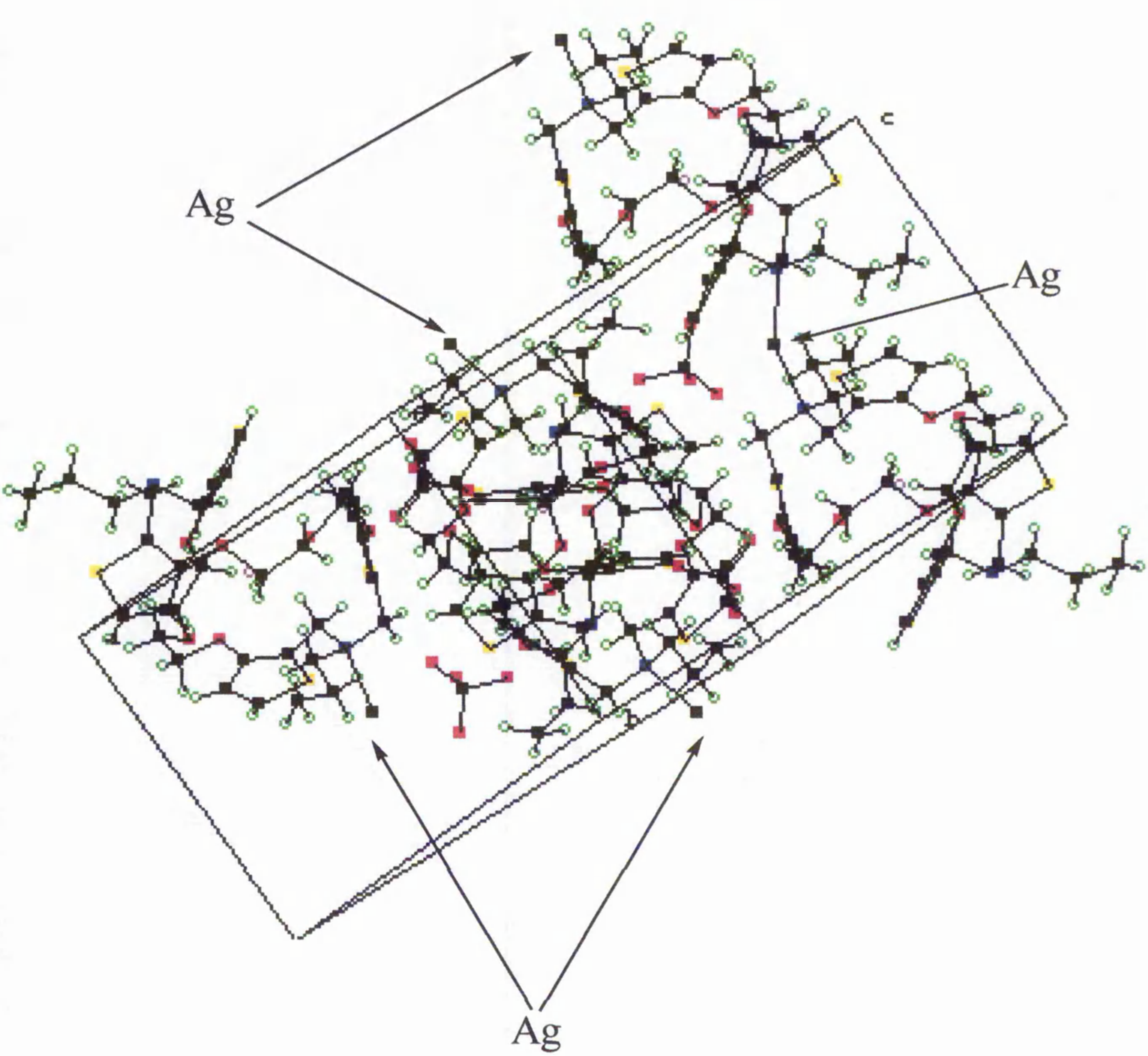
Dihedral angles between least-squares planes 4 and 6= 59.23°

Dihedral angles between least-squares planes 5 and 6= 85.85°

The view of the unit cell below shows that the ligand, the silver(I) ion and the associated perchlorate anion with symmetries (x, y, z) and (x, ½-y, ½+z) are arranged as a pair along the c-axis. This is the same for the pair of complexes with symmetries (-x, ½+y, ½-z) and (-x, -y, -z). The molecules and ions are also arranged along the a-axis as two pairs: (x, y, z) and (-x, ½+y, ½-z), (-x, -y, -z) and (x, ½-y, ½+z). The distances between the silver ions in the cell are Ag1(x, y, z)...Ag1(-x, ½+y, ½-z) and Ag1(-x, -y, -z)...Ag1(x, ½-y, ½+z)= 10.812Å, Ag1(x, y, z)...Ag1(-x, -y, -z)= 16.092Å, Ag1(-x, ½+y, ½-z)...Ag1(x, ½-y, ½+z)= 17.591Å, Ag1(x, y, z)...Ag1(x, ½-y, ½+z) and Ag1(-x, ½+y, ½-z)...Ag1(-x, -y, -z)= 12.934Å, and finally Ag1(x, y, z)...Ag1'(x, 1+y, z)= 11.019Å which is shown on the next view of the cell.



This view of the cell (below) shows that the chain formed by the silver ions, each linked to two macrocyclic ligands, is arranged along the b-axis.



The perchlorate counterions in the unit cell are attached to the different ligands by O...H contact bonds such as Cl1-O1(x, y, z)...H44-C37(x, y, -1+z)= 2.76Å, Cl1-O2(x, y, z)...H27-C53(x, y, -1+z)= 2.71Å, Cl1-O2(x, y, z)...H6-C42(-x, -y, -z)= 2.67Å, Cl1-O1(x, y, z)...H15-C24(x, ½-y, ½+z)= 2.57Å, Cl1-O3(x, y, z)...H8-C31(x, ½-y, ½+z)= 2.47Å, Cl1-O3(x, y, z)...H19-C22(x, ½-y, ½+z)= 2.65Å and Cl1-O3(x, y, z)...H18-C33(x, ½-y, ½+z)= 2.74Å. There are however large errors in the perchlorate oxygen positions so these interactions may be less significant than the distances quoted here indicate.

4.4. Metal-ion bonding – deductions from spectral data

The thiophene-based ligands studied in this work have been complexed with several different metal ions. Their proton and carbon NMR spectra were studied and are summarised in the following tables.

Table 104. ^{1}H and ^{13}C chemical shifts of compounds **16**, **19**, **20**, **26**, **27**, **28**, **29**, **30** and **31**.

