Molecular-Based Compounds Exhibiting a Spontaneous Magnetization [and Discussion]

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Molecular-based compounds exhibiting a spontaneous magnetization

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One of the main challenges in the field of the molecular materials is the design of molecular-based ferromagnets. My basic strategy along this line consists of assembling ferrimagnetic chains within the crystal lattice in a ferromagnetic fashion. This can be achieved owing to the (almost) limitless flexibility of the molecular chemistry. The chains may be either regular or alternating. Examples of both situations are presented. $MnCu(pbaOH)(H_2O)_3$ (pbaOH = 2-hydroxy-1,3-propylenebis(oxamato)) is a regular chain compound ordering ferromagnetically at $T_c = 4.6$ K, and $MnCu(obbz) \cdot 1H_2O$ (obbz = oxamido-N,N'-bis(2-benzoato)) is an alternating chain compound exhibiting a spontaneous magnetization below $T_c = 14$ K. To get information on the mechanism of the magnetic ordering, a broad spectrum of physical techniques is utilized, including magnetic susceptibility and magnetization measurements, EPR spectroscopy and heat capacity data. The perspectives in this new field are outlined.

Introduction

Several groups over the world are presently working on the design of molecular-based ferromagnets (Miller *et al.* 1987; Kahn 1987; Korshak *et al.* 1987; Lepage & Breslow 1987; Torrance *et al.* 1987; Sugawara *et al.* 1986; Izuoka *et al.* 1987) and the first compounds of this kind have recently been reported. To the best of my knowledge, three families of compounds exhibiting potentially a spontaneous magnetization below a critical temperature T_c are currently investigated and in each family one system, at least, has been found to order ferromagnetically. These families are: (i) the donor–acceptor compounds giving D^+A^- alternating stacks, in which both D^+ and A^- carry a local spin $\frac{1}{2}$. So $Fe(Me_5Cp)_2(TCNE)$ (Me_5Cp = pentamethylcyclopentadienyl and TCNE = tetracyanoethylene) orders ferromagnetically at $T_c = 4.8$ K (Miller & Epstein 1987; Miller *et al.* 1987); (ii) the Mn^{II}–nitroxide chain compounds. For instance, $Mn(hfa)_2(NITMe)$ (hfa = hexafluoroacetylacetonato and NITMe = 2-methyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl-3-oxide) orders at $T_c = 7.8$ K (Caneschi *et al.* 1988); (iii) the Mn^{II}–Cu^{II} bimetallic chain compounds with bisbidentate extended ligands (Kahn *et al.* 1988; Nakatani *et al.* 1989). This family is currently studied in my group and I briefly review the main results obtained so far.

Strategy

My specific strategy to design molecular-based compounds exhibiting a spontaneous magnetization consists of assembling ordered bimetallic chains within the crystal lattice in a ferromagnetic fashion. If, as it is most often the case, the intrachain interactions between nearest-neighbour metal ions A and B are antiferromagnetic, the chains are said to be ferrimagnetic and their ground state may be schematized as:

[123]
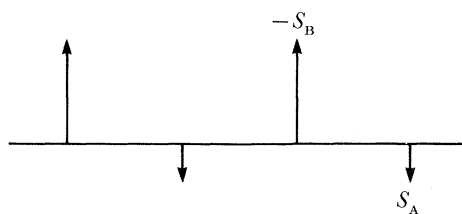
where S_A and S_B ($S_A \neq S_B$) are the local spins. In absence of any interchain interaction, the magnetic properties of such a system are quite characteristic. The $\chi_M T$ against T plot, χ_M being the molar magnetic susceptibility per AB unit and T the temperature, exhibits a minimum. Upon cooling below the temperature of this minimum, $\chi_M T$ increases in a ferromagnetic-like fashion and diverges when T approaches zero (Verdaguer et al. 1983; Gleizes & Verdaguer 1984). This divergence may be considered as the onset of a magnetic ordering at 0 K. It is indeed well established that there is no magnetic ordering at a finite temperature for a purely one-dimensional system (Carlin 1986). In fact, the chains cannot be perfectly isolated within the lattice. Either, they interact between them in an antiferromagnetic fashion and the divergence of $\chi_M T$ is stopped at a certain temperature close to the temperature of three-dimensional antiferromagnetic ordering (Pei et al. 1987), or they interact in a ferromagnetic fashion and below a critical temperature, the system behaves as a ferromagnet. My goal is to realize the conditions leading to this latter situation.

