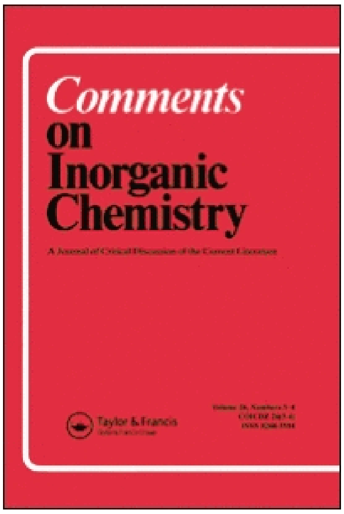

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Bimetallic Magnetic Materials

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Bimetallic Magnetic Materials

The syntheses and structural and magnetic properties of several bimetallic materials are described. Bimetallics offer a novel way to prepare a variety of interesting new magnetic compounds such as ferrimagnets, which are described in detail.

Key Words: *bimetallics, ferrimagnetism, ferromagnetism, antiferromagnetism, linear chains, clusters*

INTRODUCTION

In view of the current interest in the synthesis and characterization of new, insulating ferromagnets and ferrimagnets, I thought it would be useful to review some of the recent work in this area. While much of the effort is directed towards finding ferromagnetic materials which order at high temperatures, there have as yet been few successes in that direction. As we show below, there is at least a strategy available for the preparation of new ferrimagnets; that is also true for the preparation of new inorganic ferromagnets. One class of ferrimagnets consists of those materials which are antiferromagnetically ordered, in which there are two magnetic sublattices of unequal magnitude. An example might consist of a two-sublattice sample containing equal numbers of chromium(III) ions (spin $S = 3/2$) and of iron(III) ions ($S = 5/2$) on each sub-

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lattice. A coordination compound which might be such a ferrimagnet is provided by $[Cr(H_2O)(NH_3)_5][FeCl_6]$. The distinctive behavior of these materials arises from the supposed inability of the antiferromagnetic interaction to cancel the opposing unequal moments. Chemists have been quite successful lately in preparing novel compounds of this type; there is a variety of new materials, including both magnetic linear chains and three-dimensional materials. Most of the compounds still order at relatively low temperatures, however. Several of these systems will be discussed in this article. Throughout this article we use the standard spin-Hamiltonian for magnetic exchange,

$$H = -2J\Sigma \mathbf{S}_i \cdot \mathbf{S}_j \tag{1}$$

where the summation is taken over the entire lattice (three-dimensional ordering) or only over the two nearest neighbors (linear chain). The quantity J, called the exchange constant, measures the strength of the interactions, and has units of energy.

The kind of system mentioned above, in which there are two different metal ions, has been referred to as bimetallic or, to be more precise, heterobimetallic. The preparation of magnetic linear chains in which the different metals are chemically ordered has been a challenge to chemists which, perhaps surprisingly, has been met.[1,2] There are also three-dimensional bimetallics of several types; for example, there is the homometallic substance $[Co(C_5H_5NO)_6](CoCl_4)$ in which one metal ion resides in two different stereochemical positions with different properties (g-values, zero-field splittings) at each site.[3] This particular material is a canted antiferromagnet. Another example of a structurally ordered, three-dimensional bimetallic is provided by ferromagnetic $[Cr(NH_3)_6][Cr(CN)_6]$.[4] It is by no means necessary that this type of compound order with only two sublattices, but there is as yet no information available on this point. I have already reviewed some of these systems[1]; I shall comment here on related work that is more recent.

The nature of the syntheses of bimetallic compounds varies with the material. Thus, the straightforward addition of pyridine N-oxide to cobalt chloride yields $CoCl_2 \cdot 3C_5H_5NO$, which turns out to be, from crystallographic analysis, the previously mentioned

$[Co(C_5H_5NO)_6](CoCl_4)$. The recrystallization of $[Cr(en)_3][FeCl_6]$ from acidic solution yields single crystals, not of the starting material, but rather of $[Cr(en)_3]_3[FeCl_6]Cl_6 \cdot H_2O$, a substance which will be discussed below. On the other hand, large single crystals of $[Co(NH_3)_6][FeCl_6]$ can be grown by mixing $[Co(NH_3)_6]Cl_3$ and $FeCl_3 \cdot 6H_2O$ in a 1:5 ratio in 2.5 *M* HCl and then evaporating slowly at 50°C.

There is a great deal of crystallographic evidence for the model presented here, of cationic and anionic complex ions combining in the manner suggested above.[1,5] The series of salts $[M(H_2O)_x(NH_3)_{6-x}][CuCl_5]$ where M may be Cr(III) or Co(III) is cubic and belongs to the space group Fd3c for $x = 0,1,2$. The extensive series based on $[Cr(NH_3)_6][Cr(CN)_6]$ (replace the Cr by Co in either ion, replace part of the ammonia by water) is isomorphous and belongs to the space group $R\bar{3}$.