Compound/ NMR		CHO	C5	C4	C3	C2	$ThOCH_2$	$ThOCH_2CH_2$	OCH_2CH_2O
16	^{1}H NMR		7.18dd	6.79dd		6.27dd	4.15t	3.91t	
	^{13}C NMR		123.61	118.35	157.43	96.57	69.73	69.47	
26 $AlCl_3$	^{1}H NMR		6.75dd	6.30dd		5.87dd	3.68t	3.43t	
	^{13}C NMR		123.7	118.35	156.35	96.57	68.55	68.46	
29 $Cu(ClO_4)_2$	^{1}H NMR		7.42m	6.88m		6.32m	4.01-4.17m		
	^{13}C NMR		122.63	118.19	168.85	90.59	71.86	71.72	
19	^{1}H NMR	9.99s	7.63d	6.87d			4.34m	3.94m	
	^{13}C NMR	181.18	135.03	116.52	163.93	121.78	72.23	69.82	
27 $AlCl_3$	^{1}H NMR	9.32s	7.17d	6.39d			3.77t	3.32t	
	^{13}C NMR	179.33	134.06	115.89	163.93	121.78	69.97	68.2	
30 $Cu(ClO_4)_2$	^{1}H NMR	10.32s	7.77d	7.00d			4.29m	3.84m	
	^{13}C NMR	182.71	137.35	118.54	166.96	118.54	72.7	70.82	
20	^{1}H NMR		7.14dd	6.77d		6.24dd	4.09t	3.72s	3.83t
	^{13}C NMR		124.76	119.67	157.67	97.63	70.9	69.65	69.82
28 $AlCl_3$	^{1}H NMR		6.64dd	6.18dd		5.75dd	3.53t	3.25t	
	^{13}C NMR		123.54	118.16	156.2	96.37	69.25	68.23	68.26
31 $Cu(ClO_4)_2$	^{1}H NMR		7.54s	7.39m		7.06m	4.07m	3.52s	3.65m
	^{13}C NMR		126.33	112.18	162.87	109.65	70.83	70.63	70.74

The thiophene-based open chains studied by structural crystallography earlier in this work were reacted with aluminium(III) chloride and with copper(II) perchlorate in order to form complexes. These open chain compounds are very flexible and have a great ability to complex with metal ions such as Al^{3+} that especially prefer oxygen donors (see pages 150, 158 and 183 for illustrations of the compounds).

In the three compounds **26**, **27**, and **28**, the complexation of the corresponding free ligands **16**, **19** and **20** with $AlCl_3$ can be seen to have a similar effect on the ^{1}H NMR spectra. In complex **26**, all the ^{1}H chemical shifts are moved upfield, while the ^{13}C chemical shifts are not significantly different from those in the free ligand **16**. This shielding effect could be due to the aluminium(III) ion which is diamagnetic. The shielding effect on the ether bridge indicates that the aluminium (III) ion interacts with the oxygen donors and so has complexed with the ligand **16**. The infrared spectrum of **26** shows that the peaks at 766.4(s) cm^{-1} and a peak at 1190.1(s, C-O) cm^{-1} in the free ligand **16** are both lowered in the complex spectrum at 756.2(s) cm^{-1} and 1178.0(s, C-O) cm^{-1}. Moreover, the C-C aromatic peaks are different in the ligand and the complex spectra. Also, the crystals of the free ligand were colourless while those of the complex were blue-grey. The chemical shifts for complex **28** are similar to those for **26**. However displacements of the ^{13}C chemical shifts to the right by 1ppm occur on all the carbon atoms compared to complex **26**. This could be due to the extra oxygen donor atom included in the ether chain and maybe due to a stronger and more stable complexation of the aluminium(III) ion with the donor atoms. Compound **27** is slightly different in structure compared to compound **26**. The C2 carbon atoms are each substituted by an aldehyde group. The ^{1}H chemical shifts are moved down by around 0.5ppm, similar to the preceding complexes. However, the ^{13}C chemical shifts are differently affected. The aldehyde carbon atom is moved upfield by 2ppm compared to **19** and the unsubstituted carbon atoms, as well as the ether bridge carbon atom chemical shifts, are decreased by 1ppm and 2ppm, while the carbons C2 and C3 keep the same chemical shifts. This indicates that Al^{3+} may be more strongly bonded to the ligand **19** oxygen donors in **27** than in the previous complexes. In the case of complex **27,** compared to the starting ligand **19** the infrared peaks at 744.6(s) cm-1 and 1273.1(m) cm^{-1} are moved respectively to a higher and lower frequency 802.6(m) cm^{-1} and 1261.1(m) cm^{-1}, while for compound **28**, similar to compounds **16** and **26**, the peak at 754.6(m) cm^{-1} in the free ligand **20** is lowered to 744.5(m) cm^{-1}. Crystals of these aluminium complexes were easily obtained but they were not suitable for X-ray crystallography as they decomposed in the X-ray beam.

The effect on the NMR spectra of complexation of the ligands **16**, **19** and **20** with $Cu(ClO_4)_2$ is completely different from the changes noted for the previous complexes with $AlCl_3$. Complex **29** does not show any significant differences in its ^{1}H chemical shifts compared to the free ligand **16**, while the ^{13}C shifts are more strongly affected. Indeed, the C3 carbon atom bonded to the ether bridge is deshielded and shifts to the left by 11ppm, while the C2 and C5 carbon atoms are more shielded (by 6ppm and 1ppm) compared to **16**. Moreover, the ether bridge carbon atoms have their chemical shifts moved to the left by 2ppm. These chemical shift differences show that the copper(II) ion, which is paramagnetic, is interacting with the oxygen donors. Also, the chemical shifts are not split, which indicates that the copper(II) ion interacts symmetrically with the donor atoms of the ligand **16**. In the solid state, the infrared spectrum reveals a peak at 628.1(s) cm^{-1} typical of the perchlorate ion. In complex **31**, the ^1H chemical shifts of the thiophene rings are more deshielded than in the free ligand **20**, while the hydrogen peaks of the chain $CH_2OCH_2CH_2OCH_2$ shift to the right. However in the ether bridge, the ^1H and ^{13}C chemical shifts of the carbon atoms next to the oxy-thiophene are similar to the free ligand. The C2 and C3 carbon atom peaks respectively shift to the left by 12ppm and 5ppm. These atoms are closer to the ether bridge. The carbon C5 is also deshielded by 2ppm while the carbon C4 is moved upfield by 7ppm. In the $CH_2OCH_2CH_2OCH_2$ fragment, the ^{13}C chemical shifts move upfield by 1ppm. The typical infrared peak of the perchlorate anion for **31** is observed at 625.2(s) cm^{-1}. The four oxygen donors of the ether bridge, which is very flexible, could allow a square planar arrangement of the ligand **20** around the copper(II) ion. In compound **30**, the OCH_2CH_2O fragment carbon atom ^1H chemical shifts are slightly shielded while in the thiophene rings they are moved downfield. Again for the ^{13}C chemical shifts, the largest peak displacements occur in the thiophene rings. The C5, C4 and especially C3 carbons shift to the left respectively by 2ppm, 2ppm and 3ppm, while the carbon C2 substituted by an aldehyde group shifts to the right by 3ppm. The aldehyde carbon atom and the ether chain carbons surrounding the central oxygen donor are deshielded by 1ppm whereas the other carbon atoms only shift to the left by 0.5ppm. This indicates that the $ThOCH_2$ oxygen atoms may interact more weakly with the copper(II) ion than with the aluminium(III) ion and suggests a trigonal bipyramidal complex conformation. The perchlorate peak for **30** appears in the solid state infrared spectrum at 627.5(s) cm^{-1}.

