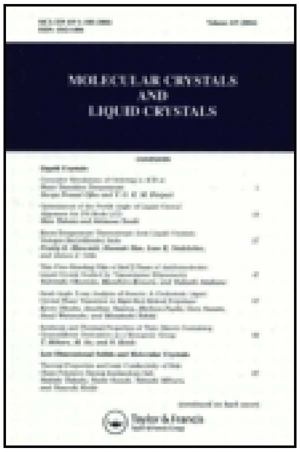

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New Oxamido Bridged Molecular Based Magnets and High-Spin Molecules

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NEW OXAMIDO BRIDGED MOLECULAR BASED MAGNETS AND HIGH-SPIN MOLECULES

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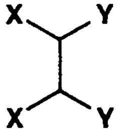
Abstract The reaction of copper(II) bis-oxamido monomers with a manganese(II) salt leads to compounds **1**, **2** and **3** of general formula $(PPh_4)_2Mn_2[CuL]_3.nH_2O$ where L= $(PhMe_2opbox)^{4-}$, $(PhPr_2opbox)^{4-}$, $(PhBu_2opbox)^{4-}$ for **1**, **2** and **3** respectively. Critical temperatures of 12.5, 11.5 and 13.5 K were measured for **1**, **2** and **3** respectively. This range of temperature likely indicates that this family of compounds assumes a 2D structure. Two tetrameric complexes **10** and **11** were prepared from the Cr(III) tamox precursor. Magnetic investigations of **10** in the 2-300 K temperature range reveal a ferromagnetic interaction between the Cr(III) and Ni(II) magnetic centers with a spin coupling constant J estimated to be +10.8 cm^{-1} which is twice the value observed for the oxalato bridge. On the other hand, an antiferromagnetic exchange is observed for the $CrMn_3$ complex **11**. The magnetic behavior can be reproduced using the interaction parameter J_{CrMn}= -3 cm-1, J_{MnMn}= -0.5 cm-1, g_{Cr}=1.98 and g_{Mn}= 2.07.

INTRODUCTION

The search for molecular-based magnets, *i.e.* compounds exhibiting a spontaneous magnetization below a critical temperature T_c, has been a field of increasing activity in the past few years.[1] Beyond the pioneering work carried out on one-dimensional compounds,[2-5] the actual interest has been focused on the obtention of two- or three-dimensional networks in order to shift T_c towards higher temperatures.[6-14] To synthesize these two or three-dimensional structure many groups are working with oxalato type bridging ligands.



X = O, S
Y = O, N

The oxalato and dithiooxalato series reported by Okawa[15] and the oxamato ones obtained by Kahn[10]. Surprisingly, the oxamido bridge which is known to mediate strong exchange interaction between two metal centers (oxalato < oxamato < dithioxalato ≈ oxamido)[16] has not been used till now to elaborate this fascinating class of molecular magnetic materials. We report here the results concerning our quest for three dimensional molecular-based magnets using the oxamido bridging ligands family.

STRATEGY

In the fifties, A. F. Wells[17] has shown that three connected nets could lead to either two or three dimensional lattices. It is well established that the oxalato type bridging ligands lead to three connected networks. Recent works from Okawa[16,18] and Descurtins[12-13] indicated that in the case of oxalato type bridging ligands the switching between 2D and 3D structures is governed by the chirality around the metal center. For instance, a 2D network is weaved for an ordered racemic mixture of Λ and Δ isomers. On the other hand, a 3D network is obtained for a pure enantiomeric form, as shown in Figure 1.

