

# Synthesis and Magnetic Studies of Copper(II)-Manganese(II) Heterobinuclear Complexes with an Oxamido Bridge

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Four new copper(II)-manganese(II) heterobinuclear complexes bridged by *N,N'*-bis[2-(dimethylamino)ethyl]oxamido dianion (dmoxae) and end-capped with 1,10-phenanthroline (phen), 5-methyl-1,10-phenanthroline (Mephen), diaminoethane (en) or 1,3-di-aminopropane (pn), respectively, namely, [Cu(dmoxae)MnL<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (L = phen, Mephen, en, pn), have been synthesized and characterized by elemental analyses, IR, electronic spectral studies, and molar conductivity measurements. The electronic reflectance spectrum indicates the presence of spin exchange-coupling interaction between bridged copper(II) and manganese(II) ions. The cryomagnetic measurements (4.2–300 K) of [Cu(dmoxae)Mn(phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (1) and [Cu(dmoxae)Mn(Mephen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (2) complexes demonstrated an antiferromagnetic interaction between the adjacent manganese(II) and copper(II) ions through the oxamido-bridge within each molecule. On the basis of spin Hamiltonian,  $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ , the magnetic analysis was carried out for the two complexes and the spin-coupling constant (*J*) was evaluated as  $-35.9 \text{ cm}^{-1}$  for 1 and  $-32.6 \text{ cm}^{-1}$  for 2. The influence of methyl substitutions in the amine groups of the bridging ligand on magnetic interactions between the metal ions of this kind of complexes is also discussed.

**Keywords** Oxamido-bridge, Cu(II)-Mn(II), heterobinuclear complexes, magnetic properties, synthesis

## Introduction

Synthesis and magnetic investigations of heterobinu-

clear transition-metal complexes containing two different paramagnetic centers are of current interest, due to the hope of mimicking the active sites of some metalloenzymes containing dissimilar metal ions and thus correlating structure with biological function, and the mechanism of spin coupling between paramagnetic metal ions in view of the electronic structures of the interacting metal ions and to find appropriate systems applicable as building units for the design of molecular-based ferromagnet.<sup>1-4</sup> So far, much effort has been devoted to the development of multiatom bridging ligands that can afford magnetic interactions. Amongst other more elaborate ligands employed in the study of magnetic interactions, *N,N'*-bis(substituent) oxamides could be good candidates in supporting magnetic exchange interactions because their coordination ability toward transition-metal ions can be modified and tuned by playing on the nature of the amide substitutions,<sup>5</sup> and the remarkable efficiency of the oxamido bridge to transmit electronic effects between the metal ions. Hence, this family of ligands has played an important role in molecular magnetism.<sup>6-10</sup> Many polynuclear complexes containing oxamido bridges have been synthesized and their magnetic properties have been studied.<sup>3-6,11-13</sup> It has been revealed by X-ray diffraction analyses and variable-temperature magnetic susceptibility investigations that magnetic coupling can occur between paramagnetic centers bridged by this type of ligand.

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However, to our knowledge, there is no study on the influence of substitutions in their amine groups of the bridging ligand on magnetic interactions between the metal ions of this kind of complexes. Taking into account the above facts, it is of considerable interest to synthesize and study polynuclear complexes with bridging oxamide. In this paper, four new heterometal binuclear complexes,  $[\text{Cu}(\text{dmoxae})\text{MnL}_2](\text{ClO}_4)_2$  ( $L = \text{phen}$ , Mephen, en, pn) have been synthesized and characterized and the cryomagnetic properties of the  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{phen})_2](\text{ClO}_4)_2$  (**1**) and  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{Mephen})_2](\text{ClO}_4)_2$  (**2**) complexes have been measured in the temperature range 4.2–300 K to examine the effect of the substitutions in oxamido bridge upon the magnetic interaction between copper(II) and manganese(II) ions.

