

Metal Catalyzed Rearrangement of a 2,2'-Bipyridine Schiff-Base Ligand to a Quaterpyridine-Type Complex.

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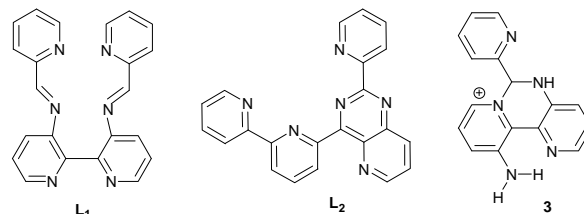
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A Co(II) quaterpyridine-type complex has been prepared via a one-pot transformation of a 2,2'-bipyridine Schiff-base ligand in the presence of a Lewis acidic metal salt.

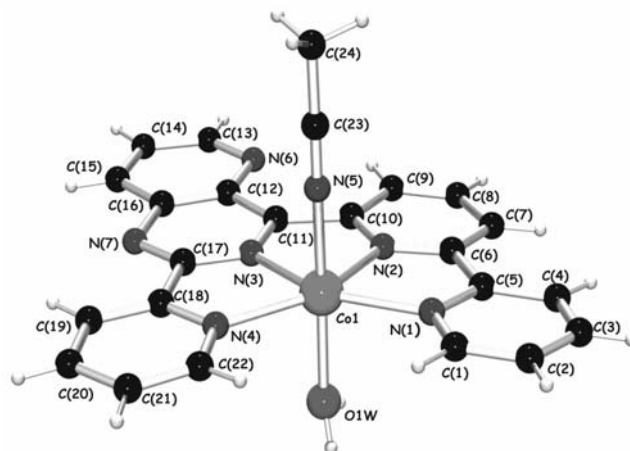
Coordination chemistry concerns metals and ligands where metals are known to have preferences for certain ligating atoms and adopt specific geometries. Ligands can be simple ions such as chloro with one pair of electrons that bind in a monodentate manner, or multidentate with multiple bridges, such as the heterotopic ligands so beautifully designed by Lehn and co-workers that have afforded a wealth of metallo-supramolecular architectures.¹ In this respect, the most common approach to coordination chemistry involves the study of how ligands of known structures combine with metal ions to form extended structures, and is used for the self-assembly of supramolecular compounds with novel properties.² One example of such materials includes magnetic molecular conductors based on the self-assembly of radical cation salts of stacked planar organosulfur compounds in between magnetic oxalate lattices.³ Other examples include molecule-based magnetic materials in which paramagnetic centres are linked by short bridging ligands such as cyanide or oxalate.⁴ While the element of 'design' in simple bridging ligands is limited, the nature of the ligand has a profound effect on the bulk magnetic behaviour and the correct choice of bridging ligand is crucial to achieve the desired effect.⁵ In contrast to the above approach, in a few cases the ligands are preferentially formed when the metal ion to which the ligand binds is present already. One example of this are the metal-templated Schiff base couplings that afford macrocyclic compounds.⁶

Here we take an alternative approach in which a chemically reactive Schiff-base ligand and a metal ion are combined, and the product formed depends on both the chemical reactivity of the ligand as well as the coordinating preferences and Lewis acidity of the added metal ion. Following on from earlier studies exploring the coordination chemistry of 3,3'-diamino-2,2'-bipyridine,⁷ we have now prepared the Schiff-base bis-imine ligand **L**₁. The susceptibility of this ligand to nucleophilic attack at its imine functionality assisted via chelation to Lewis acidic metal ions adds

an extra dimension to its coordination chemistry, especially since this attack can be intramolecular from a pyridine N atom.



