Co-ordination complexes as organic–inorganic layer magnets

Peter Day

Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS, UK

Examples are given of transition-metal co-ordination complexes that give rise to alternating layers of organic and inorganic moieties in the solid state exhibiting finite zero-field magnetisation at low temperature. The mechanisms of magnetic exchange included are ferromagnetism, ferrimagnetism and canted antiferromagnetism.

When inorganic chemistry finally emerged as a distinct discipline in the 1950s one of the driving forces was the application of physical methods to determine the fine detail of molecular electronic structure, and hence provide the basis for correlations between structure and properties. Among the methods that came especially into prominence at that time was the measurement of bulk magnetic susceptibility. In his seminal book 'The Nature of the Chemical Bond' Pauling,[1] in the 1930s, devoted a whole chapter to what he called 'the magnetic criterion for bond type', by which he meant the distinction between what we now know as high-spin and low-spin electron configurations. In the 1950s and 1960s it was Nyholm, with Figgis and Lewis,[2] who pioneered the field that became known as magnetochemistry, but since then, until the last few years, inorganic chemists have moved away from bulk magnetic studies in favour of more direct structural probes like magnetic resonance. However, there is now a distinct field of study developing around the directed synthesis of new compounds (often based on co-ordination complexes) that show varieties of long-range magnetic order. From some points of view, ordered magnets have been considered as closer to the concerns of physicists, and the key examples have tended to be, if not simple metals and alloys, then binary or ternary oxides: in short, continuous lattices. The purpose of this Perspective is to survey some of the more novel forms of magnetism that have arisen from synthetic inorganic chemistry, using mainly examples from the work of my group, and with an emphasis on molecular lattices with strongly developed layer structures.

Strategies towards Spontaneous Magnetism

A major force driving synthesis in the field of magnetism is to try and create lattices which not only show long-range magnetic order, but exhibit 'spontaneous' magnetisation, *i.e.* a non-zero net moment in the absence of an applied field. To reach this goal a variety of strategies have been tried. 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.[3] Of these many are metals and insulating magnets are quite rare. Indeed, all the molecular-based magnets prepared up to now are insulators (Table 1).

Physical mechanisms of ferromagnetic exchange coupling between localised moments are based on the notion of 'orthogonal magnetic orbitals',[4] a situation that is very difficult to achieve in a three-dimensionally continuous lattice. Many years ago it was shown[5,6] that a co-operative Jahn–Teller lattice distortion provided a suitable means of creating 'orbital ordering' in two dimensions, such that singly occupied 3d orbitals on a given metal ion are made orthogonal to the corresponding ones on all the nearest-neighbour ions. The metals concerned are Cr^{II}, Mn^{III} and Cu^{II} (Table 1). Halide and cyanide complexes of

Table 1 Some insulating ferromagnets with mono- and poly-atomic ligands

	T_c/K		T_c/K
$CrBr_3$	33	[Mn(pc)]	8.6
EuO	69	[Fe(phen)$_2$Cl$_2$]	5
$K_2[CuF_4]$	6.3	$GdCl_3$	2.2
$Cs[MnF_4]$	18.9	A_2CrX_4	50–60
$[(RNH_3)_2][CuCl_4]$	7–11	[Fe(η-C_5Me_5)$_2$]·tcne	4.8
$Tb(OH)_3$	3.7	[Mn(tpp)]·tcne	18
$Fe_4[Fe(CN)_6]_3$·14H_2O	5.5	$Cs[Cr_2(CN)_6]$	90
		$[Cr_5(CN)_{12}]$·10H_2O	220

pc = Phthalocyaninate; phen = 1,10-phenanthroline; tcne = tetracyanoethylene; tpp = 5,10,15,20-tetraphenylphorphyrinate.

these elements generate genuine ferromagnets, but still they are small in number.

