
The Bakerian Lecture, 1999

The molecular chemistry of magnets and superconductors

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Only recently have magnetism or superconductivity been associated with molecular compounds. Observing these properties in molecular-based lattices has brought chemistry to bear on the relation between crystal structure and physical properties. Recent work from The Royal Institution is used to identify features associated with the molecular-based materials that distinguish them from conventional continuous lattice solids, and which are unique to molecular solid state.

Keywords: magnetic materials; organic magnets; metal-organic solids;
superconductors; molecular materials

1. Introduction: conducting and magnetic molecular compounds

In the 224 years since its inauguration, the Bakerian Lecture has quite frequently taken as its subject matter work performed at The Royal Institution. Indeed, in the more expansive days of the early 19th century, Humphrey Davy gave no fewer than five such lectures, exceeded only by our Institution's most famous son, Michael Faraday, who gave six! In the year of its bicentenary, it is therefore particularly appropriate to survey a topic which, while its gestation goes back more than 20 years, has formed the principal activity of my own research group at The Royal Institution. Especially apposite, too, is the fact that it concerns both magnetism and conductivity, subjects that have long pedigrees in the Albemarle Street laboratories. For example, by his discovery of potassium, set out in one of his Bakerian Lectures (Davy 1808), Davy overturned at a stroke the conventional view of metals, since the material he described was both low melting and chemically extremely reactive. Likewise, the metals described in the present lecture are quite unconventional, being soft molecular crystalline compounds obtained from organic solvents at room temperature. Some contain solvent molecules, including water, trapped within their crystal lattices, or have chiral or magnetic centres as an integral part of their structures.

(a) *Conductivity in molecular crystals*

Of all the physical properties characterizing condensed matter, electrical conductivity is the one spanning the largest number of orders of magnitude, from the most

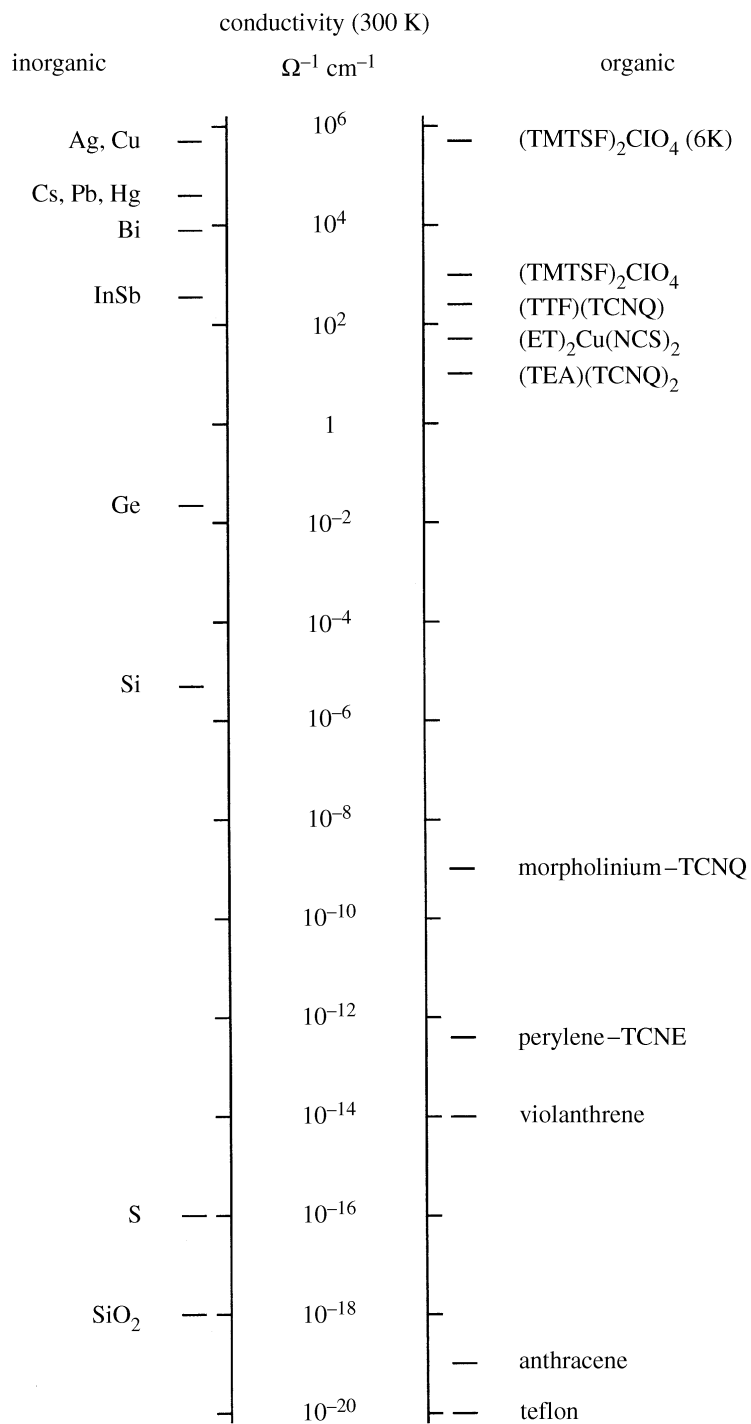


Figure 1. Room temperature specific conductivities (S cm^{-1}) of representative inorganic (left hand) and molecular organic (right hand) solids.

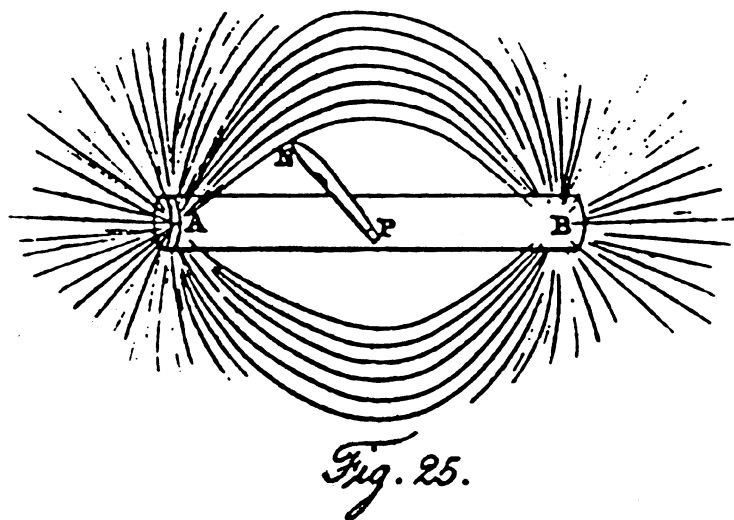


Figure 2. Lines of magnetic flux around a bar magnet (from Faraday 1832).

highly conducting metals to the most insulating solids. It may therefore appear surprising at first sight that, over the last two decades, chemical synthesis has led to the discovery of many molecular solids with room temperature electrical conductivities spanning as wide a range as those of more conventional metals, semiconductors and insulators. The left-hand side of figure 1 indicates specific conductivities at room temperature for various examples of structurally simple solids, most of them elements, whose properties have long provided paradigms of the metallic, semiconducting and insulating states. Nearly all are continuous lattice materials. In contrast, on the right-hand side of figure 1 we see a series of chemical formulae whose initial characteristic, compared with those on the left, is that they are much more complicated. Indeed most of the formulae would not be recognizable immediately by chemists, since they are based on abbreviated acronyms invented largely by physicists interested by their properties but unable to handle the complexities of the correct chemical nomenclature. Thus we have a parable of the circumstance, quite often found in science, that a topic may start by being multidisciplinary, but has further steps to take before it can properly be said to be interdisciplinary. Compounds with the highest conductivities are of two types: charge transfer complexes, consisting of an electron donor and acceptor, and charge transfer salts, typically containing an electron donor molecule in the form of a cation and an inorganic anion. The examples that we have prepared and characterized are all of the latter type. Uniting all these compounds is the observable characterizing the metallic state first pointed out by Davy in another of his Bakerian Lectures (Davy 1821), namely a negative temperature coefficient of conductivity. As Davy himself put it, 'The most remarkable general result that I obtained by these researches ... was that the conducting power of metallic bodies varied with the temperature and was lower in some inverse ratio as the temperature was higher'.

(b) *Magnetism in molecular crystals*

A quite analogous evolution, in which the role of solid state chemistry has become progressively more marked, can be seen when we examine the history of magnetic

materials. It is also a story in which The Royal Institution played a key part in the 19th century. When Michael Faraday (1832) published the first illustration of the lines of magnetic flux around a magnet (figure 2), there can be no doubt at all that the cylindrical bar in the picture was of iron, since, apart from the discovery of lodestone millennia previously, that was the only practical magnetic material available at the time. The 160 years since Faraday's picture have seen a veritable explosion in the number and variety of solids showing spontaneous magnetization below some critical temperature, from the ferro- and ferrimagnetic oxides whose synthesis created the challenge taken up in Néel's molecular field model to the most recent ferromagnets that contain no metallic elements at all, and whose ordering mechanism remains a subject of theoretical debate.