The main requirements of my strategy are the following: (i) $|S_A - S_B|$ must be as large as possible. For that, we use Mn^{II} and Cu^{II} magnetic centres with $\frac{5}{2}$ and $\frac{1}{2}$ local spins, respectively. (ii) The intrachain antiferromagnetic interactions must be as large as possible. This condition is satisfied when using bridging groups known for their ability to transmit the electronic effects, like the conjugated bisbidentate ligands (Kahn 1987). (iii) Finally, the relative positions of the chains within the crystal lattice must favour the ferromagnetic situation instead of the antiferromagnetic one.

The first two requirements led us to synthesize bimetallic chain compounds according to one of the two schemes shown below, with Mn^{II} cations reacting on Cu^{II} mononuclear anionic bricks:
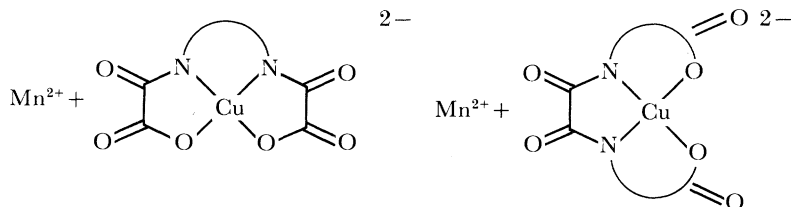

The former scheme gives equally spaced bimetallic chains of which examples are presented in the next section and the latter alternating bimetallic chains (Pei et al. 1988) as those described in the following section.

REGULAR BIMETALLIC CHAINS: $MnCu(pba)(H_2O)_3 \cdot 2H_2O$ AND $MnCu(pbaOH)(H_2O)_3$

The two compounds $MnCu(pba)(H_2O)_3 \cdot 2H_2O$ (1) and $MnCu(pbaOH)(H_2O)_3$ (2) (pba = 1,3-propylenebis(oxamato) and pbaOH = 2-hydroxy-1,3-propylenebis(oxamato))

have very similar regular chain structures. They are obtained by reaction of Mn^{II} ion on the Cu^{II} brick shown below:
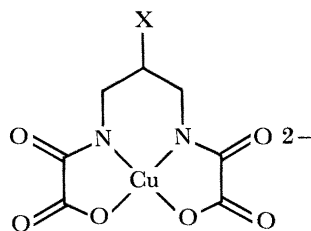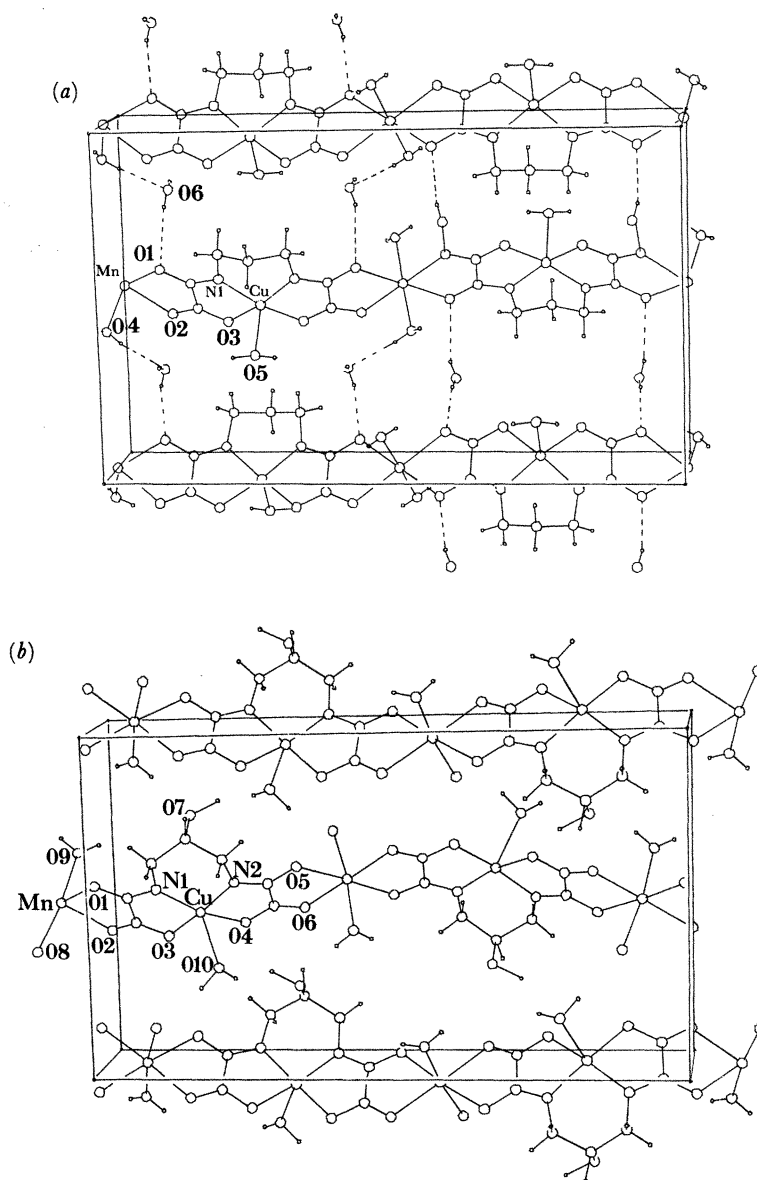
pba: X = H
pbaOH: X = OH

