Molecular magnetic semiconductors, metals and superconductors: BEDT-TTF salts with magnetic anions

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Molecular charge-transfer salts that consist of alternating layers of organic donor molecules and inorganic anions offer the opportunity of bringing together in the same crystal lattice conduction electrons localised on the donor sublattice and magnetic moments localised on the inorganic anions. A wide range of such compounds is formed by the donor molecule BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene]. Some are semiconductors, others are metals while one is a superconductor, the first containing paramagnetic 3d moments. The structures, magnetic and conductivity properties of examples from each category are reviewed.

Superconductivity was first found in molecular solids about 15 years ago[1] and since then some hundred or so examples have been found, with the critical temperature T_c rising from 1.4 to almost 13 K.[2] All of them belong to the class of compounds called charge-transfer salts, in which a conjugated molecular cation is combined with a smaller inorganic anion, or *vice versa.* The majority are formed from organo-chalcogen donor cations such as tetramethyltetraselenofulvalene (TMTSF) and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF). The latter are particularly significant, not only because they provide the highest T_cs found so far,[3] but because of the very wide range of structures that they form, which facilitates the correlation of structure with properties.

An important reason for synthesizing new molecular-based materials is to bring together in the same crystal lattice physical properties that are not normally found in continuous lattice compounds. It is a striking feature of the superconducting charge-transfer salts based on BEDT-TTF that the organic cations and inorganic anions are spatially segregated into alternating layers, which led us to cite them as examples of 'organic–inorganic molecular composites'[4] or 'chemically constructed multilayers'.[5] Because of this separation into well defined organic and inorganic components the BEDT-TTF charge-transfer salts are attractive synthetic targets for attempts to combine superconductivity in a molecular lattice with properties more often found in the inorganic solid state like cooperative magnetism. Establishing superconductivity in a crystal containing localized magnetic moments is an important objective because superconductivity and magnetism have long been thought inimical to one another: Cooper pairs are disrupted by external fields and by the internal fields generated in ferromagnets.[6]

This Feature Article summarises our efforts to make conducting molecular charge-transfer salts of BEDT-TTF containing anions consisting of transition-metal complexes of two types [tetrahalogeno- and tris(oxalato)]. Some of the resulting phases are semiconductors and others are metallic without becoming superconducting. However, in one case we find superconductivity in the presence of paramagnetic Fe^{III} centres. The latter seems to be the first example, (not only among molecular materials) of a superconductor containing localised paramagnetic 3d centres, in a stoichiometric lattice.

Semiconducting tetrahalogenoferrate(III) salts

First attempts to insert 3d ions into BEDT-TTF charge-transfer salts centred on tetrahalogeno anions, beginning with Fe^{III} because of its large paramagnetic moment ($S=5/2$).[7] Surprisingly, electrochemical synthesis under the same conditions yielded different chemical stoichiometries for the salts containing $FeCl_4^-$ and $FeBr_4^-$. The structure of (BEDT-TTF)$_2$[FeCl$_4$] consists of dimerised stacks of BEDT-TTF molecules separated by the sheets of tetrahedral $FeCl_4^-$ anions. The anions are situated in an 'anion cavity' formed by the ethylene groups of the BEDT-TTF molecules, which are arranged in the sequence … XYYXXYYX … (Fig. 1). Adjacent molecules of the same type (XX′ and YY′) stack uniformly on top of each other but with a slight displacement between neighbours along the long in-plane molecular axis. On the other hand, the long in-plane molecular axes of adjacent molecules of different type (XY′ and YX′) are rotated relative to one another. Furthermore, X and X′ (or Y and Y′) are closer to each other (*ca.* 3.60 A) than X and Y (3.81 A). The shortest distances between BEDT-TTF molecules are shorter than the sum of the van der Waals radii of two sulfur atoms (3.60 A), thus suggesting the possibility of a quasi-one-dimensional interaction along the *a* direction.

