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MOLECULAR FERROMAGNETISM : ORBITAL APPROACH AND RECENT ACHIEVEMENTS

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Abstract This paper is divided into two parts. First the various orbital patterns favoring a ferromagnetic interaction between molecular units are explored. Two types of mechanisms are distinguished according to whether they require or not an electron transfer between the molecular units. As far as the mechanisms requiring no electron transfer are concerned, a further distinction is made between spin delocalization and spin polarization. Each concept is illustrated by at least one example. The second part deals with a new family of molecular-based magnets of formula $Mn_2[Cu(opba)]_3R_2.nL$ where opba stands for orthophenylenebis(oxamato), R for a monovalent cation and L for a solvent molecule. The compound $Mn_2[Cu(opba)]_3(NBu_4)_2.6DMSO$ exhibits a spontaneous magnetization below 15 K.

In the last two years, since the meeting of Il Coccio (Italy),[1] we have pursued our endeavors concerning the molecular ferromagnetism, from both theoretical and experimental points of view. In this paper we would like to summarize briefly some of our findings. In the first part we will discuss the various orbital patterns favoring the parallel alignment of local spins, and in each case we will give at least one example. This example may arise either from our own research group or from other groups. Then, in the second part, we will present some preliminary results concerning a new family of molecular-based magnets.

PARALLEL SPIN ALIGNMENT IN MOLECULAR CHEMISTRY

To start with, we consider two molecular units noted A and B, each of them carrying an unpaired spin. The two singly-occupied orbitals around A and B are noted a and b, respectively. The interaction between A and B leads to a singlet state and a triplet state. When the latter state is the lowest, the interaction is ferromagnetic; the parallel spin alignment is favored. Whatever its nature, the interaction may be transmitted through space; it is then generally very weak. It may be also transmitted through a bridge or molecular wire joining A and B. This latter situation is the most frequently encountered when the spin carriers are transition metal ions.

We must now distinguish two types of mechanisms favoring the ferromagnetic interaction, namely those which do not require any electron transfer between A and B, and those requiring such an electron transfer.

Mechanisms requiring no electron transfer between the molecular units

Two situations must be discussed here, according to whether the interaction is due to spin delocalization or to spin polarization.

Spin delocalization The simplest form of interaction between A and B may be described by the Heitler-London approach. The singlet-triplet energy gap J is then given in a first approximation by :

$$J = 2k + 4\beta S \tag{1}$$

with :

$$k = \langle a(i)b(j)|1/r_{ij}|a(j)b(i)\rangle$$
$$\beta = \langle a(i)|h(i)|b(i)\rangle$$
$$S = \langle a(i)|b(i)\rangle \tag{2}$$

h(i) being the one-electron Hamiltonian. The first term in the right-hand side of eq. (1) is always positive; it stabilizes the triplet. The second term is negative and stabilizes the singlet. When the a and b

orbitals are orthogonal, the overlap integral S and transfer integral β are zero, such that the ground state is the triplet. Many cases of ferromagnetic interaction arising from the strict orthogonality of the magnetic orbitals have already been discussed.[2,3] We report here on two new cases. The first one concerns the compound of formula $[MnCu(dmg)_2CH_3COO)].2H_2O$ with dmg^{2-} = dimethylglyoximato studied by Lloret, Journaux et al.[4] This compound has a bimetallic chain structure with Mn(III) and Cu(II) ions bridged by oximato groups as shown in Figure 1.

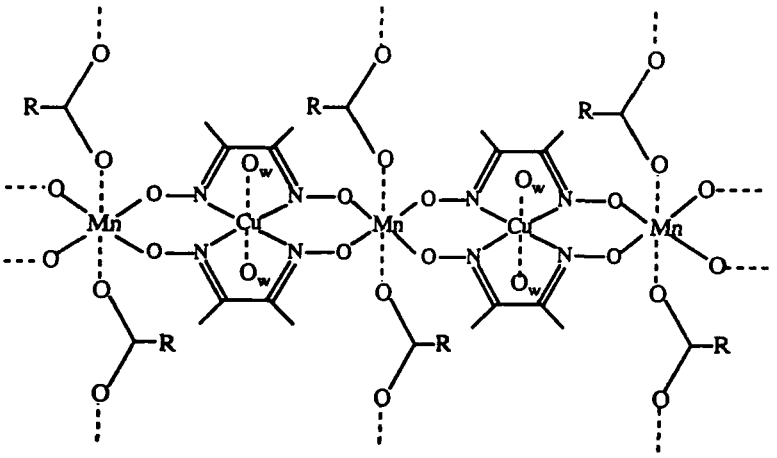


FIGURE 1 Structure of $[MnCu(dmg)_2CH_3COO)].2H_2O$. R stands for CH_3 and O_W for H_2O.

