

# Molecular conductors of BEDT-TTF with tris(oxalato)metallate anions

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## ABSTRACT

This review presents the synthesis, crystal structures and conducting properties of BEDT-TTF radical-cation salts with the tris(oxalato)metallate anion [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene]. This series has received much attention owing to the wide variety of conducting properties that have been observed. As well as including numerous metals, semiconductors and insulators, there are over twenty superconductors in this series. The series also includes several examples of multifunctionality where it has been possible to combine together particular physical properties in the same lattice such as electrical conductivity with magnetism, chirality or proton conductivity. This review presents an overview of the flexibility of the coordination chemistry of the oxalate ligand and the variety of packing arrangements of the tris(oxalato)metallate complexes in the insulating layers of these radical-cation salts.

## 1. INTRODUCTION

Since the discovery of the first metallic charge-transfer salt of TTF-TCNQ in 1973 [1] extensive research has been performed in the field of molecular conductors with TTF derivatives. Studies of these 1-dimensional and 2-dimensional (1D and 2D) molecular conductors have investigated many interesting phenomena such as spin-Peierls, charge order, Mott insulators, quantum spin-liquids, and spin density waves.[2] Organic superconductivity was first observed in a radical-cation salt of TMTSF (tetramethyltetraselenafulvalene) with the  $\text{PF}_6^-$  anion.[3] The majority of organic superconductors have been found with the donor molecule BEDT-TTF (Scheme 1), with  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br showing the highest T<sub>c</sub> at ambient pressure, 11.6 K, whilst  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl has a T<sub>c</sub> of 13.1K under applied pressure, and  $\beta'$ -(BEDT-TTF)<sub>2</sub>Cl<sub>2</sub> has the highest T<sub>c</sub> under applied pressure of 14.2K[4] Transition-metal complexes have been extensively used in radical-cation salts of BEDT-TTF because they offer the possibility of combining two or more properties in the same lattice. The most extensive family of these salts employs the tris(oxalato)metallate anion to combine conductivity with paramagnetism,[5] ferromagnetism,[6] or anti-ferromagnetism.[7] The ability of the tris(oxalato)metallate anion  $[\text{M}(\text{C}_2\text{O}_4)_3]^{3-}$  to form infinite 2D sheets in a hexagonal network offers many possibilities for making subtle changes to the crystal structure, such as changing the metal centre, the counter cation, or the guest solvent molecule which is located within the hexagonal cavities of the 2D sheet. These small changes can have a drastic effect upon the crystal structure and thus the physical properties of the material. The bridging capability of the oxalato ligand has also made it possible to introduce two different metal centres into the same layer leading to long-range magnetic order. This review will focus on the molecular superconductors, metals, semiconductors and insulators derived from BEDT-TTF with tris(oxalato)metallate anions.

## 2. 4:1 radical cation-salts of BEDT-TTF with tris(oxalato)metallate(III)

Research into magnetic molecule-based materials that also exhibit conductivity by the group of Prof. Peter Day at the Royal Institution of Great Britain led to the discovery in 1995 of the first molecular paramagnetic superconductor in the radical-cation salt  $\beta''$ -(BEDT-TTF)<sub>4</sub>[(H<sub>3</sub>O)Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·PhCN (Fig.

1).[5,8-11] This was an important discovery owing to the antagonistic relationship between superconductivity and magnetism. Several studies of the magnetic and electrical properties of this radical-cation salt observed the superconducting transition at 7.0K to 8.5K, which is the highest  $T_c$  of all known BEDT-TTF/tris(oxalato)metallate superconductors to date.

## 2.1 Monoclinic $\beta''$ superconductors, metals and semiconductors

$\beta''$ -(BEDT-TTF)<sub>4</sub>[(H<sub>3</sub>O)Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].benzonitrile crystallises in the monoclinic space group  $C2/c$ . [5,8-11] The asymmetric unit consists of two crystallographically independent BEDT-TTF<sup>0.5+</sup> molecules, half an Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>3-</sup> anion, half a solvent molecule, and half an H<sub>3</sub>O<sup>+</sup> cation. The BEDT-TTF cations and tris(oxalato)ferrate anions are segregated into alternating layers (Fig. 1) with the donor molecules adopting a  $\beta''$  packing arrangement (Fig. 2). The two crystallographically independent BEDT-TTF molecules pack in an AABBAABB sequence within each donor stack. Within each anion layer the tris(oxalato)metallate and the H<sub>3</sub>O<sup>+</sup> cation adopt a hexagonal packing arrangement with the inner oxygens of the oxalato ligand octahedrally coordinated to the metal and the outer oxygens involved in hydrogen bonding with the H<sub>3</sub>O<sup>+</sup> (Fig. 3). The benzonitrile solvent molecule occupies each hexagonal cavity with its C≡N bond directed towards an Fe metal centre.

Twenty-nine superconductors of the monoclinic  $C2/c$  type have since been prepared having the same formula,  $\beta''$ -(BEDT-TTF)<sub>4</sub>[(A)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].solvent(s), making these 4:1 salts are the most widely studied of all the BEDT-TTF-tris(oxalato)metallate radical-cation salts. Changing the counter cation (A = H<sub>3</sub>O<sup>+</sup>/K<sup>+</sup>/NH<sub>4</sub><sup>+</sup>) and changing the metal centre of the tris(oxalato)metallate (M = Fe<sup>3+</sup>, Cr<sup>3+</sup>, Ga<sup>3+</sup>, Rh<sup>3+</sup>, Ru<sup>3+</sup>, Mn<sup>3+</sup>) has only a very small effect upon the properties (Tables 1 and 2). In the benzonitrile salts changing the tris(oxalato)metallate from Fe to Cr lead to a reduction of superconducting  $T_c$  from 7.0-8.5K to 5.5-6.0K. Much more marked effects upon the physical properties changing from superconductors to metals or semiconductors occurs when changing the size and shape of the guest solvent molecule (Table 1-3). Some of the  $\beta''$ -(BEDT-TTF)<sub>4</sub>[(A)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].halobenzene salts undergo a phase transition from monoclinic  $C2/c$  to triclinic  $P-1$  at temperatures around 200K.[15,18]

Table 1 shows the variety of conducting properties possible in the  $\beta''$ -(BEDT-TTF)<sub>4</sub>[(A)Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].solvent salts. Highest superconducting  $T_c$ s are observed when larger guest solvent molecules are filling the hexagonal cavity, and specifically those which increase the  $b$  axis length the most. Benzonitrile is the guest solvent molecule which extend the  $b$ -axis of the hexagonal cavity the furthest. In the benzonitrile salt there is no BEDT-TTF ethylene disorder, even at room temperature, and superconductivity is observed. In contrast, in the pyridine salt no superconductivity is observed down to 1K. To investigate this a series of salts were synthesised containing different mole fractions of benzonitrile and pyridine (Table 3) and their conducting properties showed a sharp cut-off in the superconductivity at >65% concentrations of pyridine. Another study using mixed solvents showed that the  $T_c$  of the pure benzonitrile salt could be reduced by the inclusion of increasing amounts of a second solvent.[11,17]

## 2.2 Orthorhombic pseudo- $\kappa$ semiconductors

When using benzonitrile as solvent a 2<sup>nd</sup> phase is obtained which has the same chemical formula as the superconducting monoclinic  $\beta''$ -(BEDT-TTF)<sub>4</sub>[(A)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].PhCN but the BEDT-TTF donor molecules pack in a very different manner. Pseudo- $\kappa$ -(BEDT-TTF)<sub>4</sub>[(K or NH<sub>4</sub>)Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].PhCN crystallises in the orthorhombic space group  $Pbcn$ , with two crystallographically independent BEDT-TTF molecules, half an Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>3-</sup> anion, half a benzonitrile molecule and half of an NH<sub>4</sub><sup>+</sup> or K<sup>+</sup> cation. The pseudo- $\kappa$  BEDT-TTF packing motif is shown in Figure 4 with (BEDT-TTF<sup>1+</sup>)<sub>2</sub> dimers each surrounded by six neutral BEDT-TTF<sup>0</sup> monomers which leads to semiconducting behaviour (Table 4).

The anion layer (Fig. 5) contains  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$  and  $\text{NH}_4^+$  or  $\text{K}^+$  in a honeycomb packing arrangement with a benzonitrile molecule occupying the hexagonal cavity. The benzonitrile molecule is disordered over two positions with the  $-\text{C}\equiv\text{N}$  group directed towards the  $\text{NH}_4^+$  or  $\text{K}^+$  anions giving the hexagonal cavity an increased width compared to in the monoclinic  $\beta''$  salts to accommodate the disordered positions of the  $-\text{C}\equiv\text{N}$  group.

It is interesting to note that crystals of this orthorhombic pseudo- $\kappa$  phase grow only when using benzonitrile as a solvent. This is the case for all  $\text{M}(\text{C}_2\text{O}_4)_3^{3-}$  anions –  $\text{M} = \text{Fe}^{3+}, \text{Cr}^{3+}, \text{Al}^{3+}, \text{Co}^{3+}, \text{Ga}^{3+}, \text{Rh}^{3+}, \text{Ru}^{3+}, \text{Mn}^{3+}$  (Table 4). However, crystals of the monoclinic  $\beta''$  phase only grow when  $\text{M} = \text{Fe}$  or  $\text{Cr}$ , and not for another  $\text{M}(\text{C}_2\text{O}_4)_3^{3-}$  anions. On the other hand, when using bromobenzene as the guest solvent high-quality crystals of the monoclinic  $\beta''$  phase crystals have been obtained for  $\text{M} = \text{Fe}^{3+}, \text{Cr}^{3+}, \text{Ga}^{3+}, \text{Rh}^{3+}, \text{Ru}^{3+}$ , and  $\text{Mn}^{3+}$  (Tables 1 and 2).

### 2. 3 Bilayered triclinic $\alpha/\beta''$ and $\alpha/\text{pseudo-}\kappa$ salts

A third type of 4:1 salt has also been synthesised when using an unsymmetrical guest solvent which is too large to fit within the hexagonal cavities in the anion layer (Table 5). These unsymmetrical molecules do not sit centrally in the hexagonal cavity but instead the phenyl groups are displaced towards one face of the anion layer with a side group protruding on one side. The result is that both faces of the anion layer are not identical which leads to two different BEDT-TTF packing modes in adjacent donor layers (Fig. 6). Depending on the solvent in the hexagonal cavity the packing types are  $\alpha/\beta''$  ( $\text{PhCH}_2\text{CN}$ ,  $\text{PhN}(\text{CH}_3)\text{CHO}$ ,  $\text{PhCOCH}_3$ ,  $\text{PhCH}(\text{OH})\text{CH}_3$ ) or  $\alpha/\text{pseudo-}\kappa$  (1,2- $\text{Br}_2\text{Ph}$ ). The  $\beta''$  and pseudo- $\kappa$  donor packing modes are discussed earlier (Figs 2 and 4) whilst the  $\alpha$  packing is shown in Fig. 7.

The inclusion of *sec*-phenethyl alcohol ( $\text{PhCH}(\text{OH})\text{CH}_3$ ) in these salts is also of note owing to it being prepared from either the racemic *R/S* or chiral *S* molecule.[37] The *R/S* bilayered salts have four crystallographically independent BEDT-TTF molecules in the asymmetric unit (with two belonging to the  $\alpha$  donor packing mode and two to the  $\beta''$ ) in space group *P*-1, whilst the isostructural chiral *S* salt has eight BEDT-TTFs, with four in each donor packing mode in space group *P*1. A small difference in the metal-insulator transition temperature is observed owing to the enantiomeric disorder of the *R* and *S* molecule in the racemic salt which is not found in the chiral *S* salt.

### 2.4 Chirality of the anion layers

On the subject of chirality there is a significant difference between the tris(oxalato)metallates in the anion layers in the  $\beta''$  and pseudo- $\kappa$  salts, though at first glance they may look identical. In the  $\beta''$  salts each anion layer contains only a single enantiomer of  $\text{M}(\text{C}_2\text{O}_4)_3^{3-}$  with the adjacent anion layers containing only the opposite enantiomer to give an overall racemic lattice (Fig. 3). In the pseudo- $\kappa$  salts each anion layer contains a 50:50 mixture of the two enantiomer of  $\text{M}(\text{C}_2\text{O}_4)_3^{3-}$ , with alternating rows of  $\Delta$  or  $\Lambda$  enantiomers within a single anion layer, to once again give an overall racemic lattice (Fig. 5). When performing synthesis from racemic  $\text{M}(\text{C}_2\text{O}_4)_3^{3-}$ , crystals begin to grow within a couple of days, but during attempts to grow crystals from enantiopure  $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$  no crystals were obtained in the first 2 weeks.[31] The crystals obtained were of the racemic pseudo- $\kappa$  phase which suggests that partial racemisation occurred before crystals started to grow.

## 3. 3:1 radical cation-salts of BEDT-TTF with tris(oxalato)metallate(III)

A new family of 3:1 salts was obtained when trying to include chiral (*R*)-(-)-carvone (Scheme 2) into the hexagonal cavity as guest solvent molecule.[39-43] Using (*R*)-(-)-carvone on its own gave no crystals since it is likely that the molecule is too large to fit inside the cavity. However, using (*R*)-(-)-

carvone mixed with a second solvent resulted in chiral induction and the second solvent molecule is included in a radical-cation salt of BEDT-TTF with either a single enantiomer or an enantiomeric excess of the  $\Delta\text{-M}(\text{C}_2\text{O}_4)_3^{3-}$  anion. This method has produced a family of semiconductors having the formula  $(\text{BEDT-TTF})_3[(\text{A})\text{M}(\text{C}_2\text{O}_4)_3]\cdot\text{solvent}$  ( $\text{M} = \text{Cr}^{3+}, \text{Al}^{3+}$ ;  $\text{A} = \text{Li}^+, \text{Na}^+, \text{NH}_4^+$ ; solvent = nitromethane, acetonitrile, dichloromethane, *N,N*-dimethylformamide, ethanol) (Table 6).

These salts also consist of alternating anion and donor layers. The anion layers are similar to the 4:1 salts with a hexagonal packing of tris(oxalato)metallate and counter cation, though the hexagonal cavity size is smaller and accommodates the smaller solvents used in these salts (Fig. 8). All except the DMF salt have an asymmetric unit consisting of three crystallographically independent BEDT-TTFs; two of these BEDT-TTF molecules are parallel (A and B) whilst the third BEDT-TTF molecule (C) is at  $90^\circ$  with respect to A and B in the  $P2_12_12_1$  salts,  $45^\circ$  in the  $P2_1$  salts, or  $80^\circ$  in the  $P1$  salts (Fig. 9a-c). The parallel BEDT-TTFs do not form a dimer since there are no close S...S contacts below the sum of the van der Waals radii ( $<3.6 \text{ \AA}$ ). The charges on the donor molecules show considerable differences between the salts in this 3:1 family. Some salts show charge disproportionation with the monomer having a charge close to zero and the dimer having a higher charge close to +2 suggesting formation of a spin dimer. Meanwhile other salts show charges close to 0.66+ ( $\pm 0.1$ ) for each of the three donors. The DMF salt has the  $\theta$  packing motif (Fig. 9d) with two crystallographically independent BEDT-TTF molecules.