PARAMAGNETS

The major reason for investigating paramagnets is to characterize independently one magnetic sublattice. A bimetallic paramagnet which has recently been described is monoclinic $[Cr(en)_3](ZnCl_4)Cl$[6]; only the cation is paramagnetic. Simple Curie–Weiss behavior is observed, with *g*-values of 2 and Curie–Weiss ϑ's of about 0.2 K. The small Weiss temperatures can be explained as being due to zero-field splitting effects in the chromium(III) ions. Another such example is provided by $[Co(en)_3]_3[FeCl_6]Cl_6 \cdot H_2O$,[7] which contains a diamagnetic cation.

The specific heat of $[Cr(NH_3)_5(H_2O)][Co(CN)_6]$ has been measured[8]; again, the cobalt(III) moiety is diamagnetic. A broad Schottky anomaly due to the zero-field splitting of the $^4A_2$ ground state of the cation was observed; the measured splitting is $|0.33|$ K. This is a typical value for chromium(III).[9]

CLUSTERS

There is a variety of bimetallic clusters. We mention an unusual example here, in which a transition metal interacts with a lanthanide ion in a $GdCu_2$ cluster.[10-12] The material is $(CuSALtn)_2Gd(H_2O)(NO_3)_3 \cdot 2EtNO_2$, where CuSALtn is [N,N′-1,3-propylenebis(salicylaldiminato)]copper(II). The gadolinium ion is nine-coordinated, by four oxygen atoms of two bidentate nitrate ions, four oxygen atoms of two CuSALtn molecules and a water molecule. There is a ferromagnetic interaction of 1.22 cm^{-1} between the gadolinium ion and the copper ions, and an antiferromagnetic interaction of -3.6 cm^{-1} between the copper ions. These results suggest that the *f* orbitals of the gadolinium ion are indeed involved in a superexchange interaction with the *d* orbitals of the copper ions. The susceptibility follows the Curie–Weiss law at higher temperatures, with parameters corresponding to a spin $S = 9/2$ ground state, as anticipated. As the temperature is lowered, the susceptibility goes through a rather sharp maximum, indicating long-range magnetic ordering, and then decreases. The ordering temperature, T_c, is about 245 mK, and the major intercluster interaction appears to be magnetic dipolar.

A ferromagnetic interaction between gadolinium and copper ions has also been observed in a tetranuclear Gd_2Cu_2 cluster.[13]

ANTIFERROMAGNETS

There are several heterobimetallic substances which are antiferromagnets.[14,15] The cubic substance $[Co(NH_3)_6](CuCl_5)$, with a diamagnetic cation, acts as a three-dimensional, spin $S = 1/2$ Heisenberg antiferromagnet.[14] As it cools, the material undergoes a crystallographic transition at about 280 K; this appears to set up a domain structure and prevent the establishment of an easy axis. The substance orders at $T_c = 3.8$ K and the susceptibility data may be fit by the Heisenberg $S = 1/2$ simple cubic model with the exchange constant $J/k_B = -3.13$ K. There is as yet no microscopic determination of the magnetic unit cell or magnetic structure of one of the new bimetallic substances.

Complicated low-temperature behavior was observed for the related system, $[Cr(H_2O)(NH_3)_5](CuCl_5)$, which appears to order at 0.298 K.[16] Notice that both cation and anion are paramagnetic in this material. Since it has been shown that $[Cr(H_2O)$-

$(NH_3)_5](CuCl_5)$ and $[Co(NH_3)_6](CuCl_5)$ are isomorphous,[5] the ordering temperatures of these similar materials are remarkably different and in the wrong order.

The cubic substance $[Co(NH_3)_6][FeCl_6]$ has the sodium chloride structure, and therefore consists of two fcc interpenetrating sublattices each formed by a single counter-ion.[15] Once again, the cation is diamagnetic. The existence of an fcc magnetic lattice cannot be consistent with antiferromagnetic ordering with only first-magnetic neighbor interactions. Topological restrictions preclude the onset of parallel alignment of the magnetic moments in the whole lattice; antiparallel pairing between two *nn* sites will be opposed by the interactions of a third *nn* site of the lattice. The magnetic system is said to become frustrated. In order to stabilize the magnetic structure, next-nearest-neighbor interactions are required. The presence of frustration reduces the critical temperature, so that such systems typically exhibit an unusually large ratio of $|\vartheta|/T_c$. This is illustrated in Table I. The susceptibility data on $[Co(NH_3)_6][FeCl_6]$ may be fit between 4.2 and 30 K with the parameters $g = 2.01$ and $\vartheta = -4.6$ K. The data at lower temperatures indicate a transition temperature of about 0.5 K and may be fit with a value for the *nn* exchange interaction of $J_{nn}/k_B = -0.07$ K and a value for the *nnn* interaction of $J_{nnn}/k_B = 0.005$ K.