The local spins are $S_{Mn} = 2$ and $S_{Cu} = 1/2$. Due to the Jahn-Teller effect the two metal centers are expected to have elongated octahedral surroundings. It follows that the four singly-occupied orbitals around Mn(III) transform as the $2A_1 + A_2 + B_2$ irreducible representations, assuming a C_{2v} symmetry for the Mn(III)Cu(II) unit. The singly-occupied orbital centered on Cu(II) transforms as B_1. The strict orthogonality is achieved, and the Mn(III)-Cu(II) interaction is expected to be ferromagnetic. This is confirmed by the magnetic data shown in Figure 2 in the form of the $\chi_M T$ versus T plot, χ_M being the molar magnetic susceptibility and T the temperature. At room temperature $\chi_M T$ is already larger than expected for uncoupled

Mn(III) and Cu(II) ions, and increases when T is lowered down to 12 K. The fitting of those data leads to an intrachain interaction parameter J equal to 52 cm^{-1}, the interaction Hamiltonian being of the form $-J\sum_i \mathbf{S}_{Mn,i}\cdot\mathbf{S}_{Cu,i}$. The sharp maximum at 12 K is due to a three-dimensional antiferromagnetic ordering of the ferromagnetic chains. Interestingly, the compound behaves as a metamagnet; a magnetic field of 4.5×10^3 G overcomes the antiferromagnetic intrachain interactions, and align all local spins parallel.

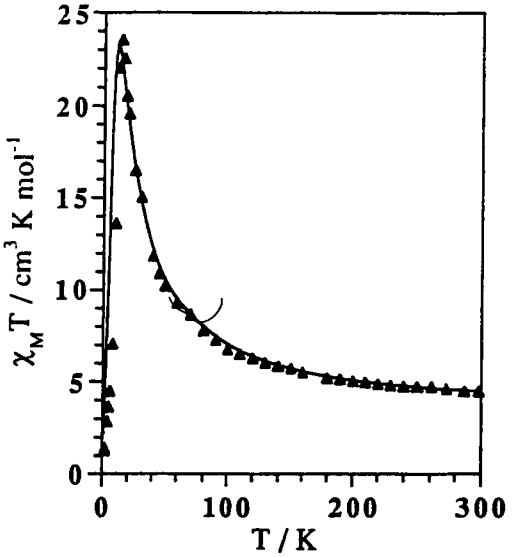
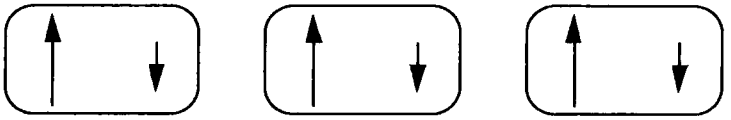


FIGURE 2 $\chi_M T$ versus T plot for $[MnCu(dmg)_2CH_3COO)].2H_2O$.

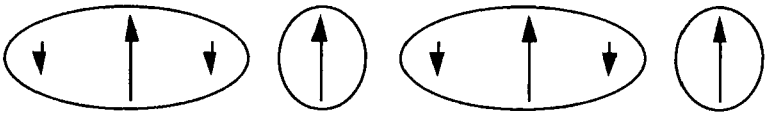
The second example concerns the Prussian-blue like compound of formula $Cs[CrNi(CN)_6].2H_2O$ studied by Verdaguer and coworkers.[5] Its structure is three-dimensional with Cr(III)-CN-Ni(II) linkages. Both ions are in octahedral surroundings. The three unpaired electrons of Cr(III) occupy the low-lying t_{2g} orbitals, and the two unpaired electrons of Ni(II) the high-lying e_g orbitals. Owing to the t_{2g}-e_g orthogonality, the Cr(III)-Ni(II) interaction is expected to be ferromagnetic. Indeed, the compound shows a long-range ferromagnetic ordering at T_c = 90 K.

