

Irregular spin state structures in heteropolymetallic systems

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Abstract. In an *ABA* symmetric and linear trinuclear system where the interaction between terminal ions is assumed to be negligible, the distribution in energy of the spin states depends on the relative values of the spins S_A and S_B . If $2S_A \leq S_B$, the spin state structure is regular in the sense where the spin multiplicity varies monotonically with the energy; if $2S_A > S_B$, it is irregular. A Cu(II)Ni(II)Cu(II) triad illustrates the former situation and a Mn(II)Cu(II)Mn(II) the latter. The concept of irregular spin state structure may be extended to the ordered bimetallic chains $(AB)_N$ with $N \rightarrow \infty$. The main theoretical ideas concerning these systems are presented as well as some typical examples. In particular, it is shown that a Cu(II)Mn(II) chain with an antiferromagnetic interaction between nearest neighbors exhibits a ferromagnetic-like behavior in the low temperature range. This corresponds to one-dimensional ferrimagnetism. Finally, it is emphasized that this concept of irregular spin state structure might lead to the first genuine molecular ferromagnets.

Keywords. Polymetallic complexes; one-dimensional compounds; ferrimagnetism; ferromagnetism; molecular ferromagnets.

1. Introduction

Since the pioneering work of Bleaney and Bowers (1952), a very large number of papers have been devoted to binuclear systems where two identical magnetic metal ions interact within the molecular unit (Willett *et al* 1985). By far, the most highly documented are the copper(II) complexes. In contrast, relatively few investigations so far have dealt with heteropolymetallic systems with more than two interacting centers. This paper is devoted to this problem, or more exactly, to a part of this problem. Our main goal is to introduce the concept of irregular spin state structure and to stress that the design and the study of heteropolymetallic systems with irregular spin state structures open quite new perspectives in the field of molecular magnetism as well as in that of molecular materials.

This paper is organized as follows: In §2, we define the concept of spin state structure in a polymetallic compound and we point out that the spin state structure of a trinuclear species may be regular or irregular. An example of each situation is then presented. Section 3 is devoted to a very important new class of magnetic systems, namely, the ordered bimetallic chains. In §4, finally, we briefly point out that the concept of irregular spin state structure might lead to the first genuine molecular ferromagnets.

2. Regular and irregular spin state structures in trinuclear systems

In this section, we propose to introduce the concept of regularity and irregularity in the spin state structure. This concept has already led to the synthesis of polymetallic

systems in which the ground state has a very high spin multiplicity. It might be a key for the design of molecular ferromagnets, as we shall see in §4.

2.1 Concept of spin state structure

Let us consider a symmetric and linear trinuclear system ABA where the interacting centers have no orbital degeneracy and let us assume that the interaction between terminal centers is negligible with regard to the interaction between nearest neighbors. The Hamiltonian suitable for determining the spin states is:

$$H = -J(\hat{S}_{A1} \cdot \hat{S}_B + \hat{S}_{A2} \cdot \hat{S}_B), \quad (1)$$

where the interactions are assumed to be purely isotropic. Several situations can be encountered concerning the distribution in energy of the spin states, according to the relative values of S_A and S_B . More precisely, three cases have to be distinguished: (i) if $2S_A \leq S_B$, we have a *regular spin state structure*, in the sense where the spin multiplicity varies monotonically with the energy. If the interaction is antiferromagnetic, the ground state has the lowest spin multiplicity and the most excited state the highest spin multiplicity, the situation being reversed for a ferromagnetic interaction. As for the magnetic behavior arising from the regular spin state structure, it is such that upon cooling down, $\chi_M T$ continuously decreases, then finally reaches a plateau corresponding to the temperature range where only the $S = S_B - 2S_A$ ground state is populated for $J < 0$, and continuously increases up to a plateau corresponding to the temperature range where only the $S = S_B + 2S_A$ ground state is populated for $J > 0$. The Cu(II)Ni(II)Cu(II) complex of §2.2 provides an example of antiferromagnetic interaction in a trinuclear system with regular spin state structure. As additional example, we give the spin state structure for an antiferromagnetically coupled ABA triad with $S_A = 1$ and $S_B = 5/2$ in figure 1. S regularly increases from $S = 1/2$ for the ground state to $S = 9/2$ for the most excited state; (ii) If $2S_A = S_B + 1/2$ with S_A and $S_B \neq 1/2$, the spin state structure becomes irregular; the spin multiplicity does not vary

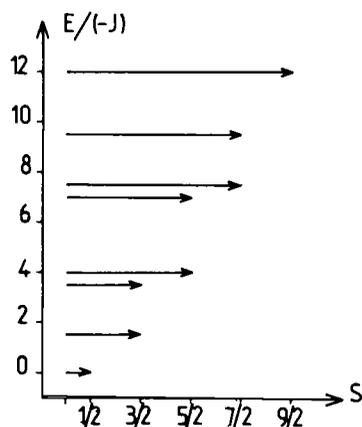


Figure 1. Spin state structure for a symmetric ABA triad with $S_A = 1$ and $S_B = 5/2$.

monotonically with energy anymore. Nevertheless, for $J < 0$, the ground state is a doublet and retains the lowest spin multiplicity; $\chi_M T$ continuously decreases upon cooling down. An example of such an intermediate case is provided by the ABA triad with $S_A = 3/2$ and $S_B = 5/2$. Its spin state structure is shown in figure 2. For $J < 0$, the ground state is a doublet and the first excited state a quartet but the second excited state is again a doublet etc . . . ; (iii) if $2 S_A > S_B + 1/2$, the spin state structure is even more irregular and for $J < 0$, the $S_g = 2 S_A - S_B$ ground state is not that of lowest spin multiplicity. On the other hand, the most excited state is always that with the largest $S (= 2 S_A + S_B)$. This may have quite an important consequence as far as the magnetic behavior is concerned. At very high temperature, when $kT > |J|$, $\chi_M T$ is constant with a value corresponding to what is expected for non coupled $2 A + B$ centers. When H begins to cool down, the first state to be thermally depopulated is that of highest spin multiplicity, so that $\chi_M T$ decreases. In the low temperature range now, when only a few excited states are populated, upon cooling down, one depopulates states with $S > S_g$ and $\chi_M T$ may increase. Therefore, $\chi_M T$ exhibits a minimum at a non zero temperature. To our knowledge, this situation has been reported for the first time, without being discussed, by Ginsberg *et al* (1968) for nickel(II) trimers. It must be emphasized here that this increase of $\chi_M T$, upon cooling below the temperature of the minimum, occurs although the interaction is antiferromagnetic. In this low temperature range, the magnetic behavior is reminiscent of what happens for a ferromagnetically coupled system. The larger $2 S_A$ with regard to S_B , the more irregular the spin state structure. Particularly interesting in this respect is the ABA triad with $S_A = 5/2$ and $S_B = 1/2$. Its spin state structure is depicted in figure 3. For $J < 0$, going down in energy, S first decreases from $11/2$ to $1/2$ then increases from $1/2$ to $9/2$. It follows that a very pronounced increase of the $\chi_M T$ versus T plot may be expected in the low temperature range. An example of this kind is given in §2.3.