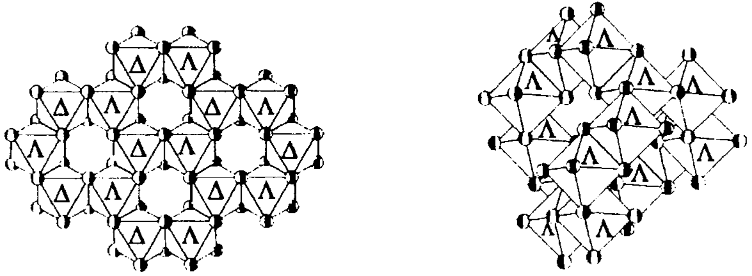
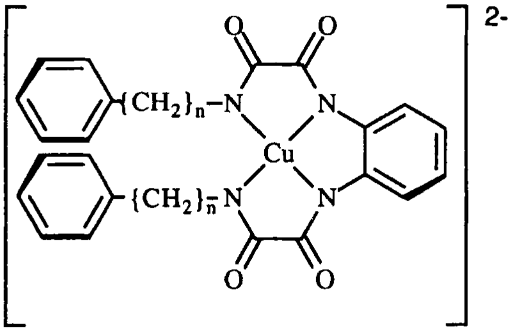


FIGURE 1 2D racemic and 3D chiral networks

Furthermore, these works have shown that experimentally the obtention of the 2D or 3D structures are intricately linked to the interaction between the negatively charged lattice and the nature of the counter cation. In the specific case of oxamato series described by Kahn et al the presence of a square planar copper(II) monomers linking two adjacent octahedral manganese(II) would lead to the formation of huge cavities with an approximate diameter of 30 Å for a 3D network. Thus it is obvious that in the latter, the interaction between the lattice and the counter cation would be extremely small which render unlikely the 3D structure. As a matter of fact, to enhance the coupling between the lattice and the cation we have developed new oxamido ligands bearing bulky substituents in the aim to fill the cavities and at the same time increase the exchange interaction between the metal centers.

TETRADENTATE LIGANDS

A series of tetradentate oxamido ligands and their corresponding copper(II) monomers were prepared (Figure 2).



n = 1; **Cu(PhMe$_2$opbox)$^{2-}$**

n = 3; **Cu(PhPr$_2$opbox)$^{2-}$**

n = 4;**Cu(PhBu$_2$opbox)$^{2-}$**

FIGURE 2 Copper(II) bis-oxamido complexes with bulky pendant groups

Reactions of these monomers with a manganese(II) salt lead to compounds **1**, **2** and **3** of general formula $(PPh_4)_2Mn_2[CuL]_3.nH_2O$ where CuL= Cu(PhMe$_2$opbox)$^{2-}$, Cu(PhPr$_2$opbox)$^{2-}$, Cu(PhBu$_2$opbox)$^{2-}$ for **1**, **2** and **3** respectively. EXAFS and XANES studies revealed that the manganese(II) ion is in an octahedral environment coordinated to six oxygen atoms and have three neighbouring copper(II) ions within a square planar surrounding. These data confirm the presence of a three connected network. Unfortunately, it is not possible to make a rational choice between one of these two basic structures (2D or 3D) for these compounds, since the EXAFS data do not provide any kind of information related to the spatial distribution of the $[Mn(CuL)_{3/2}]$ units in the crystal lattice. Only the subsequent study of the magnetic behavior of this family of compounds is able to bring interesting insights on this problem, as discussed below.

Magnetic properties

The temperature of ferrimagnetic phase transition for these compounds were determined by the measurement of the thermal dependence of both the in-phase, χ', and out-of-phase, χ'', components of the AC magnetic susceptibility, as illustrated in Figure 3. The χ' curves show an abrupt break as the temperature is lowered for each compound, *e.g.* around 12.5 K for **1**, 11.5 K for **2**, and 13.5 K for **3**, which agrees with the appearance of an out-of-phase signal in the χ'' curves (inset of Figure 3) characteristic of a magnetic ordered state existing below these temperatures. T_C is then equal to 12.5 (**1**), 11.5 (**2**) and 13.5 K (**3**).