Most of the magnetic solids synthesized by chemists of the past 40 years have not been metallic conductors (certainly not the metal-organic and organic materials that constitute the burgeoning subject of 'molecule-based magnetism' surveyed recently at a Royal Society Discussion Meeting (this issue) and a series of biennial international conferences (*Proc. Int. Conf. Mol. Magnets, Mol. Cryst. Liq. Cryst.*)). Here, the presence of ordered localized moments in an insulating lattice gives rise to numerous properties quite distinct from those of metallic (or itinerant) magnets. Not only are such materials frequently soluble in organic solvents, or even water, but their optical properties are quite unusual: it is over 20 years since we showed that the transparent ferromagnet $(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$, soluble in ethanol, changed colour visibly from green to yellow on passing through the Curie temperature near 40 K, because excitons arising from spin-forbidden ligand field transitions gained intensity by coupling to spin-waves propagating in the two-dimensional ferromagnetic lattice (Bellitto & Day (1978); for a review see Bellitto & Day (1992)).

(c) *Chemically constructed multilayers*

The present brief account cannot hope to survey all the remarkable variety of conducting and magnetic compounds synthesized by chemists (or even by our own group) over the past 20 years. Rather, by selecting a small number of examples prepared and studied at The Royal Institution in the last few years, my aim will be to illustrate a few of the unusual structures and unlooked for properties emerging from the application of supramolecular chemistry to collective electronic properties. To focus matters still further, most of the compounds chosen have strongly developed low-dimensional character, usually expressed by the presence of alternating layers of organic and inorganic material. What we have called 'organic-inorganic composites' (Day 1985) or 'chemically constructed multilayers' (Day 1990) (to distinguish them from the physicists' multilayers laid down by molecular beam epitaxy) combine many of the physical properties of both classes of solid, with the added subtlety that the organization of molecules within the layers (and hence of the interactions determining the collective electronic behaviour) depends crucially on the interfaces with the neighbouring layers. Quite small variations in the chemistry result in major changes in physical properties.

2. Metal-organic and organic molecular magnetic compounds

In this section, three distinct chemical systems are described, in each of which a spontaneous magnetization is found arising from three quite different physical mech-

anisms. In each case, too, we identify features of the magnetic behaviour peculiar to the molecular nature of the lattice.

(a) *Organophosphonato-metal(II) salts: canted antiferromagnets*

It is far from easy to construct insulating lattices from molecular building blocks that exhibit ferromagnetic exchange between neighbouring localized moments because, following the classical models of Anderson (1963), Kanamori (1959) and Goodenough (1955), it is necessary to engineer the alignment of adjacent units so that the orbitals bearing the unpaired electrons are orthogonal. Based on antiferromagnetic superexchange between localized moments, mediated through polyatomic bridging ligands, an easier task is to organize a lattice in which adjacent moments are not exactly antiparallel, but make a small angle to one another so that the resultant is a weak ferromagnetic moment (sometimes also called canted antiferromagnetism). This situation arises when the site symmetry of the ions carrying the magnetic moments is low, and there is no centre of inversion between neighbouring sites (the so-called Dzialoshinskii–Moriya mechanism (Dzialoshinskii 1958; Moriya 1960)). An excellent example of this phenomenon is provided by the organophosphonate salts of divalent 3d metals. They also exemplify one straightforward method of introducing molecular organic groups into a purely inorganic lattice.

The extensive series of ternary transition metal phosphate salts with general formula $A^I M^{II} PO_4 \cdot H_2O$ (A^I is either a Group 1 element or NH_4^+) already have well-defined layers of M^{II} coordinated to PO_4^{3-} and H_2O , forming approximately square arrays of M^{II} (Carling *et al.* 1995). By replacing one of the PO_4 atoms with an organic moiety, we arrive at the equally extensive series of organophosphonato-salts $RPO_3 M^{II} \cdot H_2O$. The R groups, which can be *n*-alkyl, aryl or other functionalized groups, extend outwards from the layers of M^{II} , $-PO_3$ and H_2O , replacing the A^I , and forming purely organic layers bound only by van der Waals interactions. Like the purely inorganic ternary phosphates, the organophosphonates are also weak ferromagnets, but with two significant differences (Carling *et al.* 1993). First, the magnitude of the ferromagnetic moment varies greatly with the organic group, increasing monotonically in the *n*-alkyl-sequence from C_1 to C_4 . Thus, we have a first instance where a change in the organic part of the lattice remote from the site of the atomic moments changes the bulk magnetic properties of the crystal. However, the second difference is even more surprising.

Naively, one might imagine that increasing the *n*-alkyl chain length, which increases the distance between the weakly ferromagnetic metal phosphonate layers, would bring about a corresponding decrease in the three-dimensional magnetic ordering temperature T_N which must be induced by interlayer interaction. On the contrary, however, T_N alternates; it *increases* from CH_4 to C_2H_5 decreasing again to C_3H_7 and increasing to C_4H_9 (Carling *et al.* 1993)! What have been called ‘alternation effects’ are well known in the structural chemistry of aliphatic molecular crystals, but this appears to be the first time such an effect has been detected in the bulk magnetism of such a solid. The most likely explanation is in the orientation of the terminal $-CH_3$ of the alkyl chain. Given that the P–C bond is almost perpendicular to the Mn–O plane, *n*-alkyl phosphonates containing odd numbers of C atoms in the alkyl group have terminal C–C bonds likewise perpendicular to that plane. On the other hand, the *n*-alkyl groups with even numbers of C atoms have terminal

C—C nearly parallel to the Mn—O plane, because of the tetrahedral C—C—C bond angles. Consequently, the $-\text{CH}_3$ groups mesh together differently in the two cases, transmitting a small variation in C—P—O angle to the plane of Mn, with consequent small modulation of the Mn—O—P—O—Mn superexchange pathway and hence the exchange constant between Mn neighbours. It is this exchange constant, which in turn determines the magnetic correlation length within each layer, whose build up with decreasing temperature provides the extended magnetic dipoles that interact across the organic molecular layer to bring about three-dimensional long-range magnetic ordering at T_N (Kurmoo *et al.* 1999). Thus, once again, a small change in an organic group remote from the locus of the moment has a significant influence on the bulk magnetic properties.

(b) *Nitronylnitroxides: purely organic ferro- and antiferromagnets*

A similar sensitivity of the electronic ground state to fine details in the molecular arrangement is found among the class of purely organic magnetic solids based on the nitronylnitroxide moiety. Until the early 1990s, all magnetic materials since the dawn of history, whether they were metallic conductors or not, had owed their magnetic properties to the presence of metal atoms within the structure, specifically to partly occupied d- or f-shells. Then Kinoshita and his colleagues (Tamamura *et al.* 1991) discovered ferromagnetism in a series of solids based on the stable, organic, nitronyl–nitroxide radicals containing only C, H, N and O, the first examples of ferromagnetism due to p-electrons. Although their Curie temperatures are extremely low (mostly below 1 K), in their bulk magnetic behaviour these molecular crystals are indistinguishable from other ferromagnets, for example, having internal fields increasing from zero to T_c to reach a saturation value as the temperature decreases. A very convenient and direct way of measuring the internal field is to record the zero field muon spin rotation (μSR), whereby positive muons are implanted in a sample and the angular asymmetry of their decay is observed using detectors in the forward and backward direction relative to the muon beam. The asymmetry arises because the magnetic moment of the muon precesses around the internal field, the precession frequency being a measure of the field strength. Typical μSR oscillations measured at the ISIS pulsed muon facility at the Rutherford Appleton Laboratory in a collaboration with colleagues in Oxford and Yokohama are shown in figure 3a, and the resulting temperature variation of the internal field in a nitronyl–nitroxide ferromagnet in figure 3b (Pratt *et al.* 1993).