The bis-imine ligand **L**₁ was prepared by reaction of 3,3'-diamino-2,2'-bipyridine with two equivalents of pyridine-2-carbaldehyde in toluene in the presence of 4 Å molecular sieves.⁸ The ligand is stable if kept in a dry box at room temperature. With six sp² N atoms, there are several possibilities for coordinating metal ions, e.g. via the bipyridine and/or via the iminopyridine groupings. It is known that 3,3'-disubstituted 2,2'-bipyridines can coordinate by their ring N atoms, even when the substituents make no attractive interaction with each other e.g. methyl.⁹ There is also the possibility of the bipyridine group adopting a *trans* conformation which opens other opportunities for metal ion coordination.¹⁰ However here we report a most remarkable transformation. Reaction of **L**₁ with an excess of cobalt(II) perchlorate in wet acetonitrile at room temperature led to the isolation of single crystals of the metal complex [Co(**L**₂)(OH₂)CH₃CN]·2ClO₄ **4** containing the rearranged tetradentate ligand **L**₂. The ligand is comprised of four contiguous heterocycles (three pyridines and one pyrido(2,3-d)pyrimidine) and chelates in a similar manner to a quaterpyridine (Figure 1). Complex **4** was obtained as the major product in 70 % yield after slow evaporation of the acetonitrile solvent.

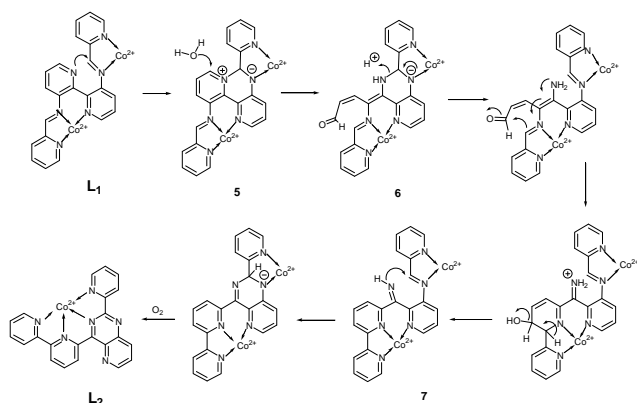


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Figure 1 Molecular structure of $[\text{Co}(\text{L}_2)(\text{OH}_2)\text{CH}_3\text{CN}]\cdot 2\text{ClO}_4$ **4** showing the appropriate labelling scheme. The counter ions are omitted for clarity.

This complex ligand was obtained in one simple step, in contrast to previously reported quaterpyridine ligands which require multi-step metal catalyzed coupling reactions.¹¹⁻¹⁴ The molecular structure of **4** reveals that the quaterpyridine ligand L_2 coordinates to the cobalt (II) metal ion in a planar tetradentate fashion with one acetonitrile and one water molecule occupying the axial coordination sites. The four Co-N distances lie in the range 2.107(7) – 2.160(7) Å, and the N-Co-N angles lie in the range 74.2(3)-76.5(3)°. The tetradentate ligand is close to perfect planarity, the maximum angle between any of the four ring systems is 5.7(4)°. The formation of this ligand from the *bis*-imine L_1 can be rationalised by the following mechanism, Scheme 1.



Scheme 1. Proposed mechanism for the rearrangement of the *bis*-imine ligand L_1 to afford the quaterpyridine type ligand L_2 .

Intramolecular attack of a bipyridine N atom on the imine belonging to the second ring creates a pyridinium cation fused to a dihydropyrimidine **5**. Coordination of the imine functionality to the Lewis acidic Co(II) metal centre most likely facilitates activation of the imine towards nucleophilic attack by the lone pair on the pyridine nitrogen.¹⁵ The pyridinium ring is then opened by water to give aldehyde **6** containing a tetrahydropyrimidine. The latter opens to form an amine and an imine, and the former drives the formation of a new pyridine ring in **7**. Finally, the Lewis catalyzed nucleophilic addition of the imine to the activated imine in **7** forms the dihydropyrimidine ring which requires a final oxidation to afford the aromatic ring. Support for the first step of this reaction comes from the X-ray crystal structure of compound **3** that was isolated from reaction of the 3,3'-diamino-2,2'-bipyridine with one equivalent of pyridine-2-carbaldehyde in the presence of a catalytic amount of HCl, Figure 2.¹⁶ The molecular structure of **3** clearly shows that one ring N atom of the bipyridine ring has added to an imine bond thus forming a pyridinium group. No second imine has formed, and the remaining amino group is hydrogen bonded to the other N atom of the bipyridine structure (N(1)⋯H(4):2.02(2) Å). The two pyridine rings of the bipyridine ring lie at 23.6° to each other, and the dihydropyrimidine ring which is fused to this system adopts a near envelope conformation with the carbon carrying the isolated pyridine ring displaced from the plane of the rest of the atoms. This pyridine ring lies roughly perpendicular to the bipyridine system. The longest ring bond in this molecule is from the pyridinium N atom to the methine C atom (1.5039(16) Å), and there is the expected widening of the angle at N in the pyridinium

