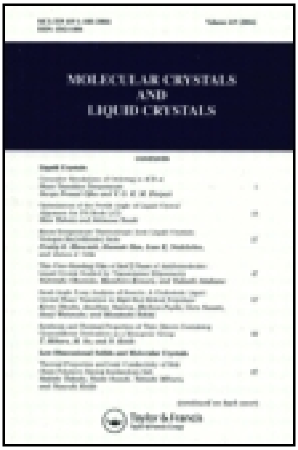

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Organic-Inorganic Layer Compounds as Molecular Functional Materials

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Organic-Inorganic Layer Compounds as Molecular Functional Materials

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Many molecular charge transfer salts synthesised over the last 20 years contain alternating layers of organic donor cations and inorganic metal-complex anions. Here we survey some features of one of the most prolific families of such salts: $(BEDT\text{-}TTF)_4[AM(C_2O_4)_3]\cdot G$, *where BEDT-TTF is bis-ethylene-dithiotetrathiafulvalene, A is a monopositive cation, M a tri-positive cation and G an organic guest molecule. The roles of anion chirality, molecular conformational disorder and the formation of superlattice ordering of layer packing are emphasised.*

Keywords: charge transfer salts; metal-complex anions; organic superconductors

INTRODUCTION

The conducting charge transfer salts whose electrical properties were first revealed in the seminal papers of Akamatu and Inokuchi [1] half a century ago contained simple inorganic anions. Since that time, however, many other inorganic anions have been used to form such salts, as well as a wide range of donor molecules. Out of all that activity came the first molecular superconductorsand a range of other exotic electronic ground states such as charge- and spin-density waves, antiferromagnets, spin-Peierls systems and so on [2]. Most of the compounds showing these unusual properties are low-dimensional, with

The work from my own group described here has been carried out by many highly motivated graduate students and postdocs, whose names will be found in the references. Financial support has come from the U.K. Engineering and Physical Sciences Research Council, the European Union (HMC, TMRI and IHP Networks), and the European Science Foundation (Programme on Molecular Magnets).

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chains or layers of closely spaced molecular units. In particular, in recent years the many salts of BEDT-TTF (bis-ethylenedithiotetrathiafulvalene) form structures consisting of alternating layers of donor cations and inorganic anions. That structural flexibility has enabled a wide variety of inorganic complex anions to be built into the structures. Hence it has proved possible to combine the two-dimensional Fermi surface derived from the donor layer with other properties characteristic of transition-metal containing solids. Examples of such 'multifunctional' materials are the first paramagnetic superconductor [3] and molecular metallic ferromagnet [4]. Another combination of properties supported by this kind of layer structure, which may have important implications for low-temperature fuel cells, is metallic conductivity and protonic conductivity [5]. In this brief overview I will survey the crystal structures and physical properties of the particularly rich family of charge transfer salts based on BEDT-TTF and tris-oxalatometallate(III) anions, with special emphasis on the stacking of the organic and inorganic layers and how they are influenced by the chirality of the anions and incorporation of organic guest molecules.

BRINGING TOGETHER ORGANIC AND INORGANIC LAYERS

The main types of bonding that contribute to the interaction between the organic and inorganic layers are no different in essence from those involved in both lower and higher dimensional lattices. That is to say they are ionic, covalent and H-bonding with, in addition, a significant contribution form steric factors in the form of a 'lock and key' arrangement of intermolecular contacts between adjacent layers.