Table 105. ^1H and ^{13}C chemical shifts of compounds **10a, 32, 33, 34** and **35**.

Compound/ NMR		C5	C4	C3	C2	$ThOCH_2$	$ThCH_2N$	$ThOCH_2CH_2$	NCH_2	CH_3
10a	^1H NMR	7.07d	6.76d			4.14-4.17m	3.96s	3.64-3.67m	2.57q	1.14t
	^{13}C NMR	122.3	117.79	153.47	121.03	70.94	48.17	69.2	46.54	13
32 $Ni(ClO_4)_2$	^1H NMR	7.66d	7.17d			3.86t	4.78s	4.31-4.49	3.33q	1.44t
	^{13}C NMR	127.34	117.42	156.41	107.64	69.56	48.37	67.66	46.49	8.08
33 $NiCl_2$	^1H NMR	7.29d	6.93d			4.19t	4.00s	3.63t	2.63q	1.17t
	^{13}C NMR									–
34 $Cu(ClO_4)_2$	^1H NMR	7.65d	7.16d			3.86t	4.75s	4.31-4.51	3.31q	1.43t
	^{13}C NMR	127.99	118.04	157.14	108.23	70.21	48.92	68.38	47.09	8.63
35 $CuCl_2$	^1H NMR	7.62dd	7.13dd			3.79m	4.69s	4.48m	3.17q	1.44t
	^{13}C NMR	129.54	117.9	156.88	109.05	71.07	48.67	68.73	45.63	15.07

Complexation of macrocycle **10a** (illustrated on pages 191-200) with metal ions such as Ni^{2+} and Cu^{2+} was attempted using two different counterions: ClO_4^- and Cl^-. As Coomber found[338], it seems that the counterion has an important effect in complex formation. Indeed, it seems that the attempted complexation with $NiCl_2$ did not work (compound **33**), while complex **32** with $Ni(ClO_4)_2$ has formed as shown by the NMR results. The infrared spectrum of compound **33** did not reveal any new peaks and this again leads to the conclusion that reaction with $NiCl_2$ did not work. Whereas for complex **35**, **10a** with $CuCl_2$, a few new peaks appear 752.3(m) cm^{-1}, 725.1(m) cm^{-1}, 655.0(m) cm^{-1} and 622.5(w) cm^{-1}. Although the chlorine ion Cl^- is smaller than the perchlorate ion ClO_4^-, it seems that the perchlorate is less strongly bonded to the metal ion and therefore favored the complexation. In both the compounds **32** and **34**, the significant infrared perchlorate ion peak appeared at 623.2(s) cm^{-1} and 624.1(s) cm^{-1} respectively. The ^1H NMR spectra as well as the ^{13}C NMR spectra show some significant shifts, which can be related to small changes in ligand geometry and to weak interactions between the metal ion and the donor atoms. Indeed, in the complexes **32**, **34** and **35**, the H aromatic, $ThOCH_2CH_2$, $ThCH_2N$, NH_2 and CH_3 chemical shifts are all deshielded, while the $ThOCH_2$ peaks are moved upfield. This indicates that the nitrogen and oxygen donors are interacting with the Ni^{2+} or Cu^{2+} ions. The carbon NMR shifts are especially important on the thiophene rings. The carbon C2 substituted by the amine bridge shifts from 12 to 14 ppm to the right in all three compounds and the carbons C3 and C5 shift to the left respectively by between 3 and 4 ppm and between 5 and 7 ppm. Furthermore, the fact that the different chemical shifts are not split in two, shows that the metal ion may have complexed the ligand **10a** in a square planar or a tetrahedral arrangement. The square planar geometry would be more likely due to the geometry of the donor atoms' disposition in the free ligand. However, the mass spectra of compounds **32** and **34** did not show the expected peak due to the complexes but only the ligand peak M+H= 340. This shows that these complexes must not be very stable, possibly due to the relatively small size of the ring in **10a** as the radius of the planar cavity calculated from the centroid is 0.708Å compared to the ionic radii of Ni^{2+}= 0.69Å and Cu^{2+}= 0.77Å. Moreover, no useable crystals for X-ray crystallography were obtained. Also, Coomber[338] in his thesis found that the metal complexes could be prepared in solution, but when they crystallised, only the ligand was there.

Table 106. ^1H and ^{13}C chemical shifts of compounds **8b**, **39**, **9b**, **40**, **10b** and **36** on the next page.

Table 106. ^{1}H and ^{13}C chemical shifts of compounds **8b**, **39**, **9b**, **40**, **10b** and **36**.

Compound/ NMR		C5	C4	C3	C2	ThOCH$_2$	ThCH$_2$N	ThOCH$_2$CH	OCH$_2$CH$_2$O	NCH$_2$CH$_2$N	NCH$_2$	CH$_3$
8b	^{1}H NMR	7.11d	6.80d			4.14t	3.71s	3.82m	3.77s	2.61s		2.32s
	^{13}C NMR	122.62	117.1	153.07	119.07	71.53	51.18	70.02	71.14	53.23		42.79
39 Cu(ClO$_4$)$_2$	^{1}H NMR	6.86d	6.45d			3.72s	3.16s	3.56m	3.25m	2.48s		2.13s
	^{13}C NMR	123.79	116.65	154.45	109.24	69.42	51.86	68.26	68.98	53.88		42.6
9b	^{1}H NMR	7.08d	6.77d			4.16m	3.73s	3.77m	3.70s	2.61s		
	^{13}C NMR	122.37	116.99	154.3	116.99	71.03	51.04	70.32	70.82	51.04		
40 Cu(ClO$_4$)$_2$	^{1}H NMR	7.17d	6.83d			4.09m	3.70s	3.65m	3.21m	2.62s		
	^{13}C NMR	124.65	117.79	156.71	117.79	71.95	51.49	71.43	71.84	51.37		
10b	^{1}H NMR	7.07d	6.74d			4.12m	3.80s	3.70m	3.66s		2.57q	1.10t
	^{13}C NMR	122.5	117.21	153.44	120.74	71.2	47.94	69.86	70.73		46.6	12.19
36 Ni(ClO$_4$)$_2$	^{1}H NMR	7.37d	6.87d			4.54m	3.66s	4.27m	3.75m		3.18s	1.34s
	^{13}C NMR	127.79	116.23	157.5	105.86	70.45	47.34	68.8	69.9		45.4	8.92

Table 107. ^{1}H and ^{13}C chemical shifts of compounds **22**, **38**, **23** and **37**.