## Experimental

### Materials

All of the reagents used in the synthesis were of analytical grade. The hydrated metal ion perchlorate salts and *N, N'*-bis[2-(dimethylamino)ethyl]oxamido ( $\text{H}_2\text{dmoxae}$ ) were prepared by the literature methods.<sup>14,15</sup> *N, N'*-dimethylethylenediamine, diethyl oxalate and the terminal ligands 1, 10-phenanthroline (phen); 5-methyl-1, 10-phenanthroline (Mephen); di-amino-ethane (en) or 1, 3-diamino-propane (pn) were used as commercially.

### Synthesis of $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{phen})_2](\text{ClO}_4)_2$ (**1**)

To a solution of  $\text{H}_2\text{dmoxae}$  (0.230 g, 1 mmol) stirred in methanol (10 mL) was added successively a solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.352 g, 0.95 mmol) in methanol (10 mL) and a solution of triethylamine (2 mL). The stirring was continued at room temperature (about 30 min) until the mixture became limp. Then this solution was filtered. To the filtrate was added a methanol solution (20 mL) of  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.362 g, 1 mmol) and a solution of phen (0.360 g, 2 mmol) in the same solvent (10 mL) under  $\text{N}_2$ . The color of the solution turned from light-blue to purple immediately and a small amount of precipitate formed. After stirring for 2 h, the purple microcrystals thus formed were filtered off, washed several times with methanol, water and diethyl

ether and dried over  $\text{P}_2\text{O}_5$  under reduced pressure. Recrystallization was carried out from a DMF/ethanol (1:3) mixture. Yield 0.772 g (85%), m. p. 206.6–207.1 °C; Anal. calcd for  $\text{MnCuC}_{34}\text{H}_{36}\text{N}_8\text{O}_{10}\text{Cl}_2$  (M. W. 906.10): C 45.07, H 4.00, N 12.37, Cu 7.01, Mn 6.06; found C 45.15, H 4.12, N 12.58, Cu 7.25, Mn 6.22.

### Synthesis of $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{Mephen})_2](\text{ClO}_4)_2$ (**2**)

This complex was obtained as pale-violet microcrystals by the same procedure and the same amount of reagents as above but by using Mephen instead of phen. Yield 0.822 g (88%), m. p. 213.3–213.7 °C. Anal. calcd for  $\text{MnCuC}_{36}\text{H}_{40}\text{N}_8\text{O}_{10}\text{Cl}_2$  (M. W. 934.15): C 46.29, H 4.32, N 12.00, Cu 6.80, Mn 5.88; found C 46.15, H 4.21, N 12.23, Cu 6.65, Mn 6.02.

### Synthesis of $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{en})_2](\text{ClO}_4)_2$ (**3**)

This complex was obtained as a brown powder by the same procedure and the same amounts of reagents as above but by using en instead of phen. Yield 0.373 g (56%), m. p. 235.8–236.2 °C; Anal. calcd for  $\text{MnCuC}_{14}\text{H}_{36}\text{N}_8\text{O}_{10}\text{Cl}_2$  (M. W. 665.88): C 25.25, H 5.45, N 16.83, Cu 9.54, Mn 8.25; found C 25.13, H 5.29, N 16.62, Cu 9.32, Mn 8.02.

### Synthesis of $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{pn})_2](\text{ClO}_4)_2$ (**4**)

This pale-red compound was prepared as described for complex **1**, except that pn was used instead of phen. Yield 0.444 g (64%), m. p. 218.6–218.9 °C; Anal. calcd for  $\text{MnCuC}_{16}\text{H}_{40}\text{N}_8\text{O}_{10}\text{Cl}_2$  (M. W. 693.93): C 27.69, H 5.81, N 16.15, Cu 9.16, Mn 7.92. found C 27.52, H 5.66, N 16.01, Cu 8.99, Mn 7.76.

