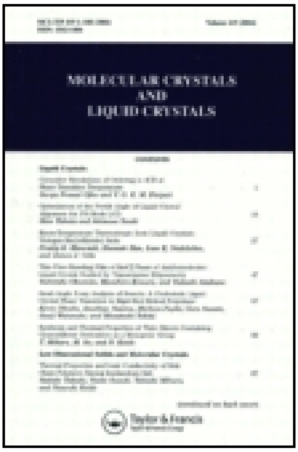

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Chemistry and Physics of Molecular Assemblies Involving Open-Shell Units: From Isolated Molecules to Three Dimensional Magnets

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CHEMISTRY AND PHYSICS OF MOLECULAR ASSEMBLIES INVOLVING OPEN-SHELL UNITS : FROM ISOLATED MOLECULES TO THREE DIMENSIONAL MAGNETS

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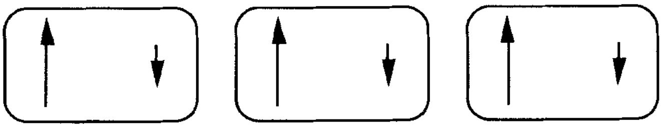
Abstract The goal of this paper is to review briefly our endeavors to increase the dimensionality of molecular-based bimetallic species. We will successively speak about antiferromagnetically coupled Mn(II)Cu(II) binuclear species, ferrimagnetic chain compounds exhibiting three-dimensional metamagnetic or ferromagnetic behavior, two-dimensional compounds, and finally a three-dimensional compound with a fully interlocked structure. We will also emphasize the importance of the local anisotropy of the spin carriers in the coercivity of the molecular-based magnets.

INTRODUCTION

For almost a decade our group has been exploring the various strategies for designing molecular-based compounds exhibiting a spontaneous magnetization below a critical temperature T_c.[1,2] One of these strategies consists first of synthesizing molecular units possessing a large positive spin density in a region and a small negative spin density in another region, then of assembling these molecular units in the crystal lattice in such a way that the large positive spin density of a unit preferably interacts with the small negative spin density of the nearest neighbor unit. The overall parallel alignment of the molecular spins may then be schematized as :



The presence of both positive and negative spin densities may arise from spin polarization effect in purely organic open-shell molecules.[3,4] It may also arise from the antiferromagnetic coupling between two different magnetic centers in a binuclear coordination compound. A compound of this kind, of formula $[Mn(Me_6\text{-}[14]ane\text{-}N_4)Cu(oxpn)]^{2+}$ with $Me_6[14]ane\text{-}N_4$ = (±)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane and oxpn = N,N'-bis(3-aminopropyl)oxamide is shown in Figure 1.[5]

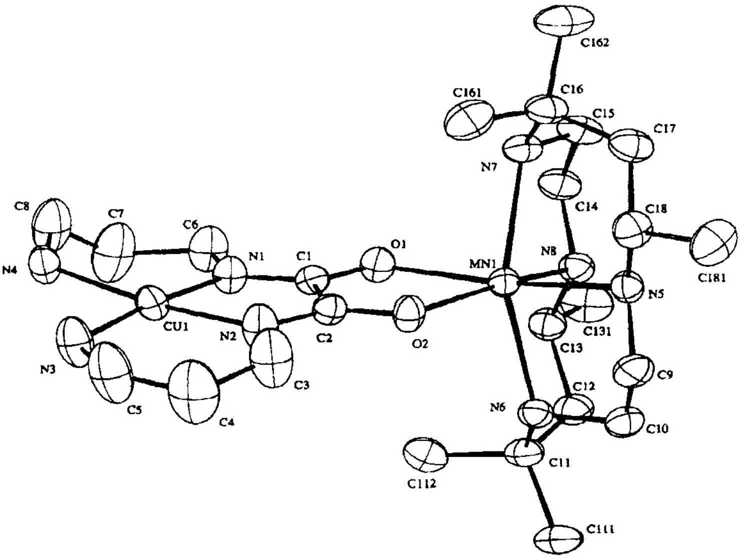


FIGURE 1 Structure of $[Mn(Me_6\text{-}[14]ane\text{-}N_4)Cu(oxpn)]^{2+}$.