Given the difficulty of engineering near-neighbour ferromagnetic exchange in the absence of conduction electrons, alternative strategies for inducing finite zero-field magnetisation are worth considering. One route lies in exploiting ferrimagnetism. A ferrimagnet contains two different magnetic ions with near-neighbour antiferromagnetic exchange coupling. Since the antiparallel moments do not cancel there is a net resultant moment in zero field below the ordering temperature T_c. The most famous examples are the ferro-spinels, including the oldest magnetic material of all, magnetite (Fe_3O_4), but some molecular-based examples are discussed below. Finally a third strategy, less exploited than the other two, consists of building lattices containing only one magnetic ion, but in which (because of competition with single-ion anisotropy induced by a low-symmetry ligand field and second-order spin–orbit coupling) the moments on neighbouring ions are not exactly antiparallel. This is called canted antiferromagnetism or 'weak ferromagnetism' because the resultant of two vectors that are nearly, but not quite, antiparallel is a small vector at right angles. Some examples will be given of all three approaches, based on synthetic co-ordination chemistry.

Transparent Insulating Ferromagnets

One of the most intensively studied of the ferromagnets based on the principle of orthogonal magnetic orbitals is the A_2CrX_4 series since they have relatively high Curie temperatures.[7–9] Their properties have been comprehensively reviewed so only a few salient points will be mentioned here. The structure consists of a two-dimensionally infinite square lattice of Cr^{II} bridged by halide ions, the A^+ being situated between the layers (Fig. 1). An important characteristic of these compounds is that they are relatively transparent in the visible and also at microwave frequencies. The intensity of the optical absorption of such materials, which is due to spin-forbidden ligand-field transi-
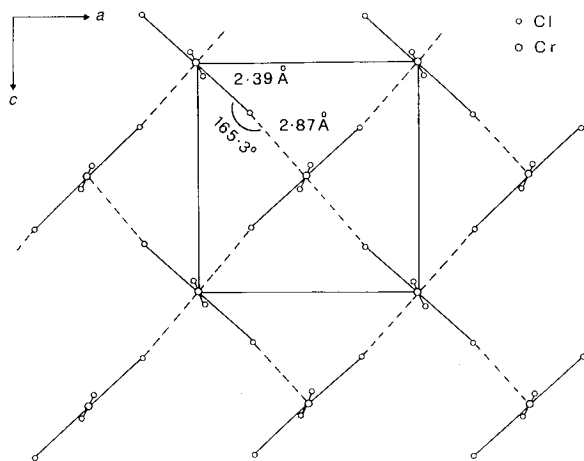
Fig. 1 The $([CrCl_4]^{2-})_\infty$ layer in $[H_3N(CH_2)_3NH_3][CrCl_4]$ [8]
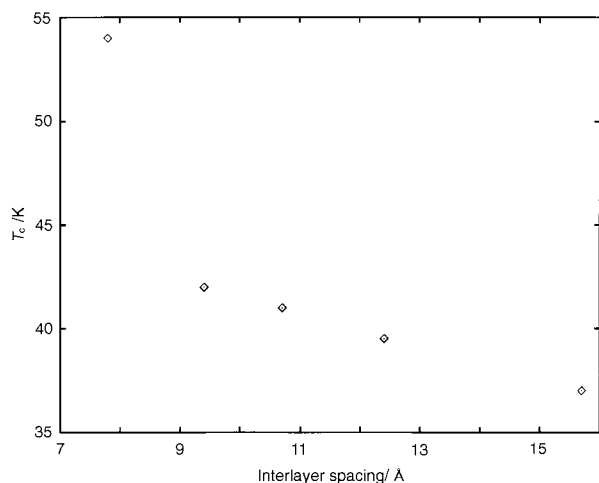
Fig. 2 Variation of the Curie temperature of A_2CrCl_4 with interlayer spacing

Fig. 3 The layer structure of $Mn(CH_3PO_3)\cdot H_2O$

tions, is extremely sensitive to the onset of the magnetic ordering.[10] This is because the transitions become allowed by coupling the electronic excitation with annihilation of thermally populated spin deviations, a mechanism which has been validated in great detail by a combination of optical and neutron experiments.

As well as exciting spin deviations thermally, they can also be excited by irradiating the compound with microwaves, and it has been demonstrated[11] that microwave pumping changes the magnetisation and hence the optical absorption intensity. Thus one could envisage using this kind of material to modulate a beam of optical frequency at a microwave frequency for communications purposes.