In (BEDT-TTF)[FeBr$_4$], on the other hand, there are no stacks and planes of closely spaced BEDT-TTF, in marked

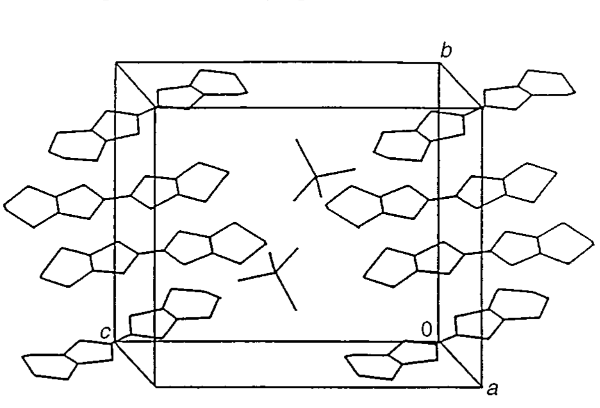

Fig. 1 The XXYYXX stacking sequence of BEDT-TTF in (BEDT-TTF)$_2$[FeCl$_4$][7]

contrast to most of the compounds containing this donor molecule. The only short S···S distances (<3.50 A) are between two BEDT-TTF molecules in different pairs but there is no continuous network of short S···S contacts through the lattice. The $FeBr_4^-$ form a three-dimensional lattice separated by the pairs of BEDT-TTF molecules. One $FeBr_4^-$ has short intermolecular distances to two donor molecules but no extended interaction between BEDT-TTF molecules through the $FeBr_4^-$ is possible, which correlates with the insulating behaviour of this compound.

The structure of the $FeCl_4^-$ salt is closely related to those of $(BEDT\text{-}TTF)_2[InBr_4]$,[8] α-$(BEDT\text{-}TTF)_2[PF_6]$,[9] β-$(BEDT\text{-}TTF)_2[PF_6]$[10] and $(BEDT\text{-}TTF)_2[AsF_6]$,[11] with the salts containing octahedral anions exhibiting interstack side-by-side contact distances nearly identical to those found in $(BEDT\text{-}TTF)_2[FeCl_4]$. There are no short contact distances between sulfur atoms along the molecular stacking direction in any of these compounds and so their conduction properties are highly one-dimensional. For example, in β-$(BEDT\text{-}TTF)_2[PF_6]$ the ratio of the conductivities along the direction of side-by-side contacts to that along the molecular stacking direction is 200:1.[9,10] $(BEDT\text{-}TTF)_2[FeCl_4]$ is also semi-conducting, like the PF_6 and AsF_6 salts, with an activation energy of 0.21 eV.

Given that the formal charge per donor molecule is $+1/2$ in the $FeCl_4^-$ salt we would expect a contribution to the susceptibility from unpaired spins on the organic cations. For example, the molar susceptibility of $(BEDT\text{-}TTF)_2[GaCl_4]$, which has a similar structure but a diamagnetic anion, has a broad maximum near 90 K, which can be fitted from 70 to 300 K either by a one-dimensional (Bonner–Fisher) or quadratic layer antiferromagnetic model to yield exchange parameters J of 66.5(5) and 89.6(1) K, respectively, similar to those found in the semiconducting α′-$(BEDT\text{-}TTF)_2X$ with $X = AuBr_2$, $Ag(CN)_2$ or $CuCl_2$,[12] where the absolute values of the susceptibility agree with expectations for localised moments corresponding to $S = 1/2$ per pair of donor molecules. Of course, in the $FeCl_4^-$ salt, the susceptibility is dominated by the anion. Thus the magnetic response of the donor sublattice is all but obscured, though with care it can be disentangled. From the low-temperature data, a value of the Weiss constant can be extracted and the parameters of the fit ($S = 5/2$, $g = 2$, $\theta = -4$ K) used to calculate the difference between observed and calculated at all temperatures to obtain the contribution from the BEDT-TTF. The resulting difference gives a good fit to a singlet–triplet model (Fig. 2).[13]

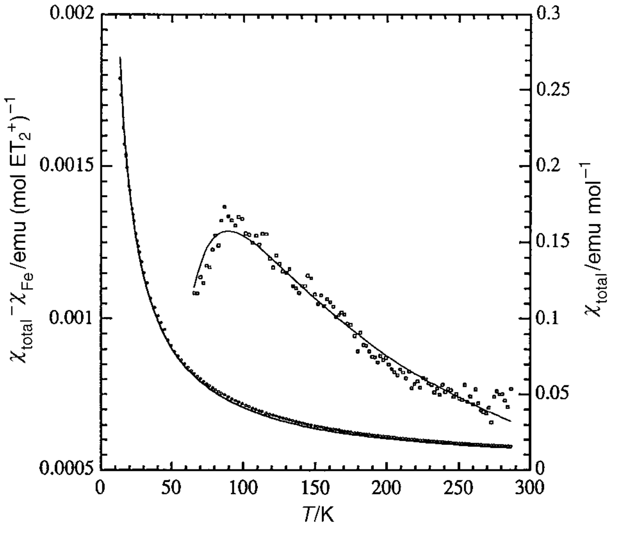

Fig. 2 Temperature dependence of the magnetic susceptibility of $(BEDT\text{-}TTF)_2[FeCl_4]$ (circles) and the BEDT-TTF contribution (squares). The solid lines are fits (see text).[13]