TABLE I

Relation between magnetic frustration and experimental values of $|\vartheta|/T_c$ for different materials (Ref. 15)

Compound[a]	$\|\vartheta\|/T_c$	Magnetic Frustration
$NiBr_2 \cdot 6H_2O$	1.8	no
$[Cu(en)_3]SO_4$	1.7	no
$[Co(NH_3)_6][CuCl_5]$	2.0	no
$[Co(en)_3][FeCl_6]$	1.6	no
$[Co(pn)_3][FeCl_6]$	2.0	no
$MnTe_2$	5.3	yes
MnS_2	12.4	yes
$(NH_4)_2IrCl_6$	9.3	yes
K_2IrCl_6	10.5	yes
$[Co(NH_3)_6][FeCl_6]$	9.2	yes

[a] pn is propylenediamine; en is ethylenediamine.

FERROMAGNETS

One of the major problems remaining in magnetochemistry research is to discover the ground rules for constructing new ferromagnets. The majority of magnetically ordered coordination compounds are antiferromagnets, but more and more ferromagnets have been found as time progresses. One advantage of studying ferromagnetic insulators is that one can carry out experiments over the entire range of the electromagnetic spectrum, without interference from eddy currents. An orthogonal exchange path between the metal ions is often cited as the source of a ferromagnetic interaction but, except for dimers, one is rarely as yet in a position to control the exchange path. A number of bimetallic coordination compounds do exhibit ferromagnetism, and it seems that it will be profitable to explore this phenomenon further by the study of more bimetallic compounds. These are discussed below.

Some of the properties of ferromagnets have been discussed elsewhere, along with the molecular field description of ferromagnetism.[17] While insulating ferromagnets are not common, bimetallic substances appear to have a greater tendency than most insulators to order ferromagnetically; why this should be so is not yet understood. The susceptibilities of ferromagnetic $[Cr(NH_3)_6][Cr(CN)_6]$ and $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ have been reported previously.[4] The compounds are isomorphic, with the water in the second material equally distributed over the six ammonia sites.[5,18] The specific heats of both compounds have now been reported[8,19] and are illustrated in Fig. 1. The data for the first compound (T_c = 0.66 K) may be interpreted with an isotropic Heisenberg bcc S = 3/2 model, while the net effect of water substitution to form $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ (T_c = 0.37 K) is to reduce the effective superexchange paths and cause a reduction of T_c. A bond-dilution model, caused by the substitution of ammonia ligands by water ligands, allows the interpretation of the data. This reduces the effective coordination number of the bcc lattice from z = 8 to 6.

FERRIMAGNETS

We begin this section by reviewing some aspects of the subject of ferrimagnetism,[20,21] which is generally less-familiar than the other

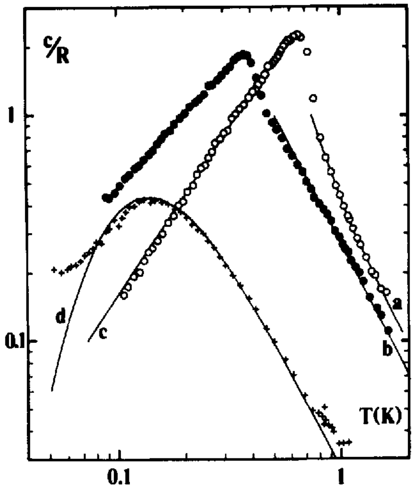

FIGURE 1 Specific heat of (○) $[Cr(NH_3)_6][Cr(CN)_6]$, (●) $[Cr(NH_3)_5(H_2O)][Cr(CN)_6]$, and (+) $[Cr(NH_3)_5(H_2O)][Co(CN)_6]$. (a) HTS predictions for a $S = 3/2$, bcc, Heisenberg ferromagnet; (b) T^{-2} term of a $z = 6$, Heisenberg ferromagnet; (c) simple spin-wave prediction for a $S = 3/2$, bcc ferromagnet; (d) Schottky curve for ZFS of $|\Delta| = 0.33$ K. From Ref. 8.

topics discussed here. A ferrimagnetic material may be defined as one which, below a certain temperature, possesses a spontaneous magnetization that arises from a nonparallel arrangement of the strongly coupled magnetic moments. The example originally considered by Neel was that of a substance composed of two lattices with the magnetic moments of one sublattice tending to be antiparallel to those of the other. When the sublattice magnetizations are not equal there will be a net magnetic moment. The classic example is magnetite, Fe_3O_4, a spinel. The two chemical or structural sublattices are

(1) iron(III) ions in tetrahedral coordination to oxygen, and
(2) iron(II) and iron(III) ions in equal proportion to octahedral oxygen coordination.

