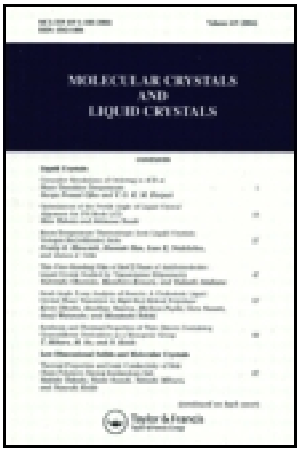

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Metal-Organic Layer Magnets with and without Metallic Conduction

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METAL-ORGANIC LAYER MAGNETS WITH AND WITHOUT METALLIC CONDUCTION

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Abstract A distinguishing feature of molecular-based magnetic materials is that the vast majority of examples are insulators, and the microscopic magnetic moments are therefore localised. Maximum connectivity between centres carrying the moments is therefore desirable to maximise ordering temperatures, so ambidentate ligands are most effective. We have been studying the bimetallic tris-oxalato series $AMFe^{III}(C_2O_4)_3$ from this point of view and the lecture will give an overview of results. We concentrate on organic cations A stabilising a hexagonal layer structure since the details of magnetic ordering are highly sensitive to changes in the packing of A between the layers. In contrast when A = BEDT-TTF the organic layer is conducting and in one case superconductivity has been found.

The large majority of materials showing spontaneous magnetisation at finite temperatures have crystal lattices continuous in three dimensions, either close packed structures or oxides, chalcogenides and halides. Of these, many are metals and insulating magnets are quite rare. One of the most intensively studied of these is the A_2CrX_4 series since they have relatively high Curie temperatures[1-3]. The structure consists of a two-dimensionally infinite square lattice of Cr(II) bridged by halide ions, the A^+ being situated between the layers. An important characteristic of the A_2CrX_4 series is that, in common with some (but not all) insulating magnets, they are relatively transparent in the visible and also at microwave frequencies. Indeed, it has been demonstrated that microwave pumping changes the magnetisation, and hence the optical absorption intensity. We could therefore envisage using this kind of material to modulate a beam of optical frequency at a microwave frequency for communications purposes[4]. Additionally, the A^+ is not confined to monatomic Group 1 ions, but can be a wide range of organic cations, principally of the RNH_3^+ type[5]. We therefore find an example of a magnetic material containing molecular entities, but in which the latter do not participate directly in the exchange interaction mechanism. However, they do participate indirectly, because the ferromagnetic state must show long range order in all three dimensions and the organic molecular cations serve to separate the $[CrX_4^{2-}]_\infty$ layers. By changing the substituent R (especially the length of an alkyl chain C_nH_{2n+1}) on can vary the interlayer spacing by a factor of more than two and T_c varies by about 30%.

In other cases the organic moieties (while not themselves either bearing or transmitting the magnetic moment) modulate the exchange process by bringing about small but crucial changes in the site symmetry around a magnetic metal ion or influencing the geometry of an exchange pathway. Two examples are given here, taken from our own recent work. The bimetallic tris-oxalato series provide such an example.

BIMETALLIC TRIS-OXALATO-SALTS

One strategy for achieving finite zero-field magnetisation in a molecular-based array, without the need for ferromagnetic near neighbour exchange, is to exploit ferrimagnetism. Compounds with general formula $AM^{II}M^{III}(C_2O_4)_3$ 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[6]. Depending on the connectivity of the $M^{III}(C_2O_4)_3^{3-}$ 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^+ [7].

Connection between $M^{III}(C_2O_4)_3^{3-}$ 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 1).

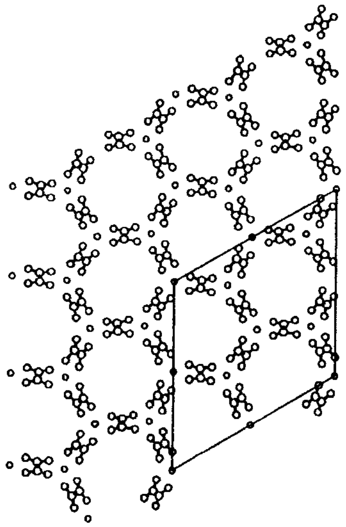

FIGURE 1. Two-dimensional honeycomb structure of $AM^{II}M^{III}(C_2O_4)_3$

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 have M^{II} = Mn or Fe and M^{III} = Fe. Averaged over the whole group the spacing between the metal ions in the plane decreases from Mn to Fe by 0.026 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 0.083 Å, most probably because the organic groups which enter the hexagonal cavities are slightly extended as the cavity becomes smaller.