Since Kinoshita's original discovery (Tamamura *et al.* 1991), many nitronylnitroxides have been synthesized to explore structure–property relations in this unusual class of magnet by systematically changing the organic substituent R attached to the nitronylnitroxide moiety. One example will suffice: when $R = 3\text{-quinolyl}$ (3QNNN) we find a ferromagnet, but for $R = 4\text{-quinolyl}$ (4QNNN) it is an antiferromagnet. The reason for the striking difference becomes apparent from the crystal structures (Sugano *et al.* 1993). Although the two substituents are very similar from an electronic point of view, the difference in the point of attachment of the quinolyl group to the nitronylnitroxide means that the molecules have quite different shapes and hence pack differently in their respective crystals. In 3-QNNN the axes of the O—N—C—N—O groups that carry the unpaired spins are approximately perpendicular suggesting the orthogonality between magnetic orbitals necessary for ferromagnetism, while

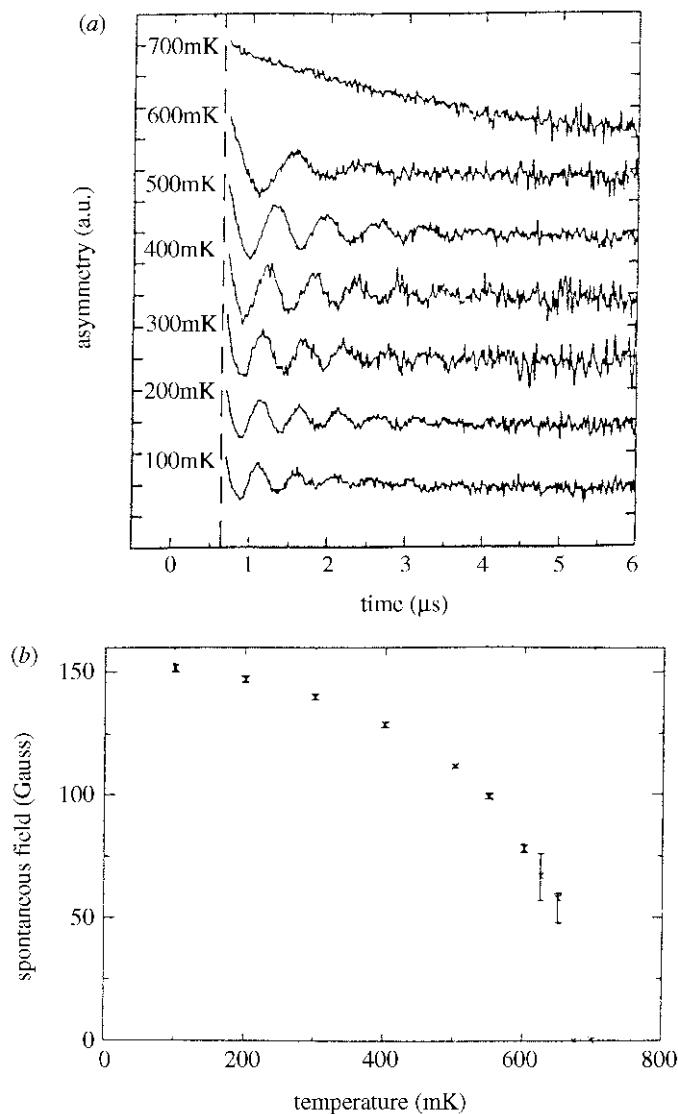


Figure 3. (a) Zero field muon spin rotation in *p*-nitrophenyl-nitronitroxide. (b) Temperature variation of internal field determined by muon spin rotation.

in 4-QNNN the N—O groups on neighbouring molecules are brought close enough for electron pairing to take place.

(c) *Bimetallic tris-oxalato-salts: honeycomb layer ferrimagnets*

A distinguishing feature of molecular-based magnetic materials is that the vast majority are insulators, and the microscopic magnetic moments are therefore localized. Maximum connectivity between centres carrying the moments is therefore desirable to maximize ordering temperatures, so ambidentate ligands are most effective. The bimetallic *tris*-oxalato series $AM^{II}Fe^{III}(C_2O_4)_3$ is particularly interesting from

Table 1. $M^{\text{II}}\text{-Fe}^{\text{III}}(d_1)$ and interlayer separation (d_2) in two-dimensional $AM^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3$

	$M^{\text{II}} = \text{Fe}$		$M^{\text{II}} = \text{Mn}$	
	d_1 (Å)	d_2 (Å)	d_1 (Å)	d_2 (Å)
$\text{N}(n\text{-C}_3\text{H}_7)_4^+$	4.667	8.218	4.686	8.185
$\text{N}(n\text{-C}_4\text{H}_9)_4^+$	4.701	8.980	4.731	8.937
$\text{N}(n\text{-C}_5\text{H}_{11})_4^+$	4.703	10.233	4.728	10.158
$\text{P}(n\text{-C}_4\text{H}_9)_4^+$	4.735	9.317	4.760	9.525
$\text{As}(\text{C}_6\text{H}_5)_4^+$	4.683	9.655	4.722	9.567
$\text{N}(\text{C}_6\text{H}_5\text{CH}_2)(n\text{-C}_4\text{H}_9)_3^+$	4.690	9.633	4.735	9.433
$(\text{C}_6\text{H}_5)_3\text{PNP}(\text{C}_6\text{H}_5)_3^+$	4.690	14.433	4.707	14.517

this point of view, since a wide range of organic cations A^+ stabilize a hexagonal layer structure and the details of magnetic ordering are highly sensitive to changes in the packing of A between the layers.

One strategy for achieving finite zero-field magnetization in a molecular-based array, without the need for ferromagnetic near-neighbour exchange, is to exploit ferrimagnetism. Compounds with general formula $AM^{\text{II}}M^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-}$ constitute a very extensive series, formed by a wide range of organic cations A^+ , as well as divalent and trivalent M both from transition metal and B-subgroup ions (Tamaki *et al.* 1992). Depending on the connectivity of the $M^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-}$ units effected by the M^{II} one can have either a two- or three-dimensional array, with the build up of the long-range order state being ‘templated’ by the organic A^+ (Decurtins *et al.* 1994b). Connection between $M^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-}$ by M^{II} in two dimensions produces a honeycomb structure in which both metal ions occupy sites of trigonally distorted octahedral geometry, with all near-neighbour M^{II} , M^{III} pairs bridged by oxalate ions (figure 4). Many compounds in this series therefore have crystal structures that are approximately hexagonal, with basal plane unit cell constants that vary only slightly with A^+ , though with strongly varying interlayer separations. Some unit cell constants are listed in table 1, which show that a factor of 2 in interlayer separation is easily achievable.

The set of compounds we have studied in detail have $M^{\text{II}} = \text{Mn}$ or Fe and $M^{\text{III}} = \text{Fe}$ (Mathionière *et al.* 1996). Averaged over the whole group, the spacing between the metal ions in the plane decreases from Mn to Fe by 0.03 Å, in line with the decrease in ionic radius expected from ligand field considerations. In contrast, though, the interplanar spacing *increases* by an average of 0.08 Å, most probably because the organic groups which enter the hexagonal cavities are slightly extended as the cavity becomes smaller.

One example studied in detail is $\text{N}(n\text{-C}_5\text{H}_{11})_4\text{MnFe}(\text{C}_2\text{O}_4)_3$, whose crystal structure consists of alternate layers of $[\text{MnFe}(\text{C}_2\text{O}_4)_3]^-$ and $\text{N}(n\text{-C}_5\text{H}_{11})_4^+$ (Carling *et al.* 1996). The former comprise honeycomb networks of alternating Mn and Fe bridged by $\text{C}_2\text{O}_4^{2-}$ (figure 5). Thus, both metal ions are coordinated by six O originating from three bidentate oxalate ions forming trigonally distorted octahedra. Similar networks have been observed in $\text{P}(\text{C}_6\text{H}_5)_4\text{MnCr}(\text{C}_2\text{O}_4)_3$ (Decurtins *et al.* 1994a) and in the $\text{P}(\text{C}_6\text{H}_5)_4^+$ compound, one P—C bond lies parallel to a threefold axis and the unit cell is rhombohedral.

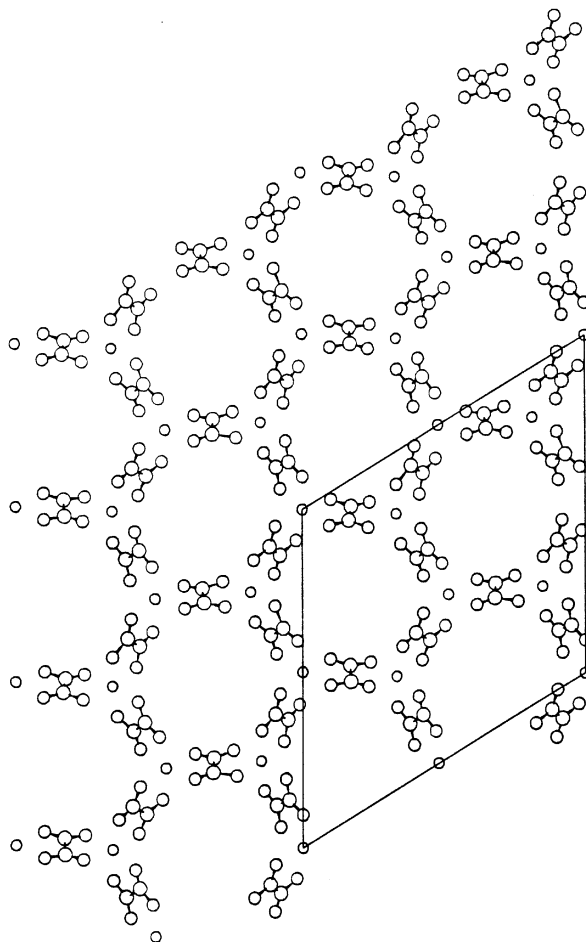


Figure 4. Layer honeycomb structure of $AM^{II}M^{III}(C_2O_4)_3$.