FIGURE 1. Perspective view of three neighbouring chains in (a) **1** and (b) **2**. The origin of the unit cell is the upper left-hand corner. The a-axis runs top to bottom and the b-axis left to right.

The relative positions of the chains within the crystal lattice are however different as shown in figure 1. Both **1** and **2** crystallize in the orthorhombic system. The chains run along the b-axis. The shortest interchain separations along the a-axis involve metal ions of the same nature in **1** (Cu ... Cu = 6.545 Å† and Mn ... Mn = 6.977 Å) and of different nature in **2** (Cu ... Mn = 5.751 and 6.398 Å). In a simplified fashion, in **2**, with respect to **1**, every other chain is displaced by slightly less than half of a repeat unit along b. In both compounds, the chains closest to one another are those related by a unit cell translation along the c-axis (Cu ... Cu^e = Mn ... Mn^e = 5.2105 Å in **1** and 5.073 Å in **2**).

In the 30–300 K temperature range, **1** and **2** show the magnetic behaviour characteristic of ferrimagnetic chains with the minimum of $\chi_M T$ around 115 K. On the other hand, upon cooling down below 30 K, $\chi_M T$ increases much faster for **2** than for **1** and below 5 K, the two compounds behave quite differently. **1** exhibits a maximum of $\chi_M T$ at 2.3 K and a maximum of χ_M at 2.2 K, due to the onset of three-dimensional antiferromagnetic ordering. In contrast, $\chi_M T$ for **2** diverges and becomes strongly field-dependent, which suggests that a ferromagnetic transition takes place. The temperature dependence of the magnetization M within a magnetic field of 3×10^{-6} T confirms that a three-dimensional ferromagnetic transition occurs at $T_c = $ 4.6 K. Below this temperature, **2** exhibits a spontaneous magnetization and a hysteresis loop $M = f(H)$ characteristic of a soft magnet.

Both the antiferromagnetic transition in **1** and the ferromagnetic one in **2** correspond to first-order phase transitions. As a matter of fact, the heat capacity curves shown in figure 2 exhibit a λ peak at T_c.
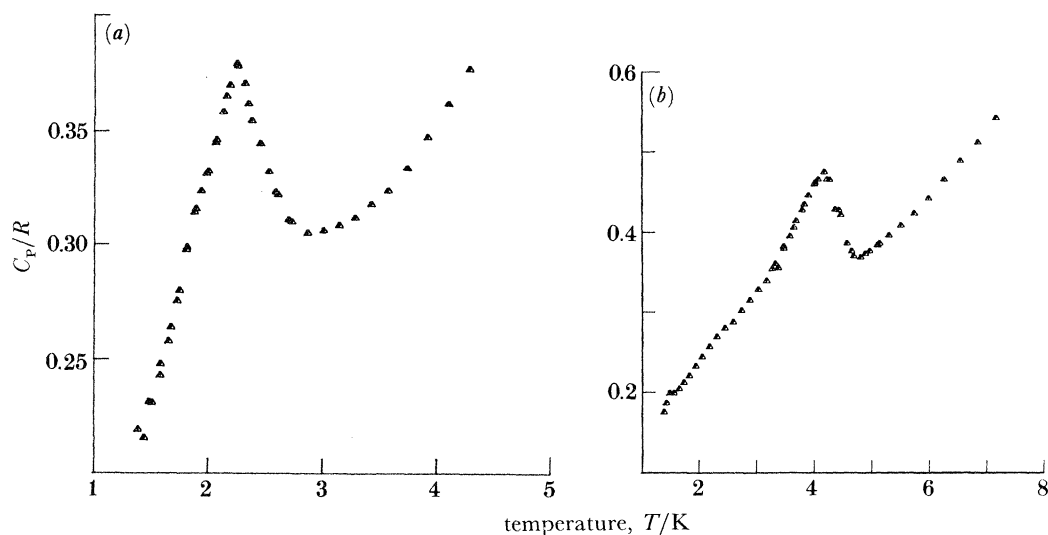