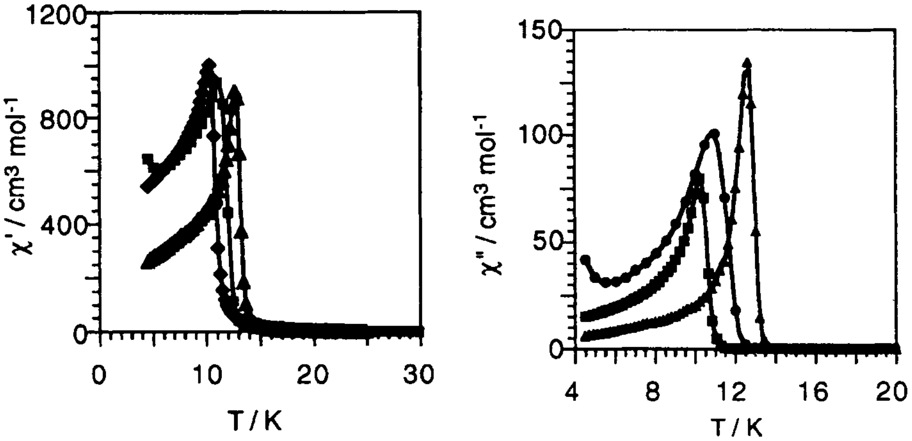
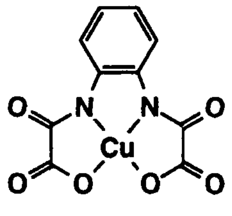


FIGURE 3 Temperature dependence of both the in-phase, χ', and out-of-phase, χ'', components of the AC molar magnetic susceptibility for **1** (circles), **2** (squares), and **3** (triangles)

Unfortunately, the observed critical temperatures in this series are in the order of ten Kelvin. This range of temperature likely indicates that this family of formula $(PPh_4)_2Mn_2[CuL]_3.nH_2O$ assumes a two dimensional structure instead of a three dimensional one where a Tc of about 50K would be expected (mean field approximation). Furthermore, the observed range of critical temperature for these oxamido bridged series is roughly equal to those measured for oxamato family. Obviously, this result does not respect the expected trend (J oxalato < J oxamato < J dithioxalato ≈ J oxamido).

In order to elucidate these disappointing results a novel series of ligands was synthesized that would allow us to compare the difference in magnitude of the magnetic exchange between oxamato and oxamido bridges.



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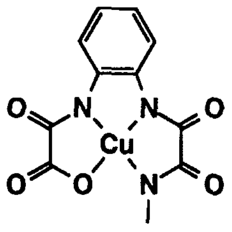

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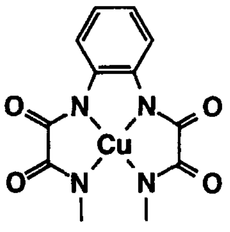


6

Compounds **7**, **8** and **9** of general formula $(PPh_4)_2Mn_2[Cu(L)]_3.nH_2O$ were obtained from reaction of the copper(II) monomers **4**, **5** and **6** respectively with manganese(II) ions. In Figure 4 are gathered the temperature dependence of both the in phase χ', and out of phase components of the AC molar magnetic susceptibility for **7**, **8** and **9**.