Zhang *et al.* have synthesised antiferromagnetic semiconductor  $(\text{BEDT-TTF})_3\text{Cu}_2(\text{C}_2\text{O}_4)_3(\text{CH}_3\text{OH})_2$  from BEDT-TTF and  $(\text{Et}_3\text{NH})_2\text{Cu}(\text{C}_2\text{O}_4)_2$ . There are three crystallographically independent BEDT-TTF molecules, one of which forms a stack along the *a* axis, with the other two forming the neighbouring stack. There is a dihedral angle of  $125\text{-}126^\circ$  between the two stacks. The anion layer includes two methanol molecules in each hexagonal cavity created by six oxalate-bridged copper atoms.[7] The antiferromagnetism arises from d-d interaction between the Jahn-Teller distorted oxalate-bridged  $\text{Cu}^{2+}$  atoms.

## 4. 2:1 radical cation-salts of BEDT-TTF with tris(oxalato)metallate(III) containing 18-crown-6

In 2017 a new superconducting phase was discovered, only the 2<sup>nd</sup> superconducting phase after the 4:1  $\beta''$  salts which were first reported in 1995. These superconductors have the formula  $\beta''\text{-}(\text{BEDT-TTF})_2[(\text{H}_2\text{O})(\text{NH}_4)_2\text{M}(\text{C}_2\text{O}_4)_3]\cdot 18\text{-crown-6}$ , with  $\text{M} = \text{Cr}^{3+}$  ( $T_c = 4.0\text{-}4.9\text{K}$ ) or  $\text{M} = \text{Rh}^{3+}$  ( $T_c = 2.7\text{K}$ ) (Table 7).[44,45]

Crystallising in triclinic space group *P*-1 the asymmetric unit consists of two crystallographically independent BEDT-TTF<sup>0.5+</sup> cations, one  $\text{M}(\text{C}_2\text{O}_4)_3^{3-}$  anion, one  $\text{H}_2\text{O}$  molecule, two  $\text{NH}_4^+$  cations, and one 18-crown-6 molecule. The BEDT-TTF molecules adopt a similar  $\beta''$ -packing arrangement to the 4:1 superconductors (Fig. 2) with the two crystallographically independent BEDT-TTF cations (A and B) having an AABBAABB pattern within each stack. Donor B is ordered whilst donor A shows disorder of a terminal ethylene group at one end only at 110K, which is directed towards the  $\text{NH}_4^+$  cation in the anion layer. The anion layer adopts a similar hexagonal packing arrangement of  $\text{NH}_4^+$  and  $\text{M}(\text{C}_2\text{O}_4)_3^{3-}$  to the 4:1 salts, but instead of a guest solvent molecule, a single 18-crown-6 molecule protrudes into the hexagonal cavity of only one adjacent anion layer. The crystal structure has a superstructure with a repeating pattern of ABCDABCD with BEDT-TTF molecules adopting a  $\beta''$  packing motif (layer A), layers of  $\text{NH}_4^+$  and  $\Delta\text{-M}(\text{C}_2\text{O}_4)_3^{3-}$  (layer B), layers of  $(\text{H}_2\text{O})(\text{NH}_4)$ 18-crown-6 (layer C), and layers of  $\text{NH}_4^+$  and  $\Delta\text{-M}(\text{C}_2\text{O}_4)_3^{3-}$  (layer D). This results in a

packing arrangement with the widest gap between conducting BEDT-TTF layers where only a single donor packing motif is present (Fig. 10).[44,45]

For the Rh salt a  $T_c$  of 2.7K was observed by transport measurement ( $T_{CT}$ ) but zero resistivity could not be observed. A  $T_c$  of 2.5K was observed on the magnetisation curve ( $T_{CM}$ ) but it was not clear and the Meissner signal was small. By contrast, zero resistivity for the Cr salt could be clearly observed below 1.8K and the Meissner signal was relatively large, although the transition was broader than those of normal superconducting salts, and the Meissner volume at 1.7 K was calculated as 11.5%. There was a large difference between  $T_{CT}$  and  $T_{CM}$  of 4.0-4.9K and 2.5K, respectively. The insulating layer of the Cr salt is thinner than that of the isostructural Rh salt which leads the Rh salt having a larger gap between BEDT-TTF layers and so the Rh salt a stronger 2D nature. The superconducting transition of the Rh salt may be extraordinarily broad because the 2D nature of the material makes the superconducting transition a Kosterlitz-Thouless (KT) transition.[56]  $I$ - $V$  measurement also suggests that the Cr salt shows a close to perfect Kosterlitz-Thouless transition.[44,45]

Another interesting 2:1 salt is the proton-conducting metal  $\beta''$ -(BEDT-TTF)<sub>4</sub>[(A)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>·[(A)<sub>2</sub>18-crown-6](H<sub>2</sub>O)<sub>5</sub> (M = Cr or Ga, A = NH<sub>4</sub><sup>+</sup> or H<sub>3</sub>O<sup>+</sup>) (Table 7). Crystallising in triclinic space group  $P-1$  the asymmetric unit consists of two crystallographically independent BEDT-TTF<sup>0.5+</sup> cations, one M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>3-</sup> anion, five H<sub>2</sub>O molecules, four H<sub>3</sub>O<sup>+</sup>/NH<sub>4</sub><sup>+</sup> cations, and half an 18-crown-6 molecule. The crystal structure also has an ABCDABCD<sub>A</sub> superstructure, like the aforementioned 2:1 salt, but in this salt the crown ether molecules in layer C form a stack containing hydrogen-bonded chains of A/H<sub>2</sub>O which is believed to mediate the proton conductivity through a diffusion mechanism (Fig. 11).[46,47]

## 5. Other radical cation-salts of BEDT-TTF with tris(oxalato)metallate(III)

Several phases have been produced by using tris(oxalato)ferrate with different counter cations:  $\beta'$ -(BEDT-TTF)<sub>5</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·(H<sub>2</sub>O)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>[48] from tetraethylammonium,  $\eta$ -(BEDT-TTF)<sub>4</sub>(H<sub>2</sub>O)LiFe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>[43] from lithium,  $\alpha'''$ -(BEDT-TTF)<sub>9</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>8</sub>Na<sub>18</sub>(H<sub>2</sub>O)<sub>24</sub>[49] from sodium,  $\alpha$ -(BEDT-TTF)<sub>10</sub>(18-crown-6)<sub>6</sub>K<sub>6</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>4</sub>(H<sub>2</sub>O)<sub>24</sub>[49] from potassium, and  $\alpha$ -(BEDT-TTF)<sub>12</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>·(H<sub>2</sub>O) <sub>$n$</sub> [50] from potassium or caesium (Table 8) ( $n = 15$  or  $16$ ).

Semiconductor  $\beta'$ -(BEDT-TTF)<sub>5</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·(H<sub>2</sub>O)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>[48] grown from tetraethylammonium tris(oxalato)ferrate has alternating donor and anion layers. The BEDT-TTF layers adopt a packing similar to  $\beta'$  with alternate donor layers having different close S...S contacts. Each anion layer consists of a single enantiomer of [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> with the next anion layer consisting of the opposite enantiomer. [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> anions are arranged in a parallelogram occupied by two water and one dichloromethane molecule (Fig. 12a). Another semiconducting 5:1 salt,  $\alpha''$ -(BEDT-TTF)<sub>5</sub>[Ga(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·(H<sub>2</sub>O)<sub>3.4</sub>·(EtOH)<sub>0.6</sub>[29] differs in that each anion layer contains a 50:50 mixture of  $\Delta$ - and  $\Lambda$ -[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> anions, which alternate in the  $a$  direction, with disorder ethanol and water molecules in a void on one side of the parallelogram.

Semiconductor  $\eta$ -(BEDT-TTF)<sub>4</sub>(H<sub>2</sub>O)LiFe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>[43] grown from lithium tris(oxalato)ferrate also has alternating donor and anion layers. The BEDT-TTF molecules adopt a  $\eta$  packing arrangement (Fig. 13a). Each anion layer consists of a single enantiomer of [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> with the next anion layer consisting of the opposite enantiomer. The anion layers have a honeycomb network of Li<sup>+</sup> and M(oxalate)<sub>3</sub><sup>3-</sup> that includes a water molecule which elongates the hexagon in the  $c$  direction compared to other salts of

this type grown from ammonium or potassium tris(oxalato)ferrate (Fig. 13b). The hexagonal cavity in this salt contains heavily disordered dichloromethane which could not be resolved.

Semiconductor  $\alpha'''$ -(BEDT-TTF)<sub>9</sub>[M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>8</sub>Na<sub>18</sub>(H<sub>2</sub>O)<sub>24</sub>[42,49] was grown from sodium tris(oxalato)ferrate or -chromate and is a multi-layered salt of type ABCDABCDA. The A layers consist of only BEDT-TTF, B and D layers consist of tris(oxalato)metallate(III) and sodium, and the C layers consist of sodium and water (Fig. 14). The two enantiomeric forms of [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup>,  $\Delta$  and  $\Lambda$ , are separated by a layer built up of columns of Na<sup>+</sup> ions and columns of water molecules (Fig. 14). In the tris(oxalato)metallate layers six [M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> anions form close contacts with two 8-coordinate sodium ions.

Semiconductor  $\alpha$ -(BEDT-TTF)<sub>10</sub>(18-crown-6)<sub>6</sub>K<sub>6</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>4</sub>(H<sub>2</sub>O)<sub>24</sub>[49] was grown from potassium tris(oxalato)ferrate and is a multi-layered salt of type ABCBABCBA. The A layers consist of only BEDT-TTF molecules, B layers consist of rows of alternating  $\Delta$ - and  $\Lambda$ -[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> with H<sub>2</sub>O, and 18-crown-6 with complexed K<sup>+</sup> ions, C layers consist of columns of 18-crown-6 molecules with complexed K<sup>+</sup> (Fig. 15).

$\alpha$ -(BEDT-TTF)<sub>12</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>·(H<sub>2</sub>O)<sub>n</sub>[50] grown from potassium or caesium tris(oxalato)ferrate differ only in the number of H<sub>2</sub>O molecules, 15 or 16, respectively. The novel anion layer packing consists of a tris(oxalato)ferrate surrounded by H<sub>2</sub>O molecules in hydrogen bonded chains (Fig. 12b).

The coexistence of ferromagnetism and metallic conductivity was discovered in the first magnetic molecular metal (BEDT-TTF)<sub>x</sub>[MnCr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].CH<sub>2</sub>Cl<sub>2</sub> (x = <3).[6] The BEDT-TTF layers show metallic behaviour down to 0.3 K whilst the bimetallic honeycomb tris(oxalato)metallate layers are responsible for ferromagnetic ordering below 5.5 K.[6] The isostructural paramagnetic metal (BEDT-TTF)<sub>2.53</sub>[MnRh(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].CH<sub>2</sub>Cl<sub>2</sub> has also been synthesized which helped to clarify the incommensurate nature of the conducting and magnetic layers.[51,52]

## 6. Radical cation-salts of BEDT-TTF with tris(oxalato)germanate(IV)

Changing the charge on the tris(oxalato)metallate to 4- produces very different structures compared to the tris(oxalato)metallate(III) radical-cation salts (Table 9). There are four examples using the tris(oxalato)germanate(IV) anion, all of which are semiconductors: (BEDT-TTF)<sub>2</sub>[Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>·PhCN,[53] (BEDT-TTF)<sub>5</sub>[Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>,[54] (BEDT-TTF)<sub>7</sub>[Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>(CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.87</sub>(H<sub>2</sub>O)<sub>0.09</sub>,[54] and (BEDT-TTF)<sub>4</sub>Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·(CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.50</sub>. [55] None of these salts have anion layers with the 2D honeycomb tris(oxalato)metallate sheets found in the 3- salts. (BEDT-TTF)<sub>2</sub>[Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>·PhCN[53] does not contain alternating anion and donor layers but instead has BEDT-TTF dimers in a checkerboard arrangement with [Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>2-</sup> anions and separate benzonitrile layers (Fig. 16). (BEDT-TTF)<sub>5</sub>[Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>[54] also has a checkerboard arrangement of donors and anions with BEDT-TTFs forming diagonal stacks of five molecules, with a crystallographically unique molecule sandwiched between two pairs of dimers (Fig. 16). Each [Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>2-</sup> is disordered between the  $\Delta$  and  $\Lambda$  enantiomers when grown from several different solvents; when using (R)-(-)-carvone a Flack parameter of 0.43(3) is observed. (BEDT-TTF)<sub>7</sub>[Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>(CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.87</sub>(H<sub>2</sub>O)<sub>0.09</sub>,[54] and (BEDT-TTF)<sub>4</sub>Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·(CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.50</sub>. [55] both have segregated anion and donor layers. The anion layers in the both are made up of [Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>2-</sup> segregated into  $\Delta$  and  $\Lambda$  enantiomer pairs separated by dichloromethane molecules (Fig. 17).

## CONCLUSIONS

This review highlights the diversity of packing arrangements of the tris(oxalato)metallate anion with the organosulphur donor molecule BEDT-TTF. These radical-cation salts combine magnetism with conductivity in an extensive family of insulators, semiconductors, metals and superconductors. No

novel effects upon the bulk physical properties have been observed owing to the interplay between the discrete anion and cation layers. The inclusion of other building blocks such as guest solvent molecules, counter cations and crown ethers have produced a wealth of multifunctional materials including properties such as proton conductivity.