### Physical measurements

Carbon, hydrogen and nitrogen elemental analyses were performed with a Perkin-Elmer elemental analyzer Model 240. The metal contents were determined on an ICP-9000 isoionic emission spectrophotometer. IR spectra were recorded with a Nicolet FT-IR 5DX spectrometer using KBr pellets. The electronic spectra were measured on a Perkin-Elmer Hitachi-240 spectrophotometer. Molar

conductances were measured with a Shanghai DDS-11A conductometer. Variable temperature magnetic susceptibilities (4.2—300 K) were measured with a Model CF-1 (sensitivity  $m = 10^{-4}$  emu.) vibrating sample magnetometer made by Neel Laboratory de CNRS, France. Diamagnetic corrections were made with Pascal's constants<sup>16</sup> for all the constituent atoms and effective magnetic moments were calculated by the equation  $\mu_{\text{eff}} = 2.828(\chi_{\text{M}} T)^{1/2}$ , where  $\chi_{\text{M}}$  is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms.

## Results and discussion

### Synthesis and coordination environment of the binuclear complexes

A promising method to design and synthesize heterobinuclear complexes is to use hetero-binucleating ligand, which offers either the coordination geometry or the ligand field strength suitable for dissimilar metal ions.<sup>17</sup> In this study, we have adopted this strategy to synthesize Cu(II)—Mn(II) heterobinuclear complexes. For this purpose, heterobinucleating ligand *N,N'*-bis[2-(dimethylamino)ethyl]oxamido ( $\text{H}_2\text{dmoxae}$ ) was chosen as a bridging ligand. Simultaneously, 1,10-phenanthroline (phen); 5-methyl-1,10-phenanthroline (Mephen); diaminoethane (en) or 1,3-diaminopropane (pn), was used as terminal ligand, respectively. In the course of preparation of these binuclear complexes the use of triethylamine as base makes the bridging ligand coordinate to copper(II) ion through the deprotonated oxamido nitrogen atoms. By adding  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in less than stoichiometric amount, the formation of the

binuclear copper(II) complexes is avoided. Indeed, elemental analyses indicate that the reaction of  $\text{H}_2\text{dmoxae}$  with  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and L (L = phen, Mephen, en, pn) in *ca.* 1:1:1:2 mole ratio yielded the heterobinuclear complexes of the general formula  $[\text{Cu}(\text{dmoxae})\text{MnL}_2](\text{ClO}_4)_2$ , as expected. On the basis of the molar conductivity measurements, spectroscopic characterization and magnetic analyses (*vide infra*), these complexes are presumed to have the coordination environment as shown in Fig. 1.

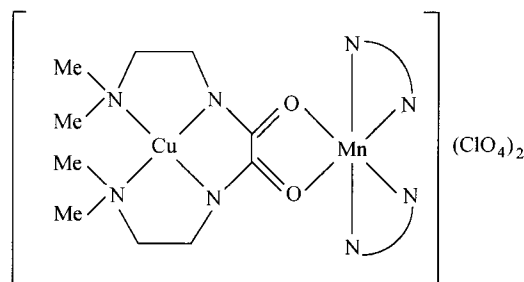


Fig. 1 Plausible coordination environment of the complexes ( $\overline{N-N}$  = phen, Mephen, en, pn).

### Molar conductance and general properties of the binuclear complexes

All the Cu(II)-Mn(II) binuclear complexes are sparingly soluble in water, ethanol, carbon tetrachloride, chloroform and benzene; but are soluble in acetonitrile, DMF and DMSO to give stable solutions at room temperature. In the solid state all complexes are fairly stable in air so as to facilitate physical measurements. For the four Cu(II)—Mn(II) binuclear complexes, the molar conductance values ( $1 \times 10^{-3}$  mol  $\cdot$  L<sup>-1</sup> acetonitrile solution) fall in the expected range for 1:2 electrolytes<sup>18</sup> (see Table 1), indicating that the two per-

Table 1 Physical data for the ligand and the Cu(II)-Mn(II) heterobinuclear complexes

Compound <sup>a</sup>	$\Delta_{\text{M}}$ ( $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ )	IR ( $\text{cm}^{-1}$ )							UV (nm)	
		$\nu(\text{C}=\text{O})$	$\nu(\text{Cu}-\text{N})$	$\nu(\text{Mn}-\text{O})$	$\nu(\text{N}=\text{C})$	$\nu(\text{NH}_2)$	$\nu(\text{Mn}-\text{N})$	$\nu(\text{ClO}_4)$	${}^6\text{A}_1 \rightarrow {}^4\text{A}_1 + {}^4\text{E}$	${}^2\text{B}_1 \rightarrow {}^2\text{A}_1$
$\text{H}_2\text{dmoxae}$		1650								
1	240	1650	478	450	1536	—	430	1100, 630	423	520
2	245	1652	476	455	1520	—	425	1085, 628	420	525
3	248	1650	470	452	—	3340	428	1100, 626	422	521
4	252	1650	475	454	—	3328	420	1098, 625	421	522