Metallic tetrahalogenocuprate(II) salts

The anions CuX_4^{2-} ($X = Cl$, Br) are unusual in the wide variety of geometries they adopt, from square-planar to flattened tetrahedral. It turns out that the crystal structures (and hence properties) of the BEDT-TTF salts with these anions are correspondingly varied. Amongst them is the first example of a metallic molecular charge-transfer salt in which magnetic resonance is observed simultaneously from conduction and localised electrons, $(BEDT\text{-}TTF)_3[CuCl_4]{\cdot}H_2O$.[14] Other examples containing $CuBr_4^{2-}$ and $CuCl_2Br_2^{2-}$ have the largest change of conductivity with pressure ever seen in conducting organic solids.

The crystal structure of $(BEDT\text{-}TTF)_3[CuCl_4]{\cdot}H_2O$ consists of stacks of BEDT-TTF parallel to the c-axis, with short interstack S···S contacts leading to the formation of layers in the ac-plane (Fig. 3).[14] These layers are interleaved by the inorganic anions and the water of crystallization in the same general arrangement as in the $FeCl_4$ salt. However, in $(BEDT\text{-}TTF)_3[CuCl_4]{\cdot}H_2O$ there are three crystallographically independent BEDT-TTF molecules and two different stacks. Stack A contains only BEDT-TTF of type I, and stack B has an alternate arrangement of II and III. Within the ac-plane, the stacks form an XYYXYYX array. The anions lie in planes parallel to the layers of the donor, within which pairs of $CuCl_4^{2-}$ anions are connected by hydrogen bonds through the two water molecules to form discrete units. The Cu—Cl bond lengths average 2.25 A with a *trans*-Cl—Cu—Cl angle of 150°, both values being quite normal for copper(II) halides with a Jahn–Teller distortion. The bond lengths and angles of the three independent BEDT-TTF molecules are almost identical while the two different overlap modes are the same in each stack. $(BEDT\text{-}TTF)_3[CuCl_4]{\cdot}H_2O$ is the only BEDT-TTF salt with 3:2 charge stoichiometry that remains metallic down to very low temperatures at ambient pressure. In general, such salts undergo metal (or semimetal) to insulator (or semiconductor) transitions, some of which are sharp {*e.g.* $(BEDT\text{-}TTF)_3[ClO_4]_2$},[15] and others broad [*e.g.* $(BEDT\text{-}TTF)_3Cl_2{\cdot}2H_2O$].[16]

Because it is metallic down to at least 400 mK $(BEDT\text{-}TTF)_3[CuCl_4]{\cdot}H_2O$ is an extremely interesting subject in which to observe the interaction between localized moments and conduction electrons, which manifests itself in two ways.[17] First, there is a shift in g value and broadening of the EPR line, the former being distinctly larger than those found in β- or α′-phase BEDT-TTF salts (2.003–2.010),[15] which strongly suggests that there is some interaction between the localised and conduction electrons. A second indication of such interaction comes from the way that the spin susceptibility of the conduction electrons falls below its Pauli limit as that of the localised electrons increases at low temperature. Most striking

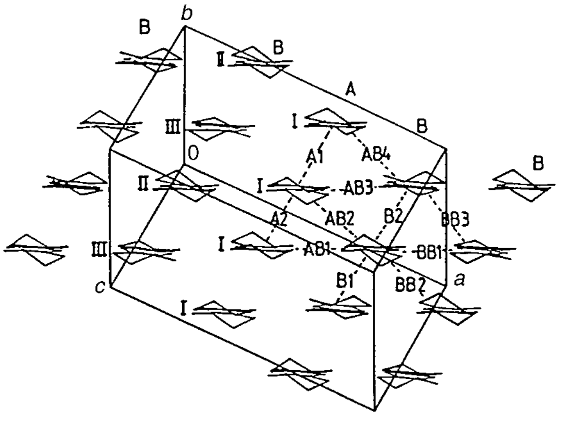

Fig. 3 Crystal structure of $(BEDT\text{-}TTF)_3[CuCl_4]{\cdot}H_2O$ projected along the c axis[14]