As far as the bimetallic *tris*-oxalato layer is concerned (figure 5), the deviation of the 3d ions from a hexagonal array is implicit in the orthorhombic space group: the angles Fe–Mn–Fe and Mn–Fe–Mn are, respectively, 112° and 138° instead of 120° . The site symmetry of the metal ions, which would be D_3 if the cell were rhombohedral, is reduced to C_2 and the metal–oxygen bond lengths are not all equal. One index of the distortion of the MO_6 units from regular octahedra is the deviation of the *trans* O–M–O bond angles from 180° : at the Fe site two such angles are 163° and one 170° . As expected for bidentate chelating oxalate groups the ‘bite angle’ O–M–O averages 78.0° around the Fe site and 79° around the Mn, similar to those found in other oxalato-complexes of Fe(III) and Mn(II) (Julve *et al.* 1984). Since the mean O–M–O angle for O atoms on adjacent oxalate groups exceeds 90° (99.4° at the Fe site and 98.6° at Mn), both MO_6 octahedra may be considered as slightly elongated perpendicular to the plane of the $[MnFe(C_2O_4)_3]^-$ layer. Alternate layers have opposite chirality (i.e. Mn(Λ) and Fe(Δ) in one layer, and Mn(Δ), Fe(Λ) in the next).

The N atoms of the $N(n-C_5H_{11})_4^+$ form rectangular planar arrays, interleaving

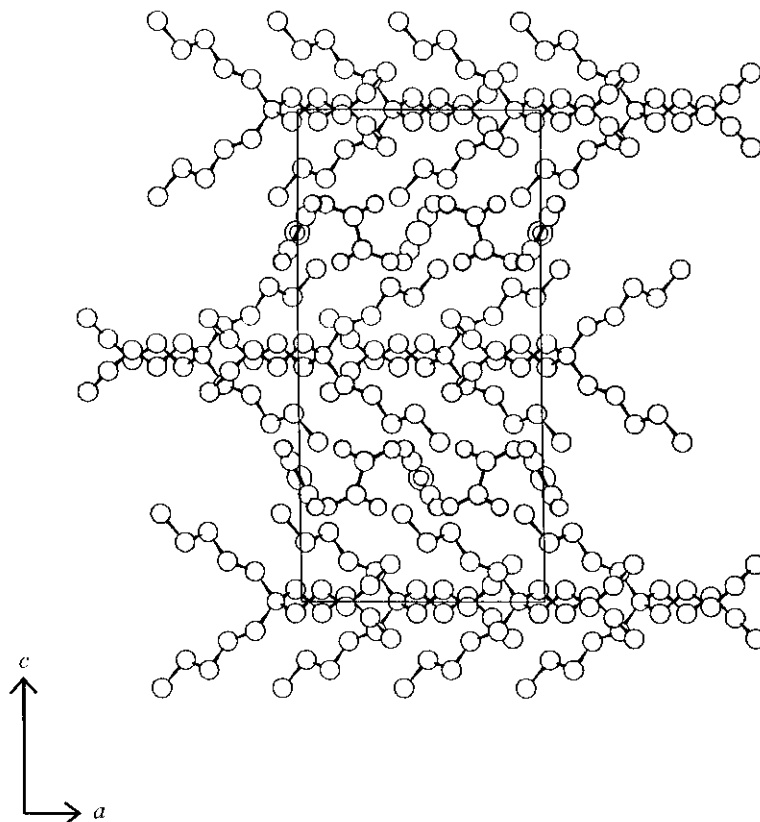


Figure 5. Projection of the crystal structure of $N(n\text{-C}_5\text{H}_{11})_4\text{MnFe}(\text{C}_2\text{O}_4)_3$ along the b -axis (Carling *et al.* 1996).

the $\text{MnFe}(\text{C}_2\text{O}_4)_3^-$ layers, with the four attached alkyl chains extended: two in the plane of the N and two perpendicular. The first four C atoms in each chain are fully extended but the terminal CH_3 is twisted away from the plane of the four CH_2 towards the *gauche* configuration. Attempts to synthesize compounds in the series $N(n\text{-C}_n\text{H}_{2n+1})_4\text{MnFe}(\text{C}_2\text{O}_4)_3$ have only been successful for $n = 3\text{--}5$, no C_6H_{14} derivative being obtained (Nuttall 1997). It would appear that the steric requirement for accommodating the alkyl chains within the hexagonal Mn_3Fe_3 cavities cannot be satisfied for $n > 5$, though in the series with $A = (n\text{-C}_n\text{H}_{2n+1})\text{P}(\text{C}_6\text{H}_5)_3^+$, compounds with $n = 6, 7$ have been prepared (I. D. Watts, unpublished work).

The $\text{M}^{\text{II}} = \text{Mn}$ compounds constitute a rather unusual kind of ferrimagnetism in that the electronic ground states of the two metal ions are the same: ${}^6\text{A}_1$ in D_3 symmetry. The near-neighbour exchange interaction is strongly antiferromagnetic, as indicated by the large negative Weiss constants, which do not vary much with A since the exchange pathway is only slightly affected by changing the organic group. Further evidence of strong antiferromagnetic spin correlations within the layers is provided by the existence of a broad maximum in the susceptibility at 55 K, again independent of A . The short-range magnetic order therefore mimics that of a two-dimensional antiferromagnet. However, with the onset of long-range order

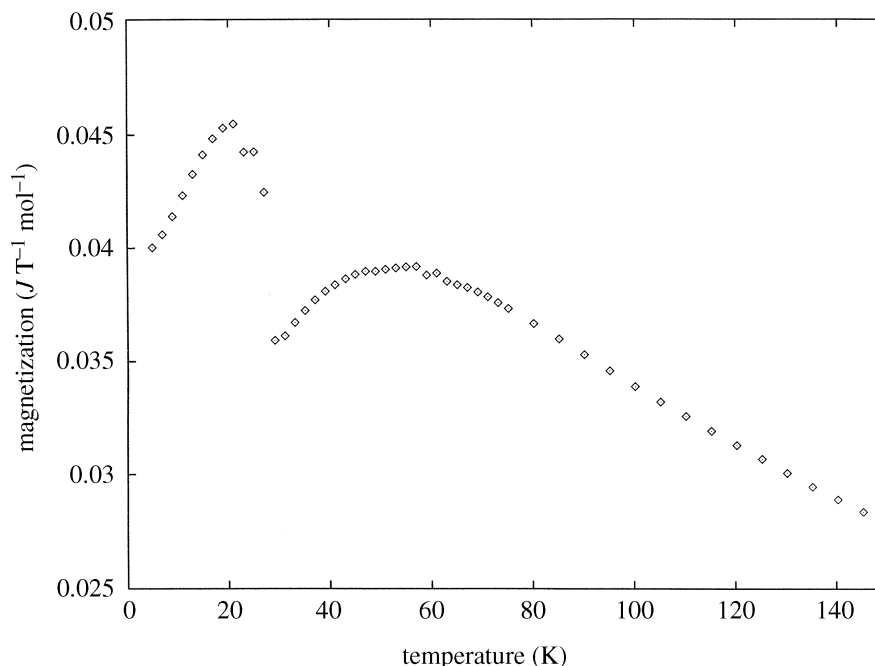


Figure 6. Temperature-dependent magnetization of $N(n-C_5H_{11})_4MnFe(C_2O_4)_3$ in a field of 10^{-2} T (Mathionière *et al.* 1996).

around 27 K (nearly independent of A), the susceptibility increases abruptly (figure 6), to reach a value which does vary strongly with A, being smallest for $N(n-C_4H_9)_4^+$ and largest for $(C_6H_5)_3PNP(C_6H_5)_3^+$ at 5 K (Mathionière *et al.* 1996). As in the Mn alkyl-phosphonates (Carling *et al.* 1993), the magnitude of the uncompensated moment is determined by an organic group which is not only not implicated in the exchange mechanism, but is spatially remote from the site of the magnetic moment, a phenomenon which has no analogue among conventional magnetic materials.