ring (124.26(11)°) compared to the other pyridine rings (117.50(9)-117.99(10)°). The primary amino group makes a shorter bond (1.3450(18) Å) to its pyridinium ring than the secondary amino group to its pyridine ring (1.3805(16) Å). This secondary amino group adopts a pyramidal structure, but the lone pair can make no anomeric interaction, and lies roughly parallel to the bond to the isolated pyridine ring. Although no HCl was added to catalyse the rearrangement of the *bis*-imine ligand L_1 , we believe that the formation of the quaterpyridine-type ligand in this case is facilitated via chelation to the Lewis acidic cobalt(II) perchlorate salt.¹⁷ Studies are currently underway to elucidate the reactivity of this *bis*-imine ligand in the presence of a range of Lewis acidic metal salts and to establish conditions for decomplexation of the final complexes to afford the free ligand.

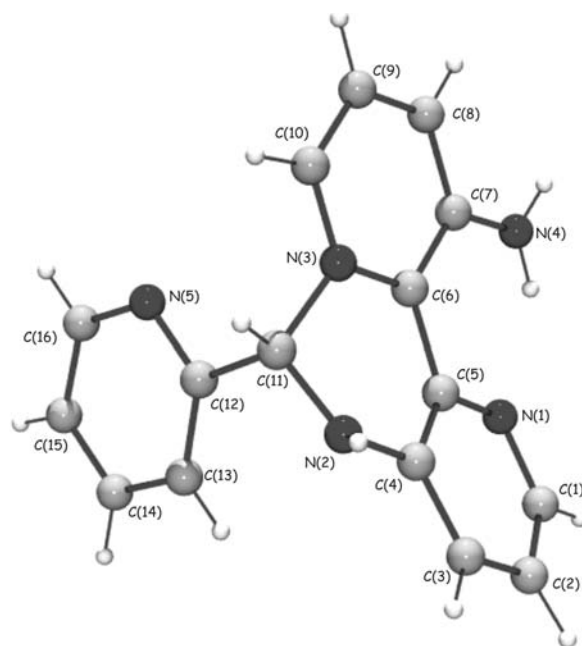


Figure 2. Molecular Structure of **3** showing the appropriate labelling scheme, the Cl⁻ counter ion is omitted for clarity.

It is pertinent to note that Manivannan *et al.*¹⁸ recently reported the formation of a 4'-(2-pyridyl)terpyridine compound via coordination of a Schiff-base ligand to a copper(II) metal ion. In this case, chelation to the copper(II) salt preorganised the Schiff-base ligand for reaction to afford a terpyridine complex. The free terpyridine ligand was isolated by reaction of the complex with an excess of Na₂EDTA. Furthermore, the rearrangement of a “salen” type Schiff-base ligand to afford a benzimidazole derivative has also been reported by Jones *et al.*¹⁹ This work highlights that there is considerable scope for the synthesis of new ligands by carrying out one-pot procedures that exploit the chemistry of reactive Schiff-base ligands.

To summarize, a variety of metal ion salts have been employed in recent years to promote reactions of nucleophiles with electrophiles.²⁰ It is well established that the promoting effects of metals ions are related to the Lewis acidity of the metal ion salts employed.¹⁷ Given the wealth of Schiff-base ligands reported in the chemical literature and their relative ease of preparation, exploiting their coordination chemistry and reactivities together with Lewis acidic and/or redox active metal salts offers a novel approach for

the preparation of new families of polydentate ligands and coordination compounds.

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Notes and references

†Crystal data for **3**: C₁₆H₁₄N₅Cl, M_r = 311.77, monoclinic, a = 12.9931(15), b = 12.4406(14), c = 9.5280(11) Å, β = 109.248(7)°, V = 1454.0(3) Å³, D_c = 1.424 g cm⁻³, space group P2₁/c, Z = 4,
160 μ(MoKα) = 0.71073, T = 173(2) K, 15114 measured refs, 4458 unique, final R₁ = 0.0385 for 3731 refs with I > 2σ(I).

