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Coordination complexes in two dimensional magnets and superconductors

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Contents

Abstract

Traditionally coordination chemists have been concerned with tailoring the properties of metal ions by modifying the ligand arrangement around single centres or small groups of ions. However, over the last 10 years or so, the properties of ordered infinite aggregates of metal ions, connected by bridging ligands, has come to the fore as a subject for synthetic study. As in classical coordination chemistry the local electronic structure at the metal ion remains important but the connectivity of the lattice and the nature of the bridging groups tuning the intermetallic interactions are vital in determining the properties of the bulk

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material. This lecture concentrates on those features of molecular-based magnets that are unique to the molecular nature of the lattice, such as connectivity and chirality.

Keywords: Intermetallic interactions; Superconductors; Two dimensional magnets

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1. Introduction

There are many reasons for synthesising lattices that exhibit long range magnetic order out of molecular building blocks (or what Kahn has called 'bricks'[1]). One is that the resulting materials will be processable in quite different ways from conventional ionic or metallic continuous lattices: thus a magnet soluble in organic solvents, or in water, would have many worthwhile applications. Another reason is to bring together two or more physical properties that are not normally found together in the same material. For example 20 years ago we made the first ferromagnetic compounds showing substantial optical transparency in the visible spectrum and found that their colour changed dramatically when they passed through the Curie temperature [2].

Other properties that only occur in lattices made of complex (i.e. molecular) rather than elementary (atomic or ionic) 'bricks' are mesomorphism and chirality. Although neither chiral nor mesomorphic magnets have yet been realised experimentally, steps towards the former are described later on. Finally we try to understand the magnetic ordering mechanism and to use chemistry to create novel forms of magnetic order. Here, the greatly enlarged possibilities of packing together metal complexes rather than spherical ions leads to beautiful new architectures that challenge theories of frustration, ground state symmetries, critical behaviour etc.

Crucial to making a long range ordered system is the question of connectivity, i.e. the number and arrangement of interaction pathways between neighbouring complexes with localised moments. In this article I will concentrate on two-dimensional lattices to simplify the topology, but the variety is still quite large. Since the interaction mechanism between localised moments connected through a chemical bonding pathway is superexchange, it is strictly speaking not only the connectivity between atoms that we should be considering, but connectivity between orbitals. This point is important when we realise that a crucial factor determining ferromagnetic exchange is the orthogonality of adjacent magnetic orbitals. One aspect of connectivity that has not been discussed very widely up till now is that of chirality. Whilst chiral magnetic order is known in quite a number of compounds where the underlying crystal lattice is not chiral [3], it is only in molecular-based magnets that we can investigate the consequences for magnetic ordering of a chiral crystal lattice. From a structural point of view, chirality can arise in two ways: either the molecular 'bricks' are themselves chiral, or achiral 'bricks' could be arranged to make a chiral lattice. This point will be developed further later on.

The final point to be dealt with concerns conductivity. Whilst many continuous lattices are metallic, very few crystalline metal complexes showing long range magnetic order are metals, although molecular-based metals (and even superconductors) have been known for many years [4]. Nevertheless, among the extensive family of BEDT-TTF (bisethylenedithiotetrathiafulvalene) charge transfer salts, we have found examples of antiferromagnetic metals (i.e. spin density waves) [5], a ground state that is extremely uncommon in close packed lattice materials. One route to introducing magnetic states into molecular-based metallic compounds is to ensure that the magnetic orbitals are of a different type, as well as being spatially segregated, from those forming the conduction band. That objective can be achieved by forming charge transfer salts from metal complexes with open d-shells, as we shall describe below.

2. Connectivity

2.1. Planar nets

Connectivity is a powerful concept because it defines the way a set of points connect to build a lattice which is infinite in one to three dimensions, like a crystal. Whilst the rules of planar or solid geometry yield ideal polygons or polyhedra, topological rules of connectivity are robust on lowering the symmetry, as often found when molecules pack together.