The synthesis of materials combining chirality and conductivity are important to explore electrical magneto-chiral anisotropy. This has been observed in bismuth helices,[57] and in carbon nanotubes,[58] where the resistivity along nanotubes of opposing chirality differs in a coaxial magnetic field. The use of tris(oxalato)metallate anions in BEDT-TTF salts offers the potential to synthesise chiral conductors. Chiral semiconductors have already been synthesised *via* chiral induction in the presence of (*R*)-(-)-carvone,[39-43] and many novel packing arrangements of  $\Delta$ - and  $\Lambda$ -[M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> enantiomers have been observed in racemic radical-cation salts. Other racemic and chiral anions that have been used to produce radical-cation salts with BEDT-TTF include Fe(croconate)<sub>3</sub>,[59] Cr(2,2'-bipy)(oxalate)<sub>2</sub>,[60] Sb<sub>2</sub>(L-tartrate)<sub>2</sub>,[61] TRISPHAT,[62] B(malate)<sub>2</sub>,[63] and Fe(C<sub>6</sub>O<sub>4</sub>Cl<sub>2</sub>)<sub>3</sub>. [64]

The use of enantiopure donor molecules based on TTF or BEDT-TTF,[65] with the tris(oxalato)metallate anion is another prospect. Electrical magneto-chiral anisotropy has recently been observed in enantiopure radical-cation salts of (*S,S*)- and (*R,R*)- (DM-EDT-TTF)<sub>2</sub>ClO<sub>4</sub>[66] which crystallise in enantiomorphic space groups *P*6<sub>2</sub>22 and *P*6<sub>4</sub>22, and show metallic behavior down to 40K. Enantiopure donors have previously been used to produce salts with the *meso* stereoisomer of [Fe<sub>2</sub>(oxalate)<sub>5</sub>]<sup>4-</sup> [67] or with racemic Fe(C<sub>6</sub>O<sub>4</sub>Cl<sub>2</sub>)<sub>3</sub>. [68]

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## HIGHLIGHTS

- Multifunctional molecular conductors of BEDT-TTF with tris(oxalato)metallate
- 2017 discovery of molecular superconductor  $\beta''$ -(BEDT-TTF)<sub>2</sub>[(H<sub>2</sub>O)(NH<sub>4</sub>)<sub>2</sub>M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].18-crown-6
- Kosterlitz-Thouless transition in 2D superconductor
- Chiral induction in molecular semiconductors
- Combination of ferromagnetism and metallic behaviour

## KEYWORDS

Tris(oxalato)metallate, BEDT-TTF, superconductor, metal, semiconductor, Kosterlitz-Thouless

## FIGURE CAPTIONS

Scheme 1 BEDT-TTF.

Scheme 2 (R)-(-)-carvone

FIG 1 Layered packing of monoclinic  $\beta''$  radical-cation salts. Sulphur atoms are yellow, carbon grey, nitrogen blue, oxygen red and hydrogen white. The metal centre atoms are turquoise and halogen atoms are brown.

FIG 2 BEDT-TTF donor layer in monoclinic  $\beta''$  radical-cation salts. The two crystallographically independent BEDT-TTF molecules are coloured red (A) and yellow (B) and show the AABBAABB packing arrangement within a stack.

FIG 3 Tris(oxalato)metallate anion layer in monoclinic  $\beta''$  radical-cation salts. All tris(oxalato)metallates within a layer are the same enantiomer, this figure shows the  $\Delta$  layer. Carbon atoms are grey, nitrogen blue, oxygen red and hydrogen white. The metal centre atoms are turquoise and halogen atoms are brown.

FIG 4 BEDT-TTF donor layer in orthorhombic pseudo- $\kappa$  radical-cation salts. The two crystallographically independent BEDT-TTF molecules are coloured red (BEDT-TTF<sup>0</sup>) and yellow (BEDT-TTF<sup>1+</sup>).

FIG 5 Tris(oxalato)metallate anion layer in orthorhombic pseudo- $\kappa$  radical-cation salts. Within a layer there are alternating rows of tris(oxalato)metallate enantiomers as indicated by  $\Delta$  and  $\Lambda$ . The benzonitrile molecules are orientationally disordered over two positions with the C $\equiv$ N group directed towards an NH<sub>4</sub><sup>+</sup>/H<sub>3</sub>O<sup>+</sup> cation. Metal atoms are turquoise, carbon grey, nitrogen blue, oxygen red and hydrogen white.

FIG 6 Layered packing of triclinic  $\alpha$ - $\beta''$  radical-cation salts. Sulphur atoms are yellow, carbon grey, nitrogen blue, oxygen red, hydrogen white and the metal centre orange. The position of the phenyl group of the unsymmetrical solvent molecule within the anion layer is indicated with an arrow.

FIG 7 BEDT-TTF  $\alpha$  packing in bilayered triclinic radical-cation salts. The two crystallographically independent BEDT-TTF molecules are coloured red and yellow.

FIG 8 3:1 Tris(oxalato)metallate anion layer in 3:1 salts (BEDT-TTF)<sub>3</sub>[NaCr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·nitromethane – *P*<sub>2</sub><sub>1</sub><sub>2</sub><sub>1</sub><sub>2</sub><sub>1</sub> (a), *P*<sub>2</sub><sub>1</sub> (b), and (BEDT-TTF)<sub>3</sub>[NaCr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·ethanol *P*<sub>1</sub> (c). The nitromethane molecule in (a) and the ethanol molecule in (c) are disordered over two positions. Na and Cr atoms are disordered on the same sites in (a). Cr atoms are blue and Na atoms are purple in (b) and (c). Carbon atoms are grey, nitrogen blue, oxygen red and hydrogen white.

FIG 9 BEDT-TTF packing in 3:1 salts (BEDT-TTF)<sub>3</sub>[(A)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·solvent – *P*<sub>2</sub><sub>1</sub><sub>2</sub><sub>1</sub><sub>2</sub><sub>1</sub> (a), *P*<sub>2</sub><sub>1</sub> (b), *P*<sub>1</sub> (c), and  $\theta$  (d). Sulphur atoms are yellow, carbon grey and hydrogen white.

FIG 10 Layered packing of 2:1 superconductor  $\beta''$ -(BEDT-TTF)<sub>2</sub>[(H<sub>2</sub>O)(NH<sub>4</sub>)<sub>2</sub>M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·18-crown-6, M = Cr<sup>3+</sup> (T<sub>c</sub> = 4.0-4.9K) or M = Rh<sup>3+</sup> (T<sub>c</sub> = 2.7K).[44,45] Sulphur atoms are yellow, carbon grey, nitrogen blue, oxygen red, hydrogen white and metal centre turquoise.

FIG 11 Layered packing of proton conductor  $\beta''$ -(BEDT-TTF)<sub>4</sub>[(A)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>·[(A)<sub>2</sub>18-crown-6](H<sub>2</sub>O)<sub>5</sub> (M = Cr or Ga, Cat = NH<sub>4</sub><sup>+</sup> or H<sub>3</sub>O<sup>+</sup>).[46,47] Sulphur atoms are yellow, carbon grey, oxygen red, hydrogen white and metal centre is blue.

FIG 12 Tris(oxalato)metallate anion layers of  $\beta'$ -(BEDT-TTF)<sub>5</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>](H<sub>2</sub>O)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>[48] (a) and  $\alpha$ -(BEDT-TTF)<sub>12</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>·(H<sub>2</sub>O)<sub>n</sub>[50] (b). Dichloromethane molecules in (a) are disordered over two positions. Water molecules are represented by red spheres in (b). Carbon atoms are grey, oxygen red, hydrogen white and chlorine green.

FIG 13 BEDT-TTF layer (a) and tris(oxalato)metallate anion layer (b) of  $\eta$ -(BEDT-TTF)<sub>4</sub>(H<sub>2</sub>O)LiFe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>[43]. Sulphur atoms are yellow, carbon grey, oxygen red, hydrogen white, lithium pink and iron orange. The hexagonal cavity in this salt contains heavily disordered dichloromethane which could not be resolved.

FIG 14 Layered packing of  $\alpha'''$ -(BEDT-TTF)<sub>9</sub>[M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>8</sub>Na<sub>18</sub>(H<sub>2</sub>O)<sub>24</sub>[42,49]. Sulphur atoms are yellow, carbon grey, oxygen red, hydrogen white, sodium purple and the metal centre orange.

FIG 15 Layered packing of  $\alpha$ -(BEDT-TTF)<sub>10</sub>(18-crown-6)<sub>6</sub>K<sub>6</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>4</sub>(H<sub>2</sub>O)<sub>24</sub>[49]. Sulphur atoms are yellow, carbon grey, oxygen red, hydrogen white, potassium purple, and iron orange.

FIG 16 Checkerboard donor-anion layer with interleaved benzonitrile layers in (BEDT-TTF)<sub>2</sub>[Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].PhCN[53] (a), and checkerboard layer in (BEDT-TTF)<sub>5</sub>[Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>[54] (b). Sulphur atoms are yellow, carbon grey, oxygen red, hydrogen white, nitrogen blue, and germanium turquoise.

FIG 17 Tris(oxalato)metallate anion layers of (BEDT-TTF)<sub>7</sub>[Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>(CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.87</sub>(H<sub>2</sub>O)<sub>0.09</sub>,[54] (a) and (BEDT-TTF)<sub>4</sub>Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·(CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.50</sub>.[55] (b). Dichloromethane molecules are disordered over two positions. Carbon atoms are grey, oxygen red, hydrogen white, chlorine green, and germanium turquoise.

**Table 1** 4:1 radical cation-salts of BEDT-TTF with tris(oxalato)ferrate(III) and their conducting properties. Salts all have the BEDT-TTF donor packing motif  $\beta''$  and have the formula  $\beta''$ -(BEDT-TTF)<sub>4</sub>[(A)Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>3</sub>·solvent. All salts crystallise in the monoclinic space group C2/c. Ph = Phenyl, Py = pyridine/pyridyl.

M <sup>3+</sup>	A <sup>+</sup>	Solvent	Conducting Properties	Reference
Fe	H <sub>3</sub> O <sup>+</sup>	PhCN	T <sub>c</sub> = 7.0-8.5 K	[5,8,9,10,11]
Fe	H <sub>3</sub> O <sup>+</sup> /NH <sub>4</sub> <sup>+</sup>	PhNO <sub>2</sub>	T <sub>c</sub> = 6.2 K	[12,13,14]
Fe	H <sub>3</sub> O <sup>+</sup>	2-BrPy	T <sub>c</sub> = 4.3 K	[15]
Fe	H <sub>3</sub> O <sup>+</sup>	PhBr	T <sub>c</sub> = 4 K	[16]
Fe	H <sub>3</sub> O <sup>+</sup>	2-ClPy	T <sub>c</sub> = 2.4 - 4.0 K	[15]
Fe	H <sub>3</sub> O <sup>+</sup>	PhF	T <sub>c</sub> = <1 K	[11,17,18]
Fe	H <sub>3</sub> O <sup>+</sup>	PhCl	Metal > 0.4 K	[11,17-20]
Fe	H <sub>3</sub> O <sup>+</sup>	3-ClPy	Metal > 0.4 K	[15]
Fe	H <sub>3</sub> O <sup>+</sup>	3-BrPy	Metal > 0.4 K	[15]
Fe	H <sub>3</sub> O <sup>+</sup>	1,2-Cl <sub>2</sub> Ph	Metal > 0.4 K	[11,21]
Fe	NH <sub>4</sub> <sup>+</sup>	(CH <sub>3</sub> ) <sub>2</sub> NC(O)H	Metal > 4.2 K	[22]
Fe	Rb <sup>+</sup>	Py	Metal > 2 K	[19]
Fe	H <sub>3</sub> O <sup>+</sup>	Py	T <sub>MI</sub> = 116 K	[10,23,24]
Fe	K <sup>+</sup>	PhI	E <sub>a</sub> = 64 meV	[18]
Fe	K <sup>+</sup>	PhCl	Semiconductor	[25]

**Table 2 4:1** radical cation-salts of BEDT-TTF with tris(oxalato)metallate(III) and their conducting properties. Salts all have the BEDT-TTF donor packing motif  $\beta''$  and have the formula  $\beta''$ -(BEDT-TTF)<sub>4</sub>[(A)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]-solvent. All salts crystallise in the monoclinic space group C2/c. Ph = Phenyl, Py = pyridine/pyridyl.

M <sup>3+</sup>	A <sup>+</sup>	Solvent	Conducting Properties	Reference
Ga	H <sub>3</sub> O <sup>+</sup>	PhNO <sub>2</sub>	T <sub>c</sub> = 7.5 K	[26,27]
Ga	H <sub>3</sub> O <sup>+</sup>	Py	T <sub>c</sub> = 1.5 K	[26,27]
Ga	H <sub>3</sub> O <sup>+</sup> /K <sup>+</sup>	PhBr	Metal > 0.5 K	[28]
Ga	H <sub>3</sub> O <sup>+</sup> /K <sup>+</sup>	2-ClPy	Metal > 0.5 K	[29]
Ga	H <sub>3</sub> O <sup>+</sup> /K <sup>+</sup>	2-BrPy	Metal > 0.5 K	[29]
Cr	H <sub>3</sub> O <sup>+</sup>	PhCN	T <sub>c</sub> = 5.5–6.0 K	[9,30,31]
Cr	H <sub>3</sub> O <sup>+</sup> /NH <sub>4</sub> <sup>+</sup>	PhNO <sub>2</sub>	T <sub>c</sub> = 5.8 K	[12]
Cr	H <sub>3</sub> O <sup>+</sup>	PhBr	T <sub>c</sub> = 1.5 K	[20]
Cr	NH <sub>4</sub> <sup>+</sup>	(CH <sub>3</sub> ) <sub>2</sub> NC(O)H	Metal > 4.2 K	[22]
Cr	K <sup>+</sup> /NH <sub>4</sub> <sup>+</sup>	(CH <sub>3</sub> ) <sub>2</sub> NC(O)H	Metal > 4.2 K	[22]
Cr	H <sub>3</sub> O <sup>+</sup>	PhCl	Metal > 130 K	[20]
Cr	H <sub>3</sub> O <sup>+</sup>	CH <sub>2</sub> Cl <sub>2</sub>	T <sub>Metal-semiconductor</sub> = 150 K	[32]
Cr	H <sub>3</sub> O <sup>+</sup>	Py	Metal > 0.5 K	[24]
Cr	H <sub>3</sub> O <sup>+</sup> /K <sup>+</sup>	2-ClPy	Metal > 0.5 K	[29]
Cr	H <sub>3</sub> O <sup>+</sup> /K <sup>+</sup>	2-BrPy	Metal > 0.5 K	[29]
Rh	NH <sub>4</sub> <sup>+</sup>	PhBr	T <sub>c</sub> = 2.5 K	[33]
Rh	H <sub>3</sub> O <sup>+</sup>	PhCl	Metal > 0.8K	[33]
Rh	H <sub>3</sub> O <sup>+</sup>	PhF	Metal > 0.8K	[33]
Ru	H <sub>3</sub> O <sup>+</sup> /K <sup>+</sup>	PhBr	T <sub>c</sub> = 2.8-6.3 K	[34]
Mn	H <sub>3</sub> O <sup>+</sup>	PhBr	T <sub>c</sub> = 2 K	[18]

**Table 3** 4:1 radical cation-salts of BEDT-TTF with tris(oxalato)ferrate(III) which include a solvent mixture and their conducting properties. Salts have the formula (BEDT-TTF)<sub>4</sub>[(A)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]-solvent. Ph = Phenyl, Py = pyridine.  $\rho T_c$  is T<sub>c</sub> measured by transport,  $\chi T_c$  is T<sub>c</sub> measured by SQUID magnetometry