TABLE 1. M^{II}-Fe^{III}(d_1) and interlayer separation (d_2) in two-dimensional $AM^{II}Fe^{III}(C_2O_4)_3$

	M^{II}=Fe		M^{II}=Mn	
	d_1	d_2	d_1	d_2
$N(n\text{-}C_3H_7)_4{}^+$	4.667	8.218	4.686	8.185
$N(n\text{-}C_4H_9)_4{}^+$	4.701	8.980	4.731	8.937
$N(n\text{-}C_5H_{11})_4{}^+$	4.703	10.233	4.728	10.158
$P(n\text{-}C_4H_9)_4{}^+$	4.735	9.317	4.760	9.525
$As(C_6H_5)_4{}^+$	4.683	9.655	4.722	9.567
$N(C_6H_5CH_2)(n\text{-}C_4H_9)_3{}^+$	4.690	9.633	4.735	9.433
$(C_6H_5)_3PNP(C_6H_5)_3{}^+$	4.690	14.433	4.707	14.517

One example that we have studied in detail is $N(n\text{-}C_5H_{11})_4MnFe(C_2O_4)_3$ whose crystal structure consists of alternate layers of $[MnFe(C_2O_4)_3]^-$ and $N(n\text{-}C_5H_{11})_4{}^+$. The former comprise honeycomb networks of alternating Mn and Fe bridged by $C_2O_4{}^{2-}$ (Figure 2). Thus both metal ions are co-ordinated by six O originating from three bidentate oxalate ions forming a trigonally distorted octahedron. Similar networks have been observed in $P(C_6H_5)_4MnCr(C_2O_4)_3$[8] and $N(n\text{-}C_4H_9)_4MnCr(C_2O_4)_3$[9] though in the latter case none of the C atoms of the quaternary ammonium cation were located, and the N was arbitrarily placed on a threefold axis. In contrast we have been able to position all the C atoms of the $N(n\text{-}C_3H_{11})_4{}^+$ and have not assumed a rhombohedral cell. In the $P(C_6H_5)_4{}^+$ compound, too, one P–C bond lies parallel to a threefold axis and the unit cell is also rhombohedral. Thus we are in a position to discuss the co-ordination geometry of the metal ions and the packing of the organic cations in this class of compound in more detail than previously.

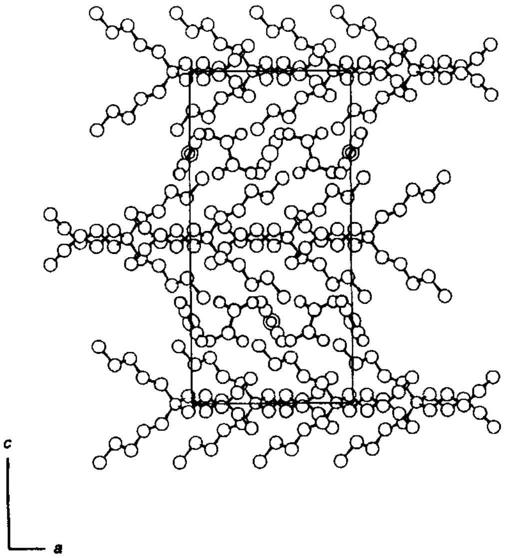

Fig. 2 Projection of the structure of $N(n\text{-}C_5H_{11})_4MnFe(C_2O_4)_3$ along the *b* axis

As far as the bimetallic tris-oxalato layer is concerned (Figure 2), 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; at both Fe and Mn sites two bonds are slightly longer than the other four. One index of the extent 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)[10]. 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 $N(n\text{-}C_5H_{11})_4^+$ form rectangular planar arrays, interleaving the $MnFe(C_2O_4)_3^-$ 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 (Figure 3). Our attempts to synthesise compounds in the series $N(n\text{-}C_nH_{2n+1})_4MnFe(C_2O_4)_3$ were only successful for n = 3-5, no C_6H_{14} derivative being obtained[11]. It would appear that the steric requirement to accommodate the alkyl chains within the hexagonal Mn_3Fe_3 cavities cannot be satisfied for n > 5.