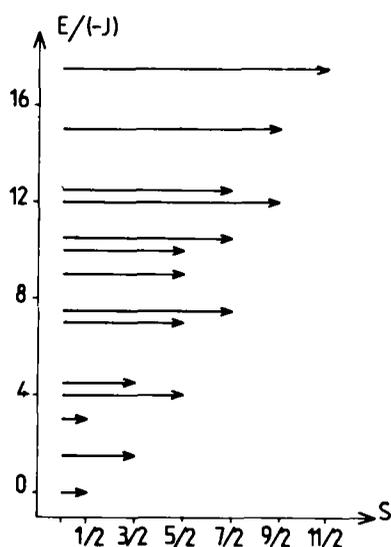


Figure 2. Spin state structure for a symmetric ABA triad with $S_A = 3/2$ and $S_B = 5/2$.

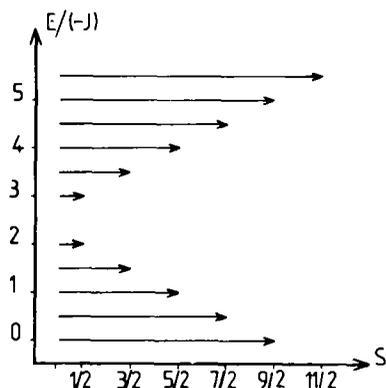


Figure 3. Spin state structure for a symmetric *ABA* triad with $S_A = 5/2$ and $S_B = 1/2$.

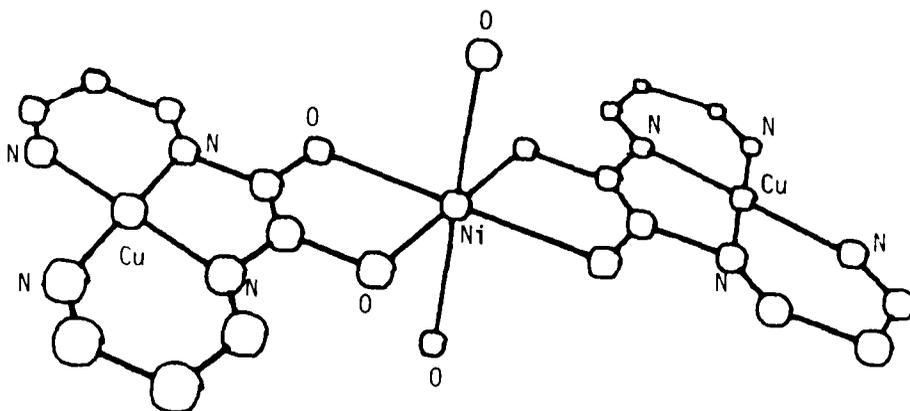


Figure 4. Structure of $[\text{Cu}_2\text{Ni}(\text{oxpn})_2(\text{H}_2\text{O})_2]^{2+}$.

2.2 $[\text{Cu}_2\text{Ni}(\text{oxpn})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$

The condensation of two moles of $\text{Cu}(\text{oxpn})$ with one mole of $\text{Ni}(\text{II})$ perchlorate affords $[\text{Cu}_2\text{Ni}(\text{oxpn})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$. (oxpn) is *N, N'*-bispropylene-diamine-oxamido (Journaux *et al* 1986). The structure of the trinuclear cation with the $\text{Cu}(\text{II})\text{Ni}(\text{II})\text{Cu}(\text{II})$ triad is schematized in figure 4.

The spin Hamiltonian in zero field for this compound is written as:

$$H = -J(\hat{S}_{\text{Cu1}} \cdot \hat{S}_{\text{Ni}} + \hat{S}_{\text{Cu2}} \cdot \hat{S}_{\text{Ni}}) - j\hat{S}_{\text{Cu1}} \cdot \hat{S}_{\text{Cu2}}, \quad (2)$$

and the relative energies $E(S, S')$ of the low lying states are:

$$\begin{aligned} E(0, 1) &= 0, \\ E(1, 1) &= -J, \\ E(1, 0) &= -2J + j, \\ E(2, 1) &= -3J, \end{aligned} \quad (3)$$

with:

$$\begin{aligned}\hat{S}' &= \hat{S}_{\text{Cu1}} + \hat{S}_{\text{Cu2}}, \\ \hat{S} &= \hat{S}' + \hat{S}_{\text{Ni}},\end{aligned}\quad (4)$$

Since the ground state of the compound is the singlet (vide infra), it is not necessary to introduce local anisotropy or anisotropic interaction terms in (2). The Zeeman perturbation is:

$$H_Z = \beta \vec{H} \cdot (\mathbf{g}_{\text{Cu1}} \cdot \hat{S}_{\text{Cu1}} + \mathbf{g}_{\text{Ni}} \cdot \hat{S}_{\text{Ni}} + \mathbf{g}_{\text{Cu2}} \cdot \hat{S}_{\text{Cu2}}), \quad (5)$$

and the magnetic susceptibility is:

$$\begin{aligned}\chi_M T &= (2N\beta^2/k) [g_{1(1)}^2 \exp(J/kT) + g_{1(0)}^2 \exp((2J-j)/kT) + \\ &5g_2^2 \exp(3J/kT)] / [1 + 3 \exp(J/kT) + 3 \exp((2J-j)/kT) + \\ &5 \exp(3J/kT)].\end{aligned}\quad (6)$$

The $\mathbf{g}_{S(S')}$ tensors are related to the local tensors through (Gatteschi and Bencini 1985):

$$\begin{aligned}\mathbf{g}_{1(1)} &= \mathbf{g}_2 = (\mathbf{g}_{\text{Cu1}} + \mathbf{g}_{\text{Cu2}} + 2\mathbf{g}_{\text{Ni}})/4, \\ \mathbf{g}_{1(0)} &= \mathbf{g}_{\text{Ni}}.\end{aligned}\quad (7)$$

The only role of j is to modify slightly $E(1, 0)$, the energies of the other three states remaining unchanged. Its influence on the magnetic properties is almost negligible, so that it cannot be determined by fitting the magnetic data of the Cu(II)Ni(II)Cu(II) species. On the other hand, j can be estimated from the magnetic properties of the Cu(II)Zn(II)Cu(II) species where Zn(II) replaces Ni(II). This compound behaves as a copper(II) binuclear complex with a singlet-triplet energy gap equal to j . j has been found to be in the range $0 > j > -1.6 \text{ cm}^{-1}$. The magnetic properties of $[\text{Cu}_2\text{Ni}(\text{oxpn})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ are shown in figure 5, where, to be homogeneous with the other curves of this paper,

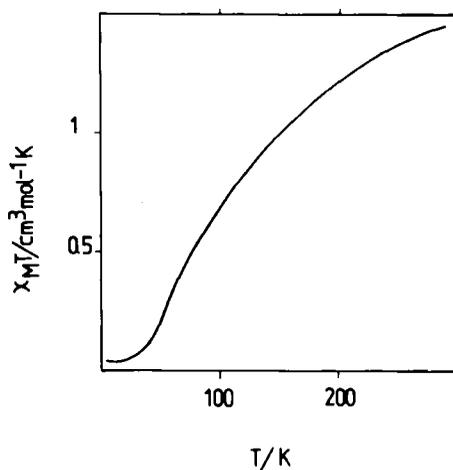


Figure 5. $\chi_M T$ versus T plot for $[\text{Cu}_2\text{Ni}(\text{oxpn})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$.