<sup>a</sup> 1:  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{phen})_2](\text{ClO}_4)_2$ ; 2:  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{Mephen})_2](\text{ClO}_4)_2$ ;  
3:  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{en})_2](\text{ClO}_4)_2$ ; 4:  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{pn})_2](\text{ClO}_4)_2$ .

chlorate anions are situated outside the metal coordination sphere. This is consistent with the presumed structure of the complexes shown in Fig. 1. The structures of the binuclear complexes were further characterized on the basis of the following facts.

#### *Infrared spectra*

The IR spectra taken in the region 4000—400  $\text{cm}^{-1}$  provide some information regarding the mode of coordination in the complexes and were analyzed in a careful comparison with those of the free ligand ( $\text{H}_2\text{dmoxae}$ ). The most relevant IR absorption bands from the IR spectra of the complexes, along with their assignments are shown in Table 1. We will only discuss here selected infrared bands. The IR spectrum of the free ligand ( $\text{H}_2\text{dmoxae}$ ) shows a sharp distinct band at 3250  $\text{cm}^{-1}$ , which is attributed to  $\nu(\text{N—H})$  stretching vibration band. However, in the IR spectra of all complexes, the band had disappeared, accompanied by the appearance of a strong band in the 470—478  $\text{cm}^{-1}$  range attributed to the  $\nu(\text{Cu—N})$  stretching mode. These facts indicated that the free ligand is coordinated to copper(II) ion through the deprotonated oxamido group. On the other hand, it is noted that the carbonyl ( $\text{C}=\text{O}$ ) stretching vibration for the free ligand remains at *ca.* 1650  $\text{cm}^{-1}$  in the IR spectra of the four binuclear complexes. This might be due to the following reasons. In general, when the deprotonated amide nitrogen is coordinated with the metal ion to form mononuclear complex, its amide I band shifts considerably towards lower wave numbers. In the case of an oxamide dianion coordinated to two metal ions as a bridging ligand, the amide I band reverts to near its original position (in the protonated species).<sup>5,11</sup> Although the amide I band is the result of a composite  $\text{N—C}=\text{O}$  vibration, it can essentially be seen as  $\nu(\text{C}=\text{O})$ . It is likely that the bond order of  $\text{C}=\text{O}$  in binuclear complexes is higher than that in its corresponding mononuclear complex. This shift has often been used as definite proof of an examine-bridge.<sup>5</sup> Thus, the above observation means that the carbonyl oxygen atoms of the ligand are coordinated with manganese(II) ion and are indicative of the oxamido-bridged structure. The facts that the  $\text{C}=\text{O}$  deformation at 728  $\text{cm}^{-1}$  of the ligand had disappeared, and accompanied by the appearance of a new band at *ca.* 450  $\text{cm}^{-1}$  due to  $\nu(\text{Mn—O})$  further confirm the coordinated nature of the carbonyl oxygens in

these binuclear complexes. Furthermore, the  $\text{N}=\text{C}$  or  $\text{NH}_2$  vibrations for the terminal ligands (phen, Mephen, en, pn) were found in the corresponding binuclear complexes (see Table 1), suggesting that the N atoms of the terminal ligands are coordinated with the Mn(II) ion. The additional band observed at around 430—425  $\text{cm}^{-1}$  due to  $\nu(\text{Mn—N})$  further supports this view. In addition, a broad and intense band centered at *ca.* 1100  $\text{cm}^{-1}$ , and a strong sharp band at *ca.* 630  $\text{cm}^{-1}$ , typical for a non-coordinated perchlorate group,<sup>19,20</sup> were observed for all the binuclear complexes. This is consistent with the conductance data of the binuclear complexes.