Compound/ NMR		C5	C4	C3	C2	ThOCH$_2$	ThCH$_2$N	ThOCH$_2$CH$_2$	OCH$_2$CH$_2$O	NCH$_2$CH$_2$O	NCH$_2$CH$_2$O	C9	C8/8'	C7/7'	C6
22	^{1}H NMR	7.27d	6.78d			4.11m	4.33s	3.70m	3.59t	3.17m	3.86t				
	^{13}C NMR	127.4	116.17	157.37	116.49	70.78	48.8	69.76	70.65	53.4	65.73				
38 Cu(ClO$_4$)$_2$	^{1}H NMR	7.31m	6.81m			4.11m	4.37m	3.68m	3.53t	3.39m	3.95m				
	^{13}C NMR	127.91	114.93	157.65	116.06	70.44	49.74	69.28	70.21	53.45	63.95				
23	^{1}H NMR	7.11d	6.70d			4.05m	4.89s	3.70m	3.62s	3.23t	3.39t		7.24d	7.68d	
	^{13}C NMR	124.52	116.1	154.95	116.26	71.14	42.06	69.97	71	47.75	68.37	143.13	129.6	127.34	137.72
37 Cu(ClO$_4$)$_2$	^{1}H NMR	7.02d	6.77d			4.13m	4.90s	3.80m	3.50s	3.08t	3.39t		7.32d	7.76d	
	^{13}C NMR	124.18	113.64	155.52	121.14	73.39	42.76	73.39	69.27	50.87	69.77	143.53	129.75	127.06	136.93

The macrocyclic ligand **10b** (illustrated on page 214), which has an extra oxygen donor atom in its ether chain compared to compound **10a**, was complexed with $Ni(ClO_4)_2$ to form complex **36** and its ^1H and ^{13}C NMR spectra were studied. The ^1H and ^{13}C chemical shift changes show, as for the previous complexes, that some small changes in the ligand geometry occur during complexation. Similarly to the complexes **32**, **34** and **35**, the thiophene ring ^1H chemical shifts are less shielded, while in the ether bridge they shift to the left. On the amine bridge, the ^1H peaks of the carbon bonded to the thiophene are moved upfield and in the ethyl group this is reversed. This could indicate an interaction between the nickel(II) ion and all five donor atoms. The ^{13}C chemical shift changes, which are similar to complex **32**, confirm this hypothesis. However, the ^{13}C chemical shifts of the $ThCH_2N$ fragments surrounding the nitrogen do not shift as much as the carbons of the ether chain, which are moved by 1ppm to the right of the spectrum. The solid state crystal structure conformation of **10b** indicates that any complex would have a square pyramidal geometry due to the planar arrangement of the oxygen atoms, which with the nitrogen atom form a cavity radius of 0.986Å and 1.263Å. The low stability of this complex could be due to the cavity radii, which are too large compared to Ni^{2+}= 0.69Å. The perchlorate infrared peak in **36** is found at 625.7(s) cm^{-1}. The complex **36** was confirmed by mass spectroscopy with a peak at $[NiL]^{2+}$ ClO_4^- m/z= 540, 542 and 544.

The ligand **8b** (illustration p236-244) contains a dimethyldiamine bridge instead of an ethylamine unit as in macrocycle **10b**. **8b** was complexed with $Cu(ClO_4)_2$ to form complex **39**. The ligand conformational changes during complexation with copper(II) ion are shown in the ^1H NMR results as a shielding on all the carbon atoms. The ^{13}C chemical shifts are differently affected. Indeed, the peak shifts on the thiophene rings are smaller than in previous complexes such as **32**, **34**, **35** and **36**. This could be due to the longer bridges and the larger cavity radius of macrocycle **8b** which induce less torsion in the molecule during complexation. The carbons C5, C2 (bonded to the diamine chain) and C3 (bonded to the ether chain) respectively shift by +1ppm, -10ppm and +1.5ppm. The $ThOCH_2$ and $CH_2OCH_2CH_2OCH_2$ fragment peaks are moved to the right of the spectrum by 1 to 2ppm, while on the diamine the $ThCH_2N$ and NCH_2CH_2N peaks are moved upfield by 0.5ppm and 0.7ppm. This could indicate that complex **39** has adopted a square planar arrangement of the nitrogen and two oxygen donors around the copper(II) ion, or a trigonal prismatic geometry if all the oxygens are included. The infrared spectrum presents a peak at 624.2(s) cm^{-1} typical of perchlorate.

The flexibility of the diamine in macrocycle **8b** was hindered by the substitution of the dimethyldiamine by a piperazine unit in ligand **9b** (illustration p245-257). The ^{1}H and ^{13}C chemical shifts in complex **40** with $Cu(ClO_4)_2$ show that the carbon atoms of the ether bridge are more affected by a change of conformation on complexation than the piperazine. Moreover, the thiophene ring ^{1}H and ^{13}C peaks are differently shifted compared to complex **39**. These differences also show that the changes in the ligand conformation on complexation are more important in the ether chain than in the rigid cyclodiamine, which is not the case in ligand **8b** where the diamine is more flexible. The cyclodiamine is in the chair conformation in the solid state (p 245-257), but in solution it could convert to the boat conformation, which is ideal for complexation as the nitrogen lone pairs would be oriented inside the cavity. In that case, the copper(II) ion should, as in compound **39**, complex with the two nitrogens and two oxygens in a square planar geometry or possibly as a trigonal prism if all four oxygen atoms were attached. The perchlorate peak in the infrared spectrum comes at 627.2(s) cm^{-1}. However, the stability of this complex must be fairly low as in the mass spectrum only the ligand peak appears (M+H= 425). This is confirmed by the fact that the crystals did not stand the X-ray beam and decomposed. This could be due to the cavity radius which calculated from the centroid is 1Å and is too large to strongly complex with Cu^{2+} (0.77Å).

In the case of compound **22** (illustration p258-259), the complexation with $Cu(ClO_4)_2$ to give complex **38** does not give much change in the ^{1}H and ^{13}C NMR spectra except for the diamine chain. Indeed, it seems that only the diamine bridge is affected by a change of conformation when complexing with the copper(II) ion.