When both the organic and inorganic components in a composite hybrid compound are molecular, several other factors come into play. In charge transfer salts of organic donors with molecular inorganic anions, coulomb interaction is obviously important. Relevant to the electron transport properties of the organic layer is the charge distribution within the inorganic layer, which may be far from uniform, especially when this layer contains guest molecules. Among many BEDT-TTF salts, a clear example is α-(BEDT-TTF)$_4$[ReCl$_6$]C$_6$H$_5$CN, which is not a metal but a semiconductor. The structures of the organic and inorganic layers in this salt are shown in Figure 1 [6]. Analysis of the BEDT-TTF bond lengths reveals that the molecules in alternate stacks have charges 0 and +1 instead of +0.5, +0.5 anticipated in conducting α-phase (BEDT-TTF)$_2$X salts. The reason for such a charge localisation becomes clear when we examine the interrelation between the cation and anion layers. In the latter, Figure 1

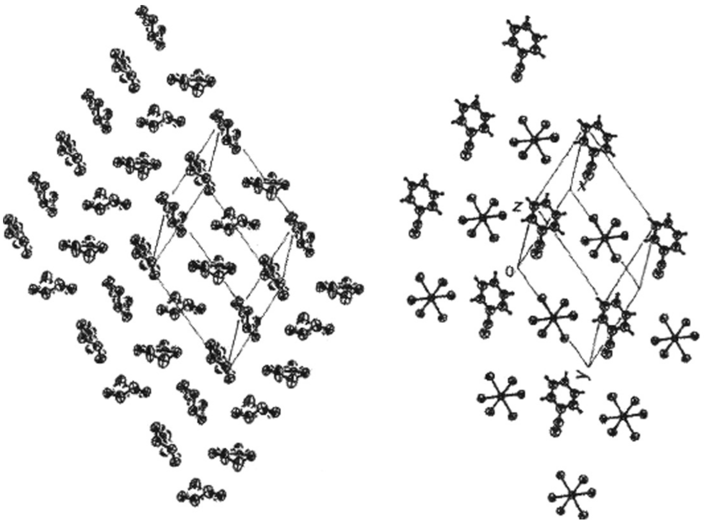

FIGURE 1 The donor (left hand side) and anion (right hand side) layers in α-$(BEDT\text{-}TTF)_4ReCl_6 \cdot PhCN$ [6].

shows how the anions and solvent molecules are disposed in alternate chains propagating in the same direction as the donor stacks. Now the +1 donor stacks lie adjacent to the columns of $[ReCl_6]^{2-}$, while the 0 charged ET are closest to the chains of neutral C_6H_5CN molecules. Since many organic-inorganic charge transfer salts have layers that contain both anions and neutral molecules, charge localisation due to this type of effect may be quite widespread.

Apart from charge fluctuation within the inorganic anion layer, straightforward steric considerations are also significant determinants of the packing arrangement in the organic donor layer and hence of the physical properties. A key example in the development of molecular conductors is provided by the $(BEDT\text{-}TTF)_2X$ series, where X is a relatively small anion that forms quite 'thin' layers, such as I_3^-, $[Cu(N(CN)_2)Cl]^-$, $[Ag(CN)_2]^-$ etc. In these compounds we find extensive polymorphism, corresponding to different stacking arrangements in the donor layer. However, analysis of the organisation of the donor molecules in relation to the packing of the anions reveals a clear steric correlation between the two sublattices [16]. For example, both $[Cu(N(CN)_2)Cl]^-$ [7] and $[Ag(CN)_2 \cdot H_2O]^-$ [8] form sheets containing networks of distorted hexagonal cavities of such a size that the terminal groups of two BEDT-TTF molecules fit inside them if they are oriented plane to plane. Since the directions of distortion of adjacent