#### *Electronic spectra*

In order to obtain further structural information, the electronic reflection spectra of these binuclear complexes were measured and the spectral data are given in Table 1. As shown in this table, the electronic spectra of the four complexes are similar to each other. For all four binuclear complexes, two absorption bands are observed (see Table 1). The band observed at 525—520 nm is characteristic of copper(II) in a square-planar environment,<sup>21</sup> which can be unambiguously assigned to the  ${}^2\text{B}_1 \rightarrow {}^2\text{A}_1$  local transition in  $\text{C}_{2v}$  site symmetry, while the band at *ca.* 420 nm corresponds to the  ${}^6\text{A}_1 \rightarrow {}^4\text{A}_1 + {}^4\text{E}$  spin-forbidden transition for manganese(II) activated by spin exchange-coupling interaction existing between copper(II) and manganese(II) ions. It is characteristic of the transition<sup>22</sup> between the low-lying pair state  $S = 2$  and the excited pair state  $S^* = 2$ , which displays a coupling band in the electronic spectrum, and in accord with the following magnetic study.

All our efforts to grow crystals of these copper(II)-manganese(II) binuclear complexes suitable for X-ray structure determination so far have been unsuccessful. However, based on the composition of these complexes, their IR and electronic spectra, molar conductivity measurements, magnetic studies (*vide infra*) and the crystal structure of an analogous complex,<sup>12</sup> these complexes are proposed to have an extended oxamido-bridged structure and to contain a manganese(II) ion and a copper(II) ion, which have an octahedral environment and a square-planar environment, respectively, as shown in Fig. 1. The plausible binuclear structure is proved by the following magnetic study.

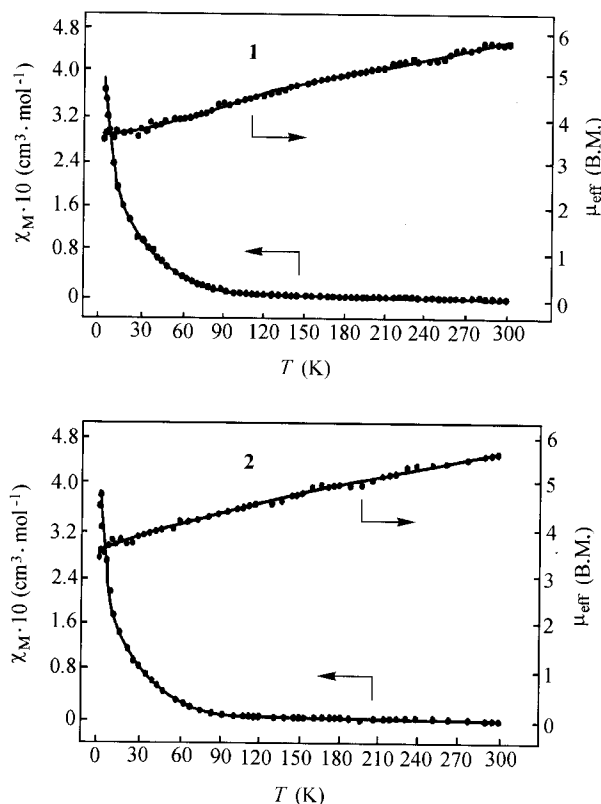
## Magnetic properties

On the basis of the above discussion of electronic spectra of these complexes, it has shown that a spin-coupled interaction exists between copper(II) and manganese(II) ions. In order to understand quantitatively the magnitude of the spin-exchange interaction, variable-temperature molar magnetic susceptibility (4.2–300 K) data were collected for complexes  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{phen})_2](\text{ClO}_4)_2$  (**1**) and  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{Mephen})_2](\text{ClO}_4)_2$  (**2**), and the magnetic analysis was performed using the susceptibility equation (1) which includes a parameter  $\theta$  to correct for the contribution from an intermolecular magnetic interaction based on the Heisenberg spin-exchange operator ( $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ ,  $S_1 = 1/2$ ,  $S_2 = 5/2$ ):