M <sup>3+</sup>	A <sup>+</sup>	Solvent	BEDT-TTF packing	Space Group	Conducting Properties	Reference
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.22</sub> (Py) <sub>0.78</sub>	β''	C2/c	$\rho T_c = 3.9$ K, $\chi T_c = ?$ K	[10]
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.23</sub> (Py) <sub>0.77</sub>	β''	C2/c	$\rho T_c = ?$ K, $\chi T_c = ?$ K	[10]
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.34</sub> (Py) <sub>0.66</sub>	β''	C2/c	$\rho T_c = ?$ K, $\chi T_c = 5.8$ K	[10]
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.38</sub> (Py) <sub>0.62</sub>	β''	C2/c	$\rho T_c = 6.9$ K, $\chi T_c = ?$ K	[10]
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.43</sub> (Py) <sub>0.57</sub>	β''	C2/c	$\rho T_c = 6.7$ K, $\chi T_c = ?$ K	[10]
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.54</sub> (Py) <sub>0.46</sub>	β''	C2/c	$\rho T_c = 5.9$ K, $\chi T_c = 6.8$ K	[10]
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.61</sub> (Py) <sub>0.39</sub>	β''	C2/c	$\rho T_c = 4.2$ K, $\chi T_c = 6.1$ K	[10]
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.90</sub> (Py) <sub>0.10</sub>	β''	C2/c	$\rho T_c = ?$ K, $\chi T_c = 7.3$ K	[10]
Fe	H <sub>3</sub> O <sup>+</sup>	PhF/PhCN	pseudo-κ	Pbcn	Semiconductor	[11,17]
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.17</sub> (PhBr) <sub>0.83</sub>	β''	C2/c	T <sub>c</sub> = 4.2 K	[11,17]
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.86</sub> (1,2-Cl <sub>2</sub> Ph) <sub>0.14</sub>	β''	C2/c	T <sub>c</sub> = 7.2 K	[11,17]
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.88</sub> (1,2-Cl <sub>2</sub> Ph) <sub>0.12</sub>	pseudo-κ	Pbcn	Semiconductor	[11,17]
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.8</sub> (PhNO <sub>2</sub> ) <sub>0.2</sub>	β''	C2/c	T <sub>c</sub> = 6.6K	[11,17]
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.8</sub> (PhNO <sub>2</sub> ) <sub>0.2</sub>	pseudo-κ	Pbcn	Semiconductor	[11,17]
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.40</sub> (PhF) <sub>0.60</sub>	β''	C2/c	T <sub>c</sub> = 6.0 K	[11,17]
Fe	H <sub>3</sub> O <sup>+</sup>	(PhCN) <sub>0.35</sub> (PhCl) <sub>0.65</sub>	β''	C2/c	T <sub>c</sub> = 6.0 K	[11,17]

**Table 4** 4:1 radical cation-salts of BEDT-TTF with tris(oxalato)metallate(III) and their conducting properties. Salts all have the BEDT-TTF donor packing motif pseudo- $\kappa$  and have the formula pseudo- $\kappa$ -(BEDT-TTF)<sub>4</sub>[(A)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·benzonitrile. All salts crystallise in the orthorhombic space group *Pbcn*. Ph = Phenyl.

M <sup>3+</sup>	A <sup>+</sup>	Solvent	Conducting Properties	Reference
Fe	NH <sub>4</sub> <sup>+</sup>	PhCN	$E_a = 140$ meV	[8,9]
Fe	K <sup>+</sup>	PhCN	$E_a = 141$ meV	[8]
Cr	H <sub>3</sub> O <sup>+</sup>	PhCN	$E_a = 153$ meV	[9,31]
Al	NH <sub>4</sub> <sup>+</sup>	PhCN	$E_a = 222$ meV	[9]
Co	NH <sub>4</sub> <sup>+</sup>	PhCN	$E_a = 225$ meV	[9]
Rh	H <sub>3</sub> O <sup>+</sup>	PhCN	$E_a = 245$ meV	[33]
Ru	H <sub>3</sub> O <sup>+</sup> /K <sup>+</sup>	PhCN	Semiconductor	[34]
Mn	K <sup>+</sup>	PhCN	$E_a = 180$ meV	[35]

**Table 5 4:1** radical cation-salts of BEDT-TTF with tris(oxalato)metallate(III) having two BEDT-TTF packing motifs and their conducting properties. Salts all have the BEDT-TTF donor packing motif pseudo- $\kappa$  and have the formula  $(\text{BEDT-TTF})_4[(\text{A})\text{M}(\text{C}_2\text{O}_4)_3]\cdot\text{solvent}$ . All salts crystallise in the triclinic space group  $P-1$ . Ph = Phenyl.

$\text{M}^{3+}$	$\text{A}^+$	Solvent	BEDT-TTF packing	Space Group	Conducting Properties	Reference
Fe	$\text{NH}_4^+$	$\text{PhCOCH}_3$	$\alpha + \beta''$	$P-1$	Non-metallic and no superconductivity > 2K	[36]
Fe	$\text{NH}_4^+$	$(R/S)\text{-PhCH(OH)CH}_3$	$\alpha + \beta''$	$P-1$	$T_{\text{MI}} = 170 \text{ K}$	[37]
Fe	$\text{NH}_4^+$	$(S)\text{-PhCH(OH)CH}_3$	$\alpha + \beta''$	$P1$	$T_{\text{MI}} = 150 \text{ K}$	[37]
Fe	$\text{H}_3\text{O}^+$	1,2- $\text{Br}_2\text{Ph}$	$\alpha + \text{pseudo-}\kappa$	$P-1$	Metal > 0.4 K	[11,38]
Ga	$\text{H}_3\text{O}^+/\text{K}^+$	1,2- $\text{Br}_2\text{Ph}$	$\alpha + \text{pseudo-}\kappa$	$P-1$	Metal > 0.4 K	[28]
Ga	$\text{NH}_4^+$	$\text{PhN(CH}_3\text{)CHO}$	$\alpha + \beta''$	$P-1$	Non-metallic and no superconductivity > 2K	[36]
Ga	$\text{NH}_4^+$	$\text{PhCH}_2\text{CN}$	$\alpha + \beta''$	$P-1$	Non-metallic and no superconductivity > 2K	[36]

**Table 6** 3:1 radical cation-salts of BEDT-TTF with tris(oxalato)metallate(III) and their conducting properties. Salts all have the formula (BEDT-TTF)<sub>3</sub>[(A)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].solvent.

M <sup>3+</sup>	A <sup>+</sup>	Solvent	BEDT-TTF packing	Space Group	Conducting Properties	Reference
Cr	Na <sup>+</sup>	CH <sub>3</sub> NO <sub>2</sub>	2 parallel & 1 perpendicular	<i>P</i> <sub>2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></sub>	<i>E</i> <sub>a</sub> = 80 meV	[39]
Cr	NH <sub>4</sub> <sup>+</sup>	CH <sub>3</sub> NO <sub>2</sub>	2 parallel & 1 perpendicular	<i>P</i> <sub>2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></sub>	<i>E</i> <sub>a</sub> = 80 meV	[41]
Cr	Na <sup>+</sup>	CH <sub>3</sub> NO <sub>2</sub>	2 parallel & 1 perpendicular	<i>P</i> <sub>2<sub>1</sub></sub>	<i>E</i> <sub>a</sub> = 79 meV	[39]
Cr	Na <sup>+</sup>	CH <sub>3</sub> CN	2 parallel & 1 perpendicular	<i>P</i> <sub>2<sub>1</sub></sub>	<i>E</i> <sub>a</sub> = 79 meV	[40]
Al	Na <sup>+</sup>	CH <sub>3</sub> NO <sub>2</sub>	2 parallel & 1 perpendicular	<i>P</i> <sub>2<sub>1</sub></sub>	<i>E</i> <sub>a</sub> ≈ 140 meV	[41]
Cr	Na <sup>+</sup>	CH <sub>2</sub> Cl <sub>2</sub>	2 parallel & 1 perpendicular	<i>P</i> <sub>1</sub>	<i>E</i> <sub>a</sub> = 69 meV	[42]
Cr	Na <sup>+</sup>	(CH <sub>3</sub> ) <sub>2</sub> NC(O)H	θ	<i>P</i> <sub>1</sub>	<i>E</i> <sub>a</sub> = 43 meV	[40]
Cr	Na <sup>+</sup>	EtOH	2 parallel & 1 perpendicular	<i>P</i> <sub>1</sub>	-	[40]
Cr	Li <sup>+</sup>	EtOH	2 parallel & 1 perpendicular	<i>P</i> <sub>2<sub>1</sub>/c</sub>	<i>E</i> <sub>a</sub> = 179 meV	[43]
Fe	Li <sup>+</sup>	EtOH	2 parallel & 1 perpendicular	<i>P</i> <sub>2<sub>1</sub>/c</sub>	<i>E</i> <sub>a</sub> = 126 meV	[43]

**Table 7** 2:1 radical cation-salts of BEDT-TTF with tris(oxalato)metallate(III) incorporating 18-crown-6 ether into the lattice and their conducting properties.

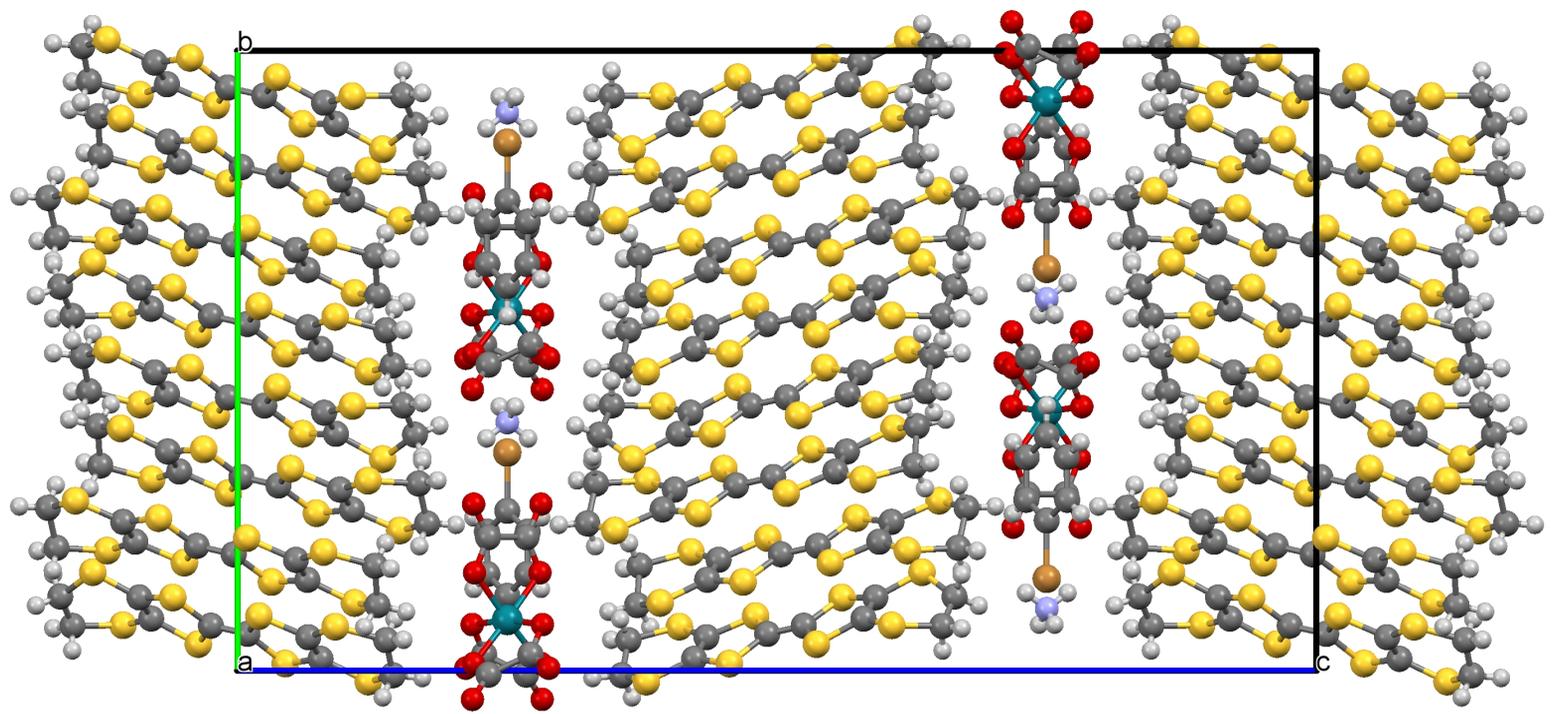
Formula	Space Group	Conducting Properties	Reference
$\beta''$ -(BEDT-TTF) <sub>2</sub> [(H <sub>2</sub> O)(NH <sub>4</sub> ) <sub>2</sub> Rh(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ]·18-crown-6	<i>P</i> -1	<i>T<sub>c</sub></i> = 2.7 K	[44]
$\beta''$ -(BEDT-TTF) <sub>2</sub> [(H <sub>2</sub> O)(NH <sub>4</sub> ) <sub>2</sub> Cr(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ]·18-crown-6	<i>P</i> -1	<i>T<sub>c</sub></i> = 4.0-4.9 K	[45]
$\beta''$ -(BEDT-TTF) <sub>4</sub> [(NH <sub>4</sub> )Cr(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] <sub>2</sub> ·[(NH <sub>4</sub> ) <sub>2</sub> 18-crown-6](H <sub>2</sub> O) <sub>5</sub>	<i>P</i> -1	<i>T<sub>MI</sub></i> = 190 K	[46,47]
$\beta''$ -(BEDT-TTF) <sub>4</sub> [(NH <sub>4</sub> )Ga(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] <sub>2</sub> ·[(NH <sub>4</sub> ) <sub>2</sub> 18-crown-6](H <sub>2</sub> O) <sub>5</sub>	<i>P</i> -1	<i>T<sub>MI</sub></i> = 240 K	[47]