The result is that the inequivalent magnetic sublattices cannot balance each other out, and a weak moment persists below T_c. Ferrites and garnets are technologically important ferrimagnets.

These substances must not be confused with canted antiferromagnets, also known as weak ferromagnets. The physics of the two situations differs greatly.[17]

The concept of inequivalent sublattices has since been broadened to include materials with more than two sublattices and with other spin configurations, such as triangular or spiral arrangements. It is an empirical fact that most of the substances which are ferrimagnetic are insulators, in contrast to ferromagnetic substances, of which so many are metals or very good conductors. The recent progress in this area that is of interest here concerns bimetallic compounds.

Even for a two sublattice system, there are several schemes that can lead to ferrimagnetism. As for the antiferromagnetic case,[17] the two sublattices are denoted by A and B. Suppose first that all the magnetic ions, N per unit volume, have identical moments, regardless of whether they are situated on A or B sites. If a fraction λ and μ ($=1 - \lambda$) occupy A and B sites, respectively, the material will possess a net moment if $\lambda \neq \mu$. An unequal partitioning of the ions can occur either if there are unequal numbers of sites on the two sublattices or if the ions prefer the sites on one sublattice over those on the other.

There will be ferrimagnetism even when $\lambda = \mu$ if the magnetic moments on the A and B sites are unequal. This inequality may develop (a) from elements in different ionic states, e.g., Fe^{2+} and Fe^{3+}; (b) from different elements in the same or different ionic states, for example, Fe^{3+} and Co^{2+}; or (c) from different crystalline fields acting at the two sites.

The molecular field theory for ferrimagnetism is similar to that described earlier[17,20] for ferromagnets and antiferromagnets. The difference from the antiferromagnetic case is that λM_A, the magnetization of one sublattice, is not equal to μM_B, the magnetization of the other sublattice, for the reasons stated above. One can follow the reasoning of Morrish[20] and arrive at the relationship, for the paramagnetic region,

$$1/\chi = T/C - 1/\chi_0 - \sigma/(T - \vartheta) \qquad (2)$$

which is a hyperbola. The quantities χ_0, σ and ϑ are defined as molecular field parameters related to the fractions of ions on the two sites; in practice, they are largely empirical constants. The constant C is the average Curie constant of the ions.

The asymptote as $T \rightarrow \infty$ of Eq. (2) is given by

$$1/\chi = T/C - 1/\chi_0. \tag{3}$$

It is usually found that the $1/\chi$ intercept of Eq. (3) is positive; the result is much like the Curie–Weiss law. Therefore, for a temperature sufficiently above T_c, the inverse susceptibility plot has essentially the same linear relationship predicted by the molecular field theory for antiferromagnetic materials, that is, the Curie–Weiss form. Furthermore, since T_c is greater than ϑ and the susceptibility is infinite at this point, the $1/\chi$ vs. T curve must have considerable curvature just above the ferrimagnetic Neel temperature. This behavior is illustrated for $[Cr(NH_3)_5(H_2O)][FeCl_6]$ in Fig. 2.

A significant feature that accounts for many of the unusual properties of ferrimagnetic materials is that the spontaneous magnetizations of the several sublattices will generally have different temperature dependences, since the sublattices see different molecular fields.

The chemical composition and metal valence of bimetallics can be controlled more precisely than that of the oxide compounds mentioned above. The lower ordering temperatures also allow experiments such as specific heat measurements to be done more profitably.

A number of ferrimagnets, such as $[Cr(NH_3)_6][FeCl_6]$, were mentioned in an earlier article.[1] Several new ferrimagnets have recently been reported.[7,22] The materials are $[Cr(NH_3)_5(H_2O)]$-$[FeCl_6]$, $[Cr(NH_3)_4(H_2O)_2][FeCl_6]$, and $[Cr(en)_3]_3[FeCl_6]Cl_6 \cdot H_2O$, where en is ethylenediamine or, more properly, 1,2-ethanediamine. The high-temperature susceptibility data indicate that indeed all three compounds contain $S = 3/2$ chromium and the iron is octahedral, $S = 5/2$. Compounds $[Cr(NH_3)_5(H_2O)][FeCl_6]$ and $[Cr(NH_3)_4(H_2O)_2][FeCl_6]$ are isomorphic to $[Co(NH_3)_6][FeCl_6]$ and undergo long-range order at 2.32 and 2.31 K, respectively.[22] Below these temperatures, the in-phase ac signal is accompanied by an out-of-phase or absorption signal, χ'', indicative of the presence of net magnetic moments. The three substances exhibit in their in-