The methyl group in **22** was substituted by a tosyl group in macrocycle **23** (illustration p260-273) to create a steric effect and to hinder the flexibility of the ligand. The complexation of **23** with a copper(II) ion to give complex **37** appears more clearly on the NMR results than for the previous complex **38**. Indeed, the thiophene ring ^{13}C chemical shifts move by between +5ppm and -2.5ppm. The ether bridge shows changes in its conformation as the ^{13}C peaks are shifted by between –2ppm and +4ppm. In the diamine bridge, the movements of the $ThCH_2N$ fragment are limited by the steric effect of the tosyl units. However, the NCH_2CH_2O fragment ^{13}C peaks are deshielded by 1.4 to 2ppm. The differences between the spectra of these complexes confirm the participation of the nitrogen atoms in complexation with the copper(II) ion. The formation of complexes **37** and **38** has been confirmed by infrared spectroscopy (perchlorate ion at 624.4(s) cm^{-1} and 624.9(s) cm^{-1}) as well as by elemental analysis which confirms formation of a 1:1 complex in both cases. Moreover, crystals of these two complexes have been obtained and are awaiting X-ray diffraction.

Table 108. ^1H and ^{13}C chemical shifts of compounds **24**, **25** and **41** to **55**.

Compound/ NMR		C5	C4	C3	C2	$ThOCH_2$	$ThCH_2N$	$ThOCH_2CH_2/OCH_2CH_2O$	$N\underline{CH_2}CH_2$	$NCH_2\underline{CH_2}$	CH_3
25	^1H	7.07d	6.76d			4.10t	3.69s	3.73m	2.44t	1.55m	0.86t
	^{13}C	124.1	112	159.4	116	71.44	50.81	70.44/70.23	58.59	18.22	11.94
41 $Cu(ClO_4)_2$	^1H	6.99s	6.57s			3.86s	3.28s	3.86s/3.42s	2.29s	1.36m	0.94s
	^{13}C	132.2	116.3	154.7	126.8	70.38	47.23	69.76/68.87	53.29	21.23	14.03
24	^1H	7.07d	6.75d			4.08t	3.76s	3.78t	2.45t	1.54q	0.87t
	^{13}C	122.6	117.3	153.5	121.4	71.41	48.42	70.21	54.83	20.34	11.78
42 $AgClO_4$	^1H	7.01d	6.64m			3.88s	3.46m	3.68s	2.74s	1.36m	0.61t
	^{13}C	124.5	116.1	155.2	118	71.29	49.05	70.79	68.77	20.75	10.89
43 $2(AgClO_4)$	^1H	7.46d	6.86d			3.98s	3.21m	3.65m	2.87m	1.67m	0.83t
	^{13}C	128.9	117.9	159.2	117.9	72.18	48.83	70.73	54.45	18.85	11.3
44 KSCN	^1H	7.12d	6.76d			4.10t	3.79m	3.79m	2.50t	1.58q	0.88t
	^{13}C	122.9	117.2	153.6	117.2	71.36	48.21	71.22	70.15	20.11	11.71
45 2(KSCN)	^1H	7.10d	6.76d			4.08m	3.79m	3.79m	2.47m	1.56q	0.87t
	^{13}C	122.8	117.3	153.8	117.3	71.37	48.28	71.2	70.16	20.14	11.74
46 $Al_2(SO_4)_3$	^1H	7.55d	6.95d			4.08m	4.36s	3.75m	2.88m	1.76m	0.93t
	^{13}C	128.4	117.9	158.8	109	72.23	49*	70.81	54.09	19.17	11.46
47 $AlCl_3$	^1H	7.34d	6.71d			3.99m	4.33m	3.63m	2.73m	1.90m	0.87m
	^{13}C	127.3	116	157.6	106.4	70.96	46.91	70.55	69.62	18.02	11.28
48 Pb(IV) ethanoate	^1H	7.22d	6.84d			4.07m	3.80s	3.73m	2.44m	1.52m	0.84t
	^{13}C	124.4	113.5	155.9	119.8	71.2	47.95	70.38	58.38	18.44	10.8
49 $Pb(ClO_4)_2$	^1H	7.48d	6.86d			3.94m	4.30s	3.65m	2.88m	1.64m	0.84t
	^{13}C	128	117.9	155.5	119.9	72.19	47.16	70.71	59.27	20.26	9.56
50 $Cu(ClO_4)_2$	^1H	7.13m	6.59d			4.01m	3.49s	3.82s	2.74m	1.40m	1.08s
	^{13}C	127.1	116.2	153.9	117.8	71.77	47.16	70.38	55.85	18.87	10.57
51A $CuCl_2$	^1H	7.30s	6.76s			4.22s	3.76s	4.07s	2.73m	1.87m	0.90s
	^{13}C	126.6	116.5	156.9	116.7	71.09	47.45	69.89	51.41	18.78	11.89
51B $CuCl_2$	^1H	7.22s	6.72s			4.09s	3.67s	3.99s	2.63s	1.70s	0.82s
	^{13}C	125.8	116.3	156.1	116.8	70.67	47.1	69.46	52.05	18.42	11.07
51C $CuCl_2$	^1H	7.24d	6.75d			4.12s	3.73s	4.04s	2.65s	1.75s	0.88t
	^{13}C	125.7	116.5	156.2	116.8	71	47.4	69.8	53.37	18.84	11.39
52 $Ni(ClO_4)_2$	^1H	6.91m	6.80m			4.20m	3.67m	3.83m	2.82m	1.26m	1.16m
	^{13}C	127.6	114.9	154.1	119.5	72.22	47.59	69.76	60.21	18.84	9.46
54 $Co(ClO_4)_2$	^1H	6.92m	6.80m			4.23m	3.86m	3.86m	2.84m	1.64m	0.92m
	^{13}C	124.1	116.5	156.1	118.9	71.68	46.33	69.77	57.69	19.2	8.29
55 $Fe(ClO_4)_2$	^1H	6.88m	6.78m			4.18m	3.81m	3.81m	2.80m	1.68m	0.89m
	^{13}C	125.5	116.8	154.8	119.5	71.09	46.55	69.67	61.35	22.01	10.09
56 $Mn(ClO_4)_2$	^1H	6.92m	6.46m			3.67m	3.35m	3.35m	2.26m	1.24m	0.84m
	^{13}C	124.4	116.4	153.8	106.6	70.08	46.93	68.72	61.35	17.58	10.15

*Hidden by methanol

Macrocycles **24** and **25** (illustrations p274-283 and 284-286) differ by an extra oxygen being present in each of the two ether bridges of compound **25**. The copper(II) complex **41** ^{1}H and ^{13}C chemical shift differences compared with the free ligand **25** show that there is an interaction of the copper(II) ion with all the possible donor atoms. The macrocyclic ligand **25**, which is already in a cage geometry, should, as should the ligand **24**, encapsulate the copper(II) ion. Indeed, all the 8 donor atoms of ligand **24** weakly interact with the metal ion in copper complex **50**, as shown by the crystallographic results (p 287-303).