In two dimensions, there are only three regularly connected nets [6]. By 'regular' we mean a network which not only has the same number of neighbours at each site, but where there is only one kind of polyhedron in the net. For 3-connected planar nets, we have a hexagonal arrangement, while the 4-connected one corresponds to a net made up of quadrilaterals (N.B. not necessarily squares) and regular 6-connected nets are an array of triangles (again, not necessarily equilateral). The most symmetrical forms of these three regular networks are shown in Fig. 1. In two-dimensions, examples of metal complexes are found with 4- and 3-connected nets. Here I want to use examples from our own work to illustrate how the long range magnetic order is established, and how sensitive it is to the packing of the metal-organic limits.

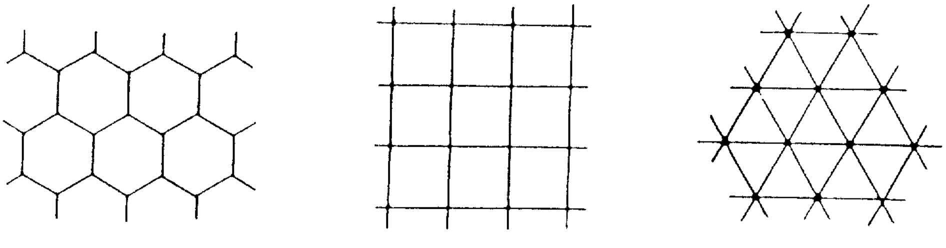

Fig. 1. The three regular planar nets, from left to right: 3, 4 and 6-connected.

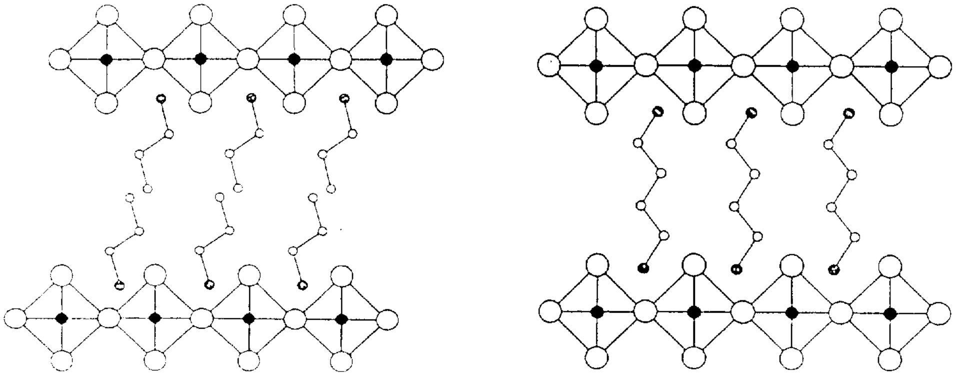

Fig. 2. Alternating organic and inorganic layers in perovskite halide salts: left hand side $(C_3H_7NH_3)_2MX_4$; right hand side $(H_3N.(CH_2)_4NH_3)MX_4$. Black circles are M, hatched NH_3, small empty C, large empty X.

2.2. 4-Connected lattices

Compounds with the general formulae $(RNH_3)_2MX_4$ or $(H_3N.R.NH_3)MX_4$ have structures related to the K_2NiF_4 structure, where the $[NiF_4]^{2-}$ layer consists of NiF_6 octahedra linked through all their equatorial vertices [7]. The molecular cations occupy the cavities between the layers, as shown in Fig. 2 [8]. If the octahedra are regular, the anion layer is not molecular, but in the ferromagnetic Cr(II) and Cu(II) compounds a cooperative Jahn–Teller distortion of the halide ions within the equatorial plane leads to alternating short and long M–X bonds. Thus the structure can be viewed as consisting of planar MX_4 molecules with their planes perpendicular to the layer and with the planes of neighbouring molecules at right angles to one another. For example, the Cr–Cl distances in the tetrachlorochromates(II) are 2.39 and 2.87 Å. Projections of two such structures (Cu(II) and Cr(II)) on to the basal planes are shown in Fig. 3 [8,12]. As described previously [9–11] the near orthogonality between the magnetic orbitals on adjacent centres gives rise to ferromagnetic exchange in these compounds, yielding T_c's of 6–8 K for the $S = 1/2$ Cu(II) series and 35–60 K for the $S = 2$ Cr(II).

