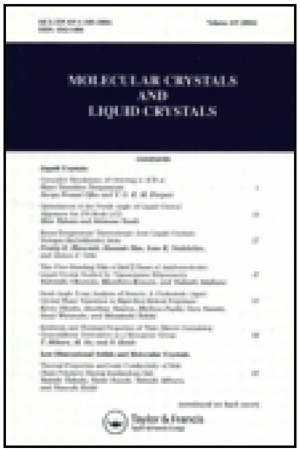

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Molecular Magnetism: A Multidisciplinary Field of Research

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MOLECULAR MAGNETISM : A MULTIDISCIPLINARY FIELD OF RESEARCH

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Abstract The goal of this paper is to emphasize the multidisciplinary character of molecular magnetism as a whole, and of our own activity in this field. For that, we have briefly described some of our results concerning the theoretical simulation of thermodynamical properties of molecular magnetic materials, the study of spin density maps, and the synergy between optical (or photophysical) and magnetic properties. We have also reported on two new chain compounds exhibiting dominant ferromagnetic interactions, one involving transition metal ions, the other one involving organic radicals.

INTRODUCTION

Molecular magnetism is a rather new field of research which has developed very rapidly in the last decade.[1] What characterizes this field is its deeply interdisciplinary character. Our own activity, schematized in Figure 1, reflects this interdisciplinarity. We are working along two main directions, namely the design of novel spin-bearing chemical objects, and the theory of open-shell systems. The spins of our chemical objects may arise from transition metal ions, organic radicals, or lanthanide ions. We are particularly concerned by the design of molecular assemblies exhibiting bulk magnetic properties such as long-range magnetic ordering, or bistability with hysteresis effects, which confers a memory effect on the system. As far as the theoretical route is concerned, our two main interests lie in the orbital mechanisms of magnetic phenomena on the one hand, and the theoretical simulation of thermodynamical properties on the other hand. Of course, theoretical and experimental routes may be strongly correlated. Figure 1 points out a facet of molecular magnetism for which both theoretical and experimental efforts are required, namely the determination of spin density maps. Finally, we would like to stress that one of the main issues in molecular magnetism deals with the design and the physical study of compounds exhibiting both magnetic and optical, or photophysical, properties, if possible in a synergistic way. For a couple of years or so, we are strongly engaged along this line.

The goal of this paper is to describe some of our very recent results which bring witness of our multidisciplinary approach of molecular magnetism.

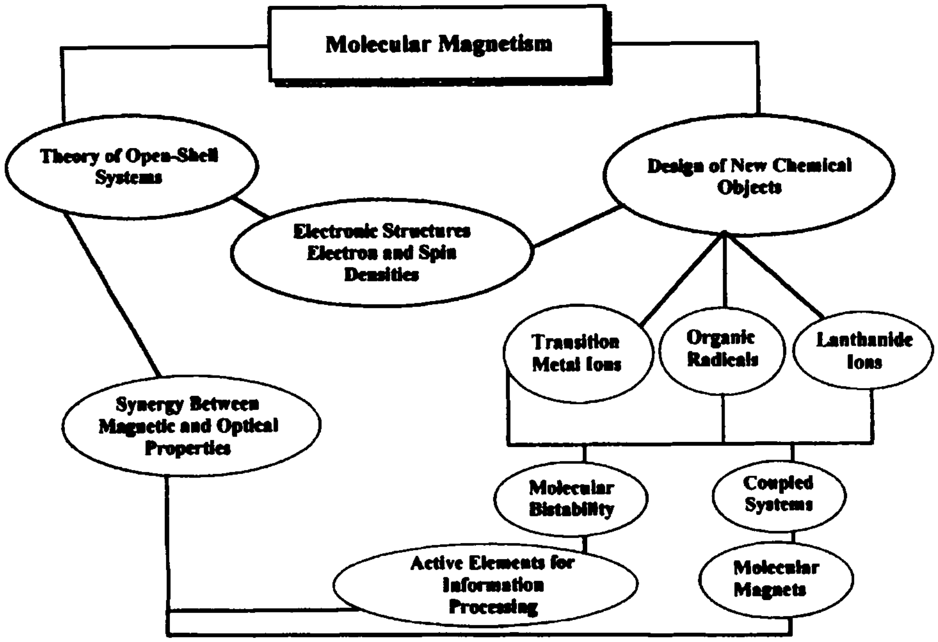


FIGURE 1 Diagrammatic representation of the activity of our research group in the field of molecular magnetism.