Spin polarization The molecular orbital approach at the SCF level in the spin-unrestricted scheme in some cases leads to an

unsatisfying description of the spin density. In such an approach the spin density within the A (or B) unit is given by a^2 (or b^2), and therefore is positive or zero in any point of the space. This approach cannot account for regions of space in which the spin density is negative whereas both NMR and EPR techniques reveal that such regions do exist. To account for this it is necessary to go beyond the SCF approximation and to perform configuration interaction (CI). One may then find paramagnetic molecular species in which there is a large positive spin density in a region of the molecule and a weak negative spin density in another region. If the species of that kind can be assembled within the crystal lattice in such a way that the negative spin density of a unit preferably interacts with the positive spin density of the adjacent unit, an overall ferromagnetic behavior may be anticipated,[6] as schematized below :



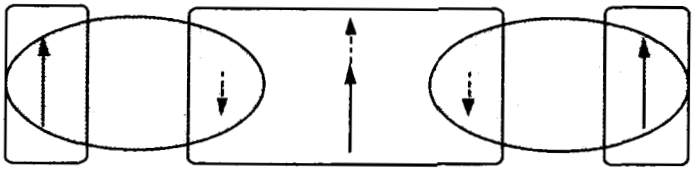
It is also possible to use two kinds of units, only one of them showing both positive and negative spin densities, and to build a ferromagnetic assembly as :



What is remarkable in this spin-polarization approach is that, if we single out a pair of units, the magnitude of the interaction is given by an expression rather similar to eq. (1), all the signs however being reverted. In the Heitler-London mechanism the overlap integral <a|b> favored the singlet state. Here the overlap integral between local orbitals carrying the positive and negative spin densities favors the triplet.[7]

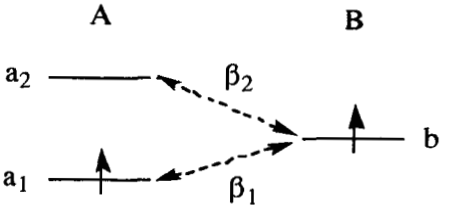
This mechanism based on spin polarization explains the parallel spin alignment observed in the metallocenium charge-transfer salts $[M(C_5Me_5)_2](TCNE)$ with M = Cr, Mn and Fe.[8-10] Let us consider the case of the decamethylferrocenium derivative. At the SCF level the unpaired electron on $[M(C_5Me_5)_2]^+$ is found to be strongly localized on the low-spin iron(III) ion, such that the spin density is positive in the immediat environment of the metal and negligible everywhere

else. In fact, an approach including the CI reveals that the Cp rings carry a significant negative spin density, the positive spin density on the metal being enhanced.[11] The ferromagnetic interaction between nearest neighbor $[M(C_5Me_5)_2]^+$ and $(TCNE)^-$ units then arises from the antiparallel alignment of the negative spin density on a ring and the positive spin density on the adjacent $(TCNE)^-$, as schematized below :



Mechanism requiring an electron-transfer between A and B

Untill now we ignored the mixing between the low-lying states arising from the AB ground configuration (GC) and the states arising from the excited A^+B^- or A^-B^+ charge-transfer configurations (CTC). To take into account this effect we now consider the orbital pattern :



The charge-transfer configurations of lowest energy correspond to the $a_1 \rightarrow b$ and $b \rightarrow a_1$ processes. Both give rise to a singlet state, and the GC-CTC coupling stabilizes the low-lying singlet state by :

$$J = -2\beta_1^2[1/U(a_1 \rightarrow b) + 1/U(b \rightarrow a_1)] \quad (3)$$

where $U(a_1 \rightarrow b)$ and $U(b \rightarrow a_1)$ are the energy costs associated with the $a_1 \rightarrow b$ and $b \rightarrow a_1$ electron transfers, respectively, and β_1 is the transfer integral between the a_1 and b orbitals.

It has been suggested that if the highest-occupied orbital level of one of the units, say A, were orbitally degenerate, then the $b \rightarrow a_1$ transfer would favor the ferromagnetic interaction.[12] Indeed, the lowest state arising from the CTC in that case is a triplet due to Hund's rule, which by mixing with the low-lying triplet should favor the parallel spin alignment. This argument, however, is oversimplified.[13] Above the triplet state arising from the A^-B^+ configuration there are three singlet states (two of them being possibly accidentally degenerate), all three coupling with the low-lying singlet state, such that most often the GC-CTC coupling stabilizes the low-lying singlet more than the low-lying triplet, as schematized in Figure 3.