Another kind of 4-connected net that we have been studying in the last few years is found in the alkyl- and alryl-phosphonate salts of divalent 3d elements, where the phosphonate group has 3-fold symmetry, but forms a distorted square lattice of metal ions by chelating to one while coordinating to a neighbour. In this way each $-PO_3$ connects three metals, a strongly distorted octahedral coordination around each metal being completed by a water molecule to give the overall formula $(RPO_3)M.H_2O$ (Fig. 4) [13].

The average magnetic structures of these compounds are antiferromagnetic, but because the site symmetry at the metal site is so distorted (C_2) and there is no mirror plane between neighbours, the Dyaloshinski–Moriya exchange mechanism operates and the structures are actually canted, giving rise to weak ferromagnetic behaviour. In fact, for a series of *n*-alkyl substitutents C_1–C_4, T_N does not vary monotonically with chain length, but alternates [14]. This is because the terminal $-CH_3$ groups in the alkyl chains mesh together differently depending on whether the chain contains an odd or even number of C atoms, yet another example of the subtle effects of molecular packing on the magnetic behaviour of molecular-based magnets.

2.3. 3-Connected lattices

So called honeycomb lattices (Fig. 1, left hand side) are not very common in inorganic chemistry although we commented some years ago on the structures and magnetic properties of the family of ternary transition metal arsenates $A^IM^{II}AsO_4$ (A = Group 1 cation or RNH_3^+; M^{II} = Mn, Fe, Ni) which are related in an interesting way to the silicate micas and which, like the micas, can be exfoliated and intercalated [15,16]. The honeycomb structure can support several long range ordered magnetic structure types, depending on the ratios of first to second and first to third near neighbour exchange constants, and whether the single ion anisotropy is of Ising or xy-type [17]. Simplest among these are the purely ferromagnetic (which has never actually been observed) and Ising antiferromagnetic, i.e. with moments perpendicular to the layer. However, an even more extensive series of