SIMULATION OF THE THERMODYNAMICAL PROPERTIES OF TWO-DIMENSIONAL FERRIMAGNETC COMPOUNDS

We have described several two-dimensional ferrimagnetic compounds, of general formula $cat_2Mn_2[Cu(opba)]_3 \cdot S$, where cat^+ stands for a cation, S stands for solvent molecules, and opba stands for *ortho*-phenylenebis(oxamato).[2-6] The structure of these compounds consists of bimetallic anionic layers $\{Mn_2[Cu(opba)]_3\}^{2-}$ shown in Figure 2 and cat^+ cations inserted between the layers. Two approaches have been developed to simulate the thermodynamical properties of such compounds, namely a high-temperature expansion up to the 12th order for the magnetic susceptibility and the 30th order for the heat capacity, and a Monte Carlo simulation, using the Wolf algorithm.[7] This algorithm is much more appropriate than the more classical Metropolis algorithm when we get closer to the critical points. In both approaches the $S_{Mn} = 5/2$ spin of Mn(II) was treated as a classical spin and the $S_{Cu} = 1/2$ spin of Cu(II) as a quantum spin. Figure 3 shows the $\chi_M T$ versus T plot for $(NBu_4)_2Mn_2[Cu(opba)]_3 \cdot 6DMSO \cdot H_2O$, χ_M being the molar magnetic susceptibility and T the temperature. The minimum of $\chi_M T$ around 120 K is the signature of a ferrimagnetic behavior. At low temperature $\chi_M T$ diverges as a result of a long-range magnetic ordering occurring at $T_c = 15$ K. The fitting of these magnetic data in the paramagnetic region with the high-temperature expansion leads to the local Zeeman factors $g_{Mn} = 2.00$ and $g_{Cu} = 2.20$, and to the interaction parameter $J = -33.1$ cm^{-1}, the interaction Hamiltonian being written as $-J\ \Sigma_i S_{Mn,i} \cdot S_{Cu,i}$. A Monte-Carlo simulation with these parameters reproduces almost perfectly the magnetic data down to about 20 K.

SPIN DENSITY MAPS

The most accurate description of the ground state for a paramagnetic species is provided by the spin density map. This map can be deduced from polarized neutron diffraction; it can also be calculated theoretically. In this respect, the Density Functional Theory (DFT) approach has been proved to be very appropriate to reproduce the main features of the spin distribution. We recently completed such a study, concerning the compound $[Mn(cth)Cu(oxpn)](CF_3SO_3)_2$.[8] This compound contains the Mn(II)Cu(II) dinuclear

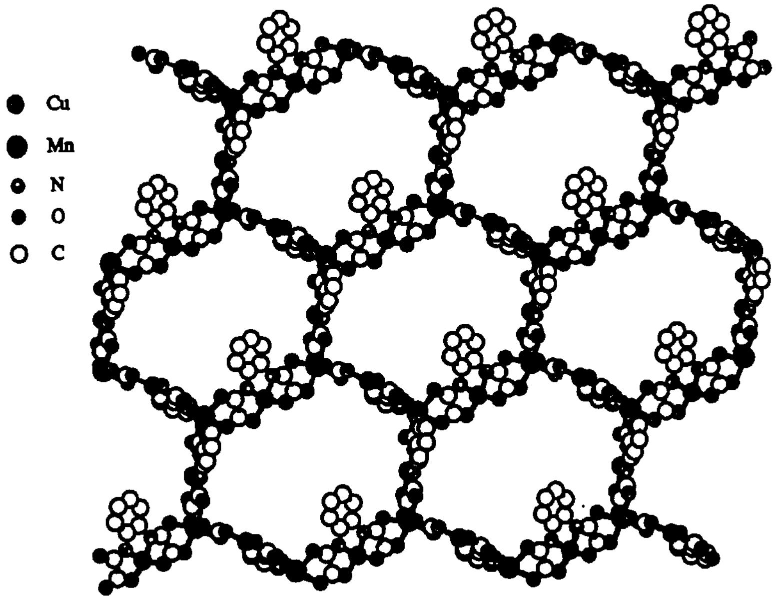


FIGURE 2 Structure of the anionic layer $\{Mn_2[Cu(opba)]_3\}^{2-}$ in two-dimensional ferrimagnets of formula $cat_2Mn_2[Cu(opba)]_3{\bullet}S$.