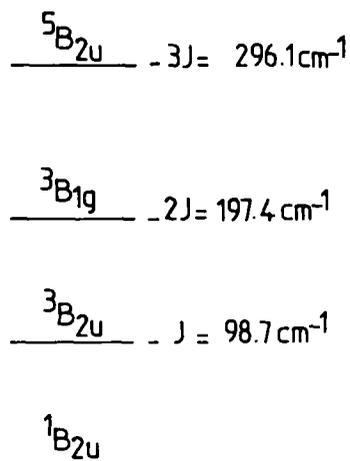


Figure 6. Spectrum of the low lying states in $[\text{Cu}_2\text{Ni}(\text{oxpn})_2(\text{H}_2\text{O})_2]\text{ClO}_4$.

we plotted $\chi_M T$ versus T . Upon cooling down, $\chi_M T$ continuously decreases and tends to a value very close to zero, confirming that the ground state is the singlet. The $\chi_M T$ versus T plot exhibits a maximum around 90 K, which is characteristic of a coupled molecular system with a diamagnetic ground state. The fitting of the data leads to $J = -98.7 \text{ cm}^{-1}$ with an average g -value of 2.12 and a spectrum of the low lying states as depicted in figure 6, where we indicated the orbital symmetry of the states, assuming a D_{2h} molecular symmetry.

The most interesting result concerning this complex is the large magnitude of the antiferromagnetic interaction between metal ions separated by about 5.1 Å. In other words, the oxamido *bis* bidentate ligand has quite a remarkable ability to transmit the electronic effects between metal ions far away from each other. This problem has recently been reviewed (Kahn 1985a) and we do not intend to discuss it again here. We simply recall that the efficiency of *bis* bidentate ligands like

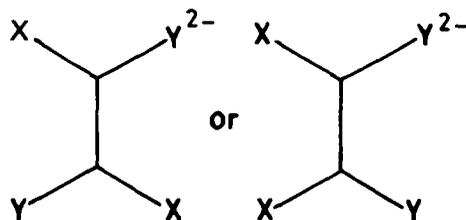


Chart 1.

with X, Y = O, S or NR to propagate an antiferromagnetic interaction is due to the favorable relative orientations of the xy -type magnetic orbitals that point from the metal toward the four nearest neighbors and overlap of either side of the bridge, as shown in chart 2. It has also been shown that the less electronegative the X and Y groups are, the more delocalized the magnetic orbitals and the stronger the antiferromagnetic interaction (Kahn 1985a, Verdaguer *et al* 1985). So, the magnitude of the phenomenon varies as dithiooxalato $\text{C}_2\text{O}_2\text{S}_2^{2-}$ > oxamido $[\text{C}_2\text{O}_2(\text{NR})_2]^{2-}$ > oxamato $[\text{C}_2\text{O}_3(\text{NR})]^{2-}$ > oxalato $\text{C}_2\text{O}_4^{2-}$.

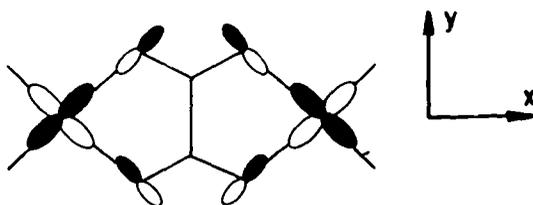


Chart 2.

2.3 $\{[Mn(Me_6[14]ane\ N_4)]_2Cu(pba)\}(CF_3SO_3)_2 \cdot 2H_2O$

A complex containing the Mn(II)Cu(II)Mn(II) triad with $S_{Mn} = 5/2$ and $S_{Cu} = 1/2$ has been synthesized (Pei *et al* 1986a). Its formula is $\{[Mn(Me_6[14]ane\ N_4)]_2Cu(pba)\}(CF_3SO_3)_2 \cdot 2H_2O$ and it is obtained by condensation of two moles of $[Mn(Me_6[14]ane\ N_4)](CF_3SO_3)_2$ with one mole of $Na_2[Cu(pba)] \cdot 6H_2O$. $Me_6[14]ane\ N_4$ is *d, l, 5, 7, 7, 12, 14, 14*-hexamethyl-1, 4, 8, 11-tetraazacyclotetradecane (Tait and Busch 1972) and *pba* is 1,3-propylene *bis* (oxamato) (Nonoyama *et al* 1976). The skeleton of the trinuclear unit is schematized in figure 7. Owing to the nature of the bridges, the Mn(II)Cu(II) interaction is expected to be strongly antiferromagnetic (see §2.2), which gives rise to a 9/2 ground state with the (5/2, -1/2, 5/2) symbolic notation for the local spins. The magnetic behavior of this compound is shown in figure 8. As expected, $\chi_M T$ first decreases upon cooling with a very rounded minimum about 170 K, then increases in a rather abrupt fashion up to a high plateau with $\chi_M T = 12.1\text{ cm}^3\text{ mol}^{-1}\text{ K}$. This plateau exactly corresponds to what is expected for an $S = 9/2$ isolated state ($\chi_M T = 33 N\beta^2 g_{9/2(5)}^2 / 4k$) with $g_{9/2(5)} = 1.98$. $g_{9/2(5)}$ is related to the local tensors by:

$$g_{9/2(5)} = (6g_{Mn1} - g_{Cu} + 6g_{Mn2})/11 \quad (8)$$

Apparently, the zero field splitting within the ground state is very weak since $\chi_M T$ does not exhibit any deviation from the Curie law. This is confirmed by the EPR spectrum at 4.2 K where no fine interaction is detected. This spectrum exhibits the $\Delta M_s = \pm 1$ allowed transition at $g = 1.991$ and the $\Delta M_s = \pm 2, \pm 3$ and ± 4 forbidden transitions of decreasing intensity at half, third and quarter-field respectively. The theoretical expression for the magnetic susceptibility has been established from the spin state structure of figure 3 and the Zeeman perturbation expressed as:

$$H_Z = \beta \vec{H} \cdot (g_{Mn1} \cdot \hat{S}_{Mn1} + g_{Cu} \cdot \hat{S}_{Cu} + g_{Mn2} \cdot \hat{S}_{Mn2}) \quad (9)$$

The *g*-factors of the eleven spin states have been calculated as a function of the

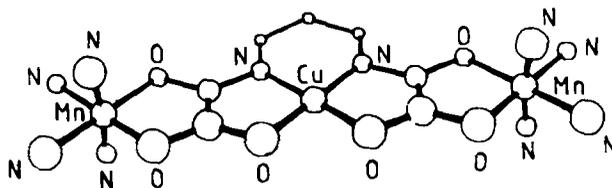


Figure 7. Trinuclear unit in $\{[Mn(Me_6[14]ane\ N_4)]_2Cu(pba)\}(CF_3SO_3)_2 \cdot 2H_2O$.