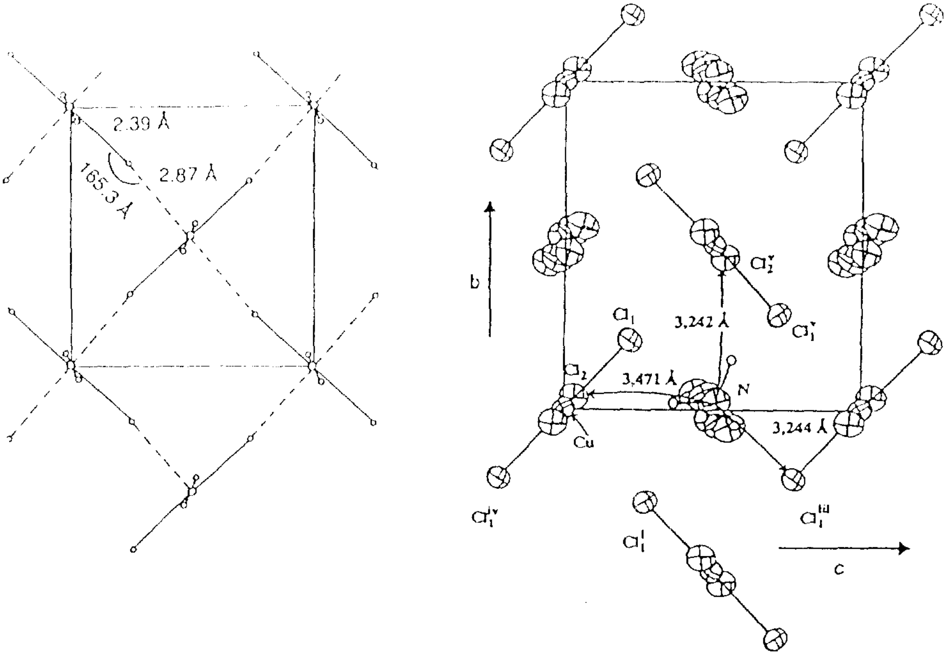

Fig. 3. Layer salts showing cooperative Jahn–Teller distortions: left hand side $(H_3N(CH_2)_3NH_3)\ CrCl_4$ [12]; right hand side $(H_3N(CH_2)_4NH_3)\ CuCl_4$ [8].