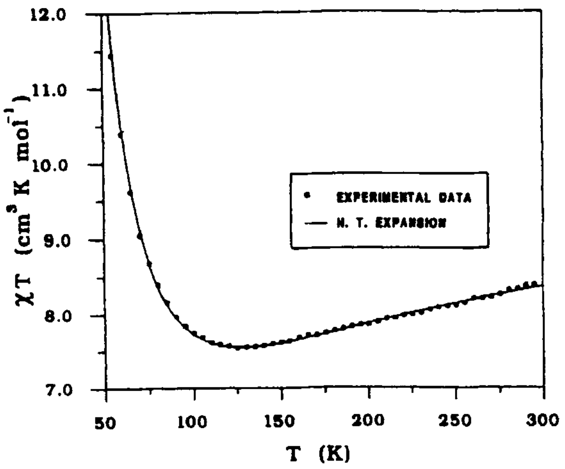


FIGURE 3 Experimental and calculated $\chi_M T$ versus T curves for $(NBu_4)_2Mn_2[Cu(opba)]_3{\bullet}6DMSO{\bullet}H_2O$.

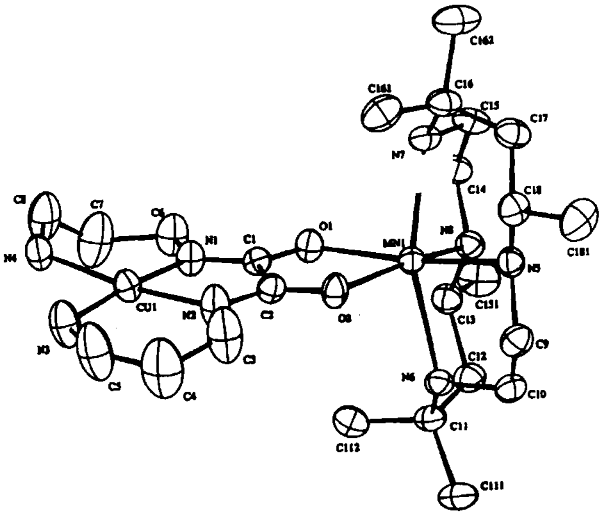


FIGURE 4 Structure of the binuclear cation $[Mn(cth)Cu(oxpn)]^{2+}$.

cation whose structure is represented in Figure 4. The interaction between $S_{Mn} = 5/2$ and $S_{Cu} = 1/2$ local spins is antiferromagnetic; the $S = 2$ pair state is the ground state, and the $S = 3$ pair state is located at 93 cm^{-1} above.[9] Figure 5 shows the spin density map deduced from polarized neutron diffraction. As expected, a large positive spin density is observed on the manganese side, and a weaker negative spin density is observed on the copper side. This negative spin density is much more diffuse than the positive one, so that the surface of zero spin density (or nodal surface) passes much closer to the manganese than to the copper atom. The results may also be presented in the form of atomic spin populations (see Figure 6), which specifies the degree of spin delocalization from the magnetic ions toward the peripheral and bridging ligands. Interestingly, the sum of the positive spin populations on the manganese side is equal to 4.67 μ_B, and the sum of the negative spin populations on the copper side is equal to -0.67 μ_B. These values exactly correspond to the Heitler-London description of the $S = 2$ ground state. In this description the $M_S = 2$ component of the wavefunction for the ground state may be written in the $|S,M_S>$ braket form as :

$$|2,2> = \sqrt{\frac{5}{6}}|5/2,5/2>|1/2,-1/2> - \sqrt{\frac{1}{6}}|5/2,3/2>|1/2,1/2>$$

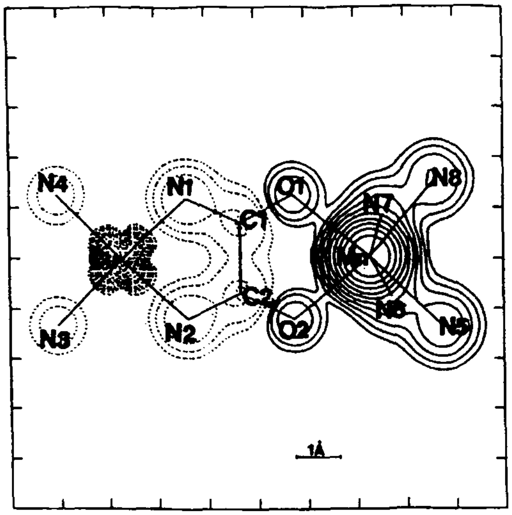
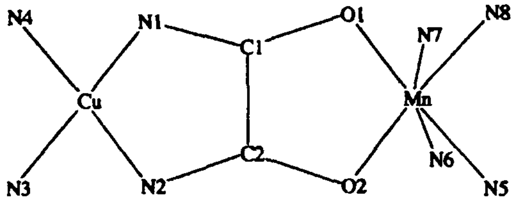


FIGURE 5 Spin density map deduced from polarized neutron diffraction for $[Mn(cth)Cu(oxpn)](CF_3SO_3)_2$. The full lines represent the positive spin density contours, and the dotted lines the negative spin density contours.