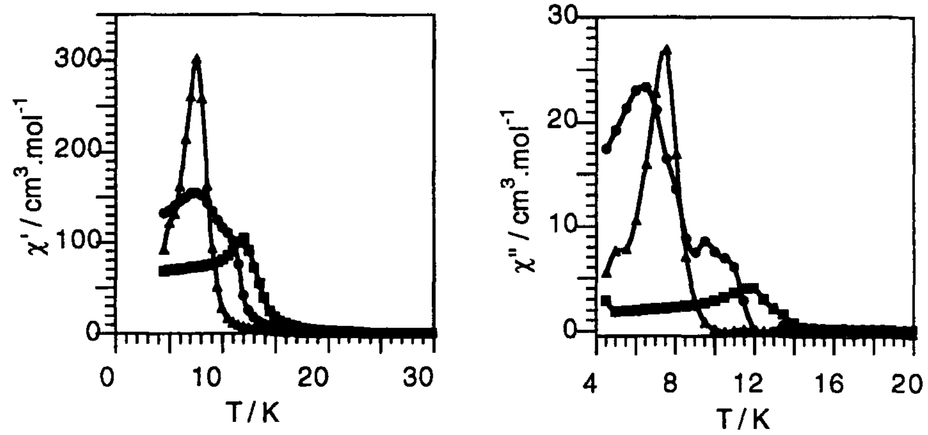


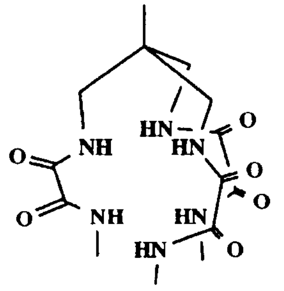
FIGURE 4 Temperature dependence of both the in-phase, χ', and out-of-phase, χ'', components of the AC molar magnetic susceptibility for **7** (circles), **8** (squares), and **9**(triangles)

Here again the critical temperatures obtained for **7**, **8** and **9** (12, 14 and 10 K respectively) suggested strongly for a two dimensional phase. To our great surprise, the mono oxamido compound was characterized with a higher Tc than the bis oxamido precursor. This spectacular fall in the coupling exchange for the bis oxamido ligand can actually be explained in terms of the steric congestion of the two methyl groups. Molecular modelization and cristallographic data show unambiguously that the steric

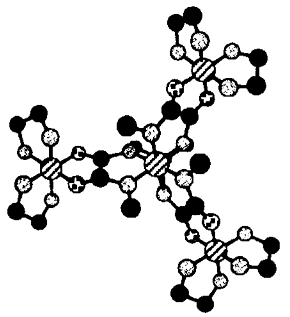
From these results it seems unlikely to increase the magnetic exchange between the metal centers by using tetradentate oxamido ligands owing to the ruffling of the copper(II) coordination environment.

HEXADENTATE LIGANDS

Following the results obtained in the tetradentate ligands, one elegant strategy to reach oxamido ligands that would not suffer from steric hindrance is to use tripodal structured ligands. Molecular modelization has shown that for a mononuclear complex with this tripodal chelate, there exists hardly any interaction between the three pendant methyl groups. Furthermore, from a topological point of view, we should be able to increase the connectivity between the two paramagnetic centres and thereby leading to higher Tc material. Within the plethora of organic molecules, only the tris-ammino derivatives were of particular interest for the preparation of our target molecules. Thus, a series of tris oxamido ligands have been prepared from Tren (tris(2-aminoethyl)-amine), Tame (tris(aminomethyl)-ethane) and the Tach (cis, cis, cis 1.3.5-tris-amino-cyclohexane). Unfortunately, the synthesis of monomeric complexes using the Tren based ligand turned out to be ineffective. Most probably due to the presence of the tertiary amine. In this report we are going to focus only on the chemistry of the complexes within the Tamox series.



Tamox ligand



$\{Cr(tamox)\}[M(L)_x]_3^{3+}$

Tetranuclear complexes

To complete our study concerning the magnetic exchange through the oxamido bridge, we have in the first place prepared two tetranuclear complexes using the Chromium(III) Tamox monomer. According to the symmetry of the magnetic orbitals we should observe a ferromagnetic coupling in the case of the CrNi3 complex and an antiferromagnetic interaction for the CrMn3 compound.

Tamox monomer. According to the symmetry of the magnetic orbitals we should observe a ferromagnetic coupling in the case of the CrNi3 complex and an antiferromagnetic interaction for the CrMn3 compound.

Magnetic properties of CrNi3 complex

The reaction of the Cr(III) monomer with a Ni(II)cyclam leads to the tetranuclear compound of formula $\{Cr(tamox)\}[Ni(cyclam)]_3 (ClO_4)_3.n H_2O$ (**10**). The temperature dependence of the magnetic susceptibility for **10** is depicted in Figure 5 in the form of the $\chi_M T$ versus T plot, χ_M being the molar magnetic susceptibility.