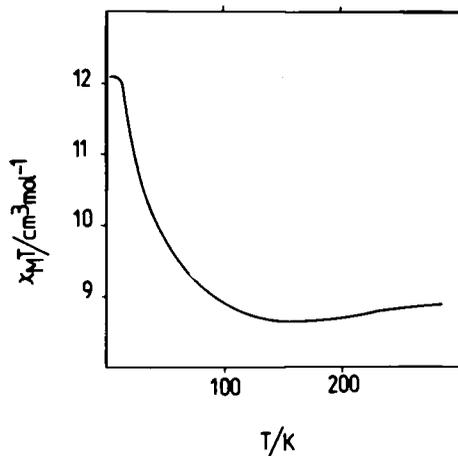


Figure 8. $\chi_M T$ versus T plot for $\{[\text{Mn}(\text{Me}_6[14]\text{ane } N_4)]_2\text{Cu}(\text{pba})\} (\text{CF}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$.

$g_{\text{Mn}} = 2.03$ and $g_{\text{Cu}} = 2.10$. This Mn(II)Cu(II)Mn(II) complex is to our knowledge the molecular unit exhibiting the largest spin multiplicity in its ground state.

A Ni(II)Cu(II)Ni(II) complex similar to that of figure 7 has also been synthesized, Ni(II) replacing Mn(II). It has an $S = 3/2$ ground state and the $\chi_M T$ versus T plot exhibits the characteristic minimum of this type of antiferromagnetically coupled trinuclear species with irregular spin state structure. In this compound, the isotropic interaction parameter is found to be equal to $J = -135 \text{ cm}^{-1}$.

3. Ordered bimetallic chains

We have seen in §2.1 that a trinuclear species can have an irregular spin state structure with, in the case of antiferromagnetic interaction, a ground state which has not the lowest spin multiplicity. It follows that the temperature dependence of $\chi_M T$ displays a characteristic minimum. The most spectacular example is the antiferromagnetically coupled Mn(II)Cu(II)Mn(II) triad. This concept of irregular spin state structure can be extended to more complex systems like the ordered bimetallic chains. The first compound of this kind was reported in 1981 and opened new and very exciting perspectives in the field of magnetic systems (Gleizes and Verdaguer 1981). In the forthcoming sections, we shall present first the main theoretical ideas both at a qualitative, then the quantitative level: afterwards, we shall discuss the most significant experimental results reported so far.

3.1 Theory: qualitative approach

To introduce the main ideas (Verdaguer *et al* 1983), we consider an ordered and regular bimetallic ring $(AB)_N$ where N may become infinitely large. A and B symbolize magnetic metal ions surrounded by their nearest neighbor ligands, including the bridging ligands, with spins S_A and $S_B \neq S_A$ respectively. We also

assume that A and B have no first order angular momentum. The spin Hamiltonian in zero field appropriate to the problem is:

$$H = -J \sum_{i=1}^{2N} S_i \cdot S_{i+1}, \quad (10)$$

with :

$$S_{2i-1} = S_A,$$

$$S_{2i} = S_B,$$

$$\hat{S}_{2N+i} = \hat{S}_i.$$

In (10) local anisotropies and anisotropic interactions have been ignored.

We suppose first that J is negative. In this case, the state of lowest energy E_g may be schematized as:

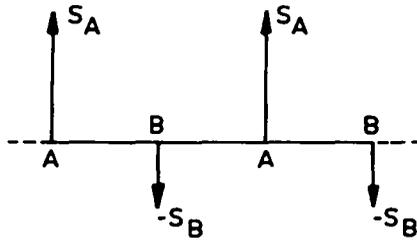


Chart 3.

with the spin $S_g = N(|S_A - S_B|)$. The state of highest energy E_e is as:

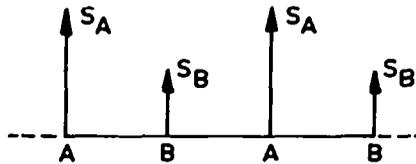


Chart 4.

with the spin $S_e = N(S_A + S_B)$. Between the two limits E_g and E_e , states with spins inferior to S_g do exist. In particular, there are states with $S = 0$ if the total number of unpaired electrons $2N(S_A + S_B)$ is even, one of them is schematized hereunder:

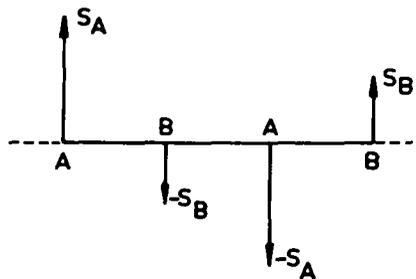


Chart 5.

or with $S = 1/2$, if this number is odd: In other words, for any $N \neq 1$, the spin state structure is always irregular. This irregularity increases with N and $|S_A - S_B|$ since

S_g is proportional to those two quantities whereas the lowest spin is always 0 or 1/2. Let us examine now the consequences of this irregularity as far as the temperature dependence of $\chi_M T$ is concerned, χ_M being the magnetic susceptibility per AB unit. The Zeeman perturbation to add to (10) is:

$$H_Z = \beta \hat{H} \cdot \sum_{i=1}^N (\mathbf{g}_{A2i-1} \cdot \hat{S}_{2i-1} + \mathbf{g}_{B2i} \cdot \hat{S}_{2i}). \quad (11)$$

Since, in this section, we restrict ourselves to a qualitative approach, we assume that the \mathbf{g}_A and \mathbf{g}_B tensors are isotropic with the same principal value g . At very high temperature, when $kT \gg |J|$, $\chi_M T$ tends to the $(\chi_M T)_{HT}$ limit corresponding to the superposition of the uncoupled A and B fragments. This limit is:

$$(\chi_M T)_{HT} = (N\beta^2 g^2 / 3k) \cdot [S_A(S_A + 1) + S_B(S_B + 1)]. \quad (12)$$

The low temperature limit, when $kT/|J|$ approaches zero, is:

$$(\chi_M T)_{LT} = (N\beta^2 g^2 / 3k) [N(S_A - S_B)^2 + |S_A - S_B|]. \quad (13)$$

For $N = N_0$ defined as:

$$N_0 = (S_A^2 + S_B^2 + 2S_<)/(S_A - S_B)^2, \quad (14)$$

where $S_<$ is the smaller of S_A and S_B , the limits $(\chi_M T)_{HT}$ and $(\chi_M T)_{LT}$ are equal. For $N > N_0$, $(\chi_M T)_{LT}$ is superior to $(\chi_M T)_{HT}$ and when N tends to the infinite, $(\chi_M T)_{LT}$ diverges. Upon cooling down from the high temperature, one depopulates first the state of highest spin multiplicity so that $\chi_M T$ decreases. Therefore, one is led to the following fundamental result: *For a chain of alternated and antiferromagnetically coupled spins S_A and S_B , upon cooling down, $\chi_M T$ first decreases, then reaches a minimum for a finite temperature and finally diverges when T approaches zero.* This behavior is valid for any couple S_A and $S_B \neq S_A$, provided that there is no compensation of the local magnetic moments (see §3.2). Another way to express the same result is to say that at high temperature, $\chi_M T$ tends toward the paramagnetic limit; the minimum of $\chi_M T$ corresponds to a short-range order state where the spins S_A and S_B of adjacent ions are antiparallel, but without correlation between neighboring AB units. When T decreases, the correlation length within the chain increases, leading to a magnetic short-range order symbolized by $(S_A, -S_B)_N$. Such a situation may be defined as the *one-dimensional ferrimagnetism*. Below the temperature of the minimum of $\chi_M T$, the magnetic behavior is qualitatively equivalent to what happens in a chain of N spins $|S_A - S_B|$ ferromagnetically coupled. This point, which is of utmost importance, will be developed further.