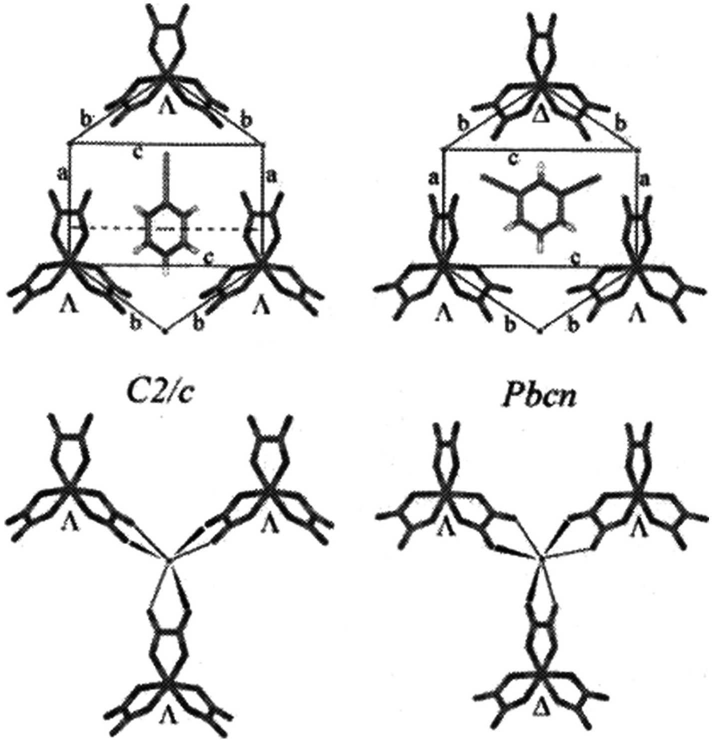

FIGURE 2 The anionic layer in (BEDT-TTF)$_4$[AM(C$_2$O$_4$)$_3$]PhCN [9]. Left hand side, C2/c phase; right hand side, Pbcn phase.

hexagons are almost orthogonal, this leads to the BEDT-TTF dimers being similarly orthogonal, thus generating the so-called κ-structure. Correspondingly, less extended anions such as I_3^-, $[AuI_2]^-$ etc., form more densely packed two-dimensional arrays that act as templates for a more closely packed arrangement of BEDT-TTF containing stacks of molecules that interact through inter-stack $S \cdots S$ contacts.

When the anion layer is even more densely packed, or is thicker, a further principle directing the assembly of the organic donor layer comes into play. Since inorganic anions by definition contain electronegative atoms, weak H-bonding may exert a significant structure directing effect, when the donors contain suitably oriented H atoms. An example is provided by BEDT-TTF salts of *tris*-oxalato-metallates. In this case the anion layers consist of $[M(C_2O_4)_3]^{3-}$ arranged in a triangular array, separated by further cations such as K^+, NH_4^+ or H_3O^+. The M^{3+} and A^+ therefore form an approximately hexagonal layer, between each pair of which lies one $[C_2O_4]^{2-}$, with two O coordinated to M to form a five-membered chelate ring and the other two making weak H-bonds with the H_3O^+ or NH_4^+ (Fig. 2). Since the preferred coordination of M is octahedral the $[C_2O_4]^{2-}$, which are planar, make angles of about 70° to the plane defined by the M. Consequently the $[AM(C_2O_4)_3]^{2-}$ layer has two 'surfaces', each consisting of O atoms in pairs. Above and below this layer the BEDT-TTF lie in stacks with the β'' packing motif. The long axes of the molecules make angles of roughly 80° to the anion plane, and their terminal $-CH_2CH_2-$ groups lie at the organic-inorganic interface, stabilized by a network of $-C-H\cdots O-$ short links. Definitive evidence that the latter indeed stabilize the BEDT-TTF packing comes from the orientation of the stacking axes, which make an angle of 62–64° between adjacent donor layers. This is precisely the same as the angle of twist of the $[C_2O_4]^{2-}$ (and hence of the pairs of O) between the top and bottom of the anion layer.

ADDITIONAL STRUCTURAL FEATURES OF ORGANIC-INORGANIC LAYERS

One of the lessons about collective electronic properties of molecular lattices is the extreme sensitivity of the behaviour to chemically minor variations. Here we examine the influence of two further factors on the packing of the organic and inorganic layers, and hence on the resulting properties of the crystals.