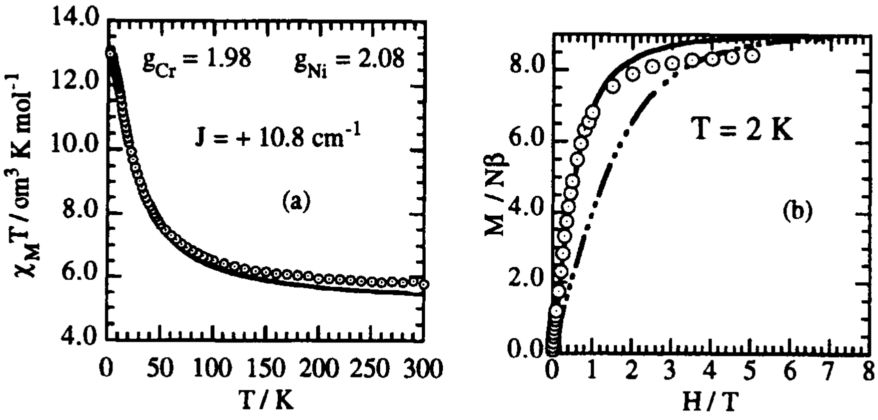


FIGURE 5 Magnetic properties of **10**. (a) circles experimental data and solid line theoritical curve; (b) circles experimental data, solid line Brillouin function for S=9/2 and broken line Brillouin function for uncoupled system

At room temperature $\chi_M T$ is equal to 5.8 $cm^3 mol^{-1} K$ which is a sligthly higher value than the expected one for magnetically isolated three Ni(II) and one Cr(III) ions. $\chi_M T$ increases when the temperature is lowered and reaches a plateau at 4 K with $\chi_M T$ = 12.9 $cm^3 mol^{-1} K$ which is the expected value for a S=9/2 state. The $\chi_M T$ plot clearly shows that the Cr(III)Ni(II) interaction is ferromagnetic. The magnetic behavior can be reproduced using the interaction parameter J= 10.8 cm^{-1} ($H=-J\Sigma(S_{Cr}.S_{Ni(j)})$), $g_{Cr} = 1.98$ and $g_{Ni} = 2.07$. In order to confirm that **10** has a S=9/2 ground state, we measured the field dependence of magnetization for **10** at 2 K. Up to 1 Tesla, the experimental points perfectly follow the Brillouin function for S = 9/2, the observed deviation at higher field is likely related to the presence of anisotropy in the S = 9/2 ground state.

The ferromagnetic interaction in this complex is easily understood in term of strict orthogonality of the magnetic orbitals of the metal ions (t_{2g} for Cr(III) and e_g for Ni(II)). Two other $CrNi_3$ complexes of the same toplogy are known in the litterature[21-22], one with oxalato bridges and the other with dithiooxalto bridges. The J value for **10** is twice the value measured for the oxalato-bridged complex (J = 5.3 cm^{-1}) and as expected close to the observed one for the dithiooxalato-bridged $CrNi_3$ analogue (J = 11.8 cm^{-1}).

Magnetic properties of CrMn3 complex

In the paper by Pei et al.[21], the authors end by saying "we have not succeeded in synthesizing the $CrMn_3$ tetranuclear complex". Herein we discussed the magnetic properties of such a complex obtained by the reaction of the Cr(III) monomer with Mn(II) ions and bipy which leads to the tetranuclear compound of formula $\{Cr(tamox)\}[Mn(bipy)_2]_3\ (ClO_4)_3.n\ H_2O$ (**11**). The magnetic behavior of **11** in the form $\chi_M T$ versus temperature is shown in Figure 6.