If the intrachain interaction is ferromagnetic ($J > 0$), the order of the spin levels is reversed and no extremum of the $\chi_M T$ versus T plot can be predicted a priori. In fact, no compound of that sort has been reported so far and in the following, we shall ignore this situation.

3.2 Theory: quantitative approach

Several quantitative approaches of the magnetic susceptibility of ordered bimetallic chains have been proposed so far. The first one consists of carrying out the

calculation on $(AB)_N$ rings of increasing size with quantum spins S_A and S_B and to extrapolate to $N \rightarrow \infty$ (Verdaguer *et al* 1983; Drillon *et al* 1983b). This requires that for each N the Hamiltonian (10) is diagonalized by using the microstates as basis sets with M_s varying from 0 or 1/2, according as $2N(S_A + S_B)$ is even or odd, up to $N(S_A + S_B)$, as done for the first time by Orbach (1959) for a chain of spins 1/2. This leads to the energies $E_i(S)$ of the spin states and to their multiplicity. In the hypothesis where the average g -factors, g_A and g_B , are equal, the calculation of the magnetic susceptibility is then straightforward since all the spin states have the same g -factor and the spin labels S are good quantum numbers even in the presence of the Zeeman perturbation. The method is an extension of the work of Bonner and Fisher (1964) concerning regular chains of spins 1/2. For $g_A \neq g_B$, not only each spin state has a given g_s -factor but also the Zeeman perturbation couples the components of the same M_s belonging to different spin states, which introduces nonzero second-order Zeeman coefficients in the calculation of the susceptibility. This method, even by taking into account the full D_N symmetry of the problem, is severely limited by the storage capacity of the computers, as well as by the computing time. The problem which has been studied best is the one with $S_A = 1/2$, $S_B = 1$. Drillon *et al* (1983b) performed the calculation up to $N = 5$ and extrapolated for $N \rightarrow \infty$. The result for $g_A = g_B$ is shown in figure 9. The minimum of $\chi_M T$ is obtained for $kT/|J| = 0.570$. In the very low temperature range, $\chi_M T$ diverges according to a power law $T^{-0.80}$, which coincides with the law found for a chain of ferromagnetically coupled spins 1/2. Drillon *et al* (1983b) also investigated the effect of $g_A/g_B \neq 1$ and found that for $g_A/g_B = 2.66$, there is an exact compensation of the magnetic moments associated with A and B respectively. The ground state becomes nonmagnetic and $\chi_M T$ continuously decreases down to zero upon cooling. The $(AB)_N$ ring chain technique has also been utilized for the $S_A = 1/2$, $S_B = 5/2$ (Drillon *et al* 1984) and $S_A = 1$, $S_B = 5/2$ (Drillon *et al* 1986) situations but in both cases only up to $N = 3$. Very quickly, the problem becomes untractable and alternative methods are indispensable.

The simplest method consists of considering that both S_A and S_B are classical spins with g_A^e and g_B^e effective g -factors and a J^e effective interaction parameter. The

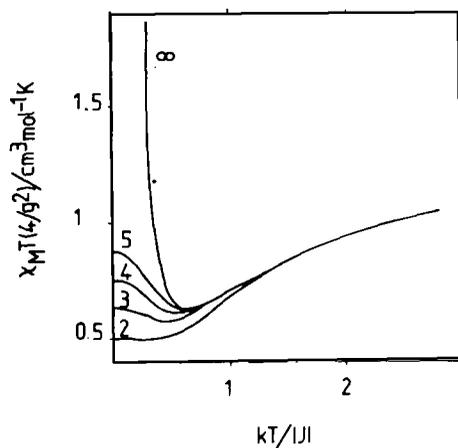


Figure 9. $\chi_M T(4/g^2)$ versus $kT/|J|$ plot for antiferromagnetically coupled $(AB)_N$ ring chains of spins $S_A = 1/2$, $S_B = 1$.

effective parameters are related to the actual parameters through:

$$g_A^e = g_A [S_A(S_A + 1)]^{1/2}, \quad (15)$$

and a similar relation for g_B^e , and:

$$J^e = J [S_A(S_A + 1)S_B(S_B + 1)]^{1/2}. \quad (16)$$

An analytical expression for the magnetic susceptibility has been derived by Drillon *et al* (1983a). This expression is:

$$\chi_M T = \frac{N\beta^2}{3k} \left(g^2 \frac{1+u}{1-u} + \delta^2 \frac{1-u}{1+u} \right), \quad (17)$$

with:

$$\begin{aligned} g &= \frac{1}{2}(g_A^e + g_B^e), \\ \delta &= \frac{1}{2}(g_A^e - g_B^e), \\ u &= \coth(J^e/kT) - (kT/J^e) \end{aligned} \quad (18)$$

For $\delta = 0$, (17) reduces to the known expression for a regular chain of classical spins (Fischer 1974). For $\delta \neq 0$ and $J < 0$, a minimum in the $\chi_M T$ versus T plot appears and when T approaches zero, $\chi_M T$ diverges in a ferromagnetic-like fashion. The divergence law is $\delta^2 T^{-1}$. The validity of (17) is the same as the validity of the classical spin approximation. The larger S_A and S_B are, the better the relation (17). For $S_B = 5/2$, (17) is likely to be valid if $S_A = 2$, may be also if $S_A = 3/2$ or 1 but is certainly a very poor approximation if $S_A = 1/2$.

The $S_A = 1/2$, $S_B = 5/2$ case has been treated in quite an elegant way by Seiden (1983) and Verdaguer *et al* (1984). The method consists of taking S_A as a quantum spin and S_B as a classical spin. We cannot present here the details of the calculation that is very elaborated. This calculation does not lead to an analytical expression but can be solved numerically. The following empirical relation has been proposed to fit the numerical results (Gleizes and Verdaguer 1984).

$$\begin{aligned} \chi_M T &= (g^2/4)(4.75 - 1.62370X + 2.05042X^2 - 4.52588X^3 \\ &\quad - 8.64256X^4)/(1 + 0.77968X - 1.56527X^2 - 1.57333X^3 \\ &\quad - 0.11666X^{4.5}) \end{aligned} \quad (19)$$

with:

$$X = |J|/kT. \quad (20)$$

Equation (19) is only valid for $J < 0$. The plot of $\chi_M T (4/g^2)$ versus $kT/|J|$ is represented in figure 10. $\chi_M T$ exhibits a rounded maximum for $kT/|J| = 2.98$. Upon cooling below the temperature of the minimum, $\chi_M T$ diverges in an abrupt way, following a law in $T^{-0.69}$. In this quantum-classical approach, the g_A and g_B factors were assumed to be equal.