$$\chi_M = \frac{N\beta^2 g^2}{k(T - \theta)} \left[ \frac{28 + 10\exp(-6J/kT)}{7 + 5\exp(-6J/kT)} \right] \quad (1)$$

where  $\chi_M$  denotes the susceptibility per binuclear complex and the remaining symbols have their usual meaning. As shown in Fig. 2, good least-square fits to the experimental data were attained with equation (1). The magnetic parameters thus determined are  $J = -35.9 \text{ cm}^{-1}$ ,  $g = 2.02$ ,  $\theta = 1.27 \text{ K}$  for **1**, and  $J = -32.6 \text{ cm}^{-1}$ ,  $g = 2.01$ ,  $\theta = 0.98 \text{ K}$  for **2**. The agreement factors  $F$ , defined here as  $F = \sum([\chi_M]_{\text{obs.}} - [\chi_M]_{\text{calc.}}]^2 / \sum([\chi_M]_{\text{obs.}})$ , are then equal to  $1.26 \times 10^{-5}$  (**1**),  $1.39 \times 10^{-5}$  (**2**), respectively. The results have confirmed that the spin coupling between manganese(II) and copper(II) ions through an oxamido-bridge is antiferromagnetic. The magnetic spin-exchange interaction between manganese(II) and copper(II) ions within the complexes may be explained by several models which have so far been proposed.<sup>23,24</sup> According to these models, strict orbital orthogonality results in ferromagnetism ( $J > 0$ ), otherwise antiferromagnetic coupling ( $J < 0$ ) should be involved in the system. On the basis of the crystal structure of complex<sup>12</sup> that is analogous to the present complexes, if the whole molecular symmetry is considered to be  $C_{2v}$ , the 3d metallic orbitals of copper(II) and manganese(II) ions transform as  $a_1(d_z^2 \text{ and } d_{x^2-y^2})$ ,  $a_2(d_{yz})$ ,  $b_1(d_{xy})$  and  $b_2(d_{zx})$ .<sup>25</sup> Around the copper(II) ion, there is just one unpaired electron which occupies the  $b_1$  orbital, and around manganese(II) ion there are

five unpaired electrons which populate the  $a_1$ ,  $a_2$ ,  $b_1$  and  $b_2$  orbitals. According to point group theory, because there is no orthogonality between  $b_1(\text{Cu})$  and  $b_1(\text{Mn})$ , namely  $S = \langle b_1(\text{Cu}) | b_1(\text{Mn}) \rangle \neq 0$ , the antiferro-magnetic exchange interaction should be observed in the complexes.



**Fig. 2** Temperature variation of  $\chi_M$  (lower curve) and  $\mu_{\text{eff}}$  (upper curve) for the complexes  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{phen})_2](\text{ClO}_4)_2$  (**1**) and  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{Mephen})_2](\text{ClO}_4)_2$  (**2**). The curves are based on equation (1) using the parameters given in the text. (●), experimental data; (—), calculation curves as described in the text.

If we compare the  $J$  value with that previously reported for the analogous  $\mu$ -oxamido heterobinuclear copper(II)-manganese(II) complex<sup>26</sup>  $[\text{Cu}(\text{oxae})\text{Mn}(\text{phen})_2](\text{ClO}_4)_2$  [where oxae denotes the  $N, N'$ -bis(2-aminoethyl)oxamido dianion], we obtained the following results for the magnetic interactions:  $[\text{Cu}(\text{oxae})\text{Mn}(\text{phen})_2](\text{ClO}_4)_2$  ( $J = -31.1 \text{ cm}^{-1}$ )  $<$   $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{phen})_2](\text{ClO}_4)_2$  ( $J = -35.9 \text{ cm}^{-1}$ ). In fact, the two complexes have similar bridging ligands and the same terminal ligand. The only difference between