For a long time, the conjugated bisbidentate ligands like oxamido have been known to be very efficient antiferromagnetic couplers.[6] The interaction between the $S_{Mn} = 5/2$ and $S_{Cu} = 1/2$ local spins gives rise to a ground $S = 2$ and an excited $S = 3$ pair states. The fitting of the magnetic susceptibility data leads to a quintet - septet energy gap of $3J = -93.9\ cm^{-1}$. This energy gap may be also deduced from the temperature dependence of the sharp and intense band corresponding to the $^6A_1 \rightarrow {}^4A_1 + {}^4E$ spin-forbidden transition for Mn(II) activated by an exchange mechanism, as shown in Figure 2. It is worthwhile to mention that the magnetic and optical methods lead to the same value for the energy gap between the two low-lying pair states. This giant enhancement of the formally spin-forbidden Mn(II) transitions is observed in all the Mn(II)Cu(II) compounds mentioned in this paper. The intensity of these transitions always increases as the temperature is lowered. In the compounds containing aromatic rings (from the opba ligand) the π → π* transitions of the rings partially hide the Mn(II) transitions.

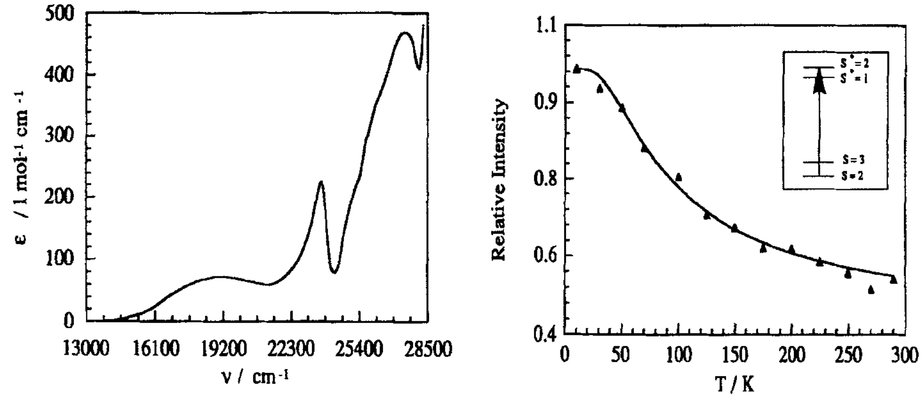
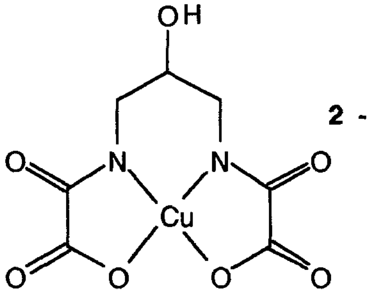


FIGURE 2 Absorption spectra in acetonitrile solution of $[Mn(Me_6\text{-}[14]ane\text{-}N_4)Cu(oxpn)](CF_3SO_3)$ and temperature dependence of the Mn(II) spin-forbidden transition at 23,697 cm-1.

Mn(II)Cu(II) LINEAR CHAINS

One of our first attempts to assemble such Mn(II)Cu(II) units was reported in 1986.[7,8] The reaction of the precursor $[Cu(pbaOH)]^{2-}$:



pbaOH being 2-hydroxy-1,3-propylenebis(oxamato), with Mn(II) ions affords the one-dimensional compound $MnCu(pbaOH)(H_2O)_3$ exhibiting a ferromagnetic alignment of *the ferrimagnetic* chains at T_c = 4.6 K. Recently, we discovered a new phase arising from the same reaction, of formula $MnCu(pbaOH)(H_2O)_3{\cdot}2H_2O$, exhibiting an antiferromagnetic ordering of the ferrimagnetic chains at 2.4 K. Actually, this compound may be described as a metamagnet.[9] A critical field of 900 Oe overcomes the weak interchain antiferromagnetic interactions. The difference of magnetic behavior between $MnCu(pbaOH)(H_2O)_3{\cdot}2H_2O$ and $MnCu(pbaOH)(H_2O)_3$, is assigned to the fact that along one of the directions perpendicular to the chain axis, the adjacent chains are in registry (with Mn - Mn and Cu - Cu shortest interchain separations in the former compound, and out of registry (with Mn - Cu shortest interchain separations) in the latter, as shown in Figure 3.