Chirality of the Layers

Chirality is quite easy to introduce into molecular lattices by building them from chiral molecules, but is more or less unknown in continuous lattices. In principle it could be built into either the organic or inorganic layer since there are many enantiomeric metal complexes. In fact the $[M(C_2O_4)_3]^{3-}$ anions referred to above are of this type since their point symmetry is D_3 and they have been known to exist in Λ and Δ enantiomers since the work of Werner 90 years ago [10]. In the BEDT-TTF salts with these anions, both enantiomers are found in the lattice, i.e., the crystals do not belong to a chiral space group. Nevertheless, the chiral nature of the anions exerts a powerful influence on the molecular packing in the crystals, as discussed below. In the bimetallic *tris*-oxalato-metallate salts $AMM'(C_2O_4)_3$ it should also be noted that in order to arrive at a two-dimensional hexagonal lattice, if one of the metal centres has a Λ configuration, the other has to be Δ [11]. Where both M and M′ sites have the same configuration (for

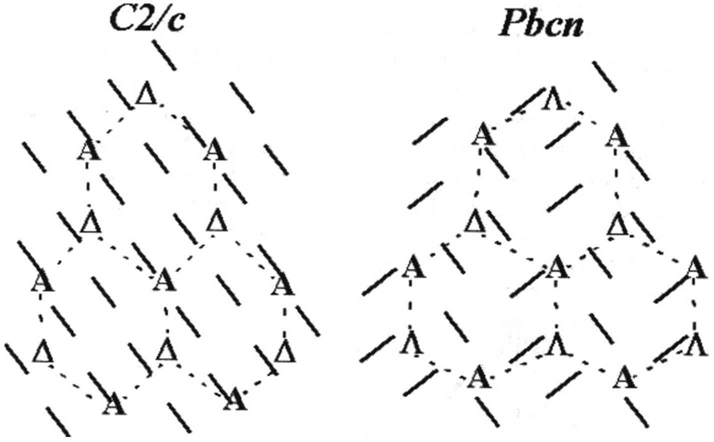

FIGURE 3 Relation between BEDT-TTF donors (thick layers) and anionic honeycomb layer for (left) C2/c and (right) Pbcn phases of (BEDT-TTF)$_4$[AM(C$_2$O$_4$)$_3$]PhCN [9].

example if the A cation is chiral) then the structure propagates as a helix instead of a layer.

The extensive series of layer charge transfer salts with the general formula (BEDT-TTF)$_4$[AM(C$_2$O$_4$)$_3$]G, where $A = H_3O^+$, NH_4^+, K^+; M = Cr, Fe, Ga, Al; G = guest molecule, provides an excellent example of the influence of anion chirality on the packing of the donor layer. Two phases are known, in one or two cases even for the same combination of A, M, and G. The monoclinic (C2/c) phase has a β'' packing of the BEDT-TTF while an orthorhombic one (Pbcn) has a completely different donor packing consisting of orthogonally arranged dimers (whose bond lengths confirm a charge of $+1$) surrounded by monomers with zero charge. Hence the properties of the two phases make a startling contrast: the C2/c ones are superconductors, while the Pbcn ones are insulating. So what is the difference between the anion layers that produces such a difference in the packing of the donor layer? In fact both layers consist of a near-hexagonal array of alternating A and M, with one $C_2O_4^{2-}$ between each A-M pair, and the G molecule occupying the centre of each hexagon. However it is the distribution of the Λ and Δ stereoisomers of the *tris*-oxalato-anions that differs. As noted already, in the C2/c phase, each anion layer consists of $[M(C_2O_4)_3]^{3-}$ of the same chirality, alternating between layers. On the other hand, the Pbcn have Λ and Δ within each layer arranged in alternate rows. That small but crucial difference changes the arrangement of O atoms on the 'surface' of the layer and hence (via the weak H-bonds already mentioned) the preferred donor packing (Fig. 3). In parenthesis, this appears to be the only example known at present of polymorphism arising from different spatial arrangements of the chiral enantiomers in a racemic crystal [12].