Spin populations (in μ_B)

Mn	4.32(2)	
O1	0.03(1)	
O2	0.03(1)	
N5	0.09(1)	Sum of the positive
N6	0.08(1)	spin populations : 4.67
N7	0.07(1)	
N8	0.05(1)	
Cu	-0.47(1)	
N1	-0.05(1)	
N2	-0.05(1)	Sum of the negative
N3	-0.02(1)	spin populations : -0.67
N4	-0.02(1)	
C1	-0.03(1)	
C2	-0.03(1)	

FIGURE 6 Atomic spin populations for $[Mn(cth)Cu(oxpn)](CF_3SO_3)_2$.

so that the spin populations (in μ_B units) on the manganese and copper sides, p_{Mn} and p_{Cu}, are given by :

$$p_{Mn} = 7g_{S=2}/3$$
$$p_{Cu} = -g_{S=2}/3$$

where $g_{S=2}$ is the Zeeman factor for the S = 2 pair ground state. This result confirms, if it was still necessary, that the best first-order description of low-lying states in coupled systems is the Heitler-London description.[1]

COMPLEMENTARITY BETWEEN OPTICAL AND MAGNETIC PROPERTIES OF Mn(II)Cu(II) COMPOUNDS

All the Mn(II)Cu(II) compounds we synthesized so far, whatever their dimensionality may be, exhibit formally spin-forbidden Mn(II) optical transitions activated by the Mn(II)-Cu(II) antiferromagnetic interaction.[9,10] The most intense of these transitions corresponds to $^6A_{1g} \rightarrow {}^4A_{1g} + {}^4E_g(G)$, referring to the O_h local symmetry. The temperature dependence of the intensity of this transition allows to determine the interaction parameter J between the $S_{Mn} = 5/2$ and $S_{Cu} = 1/2$ local ground states. The temperature dependence of the energy of this transition allows to determine the interaction parameter J* between the $S^*_{Mn} = 3/2$ local excited state of Mn(II) corresponding to the spin flip of an electron on its orbital and the $S_{Cu} = 1/2$ local ground state of Cu(II). The J value deduced from optical spectroscopy may be compared to that deduced from magnetic measurements. On the other hand, J* cannot be obtained by any magnetic technique.

Let us apply these ideas to the species $\{Mn[Cu(oxpn)]_3\}(ClO_4)_2 \cdot 2H_2O$ containing the tetranuclear cation shown in Figure 7.[11] The low-lying states arising from the $S_{Mn} = 5/2 \leftrightarrow S_{Cu} = 1/2$ interaction as well as the excited states arising from the $S^*_{Mn} = 3/2 \leftrightarrow S_{Cu} = 1/2$ interaction are also indicated in Figure 7 along with the allowed transitions. The solution spectrum at room temperature together with the temperature dependence of the transition around 24,310 cm^{-1} in cellulose acetate pellets are represented in Figure 8.[12]

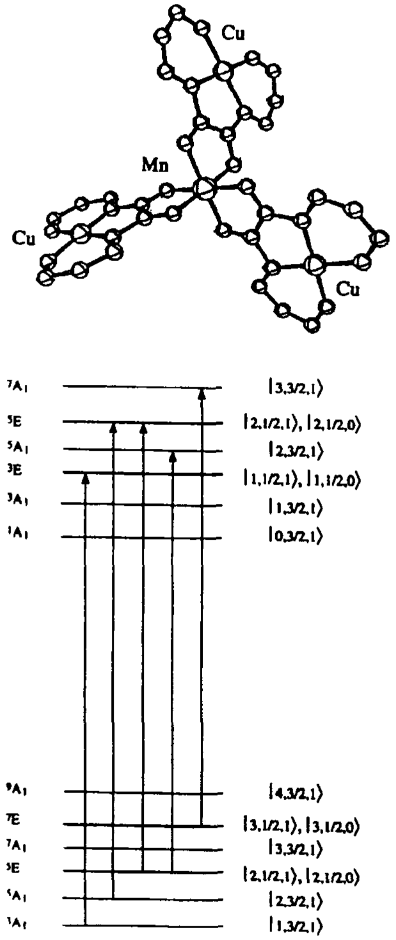


FIGURE 7 Structure of the tetranuclear cation $\{Mn[Cu(oxpn)]_3\}^{2+}$, and allowed transitions between low-lying and excited states.