of all, however, the product of the spin susceptibility of the Cu resonance and the temperature rises at low temperature, indicating a short-range ferromagnetic interaction. Fitting the data to the Bleaney–Bowers[18] model indicates a ferromagnetic exchange constant of 4(1) K. Since the shortest Cu···Cu distance is 8.5 Å, direct exchange interaction between the Cu moments is very small. On the other hand, the $CuCl_4^{2-}$ are arranged as dimers bridged by H_2O, which may provide an exchange pathway. Nor can we rule out the possibility that exchange between Cu moments is mediated by the free carriers of the BEDT-TTF layers (the so-called RKKY mechanism).

Whilst the interaction between the BEDT-TTF and the metal ion spins is weak though observable in $(BEDT\text{-}TTF)_3[CuCl_4]\cdot H_2O$, in semiconducting $(BEDT\text{-}TTF)_2[FeCl_4]$ and insulating (BEDT-TTF)$[FeBr_4]$, it is negligible. By contrast, in $(BEDT\text{-}TTF)_3[CuBr_4]$ and $(BEDT\text{-}TTF)_3[CuBr_2Cl_2]$ the interaction between the two sublattices is strong, and structural phase transitions transform the electrical and magnetic properties.[19] The $CuBr_4^{2-}$ and $CuCl_2Br_2^{2-}$ salts are very different structurally from the $CuCl_4^{2-}$ salt, and their electronic properties are unrelated. Whereas the $CuCl_4^{2-}$ are distorted from square planar, as is usually expected for Jahn–Teller d^9 ions (the *trans*-Cl—Cu—Cl angle being 150°), the anions in the bromo salts are, very unusually, square planar. In fact, to our knowledge this is the first compound in which planar $CuBr_4^{2-}$ has been found.[20] Nevertheless the stoichiometry of all three salts is 3:1. Two crystallographically independent BEDT-TTF molecules (X and Y) are found in both bromo compounds; comparing the bond lengths with salts containing BEDT-TTF molecules with well defined charges one finds that they are 0 and +1.[21,22] Both crystal structures consist of layers of BEDT-TTF, stacked in XYYXYY sequence and adopting the α-phase mode of packing. They are separated by pseudo-square-planar tetrahalogenocuprate(II) (Fig. 4).

The room-temperature conductivities are very similar, being low for metallic organic conductors and high for semiconductors but they are affected dramatically by pressure.[19,23] In fact, they show the largest changes in conductivity with pressure of any known organic conducting solids: 25 S cm^{-1} kbar^{-1} up to 8 kbar, finally attaining a plateau at 22 kbar with 500 times the ambient pressure value. At low temperatures (<100 K) there are phase transitions that take both salts from the semimetallic to a semiconducting regime at pressures above 3 kbar.

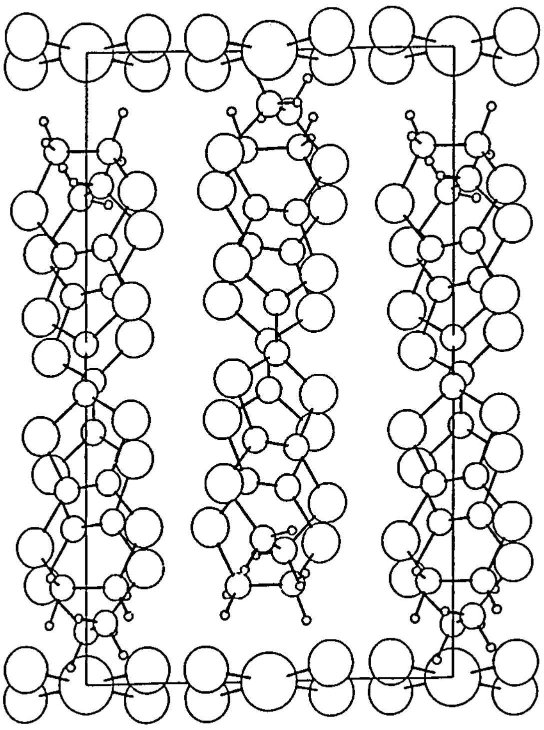

Fig. 4 Crystal structure of $(BEDT\text{-}TTF)_3[CuBr_4]$ projected along the *c* axis[23]