The A^+ separating the layers are not confined to monoatomic Group 1 ions, but can be a wide range of organic cations, principally of the RNH_3^+ type.[12] This leads to the unusual situation of a magnetic material containing molecular entities, but in which the latter do not participate directly in the exchange mechanism. However, they do participate indirectly, because the ferromagnetic state must show long-range order in all three dimensions and the organic molecular cations separate the $([CrX_4]^{2-})_\infty$ layers. By changing R (especially the length of an alkyl chain C_nH_{2n+1}) one can vary the interlayer spacing by a factor of more than two. This kind of chemistry makes accessible a structural change much larger than would be possible in a purely inorganic non-molecular lattice. The variation of Curie temperature with interlayer spacing in the series is shown in Fig. 2.
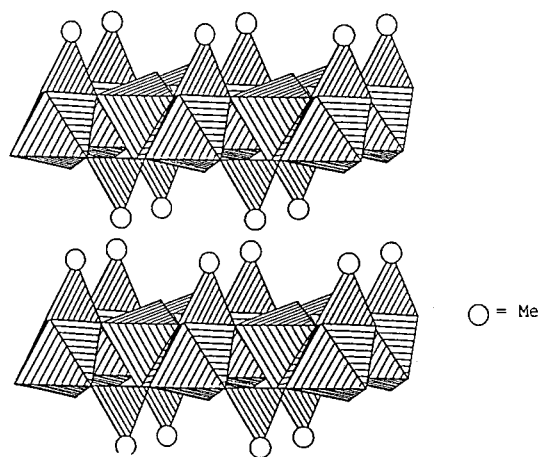
Canted Antiferromagnets

When a paramagnetic ion is surrounded by a low-symmetry ligand environment, spin–orbit coupling results in a small component of excited states being mixed into the ground state giving a zero-field splitting of the lowest electronic levels. This splitting mimics the effect of a large static magnetic field, along the principal axis of the local ligand field.[13] The moments are therefore constrained to that direction and we find a single-ion anisotropy. Should the local distortion axes on neighbouring sites not be parallel, in the presence of near-neighbour antiferromagnetic exchange the moments will not be aligned in an exactly parallel fashion, but will make an angle to each other. Consequently the moments do not cancel in the antiferromagnetically ordered state, and there is a small net moment, hence weak ferromagnetism.[14]

A few years ago we examined[15] the series of alkylphosphonate salts $Mn(C_nH_{2n+1}PO_3)_2\cdot H_2O$ which have layer structures quite similar to the ternary phosphates $M^IM^{II}PO_4\cdot H_2O$.[16] The metal ion is again surrounded by a very low-symmetry coordination of oxygen (site group C_2), five from phosphonate groups and one from H_2O. Neighbouring metal ions are connected by exchange paths through O–P–O linkages of the anions into a nearly square two-dimensional lattice almost identical to that of the phosphates, while the P–C bonds of the phosphonate groups are directed perpendicular to the planes defined by the metal ions (Fig. 3). Exchange within the layers is antiferromagnetic and the susceptibilities also pass through a broad maximum around 20 K characteristic of a low-dimensional antiferromagnet. Near 15 K the susceptibility increases abruptly, finally saturating at low temperature at a value which varies markedly with the length of the alkyl chain, being smallest for CH_3 and largest for C_4H_9. The limiting low-field magnetisation at low temperature yields a direct estimate of the canting angle between the moments. For example that for C_4H_9 is 2.9°. Close examination shows that the onset temperature of the canted state also changes with the alkyl group, those of the C_2H_5 and C_4H_9 compounds being higher than those of CH_3 and C_3H_7 (Fig. 4).