The fitting of the temperature dependence of the intensity (see Figure 9, top) leads to $J = -33.2\ cm^{-1}$, a value very close to that deduced from the magnetic data, and the fitting of the temperature dependence of the energy of this band (see Figure 9, bottom) leads to $J^* = -45\ cm^{-1}$. Both the $S_{Mn} = 5/2 \leftrightarrow S_{Cu} = 1/2$ and $S^*_{Mn} = 3/2 \leftrightarrow S_{Cu} = 1/2$ interactions are antiferromagnetic.

Let us also mention that by irradiating a Mn(II)Cu(II) species with the wavelength corresponding to this $^6A_{1g} \rightarrow {}^4A_{1g} + {}^4E_g(G)$ transition, we can populate the $S^*_{Mn} = 3/2$ local excited state, and modify accordingly the magnetic properties of the material.

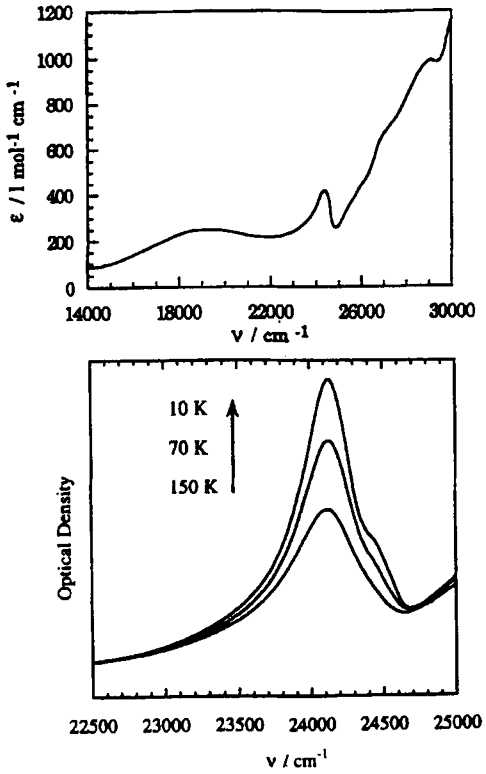


FIGURE 8 Top : Solution spectrum of $\{Mn[Cu(oxpn)]_3\}(ClO_4)_2 \cdot 2H_2O$. Bottom : Spectra in cellulose acetate pellets at various temperatures around 24,100 cm^{-1}.

SYNERGY BETWEEN MAGNETIC AND PHOTOPHYSICAL PROPERTIES; LUMINESCENT MAGNETS

The two-dimensional materials with the anionic layers $\{Mn_2[Cu(opba)]_3\}^{2-}$ shown in Figure 2 can be synthesized with almost any kind of cations inserted between the layers. It is in particular possible to use photophysically active cations such as $[Ru(bipy)_3]^{2+}$ with bipy = 2,2'-bipyridine, and to obtain a compound of formula $[Ru(bipy)_3]Mn_2[Cu(opba)]_3 \cdot S$ schematized in Figure 10.[13] Moreover, the Mn(II) ion within the layer can be replaced by the Co(II) ion, and the opba ligand can be replaced by pba = 1,3-propylenebis(oxamato) or pbaOH = 2-hydroxy-1,3-propylenebis(oxamato) ligands. Our main interest concerning these compounds is to see whether a synergy between magnetic and photophysical properties can be observed.