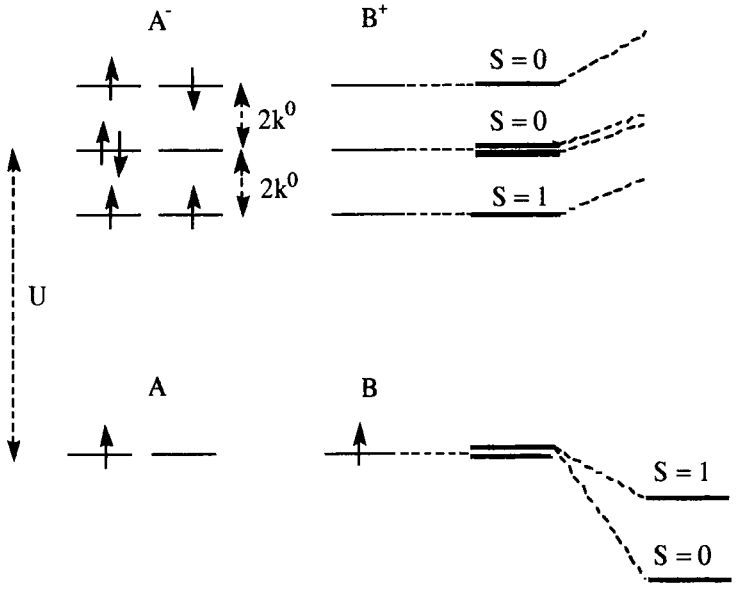


FIGURE 3 Interaction between two molecular units A and B, both carrying an unpaired electron, in the case where the highest-occupied level of A is doubly degenerate. U is the energy cost for the electron transfer and k^0 the one-site-two-electron exchange integral. Only when $k^0 > U$, can the low-lying triplet state be the ground state.

To sum up, we can say that the charge-transfers between the

highest-occupied orbital levels of the interacting units most generally favor the antiparallel spin alignment, even if one of those levels is orbitally degenerate.

There is however one type of charge transfer which may favor the ferromagnetic interaction, namely the transfer $b \rightarrow a_2$ from a singly-occupied orbital on a site toward an empty orbital on the other site (or, which is strictly equivalent, from a doubly-occupied orbital toward a singly-occupied orbital). Two states, a singlet and a triplet, arise from this charge-transfer configuration. The latter is lower in energy due to Hund's rule. The coupling between low-lying and excited triplet states is more pronounced than between low-lying and excited singlet states. The interaction is therefore ferromagnetic.[14] The singlet-triplet energy gap is roughly given by :

$$J = \beta_2^2 k^0 / U(b \rightarrow a_2)^2 \tag{4}$$

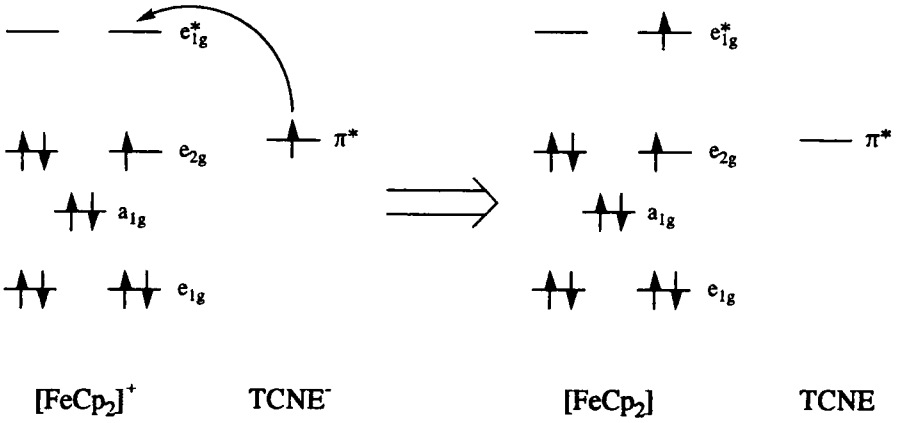
with :

$$\beta_2 = \langle a_2|h|b\rangle$$
$$k^0 = \langle a_1(i)a_2(j)|1/r_{ij}|a_1(j)a_2(i)\rangle \tag{5}$$