Alternation effects are a well known structural feature of crystals containing aliphatic hydrocarbon chains, for example the interplanar spacing in the layer perovskite halide salts $[C_nH_{2n+1}NH_3]_2[MX_4]$ when plotted against n is not a straight line but a zigzag.[17] Put another way, the increase in interlayer spacing caused by adding one CH_2 group to the chain is larger from an even to an odd number of C atoms than *vice versa*. The difference arises from the contrasting ways in which the terminal CH_3 groups mesh together in the two cases: the terminal C–C bond of a C_{2n} chain is nearly parallel to the layer while that of a C_{2n+1} chain is nearly perpendicular. Fig. 4 shows the first example of an alternation effect in magnetic properties.
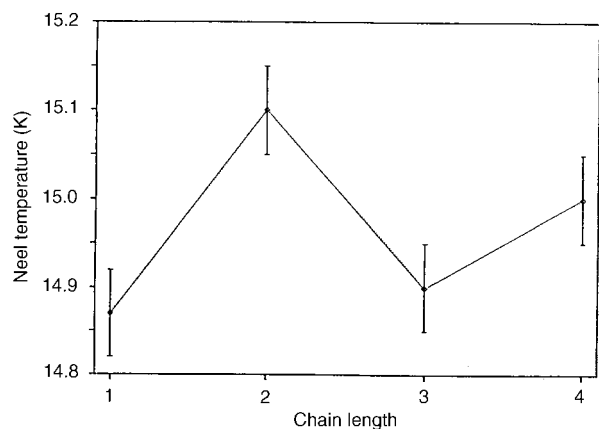
Fig. 4 Magnetic ordering temperatures of $Mn(n\text{-}C_nH_{2n+1}PO_3)\cdot H_2O$ as a function of n (ref. 15)

Although full crystal structures are not available for the four compounds, one must suppose that the different packing of the chain ends causes a small change in the orientation of the PO_3 group. That would change the M–O–P bond angle, affecting the superexchange pathway and hence T_N. Thus we have a clear case of intervention of an organic substituent far from the magnetic site in influencing the ordering process.

Varying the chain length of the alkylphosphonate group leads to a much larger variation in the interlayer spacing than changing the Group 1 ion in the ternary phosphates. For example in $Mn(CH_3PO_3)\cdot H_2O$ it is 8.82 Å and in $Mn(C_4H_9\text{-}PO_3)\cdot H_2O$ in 14.71 Å. This makes the phosphate and phosphonate salts a very attractive series in which to monitor the transition from two- to three-dimensional order by measuring the critical exponent of the magnetisation β as T_N is approached from lower temperatures. Thus the critical behaviour of $[NH_4][Mn(PO_4)]\cdot H_2O$ and its deuteriated analogue was studied[18] by neutron diffraction and bulk magnetometry, finding that β underwent a crossover from a value of 0.20 when the reduced temperature $\varepsilon = (T_N - T)/T_N$ was >0.03–0.07 to a much higher value (0.39–0.40) on approaching T_N. Then the alkylphosphonates were examined[19] to see whether there is a corresponding crossover and if so how it varies with interlayer spacing.

Data more remote from T_N obey the relationship $M_\varepsilon = M_0\varepsilon^\beta$ with β in the region of 0.20 for $Mn(C_nH_{2n+1}PO_3)\cdot H_2O$ ($n = 2$–4). However, as T_N is approached from below the exponential relationship changes and a much higher exponent β′ becomes evident. The value of β is close to that found in $M^I[Mn(PO_4)]\cdot H_2O$ (M^I = NH_4, ND_4 or K) and far from any of the estimates of two- or three-dimensional magnetic models. Thus in three dimensions the Ising, XY and Hesienberg models predict respectively 0.31, 0.33 and 0.35 while the two-dimensional Ising model predicts 0.125. The related compound $Mn(HCO_2)_2\cdot 2D_2O$, also a quadratic layer Heisenberg antiferromagnet, gives $\beta = 0.22(1)$, with a crossover to $\beta' = 0.31(2)$ at $\varepsilon \approx 0.02$. Recently, Bramwell and Holdsworth[20] have shown how β values in the region of 0.23 can arise from a two-dimensional model. Whilst the measured β′ are larger than predicted for any of the three-dimensional models the crossover clearly demonstrates evolution from two- to three-dimensional behaviour.