The perchlorate counterion was replaced by a chloride ion to form copper complex **51**. Three different samples of complex **51** were obtained, **51A**, **51B** and **51C**. Complex **51B** (infrared chloride band at 738.7(w, sp) cm^{-1}) and **51C** (infrared chloride band at 739.6(w, sp) cm^{-1}) have similar ^{1}H and ^{13}C NMR and infrared spectra, while the infrared spectrum of compound **51A** differs and shows extra new peaks (802.2(s) cm^{-1}, 744.7(s) cm^{-1}, 665.7(w, sp) cm^{-1} and 593.0(w) cm^{-1}). Complex **51A** could be in a different conformation than complexes **51B** and **51C**, indeed **51A** was obtained as a green powder whereas compounds **51B** and **51C** crystallised as fine yellow needles. However, the mass spectra of all these compounds only contain the free ligand peak; it is possible that the copper(II) ion is not strongly attached to the macrocycle as in the nickel complex **33** discussed earlier, and the complex was not stable under the mass spectroscopy experimental conditions.

The crystal structure of complex **54**, macrocycle **24** complexed with a cobalt(II) ion instead of a copper(II) ion has been obtained (p304-320). The ligand **24** encapsulates the cobalt(II) ion in a fairly similar way to complex **50** and the complex also has similar ^{1}H and ^{13}C NMR spectra. Ligand **24** was afterwards complexed with a series of metal ions such as Ni^{2+}, Fe^{2+}, Mn^{2+} and Pb^{4+} which all have similar ionic radii. The similarity of the spectra with those of compounds **50** and **54** lead to the supposition of a similar geometry of the ligand as a cryptand around the metal ions although crystals suitable for X-ray diffraction could not be obtained.

The macrocycle **24** was then complexed with a larger metal ion, Pb^{2+} (ionic radius= 1.19 Å). Crystallographic data for complex **49**, formed between **24** and $Pb(ClO_4)_2$ was obtained, but the structure could not be solved due to the poor quality of the data caused by very high absorption factors and a degradation of the crystal under the X-ray beam. However, some important structural information was obtained such as the crystal system (monoclinic), the lattice type (centrosymmetric), the unit cell dimensions (a= 14.305 Å, b= 9.183 Å, c= 16.865 Å, α= 89.674°, β= 112.205° and γ= 90.879°), the Z value (Z=2) and the space group ($P2_1/a$). As the number of molecules in the unit cell(Z)= 2 and the space group contains four asymmetric units, it could be deduced that if there was only one lead(II) ion per molecule, the lead(II) ions must lie on a special positions of symmetry within the unit cell. This and the unit cell dimensions enabled some indication of the macrocycle geometry in the structure to be obtained. The lead(II) ion is known to favour the 6 or even 8 coordinate geometry which can be obtained with the ligand **24** in case of an encapsulation of the metal ion[367]. The 8 coordination is confirmed by the ^1H and ^{13}C chemical shifts, which are all affected. Indeed, the ether bridge ^1H and ^{13}C peaks are respectively moved downfield and upfield, while for the $ThCH_2N$ fragment this is reversed. The largest shifts appear for the $N\underline{CH_2}CH_2$ fragment as its ^1H and ^{13}C chemical shifts are deshielded by +0.43ppm and +4.5ppm.

Ligand **24** was then complexed with $Ag(ClO_4)$ in a ratio of 1:1 (complex **42**) and a ratio of 2 silver(I) ions for 1 ligand (complex **43**). The crystal structure of complex **42** was obtained and revealed that the silver(I) ion was bonded to two macrocycles by their nitrogen atoms, while the metal-free cavity conformation is similar to the ligand geometry in complex **50** and **54**. This bonding between the silver(I) ion and the nitrogens is reflected in the ^{13}C chemical shifts as the $N\underline{CH_2}CH_2CH_3$ fragment carbons are deshielded by +14ppm. The complex **43** NMR spectra have different peak shifts than for complex **42**. This could be due to an effective complexation of two silver(I) ions with the ligand **24**. The two silver(I) ions could both be included in the cavity, which should be more more planar than in complex **42** as the macrocycle **24** cavity size is large and flexible enough to include between 1 and 3 metal ions (p283).

The salt KSCN was used to form a potassium complex with ligand **24** in a ratio of 1:1 (compound **44**) and 2:1 (compound **45**). The chemical analysis of these complexes showed that in fact the potassium(I) ion did only complex in a 1:1 ratio. This ratio was confirmed in compounds **44** and **45** by elemental analysis. The ^{13}C chemical shifts of the $N\underline{CH_2}CH_2CH_3$ fragment carbons, in both **44** and **45**, are deshielded by +16ppm. This shows that the potassium(I) ion should be interacting strongly with the nitrogen atoms. This indicates a possible similar complexation to **42** and this could be why the 2:1 form is not stable. Both of the prepared complexes presented the typical peaks of the isocyanate ion in their infrared spectra (**44**: 2078.8(s, vCN) cm^{-1}, 2051.0(s, vCN)cm^{-1}, 755.1(w, vCS) cm^{-1} and 470.4(w, vNCS) cm^{-1}; **45**: 2054.4(s, vCN) cm^{-1}, 748.6(w, vCS) and 470.8(w, vNCS) cm^{-1}).

Finally, two complexations were attempted on macrocycle **24** using $Al_2(SO_4)_3$ (complex **46**) and $AlCl_3$ (complex **47**). The mass spectrum of complex **46** presents a peak at M+H= 1049, which corresponds to a 2:1 ratio of aluminium/ligand. This 2:1 ratio is confirmed by elemental analysis. The proton and carbon NMR spectra show some significant peak shifts on the thiophene rings, while the ^{1}H chemical shifts of the amine bridge are, as for the thiophenes, move downfield. This indicates changes in the amine conformation and also that the aluminium(III) ions may interact more strongly with the nitrogen atoms. In the NMR spectra of complex **47**, the $N\underline{CH_2}CH_2CH_3$ peaks are strongly deshielded by +15ppm. It can be presumed that the aluminium(III) ion is bonded to the nitrogens. Furthermore, these complexes present similar infrared peaks that should be due to the Al(III)-O bond (**46**: 820.9(m)cm^{-1}, 740.5(m)cm^{-1}, 722.4(m)cm^{-1} and 604.4(m) cm^{-1}; **47**: 820.0(m) cm^{-1}, 744.7(m) and 723.2(m) cm^{-1}). The complex **47** precipitated in a yellow powder and could not be recrystallised in a suitable form for X-ray diffraction.