When $M^{II} = Fe$ in the bimetallic *tris*-oxalato-Fe(III) series, we have the interesting situation of a mixed valency compound (Day 1980). The physical properties are those of Class II in the Robin–Day classification (Robin & Day 1966), but unexpectedly a bizarre magnetic phenomenon is seen. The two magnetic ions being $S = 2$ and $S = 5/2$, the resulting behaviour is that of a conventional ferrimagnet. However, depending on the nature of the organic cation A, one either has a conventional magnetization at low temperature, increasing monotonically from zero at T_c to a limiting value at $T \rightarrow 0$ (figure 7a), or a magnetization that increases at first from zero below T_c but then reaches a maximum. At lower temperatures, the magnetization then falls again, passing through zero and becoming strongly negative (Mathionière *et al.* 1994; Nuttall & Day 1998) (figure 7b). This behaviour is extremely rare among molecular-based magnetic materials but finds a precedent among continuous lattice oxides (Goodenough 1963). As long ago as the 1940s there was great interest in ferrimagnetic mixed-valency Fe oxides with spinel and garnet structure because they were among the first materials discovered with non-zero spontaneous magnetization which were not metallic.

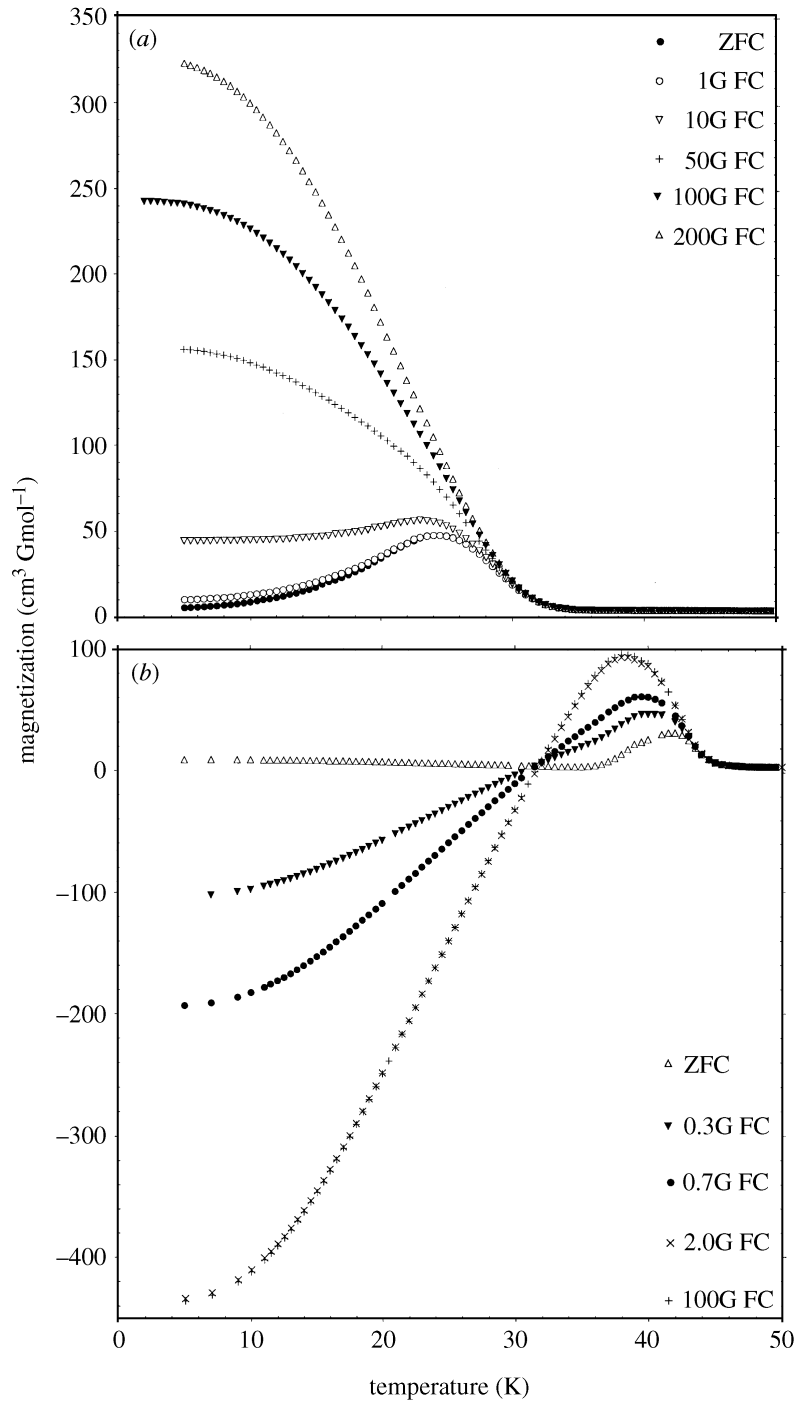


Figure 7. Temperature-dependent magnetization of ferrimagnets $\text{AFe}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3$ measured in a 100 G field after cooling in different fields: (a) $\text{A} = \text{P}(\text{C}_6\text{H}_5)_4$; 'normal' behaviour; (b) $\text{A} = \text{N}(n\text{-C}_4\text{H}_9)_4$, negative magnetization (Nuttall & Day 1998).

The origin of the apparently bizarre situation that the net magnetization of a sample could be antiparallel to the applied measurement field was actually described as long ago as 1948 by Néel (1948). In a ferrimagnet the net magnetization at a given temperature is the vector sum of the magnetizations of each sublattice. Should the temperature dependence of the magnetizations of each sublattice be similar, the resultant will be a monotonic increase from T_c to absolute zero as shown in figure 7 for $\text{P}(\text{C}_6\text{H}_5)_4\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3$. On the other hand if the temperature derivatives of sublattice magnetization $\text{d}M_{\text{Fe(II)}}/\text{d}T$ and $\text{d}M_{\text{Fe(III)}}/\text{d}T$ have a different dependence on temperature, then the temperature derivative of the resultant $\text{d}(M_{\text{Fe(II)}} - M_{\text{Fe(III)}})/\text{d}T$ can change sign. It is also feasible for the magnetizations of the two sublattices to cancel at a ‘compensation temperature’. However, the feature distinguishing the bimetallic *tris*-oxalato compounds from the oxides is that once again the drastically varying magnetic behaviour comes about by changing organic groups situated quite far away in the lattice from the magnetic centres.

3. Superconducting and semiconducting molecular charge transfer salts

Superconductivity, certainly an unlooked-for phenomenon when it was first discovered in 1910, was first found in an organic molecular solid in the early 1980s (Jerome *et al.* 1980), bringing the topic into the realm of synthetic chemistry. The compounds in question are molecular charge transfer salts, defined as substances derived from an electron donor molecule in the form of a cation and an inorganic anion of defined charge, such as I_3^- , ClO_4^- . (A much smaller number of salts arise from anionic molecular acceptors and small cations such as NH_4^+ .) At first sight, superconductivity might appear as unlikely a property to find in a molecular material as ferromagnetism, and for the same reason, namely that by definition intramolecular electronic interactions are much stronger than intermolecular ones in such a solid. Nevertheless, the past 15 years have seen many such compounds synthesized, and broad structure–property relationships emerge (see, for example, Williams *et al.* 1992). Critical temperatures for the onset of superconductivity have risen from 1.5 to 13 K (33 K in fulleride salts) which, although far lower than the high T_c cuprates, lies well within the upper quartile of all known superconductors with the exception of the cuprates, which still remain a distinct and enigmatic group.

Given that the T_c of the molecular superconductors are relatively low, it is pertinent to ask why it is worth devoting much effort to them. The question can be answered in several ways. First, from the straightforward standpoint of synthesis and processing, it is undoubtedly appealing to be able to envisage making superconductors from solution at room temperature, in contrast to conventional metallurgical or ceramic methods. Second, it is attractive to be in a position to modify (and in some cases completely transform) the electronic ground state by small chemical changes. Third, because of their molecular make-up, they are highly compressible, so that the electronic ground state can be altered drastically by quite modest applied pressures. Fourth, and perhaps most significant for scientific novelty, is the opportunity presented by the molecular nature of the lattice to introduce properties that would scarcely be feasible in a simple close-packed continuous lattice. Two examples taken up below are structural chirality and magnetism.