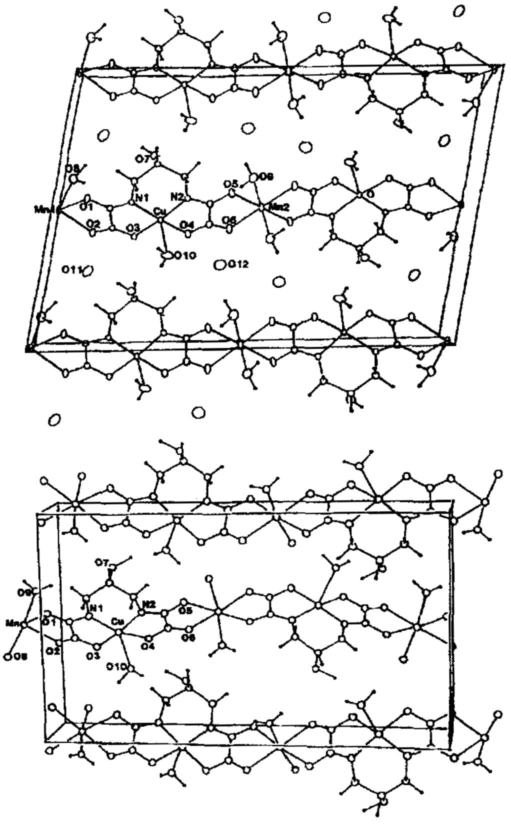
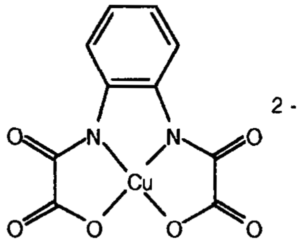


FIGURE 3 Perspective view of three neighboring chains in $MnCu(pbaOH)\ (H_2O)_3{\cdot}2H_2O$ (top) and $MnCu(pbaOH)(H_2O)_3$ (bottom).

Rather similar results concerning two phases of $Mn(C_5Me_5)(TCNQ)$ have been reported by Broderick during this Conference.[10]

For two or three years, we have explored the chemistry of another copper(II) precursor, namely $[Cu(opba)]^{2-}$, with opba = orthophenylenebis(oxamato) :



The reaction of $[Cu(opba)]^{2-}$ with Mn(II) in a DMSO/H_2O mixture affords the linear chain compound $MnCu(opba)(H_2O)_2$•DMSO shown in Figure 4.[11] Along one of the directions perpendicular to the chain axis, the chains are in registry, and along the other direction, they are efficiently isolated by noncoordinated DMSO molecules. This compound is also a metamagnet. In zero field, the ferrimagnetic chains order antiferromagnetically at T_c = 8 K. A critical field of 5 kOe overcomes the interchain interactions, as shown by the field and temperature dependences of the magnetization in Figure 5.

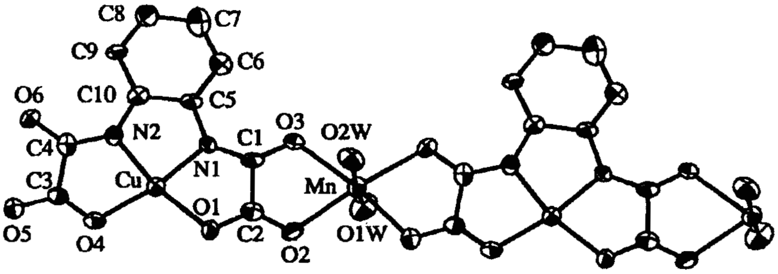


FIGURE 4 Structure of the linear chain compound $MnCu(opba)(H_2O)_2$•DMSO.

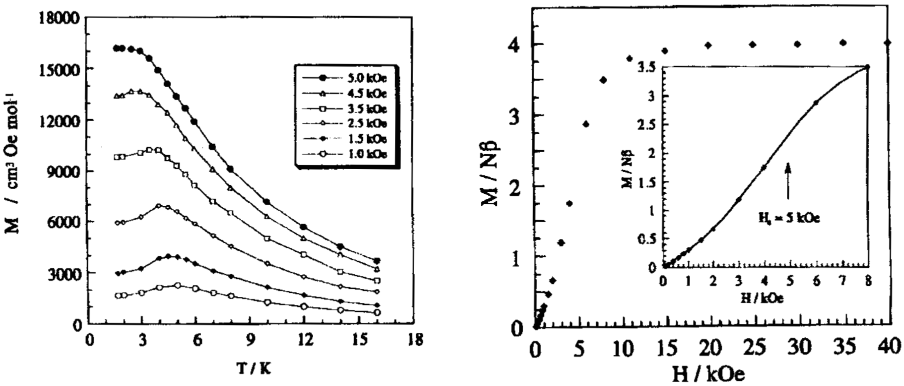


FIGURE 5 Temperature dependence at various fields (left) and field dependence (right) of the magnetization for $MnCu(opba)(H_2O)_2$•DMSO.