Conclusion

The relative sizes of the macrocycle "hole" and the cation, and also the number and symmetrical arrangement of the donor atoms have an effect on the stability of the metal complexes.

- The conventional approach consists of defining the diameter of the cavity as the distance between diametrically opposed donors[98-102].
- For macrocyclic ligands, which have an odd number and/or a non-planar arrangement of donor atoms, a more realistic estimate of hole size is obtained, when the radius of the "hole" is calculated as the mean distance of the donor atoms from their centroid[98-102].

Table 109. Macrocyclic cavity sizes

Free macrocyclic ligand	"Hole" radius (Å) in crystallographic structures	shortest distance to centroid (Å) for X-ray structures	"Hole" radius (Å) in modelled structures
8b	0.773	1	-
9a	-	-	0.898 and 1.083
9b	0.855	1.029	-
10a	0.924	0.708	1.0465 and 0.9565
10b	0.986 and 1.263	0.523 and 1.022	-
12	-	-	0.6695
13	-	-	0.198
14	0.85	0.772	-
21	-	-	0.1925
22	-	-	1.836
23	0.9025 and 0.917	0.808 and 0.686	-
24	0.995 and 1.267	1.045 and 1.044	-
25	-	-	1.189

The macrocyclic cavities found in this work are similar in size to those in macrocycles with similar numbers of ring atoms found in the literature[95-102]. The macrocycles, except the compounds **13** and **21**, have cavities suitable for accepting metal ions such as Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^{+} and K^{+}. The radii of those metal ions are reported in Table 1 (p23). The macrocycles reported here have a number of different ring sizes, different number of donor atoms, different substitution and conformation, which was expected to have an effect on their selectivities and abilities to complex with one or more metal ions, since "hole" radius is not the only determining factor.

The two different approaches to the macrocyclic cavity size give slightly different complexing ability to the macrocycles. In the case of **10a**, **10b**, **14** and **23** using the centroid method gives a much smaller cavity diameter than simply considering the maximum or minimum distance between the donor atoms and indicates that a metal complex should not be formed with the conformation **10bA** of macrocycle **10b**, since all the metal ion radii are too large, whereas the conventional approach gives a larger cavity size for **8b** and **9b**. The flexibility of the macrocycle in solution also plays an important part since some metal complexes have been obtained which might be considered impossible to prepare from the distances in table 109. Moreover, macrocycle **24** has complexed with several different metal ions with quite different sizes and coordination ability. Indeed, **24** and **25** have cavities which should enable them to complex with 1 to 3 metal ions. In the case of complexes **50** to **56**, macrocycle **24** reacts as a cryptand while in complex **42** the silver(I) ion is not inside the cavity but forms a sandwich with two ligands.

Table 110. Macrocyclic cavity sizes

Free ligand	Complex	no. of atoms in the macrocycle ring	cavity size(Å)	metal ion radius(Å)
8b	39	20	0.773/1	Cu^{2+} 0.77
9b	40	20 or 22?	0.855/1.029	Cu^{2+} 0.77
10a	32	14	0.924/0.708	Ni^{2+} 0.69
10a	34	14	0.924/0.708	Cu^{2+} 0.77
10a	35	14	0.924/0.708	Cu^{2+} 0.77
10b	36	17	0.986 and 1.263/ 0.523 and 1.022	Ni^{2+} 0.69
22	38	23	1.836	Cu^{2+} 0.77
23	37	23	0.9025 and 0.917/ 0.808 and 0.686	Cu^{2+} 0.77
25	41	34	1.189	Cu^{2+} 0.77
24	42	28	0.995 and 1.267/ 1.045 and 1.044	Ag^{+} 1.15
24	43	28	0.995 and 1.267/ 1.045 and 1.044	$2Ag^{+}$ 1.15
24	44	28	0.995 and 1.267/ 1.045 and 1.044	K^{+} 1.38
24	45	28	0.995 and 1.267/ 1.045 and 1.044	K^{+} 1.38
24	46	28	0.995 and 1.267/ 1.045 and 1.044	$2Al^{3+}$ 0.53
24	47	28	0.995 and 1.267/ 1.045 and 1.044	Al^{3+} 0.53
24	48	28	0.995 and 1.267/ 1.045 and 1.044	Pb^{4+} 0.78
24	49	28	0.995 and 1.267/ 1.045 and 1.044	Pb^{2+} 1.19
24	50	28	0.995 and 1.267/ 1.045 and 1.044	Cu^{2+} 0.77
24	51	28	0.995 and 1.267/ 1.045 and 1.044	Cu^{2+} 0.77
24	52	28	0.995 and 1.267/ 1.045 and 1.044	Ni^{2+} 0.69
24	53	28	0.995 and 1.267/ 1.045 and 1.044	Zn^{2+} 0.74
24	54	28	0.995 and 1.267/ 1.045 and 1.044	Co^{2+} 0.75
24	55	28	0.995 and 1.267/ 1.045 and 1.044	Fe^{2+} 0.78
24	56	28	0.995 and 1.267/ 1.045 and 1.044	Mn^{2+} 0.83

These complexes have been shown not to be very stable, usually due to a too small cavity which is flexible in solution but on crystallisation the ligand collapses into the most energetically stable configuration and the metal is ejected. This also occurs under the X-ray beam or under the mass spectroscopy experimental conditions, where atomic vibrations induced by the technique cause weak metal-ligand bonds to break. In reverse the loss of the metal could be due to a too large cavity and the metal ion is then "falling out" on crystallisation. Also, Coomber[338] found that metal complexes could be prepared in solution, but when they crystallised only the ligand was there. He also found that the counterion has an important effect on the complex formation. This has been confirmed in the present work as macrocycle **10a** complexed with $Ni(ClO_4)_2$ (complex **32**) while the complexation did not occur with $NiCl_2$ (complex **33**), on the contrary to complexes **34** and **35** with $Cu(ClO_4)_2$ and $CuCl_2$. Moreover, macrocycle **24** complexed with $Cu(ClO_4)_2$ (complex **50**) and $CuCl_2$ (complex **51**) in a slightly different way as only one conformation was obtained for complex **50** while two different conformations seem too occur for **51**. It can be seen in the complex structures **50** and **54** that the Cu^{2+} (**50**) and Co^{2+} (**54**) ions do not interact strongly with the donor atoms of the ligand **24** which shows that the stability of these complexes should be quite low due to the very large cavity size.