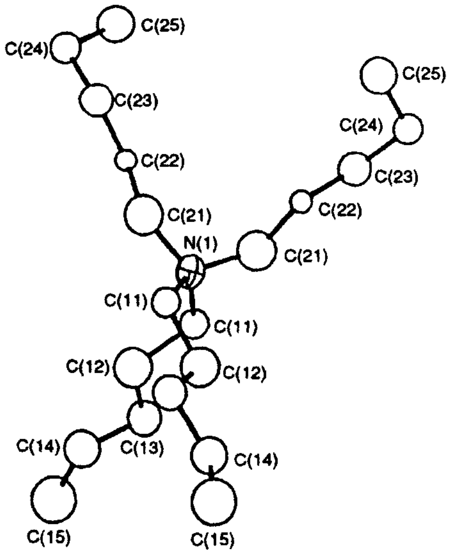

FIGURE 3 The $N(n\text{-}C_5H_{11})_4^+$ group in $N(n\text{-}C_5H_{11})_4MnFe(C_2O_4)_3$

MAGNETIC PROPERTIES

M^{II} = Mn

The M^{II} = Mn compounds constitute a rather unusual kind of ferrimagnetism in that the electronic ground states of the two metal ions are the same, $^6A_1$ 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 around 27 K (nearly independent of A), the susceptibility increases abruptly (Figure 4), to reach a value which does vary strongly with A, being smallest for $N(n\text{-}C_4H_9)_4^+$ and largest for $(C_6H_5)_3PNP(C_6H_5)_3^+$ at 5 K[11]. As in the Mn alkyl-phosphonates[12], 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.

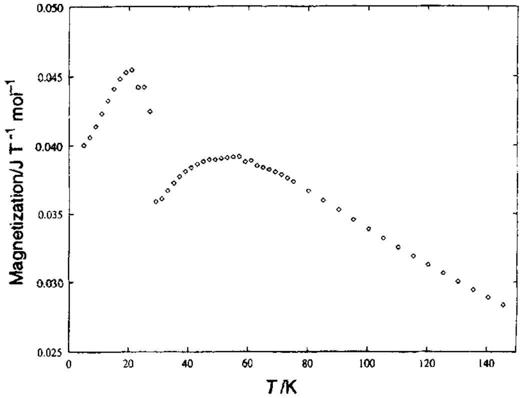

Fig. 4 Temperature dependent magnetization of polycrystalline $N(n\text{-}C_5H_{11})_4MnFe(C_2O_4)_3$ from 4 to 150 K

M^{II} = Fe

When M^{II} = Fe in the bimetallic tris-oxalateo-Fe(III) series 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 magnetisation at low temperature, increasing monotonically from zero at T_c to a limiting value at $T \longrightarrow 0$, or a magnetisation that increases at first from zero below T_c but then reaches a maximum. At lower temperatures, the magnetisation then falls again, passing through zero and becoming strongly negative[13] (Figure 5). This behaviour is extremely rare among molecular-based magnetic materials but finds a precedent among continuous lattice oxides[14]. As long ago as the 1940s there was great interest in ferrimagnetic mixed valency Fe oxides with spinel and garnet structures because they were among the first materials discovered with non zero spontaneous magnetisation which were not metallic.

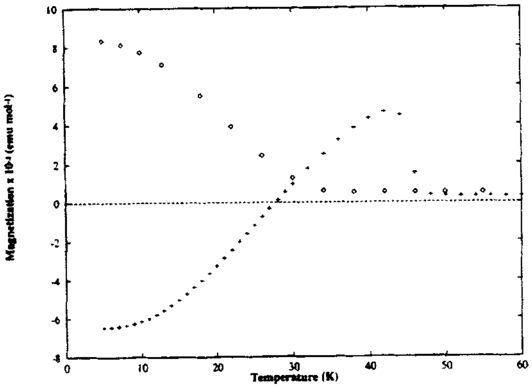

Figure 5 Negative magnetisation of $(C_6H_5)_3PNP(C_6H_5)_3Fe^{II}Fe^{III}(C_2O_4)_3$ at low temperature and 'normal' behaviour of $As(C_6H_5)_4Fe^{II}Fe^{III}(C_2O_4)$