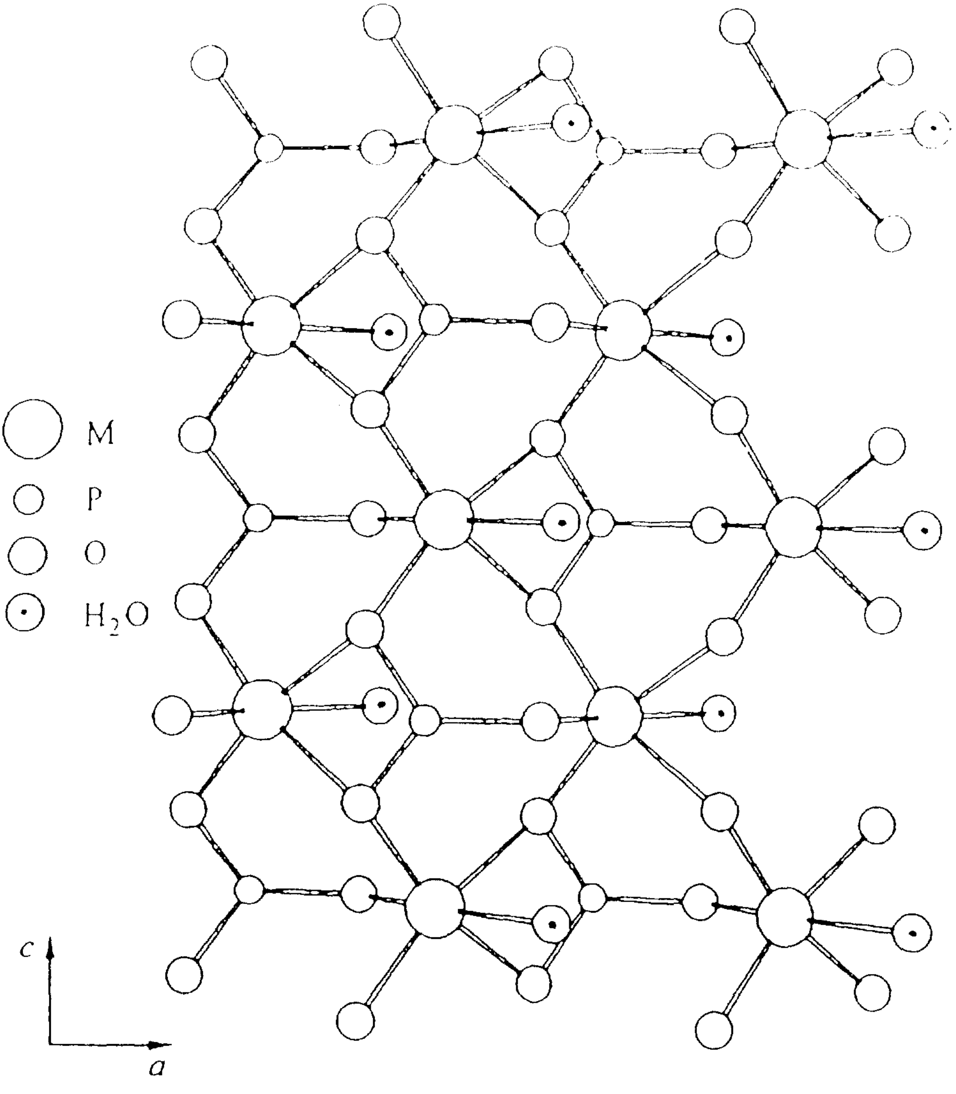

Fig. 4. The 4-connected net in the basal plane of $(RPO_3)M.H_2O$ [13].

honeycomb structures has come to light in the last few years in the form of the bimetallic tris–oxalato salts $A^{I}M^{II}M^{III}(C_2O_4)_3$ [18] (Fig. 5).

In the tris–oxalato salts the honeycomb is built from alternate M and M′ (which can be, but usually are not, the same metal) bridged by ambidentate oxalate anions. Each metal ion site therefore has trigonally distorted octahedral coordination (see Section 3). For ions with significant ground state anisotropy the latter is crucial in determining the magnetic order and is itself strongly influenced by the size and shape of the organic cation A [19]. As in the 4-connected lattices, the packing of A (and, in particular, how it nests into the cavities in the anion layer) determines the fine detail of the electronic ground state because of the way it lowers the symmetry of the metal ion site. This is shown clearly in the structures of the two compounds $N(C_nH_{2n+1})_4$ and $MnFe(C_2O_4)_3$ where $n = 3$ or 5 [20,21]. In the C_3 compound, the N is centred above the hexagonal cavity, with one alkyl chain descending into it and the remaining three occupying the interlamellar space while in the C_5 one, the N atom lies above one side of the hexagon (Fig. 5, left hand side). One alkyl chain points sideways into the cavity and another points upwards into a cavity in the next layer, leaving two chains in the interlamellar space (Fig. 5, right hand side). Also, in the C_5 compound the terminal C–C bond in each chain is in the *gauche* conformation to maximise the space filling. Indeed, it is significant that among tetra-*n*-alkylammonium cations from C_1 to C_{10}, only C_3–C_5 form bimetallic tris–oxalato-salts, although with unsymmetrically substituted cations such as $P(C_6H_5)_3$ $(n\text{-}C_nH_{2n+1})$, compounds are formed up to $n = 7$ [22]. As a result of the different positions of the cations, the tetra-*n*-pentylammonium salt is orthorhombic (*Pbcn*) while the tetra-*n*-propylammonium one is rhombohedral (*R*3*c*).

The existence of varied stacking sequences is endemic in layer compounds, and the bimetallic tris–oxalates are no exception. The commonest ones correspond to ABAB.... ($P6_3$) or ABCABC.... (*R*3*c*), and according to the method of crystallisation, more or less faulted structures are obtained, which consist of intergrown domains of both sequence types [23]. An additional complication, chirality of each layer, is dealt with in Section 3.

3. Chirality

The simplest definition of chirality in a molecule or a lattice is that it cannot be superposed on its mirror image. Structural chirality has important consequences for the macroscopic physical properties principally through optical activity. Since no