$U(b \rightarrow a_2)$ being the energy cost associated with the $b \rightarrow a_2$ process. What is important to realize is that the ferromagnetic stabilization due to this mechanism is one order of magnitude smaller in absolute value than the antiferromagnetic stabilization due to the transfer between singly-occupied orbitals, and consequently is most often masked. There are, however, some cases where the overlap density $a_1 b$ is negligibly small in any point of the space. The transfer integral β_1 is then zero. The ferromagnetic coupling due to the $b \rightarrow a_2$ electron transfer may then be detected, even if in any case it will be small.

Let us present two examples where this mechanism has been invoked to account for a ferromagnetic interaction. The first example deals with the compound $[Fe(C_5Me_5)_2](TCNE)$ we already mentioned. Tchougreeff suggested that the backward charge transfer of the unpaired electron from the π^* orbital of $(TCNE)^-$

toward the e_{1g}^* empty orbitals of $[Fe(C_5Me_5)_2]^+$, schematized below, could be at the origin of the observed ferromagnetic interaction between the two units.[15]



We must point out that this mechanism is quite plausible. As a matter of fact, the e_{1g}^* orbitals have a significant Cp ring contribution, such that the transfer integrals $<\pi^*|h|e_{1g}^*>$ may be rather large. In contrast, the e_{2g} orbitals of $[Fe(C_5Me_5)_2]^+$ are almost pure metal orbitals and the transfer integrals $<\pi^*|h|e_{2g}>$ are negligibly small, the separation between the iron(III) ion and the (TCNE) unit, about 5 Å, being too large.

Our second example is of completely different nature. It concerns the Gd(III)-Cu(II) interaction. Quite a few clusters or low-dimensional compounds containing both Gd(III) and Cu(II) ions have been described.[16,17] In any case, whatever the details of the structure may be, the interaction is ferromagnetic. The structure of one of those clusters containing two noninteracting $GdCu_2$ triads is shown in Figure 4.[18] Its formula is $[Gd_2Cu_4(fsaaep)_4(NO_3)_6]$ where $(fsaaep)^{2-}$ is the ligand deriving from 3-(N-2-pyridylethyl-formimidoyle)salicylic acid.

The temperature dependence of $\chi_M T$ (see Figure 5) and the field dependence of the magnetization at various temperatures unambiguously indicate that the ground state for the $GdCu_2$ triad has the spin 9/2. The Gd(III)-Cu(II) interaction parameter is found equal to 6.0 cm^{-1}.

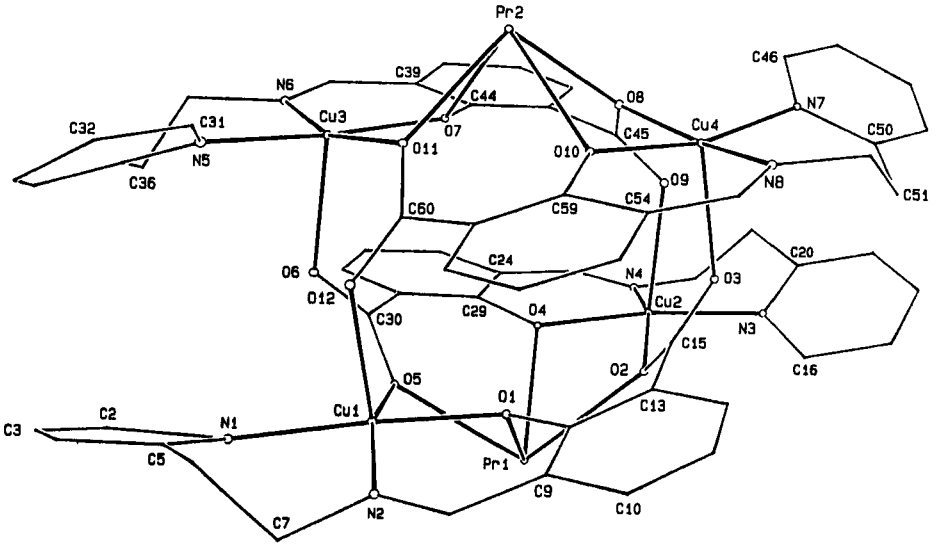


FIGURE 4 Structure of a Gd_2Cu_4 cluster. In fact the structure was refined for the isomorphous praseodymium derivative.