The Role of Guest Molecules

Compounds of the kind described in the last section incorporate a wide variety of guest molecules G within the relatively rigid cavities generated by the A^+ and $[M(C_2O_4)_3]^{3-}$ and, for a given A and M, the physical properties can vary substantially with G. For example, in the C2/c phase the superconducting T_c falls from 6.5 K to less than 1 K on replacing nitrobenzene with pyridine for $A = H_3O^+$, $M = Cr$. Furthermore, compounds with the same space group but $G = CH_2Cl_2$ [13] or DMSO [14] are not superconducting at all, but show localisation at low temperature, although they are metallic at room temperature. The reason for these differences lies in quite subtle changes in the donor layer brought about by steric factors at the interface between the organic and inorganic layers.

Chronologically the first superconductor in the series, with $A = H_3O^+$, $M = Fe$, $G = C_6H_5CN$, shows monotonically decreasing resistance from room temperature down to T_c (8.3 K) [3]. It has a fully ordered structure at all temperatures. In all the other cases we have investigated the temperature dependence of the normal state resistance is far from monotonic. For $A = H_3O$; $M = Fe$, Cr, Ga; $G =$ pyridine below room temperature, the resistance falls as in a metal, then rises to a maximum around 60 K before falling again [15,16]. At temperatures below 4 K these materials undoubtedly exhibit well-defined Fermi surfaces, in spite of the non-monotonic behaviour of the resistance at higher temperatures, because the magneto-resistance shows stray Schubnikov-de Haas oscillations [17]. Refinement of the crystal structures as a function of temperature shows that there is disorder in the conformation of the terminal $-CH_2CH_2-$ in one of the four crystallographically inequivalent BEDT-TTF in each unit cell, in fact the one which is situated closest to the pyridine. The disorder resides in two equivalent orientations of the C−C bond, corresponding to eclipsed and staggered conformations with respect to the two ends of the molecule. Even at 60 K the disorder is still present, and must therefore be considered as static.

In contrast to the pyridine adducts, the corresponding salts containing $C_5H_5NO_2$ show disorder in the BEDT-TTF methylene groups that is temperature dependent, so at low temperature the phases are ordered (Fig. 4). In that case the resistivity still has a minimum,

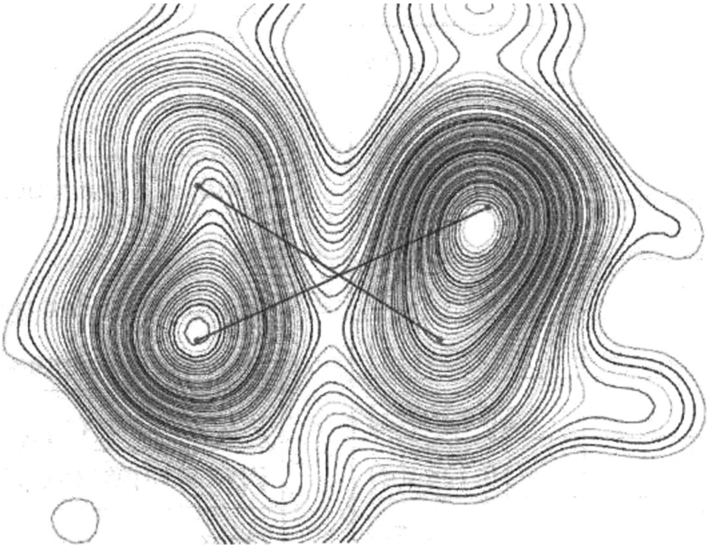

FIGURE 4 Disorder of the –CH2CH2– group of one of the BEDT-TTF in (BEDT-TTF)$_4$[(H$_3$O)Ga(C$_2$O$_4$)$_3$]PhNO$_2$ [24].

though at lower temperature than the pyridine-containing compounds. However, the rising resistance with decreasing temperature below this minimum does not lead to a maximum, but directly into a superconducting transition, as shown in Figure 5. The resistance in the neighbourhood of the transition to superconductivity is nearly 10 times that at room temperature, a remarkable result. Again, Schubnikov-de Haas magneto-resistance oscillations confirm that there is a well-defined Fermi surface at low temperature [18], while susceptibility measurement indicates a substantial (>30%) superconducting volume fraction in a poly-crystalline sample. Equally remarkable is the value of the upper critical field. At 32 T, for fields directed perpendicular to the superconducting planes, it is very much higher than found in any other BEDT-TTF salt with β″ packing.