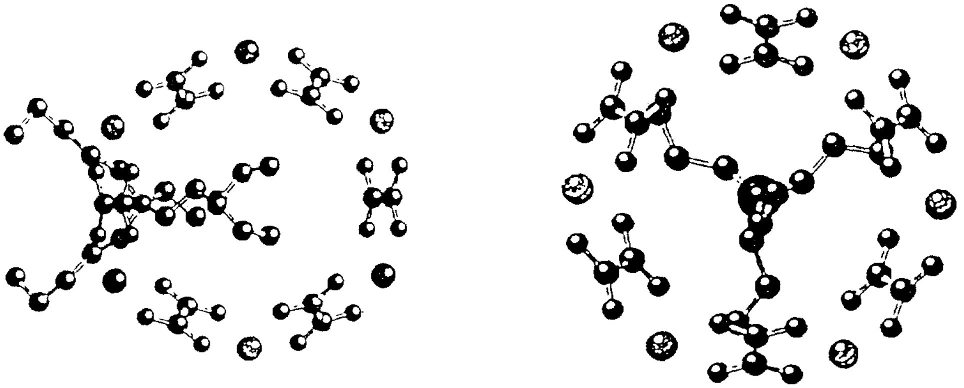

Fig. 5. Arrangement of the organic cations relative to the complex anion layers in $N(n\text{-}C_nH_{2n+1})_4$-$MM'(C_2O_4)_3$: left hand side, $n = 5$; right hand side, $n = 3$.

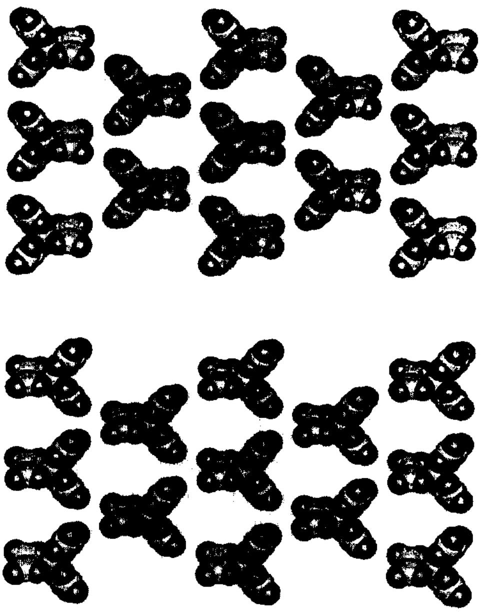

Fig. 6. Layers of tris–oxalato-ferrate(III) anions in β''-(BEDT-TTF)$_4$[(H$_3$O))Fe(C$_2$O$_4$)$_3$]C$_6$H$_5$CN.

one has yet made a magnetically ordered solid that is structurally chiral, we cannot discuss the physical consequences of any magnetic chirality that might be introduced in this way. However, chiral magnetic structures have been known in achiral crystal lattices for some time. In those cases though, the crystal consists of domains of equal volume and opposite chirality [3].

A crystal lattice may be chiral either because the constituent molecules are chiral, or because of the arrangement of achiral units; $K_3Cr(C_2O_4)_3.3H_2O$ is an example of the former and α-$NiSO_4.7H_2O$ of the latter. Here we indicate a few examples of how chirality can be introduced into lattices containing magnetic ions, and some of the structural consequences. The examples concentrate on 3-connected nets, specifically the tris–oxalato salts mentioned in Section 2.3.

Neglecting any lowering of symmetry that may arise from the packing of the organic cations, the site symmetry of the $M(C_2O_4)_3^{3-}$ in Fig. 6 is D_3, i.e. a chiral point group. A two-dimensional net can only be obtained in such a case if all the M sites are Λ and all the M′ are Δ. Since the M and M′ are distinguishable, the effects of the opposite handedness will not cancel. However, there is a crucial difference between the packing of the layers in compounds which are synthesised from racemic or chiral starting materials. If the preparation is carried out with racemic $Cr(C_2O_4)_3^{3-}$ the product contains alternate layers consisting of Λ(M)Δ(Cr) and Δ(M)Λ(Cr). If, on the other hand, we start with preresolved material, then perforce the product must contain layers all of the same type, say Λ(M)Δ(Cr).