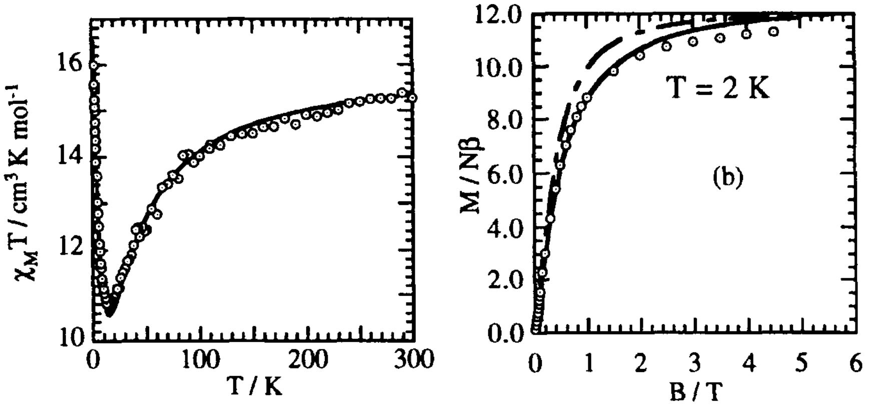


FIGURE 6 Magnetic properties of **11**. (a) circles experimental data and solid line theoritical curve; (b) circles experimental data, solid line calculated magnetization for J_{CrMn}=-3 cm^{-1}, J_{MnMn}= -0.5, g_{Cr}=1.98 and g_{Mn}= 2.07 and broken line Brillouin function for S=6 .

$\chi_M T$ is equal to 15.4 $cm^3\ mol^{-1}$ K at room temperature which corresponds to the expected value for three magnetically isolated Mn(II) and one Cr(III) ions. The $\chi_M T$ value decreases as the temperature is lowered and reaches a minimum of 10.8 cm^3 K mol^{-1} at 15 K and increases up to 16 $cm^3\ mol^{-1}$ K at 2K. This latter value does not correspond to S=6 which is the expected spin value for the ground state of **11** in the case clearly shows that the Cr(III)Mn(II) interaction is antiferromagnetic. The magnetic behavior can be reproduced using the interaction parameter J_{CrMn}= -3 cm^{-1}, J_{MnMn} = -0.5 cm^{-1} ($H=-J_{CrMn}\Sigma(S_{Cr}\cdot S_{Mn(j)})-J_{MnMn}\Sigma(S_{Mn(i)}\cdot S_{Mn(j)})$, g_{Cr} = 1.98 and g_{Mn} = 2.07. These parameters allow to nicely fit low field magnetization versus field curve as shown in Figure 6 (b). The observed deviation between the solid line and the experimental points at high field are likely due to anisotropy which has not been taken into account. An alternative good fit of the $\chi_M T$ plot is obtained when we considered only J_{CrMn} and an intermolecular interaction (J_{CrMn}=-3.1 cm^{-1}, $\theta = -3$ K,g_{Cr} = 1.98 and g_{Mn} = 2.07). To the best of our knowledge, it is the first time that such an antiferromagnetic interaction between Cr(III) and Mn(II) ions is observed with oxalato type bridging ligand. Up to now, such compounds known in the litterature[19] present a ferromagnetic coupling. This antiferromagnetic interaction most probably stems from a distortion of octahedral coordination sphere around the Cr(III) ion due to the rigidity of the tamox ligand.

CONCLUSION

To conclude, we recall that one of our target is to reach high Tc molecular based magnets. The strategy which consists in using tetradentate oxamido ligands has revealed to be of little success. Most probably, as discussed above, due to the steric hindrance of alkyl groups on the oxamido bridges. However, the results obtained with the tripodal type ligand are very encouraging. Two high spin molecules ($CrNi_3$ and the $CrMn_3$) have been synthesized and as expected we have shown that the magnetic exchange is enhanced through oxamido bridging ligands. Work is in progress towards the elaboration of extended network based on tris-oxamido tripodal ligands.

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