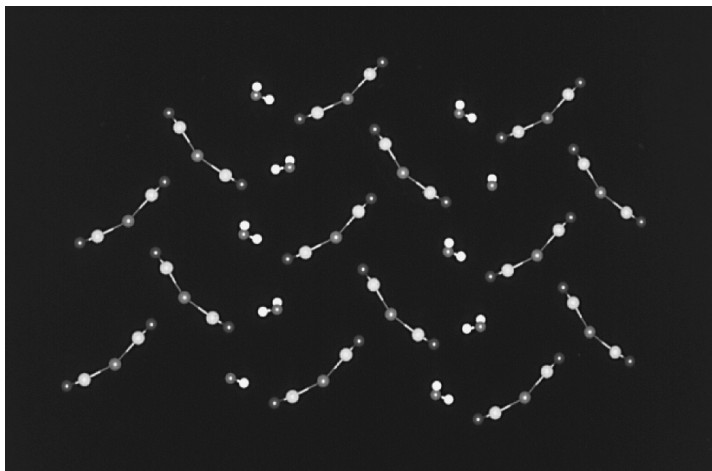


Figure 8. The anion layer in κ -(BEDT-TTF) $_2$ Ag(CN) $_2$ · H $_2$ O (Kurmoo *et al.* 1990). Note the cavities which contain the BEDT-TTF –CH $_2$ CH $_2$ – groups.

(a) *Bis-ethylenedithio-tetrathiafulvalene (BEDT-TTF) salts:
structures and properties*

The first molecular superconductors were salts of tetramethyl-tetraselenofulvalene (TMTSF), but in the mid-1980s the organo-sulphur donor BEDT-TTF came on the scene (Mizuno *et al.* 1978) and its salts now provide the physicist with examples of virtually every collective electronic ground state known: semiconductors, metals, superconductors, charge density waves, spin-density waves, spin–Peierls transitions, etc. Such richness comes from the fact that the collective properties emanate from two main parameters: the mean charge on the BEDT-TTF molecules, which determines the Fermi energy, and the molecular packing (i.e. the distances and angles between neighbouring molecules), which determines the overlap between frontier molecular orbitals and hence the intermolecular transfer integrals.

BEDT-TTF charge transfer salts are known with mean cation charges of 0.5, 0.67, 1.0 and 2.0 and a precise, if empirical, correlation has been found with the C–C and C–S bond lengths in the central tetra-thiafulvalene part of the molecule, so that effective cation charges can now be estimated reliably from crystallographic data (Guionneau *et al.* 1997). This is especially valuable in the not infrequent cases where inequivalent molecules in the unit cell bear significantly different charges. For example (BEDT-TTF) $_4$ ReCl $_6$ · C $_6$ H $_5$ CN, with a mean cation charge of +0.5, contains alternate stacks of donor molecules with charges of 0 and +1; the former lying close to the neutral solvent molecules and the latter to the ReCl $_6^{2-}$. Physically, the compound is a semiconductor with (apart from the 5d moment on the Re) a one-dimensional antiferromagnetic interaction between the BEDT-TTF $^+$ ($S = 1/2$) (Kepert *et al.* 1997).

Among the superconducting BEDT-TTF salts two main structure types have emerged, labelled β and κ , in both of which (as is commonly the case with salts of this donor) the organic donor cations and inorganic anions form separate alternate layers. We illustrate each by examples from our earlier work. Salts of both categories have mean cation charges of +0.5, so that in β -(BEDT-TTF) $_2$ AuBr $_2$, for instance, the donor molecules are organized into stacks with the mean planes of the

TTF groups parallel (Talham *et al.* 1987; Chasseau *et al.* 1993). However, because of numerous interstack S . . . S contacts below the van der Waals distance, the Fermi surface is closer to being two dimensional than one, so that the ratio of the normal-state metallic conductivity within the donor layer, parallel and perpendicular to the stacks, is only about 3:1. In contrast, in κ -phase salts, exemplified by κ -(BEDT-TTF)₂Ag(CN)₂ · H₂O (Kurmoo *et al.* 1990), the BEDT-TTF are not arranged in stacks but as discrete plane–plane dimers, with the planes of adjacent dimers orthogonal. Conductivity parallel to the donor layer is then isotropic. This compound, which has a T_c of 5.5 K, is the first ambient pressure superconductor of any kind to have water in the crystal lattice. Another, (BEDT-TTF)₃Cl₂ · 2H₂O, prepared earlier, only becomes superconducting under pressure (Rosseinsky *et al.* 1988; Kurmoo *et al.* 1988).

At once the question arises as to why salts with two such similar anions, both linear and with the same charge, should induce such different packing motifs in the donor layers. The answer lies in the arrangement of the Ag(CN)₂[−] in the anion layer, linked together by H-bonds to the H₂O (figure 8). The resulting planar array contains cavities into which the terminal –CH₂CH₂– groups ‘dock’. As we shall see below, such interactions between the donor and anion layers are a crucial factor determining the orientation of the donors, and hence the bulk physical properties of BEDT-TTF salts.

(b) *BEDT-TTF salts with tris-oxalato-metallate(III) anions:
magnetism, chirality and solvent templating*

Superconductivity and long-range magnetic order have long been thought to be ground states incapable of coexistence because the internal field generated by magnetic centres would break up the superconducting Cooper pairs. It is therefore of interest to use the chemical flexibility available in a molecular-based compound to try and synthesize superconductors containing magnetic centres. In the charge transfer salts an obvious approach is to make salts with paramagnetic anionic transition metal complexes, and over a period of years we pursued this strategy by preparing and characterizing a large number of BEDT-TTF salts with anions ranging from simple halogeno-species such as FeCl₄[−] (Mallah *et al.* 1990) and ReCl₆^{2−} (Kepert *et al.* 1997) to large metal clusters such as Mo₆Cl₁₄ (Kepert *et al.* 1998) and PW₁₂O₄₀^{6−} (Bellitto *et al.* 1995). This work has been reviewed (Kurmoo & Day 1997). Most compounds of this kind are semiconductors because of charge disproportionation within the donor sublattices, but one, (BEDT-TTF)₄CuCl₄ · H₂O (Day *et al.* 1992), is a metal from ambient temperature down to 400 mK, though without any transition to superconductivity, and also shows evidence for short-range ferromagnetic correlations between the Cu moments. However, more recently we have prepared an extensive series of compounds with the general formula (BEDT-TTF)₄[A^IM^{III}(C₂O₄)₃] (solvent), among which are the first ever superconductors containing paramagnetic 3d ions (Graham *et al.* 1995). As with the bimetallic *tris*-oxalato-salts described in § 3 a, the chirality of the M(C₂O₄)₃^{3−} is a crucial factor in determining the crystal structure and indeed, there are two different ways of incorporating Λ and Δ stereoisomers into the ultimately racemic lattice. The two phases are also strikingly different in their physical properties, one being superconducting and the other semiconducting.

The compound β'' -(BEDT-TTF)₄[(H₃O)Fe(C₂O₄)₃]C₆H₅CN was the first molecular superconductor containing paramagnetic metal centres, an important precedent

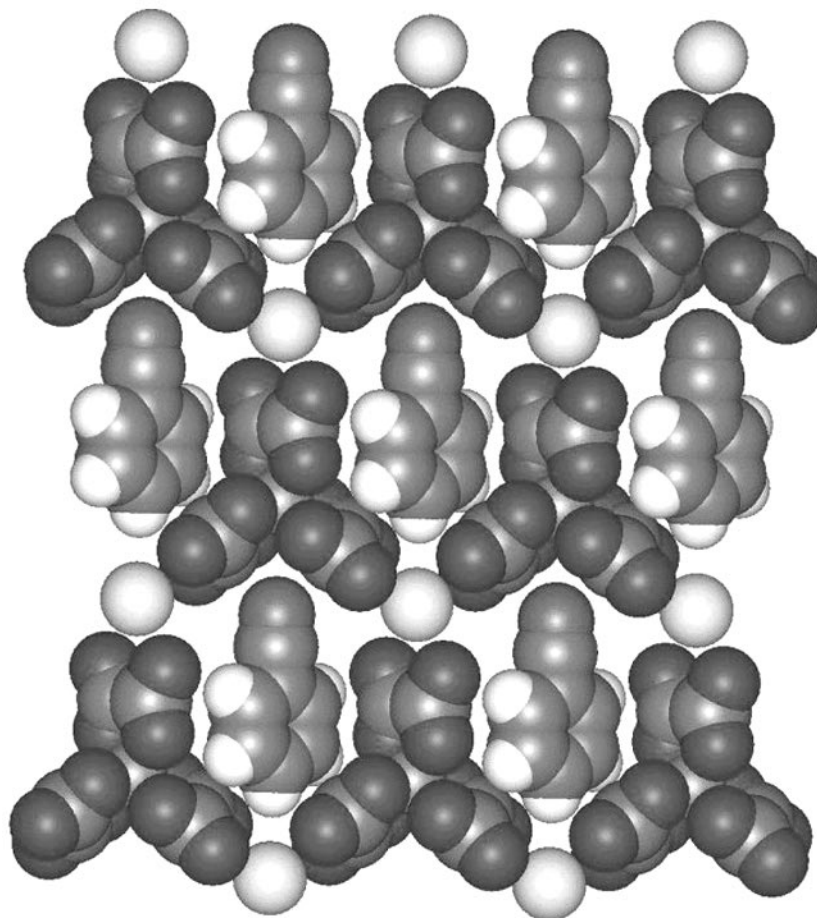


Figure 9. The anion layer in β'' -(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]C₆H₅CN; M = Cr, Fe (Kurmoo *et al.* 1995; Martin *et al.* 1997).

because of the conflict between superconductivity and magnetism in solids (Fisher & Maple 1983). The crystal consists of alternating layers of BEDT-TTF within which the cations form stacks in the β'' -packing motif and layers of anions and solvent molecules very similar to that found in the bimetallic *tris*-oxalate-salts, except that one of the metal sites is occupied by H₃O⁺ and the hexagonal cavity between the oxalate ions contains the C₆H₅CN rather than the organic cation (Kurmoo *et al.* 1995). If, however, the H₃O⁺ is replaced by K⁺ or NH₄⁺, the resulting compounds are semiconductors, although superficially at least, the hexagonal arrangement of the anion layer is almost the same.