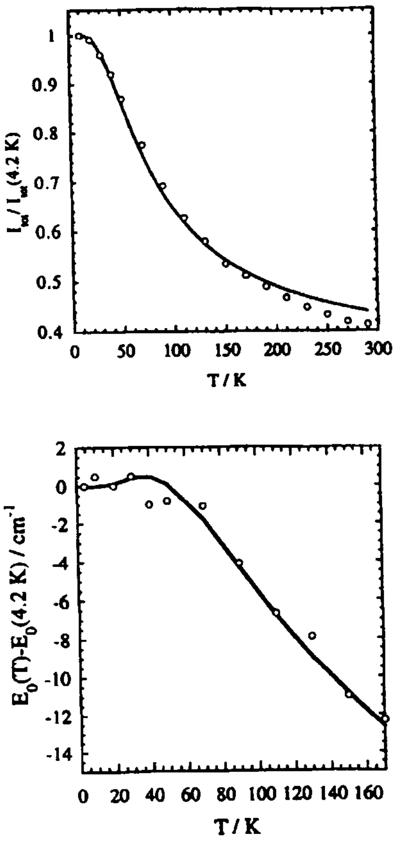


FIGURE 9 Temperature (top) and energy (bottom) dependences of the $^6A_{1g} \rightarrow {}^4A_{1g} + {}^4E_g(G)$ transition for $\{Mn[Cu(oxpn)]_3\}(ClO_4)_2 \cdot 2H_2O$. The points represent the experimental data and the full lines the theoretical curves.

Let us consider a compound of that kind, of formula $[Ru(bipy)_3]Co_2[Cu(pbaOH)]_3 \cdot 10H_2O$. The $\chi_M T$ versus T plot for this compound is shown in Figure 11. A minimum of $\chi_M T$ at 65 K characterizes a ferrimagnetic behavior, and the very rapid increase of $\chi_M T$ at low temperature reveals a long-range magnetic ordering. The critical temperature is found as T_c = 19 K from the temperature dependence of the in-phase, χ', and out-of-phase, χ'', ac magnetic susceptibilities also shown in Figure 11.

At room temperature the luminescence of the $[Ru(bipy)_3]^{2+}$ chromophore is largely quenched by the two-dimensional bimetallic skeleton. The intensity of the luminescence

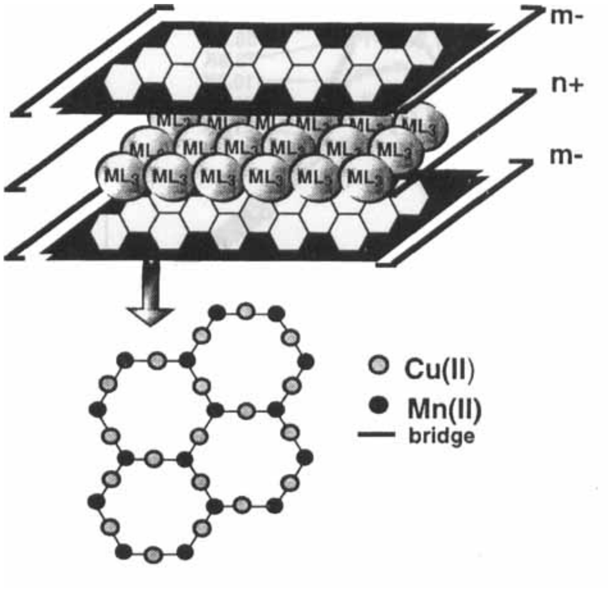


FIGURE 10 Schematic representation of a two-dimensional magnet incorporating a luminescent chromophore.

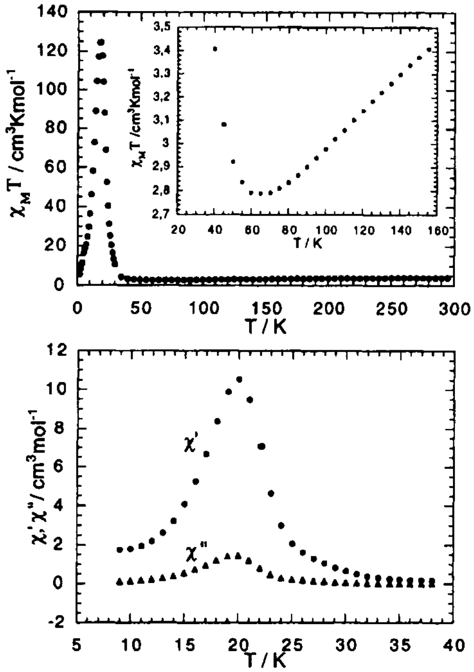


FIGURE 11 $\chi_M T$ (top) and χ' and χ'' (bottom) versus T plots for $[Ru(bipy)_3]Co_2[Cu(pbaOH)]_3 \cdot 10H_2O$