In all the approaches mentioned above, the local anisotropies of the ions with S_A (or S_B) $> 1/2$ were neglected. Such an approximation can lead to a poor description of the low temperature range if $|D/J|$ is not very small. In the specific case $S_A = 1/2$, $S_B = 1$, it has been shown that the larger $|D/J|$ is, the more the

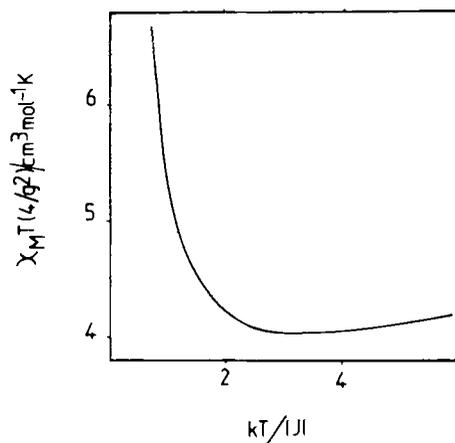


Figure 10. $\chi_M T$ ($\text{cm}^3 \text{mol}^{-1} \text{K}$) versus $kT/|J|$ plot for an infinite $(AB)_N$ chain with $S_A = 1/2$, $S_B = 5/2$.

minimum of $\chi_M T$ is shifted toward the low temperatures (Verdaguer *et al* 1983). An eventual anisotropic interaction would have the same effect. Finally, all the calculations deal with perfectly isolated $(AB)_N$ chains. In fact, much above the critical temperature where a three-dimensional order appears, the interchain interaction may substantially modify the magnetic behavior. If the interchain interaction couples the chains in an antiparallel fashion, as it is most often the case, the divergence of $\chi_M T$ is stopped with a maximum of $\chi_M T$ occurring just above the critical temperature. If this interchain interaction is large, the minimum of $\chi_M T$ can be hidden.

3.3 $\text{CuMn}(\text{dto})_2(\text{H}_2\text{O})_{3.4} \cdot 5\text{H}_2\text{O}$

The first structurally characterized ordered bimetallic chain is $\text{CuMn}(\text{dto})_2(\text{H}_2\text{O})_{3.4} \cdot 5\text{H}_2\text{O}$ with dto = dithiooxalato. This compound has been investigated by Gleizes and Verdaguer (1984) and Verdaguer *et al* (1984). The structures of two adjacent chains as well as the detail of the structure of one of the chains are shown in figure 11. Cu(II) is tetracoordinated with a planar environment and Mn(II) is heptacoordinated in a rather unusual fashion. The metal centers are bridged by the dithiooxalato ligand, the oxygen atoms being bound to manganese and the sulfur atoms to copper. The magnetic data shown in figure 12 closely follow the theoretical predictions. Upon cooling down, $\chi_M T$ decreases, reaches a weakly pronounced minimum around 130 K and increases down to 7.5 K. $\chi_M T$ is then equal to $11.3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. Finally, below 7.5 K, $\chi_M T$ decreases rapidly. In the range 7.5–300 K, these magnetic data are well fitted by the quantum-classical approach presented in the preceding section, with $J = -30.3 \text{ cm}^{-1}$ and $g = 1.90$. The maximum of $\chi_M T$ at 7.5 K is clearly due to an antiferromagnetic interaction between ferrimagnetic like chains. Magnetization studies at 1.3 and 4.2 K show a saturation corresponding to the spin $|S_A - S_B| = 2$ per CuMn unit. The relatively large $|J|$ value found in $\text{CuMn}(\text{dto})_2(\text{H}_2\text{O})_{3.4} \cdot 5\text{H}_2\text{O}$ is due to the remarkable efficiency of the dithiooxalato bridge to propagate an antiferromagnetic interaction between metal centers with xy -type magnetic orbitals.

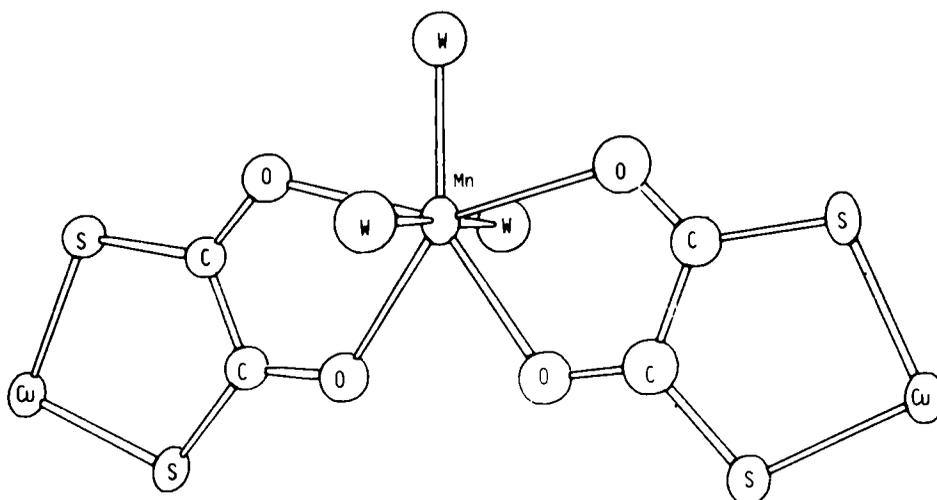
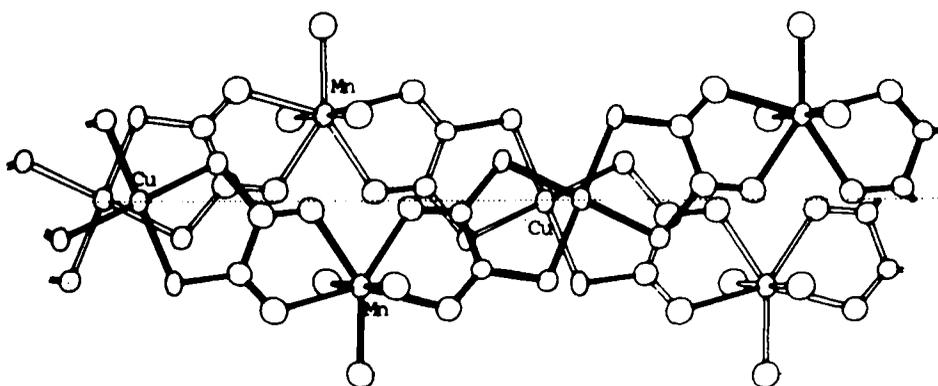


Figure 11. Crystal structure of $\text{CuMn(dto)}_2(\text{H}_2\text{O})_3 \cdot 4 \cdot 5\text{H}_2\text{O}$.