Close inspection reveals a most significant difference. Both compounds are racemates: the lattices contain equal proportions of Δ and Λ enantiomers of Fe(C₂O₄)₃³⁻, but distributed in different ways. In the superconducting compound, which is monoclinic (*C2/c*), we find alternate layers consisting of only Λ or Δ molecules (figure 9); in the semiconducting phase, on the other hand, which is orthorhombic (*Pbcn*), rows of Δ and Λ molecules alternate within each layer (figure 10). In consequence, the site

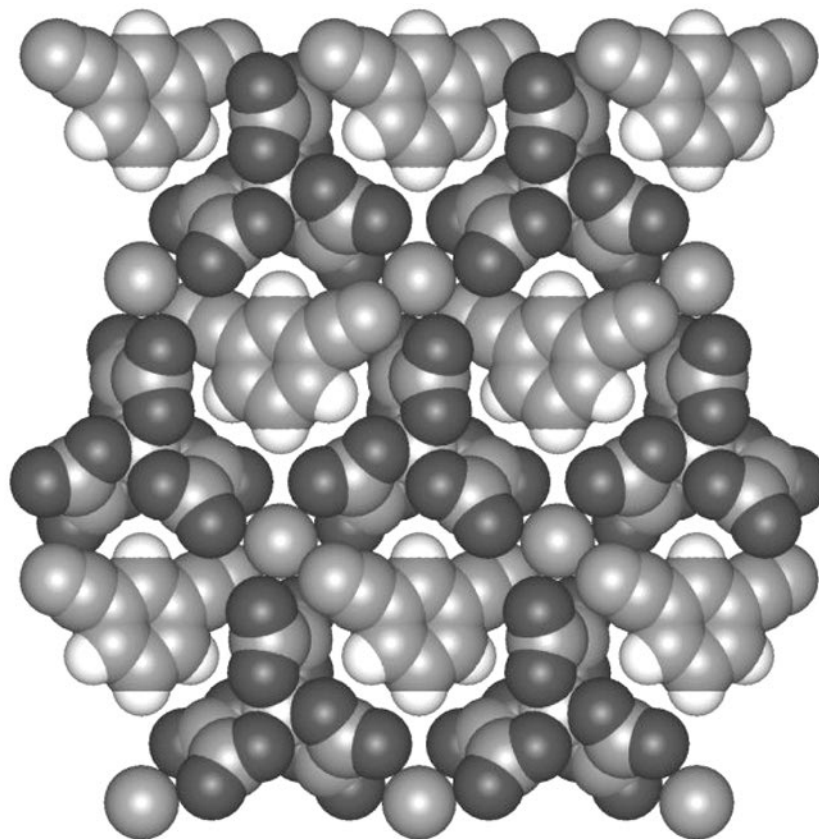


Figure 10. The anion layer in semiconducting (Pbcn): $(\text{BEDT-TTF})_4[\text{AM}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{CN}$; A = K, NH_4 , H_3O ; M = Cr, Fe, Co, Al (Kurmoo *et al.* 1995; Martin *et al.* 1997).

occupied by the A^+ , though surrounded by six O atoms from oxalate anions in both cases, has quite a different symmetry from that found in the monoclinic phase, and in fact has a cavity on one side which accommodates the $-\text{CN}$ group of the $\text{C}_6\text{H}_5\text{CN}$, thus rendering the site seven coordinate.

Thus, 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 $(\text{BEDT-TTF})_4[\text{AM}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{CN}$, five examples are known to date which crystallize in the Pbcn space group, with the anion sublattice illustrated in figure 9 (Kurmoo *et al.* 1995). They are listed in table 2 (Martin 1999), where it should be noted in particular that the $(\text{H}_3\text{O})\text{Cr}$ phase is polymorphic (Martin *et al.* 1997).

The arrangement of BEDT-TTF molecules in the Pbcn phase is illustrated in figure 11. Analysis of the C—C and C—S bond lengths using the algorithm of Guionneau *et al.* (1997) 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 $(\text{BEDT-TTF})^+$ are paired. The result,

Table 2. Phases of $(\text{BEDT-TTF})_4[\text{AM}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{CN}$

M =	Cr	Fe	Co	Al
A = K	—	Pbcn	—	—
NH ₄	—	Pbcn	—	Pbcn
H ₃ O	Pbcn C2/c	C2/c	Pbcn	—

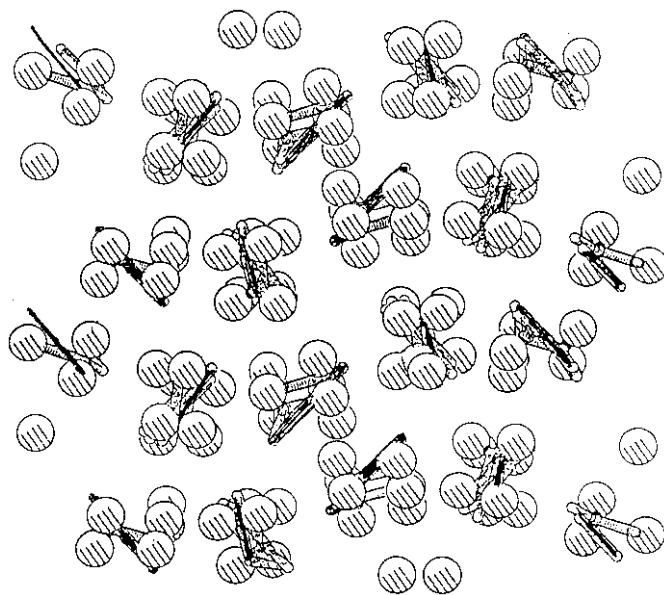


Figure 11. The BEDT-TTF sublattice in $(\text{BEDT-TTF})_4[\text{AM}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{CN}$, Pbcn phase. Shaded spheres are H atoms.

confirmed by band structure calculation (Kurmoo *et al.* 1995), 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 $-\text{CH}_2\text{CH}_2-$ moieties of the BEDT-TTF, together with the 'top' layer of O coming from the oxalate anions.

The second phase of $(\text{BEDT-TTF})_4[\text{AM}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{CN}$, which crystallizes in the $C2/c$ space group, has been identified in $(\text{H}_3\text{O})\text{M}$ examples with $\text{M} = \text{Fe}$, Cr (table 2). The difference between the distribution of chiral anions compared with the semiconducting phase transforms the packing of the donor layer, inducing a β'' arrangement of BEDT-TTF (Kurmoo *et al.* 1995). As mentioned earlier, the β -stacking arrangement leads to superconductivity in numerous salts with mean BEDT-TTF changes of +0.5, 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 (Martin *et al.* 1999). All the anions in each layer now have the same chirality (figure 9) so the network of terminal O atoms on the oxalate ions is quite different from that of the orthorhombic phase. The temperature dependent resistance (typical of a metal) and