FIGURE 2. Temperature dependence of the heat capacity curves for (a) **1** and (b) **2**.

To get information on the mechanism of the three-dimensional magnetic ordering and on the spin distribution in both compounds, I investigated the single crystal EPR spectra. The angular dependence of the linewidths is governed by the dipolar interactions between local spins. The EPR data also suggest that the main dipolar interaction must be parallel to the c-axis and this orients the local spins parallel to each other along this direction. It follows that the spin distributions should be as shown in figure 3. The bc ferromagnetic planes alternate along the
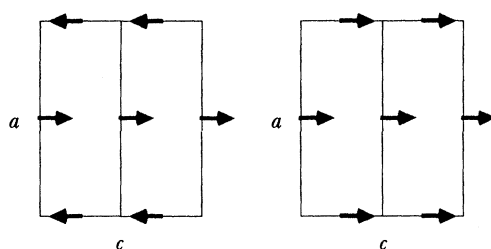
† 1 Å = 10^{-10} m.

FIGURE 3. Schematic representation of the preferred spin orientation for **1** (left) and **2** (right) in the ac-plane. The arrows indicate the Mn^{II} local spins; those of Cu^{II} ions are oriented in the opposite directions. To make easier the comparison between the two spin distributions, the coordinates of the atoms for **2** have been translated by $x/a = -0.0310$ and $z/c = -0.2625$.

a-axis in an antiferromagnetic fashion in **1** and in a ferromagnetic fashion in **2**, leading to the ferromagnetic ordering observed at 4.6 K (Gatteschi *et al.* 1989).

These differences of magnetic properties are related to the differences concerning the packing along the a-axis. This may be chemically proved in a clearcut fashion. Both **1** and **2** react with pyrazine (pz) in sealed tubes to give $MnCu(pba)(pz)$ (**3**) and $MnCu(pbaOH)(pz)$ (**4**), respectively. To respect the octahedral environment of Mn^{II} ions, pz must bridge these ions, which leads to molecular planes as shown below:
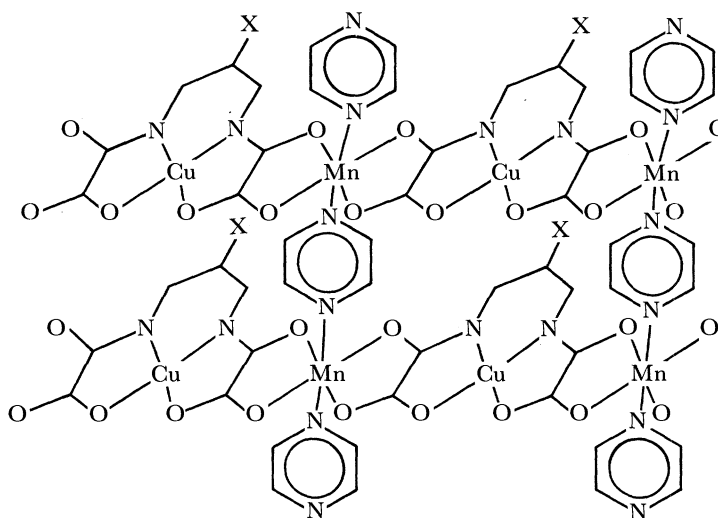
In a certain sense, the action of pyrazine corresponds to molecular weaving. The pyrazine bridge provides an antiferromagnetic exchange pathway between the Mn^{II} ions, so that each plane has a zero resulting spin, and whatever the nature of the interaction in the direction perpendicular to the plane, the compound should order antiferromagnetically. Furthermore, **3** and **4** have very similar powder X-ray patterns, which indicates that the crystal structures, including the packing of the planes, are probably identical. The magnetic data confirm these predictions. Both **3** and **4** exhibit the behaviour characteristic of ferrimagnetic chains down to about 5 K, then order antiferromagnetically at 2.9 K, owing to the Mn...Mn interaction through pz.