[Cu(dmoax)Mn(phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> and [Cu(oxae)Mn(phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> is that four methyl (CH<sub>3</sub>) substituents are present in the former and this may increase the electron density on the bridged ligand. It is well known that the delocalization of the d electrons of the metal towards the bridging atom is one of the main factors affecting the magnetic exchange interaction, while the delocalization extent is determined by the energy gap between the d orbital and bridgedatom orbital.<sup>27</sup> The electronic releasing effect of the methyl substituents increases the electron density on the bridging ligand in the present complex, raising the ligand orbital level. This will, in turn, lead to a smaller energy gap between the d orbitals of the metal ions and the highest occupied molecular orbitals of the bridging ligand<sup>28</sup> and to larger delocalization of the d electrons towards the bridged atoms in the present complex, so as to increase the antiferromagnetic interaction between copper (II) and manganese (II) ions. This would explain the difference in *J* values for these complexes. Further investigation using various substituents is required in order to confirm this effect and is in progress in our laboratory.

## References

- Gatteschi, D.; Kahn, O.; Miller, J. S.; Palacio, F. *Molecular Magnetic Materials*, NATO ASI Series, Kluwer, Dordrecht, **1991**.
- Kahn, O. *Molecular Magnetism*, Verlag-Chemie, New York, **1993**.
- Yan, C.-W.; Li, Y.-T.; Liao, D.-Z. *Transition Met. Chem.* **1997**, *22*, 475.
- Li, Y.-T.; Yan, C.-W.; Miao, S.-H.; Liao, D.-Z. *Polyhedron* **1998**, *15*, 2491.
- Ojima, H.; Nonoyama, K. *Coord. Chem. Rev.* **1988**, *92*, 85.
- Journaux, Y.; Sletten, J.; Kahn, O. *Inorg. Chem.* **1985**, *24*, 4063.
- Yu, P.; Kahn, O.; Nakatani, K.; Codjovi, E.; Mathoniere, C.; Sletten, J. *J. Am. Chem. Soc.* **1991**, *113*, 6558.
- Lloret, F.; Julve, M.; Ruiz, R.; Journaux, Y.; Nakatani, K.; Kahn, O.; Sletten, J. *Inorg. Chem.* **1993**, *32*, 27.
- Lloret, F.; Journaux, Y.; Julve, M. *Inorg. Chem.* **1990**, *29*, 3967.
- Ribas, J.; Costa, R.; Journaux, Y.; Mathoniere, C.; Kahn, O.; Gleizes, A. *Inorg. Chem.* **1990**, *29*, 2042.
- Li, Y.-T.; Liao, D.-Z.; Jiang, Z.-H.; Wang, G.-L. *Polyhedron* **1995**, *14*, 2209.
- Mathoniere, C.; Kahn, O.; Daran, J.-C.; Hilbig, H.; Kohler, H. *Inorg. Chem.* **1993**, *32*, 4057.
- Benelli, C.; Fabretti, A. C.; Giusti, A. *J. Chem. Soc., Dalton Trans.* **1993**, 409.
- Bethrent, J. R.; Madan, S. K. *J. Inorg. Nucl. Chem.* **1950**, *20*, 195.
- Ojima, H.; Yamada, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3018.
- Selwood, P. W. *Magnetochemistry*, Intersciences, New York, **1956**, pp. 78–79.
- Gunter, M. J.; Berry, K. J.; Murray, K. S. *J. Am. Chem. Soc.* **1984**, *106*, 4227.
- Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.
- Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley, New York, **1986**.
- Radecka-Paryzek, E. *Inorg. Chim. Acta* **1979**, *34*, 5.
- Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, Amsterdam, **1984**.
- McCarthy, P. J.; Gudel, H. U. *Coord. Chem. Rev.* **1988**, *88*, 69.
- Hay, P. J.; Thibeault, J. C.; Hoffman, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.
- Kahn, O.; Charlot, M. F. *Nouv. J. Chim.* **1980**, *4*, 567.
- Morgenstern-Badarau, I.; Rerat, M.; Kahn, O.; Jaud, J.; Galy, J. *Inorg. Chem.* **1982**, *21*, 3050.
- Ma, S.-L.; Jiang, Z.-H.; Liao, D.-Z.; Yan, S.-P.; Wang, G.-L. *J. Coord. Chem.* **1994**, *31*, 321.
- Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834.
- Ward, M. D. *Inorg. Chem.* **1996**, *35*, 1712.

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