The reduced temperatures ε_{X0} at which the cross-overs occur also vary significantly from one compound to another within the manganese phosphate (phosphonate) hydrate series. Among the metal(I) compounds ε_{X0} is a little larger in $K[Mn(PO_4)]\cdot H_2O$ [0.09(1)] than in the NH_4 compound [0.07(1)], no doubt to be correlated with the smaller interlayer separation in the former. For the alkylphosphonates ε_{X0} decreases as the interlayer separation increases, corresponding to a decrease in the ratio of in-plane to out-of-plane exchange constants. This was the first systematic study of the critical exponents and crossover
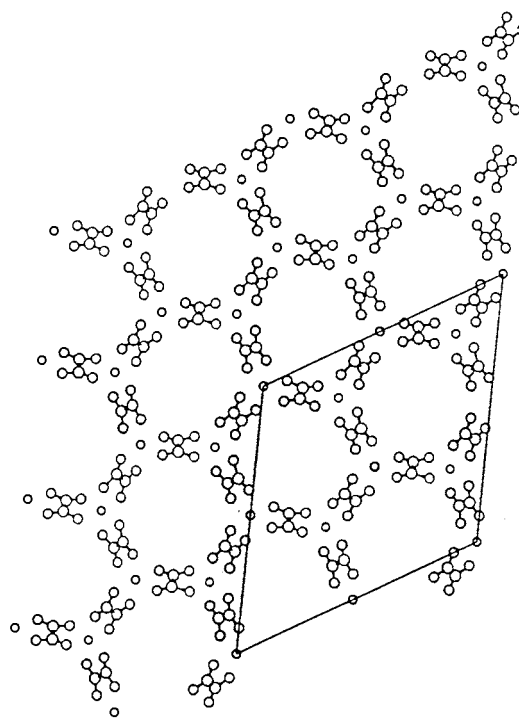

Fig. 5 Honeycomb layer structure of $A^IM^{II}M^{III}(C_2O_4)_3$

Table 2 Intralayer (d_1) and interlayer $M^{II}Fe^{III}$ separation (d_2) in $AM^{II}Fe^{III}(C_2O_4)_3$ in Å (ref. 23)

A	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	8.990	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
$[N(CH_2C_6H_5)(n\text{-}C_4H_9)_3]^+$	4.690	9.633	4.735	9.433
$[(C_6H_5)_3PNP(C_6H_5)_3]^+$	4.690	14.433	4.707	14.517

temperatures for a series of two-dimensional weak ferromagnets.

Ferrimagnets

In the previous section non-zero spontaneous magnetisation was achieved in compounds where there was only one type of metal-ion site. When two different metal ions (or two oxidation states of the same metal) are coupled antiferromagnetically ferrimagnetism provides an alternative route to the same end. Ferrimagnetic bulk magnetic properties of metal–organic compounds can be sensitive to very small changes in the organic substituents, and hence the molecular packing. 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 di- and tri-valent M both from transition metal and B-subgroup ions.[21]

Cross-linking of the $[M^{III}(C_2O_4)_3]^{3-}$ 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 (Fig. 5).

Many compounds in this series therefore have approximately hexagonal crystal structures with basal-plane unit-cell constants that vary only slightly with A^+, though with strongly varying interlayer separation. Some unit-cell constants are listed in Table 2, which shows that a factor of 2 in interlayer
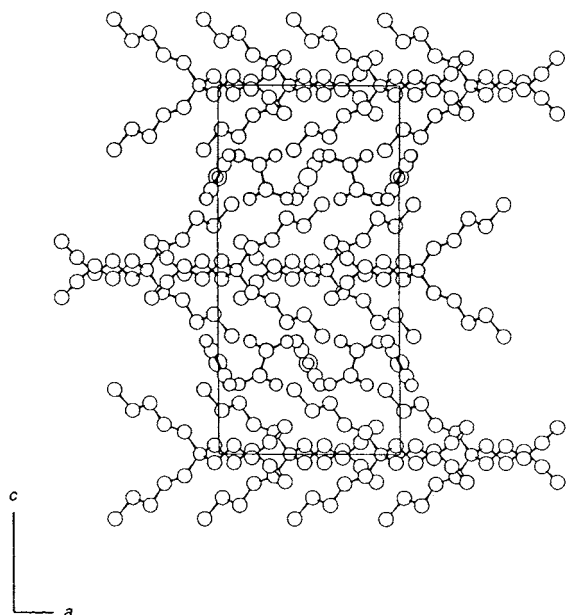
Fig. 6 Crystal structure of [N(n-C$_5$H$_{11}$)$_4$][MnFe(C$_2$O$_4$)$_3$] projected along the *b* axis