Clearly the two bromo salts are on the borderline between metallic and semiconducting behaviour. Their magnetic properties are also unusual in that the susceptibility associated with the conduction electrons on the BEDT-TTF stacks is very high. The drop of 2.5×10^{-3} emu mol^{-1} in susceptibility at the low-temperature transition is due to the loss of the contribution from these electrons (Fig. 5). To account for a contribution of this magnitude one must assume two spins per formula unit which are antiferromagnetically coupled. These facts suggest strongly that the $CuBr_4^{2-}$ and $CuCl_2Br_2^{2-}$ salts are just on the insulator side of the Mott–Hubbard transition. Semiconducting behaviour is not due to a gap in the one-electron density of states, but arises because the holes on the BEDT-TTF stacks localise due to the strong Coulomb interaction. The 3:2 charge stoichiometry of these salts requires that two holes are accommodated per three BEDT-TTF sites. As noted already, the bond lengths show that two of the BEDT-TTF molecules are charged and that one is close to neutral. The transport properties are therefore those of a 'magnetic' semiconductor, with an activation energy $U_{\text{eff}}/2$, where U_{eff} is the on-site Coulomb energy (Hubbard energy) associated with the transfer of a charge to place two charges on a single site.

In contrast to metallic $(BEDT\text{-}TTF)_3[CuCl_4]\cdot H_2O$ only a single EPR line is seen in the bromo salts, though the *g* values above the 55–60 K transition are intermediate between those expected for a Cu^{II} moment and for spins on BEDT-TTF sites. Hence the two spin systems interact significantly, in contrast to the other magnetic anion salts.[7,14]

Superconducting and semiconducting tris(oxalato)ferrate(III) salts

Recently instances have come to light of two-dimensional bimetallic layers containing uni- or di-positive cations and $[M^{III}(C_2O_4)_3]^{3-}$ in which the oxalato ion acts as bridging ligand, forming infinite sheets of approximately hexagonal symmetry, separated by bulky organic cations.[24,25] In view of the unusual magnetic properties of these compounds it is worth exploring the synthesis of compounds containing similar anion lattices but interleaved with BEDT-TTF molecules. Three such compounds have been fully characterised to date, $(BEDT\text{-}TTF)_4[AFe(C_2O_4)_3]\cdot PhCN$ ($A=H_2O$, K, NH_4).[26] While the stoichiometry of BEDT-TTF to Fe is the same in

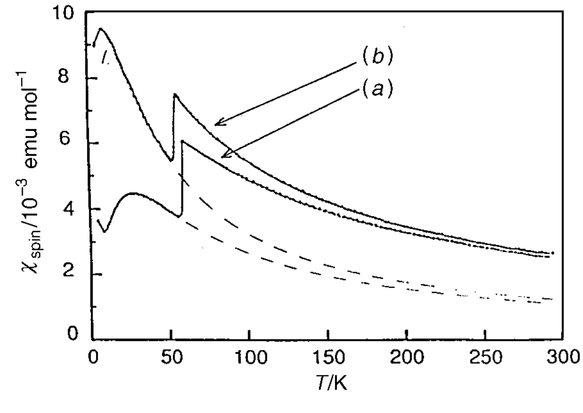

Fig. 5 Magnetic susceptibilities of (*a*) $(BEDT\text{-}TTF)_3[CuBr_4]$ and (*b*) $(BEDT\text{-}TTF)_3[CuCl_2Br_2]$. Broken lines are fits to the quadratic layer antiferromagnetic model.[23]

all three, the presence or absence of a monopositive cation not only changes the electron count (and hence the band filling) in the organic layer but also drastically alters the packing of the BEDT-TTF. Thus, the compounds with $A = K$ or NH_4 are semiconductors with the organic molecules present as $(BEDT\text{-}TTF)_2{}^{2+}$ and $(BEDT\text{-}TTF)^0$, while that with $A = H_2O$ has BEDT-TTF packed in the β'' arrangement[27] and is the first example of a molecular superconductor containing a lattice of magnetic ions.[28]

The crystal structures of all three compounds consist of alternate layers containing either BEDT-TTF or $[AFe(C_2O_4)_3]\cdot PhCN$. The anion layers contain alternating A and Fe forming an approximately hexagonal network (Fig. 6). The Fe are octahedrally coordinated by three bidentate oxalate ions, while the O atoms of the oxalate which are not coordinated to Fe form cavities occupied either by K or H_2O. The benzonitrile molecules occupy roughly hexagonal cavities in the $AFe(C_2O_4)_3$ lattice and there can be little doubt that it performs an important 'templating' role. Chirality is a further unusual feature of the anion layers. The point symmetry of $Fe(C_2O_4)_3{}^{3-}$ is D_3, and the ion may exist in two enantiomers. In fact alternate anion layers are composed exclusively either of one or the other.