Searching for magnetic molecular-based materials that are also conducting, we synthesised tris–oxalato-metallate(III) salts in which the organic cation is the organo–sulphur donor BEDT-TTF (see Section 4) and find two different fashions of incorporating the chiral anions into an ultimately racemic lattice. The compound β''-(BEDT-TTF)$_4$[(H$_3$O))Fe(C$_2$O$_4$)$_3$]C$_6$H$_5$CN is the first molecular superconductor containing paramagnetic metal centres, an important precedent because of the conflict between superconductivity and magnetism in solids [24]. The crystal consists of alternating layers of BEDT-TTF within which the cations form stacks and layers of anions and solvent molecules very similar to that found in the bimetallic tris–oxalate-salts [25]. If, however, the H_3O^+ is replaced by a cation such as K^+ or NH_4^+, the resulting compounds are semiconductors although superficially at least, the hexagonal arrangement of the anion layer is almost the same.

However, in fact there is a most significant difference. The compounds are racemates, so the lattices contain equal proportions of Δ and Λ configurations of $Fe(C_2O_4)_3^{3-}$, but the enantiomers are distributed in different ways. In the superconducting compound, which is monoclinic (*C*2/*c*), alternate layers consist of only Λ or Δ molecules (Fig. 8); in the semiconducting phase, on the other hand, which is orthorhombic (*Pbcn*), rows of Δ and Λ molecules alternate within each layer (Fig. 9). In consequence, the site occupied by the M^+, though surrounded by six O atoms from oxalate anions in both cases, has quite a different symmetry from that found in the monoclinic phase.

4. Conductivity

Magnetic exchange mechanisms in metallic lattices are fundamentally different from those in insulators, so it is of interest to synthesise molecular-based magnetic materials with high conductivity. Some hundreds of metallic molecular charge transfer salts have been synthesised and characterised over the last 20 years (see e.g. Ref. [4]) but only a very small minority of these contain ‘bricks’ with unpaired electrons. Among them, the BEDT-TTF salts with tris–oxalato-metallate(III) anions described in Section 3 are particularly significant, because the series contains the first examples of paramagnetic molecular superconductors. We referred above to the layers of chiral complex anions, we now turn to the corresponding packing of the organic donors.

4.1. Semiconducting compounds

Many different packing modes of the donor molecules have been identified in BEDT-TTF salts [26] and it is this great variety which leads to the wide range of physical properties observed. It has become clear that the most important factor driving this multiplicity of packing types is the docking of the BEDT-TTF on to the layers of anions. In some cases, where there are polymeric planar networks of anions, such as the $Cu(NCS)_2^-$ salt, it is the shape of the cavities in the anion network that orients the terminal-CH_2CH_2-moieties of the BEDT-TTF, leading (in that instance) to an array of orthogonally oriented face-to-face dimers [27]. In the present instance, we have the apparently paradoxical situation of two remarkably similar tris–oxalato-metallate(III) anion sublattices leading to two quite different BEDT-TTF packing types, and hence to totally different properties. In the series with general formula (BEDT-TTF)$_4$[AM(C$_2$O$_4$)$_3$]C$_6$H$_5$CN, five examples are known to date which crystallise in the *Pbcn* space group, with the anion sublattice illustrated in Fig. 7 [28].

The arrangement of BEDT-TTF molecules in the *Pbcn* phase is illustrated in Fig. 8. Analysis of the C–C and C–S bond lengths [29] reveals that half the BEDT-TTF are uncharged, while the other half, which form face-to-face dimers, carry a charge of + 1. From magnetic susceptibility measurements we find there is no contribution from the donor layer so the single unpaired electrons expected on each (BEDT-TTF)$^+$ are paired. The result, confirmed by band structure calculation [25], is a semiconductor. In seeking the reason for this unusual packing motif we focus on the interface between the donor and anion sublattices, and in particular on the terminal CH$_2$CH$_2$-moeities of the BEDT-TTF, together with the 'top' layer of O coming from the oxalate anions. The nesting of the H into pockets between the O is shown in Fig. 9.