Fig. 7 Variation of the magnetisation of [N(n-C$_5$H$_{11}$)$_4$][MnFe(C$_2$O$_4$)$_3$] measured at 10 mT with temperature

Fig. 8 Temperature dependence of the magnetisation of A^{I}Fe^{II}Fe^{III}-(C$_2$O$_4$)$_3$ measured at 10 mT: 'normal' behaviour, A^I = As(C$_6$H$_5$)$_4$; 'negative' behaviour, A^I = (C$_6$H$_5$)$_3$PNP(C$_6$H$_5$)$_3$

separation is easily achievable. In fourteen compounds with M^{II} = Mn or Fe and M^{III} = Fe 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, while 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. One example is [N(n-C$_5$H$_{11}$)$_4$][MnFe-(C$_2$O$_4$)$_3$] the crystal structure of which consists of alternate layers of [MnFe(C$_2$O$_4$)$_3$]$^-$ and [N(n-C$_5$H$_{11}$)$_4$]$^+$, the former comprising honeycomb networks of alternating Mn and Fe bridged by C$_2$O$_4{}^{2-}$ (Fig. 6).[22] 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$_6$H$_5$)$_4$][MnCr(C$_2$O$_4$)$_3$][24] and [N(n-C$_4$H$_9$)$_4$]-[MnCr(C$_2$O$_4$)$_3$][25] though in the latter case none of the C atoms of the cation was located, and the N was arbitrarily placed on a three-fold axis. In the [P(C$_6$H$_5$)$_4$]$^+$ compound, too, one P–C bond lies parallel to a three-fold axis and the unit cell is also rhombohedral.

In the [N(n-C$_5$H$_{11}$)$_4$]$^+$ compound 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 is the deviation of the *trans* O–M–O bond angles from 180°: at the iron site two such angles are 163 and 170°. The 'bite angle' O–M–O for bidentate chelating oxalate groups averages 78.0° around the iron site and 79° around the Mn, similar to those found in other oxalato-complexes of Fe^{III} and Mn^{II}.[26] Since the mean O–M–O angle for O atoms on adjacent oxalate groups exceeds 90° (99.4° at the iron site and 98.6° at Mn) both MO$_6$ octahedra are elongated perpendicular to the plane of the [MnFe(C$_2$O$_4$)$_3$]$^-$ 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 ferrimagnetism of the M^{II} = Mn compounds is a rather unusual kind in that the ground states of the two metal ions are both $^6A_1$ 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. Existence of strong antiferromagnetic spin correlations within the layers is confirmed by a broad maximum in the susceptibil-
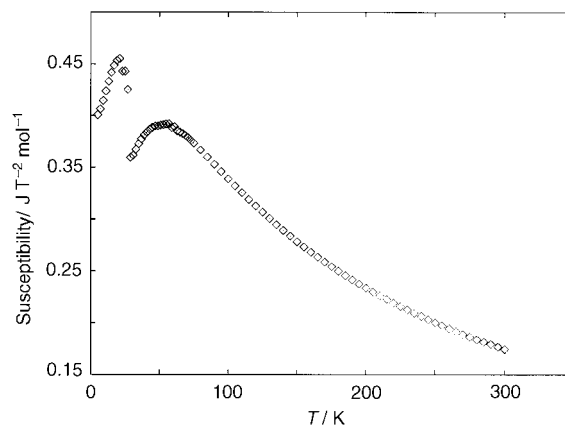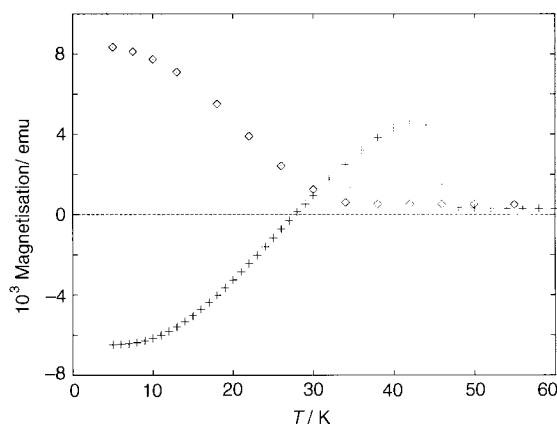
ity at 55 K, again independent of A. The short-range magnetic order therefore mimics that of a two-dimensional antiferromagnet. However, with the onset of three-dimensional order at 27 K (nearly independent of A) the susceptibility increases abruptly (Fig. 7), to reach a value which does vary strongly with A, being smallest for [N(n-C$_4$H$_9$)$_4$]$^+$ and largest for [(C$_6$H$_5$)$_3$-PNP(C$_6$H$_5$)$_3$]$^+$ at 5 K.[23] As in the manganese alkylphosphonates[15] this is due to canted antiferromagnets. Furthermore, the magnitude of the uncompensated moment is determined by an organic group which not only takes no part in the exchange mechanism, but is far removed from the site of the magnetic moment. Clearly, this phenomenon has no analogue among conventional magnetic materials.