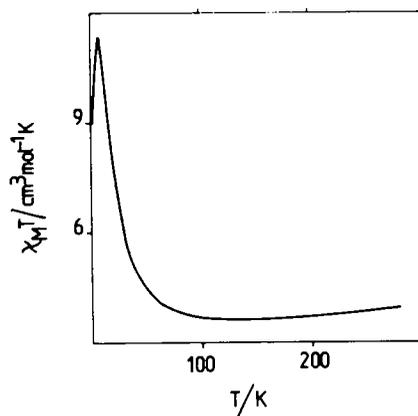


Figure 12. $\chi_M T$ versus T plot for $\text{CuMn(dto)}_2(\text{H}_2\text{O})_3 \cdot 4 \cdot 5\text{H}_2\text{O}$.

3.4 $\text{CuMn}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ and related compounds

Another example of Cu(II)Mn(II) ordered bimetallic chain is provided by $\text{CuMn}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$, with pba = 1,3-propylene bis(oxamato). The structure of the chain is given in figure 13 and that of the crystal lattice in figure 14 (Pei *et al* 1986b). Cu(II) is here in a square pyramidal environment and Mn(II) in a more classical octahedral environment. The metal centers are aligned along the *b* axis of

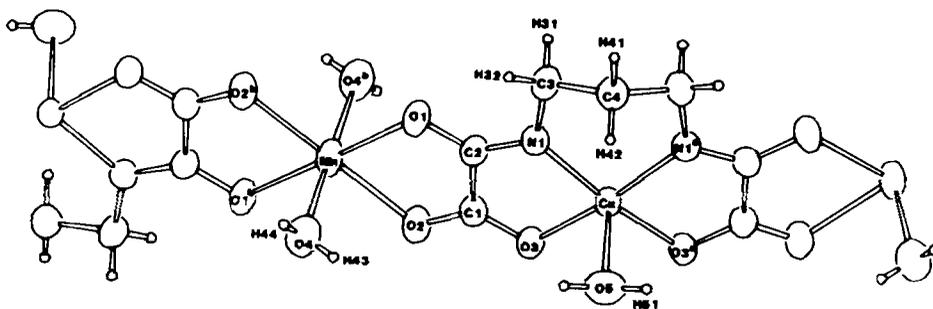


Figure 13. Crystal structure of $\text{CuMn}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$.

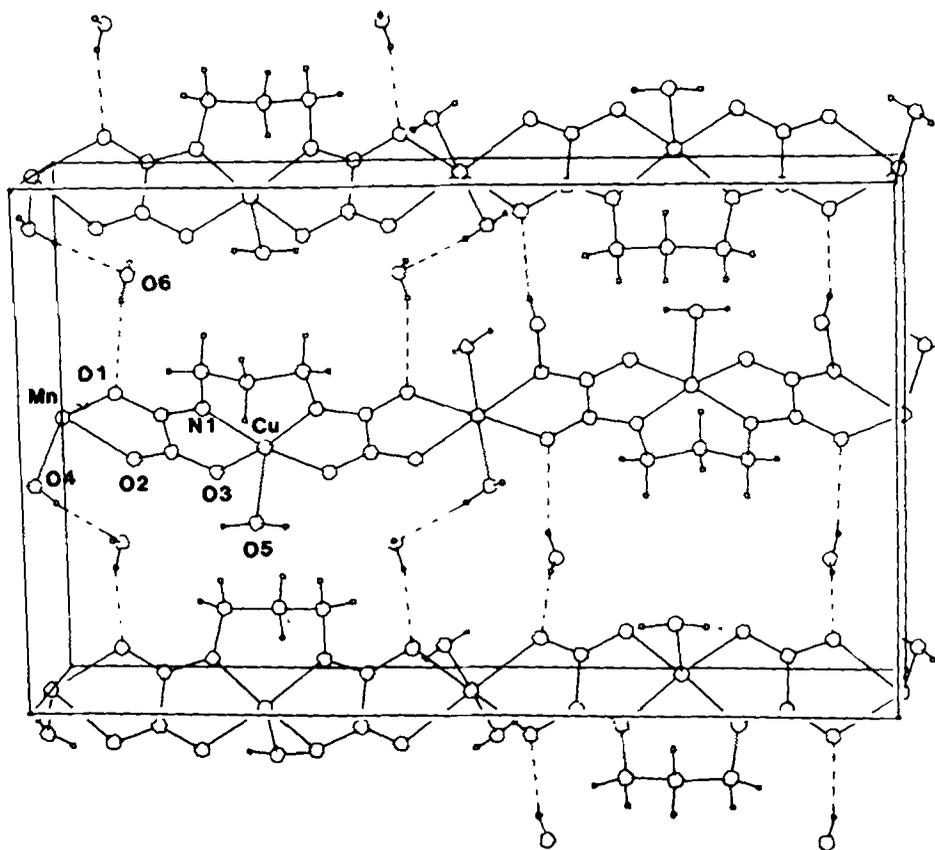


Figure 14. Crystal packing for $\text{CuMn}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$.

the orthorhombic structure, whereas in the previous example they form zigzag chains. Within the chains, two nearest neighbor metal ions are bridged by an oxamato group with a Cu . . . Mn separation of 5.41 Å. The chains are linked together by hydrogen bonding involving the oxygen atoms of the bridge and the coordinated as well as the non-coordinated water molecules. The relative positions of two adjacent chains are such that, if one takes an ion of a given type, Cu(II) or Mn(II), belonging to a chain, the nearest neighbor ion belonging to the other chain is an ion of the same type.

As expected, the $\chi_M T$ versus T plot exhibits a rounded minimum about 115 K and below this temperature a very fast increase upon cooling. Again a maximum of $\chi_M T$ is observed, but at a much lower temperature than in the previous case, namely 2.3 K instead of 7.5 K. This indicates that the interchain interaction is weaker in this compound than in the previous one. The fitting of the magnetic data above 4.2 K leads to $J = -23.4 \text{ cm}^{-1}$ with $g = 1.96$ (Pei *et al.*, 1987). This J value, although still important, is significantly smaller in its absolute value than that found in $\text{CuMn}(\text{dto})_2 \cdot (\text{H}_2\text{O})_{3.4-5}$. This is due to the fact that the magnetic orbital around copper(II) is delocalized more towards the sulfur atoms of the dithiooxalato bridge in the dto derivative than towards the nitrogen and oxygen atoms of the oxamato bridge in the pba derivative, owing to the weak electronegativity of sulfur with regard to nitrogen and oxygen.