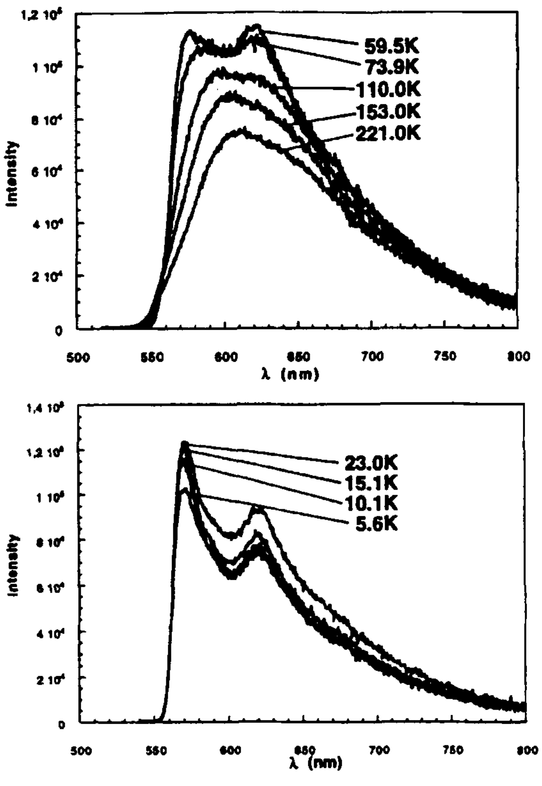


FIGURE 12 Temperature dependence of the intensity of the luminescent spectra for $[Ru(bipy)_3]Co_2[Cu(pbaOH)]_3 \cdot 10H_2O$.

spectra, however, increases as the temperature is lowered, as shown in Figure 12. The most striking feature is that this intensity reaches a maximum around T_c, and decreases as T is lowered further. Similarly, the intensity of the excitation spectra presents a maximum around T_c, and vanishes as T is lowered further. One sees that there is clearly a synergy between magnetic and photophysical properties. In the magnetically ordered state, the luminescence diminishes. The reasons why such a synergy is observed are far from being clear yet for us. However, we can say that in the magnetically ordered phase, below T_c, a large internal field is created within the material. Its value was estimated as about 30 T from other experiments.[6] This internal field perturbes the luminescent states of $[Ru(bipy)_3]^{2+}$, and strongly influences the intensity of the luminescent spectrum.[14]

TWO NEW CHEMICAL OBJECTS

In this last section we would like to present briefly two new chain compounds exhibiting intrachain ferromagnetic interactions, one involving transition metal ions, the other one involving organic radicals.

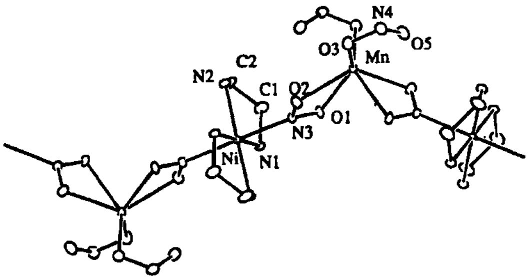


FIGURE 13 Structure of a bimetallic chain in $Mn(NO_2)_4Ni(en)_2$.

$Mn(NO_2)_4Ni(en)_2$

The reaction of the precursor $Ni(en)_2(NO_2)_2$ with en = ethylenediamine on a Mn(II) salt in the presence of an excess of NO_2^- affords the bimetallic compound $Mn(NO_2)_4Ni(en)_2$. The structure consists of alternating Mn(II)Ni(II) chains, as shown in Figure 13. The Ni(II) ion is surrounded by six nitrogen atoms, four arising from en ligands in *trans* positions and two from nitrito bridges. The Mn(II) ion is surrounded by six oxygen atoms arising from four nitrito groups, two of them being bridging, the other two being terminal. This Mn(II) ion has a *cis* environment.[15]

The $\chi_M T$ versus T plot shown in Figure 14 reveals intrachain Mn(II)-Ni(II) ferromagnetic interactions and antiferromagnetic coupling of the ferromagnetic chains within the lattice. Using a classical-quantum spin model,[1] the intrachain interaction parameter was found as $J = 1.33\ cm^{-1}$ (with $\mathbf{H} = -J\ \Sigma_i S_{Mn,i} \cdot S_{Ni,i}$). This compound may be considered as a metamagnet; the field dependence of the magnetization at 2 K also shown in Figure 14 indicates that the critical field necessary to overcome the antiferromagnetic interchain interaction and to lead to a ferromagnetic-like state is equal to 1,200 Oe.