When the same reaction between $[Cu(opba)]^{2-}$ and Mn(II) is carried out in pure DMSO, another chain compound is obtained, whose formula is $MnCu(opba)(DMSO)_3$. The structure of this compound is shown in Figure 6. The main feature is that the chain is not linear anymore, but has a zig-zag shape. The two oxamato groups around a Mn(II) ion are in *cis* position while they are in *trans* position in the linear chains.[12]

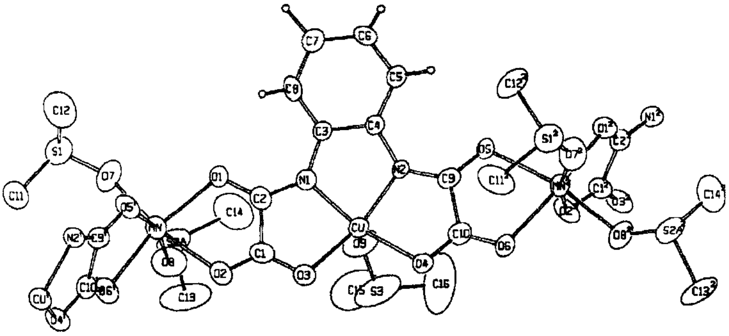


FIGURE 6 Structure of the zig-zag chain compound $MnCu(opba)(H_2O)_3$.

This structure is quite interesting; indeed, it suggests that adding another $[Cu(opba)]^{2-}$ unit may result in a cross-linking of the chains, and the formation of layers as schematized in Figure 7. As for the magnetic properties of $MnCu(opba)(DMSO)_3$, they very closely follow what is expected for a Mn(II)Cu(II) ferrimagnetic chain,[2] without any indication of three-dimensional magnetic ordering down to 1.7 K; $\chi_M T$ (χ_M being the molar magnetic susceptibility and T the temperature) shows a minimum at 115 K, characteristic of a ferrimagnetic behavior, and increases more and more rapidly as T is lowered below this temperature. The chains are very efficiently isolated in the crystal lattice owing to the presence of the bulky DMSO ligands.

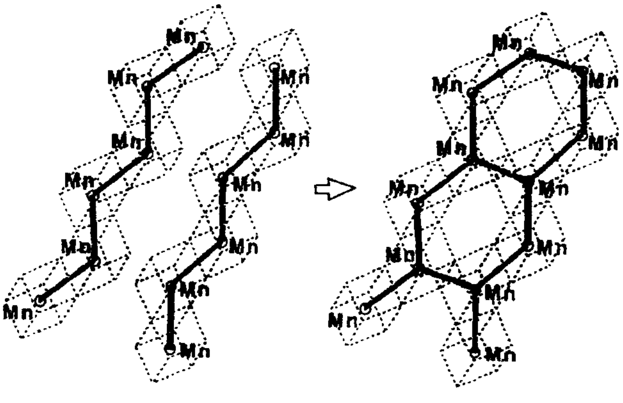


FIGURE 7 Formation of a honeycomb two-dimensional structure from zig-zag linear chains where ▬ symbolizes Cu(opba).

TWO-DIMENSIONAL COMPOUNDS

The reaction of the copper(II) precursor (cat)$_2$[Cu(opba)], cat$^+$ being a monovalent cation, with Mn(II) in the proportions 3Cu/2Mn, affords new phases of general formula (cat)$_2$Mn$_2$[Cu(opba)]$_3$•L where L stands for solvent molecules.[12] A series of compounds of that kind were obtained with cat = Na, NR$_4$ (R being Me, Et, or N-Bu), PPh$_4$ etc.... All those compounds exhibit a long range magnetic ordering with T_c ranging from 12 to 16 K. When some solvent molecules are removed through a mild thermal treatment, T_c may be shifted up to 22 K. The field dependence of the magnetization of one of the compounds, namely (NBu$_4$)$_2$Mn$_2$[Cu(opba)]$_3$ •6DMSO•H$_2$O, is represented in Figure 8. The saturation magnetization, 7.1 Nβ, agrees with what is expected for all the S_{Mn} = 5/2 local spins aligned along the field direction, and all the S_{Cu} = 1/2 local spins aligned along the opposite direction. By analogy with the structure of (rad)$_2$Mn$_2$[Cu(opba)]$_3$(DMSO)$_2$•2H$_2$O (vide infra), the structure of these (cat)$_2$Mn$_2$[Cu(opba)]$_3$•L phases may be described as two-dimensional with Mn$_6$Cu$_6$ edge-sharing hexagons. The two-dimensional skeleton is negatively charged, and the cat$^+$ cations are most likely located between the layers.