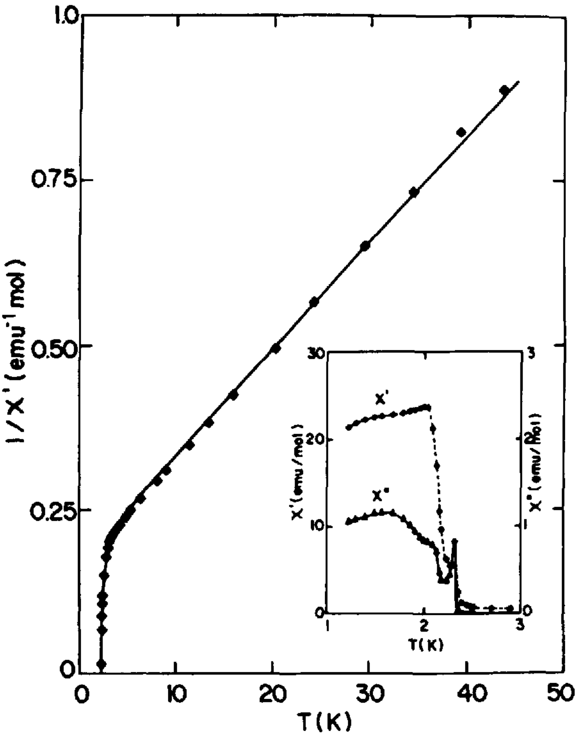

FIGURE 2 Temperature dependence of the reciprocal magnetic susceptibility of $[Cr(NH_3)_5(H_2O)][FeCl_6]$; the continuous line is a theoretical fit to the data. From Ref. 22.

verse susceptibility curves the Neel hyperbola which is characteristic of ferrimagnetic behavior; the data on $[Cr(NH_3)_5(H_2O)][FeCl_6]$ are illustrated in Fig. 2. The experimental data above T_c can be fit using standard molecular field theory[23] to yield the parameters $J(\text{Fe-Fe})/k_B = -0.12$ and -0.11 K, respectively, for $[Cr(NH_3)_5(H_2O)][FeCl_6]$ and $[Cr(NH_3)_4(H_2O)_2][FeCl_6]$, $J(\text{Cr-Cr})/k_B = -0.02$ and $+0.03$ K, again respectively, and $J(\text{Cr-Fe})/k_B = -0.24$ and -0.10 K. These are small interactions.

While $[Co(pn)_3][FeCl_6]$ orders as an antiferromagnet at about 9 K, there appear to be no magnetic measurements as yet on the analogous material, $[Cr(pn)_3][FeCl_6]$.

The interesting compound $[Cr(en)_3]_3[FeCl_6]Cl_6 \cdot H_2O$ has recently been prepared by recrystallizing samples of $[Cr(en)_3][FeCl_6]$. The salt, which presents a new kind of structure,[7] is a trigonal system that crystallizes in the space group R3 and consists of a three-dimensional network of triangular antiprisms formed by the $[Cr(en)_3]^{3+}$ ions and connected with each other by sharing corners. An $[FeCl_6]^{3-}$ ion is placed at the center of each antiprism, as illustrated in Figs. 3 and 4. The complex cations, anions and water molecules are held together by ionic forces and by a three-dimensional network of hydrogen bonds. The chromium may be isomorphously replaced by cobalt(III). The transition temperature to long range order of $[Cr(en)_3]_3[FeCl_6]Cl_6 \cdot H_2O$ is 0.91 K.

FERRIMAGNETIC LINEAR CHAINS

Major progress has recently been made in the synthesis and study of ferrimagnetic chains.[2] The distinguishing feature of all magnetic linear chains is the high degree of short range order. The individual chains are usually linked antiferromagnetically, and the distinctive

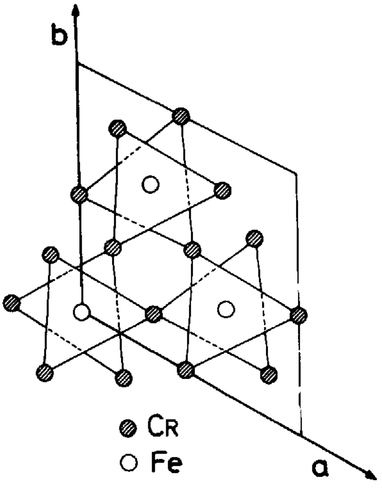

FIGURE 3 (001) projection (to scale) of a portion of the crystalline structure of $[Cr(en)_3]_3[FeCl_6]Cl_6 \cdot H_2O$. Only the metal atoms are shown; open circles are iron atoms while filled circles are chromium atoms. From Ref. 7.