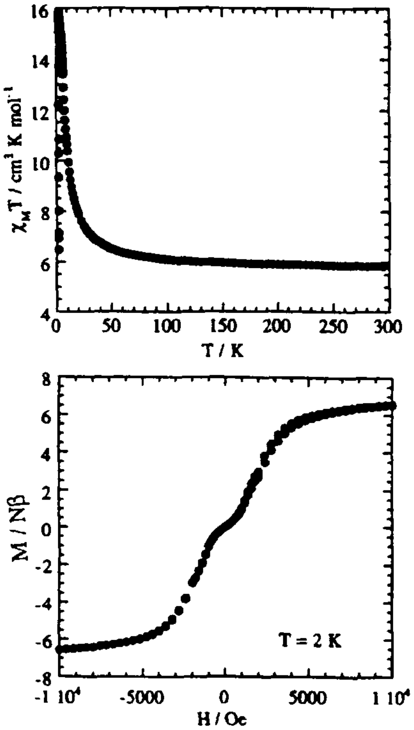


FIGURE 14 $\chi_M T$ versus T (top) and magnetization versus field (bottom) curves for $Mn(NO_2)_4Ni(en)_2$.

5-methyl-1,2,4-triazole nitronyl-nitroxide

The nitronyl-nitroxide radicals are extensively used as bricks to construct magnetic molecular assemblies. In other respects, the triazole derivatives for quite some time have been used as both terminal and bridging ligands in transition metal chemistry. They play an important role in the field of spin transition materials.[16] One of our projects of research is to combine nitronyl nitroxide and triazole functions.[17] We report here on a compound of that kind, namely 5-methyl-1,2,4-triazole nitronyl-nitroxide whose molecular structure is shown in Figure 15.[18] Within the crystal lattice the molecules form hydrogen-bonded chains. The $\chi_M T$ versus T curve shown in Figure 16 reveals an exceptionally strong intrachain (but intermolecular) ferromagnetic interaction, with an interaction parameter equal to 14.8 cm^{-1}. Most likely, the hydrogen bonds play an important role in this magnetic behavior. We are presently studying theoretically this problem. The $\chi_M T$ versus T curve presents a maximum at 4.5 K, due to weak antiferromagnetic interchain interactions. Again, this compound may be described as a metamagnet.

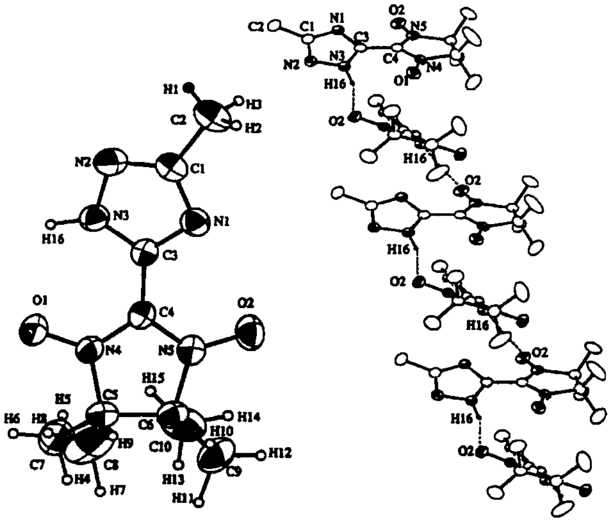


FIGURE 15 Structure of the molecule (left) and the hydrogen-bonded chain in 5-methyl-1,2,4-triazole nitronyl-nitr de.

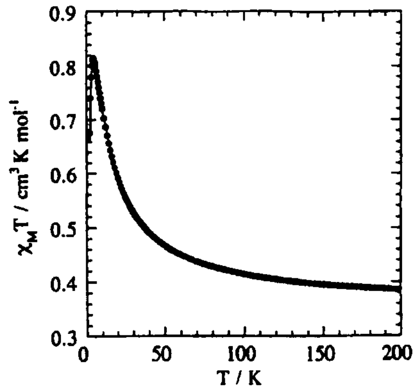


FIGURE 16 $\chi_M T$ versus T curve for 5-methyl-1,2,4-triazole nitronyl-nitroxide.

CONCLUSION

This paper represents only a small part of our activity in the field of molecular magnetism. Its goal was not to give an overview on this activity, but to emphasize its multidisciplinary character. This multidisciplinarity is for sure a wealth. It significantly contributes to the interest of the field. What is also fascinating is that molecular magnetism combines the beauty of the molecular design, the easthetic appeal of supramolecular chemistry, and the excitement of a novel physics.[19]

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