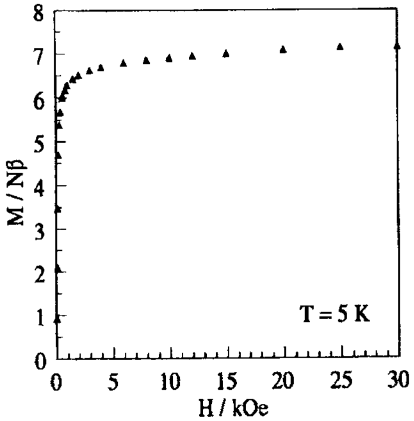


FIGURE 8 Field dependence of the magnetization for (NB$_4$)$_2$Mn$_2$[Cu(opba)]$_3$ •6DMSO•H$_2$O

What we are trying to do right now is to use cat$^+$ cations possessing some interesting properties instead of "innocent" cations like NBu$_4^+$. We expect to observe a synergy between the magnetism of the $\{$Mn$_2$[Cu(opba)]$_3\}^{2-}$ anionic skeleton and the properties of the cat$^+$ inserted species. Along this line, we have synthesized a new compound of formula [Ru(bipy)$_3$]Mn$_2$[Cu(opba)]$_3$•3H$_2$O, with bipy = 2,2'-bipyridine, in which the optically active $[Ru(bipy)_3]^{2+}$ species are inserted between the ferrimagnetic layers. The structure of this compound is not known yet. On the other hand, that of its precursor $[Ru(bipy)_3][Cu(opba)]\cdot 9H_2O$ has been solved. This structure is shown in Figure 9.

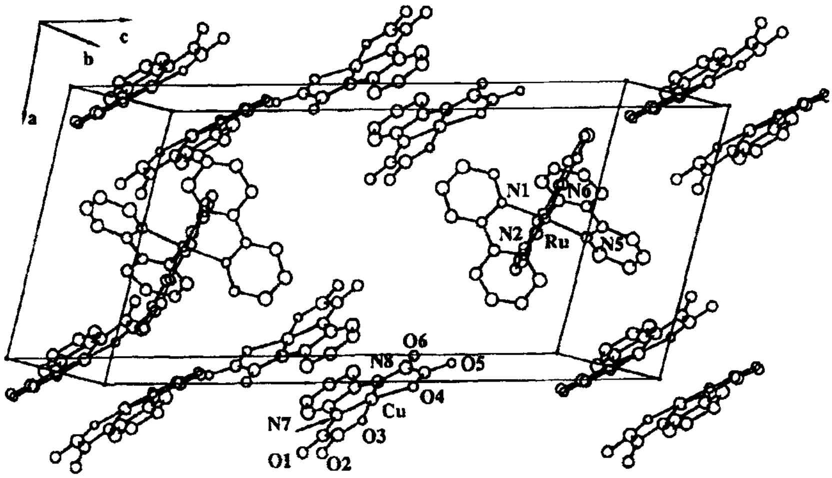
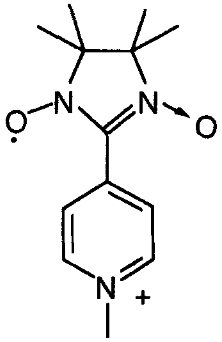


FIGURE 9 Structure of $[Ru(bipy)_3[Cu(opba)]\cdot 8H_2O$. For clarity the noncoordinated water molecules have been omitted.