Crystal data for **4**: [Co(L₂)(OH₂)(CH₃CN)]·2ClO₄, M_r = 679.3, monoclinic, a = 14.311(2), b = 13.4071(16), c = 14.598(2) Å, β = 103.464(17)°, V = 2723.9(7) Å³, D_c = 1.66 g cm⁻³, space group
165 Cc, Z = 4, μ(MoKα) = 0.71073, T = 173(2) K, 8587 measured refs, 4930 unique, final R₁ = 0.055 for 2656 refs with I > 2σ(I). For crystallographic data in CIF electronic format see DOI: 10.1039/xxxxxxx

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- 8 The bispyridylimine **L**₁ has been fully characterised by HRMS and correct elemental analysis. δ_H(600 MHz, CDCl₃): 8.71 (2H, dd, J = 4.7, 1.2 Hz, 2 x 6-H, bipy), 8.51 (2H, d, J = 4.7 Hz, 2 x 6-H, pyr), 8.34 (2H, s, 2 x CH imine), 7.79 (2H, d, J = 7.8 Hz, 2 x 3-H, pyr), 7.69 (2H, dd, J = 7.8, 1.2 Hz, 2 x 4-H, pyr), 7.47 (2H, dd, J = 7.8, 1.2 Hz, 2 x 4-H, bipy), 7.43 (2H, dd, J = 7.8, 4.6 Hz, 2 x 5-H, bipy), 7.30 (2H, dd, J = 7.8, 4.7 Hz, 2 x 5-H, pyr); δ_C(150 MHz, CDCl₃): 162.3 (2 x C, imine), 154.1 (2 x 2-C pyr), 151.5 (2 x 2-C bipy), 149.4 (2 x 6-C, pyr), 147.5 (2 x 6-C, bipy), 146.1 (2 x 3-C, bipy), 136.7 (2 x 4-C, pyr), 125.7 (2 x 3-H, pyr), 125.3 (2 x 4-C, bipy), 124.1 (2 x 5-C, pyr), 121.6 (2 x 5-C, bipy); ν_{max}(KBr): 3053, 1630, 1566, 1501, 1458, 1418, 1401, 1224, 1188, 993, 879, 797, 756, 622 cm⁻¹; m/z (EI): 364 (M⁺, 100); HRMS (EI): found 364.1435, C₂₂H₁₆N₆ requires 364.1436. C₂₂H₁₆N₆ (364.43) calcd. C 72.50 H 4.43 N 23.07 %; found C 71.97 H 4.43 N 23.43 %.
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- 16 Spectroscopic data for 1-amino-5,6-dihydro-5-(2'-pyridyl)dipyrido[1,2-c:2',3'-c]pyrimidinium chloride **3**. δ_H (600 MHz, CDCl₃): 9.19 (1H, d, J = 3.6 Hz, 7-H), 8.44 (1H, d, J = 6.0 Hz, 4-H), 8.37 (1H, d, J = 4.8 Hz, 6'-H), 8.17 (1H, d, J = 4.5 Hz, 10-H), 7.85 (3H, m, 3-,3',4'-H), 7.62 (1H, d, J = 7.8 Hz, 2-H), 7.61 (1H, d, J = 8.2 Hz, 8-H), 7.52 (1H, d, J = 3.6 Hz, 6-H), 7.43 (1H, dd, J = 4.5, 8.2 Hz, 9-H), 7.33 (1H, dd, J = 4.8, 7.8 Hz, 5'-H). δ_C (150 MHz, CDCl₃): 155.4 (2'-C), 149.7 (6'-C), 147.0 (1-C), 140.4 (10-C), 139.5 & 135.8 (11a-,11b-C), 138.1 (4'-C), 132.3 (4-C), 131.0 (7a-C), 130.7 (3-C), 126.7 (9-C), 126.3 (3'-C), 124.7 (5'-C), 124.1 (8-C), 121.5 (2-C), 75.5 (6-C); ν_{max}(KBr): 3277, 3237, 3115, 2914, 1591, 1502, 1452, 1360, 1248, 805, 758, 681 cm⁻¹; m/z (FAB): 276 (C₁₆H₁₄N₅⁺, 100); HRMS (FAB): found 276.1249, C₁₆H₁₄N₅ requires 276.1251.
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