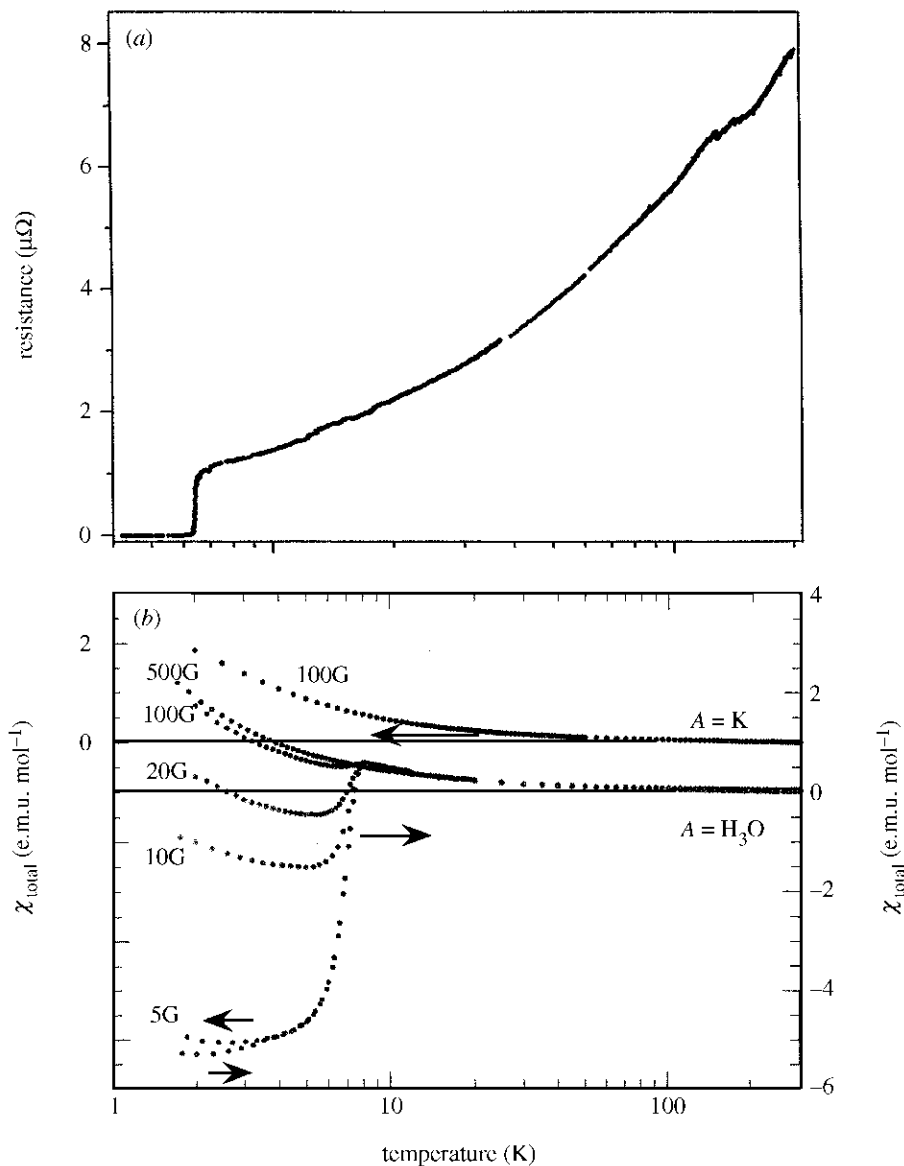


Figure 12. Superconductivity of β'' -(BEDT-TTF) $_4$ [(H $_3$ O)Fe(C $_2$ O $_4$) $_3$]C $_6$ H $_5$ CN (Kurmoo *et al.* 1995). (a) Temperature dependence of resistance ($\mu\Omega$). (b) Temperature dependence of magnetic susceptibility measured after cooling in different fields (BEDT-TTF) $_4$ [AFe(C $_2$ O $_4$) $_3$]C $_6$ H $_5$ CN (left-hand scale, A = K; right-hand scale, A = H $_3$ O).

the superconductivity transition in the (H $_3$ O)Fe salt are shown in figure 12a while the magnetic susceptibility (figure 12b) shows typical Curie–Weiss behaviour at high temperature, because of the Fe moment, with sudden onset of diamagnetism at low temperature when the sample becomes superconducting.

Other molecules may be substituted for C $_6$ H $_5$ CN in the hexagonal cavity formed by A $^+$ and M(C $_2$ O $_4$) $_3^{3-}$. In particular, C $_6$ H $_5$ NO $_2$ and C $_5$ H $_5$ N form β'' -BEDT-TTF

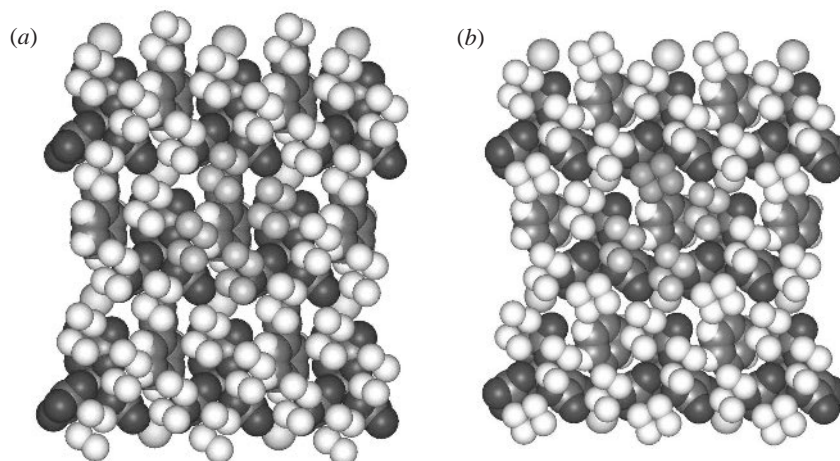


Figure 13. Terminal H atoms of BEDT-TTF in β'' -(BEDT-TTF)₄[(H₃O)Fe(C₂O₄)₃] (solvent): (a) solvent = C₆H₅CN; (b) solvent = C₅H₅N (Turner *et al.* 1999). Light spheres are H atoms.

salts with H₃O⁺ and M = Cr and Fe, which crystallize in the $C2/c$ space group with unit cell parameters very similar to the corresponding C₆H₅CN compounds. The C₆H₅NO₂ salts are superconducting, albeit with lower T_c and critical fields (S. Rashid, unpublished work), but the pyridine solvate presents an even more fascinating aspect. At room temperature it has metallic conductivity similar to the C₆H₅CN compound, but instead of becoming superconducting at low temperature it undergoes a sharp metal-to-insulator transition at 116 K (Turner *et al.* 1999). At 150 K, when both materials are in the metallic regime, they have β'' -BEDT-TTF stacking, but in the pyridine solvate one-quarter of the BEDT-TTF have an unresolved-twisted conformation in contrast with the C₆H₅CN one, where they are all twisted-twisted and eclipsed with low thermal parameters. All bond distances and angles within the anionic layers are closely similar in the two (H₃O)Fe compounds except that in the pyridine solvate there is a void in each hexagonal cavity, corresponding to the position of the unresolved -CH₂CH₂- grouping in the BEDT-TTF layers on each side. Below the metal-insulator transition temperature the molecular conformation is resolved into two distinct sites, so that all the BEDT-TTF molecules have twisted-twisted conformations, but one-quarter are staggered and the remainder are eclipsed, as indicated in figure 13 by the positions of the H-atoms. At corresponding temperatures the C=C and C-S bond lengths within the TTF moieties are almost the same in both compounds, so we can rule out charge localization as a reason for the contrasting physical behaviour. This appears to be the first example of a change in molecular conformation bringing about such large change in electrical properties in a molecular conductor, illustrating once again how subtle is the relationship between supramolecular organization and physical behaviour in the molecular solid state.

4. Conclusion: supramolecular chemistry and solid state physics

Let me end where I began, with Humphry Davy. His Bakerian Lecture introduced a wider audience to what must have seemed at the time some highly unusual metals.

It is to be hoped that the present brief survey of some examples of molecular-based superconductors and magnets has achieved the same objective. In one small respect, at least, it has surpassed Davy's endeavour: in his lecture on the properties of potassium Davy refers to it as being 'a perfect conductor of electricity' (Davy 1808). Now, of course, we know that it is not; good, yes, but perfect, no. At low temperature, potassium is not among the metals that becomes superconducting, the only category of conductor that can strictly be called 'perfect'. However, as we have seen, there are numerous organic and metal-organic molecular solids that are superconductors, and others that have long-range-ordered magnetic ground states. The molecular nature of these materials has not only provided a wealth of opportunities for synthetic chemists, but served to introduce completely new aspects into this area of physical and materials science: solubilities, compressibility, chirality and intercalation, to name just a few. No doubt in the years to come this new interface between supramolecular chemistry and materials science will uncover many more.

The examples cited in this article are taken from the work of my own research group, first at Oxford and more recently at The Royal Institution. They have been made possible by the ingenuity and enthusiasm of many colleagues, principally Dr Mohamedally Kurmoo, Dr Simon Carling and Dr Scott Turner, and talented graduate students Anthony Graham, Cameron Kepert, Chris Nuttall, Lee Martin, Ian Watts, Samina Rashid and Justin Bradley. We have also benefited from many invaluable collaborations with crystallography and physics groups, especially Professor Michael Hursthouse and Professor Daniel Chasseau, and Dr John Singleton, Dr Stephen Blundell and Dr Bill Hayes. Our group has been supported by the Engineering and Physical Sciences Research Council, the European Commission Human Capital and Mobility, and Training and Mobility of Researchers Programmes and the British Council.

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