A FULLY INTERLOCKED THREE-DIMENSIONAL STRUCTURE

Until now in this short review we have spoken about zero-, one-, and two-dimensional Mn(II)Cu(II) compounds. To further increase the dimensionality, it is necessary to link together metal centers belonging to different layers. To do so, we used the radical cation denoted rad^+ shown below :



This radical cation belongs to the family of the nitronyl nitroxides, whose ability to bridge metal centers is well documented. The reaction of $MnCl_2 \cdot 4H_2O$ with a large excess of $(rad)_2[Cu(opba)] \cdot H_2O$ in a $DMSO/H_2O$ mixture affords a compound of formula $(rad)_2Mn_2[Cu(opba)]_3(DMSO)_2 \cdot 2H_2O$ whose structure to the best of our knowledge is unprecendented.[13] The structure consists of two nearly perpendicular graphite-like networks with Mn_6Cu_6 edge-sharing hexagons. The corners of each hexagon are occupied by Mn(II) ions, and the middles of each edge by Cu(II) ions. The Mn(II) sites are chiral, and the structure presents a perfect alternation of Λ and Δ chiral sites, so that the structure as a whole is nonchiral. A $Mn_2[Cu(opba)]_3$ layer is shown in Figure 10.

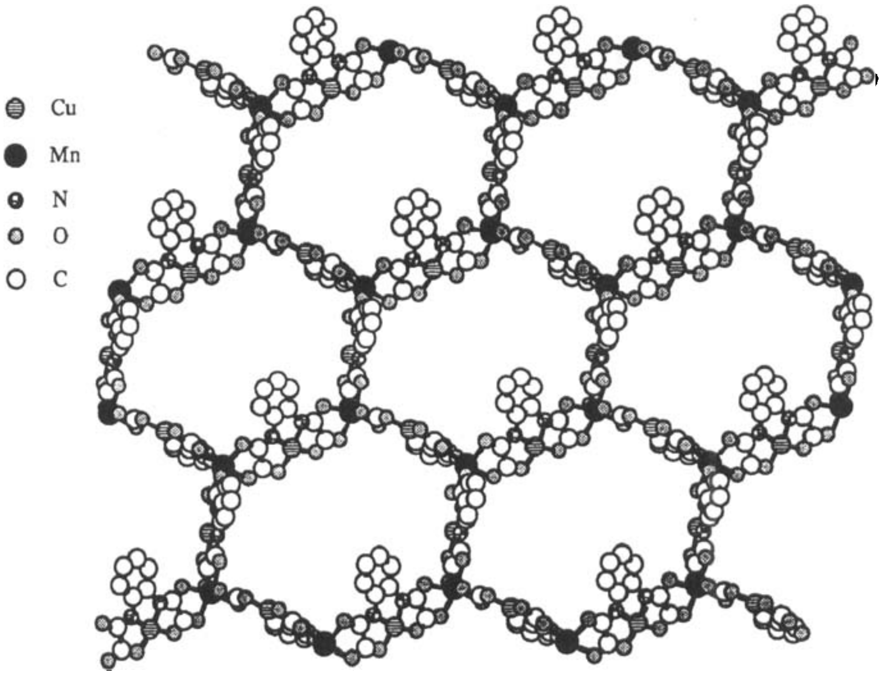


FIGURE 10 Structure of a layer in $(rad)_2Mn_2[Cu(opba)]_3(DMSO)_2 \cdot 2H_2O$.

The two networks are interlocked, the center of each hexagon being occupied by a Cu(II) ion belonging to a perpendicular hexagon as shown in Figure 11. The structure as a whole may be described as a three-dimensional chicken-wire. This compound contains three kinds of spin carriers : Mn(II) and Cu(II) ions antiferromagnetically coupled through oxamato bridges, and rad^+ radical cations, bridging the Cu(II) ions through the nitronyl nitroxide groups, and forming rad^+-Cu(II) chains.

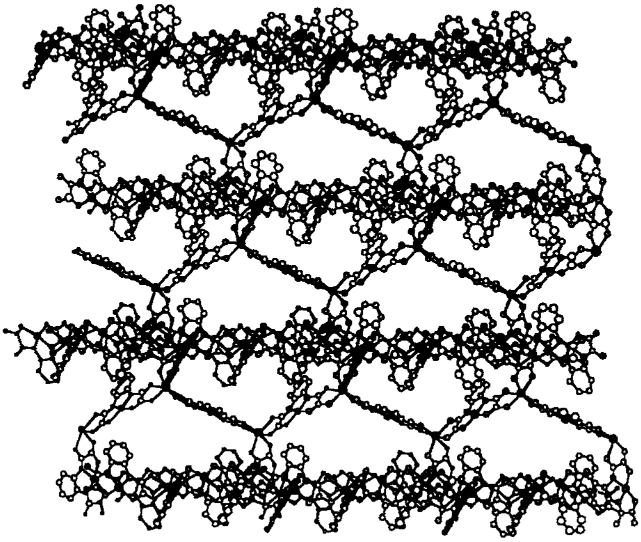


FIGURE 11 Interpenetration of the two networks in $(rad)_2Mn_2[Cu(opba)]_3(DMSO)_2{\bullet}2H_2O$.