When M^{II} = Fe in the bimetallic tris(oxalato)ferrate(III) series the two magnetic ions have $S = 2$ and $\frac{5}{2}$, giving rise to a conventional ferrimagnet. However, depending on the nature of the organic cation A, one either has a normal magnetisation at low temperature that increases monotonically from zero at T_c to a limiting value at $T = 0$, or one that increases below T_c but reaches a maximum. At lower temperatures the magnetisation then falls again, passing through zero and becoming strongly negative[27] (Fig. 8). This behaviour is highly unusual but finds a precedent among ferrimagnetic mixed-valent iron oxides with spinel and garnet structures, which were widely studied in the 1950s because they were among the first materials with non-zero spontaneous magnetisation which were not metallic.[28]

The origin of the apparently bizarre situation that the net magnetisation of a sample should be antiparallel to the applied measurement field was rationalised by Néel[29] on the basis of molecular field theory. In a ferrimagnet the net magnetisation at a given temperature is the sum of the magnetisations of each sublattice. If the temperature dependences of the sublattice
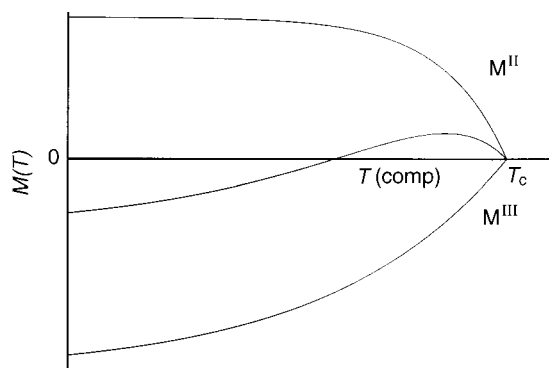
Fig. 9 Schematic temperature dependence of the sublattice magnetisations in a $M^{II}M^{III}$ ferrimagnet and the resulting measured magnetisation

magnetisations are similar the resultant is a monotonic increase from T_c to absolute zero as shown in Fig. 8 for $[As(C_6H_5)_4]$-$[Fe^{II}Fe^{III}(C_2O_4)_3]$. On the other hand, if the temperature derivatives of sublattice magnetisation $dM_{Fe^{II}}/dT$ and $dM_{Fe^{III}}/dT$ vary differently with temperature, the resultant $d(M_{Fe^{II}} - M_{Fe^{III}})/dT$ may change sign (Fig. 9). It may also happen (as shown in Fig. 9) that the magnetisations of the two sublattices 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.

Conclusion

This Perspective has used examples from transition-metal coordination chemistry to illustrate how it is possible to construct layer lattices, interleaved with organic molecular moieties, that exhibit spontaneous magnetisation. All the magnetic exchange mechanisms known to quantum mechanics, *i.e.* ferromagnetic, ferrimagnetic and canted antiferromagnetic, are found among organic–inorganic layer compounds, but with features unique to the molecular solid state. Apart from the obvious, that one can synthesize materials showing spontaneous magnetisation from solution at room temperature (in contrast to high temperatures needed to obtain halide and chalcogenide magnets), there are other features common to metal–organic magnets that distinguish them from more conventional magnetic materials.[30] Among these are optical transparency, opening up the possibility of unusual magneto-optical behaviour, and extreme sensitivity to small changes in the packing of organic groups between the layers that contain the magnetic ions. Such features enable lattice engineering to be exploited to design compounds with optical and magnetic properties capable of being switched by temperature, pressure and applied fields. If we can achieve this goal not only will the science of inorganic chemistry be enlarged, but many applications lie in waiting.