Let us examine now the mechanism of the interchain coupling. Owing to the relative positions of two adjacent chains, the dominant interchain interactions are Cu(II)Cu(II) and Mn(II)Mn(II). If these interactions are antiferromagnetic, then the spin structure will be as:

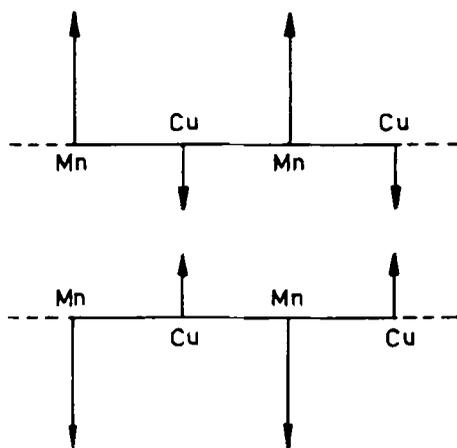


Chart 6.

with a cancellation of the spins at the scale of the lattice. This leads to the fall of $\chi_M T$ below 2.3 K. Now, if by using some chemical stratagem, we can displace every other chain in the crystal lattice by half of a repeat unit along the b axis, then the interchain interactions will occur between metal ions of different nature and, provided that these interactions are again antiferromagnetic, the spin structure will be as:

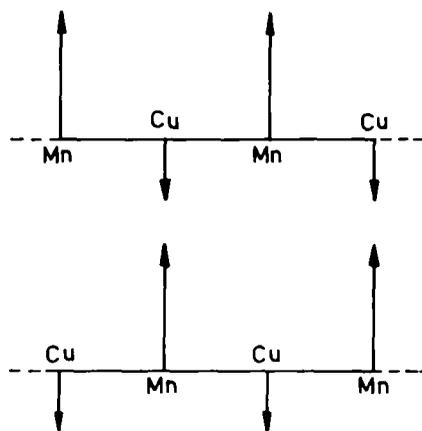
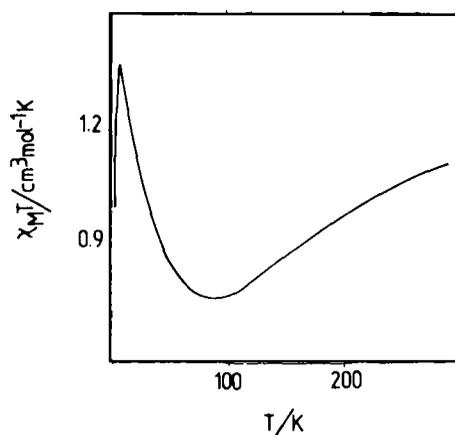


Chart 7.

with, at the scale of the lattice, all the $5/2$ spins aligned along the same direction. Such a system should exhibit a three-dimensional ferromagnetic (or ferrimagnetic) order below a critical temperature. Such a situation could be at the origin of the quite remarkable magnetic properties of $\text{CuMn}(\text{bpaOH}) \cdot 3\text{H}_2\text{O}$ (Pei *et al.*, 1986c). Chemically, the only difference between this compound and $\text{CuMn}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ is the replacement of the methylene group of the propylene chain by CHOH . Above 60 K, the pba and pbaOH derivatives exhibit the same magnetic properties with the characteristic minimum of $\chi_M T$ around 115 K. On the other hand, below 60 K, $\chi_M T$ for $\text{CuMn}(\text{bpaOH}) \cdot 3\text{H}_2\text{O}$ increases in a much more abrupt fashion and reaches an extraordinarily high value at 4.2 K. $\chi_M T$ is then larger than $100 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. Magnetization studies in very low field ($H = 0.03 \text{ G}$) show that the compound orders ferromagnetically at 4.6 K. As is usual, the ferromagnetic order is destroyed by the magnetic field, even when H is as small as 1G. $\text{CuMn}(\text{bpaOH}) \cdot 3\text{H}_2\text{O}$ may be considered as one of the first genuine molecular ferromagnets. The crystal structure of $\text{CuMn}(\text{pbaOH}) \cdot 3\text{H}_2\text{O}$ has now been solved. It actually shows a displacement of every other chain by roughly half

Figure 15. $\chi_M T$ versus T plot for $\text{CuNi}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$.

of a repeat unit along one of the directions perpendicular to the chain axis (Pei *et al.*, 1986c).

The $\text{CuNi(pba)(H}_2\text{O)}_3 \cdot 2\text{H}_2\text{O}$ chain with Ni(II) replacing Mn(II) in the structure of figure 13 has also been prepared and studied (Pei *et al.*, 1987). The $\chi_M T$ versus T plot is shown in figure 15. It exhibits the characteristic minimum at 83 K and below this temperature $\chi_M T$ increases rapidly up to a maximum at 7.3 K, reflecting again an interchain interaction. The fitting of the magnetic data in the 10–300 K temperature range using the ring chain approach leads to $J = -82.7 \text{ cm}^{-1}$ with $g = 2.17$.

4. Toward the design of molecular ferromagnets

One of the main challenges in the field of molecular materials is the design of molecular ferromagnets. For that, a strategy immediately comes to mind, namely the achievement of ferromagnetic interactions between the nearest neighbor ions at the scale of the whole lattice. If so, the system will order ferromagnetically below a critical temperature. Such ferromagnetic interactions between nearest neighbors may arise either from the strict or from the accidental orthogonality of the magnetic orbitals (Kahn 1985a; Journaux *et al.* 1983). Both types of orthogonality are difficult to realize. It is indeed well established that in most of the cases, the interaction between two nearest neighbor ions is antiferromagnetic. In a certain sense, the achievement of a ferromagnetic interaction requires going against a natural trend which favors pairing of the electrons in molecular orbitals of low energy. Therefore, it was important to find an alternative strategy to design molecular systems with high spin multiplicity in the ground state and to develop this strategy up to the design of molecular ferromagnets. Such a strategy emerges from the concept of irregular spin state structure. It consists of imposing the parallel alignment of local spin 5/2 [Mn(II) or Fe(III)] owing to an antiferromagnetic interaction with local spin 1/2[Cu(II)]. In some way, the small spins 1/2 polarize the big spins 5/2 along the same direction. This leads to a 9/2 ground state for a Mn(II)Cu(II)Mn(II) trinuclear unit, to a one-dimensional ferrimagnetic short range order for the Cu(II)Mn(II) chain and to the onset of a ferromagnetic order when a small Cu(II)Mn(II) interchain interaction superimposes on the dominant Cu(II)Mn(II) intrachain interactions. It is quite remarkable that the $S_A = 1/2$, $S_B = 5/2$ couple is the most appropriate for obtaining a ferromagnetic like behavior in the frame of this strategy whereas the interaction between those two ions is most likely antiferromagnetic (Journaux *et al.* 1983). In fact, the more pronounced the Cu(II)Mn(II) antiferromagnetic interaction is, the more efficient the polarization of the S/2 spins along the same direction. In this respect, the *bis* bidentate ligands like dithiooxalato or oxamato are particularly suitable for this purpose. Not only do they give strong antiferromagnetic interactions (see §2.2) but their chemistry is also very flexible.

$\text{CuMn(bpaOH)}_3 \cdot 3\text{H}_2\text{O}$ is apparently the first molecular ferromagnet obtained according to this strategy, with a Curie temperature of 4-6 K. This result is quite preliminary in the sense that the other physical properties of the compound are not yet known. The thorough investigation of this compound as well as the design of other systems of this kind with, if possible, a higher magnetic order temperature,

are two directions along which several groups are engaged. The difficulty along this way arises from the fact that there is no magnetic order at one or two dimensions, but only at three dimensions. Therefore the chemist has to work in terms of crystal engineering, and not only of molecular engineering.

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