The temperature dependences of the field-cooled, zero-field-cooled and remnant magnetizations shown in Figure 12 indicate that a long range magnetic ordering occurs at $T_c = 22.5$ K. The field dependence of the magnetization (Figure 12) shows a very high zero-field susceptibility, as expected for a magnet, and then a smooth increase of the magnetization as the field increases up to 200 kOe. This behaviour has been attributed to a progressive alignment of the rad^+ spins along the field direction. In zero field the radical cations are ferromagnetically coupled with the Cu(II) ions, i.e. antiferromagnetically coupled with the $Mn_2[Cu(opba)]$ metal core. Using a mean-field approach, the magnitude of the rad-Cu(II) ferromagnetic interaction parameter has been estimated as $J_{radCu} = 11.5\ cm^{-1}$ ($H = -JS_{rad}{\bullet}S_{Cu}$).[14]

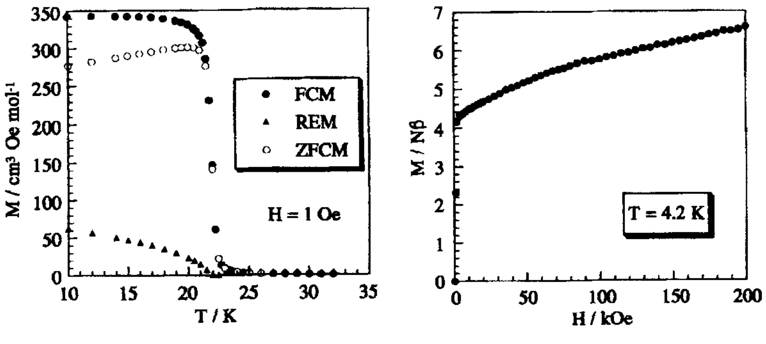


FIGURE 12 Temperature (left) and field (right) dependences of the magnetization for $(rad)_2Mn_2[Cu(opba)]_3(DMSO)_2{\bullet}2H_2O$.

LARGE COERCIVITY IN A Co(II)Cu(II) MOLECULAR-BASED MAGNET

All the Mn(II)Cu(II) compounds exhibiting a spontaneous magnetization we already mentioned in this paper may be considered as very soft magnets. The magnetization versus magnetic field hysteresis loops below T_c reveal coercive fields of a few tens of Oe at the best. Until a few month ago, we were wondering whether a molecular-based magnet could display a large cooercivity. The value of the coercive field at the given temperature for a polycrystalline magnet depends on both the chemical nature of the compound and some structural factors like the size and the shape of the grains within the sample. Concerning the chemical nature of the sample, the key role is played by the magnetic anisotropy of the spin carriers which prevents the domains from rotating freely when applying the magnetic field. Replacing Mn(II) with a $^6A_1$ orbital singlet ground state by Co(II) with a $^4T_1$ orbital triplet ground state should result in an increase of the coercive field. We synthesized the compound $(rad)_2Co_2[Cu(opba)]_3 \cdot 0.5DMSO \cdot 3H_2O$ where rad$^+$ is the radical cation shown above.[15] The temperature dependence of the magnetization shown in Figure 13 reveals a long range magnetic ordering below T_c = 34 K. It also reveals that the remnant (REM) magnetization is strictly equal to the field-cooled magnetization (FCM) below Tc, hence that all the information is retained. As for the zero-field-cooled magnetization (ZFCM), it is negligibly small down to ca. 15 K, then remains very weak in the 15-24 K temperature range. The field dependence of the magnetization at 1.7 K (see Figure 13) reveals a coercive field as large as 3.1 kOe.