Although the anion layers are very similar, the molecular arrangements in the BEDT-TTF layers are quite different in the K and NH_4 salts from the H_2O one. In the former there are two independent BEDT-TTF, whose central C=C bond lengths differ markedly, indicating charges of 0 and +1. The +1 ions occur as face-to-face dimers, surrounded by monomeric neutral molecules (Fig. 7). Molecular planes of neighbouring dimers along [011] are oriented nearly orthogonal to one another, as in the κ-phase structure of $(BEDT\text{-}TTF)_2X$,[29] but the planes of the dimers along [100] are parallel. This combination of $(BEDT\text{-}TTF)_2{}^{2+}$ surrounded by $(BEDT\text{-}TTF)^0$ has not been observed before. The $(BEDT\text{-}TTF)^0$ describe an approximately hexagonal network, while the $(BEDT\text{-}TTF)_2{}^{2+}$ are positioned near the oxalate ions, with weak hydrogen bonding between the terminal ethylene groups and oxalate O (2.51–3.05 A). Packing of the BEDT-TTF in the H_2O salt is quite different: there are no discrete dimers but stacks with short S···S distances between them, closely resembling the β''-structure in metallic $(BEDT\text{-}TTF)_2AuBr_2$[27] and the pressure-induced superconductor $(BEDT\text{-}TTF)_3Cl_2\cdot 2H_2O$.[16]

The K and NH_4 salts are both semiconductors but the H_2O salt is a metal with resistivity of *ca.* 10^{-2} Ω cm at 200 K, decreasing monotonically by a factor of about 8 down to 7 K, at which temperature it becomes superconducting (Fig. 8).

In line with their contrasting electrical behaviour the magnetic properties of the K and H_2O compounds are also quite different. The susceptibility of the semiconducting $A = K$ compound obeys the Curie–Weiss law from 2 to 300 K with the Fe dominating the measured moment. In particular, there is little contribution from the BEDT-TTF, including those molecules whose bond lengths suggest a charge of +1. Hence the $(BEDT\text{-}TTF)_2{}^{2+}$ are spin-paired in the temperature range studied (the singlet–triplet energy gap is expected to be >500 K), while the remaining BEDT-TTF contribute nothing

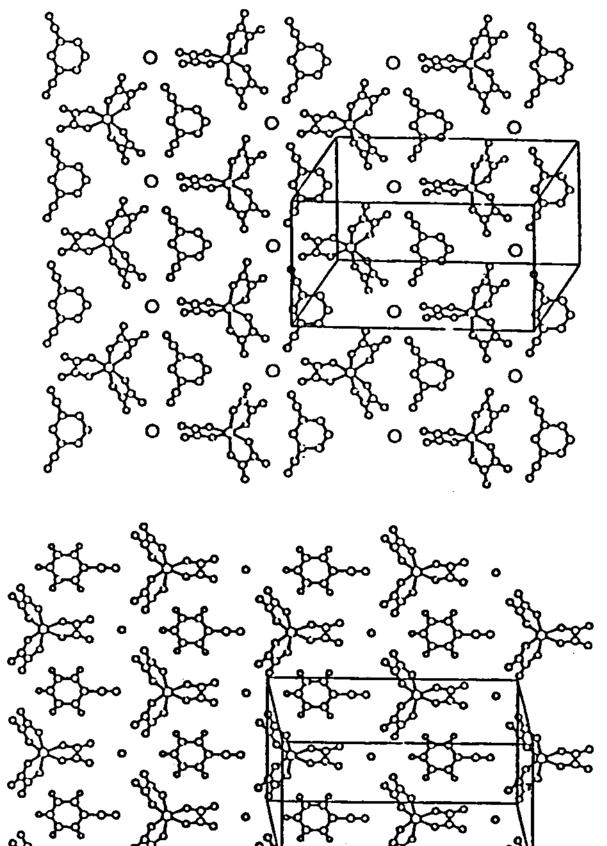

Fig. 6 Anion and solvent layers in $(BEDT\text{-}TTF)_4[AFe(C_2O_4)_3]\cdot PhCN$; top, $A = K$; bottom, $A = H_2O$[26]