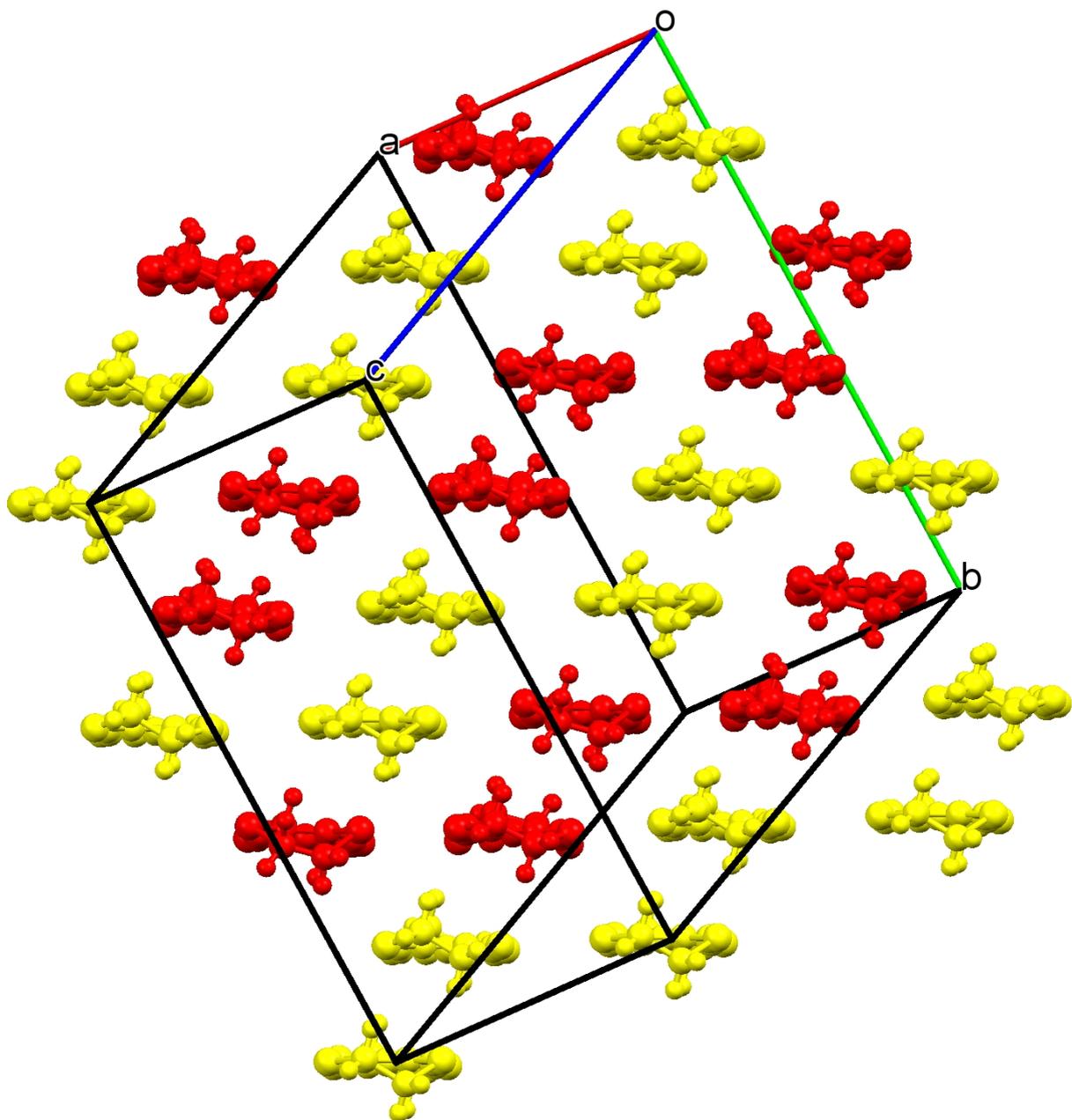
**Table 8** Radical cation-salts of BEDT-TTF with tris(oxalato)metallate(III) and their conducting properties.

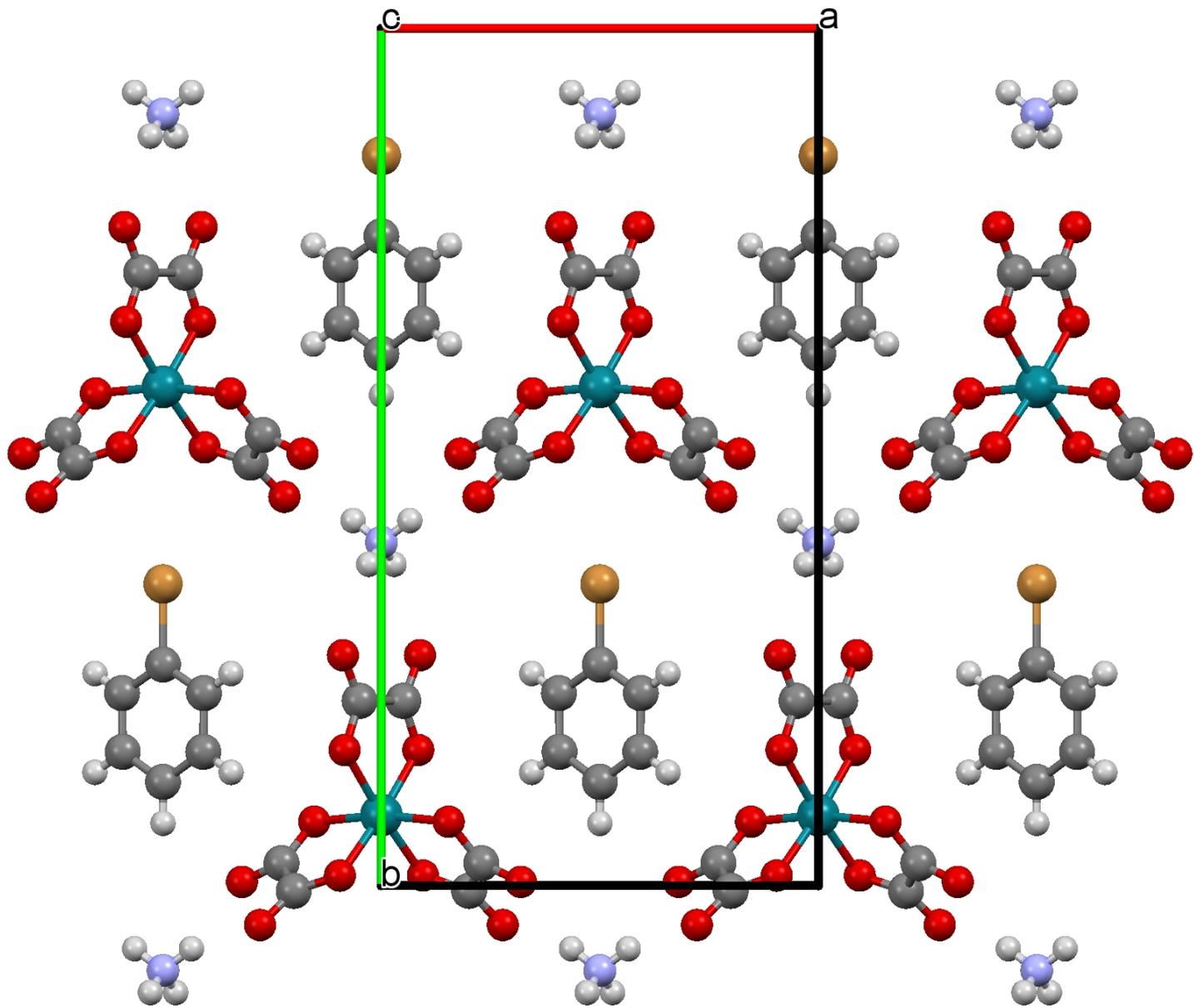
Formula	Space Group	Conducting Properties	Reference
$\beta'$ -(BEDT-TTF) <sub>5</sub> [Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] $\cdot$ (H <sub>2</sub> O) <sub>2</sub> $\cdot$ CH <sub>2</sub> Cl <sub>2</sub>	<i>P</i> -1	$E_a = 30$ meV	[48]
$\alpha'''$ -(BEDT-TTF) <sub>9</sub> [Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] <sub>8</sub> Na <sub>18</sub> (H <sub>2</sub> O) <sub>24</sub>	<i>P</i> -1	$E_a = 77$ meV	[49]
$\alpha'''$ -(BEDT-TTF) <sub>9</sub> [Cr(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] <sub>8</sub> Na <sub>18</sub> (H <sub>2</sub> O) <sub>24</sub>	<i>P</i> -1	$E_a = 66$ meV	[42]
$\alpha$ -(BEDT-TTF) <sub>12</sub> [Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] <sub>2</sub> $\cdot$ (H <sub>2</sub> O) <sub>15</sub>	<i>C</i> 2/ <i>c</i>	Semiconductor	[50]
$\alpha$ -(BEDT-TTF) <sub>12</sub> [Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] <sub>2</sub> $\cdot$ (H <sub>2</sub> O) <sub>16</sub>	<i>C</i> 2/ <i>c</i>	Semiconductor	[50]
$\alpha$ -(BEDT-TTF) <sub>10</sub> (18-crown-6) <sub>6</sub> K <sub>6</sub> [Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] <sub>4</sub> (H <sub>2</sub> O) <sub>24</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	$E_a = 105$ meV	[49]
$\eta$ -(BEDT-TTF) <sub>4</sub> (H <sub>2</sub> O)LiFe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	$E_a = 80$ meV	[43]
(BEDT-TTF) <sub>2.53</sub> [MnRh(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] $\cdot$ CH <sub>2</sub> Cl <sub>2</sub>	<i>P</i> -1	Metal > 2 K	[51]
(BEDT-TTF) <sub><i>x</i></sub> [MnCr(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] $\cdot$ CH <sub>2</sub> Cl <sub>2</sub> $x = < 3$	<i>P</i> -1	Metal > 0.3 K	[6,51,52]
$\alpha''$ -(BEDT-TTF) <sub>5</sub> [Ga(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] $\cdot$ (H <sub>2</sub> O) <sub>3.4</sub> $\cdot$ (EtOH) <sub>0.6</sub>	<i>Pbca</i>	$E_a = 71$ meV	[29]

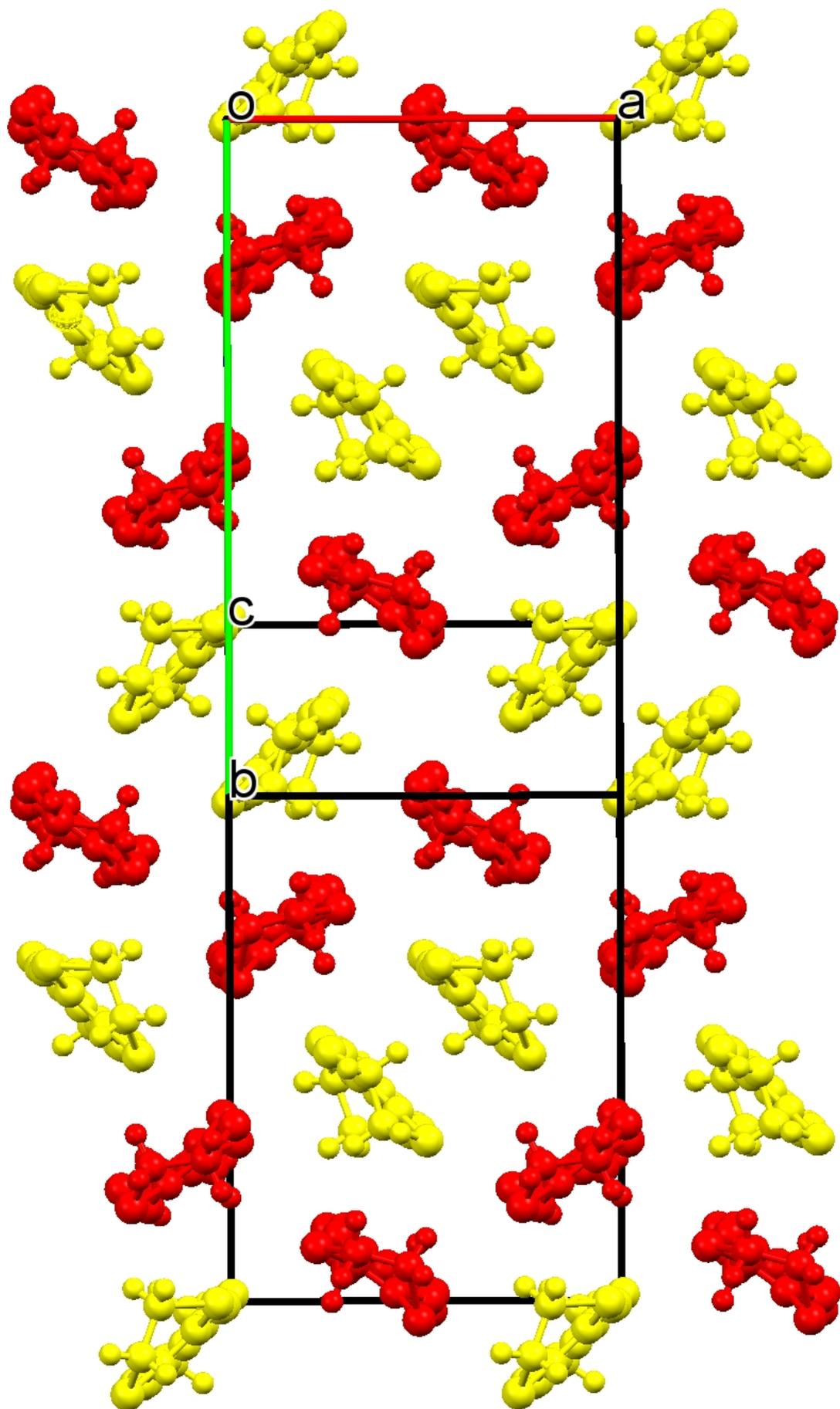
**Table 9** Radical cation-salts of BEDT-TTF with tris(oxalato)germanate(IV) and their conducting properties. Ph = Phenyl.