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ALTERNATING BIMETALLIC CHAINS: $MnCu(obbz) \cdot 5H_2O$ AND $MnCu(obbz) \cdot 1H_2O$

The action of Mn^{II} on the Cu^{II} 'brick' $[Cu(obbz)]^{2-}$ shown below:
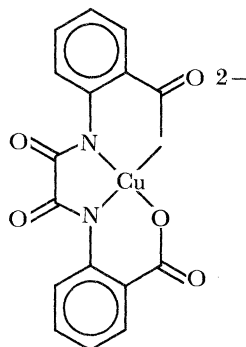
(obbz = oxamido-N,N'-bis(2-benzoato)) affords two compounds of formula $MnCu(obbz) \cdot 5H_2O$ (**5**) and $MnCu(obbz) \cdot 1H_2O$ (**6**). The four additional water molecules in **5** as compared with **6** are not coordinated to the metal ions. Otherwise, the two compounds have very similar structures as revealed by powder X-ray patterns, and XANES and EXAFS spectra at both Mn and Cu edges. Cu^{II} is in elongated tetragonal surroundings and Mn^{II} in octahedral surroundings. The radius of the first shell around Mn^{II} is equal to 2.16(3) Å. Those data allow to propose the following structure: first I consider the chain shown in figure 4 with Mn^{II} and Cu^{II} ions alternately bridged by oxamido and carboxylato groups. The equatorial plane around Mn^{II} would consist of four oxygen atoms belonging to an oxamido group, a carboxylato group and a water molecule. The apical sites are two other oxygen atoms belonging most probably to carboxylato groups of an adjacent chain, so that we have a two- or three-dimensional packing.
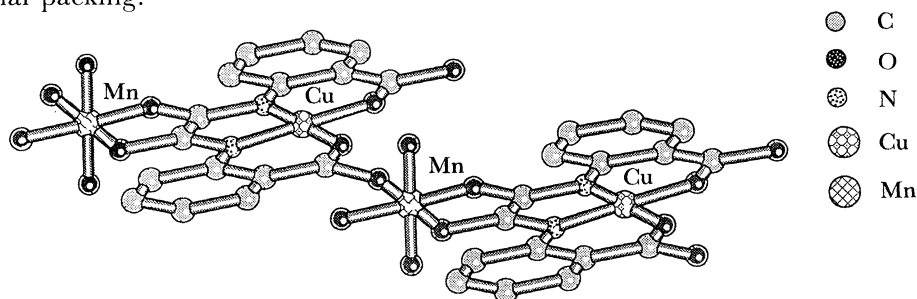

FIGURE 4. Basic structure proposed for $MnCu \cdot 5H_2O$ and $MnCu \cdot 1H_2O$. The oxygen atoms occupying the apical positions around the Mn^{II} ions belong probably to carboxylato groups of adjacent chains.