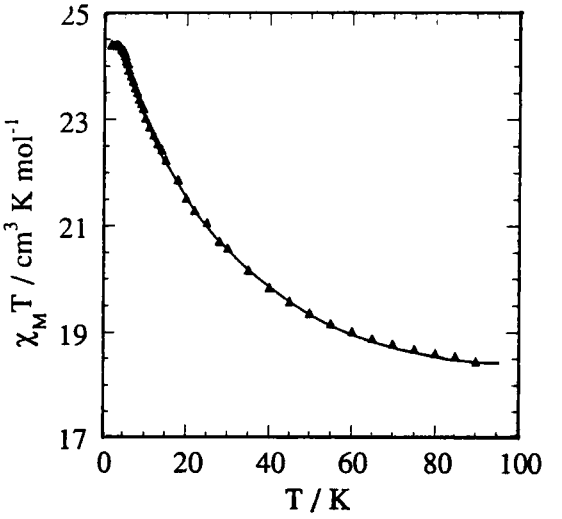


FIGURE 5 $\chi_M T$ versus T plot for the Gd_2Cu_4 cluster the structure of which is isomorphous to that shown in Figure 4.

The ferromagnetic nature of the interaction is attributed to the coupling between the Gd(III)Cu(II) ground configuration and the

Gd(II)Cu(III) charge-transfer configuration in which an electron is transferred from the singly-occupied 3d-type copper orbital toward an empty 5d-type gadolinium orbital, as schematized in Figure 6. What is important to realize, it is that the Gd(II)Cu(III) charge-transfer configuration of lowest energy, resulting from the 3d → 4f process, does not couple with the ground configuration. Indeed, the 4f gadolinium orbitals are very contracted around the nucleus and efficiently shielded by the fully-occupied 5s and 5p orbitals. As a consequence of this, the $\beta_{4f\text{-}3d}$ transfer integrals are negligibly small. On the other hand, the 5d-type gadolinium orbitals may be significantly delocalized toward the bridging atoms, and interact with the 3d-type copper orbitals. In other words the $\beta_{5d\text{-}3d}$ transfer integrals may be rather large.

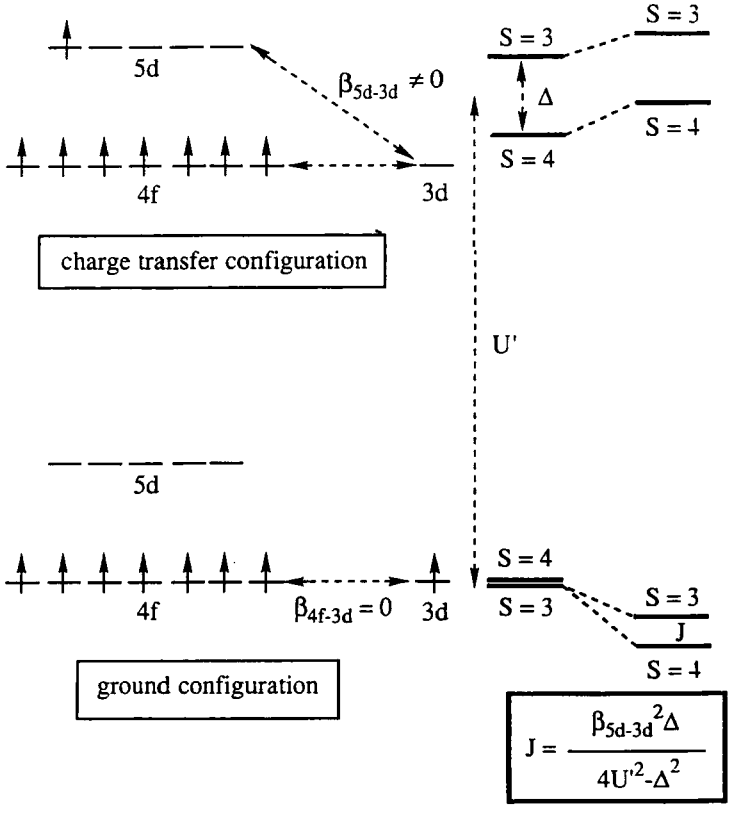
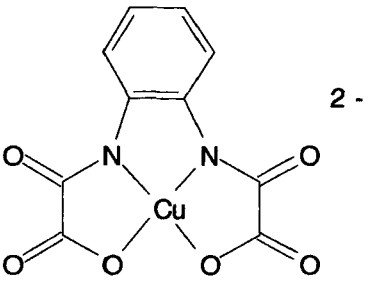


FIGURE 6 Schematic representation of the orbital mechanism explaining the ferromagnetic nature of the Gd(III)-Cu(II) interaction.