The origin of the apparently bizarre situation that the net magnetisation of a sample should be antiparallel to the applied measurement field was actually described as long ago as 1948 by Néel in his classic paper on the theory of ferrimagnetism[15]. In a ferrimagnet the net magnetisation at a given temperature is the vector sum of the magnetisations of each sublattice. Should the temperature dependence of the magnetisations of each sublattice be similar the resultant will be a monotonic increase from T_c to absolute zero as shown in Figure 5 for $As(C_6H_5)_4Fe^{II}Fe^{III}(C_2O_4)_3$. On the other hand if the temperature derivatives of sublattice magnetisation $dM_{Fe(II)}/dT$ and $dM_{Fe(III)}/dT$ have a different dependence on temperature, then the temperature derivative of the resultant $d(M_{Fe(II)} - M_{Fe(III)})/dT$ can change sign. Figure 6 shows the situation schematically. It is also feasible (as shown in Figure 6) for the magnetisations of the two sublattices to cancel at some temperature called the compensation temperature. However, the feature distinguishing the bimetallic tris-oxalato compounds from the oxides is that the drastically varying magnetic behaviour comes about by changing organic groups situated quite far away in the lattice from the magnetic centres.

TRIS-OXALATO-METALLATE LAYERS INTERCALATED WITH BEDT-TTF

Up to this point we have considered tris-oxalato-layers separated by organic cations where the latter do not contribute directly to the electronic properties. However, it is also possible to put electronically active molecules between the layers and we have characterised three such compounds, $(BEDT\text{-}TTF)_4AFe(C_2O_4)_3{\cdot}C_6H_5CN$ ($A= H_2O, K^+, NH_4^+$)[14]. While the stoichiometry of BEDT-TTF to Fe is the same in 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 $A = K^+, NH_4^+$ 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[17] and is the first example of a molecular superconductor containing magnetic ions[18].

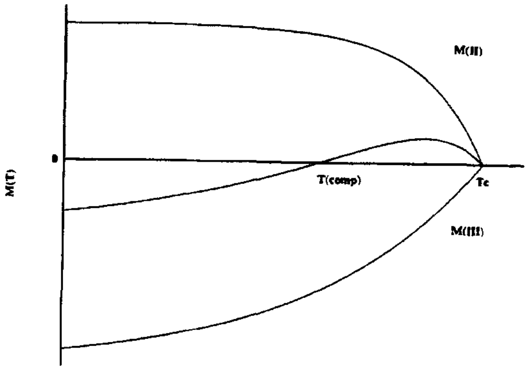

Figure 6 Schematic temperature dependence of sublattice magnetisation in a ferrimagnet and resultant zero-field magnetisation

The anion layers contain alternating A and Fe forming an approximately hexagonal network (Figure 7). The Fe are octahedrally co-ordinated by three bidentate oxalate ions, while the O atoms of the oxalate which are not co-ordinated to Fe form cavities occupied either by K^+ or H_2O. The benzonitrile molecules occupy roughly hexagonal cavities.

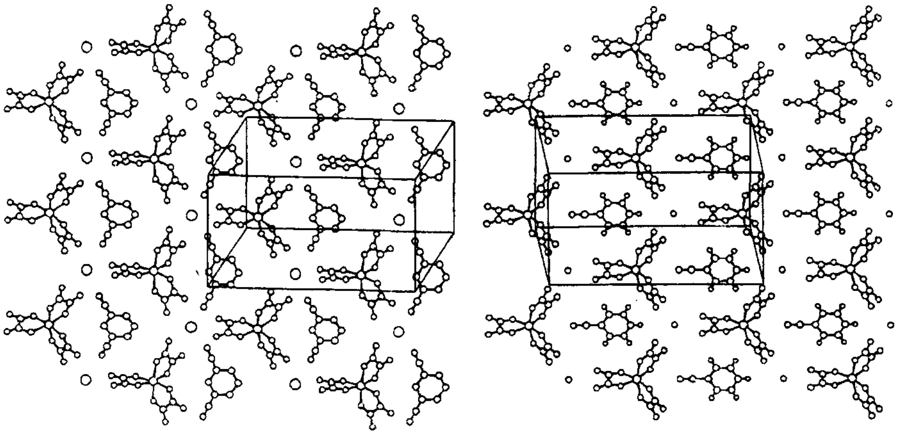

FIGURE 7. The anion and solvent layers in $(BEDT\text{-}TTF)_4AFe(C_2O_4)_3 \cdot C_6H_5CN$: (a, left) A = $K^+$and (b, right) A = H_2O.