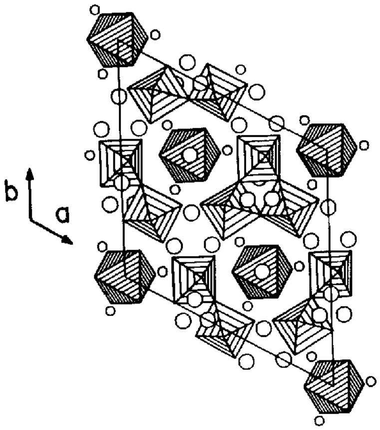

FIGURE 4 Projection of the structure of $[Cr(en)_3]_3[FeCl_6]Cl_6 \cdot H_2O$ on the (001) plane. The octahedra represent Cr cations (light hatching) and Fe anions (heavy hatching). Isolated chlorine atoms and water molecules are represented by large and small circles, respectively. From Ref. 7.

ferrimagnetic behavior arises from the inability of the antiferromagnetic interaction to cancel the alternating, unequal moments. As the temperature is decreased, the antiferromagnetic coupling first reduces the effective moment as the adjacent spins are rendered antiparallel. At still lower temperatures, the net moments begin to align parallel as the correlation length grows, causing a divergence of the product χT; in between the divergence and the decline is a minimum in χT. This may be taken as the characteristic of the ferrimagnetic chain.

An unusual effect has been observed in two copper samples, $Sr_3Cu_3(PO_4)_4$ and $Ca_3Cu_3(PO_4)_4$.[24,25] While one-dimensional ferrimagnetism is generally related to uncompensated spin sublattices, ferrimagnetic chains may also be observed in homometallic systems. This can happen when the *g*-factors alternate or when a particular stacking of metal ions, such as intertwining double chains, occurs. In these compounds, which consist of trimers of copper ions linked together, the leading interaction occurs within the trimers, but because of the relative stacking of the trimers, the noncompensated spins are parallel in the ground state. This gives a ferromagnetic-like behavior below 10 K. Thus, although only one metal is involved and all the couplings are antiferromagnetic, the chain is characterized by a high-spin ground state.

Another example of this sort of behavior is provided by Co(bpy)$(NCS)_2$, where bpy is 2,2'-bipyridine.[26] Only one type of site is found for the metals, but the structure consists of polymeric zigzag chains with stepwise cobalt-thiocyanate bridging groups and octahedral metal centers. Cobalt(II) is of course a very anisotropic ion at low temperatures and the Ising model should be closely approximated. The susceptibility data can be fit by assuming alternating *g* components along the chain.

An attractive approach for the construction of molecular ferromagnets consists of assembling ordered bimetallic chains so as to obtain two- or three-dimensional ordered bimetallic lattices. A great deal of effort has gone into the study of bimetallic linear chains.[2] We concentrate on the EDTA series of compounds, of which there are to date two distinct sets, one of stoichiometry $M'M(M'EDTA)_2 \cdot 4H_2O$[27–31] and the second, MM' (EDTA)$\cdot 6H_2O$.[32–35] In the first case, which can be abbreviated as [M'MM'], M' refers to a divalent metal ion (Zn, Co) on a tetrahedral site and M, M' may be octahedral Co(II) or Ni(II). The structure of these compounds consists of ordered bimetallic layers of alternating octahedral sites M and M', with tetrahedral sites M' connecting different layers. This is illustrated in Fig. 5. Through a selective accommodation of diamagnetic and paramagnetic ions in the appropriate sites, magnetic lattices ranging from isolated trimers to three-dimensional systems would appear.

The material [ZnNiNi] consists of bimetallic layers of nickel ions, which are separated by the diamagnetic zinc ions. Its magnetic moment decreases continuously as the temperature is decreased. Since the substance contains what looks like a ferrimagnetic layer, this antiferromagnetic behavior appears surprising and may be due to the existence of a relatively large zero-field splitting of the nickel ions. A value of D/k_B of 3.9 K, a value comparable in magnitude to the nearest neighbor exchange interactions, may be estimated.

The [CoCoCo] compound is more complicated; the magnetic moment exhibits a minimum around 0.3 K and a divergence at lower temperatures. Three-dimensional ordering appears to take place at 0.08 K. The system appears to consist of ferrimagnetic Ising layers connected by tetrahedral cobalt(II). Then the three-