Acknowledgements

References

1 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, 1948.
2 See, for example, B. N. Figgis and J. Lewis, in *Modern Coordination Chemistry*, eds. J. Lewis and R. G. Wilkins, Interscience, New York, 1960, ch. 6.
3 See, for example, J. B. Goodenough, *Magnetism and the Chemical Bond*, Interscience, New York, 1963.
4 A. Ginsberg, *Inorg. Chim. Acta Rev.*, 1971, **5**, 45.
5 P. Day, A. K. Gregson, D. H. Leech and M. J. Fair, *J. Chem. Soc., Dalton Trans.*, 1975, 1306.
6 P. Day, *J. Magn. Magn. Mater.*, 1986, **54** and **57**, 1442.
7 P. Day, *Acc. Chem. Res.*, 1979, **12**, 236.
8 C. Bellitto and P. Day, *J. Mater. Chem.*, 1992, **2**, 265.
9 P. Day, *Chem. Soc. Rev.*, 1993, **22**, 51.
10 C. Bellitto, M. J. Fair, T. E. Wood and P. Day, *J. Chem. Soc., Faraday Trans. 2*, 1980, 1579.
11 P. J. Fyne, P. Day, M. T. Hutchings, S. Depinna, B. C. Cavenett and R. Pynn, *J. Phys. C.*, 1984, **17**, L245.
12 P. Day, *Philos. Trans. R. Soc. London, Ser. A*, 1985, **314**, 145.
13 See, for example, R. L. Carlin, *Magnetochemistry*, Springer, Berlin, 1986, p. 30.
14 T. Moriya, *Phys. Rev.*, 1960, **117**, 635; **120**, 91.
15 S. G. Carling, P. Day and D. Visser, *J. Solid State Chem.*, 1993, **106**, 111.
16 S. G. Carling, P. Day and D. Visser, *Inorg. Chem.*, 1995, **34**, 3917.
17 H. Arend, W. Haber, F. H. Mischgvorsky and G. K. Richter-van Leeuwen, *J. Cryst. Growth*, 1978, **42**, 213.
18 S. G. Carling, P. Day and D. Visser, *Solid State Commun.*, 1992, **88**, 135.
19 S. G. Carling, P. Day and D. Visser, *J. Phys.: Condens. Matter*, 1995, **7**, L109.
20 S. T. Bramwell and P. C. W. Holdsworth, *J. Phys.: Condens. Matter*, 1992, **5**, L53.
21 H. I. Tamaki, Z. J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto and H. Okawa, *J. Am. Chem. Soc.*, 1992, **114**, 6974.
22 S. G. Carling, C. Mathoniere, P. Day, K. M. A. Malik, S. J. Coles and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1996, 1839.
23 C. Mathoniere, C. J. Nuttall, S. G. Carling and P. Day, *Inorg. Chem.*, 1996, **35**, 1201.
24 S. Descurtins, H. W. Schmalle, H. R. Oswald, A. Linden, J. Enslig, P. Gütlich and A. Hauser, *Inorg. Chim. Acta*, 1994, **216**, 65.
25 L. O. Atovmyan, G. V. Shilov, R. N. Lyubovskaya, E. I. Zhilyaeva, N. S. Ovanesyan, S. I. Piramova and I. G. Gusakovskaya, *JETP Lett.*, 1993, **58**, 766.
26 M. Julve, J. Faus, M. Verdaguer and A. Gleizes, *J. Am. Chem. Soc.*, 1984, **106**, 8306.
27 C. Mathoniere, S. G. Carling, Y. Dou and P. Day, *J. Chem. Soc., Chem. Commun.*, 1994, 1551.
28 J. B. Goodenough, *Magnetism and the Chemical Bond*, Interscience, New York, 1963.
29 L. Néel, *Ann. Phys.*, 1948, **1**, 137.
30 P. Day, in *Magnetism: a Supramolecular Function*, ed. O. Kahn, Kluwer, Dordrecht, 1996, p. 467.