Conversely, when the guest molecule G fits less tightly in the hexagonal cavity of the oxalato-lattice (for example molecules not containing aromatic rings), not only is G itself disordered, but the disorder in the conformation of the terminal methylene groups of the BEDT-TTF donor layer becomes even more pronounced. How subtle is the relation between organic and inorganic layers becomes evident when we observe that the one BEDT-TTF whose methylene groups are disordered are actually not the same one that is disordered in the pyridine adducts.

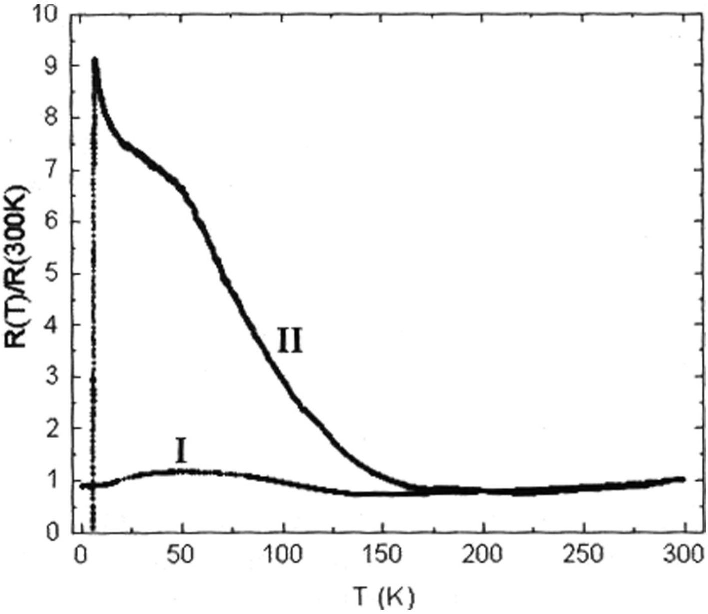

FIGURE 5 Temperature dependence of the resistance of β″-(BEDT-TTF)$_4$ [(H$_3$O)Ga(C$_2$O$_4$)$_3$]G with G = pyridine and nitrobenzene, from 2–300 K normalised to 300 K [16].

Nevertheless, the effect is analogous: an upturn in resistance at low temperature [16].

In general, therefore, it is clear that disorder (even in a part of the donor molecules that appears to have little to do with the orbitals forming part of the Fermi surface) exerts a dramatic effect on both the normal state and superconducting properties of 2D charge transfer salts. Structurally, such disorder is induced by chemically minor variations in the structure, such as changing included guest molecules.

SUPERLATTICES OF ORGANIC LAYERS

Up to this point the superlattices within the organic-inorganic salts that we have been considering have consisted of the organic and inorganic components, with the assumption that all organic or inorganic layers are the same, in other words that there are just two layer types repeating as ABAB.... In principle, however, there are many ways in which more elaborate stacking sequences could occur. Here we comment on just two that occur in the BEDT-TTF tris-oxalato-metallates.

They involve, on the one hand, different ways of packing the same molecules and, on the other, the packing of two different kinds of molecule. In other words, cases correspond to the stacking sequence ABCBABC..., the difference being whether the C layer is made out of the same molecules as A, or different ones. In the latter case we also introduce the additional phenomena of ionic conductivity alongside the metallic conductivity more characteristic of these salts.