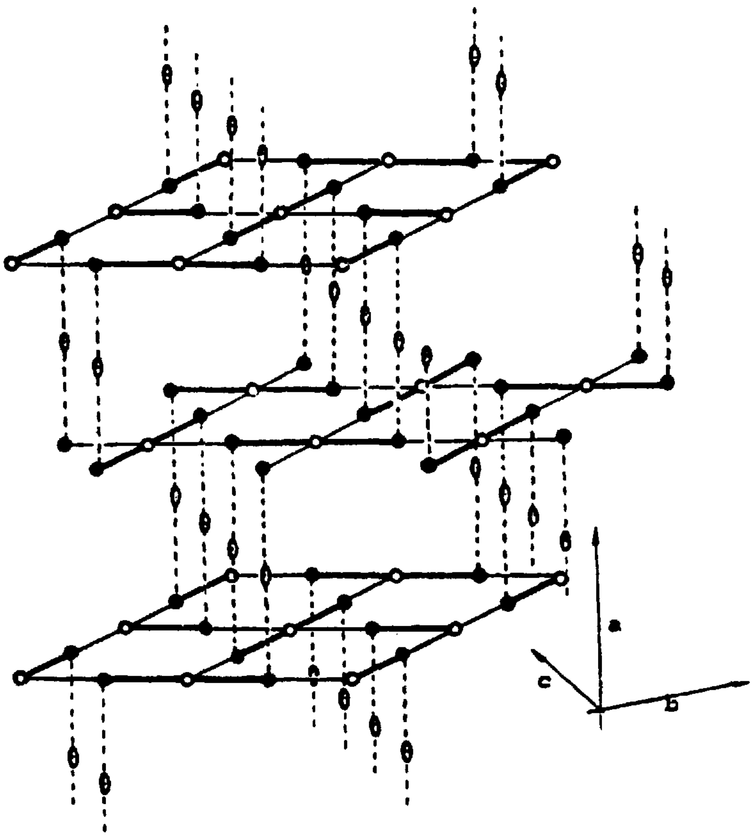

FIGURE 5 Schematic diagram of the structure of $CoCo(NiEDTA)_2 \cdot 4H_2O$, showing the layers of alternating octahedral sites (Ni, filled circles; Co, open circles) and tetrahedral Co sites connecting them (ellipses). From Ref. 31.

dimensional ordering is expected to be ferromagnetic if an antiferromagnetic exchange coupling between the Co′ and the Co′ sites is assumed.

We mention also the second EDTA series of compounds,[32–35] which is an isostructural family MM′ (EDTA)$\cdot 6H_2O$ (abbreviated as [MM′]), where M = Mn, Co, Ni and Mg and M′ = Co, Ni, Cu and Zn(II). The structure of these materials (Fig. 6) consists of infinite zigzag chains built up from two alternating octahedral

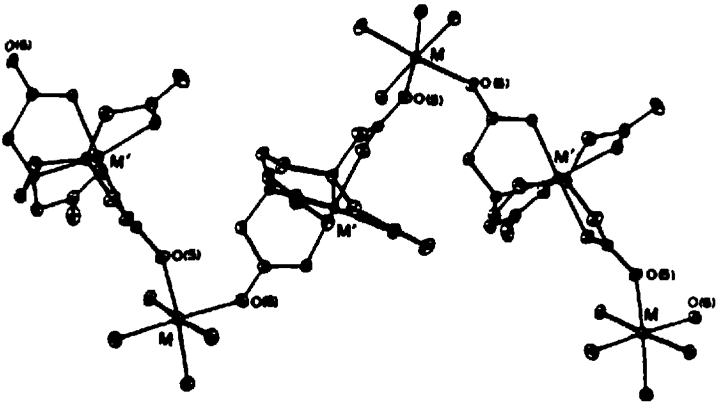

FIGURE 6 The alternating bimetallic chain in the MM′ (EDTA) · $6H_2O$ complexes. From Ref. 34.

sites, one of which is referred to as "hydrated" and the other as "chelated"; that is, the local environments of the two metal ions are different. In the former, M is coordinated to four water molecules and the oxygen atoms of carboxylate groups, while in the latter M′ is hexacoordinated by the EDTA ligand. In bimetallic substances each site is selectively occupied by metal ions giving rise to bimetallic ordered chains. Furthermore, slight alternating M–M′ distances occur along the chain which are related to different bridging carboxylate topologies.

The alternating chain may be schematically illustrated as

$$—M(H_2O)_4O_2\text{–}M'\ (EDTA)—M(H_2O)_4O_2\text{–}M'\ (EDTA)—$$

where longer and shorter lines refer to alternating metallic distances; see Fig. 6. Many choices of metals can easily be accommodated without significant structural change. The Landé factors alternate down the chain because of the inequivalent sites, and it has been shown that this can give rise to ferrimagnetism. In the case of [NiNi],[32] the successive g-factors are in the ratio of $g_a/g_b = 1.1$, and the susceptibility data may be fit by an (Ising) exchange constant of $2J/k_B = -8.25$ K, $g_a = 2.21$ and $g_b = 2.09$.