4.2. Superconducting compounds

The second phase of (BEDT-TTF)$_4$[AM(C$_2$O$_4$)$_3$]C$_6$H$_5$CN, which crystallises in the *C*2/*c* space group, has been identified so far in (H$_3$O)Fe and (H$_3$O)Cr examples. The difference between the distribution of chiral anions compared with the semi-

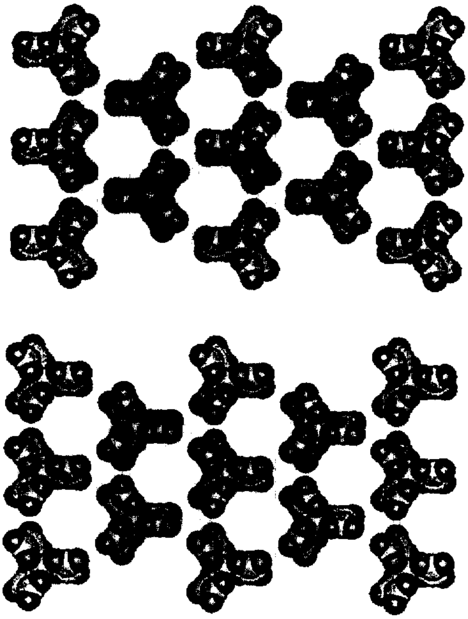

Fig. 7. Layers of tris–oxalato-ferrate(III) anions in (BEDT-TTF)$_4$[KFe(C$_2$O$_4$)$_3$]C$_6$H$_5$CN.

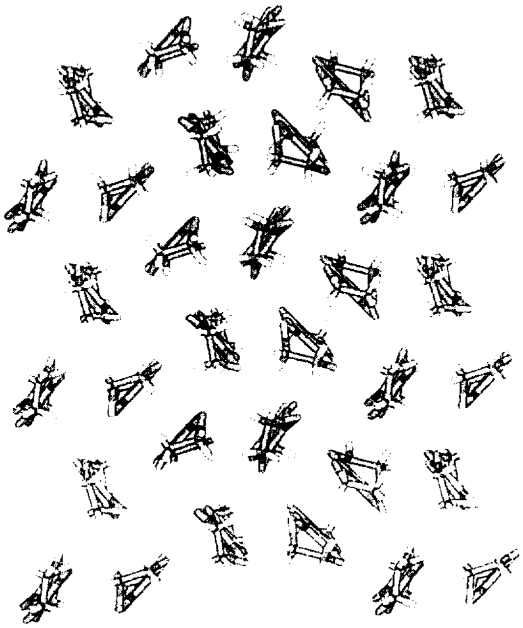

Fig. 8. The BEDT-TTF sublattice in $(BEDT\text{-}TTF)_4[KFe(C_2O_4)_3]C_6H_5CN$.

conducting phase transforms the packing of the donor layer, inducing a stacked arrangement of BEDT-TTF [26]. From this particular polymorph came a large number of superconducting phases, for example the I_3 and AuI_2 salts [30], so it is not a surprise that the tris–oxalato-metallate(III) salts with this structure are also superconducting. The Fe salt has $T_c = 8$ K while the Cr one has T_c 6 K and a smaller critical field [31]. All the anions in each layer now have the same chirality

Fig. 9. The nesting of H (small circles) and O (large circles) in $(BEDT\text{-}TTF)_4[KFe(C_2O_4)_3]C_6H_5CN$.

(Fig. 8) so the network of terminal O atoms on the oxalate ions is quite different from that of the orthorhombic phase.

5. Conclusions

The limited number of examples that have been described here reveal that layers of magnetic ions in transition metal complexes [32] organise into 3- and 4-connected nets to give a variety of long range-ordered systems. The organisation of the organic molecules around the layers of coordination complexes is crucially directed by the latter, even in such subtle aspects as the spacial distribution of chiral enantiomers. Upon the packing of the organic counterion depends whether the crystal is superconducting or semiconducting. No doubt further subtleties of supramolecular organisation await us as we continue to explore these unusual coordination complexes.

Acknowledgements

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