Coomber[338] studied the thermodynamics of modelled macrocyclic complexation of macrocycles **10a**, **10b**, **8b**, **9b** and **24** respectively with several different metal ions such as Cu^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+}. In the case of macrocycle **10a**, he found that with Cu^{2+} and Ni^{2+} the reaction would be exothermic with an increase in entropy. Moreover, the complex stability constant should be considerably higher with Ni^{2+} compared to Cu^{2+}. However, the Ni^{2+} radius is only 0.69Å (high spin) and the Cu^{2+} radius is 0.77 Å, while the macrocycle **10a** cavity radius is 0.924 Å. These differences between the metal ion radii compared to the macrocycle **10a** cavity could be too great and the ligand would need more energy to form a tetrahedral or an octahedral configuration. This may cause too much steric strain on the macrocycle, so the metal ion could be "falling out" as it is unable to bond effectively.

In the case of **10b**, the complexation reaction with Ni^{2+} would be expected to be exothermic with a decrease in entropy at low temperatures but would reverse at high temperature. Furthermore, the molecularly modelled structure for nickel showed that the nickel ion was trying to form a square planar complex with three oxygens and one nitrogen, but was slightly distorted. This might be due to the last oxygen donor, which could compete with the other donor atoms and could make the cavity too large.

The complexation reaction between macrocycle **8b** and Cu^{2+} would be similar to that for **10b** and Ni^{2+}, exothermic at low temperature then reversed at high temperature despite the fact that the cavity size is ideal for the inclusion of Cu^{2+} (Cu^{2+}= 0.77 Å and **8b**= 0.773 Å) and the presence of six donor atoms.

The thermodynamic factors of macrocycle **9b** with Cu^{2+} showed similar properties to **8b**. In addition to the reversibility of the complexation, the fact that the piperazine is in the chair conformation might cause too much steric strain on the macrocycle.

The higher flexibility of macrocycle **24** gave lower calculated stability constants. However, the complexation does not cause too much steric strain in the macrocycle compared to the previous compounds. **24** has a large cavity and contains six oxygen donors, which make it ideal for the large lead(II) ion, which prefers oxygen donors. The resulting stability complexes found were higher for Pb^{2+} (complex **49**) over Cu^{2+} (complexes **50** and **51**). The stability of complexes **50**, **51**, **52**, **53**, **54**, **55** and **56** respectively with Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+} and Mn^{2+} should be fairly similar. These metal ions are into a borderline category between hard and softness[368,369], so they are more likely to complex with a less hard base[370,371] such as nitrogen, but can also bond to harder bases such as oxygen, or a soft base like sulphur. Soft acids like Ag^+ will generally complex with a soft base such as nitrogen or sulphur, which is shown in complexes **42** and **43** as Ag^+ is bonded to the nitrogens and interacts with the sulphur atoms, but does not interact with the oxygen donors as the Ag^+ is outside the cavity.

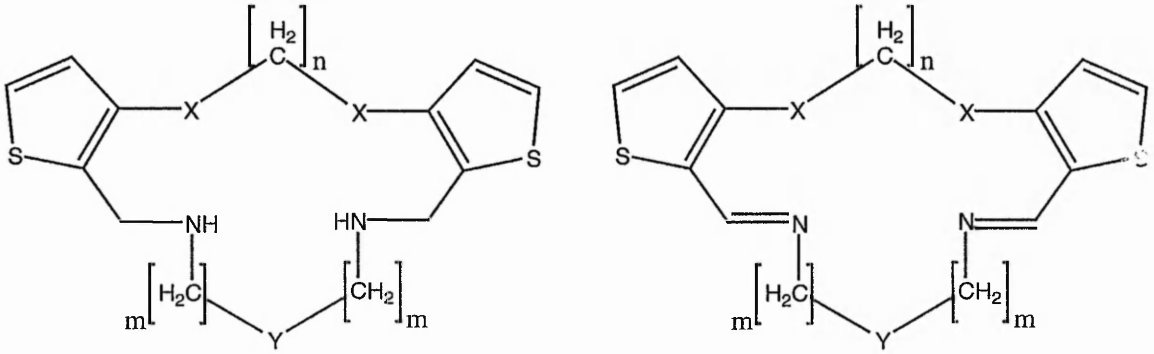
The macrocyclic ligands **12**, **13** and **14** synthesized by Weddell[4] and Sloman[5] did not complex with metal ions probably due to their too small cavity sizes and due to the too large steric strain caused in the macrocycle by reorientation of the donor atoms during complexation. Some of these macrocycles however did form complexes with Ni^{2+} in solution as colour changes were observed.

In the open-chain, compounds **16**, **19** and **20**, the donor atoms are more spread than in the macrocycles. Moreover, the large flexibility of these chains, which also appears in macrocycles **24** and **25**, hinders the steric effect of the thiophene rings and allows the open-chains to easily complex with Cu^{2+} (complexes **29**, **30** and **31**) and Al^{3+} (complexes **26**, **27** and **28**) in a ratio of 1:1 (ligand/metal ion) without too much steric strain and distortions in the molecule.

In the literature, Lindoy[96] showed that with similar macrocycles, which contain benzene instead of thiophene, the difference between the metal-free system and the complex is an important consideration. The ligand and especially the donor atom lone pairs should be close to an ideal conformation before complexation. He also showed that 16 to 19 membered-ring macrocycles[117], which contain secondary amine or imine groups form more stable complexes with 'borderline' metal ions such as Ni^{2+}, Cu^{2+} and Fe^{2+}.

It could be interesting to try bonding macrocycles **24** and **25** to a polymeric resin or a Merrifield resin and to examine their selectivity of extraction using the same method as Weddell[4]. These macrocycles should have greater extracting power than those with smaller ring sizes but would probably show limited selectivity as this work has shown that they are able to complex with metals of very different charge and size.

For optimum complexation, new thiophene-based macrocycles should be constructed containing imines or secondary amines instead of tertiary amines. Moreover, the substitution should occur on the carbon atoms or on Y as shown on the following scheme. The donor atoms, which form the complex, should then have their lone pairs ideally oriented in the cavity.



n, m= 1,2,3...
X= O,NH,S
Y= O, NH, NR, S
R= Me, Et...

The changes in the ^{1}H and ^{13}C NMR spectra on complex formation are distinctive, as reported earlier (p 337-347) and this should enable further studies of complexation in solution and also in circumstances where it is not possible to obtain suitable crystals for the X-ray diffraction. This work has also shown that it is possible to obtain accurate measurements of cavity size by molecular modelling using the 6-31G** basis set and again this will facilitate further studies both in solution and in the solid state.

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$\sigma_c(F_o)$ = e.s.d. based on counting statistics

p = p-factor

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where: N_o = number of observations

N_v = number of variables

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For a monoclinic cell:

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{13}(aa^*cc^*)\cos\beta)$

For an orthorhombic cell:

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2)$

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$U_{ij} = \exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

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