Superlattices of Donor Molecules

In all the layer compounds dealt with so far, the two sides of the inorganic layer are the same and therefore, insofar as they steer the molecular assembly in the organic layers, the latter are also going to be the same. One way of making the inorganic layer unsymmetrical is to incorporate into it guest molecules that protrude differently on each side. So, in the $(BEDT\text{-}TTF)_4[AM(C_2O_4)_3]G$ series, G molecules like pyridine, benzonitrile and nitrobenzene lie with their phenyl rings equidistant from each side of the hexagonal cavities. On the other hand, if we make G unsymmetrical, either by adding tetrahedral C atoms, as in $C_6H_5CH_2CN$, or side-chains that are too big to reside completely inside the cavity, as with $C_6H_5N(CH_3)CHO$, the C_6H_5 group is displaced towards one side. Under these circumstances the steric requirements of the donor molecules are different on each side of the layer, so a superlattice of packing motifs develops. Cases known to date with $A = H_3O^+$; $M = Ga$; $G = C_6H_5CH_2CN$, $C_6H_5N(CH_3)CHO$ and $C_6H_5CONH_2$ consist of alternating α and β'' packing (Fig. 6) [19].

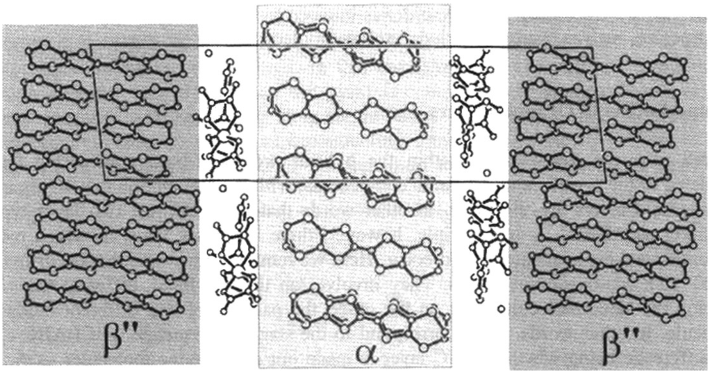

FIGURE 6 Superlattice packing of α and β'' donor layers in $(BEDT\text{-}TTF)_4[(H_3O)Ga(C_2O_4)_3]\cdot PhCH_2CN$ [19].

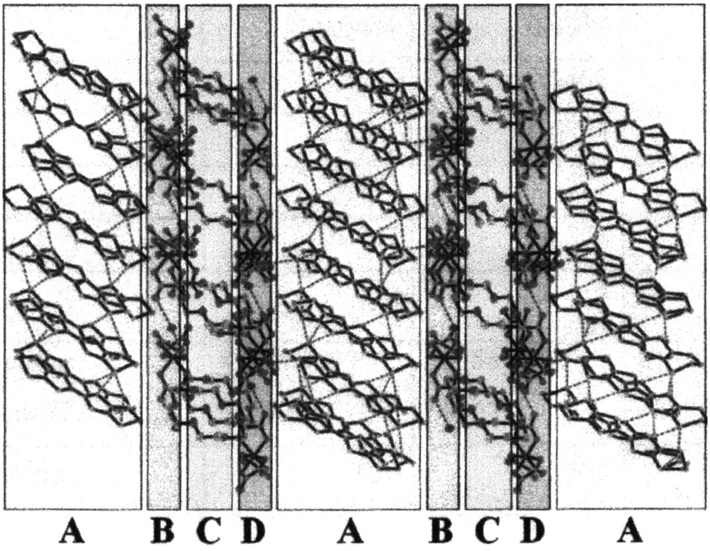

FIGURE 7 Packing sequence of layers in β″-$(BEDT\text{-}TTF)_4[(H_3O)M(C_2O_4)_3]_2$. (18-crown-6) · $(H_2O)_5$ [24].