A NEW FAMILY OF MOLECULAR-BASED MAGNETS

The strategy followed in our group to design molecular-based magnets has some similarity with the spin-polarization approach we spoke about. The large positive and weak negative spin densities are provided by antiferromagnetically coupled Mn(II) (S_{Mn} = 5/2) and Cu(II) (S_{Cu} = 1/2) ions, respectively. In this second part we would like to report on preliminary results concerning novel Mn(II)Cu(II) compounds obtained from the precursor :



of formula $[Cu(opba)]^{2-}$, opba standing for *ortho*-phenylene-bis(oxamato). This precursor reacts on a Mn(II) ion, in dimethyl-sulfoxide (DMSO), in a 1/1 ratio, to afford the compound $MnCu(opba)(DMSO)_3$. Its structure consists of ordered bimetallic chains running in a zig-zag fashion, as shown in Figure 7.

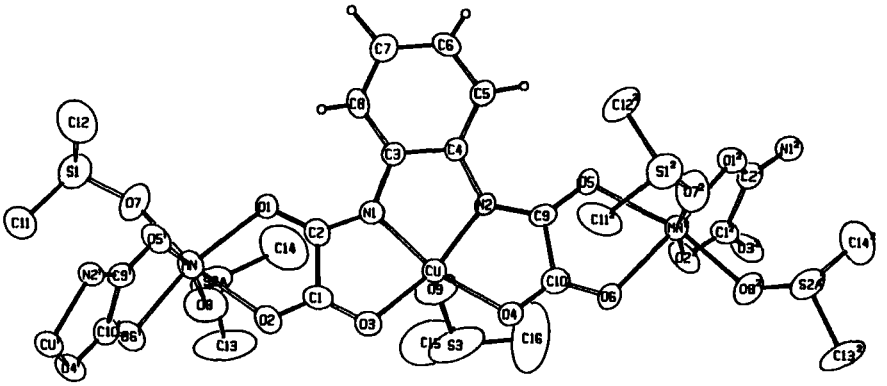


Figure 7 Structure of a section of chain for $MnCu(opba)(DMSO)_3$.

The copper atom has a square pyramidal environnement with a DMSO molecule at the apex. The manganese atom has a somewhat

distorted octahedral environment with two DMSO molecules in a *cis* position. Due to the bulky character of the DMSO ligands, the shortest interchain separations between spin carriers is as large as 7.2 Å. It turns out that the chains are almost perfectly isolated from each other. As a matter of fact, the magnetic behavior down to the very low temperatures corresponds to what is expected for a Mn(II)Cu(II) ferrimagnetic chain with the characteristic minimum of the $\chi_M T$ versus T plot around 115 K. Down to 4.2 K, no indication of long range ordering is detected. The DMSO molecules can be removed by a thermal treatment under vacuum. The new material then exhibits a magnetic transition at T_c = 6.5 K, with a spontaneous magnetization below this temperature. The field dependence of the magnetization below T_c suggests that we are faced with a canted magnet. Indeed, the magnetization does not reach the value expected for all S_{Mn} local spins aligned along a direction, and all S_{Cu} local spins aligned along the opposite direction.

In any case the one-dimensional nature of $MnCu(opba)(DMSO)_3$ prevents to obtain a high critical temperature. This is why we looked for increasing the dimensionality of our compounds. The basic idea is that it should be possible to link three Cu(opba) units to each manganese atom instead of two in the chain-compounds. The reaction in DMSO of two Mn(II) ions with three $A_2[Cu(opba)]$ units where A^+ is a monovalent cation affords small crystals of compounds of which the general formula is $A_2\{Mn_2[Cu(opba)]_3\}$. nDMSO. A may be a tetraalkylammonium as well as an alkaline ion. The determination of the structure of one of those compounds is in progress. We report here on the magnetic properties of the tetrabutylammonium derivative. The $\chi_M T$ versus T plot in the 15-300 K temperature range presents the minimum characteristic of a ferrimagnetic situation, the S_{Mn} and S_{Cu} local spin tending to align in opposite directions. When the temperature is lowered down to ca. 15 K, $\chi_M T$ reaches extremely large values and becomes field dependent, which suggests that a long-range magnetic transition takes place. This is confirmed by the magnetization versus T curves of Figure 8, recorded at a field of 1 G. The field-cooled magnetization (FCM) shows a break at 15 K, and the zero-field-cooled magnetization (ZFCM) a maximum just below T_c.