In spite of the structural analogies, **5** and **6** have completely different magnetic properties. Whereas **5** orders antiferromagnetically at 2.3 K, the deshydrated form **6** presents a ferromagnetic transition at 14 K. The temperature dependence of the molar magnetization M in a field of 10^{-5} T is shown in figure 5. The field-cooled magnetization (FCM) obtained by cooling down in the field shows the typical feature of a ferromagnetic transition, i.e. a rapid increase of M when T decreases below 15 K, then a break in a curve around $T_c = 14$ K. The remnant magnetization was then measured by switching off the field at 5 K and warming up. The remnant magnetization, as expected, vanishes at T_c. Finally, the zero-field-cooled
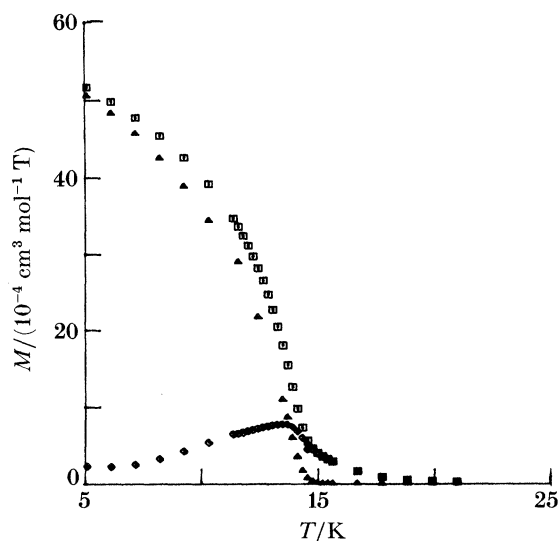
FIGURE 5. Temperature dependence of the magnetization M for **6** in the 5–20 K range and with a field of 10^{-5} T. $\square$, field cooled magnetization; $\triangle$, remnant magnetization; $\diamond$, zero field cooled magnetization (see text).
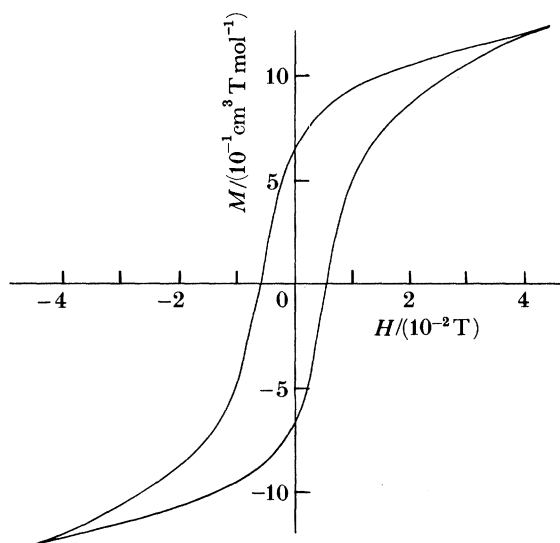

FIGURE 6. Hysteresis loop $M = f(H)$ for a polycristalline sample of **6** at 4.2 K.

magnetization (ZFCM) was measured by cooling down in zero field, then warming up within the field. At any temperature below T_c, the ZFCM is smaller than the FCM, due to the fact that in this low-temperature range the applied field is too weak to move the domain walls. The ZFCM exhibits a maximum around T_c, as expected for a polycrystalline ferromagnet (see, for example, Hitzfield *et al.* 1984).

I also studied the magnetic hysteresis for **6**. The hysteresis loop at 4.2 K is shown in figure 6. The remnant magnetization is equal to 6.3×10^{-1} cm^3 T mol^{-1}, i.e. about 30 % of the saturation magnetization (see below) and the coercive field is about 6×10^{-3} T.

The last experiment concerning the magnetization compares the variations of M with the applied magnetic field for **5** and **6**. The results at 4.2 K are shown in figure 7. They reveal what follows: (i) the high-field limits are identical for both compounds and equal to about
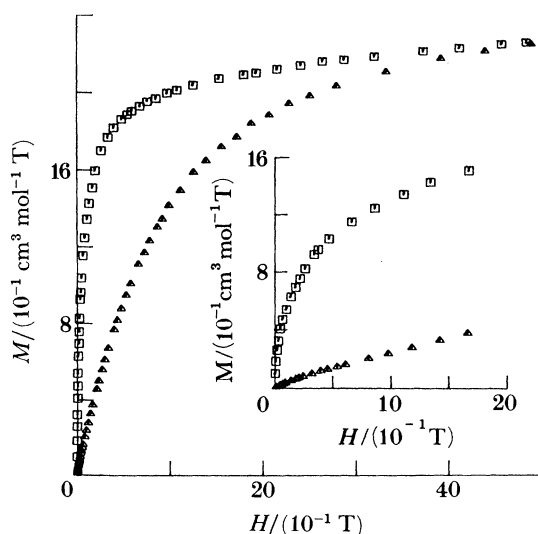
[129]

FIGURE 7. Field dependences of the magnetization M for polycristalline samples of **5** ($\triangle$) and **6** ($\square$).