Superlattices of Donors and Other Molecules

An early example of alternate layers of donor molecules and crown ether was found in (TTF)$[Cr(NCS)_4$bipyrim]18-crown-6, [20], although the physical properties of this compound are not of great interest because of the TTF form closed shell dimers and the Cr(III) interact antiferromagnetically only weakly. Of much greater interest are the series β″-$(BEDT\text{-}TTF)_4[(H_3O)M(C_2O_4)_3]_2 \cdot (H_3O)$(18-crown-6)$(H_2O)_5$ (M = Cr, Fe, Ga) (Fig. 7) [5,21,22]. Here the C-layer consists of parallel channels formed from 18-crown-6 stacked one above the other with an H-bonded network consisting of a mixture of H_3O^+ and H_2O along the centre (Fig. 8). Thus the crown ether molecules constitute a kind of 'pipe'. Not only is this structure highly unusual for a molecular charge transfer salt, but it also points towards the possibility of simultaneous conduction by electrons and protons. In fact, as anticipated, from the β″ packing motif, the compounds are indeed metallic at room temperature, with quite high conductivities (Cr 300, Fe 200, Ga 500 $S\,cm^{-1}$), though below about 200 K the resistance increases. The anion layers are essentially the same as those found in the superconductors, with the hexagonal cavities partly occupied by $-CH_2CH_2-$ groups from the crown ether. This combination of two molecular

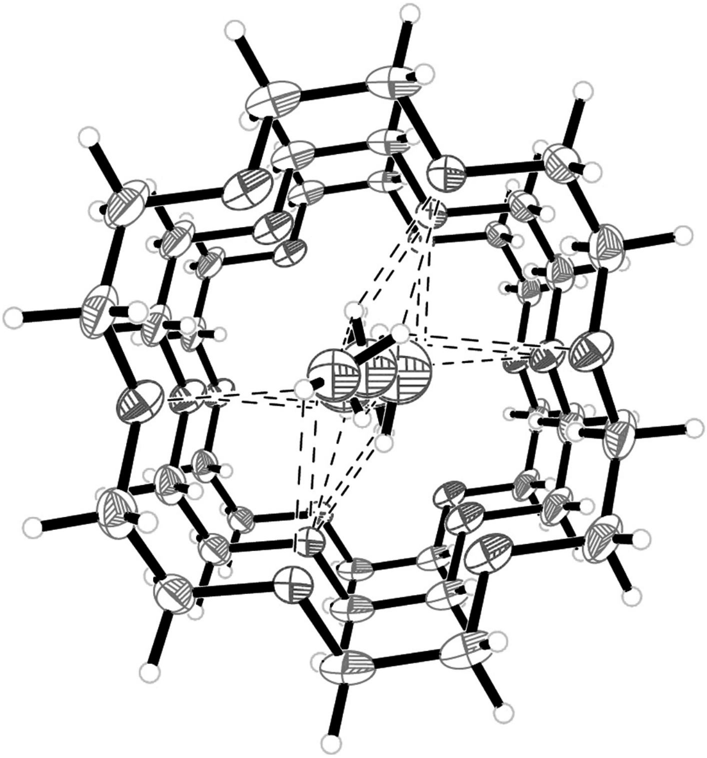

FIGURE 8 Chain of water molecules within the crown-ether 'pipe' in the compound shown in Fig. 7 [5].

conducting arrays, one electronic and the other ionic, is reminiscent of the Li(18-crown-6)[Ni(dmit)$_2$] salts reported by Nakamura [23]. It appears that we are seeing here the beginning of a new level of complexity in structures of organic-inorganic layer salts, offering the opportunity to combine two types of charge transport not previously found in this class of solid.

CONCLUSIONS

In this article we have used a specific family of organic-inorganic hybrid compounds, the conducting charge transfer salts of BEDT-TTF with *tris*-oxalato-metallates, to emphasise numerous subtle effects that can occur when one or other of the layers contains chiral components or guest molecules. In some cases the physical properties, such as superconductivity or magnetic ordering, are very strongly affected by what appear to be tiny changes in the chemistry, such as the addition of a single $-CH_2-$ group to a chain or the spatial disposition of two chiral enantiomers. Such sensitivity reminds us of analogies with large biological molecules. As the science of molecular electronics (now more than 20 years old) moves into technology, there will be an increasing need to enlarge the materials base beyond the simplest prototype conducting solids towards more precisely and elaborately engineered systems. The case made here is that organic-inorganic hybrids are a class of material that strongly merits consideration for their range and specificity of properties.

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