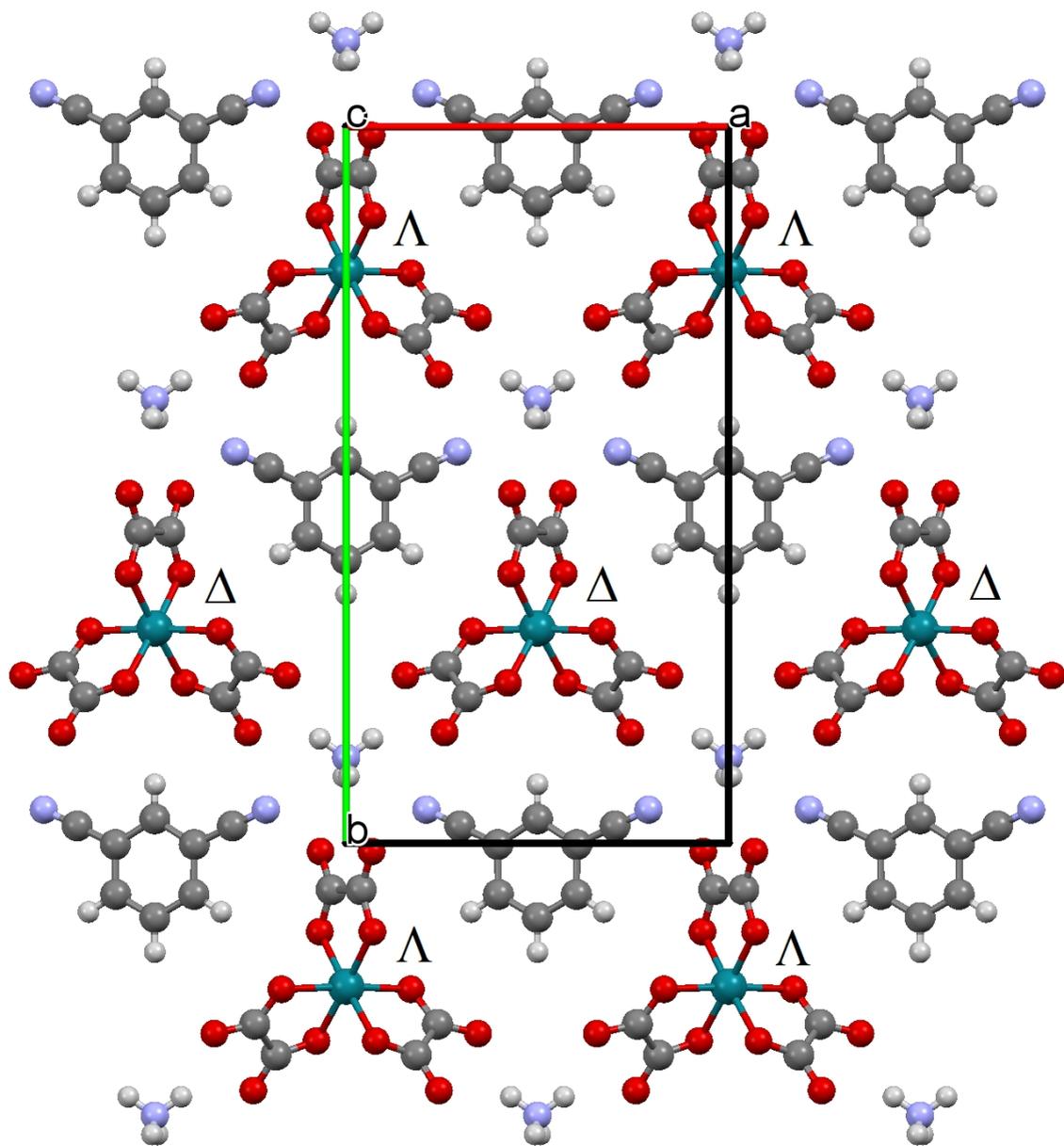
Formula	Space Group	Conducting Properties	Reference
$(\text{BEDT-TTF})_2[\text{Ge}(\text{C}_2\text{O}_4)_3]\cdot\text{PhCN}$	$P2_1/c$	$E_a = 127 \text{ meV}$	[53]
$(\text{BEDT-TTF})_5[\text{Ge}(\text{C}_2\text{O}_4)_3]_2$	$C2$	$E_a = 225 \text{ meV}$	[54]
$(\text{BEDT-TTF})_7[\text{Ge}(\text{C}_2\text{O}_4)_3]_2(\text{CH}_2\text{Cl}_2)_{0.87}(\text{H}_2\text{O})_{0.09}$	$C2/c$	$E_a = 172 \text{ meV}$	[54]
$(\text{BEDT-TTF})_4\text{Ge}(\text{C}_2\text{O}_4)_3\cdot(\text{CH}_2\text{Cl}_2)_{0.50}$	$P2_1/c$	$E_a = 224 \text{ meV}$	[55]