Figure 8 also shows the remnant magnetization obtained in cooling within the field below T_C = 15 K, then turning the field off.

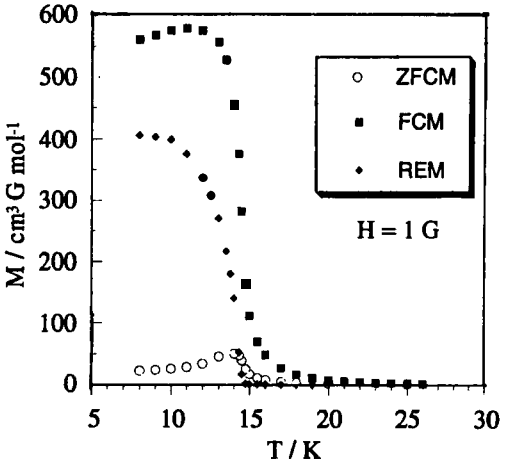


Figure 8 : Magnetization versus temperature curves for $(NBu_4)_2\{Mn_2[Cu(opba)]_3\}.6DMSO$ within a field of 1 G.

The magnetization versus magnetic field curve for $(NBu_4)_2\{Mn_2[Cu(opba)]_3\}.6DMSO$ is shown in Figure 9. The zero-field susceptibility $(\partial M/\partial H)_{H=0}$ of the compound is extremely large, and the saturation is quickly reached. Three quarters of the saturation magnetization is reached within 100 G. The value of the saturation magnetization, ca. 7 Nβ mol^{-1}, nicely corresponds to what is expected for the opposite alignment of the S_{Mn} and S_{Cu} local spins.

The crystal structure of $(NBu_4)_2\{Mn_2[Cu(opba)]_3\}.6DMSO$ should be known soon. This structure will provide some crucial information on the relation between dimensionality and T_C, for this family of compounds as well as for the oxalato-bridged bimetallic magnets obtained by Matsumoto, Okawa and coworkers.[19]

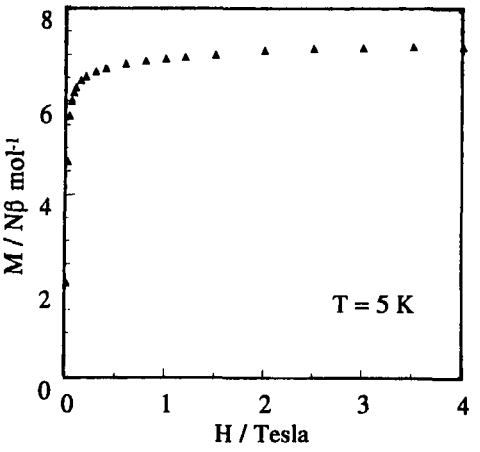


Figure 9 Magnetization versus magnetic field curve at 5 K for $(NBu_4)_2\{Mn_2[Cu(opba)]_3\}.6DMSO$.

As a conclusion of this short overview on the work performed in our group in the very last period, we would like to underline two problems : (i) Right now we know fairly well the orbital patterns favoring the parallel spin alignment. However, those patterns are still difficult to control; it is not an easy task to impose the relative energies and symmetries of the orbitals involved in the interaction phenomenon. In a certain sense, we know the rules of the game, but we are not perfectly able yet to apply them. (ii) It is now obvious that to increase the critical temperatures it is necessary to increase the dimensionality of the molecular-based materials. But the crystal engineering is still an art in molecular chemistry. Furthermore, when increasing the dimensionality, some specificities of the molecular chemistry like solubility, transparence, processability tend to disappear and the originality of the molecular-based magnets as compared to the classical insulating magnets like F_3O_4 may then vanish.

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