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 indicate charges of 0 and +1, the latter as face-to-face dimers, surrounded by monomeric neutral molecules (Figure 8). Molecular planes of neighbouring dimers are oriented nearly orthogonal to one another, as in the κ-phase structure of $(BEDT\text{-}TTF)_2X$[19], 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. 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[17].

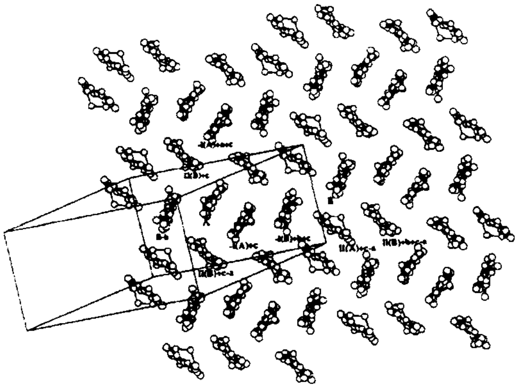

FIGURE 8. View of the BEDT-TTF layer in $(BEDT\text{-}TTF)_4KFe(C_2O_4)_3{\cdot}C_6H_5CN$ projected along the central C=C bonds.

The K^+ and NH_4^+ salts are both semiconductors but the H_2O salt is a metal with resistivity of $\sim 10^{-2}\ \Omega$ cm at 200 K, decreasing monotonically by a factor of about 8 down to 7 K, at which temperature it becomes superconducting (Figure 9).

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, and no contribution from the BEDT-TTF, including those with a charge of +1. Hence the $(BEDT\text{-}TTF)_2^{2+}$ are spin-paired, while the uncharged molecules contribute nothing to the paramagnetic susceptibility. On the other hand the superconducting A= H_2O salt obeys the Curie-Weiss law from 300 to about 1 K above T_c, with a temperature independent paramagnetic contribution. The Curie constant is close to that predicted for Fe^{3+} ($^6A_1$), and there is only very weak antiferromagnetic exchange between the Fe. 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

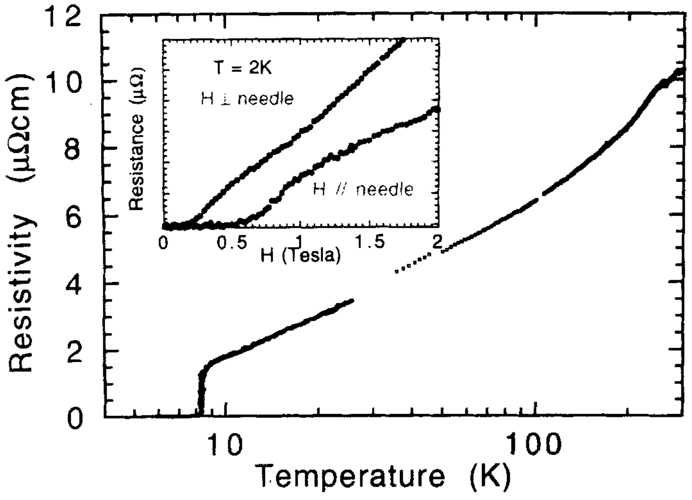

FIGURE 9. Temperature dependence of the resistance of $(BEDT\text{-}TTF)_4(H_2O)Fe(C_2O_4)_3{\cdot}C_6H_5CN$ from 5-200 K

reminiscent of what we found in $(BEDT\text{-}TTF)_3CuCl_4, H_2O$[20].

In the series $(BEDT\text{-}TTF)_4AFe(C_2O_4)_3{\cdot}\ C_6H_5CN$ (A= H_2O, K, NH_4), the lattice is stabilised by the C_6H_5CN in the hexagonal cavities. The oxalato-bridged network of A and M^{III} is an elegant way of introducing transition metal ions with localised magnetic moments into the lattice of a molecular charge transfer salt. In the case of the A= H_2O compound it has enabled us to prepare the first molecular superconductor containing localised 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.

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