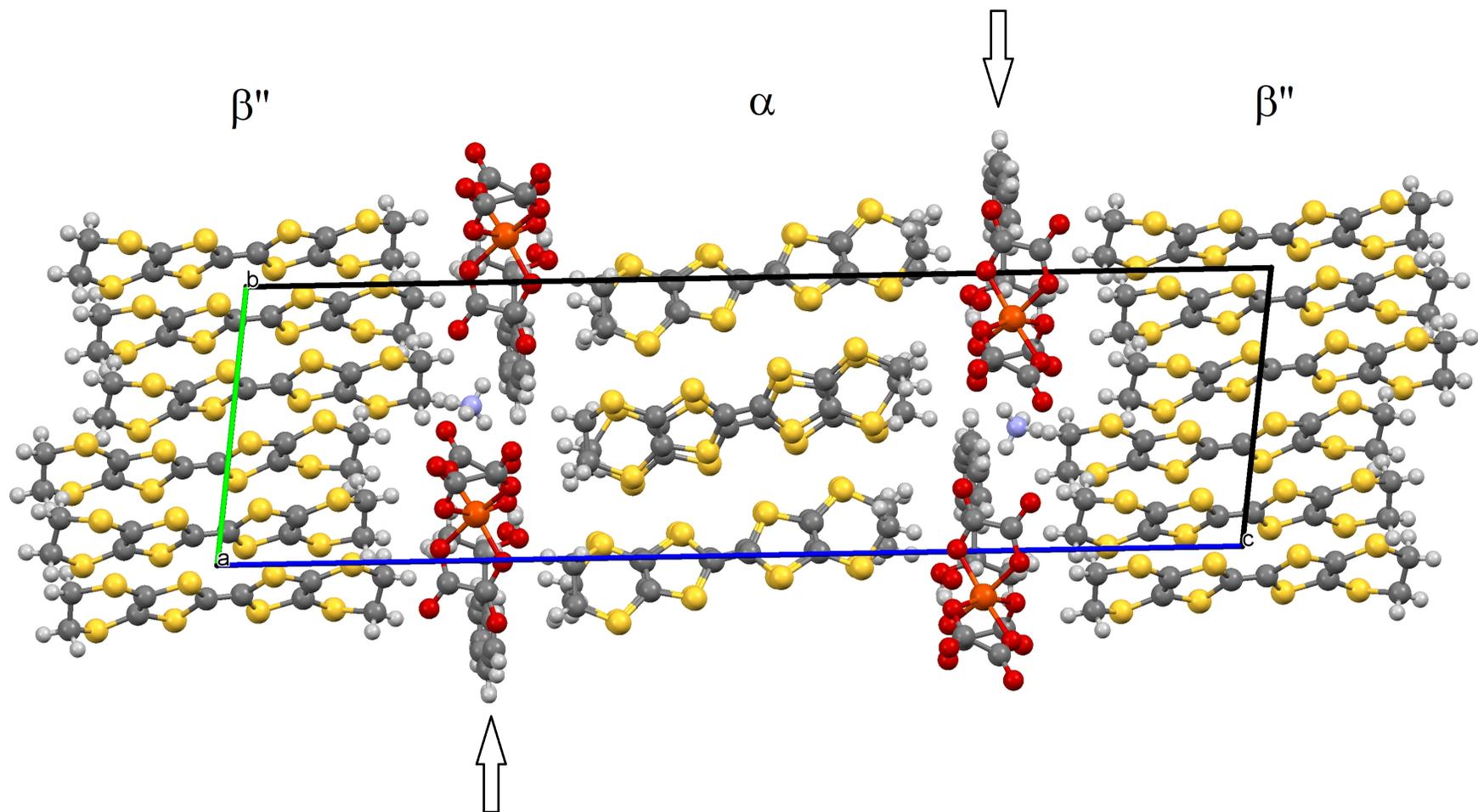


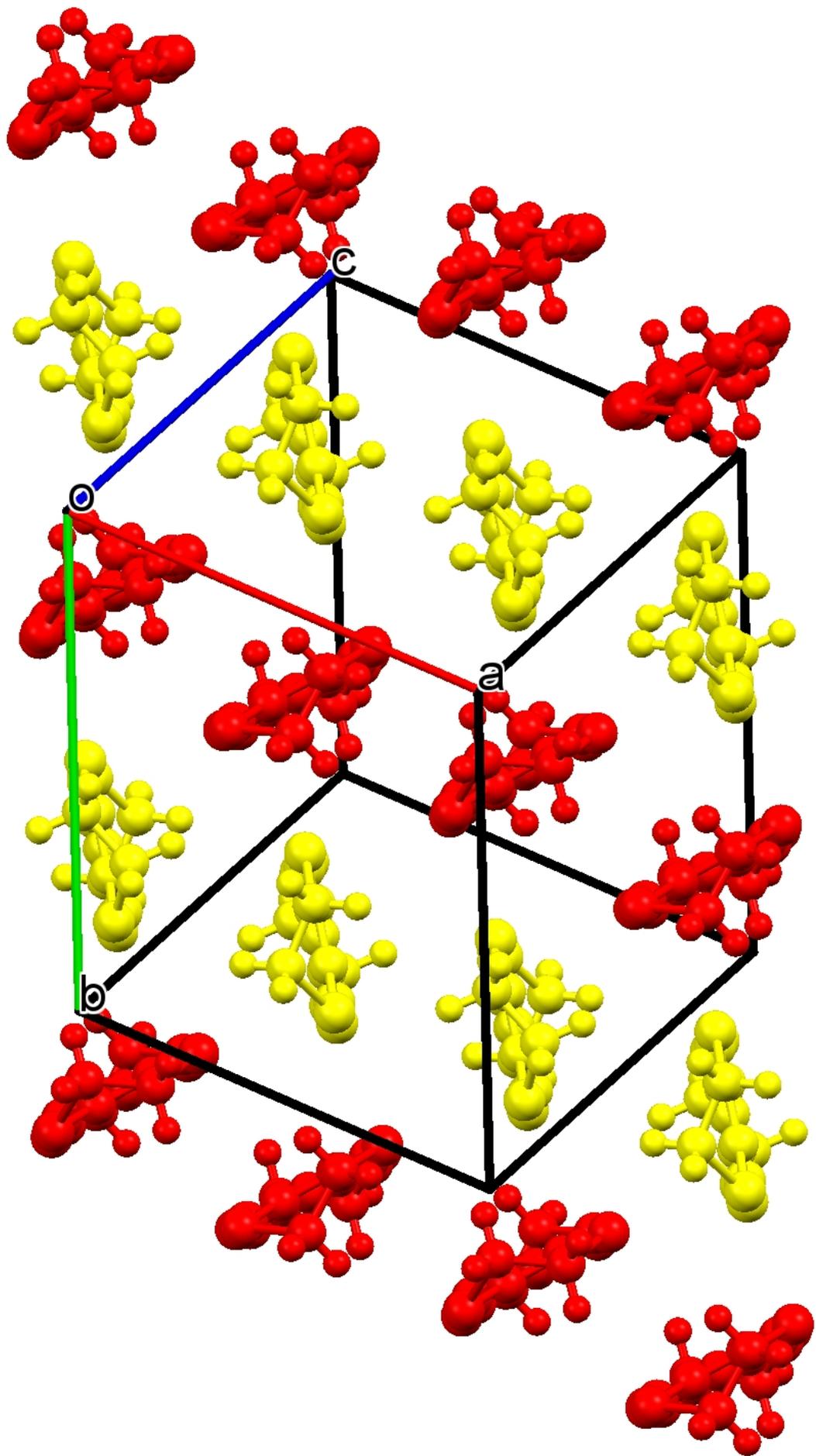


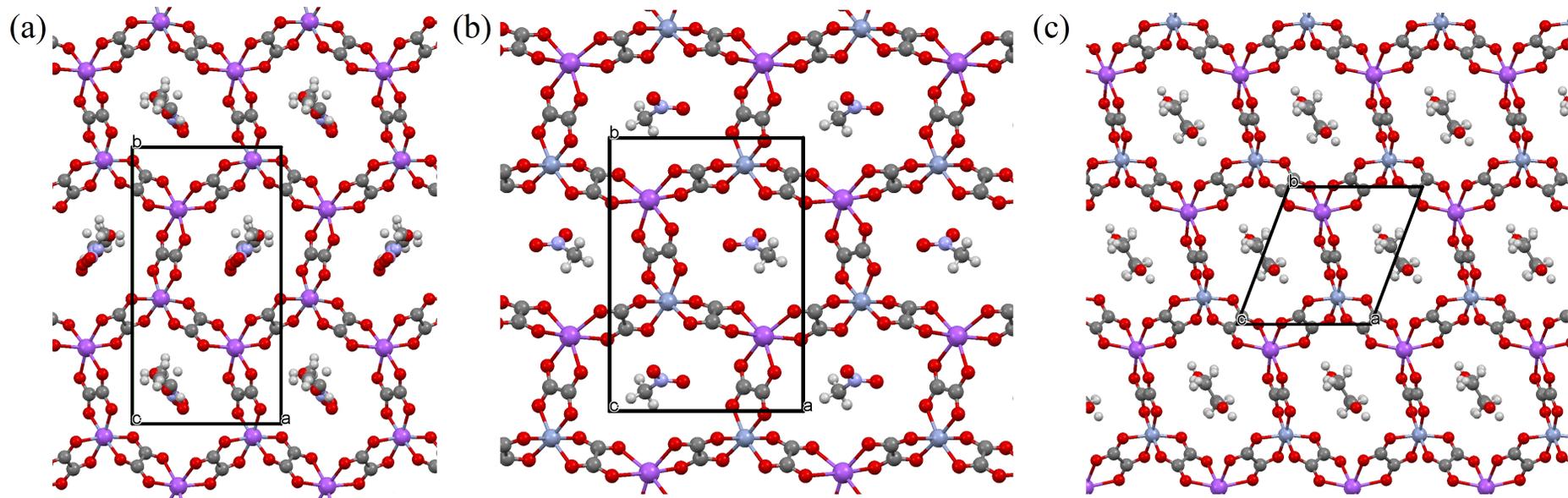


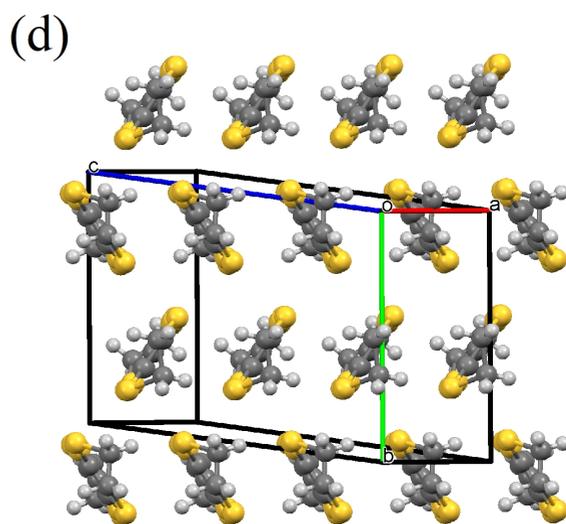
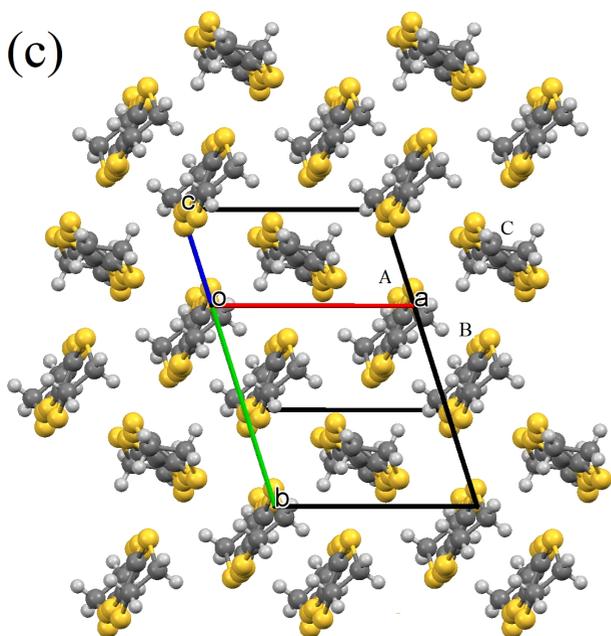
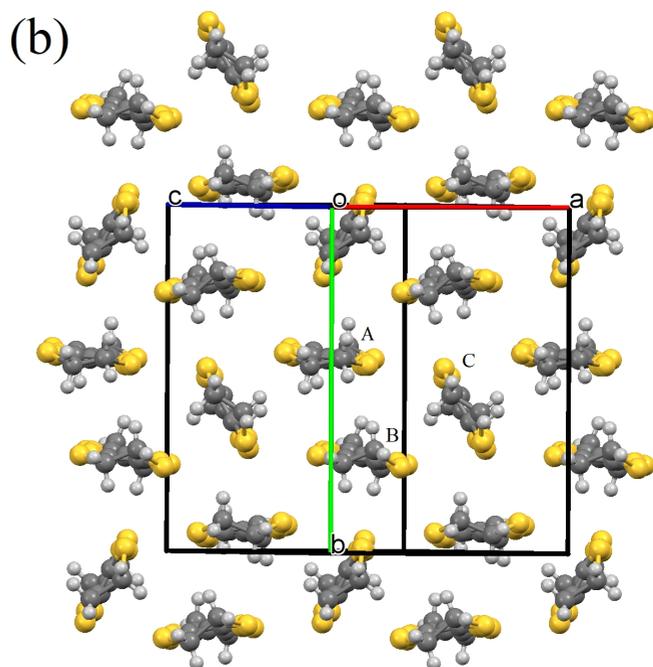
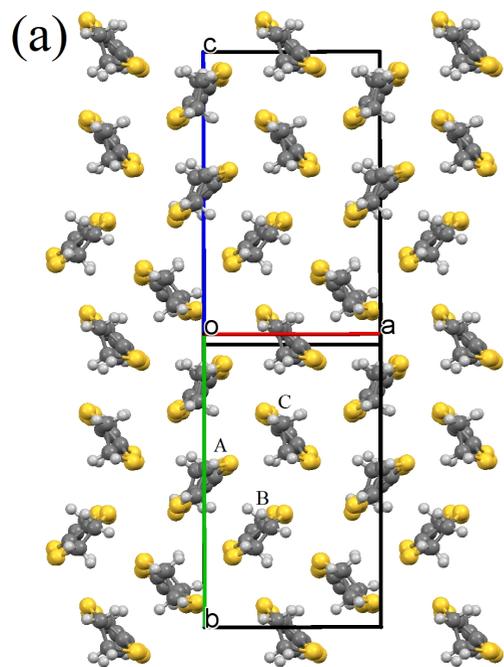


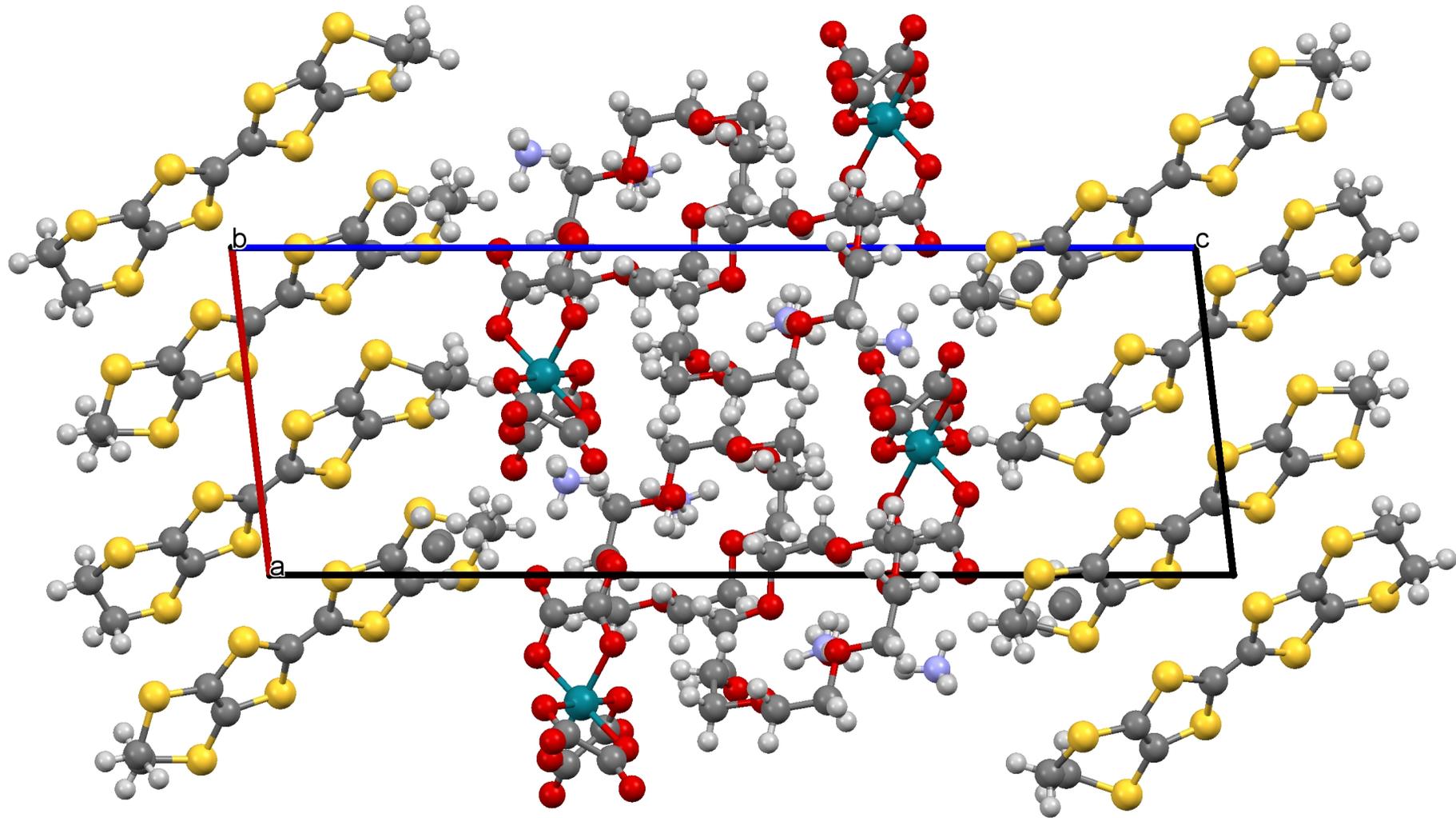












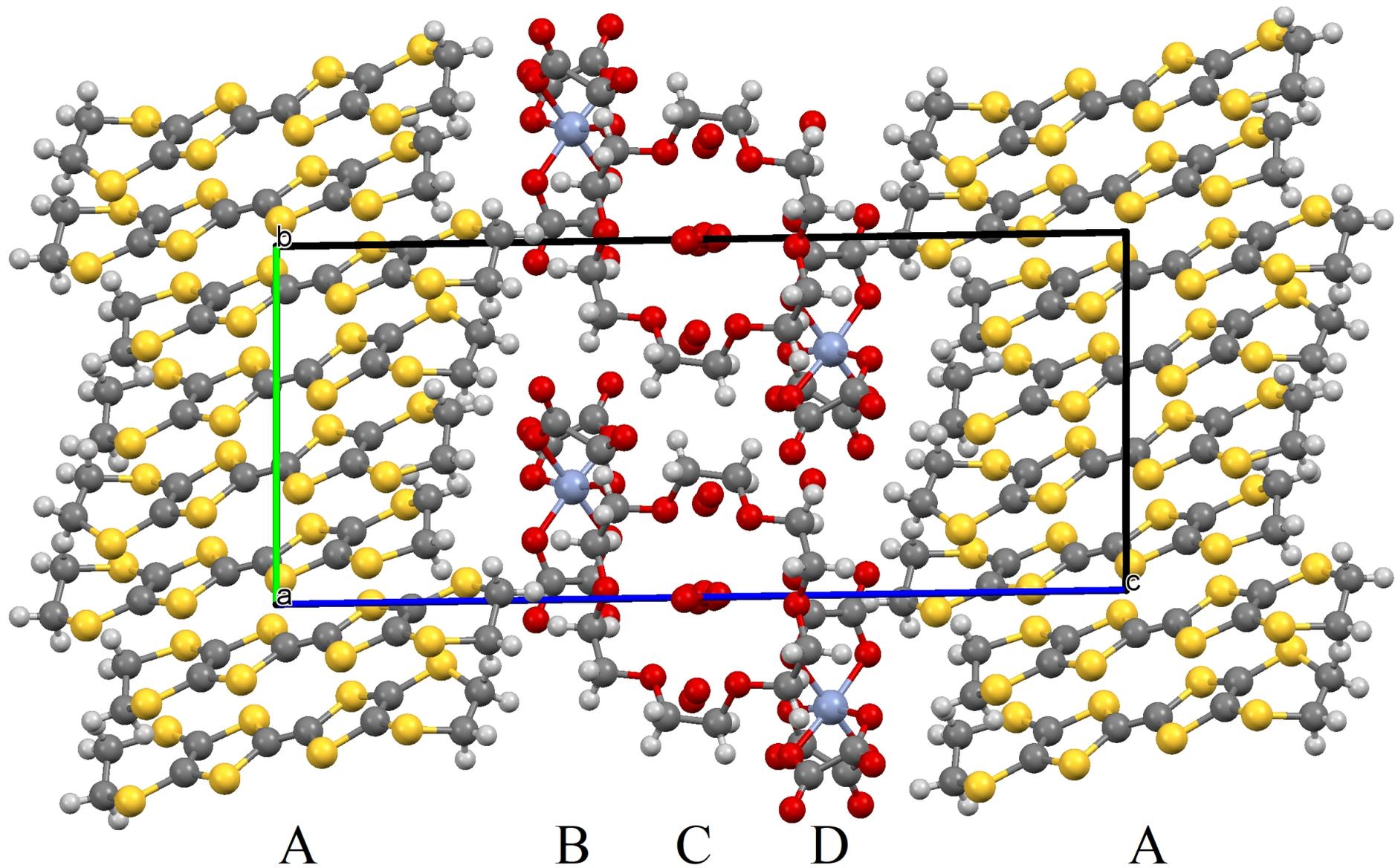
A

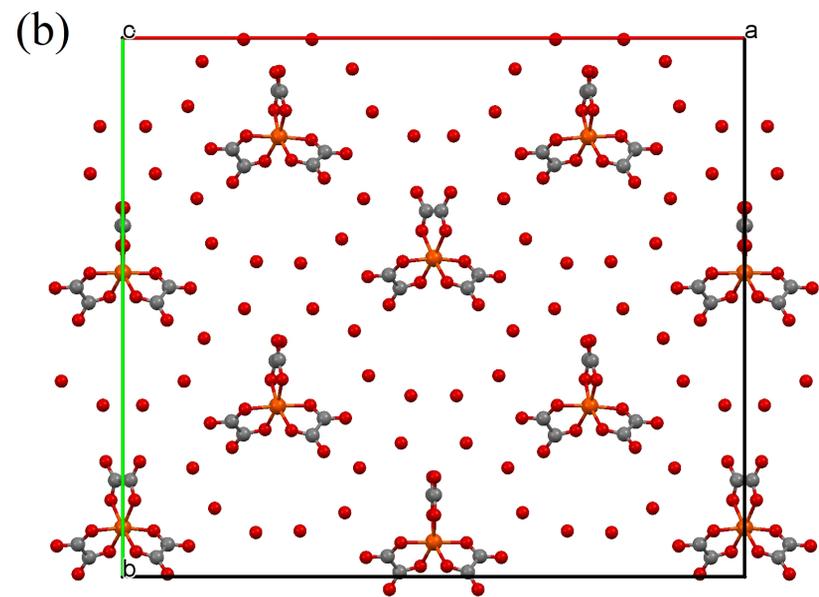
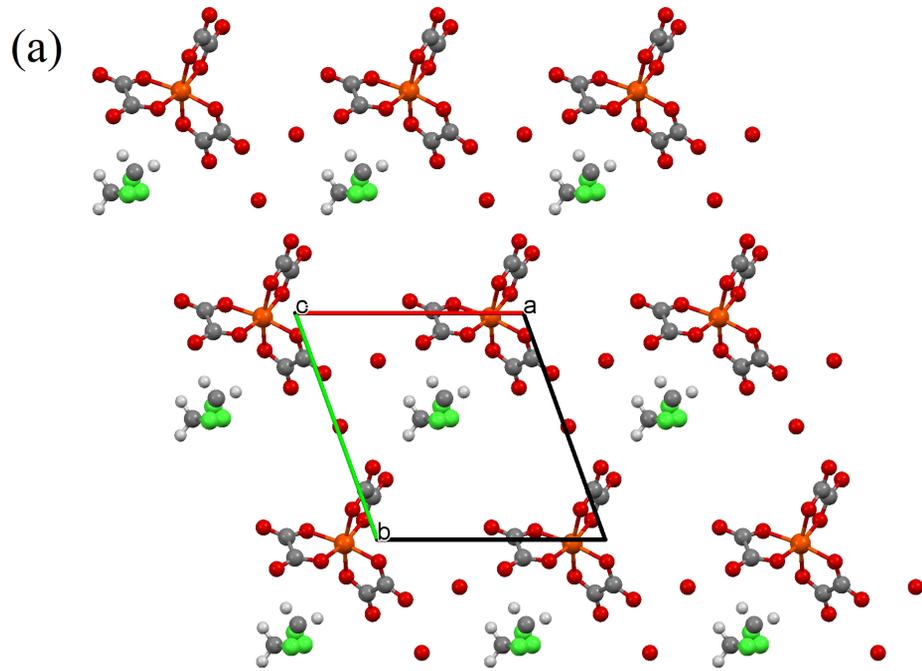
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C