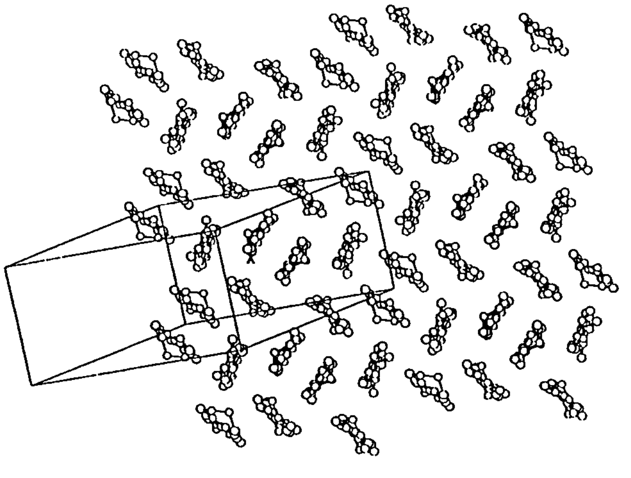

Fig. 7 View of the BEDT-TTF layer in $(BEDT\text{-}TTF)_4[KFe(C_2O_4)_3]\cdot PhCN$ projected along the central C=C bonds[26]

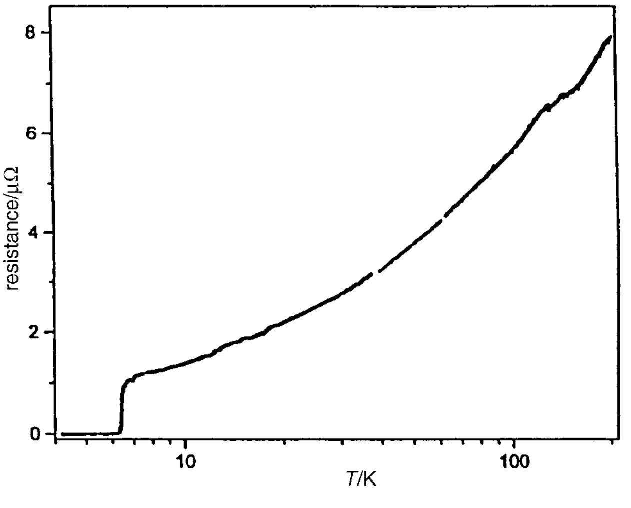

Fig. 8 Temperature dependence of the resistance of $(BEDT\text{-}TTF)_4[(H_2O)Fe(C_2O_4)_3]\cdot PhCN$ from 5 to 200 K[26]

to the paramagnetic susceptibility, in agreement with the assignment of zero charge. On the other hand, the superconducting $A=H_2O$ salt obeys the Curie–Weiss law from 300 to *ca.* 1 K above T_c, though with a temperature independent paramagnetic contribution. The measured Curie constant of 4.38 emu K mol^{-1} is close to that predicted for Fe^{3+} ($^6A_1$), while the Weiss constant (−0.2 K) signifies very weak antiferromagnetic exchange between the Fe moments. However, there is a strong diamagnetic contribution in the superconducting temperature range, returning to Curie–Weiss behaviour above 10 K. Whilst the EPR spectrum of the semiconducting A = K compound consists of a single narrow resonance, that of the $A=H_2O$ compound consists of two resonances: a narrow one assigned to the Fe^{3+} by analogy with the A = K compound, and a much broader resonance from the conduction electrons. This situation is reminiscent of what we found in (BEDT-TTF)$_3$[CuCl$_4$]·H$_2$O.[14]

In the series (BEDT-TTF)$_4$[AFe(C$_2$O$_4$)$_3$]·PhCN ($A=H_2O$, K, NH_4), the lattice is stabilized by PhCN molecules included in the hexagonal cavities. The oxalato-bridged network of A and M^{III} provides an elegant means of introducing transition-metal ions carrying localized magnetic moments into the lattice of a molecular charge-transfer salt. In the case of the $A=H_2O$ compound it led to the discovery of the first molecular superconductor containing localized magnetic moments within its structure, while the A = K, NH_4 compounds are semiconducting. We are now working to incorporate other transition-metal ions at the A site to create a two-dimensional magnetically ordered array between the BEDT-TTF layers as well as introducing 3d metal ions other than Fe.

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