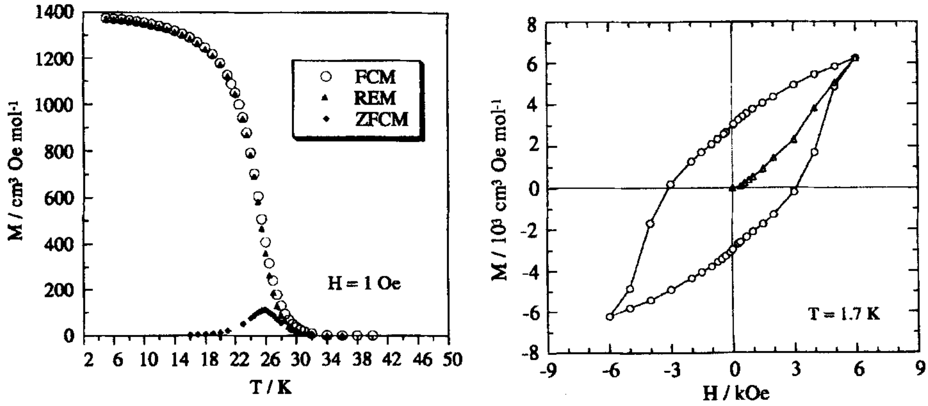


FIGURE 13 Temperatue (left) and field (right) dependences of the magnetization for $(rad)_2Co_2[Cu(opba)]_3 \cdot 0.5DMSO \cdot 3H_2O$.

CONCLUSION

Molecular magnetism has emerged as a new field of research over the past decade. This field concerns the synthesis and the study of the physical properties of molecular assemblies containing open-shell units. It is essentially interdisciplinary, involving organic, organometallic, and inorganic chemists, as well as theoreticians, physicists, and material scientists. Molecular magnetism also has strong links with field of molecular electronics.

Probably, the heart of molecular magnetism deals with the design and the synthesis of new molecular assemblies exhibiting bulk properties such as long-range magnetic ordering, as is the topic of this Conference, or bistability with hysteresis, which confers a memory effect on the system. This facet of molecular magnetism may be considered as one of the components of supramolecular chemistry, and we are deeply convinced that we are just at the very beginning of a long standing effort. Till now, supramolecular chemists have been rather reluctant to involve open-shell units in their chemistry, among other reasons because NMR then becomes more difficult to utilize. However, the presence of open-shell units in supramolecular assemblies may lead to quite exciting novel physical properties, which add to the beauty of the three-dimensional structures. What we have attempted to do in this short paper, it is to bring witness of this situation.

REFERENCES

1 O. Kahn, H. Stumpf, Y. Pei, J. Sletten, Mol. Cryst. Liq. Cryst., 233, 231 (1993)

2 O. Kahn, Molecular Magnetism, VCH, New York, 1993.

3 M. McConnell, J. Chem. Phys., 39, 1910 (1963).

4 C. Kollmar, O. Kahn, Acc. Chem. Res., 26, 259 (1993).

5 C. Mathonière, O. Kahn, Inorg. Chem., 32, 4057 (1993).

6 O. Kahn, Angew. Chem. Int. Ed. Engl., 24, 834 (1985).

7 Y. Pei, M. Verdaguer, O. Kahn, J. Sletten, J.P. Renard, J. Am. Chem. Soc., 108, 7428 (1986).

8 O. Kahn, Y. Pei, M. Verdaguer, J.P. Renard, J. Sletten, J. Am. Chem. Soc., 110, 780 (1988).

9 V. Baron, B. Gillon, J. Sletten, C. Mathonière, E. Codjovi, O. Kahn, Inorg. Chim. Acta, in press.

10 W.E. Broderick, B.M. Hoffman, Mol. Cryst. Liq. Cryst., in this issue.

11 H. Stumpf, Y. Pei, L. Ouahab, F. Le Berre, E. Codjovi, O. Kahn, Inorg. Chem., 32, 5687 (1993).

12 H. Stumpf, Y. Pei, O. Kahn, J. Sletten, J.P. Renard, J. Am. Chem. Soc., 115, 6738 (1993).

13 H.O. Stumpf, L. Ouahab, Y. Pei, D. Grandjean, O. Kahn, Science, 261, 447 (1993).

14 H.O. Stumpf, L. Ouahab, Y. Pei, P. Bergerat, O. Kahn, J. Am. Chem. Soc., 116, 3866 (1994).

15 H.O. Stumpf, Y. Pei, C. Michaut, O. Kahn, J.P. Renard, L. Ouahab, Chem. Mater., 6, 257 (1994).