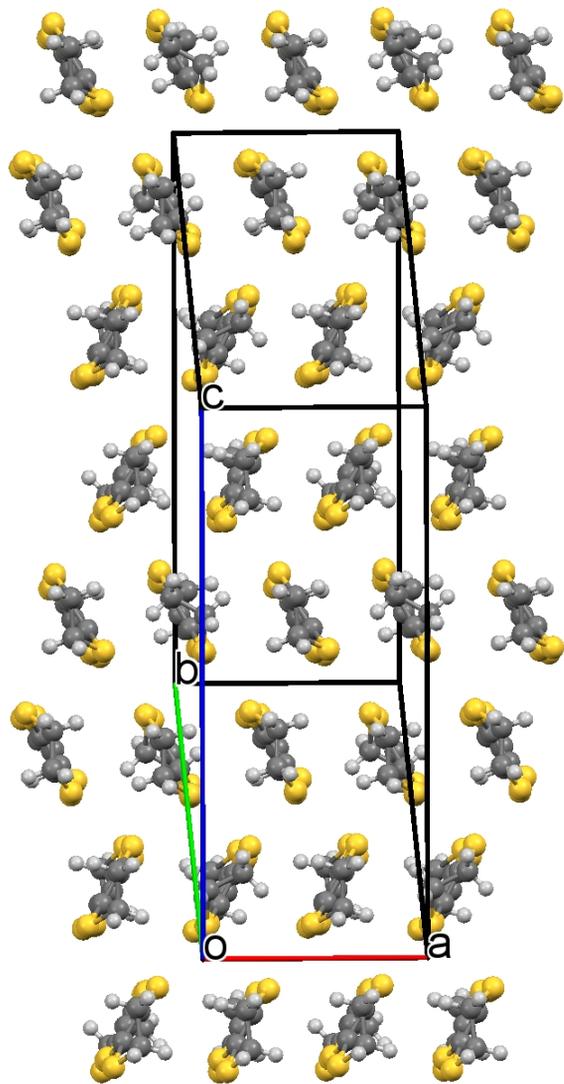
D

A

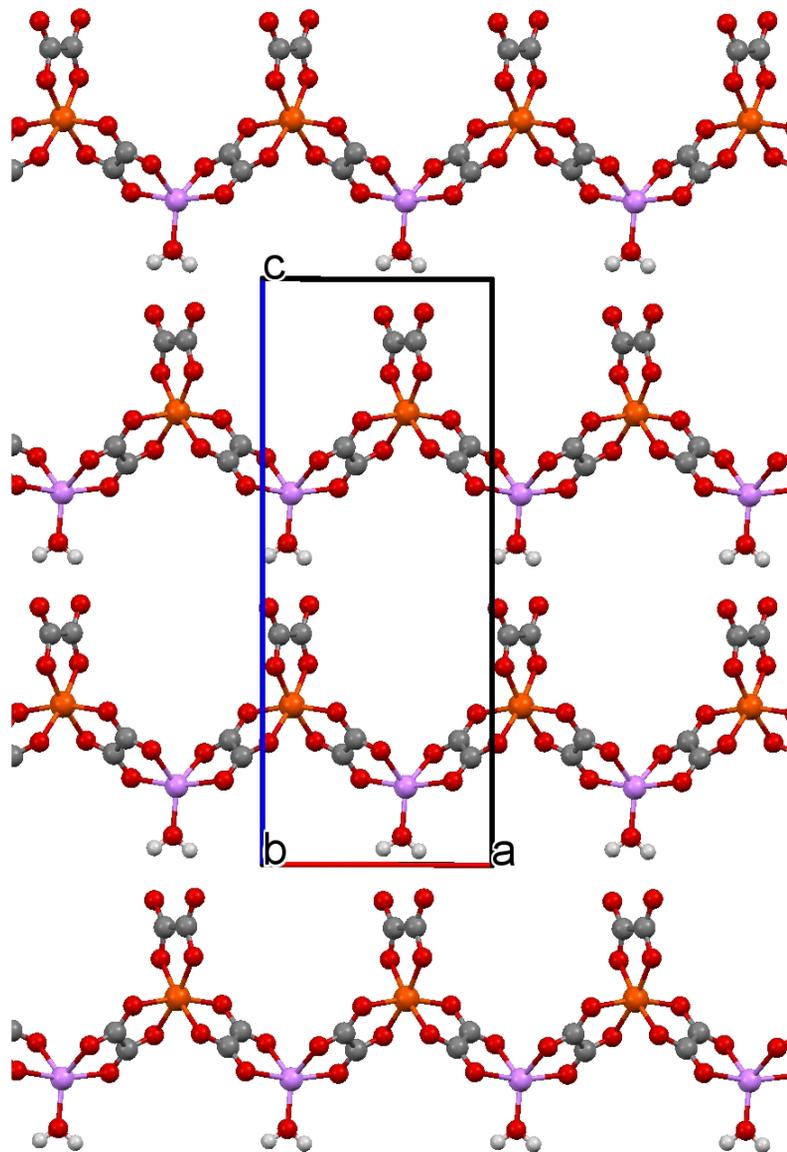


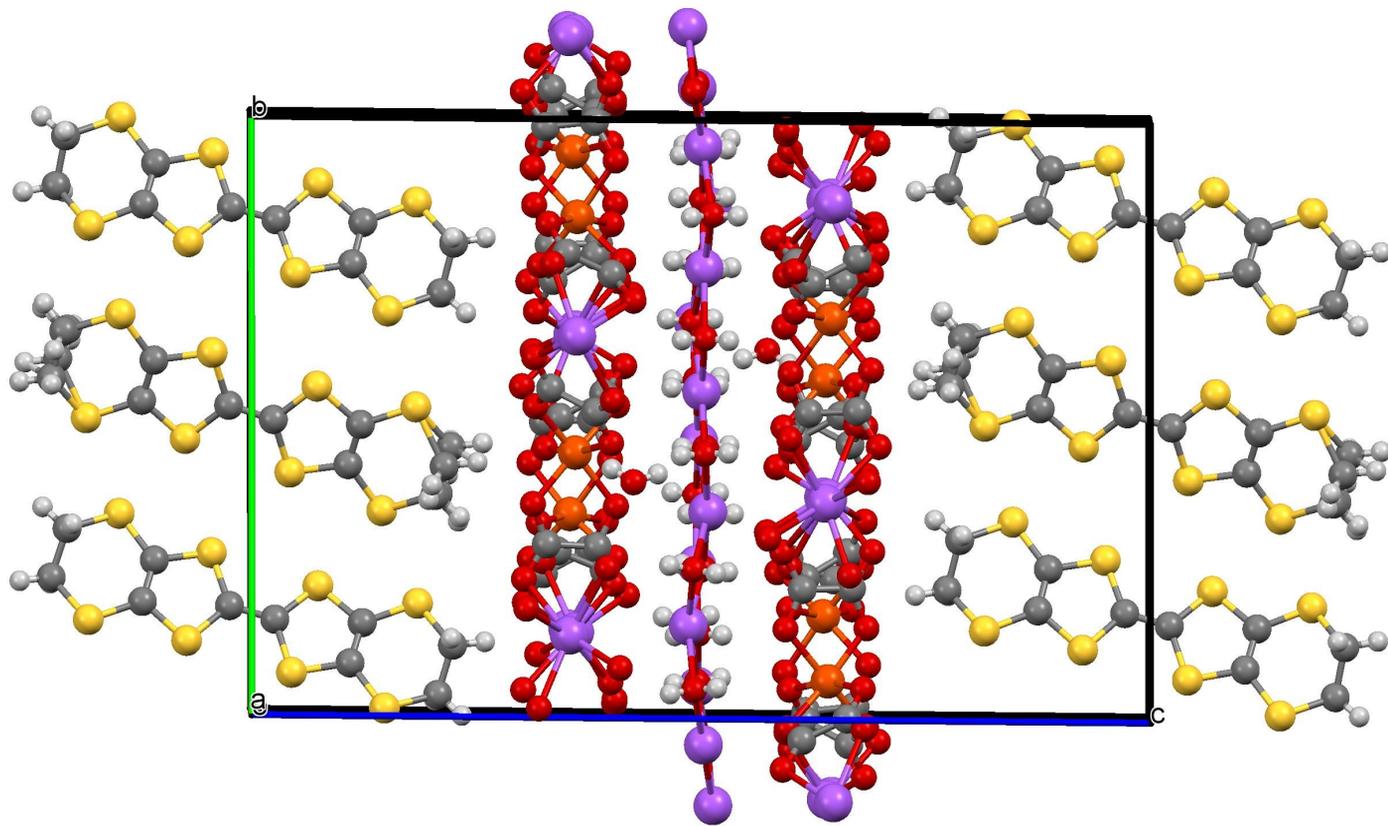


(a)



(b)





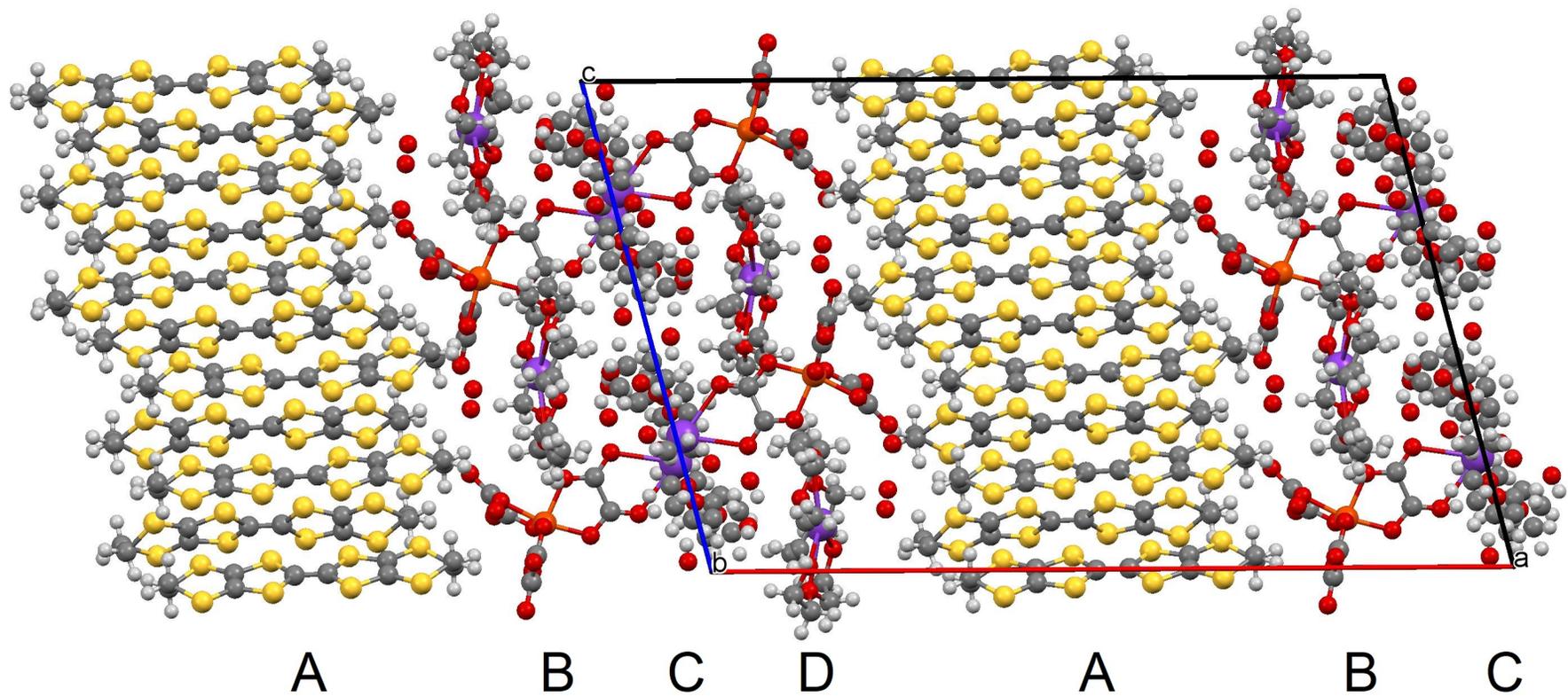
A

B

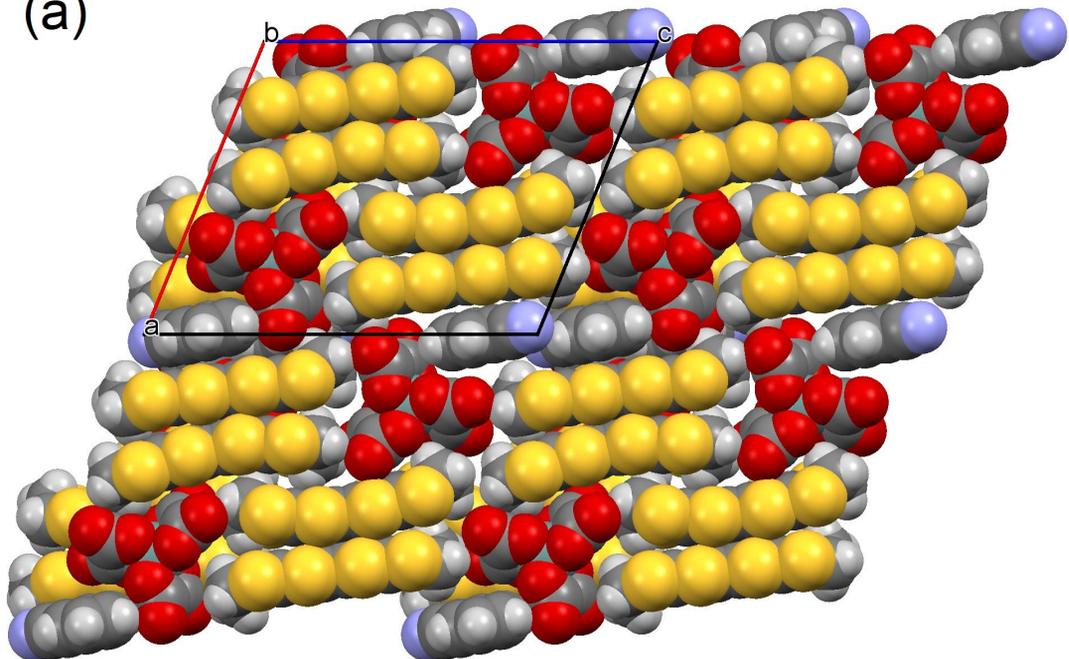
C

D

A



(a)



(b)