Much the same happens with the [CoCo] and [CoCu] analogs.[33] With cobalt(II), which is spin $S = 1/2$ at low temperatures, there is large single-ion anisotropy[17] and the g-value alternation necessary to form a ferrimagnetic linear chain is easily obtained. Neither compound undergoes long-range order above 70 mK. The related systems [MnCo], [MnNi] and [MnCu] do, however, undergo long-range order,[34] at, respectively, 1.06, 0.65 and 0.20 K. The specific heat measurements for the latter compounds are illustrated in Fig. 7, where the λ-features characteristic of transitions to long-range order may be seen. The small maximum at slightly higher temperatures is due to the one-dimensional contribution.

CONCLUSIONS

As always, I emphasize the fact that much of the recent progress in the study of magnetic materials arises from the fact that chemists have been able to prepare and characterize the often-exotic materials which are required in order to demonstrate the magnetic phenomena which are being sought. We still need more new materials! The challenge of making chemically ordered bimetallic salts has been amazingly successful to date, but more are needed. New synthetic methods should also be devised.

We have largely neglected here the subject of molecular ferromagnetism only because of the relative lack of success to date. Many ferromagnetic chains have been prepared, but they have not yet been incorporated into materials which yield the desired result: long-range ferromagnetic order in insulators at (relatively) high temperatures.

The concepts used in this report in describing ferrimagnets are based on the earlier studies of the classical ferrimagnets, the spinels and garnets. While this appears to be justified to date, some microscopic determination of magnetic structures by NMR, say, or neutron diffraction is still lacking. This situation must change. As was mentioned earlier, it is by no means necessary that any or all of these materials order in a simple two-sublattice fashion.

There are as yet few other chemical or physical studies of bimetallic magnets; careful study of the electronic spectra of some of these compounds, for example, ought to be enlightening.

Clearly, combining metallic materials of different spin in a 1:1 ratio does not guarantee that a ferrimagnet will result; that does

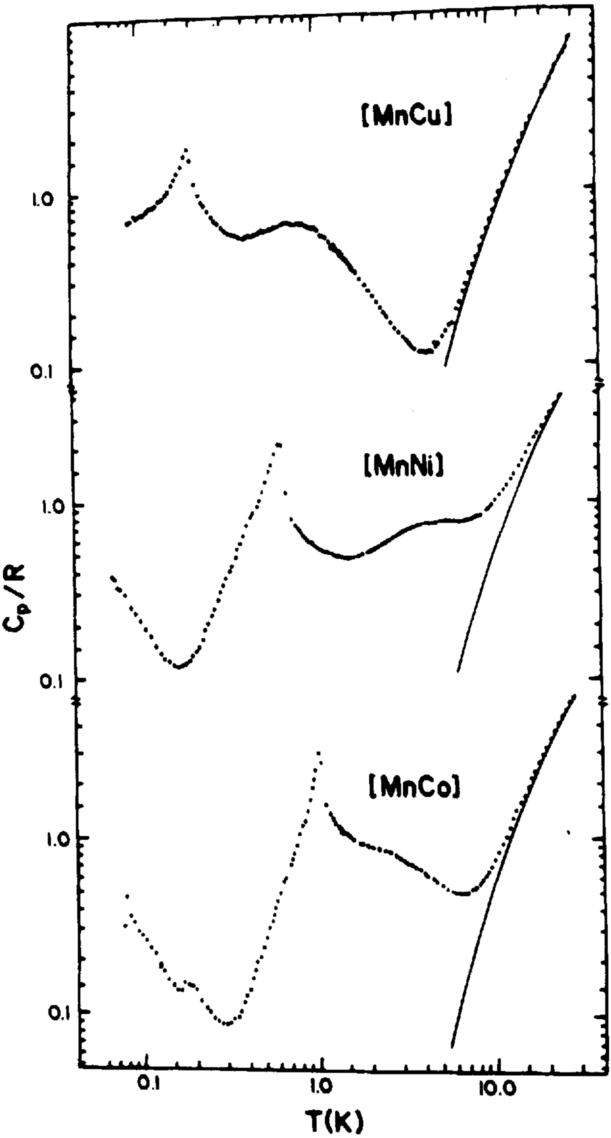

FIGURE 7 Specific heat data of the [MnM′] compounds. Full line corresponds to the specific heat of the isomorphous nonmagnetic compound [ZnZn]. From Ref. 34.

happen in the case of $[Cr(H_2O)(NH_3)_5][FeCl_6]$ but not in the case of $[Cr(en)_3][FeCl_6]$, which appears to be an antiferromagnet. Obviously, the sublattice structure of all these substances remains to be defined.

We emphasize transition temperatures throughout, rather than exchange constants for characterizing a system, for two reasons. The transition temperature T_c is in fact related to the exchange constant J/k_B by, say, the molecular field relationship

$$T_c = 2S(S + 1)\, zJ/3k_B \tag{4}$$

where z is the (generally unknown) magnetic coordination number for a given system. More importantly, T_c is a directly measured empirical quantity, while some kind of model must always be invoked in order to determine the exchange constant.

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