$2.3 \text{ cm}^3 \text{ T mol}^{-1}$. This value agrees with the saturation magnetization M_s expected for a spin $S = S_{Mn} - S_{Cu} = 2$ per Mn–Cu unit. M_s is then given by $M_s = Ng\beta S$, where N is Avogadro's number and β the electronic Bohr magneton. The theoretical value of M_s for $S = 2$ and $g = 2$ is $2.3 \text{ cm}^3 \text{ T mol}^{-1}$; (ii) the increase of M against H is much slower for **5** than for **6**. For instance, half of the saturation magnetization is reached at $7.5 \times 10^{-1} \text{ T}$ for the former compound and at only $5 \times 10^{-2} \text{ T}$ for the latter; (iii) the slope in zero-field of the M against H plot for **6** is extremely large, actually of the order of $2 \times 10^2 \text{ cm}^3 \text{ mol}^{-1}$. The fact that the zero-field susceptibility $(\mathrm{d}M/\mathrm{d}H)_{H=0}$ is not infinite is essentially due to the demagnetization field created by the surface of the sample. Moreover, the experiment is carried out with a polycrystalline powder, so that the susceptibility is averaged over all directions, including the hard magnetization direction.

The reasons why **5** and **6** behave so differently are not perfectly clear yet. Maybe, the non-coordinated water molecules in **5** prevent through-space interactions. Maybe, also, the bond angles around the carboxylato bridge are substantially different according as these water molecules are present or not, which could affect the magnitude of the Mn...Cu interaction through the carboxylato group. Furthermore, the EPR data recorded on powder samples suggest that the interchain interactions in **6** are due to exchange rather than to dipolar effects.

CONCLUSION AND OUTLOOK

The field of molecular-based magnetic materials is still in its first infancy. Several groups over the world work along this perspective, using various strategies. The emulation and the collaboration between them should favour a fast development. In my opinion, the main goals are the following.

1. To shift T_c toward higher temperatures. Reaching liquid nitrogen temperature would be obviously a major step in this area.

2. To design stable systems, easy to handle, giving well-defined hysteresis loop with large remnant magnetization and coercive fields.

3. To obtain transparent thin films retaining the ferromagnetic properties below T_c. Such films could be designed either from compounds soluble in organic solvents, or by using the Langmuir–Blodgett technique.

My specific approach utilizing both the efficiency of organic-based ligands to transmit the electronic effects on long distances and the specific ability of the d-metal orbitals to provide high local magnetic moments should allow us to make progress along the three directions underlined above.

Right now, I think that the molecular weaving of which a first example is reported in this paper opens very promising perspectives. Owing to its symmetry, pyrazine bridges two ions of the same nature belonging to adjacent chains. Replacing pyrazine by dissymmetrical bridges, X, could result ferrimagnetic planes as shown below:

```
        X           X           X           X
        |           |           |           |
————————Mn——————————Cu——————————Mn——————————Cu——————
        |           |           |           |
        X           X           X           X
        |           |           |           |
————————Cu——————————Mn——————————Cu——————————Mn——————
        |           |           |           |
        X           X           X           X
        |           |           |           |
————————Mn——————————Cu——————————Mn——————————Cu——————
        |           |           |           |
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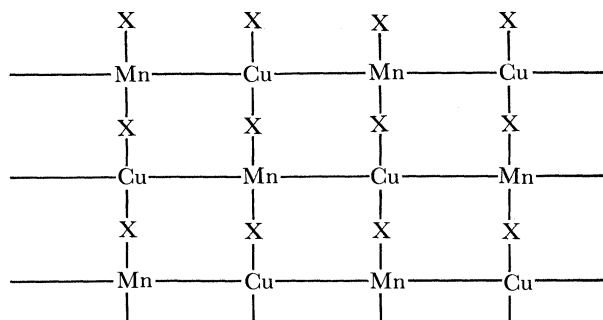
The three-dimensional ferromagnetic ordering of these ferrimagnetic planes could then be achieved owing to dipolar interactions along the direction perpendicular to the planes.

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Discussion

S. A. LAWRENCE (*Development Department, Johnson Matthey p.l.c., Middlesex, U.K.*). Results of my own work on polymeric complexes of Rh^I–Co^{II} and 4,4′-diisocyanobiphenyl (Lawrence *et al.* 1988) have shown electrical resistivities as low as $200 \, \Omega$ cm that originate in part from delocalization of unpaired electron density on Co^{II} centres to bridging π-bonded ligands. Would Professor Kahn comment on the possibility of electronic delocalization occurring within the lattice of the ferromagnetic Mn–Cu complexes that he has prepared?

O. KAHN. Till now, my Mn^{II}–Cu^{II} chain compounds exhibiting a spontaneous magnetization are insulators. In some copper precursors, it is possible to stabilize Cu^{III} and I intend to synthesize compounds in which some copper centres would be Cu^{III}. Maybe those compounds will present interesting electrical properties in addition to the magnetic properties.

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