

Synthesis and Magnetic Properties of Heterobinuclear Copper(II)–Manganese(II) Complexes with N,N'-Bis[2-(dimethylamino)ethyl]oxamide as Ligand

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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 2,2'-bipyridine (bpy); 4,4'-dimethyl-2,2'-bipyridine (Me₂-bpy); 5-chloro-1,10-phenanthroline (Cl-phen) or 5-bromo-1,10-phenanthroline (Br-phen), respectively, namely, [Cu(dmoxae)MnL₂](ClO₄)₂ (L = bpy, Me₂-bpy, Cl-phen, Br-phen), have been synthesized and characterized by elemental analyses, IR and electronic spectra studies and molar conductivity measurements. The electronic reflectance spectrum indicates the presence of exchange-coupling interaction between bridging copper(II) and manganese(II) ions. The cryomagnetic measurements (4.2–300 K) of [Cu(dmoxae)Mn(bpy)₂](ClO₄)₂ complex demonstrated the operation of an antiferromagnetic interaction between the adjacent manganese(II) and copper(II) ions through the oxamido-bridge within the complex. On the basis of spin Hamiltonian, $\hat{H} = -2JS_1S_2$, the magnetic analysis was carried out for the complex and the spin-coupling constant (J) was evaluated as -36.9 cm^{-1} . The influence of methyl substituents in amine groups of the bridging ligand on magnetic interactions between the metal ions of this kind of complexes is also discussed.

Key words: oxamido-bridge, copper(II)–manganese(II), heterobinuclear complexes, magnetic properties, synthesis

Syntheses and magnetic properties of heterobinuclear transition-metal complexes are of current interest, due to its relevance to electron transfer in biological systems and to the design of molecular-based ferromagnet [1]. So far, much effort has been devoted to the development of multi-atom 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 coordinating ability towards transition-metal ions can be modified and tuned by playing on the nature of the amide substituents [2] 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 [3,4]. Many polynuclear complexes containing oxamido bridges have been synthesized and their magnetic properties studied

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[2,5–7]. However, there are few studies on the influence of substituents 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 order to gain some insight into the effect of substituents in this kind of ligand on magnetic interaction.

In this paper, four new heterometal binuclear complexes, $[\text{Cu}(\text{dmoxae})\text{MnL}_2](\text{ClO}_4)_2$ ($L = \text{bpy}, \text{Me}_2\text{-bpy}, \text{Cl-phen}, \text{Br-phen}$) have been synthesized and characterized by using $\text{N,N}'\text{-bis}[2\text{-}(\text{dimethylamino})\text{ethyl}]\text{oxamido}$ dianion as a bridging ligand and the cryomagnetic property of the $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$ complex was measured between 4.2–300 K to examine the effect of the substituents 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 perchlorates and $\text{N,N}'\text{-bis}[2\text{-}(\text{dimethylamino})\text{ethyl}]\text{oxamido}$ (H_2dmoxae) were prepared by the methods [8,9]. $\text{N,N}'\text{-dimethylethylene-diamine}$, diethyl oxalate and the terminal ligands 2,2'-bipyridine (bpy); 4,4'-dimethyl-2,2'-bipyridine ($\text{Me}_2\text{-bpy}$); 5-chloro-1,10-phenanthroline (Cl-phen) and 5-bromo-1,10-phenanthroline (Br-phen) were purchased from the Beijing Chemical Company.

Synthesis of $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$ (1): To a solution of H_2dmoxae (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 triethyl-amine (2 mL). The stirring was continued at room temperature (about 30 minutes) until the mixture became limpid. 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 bpy (0.312 g, 2 mmol) in the same solvent (10 mL) under N_2 . The color of the solution turned from green 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 P_2O_5 under reduced pressure. Recrystallization was carried out from a MeCN/ethanol (1:2) mixture. Yield, 0.669 g (78%), mp, 216.3°C.

Synthesis of $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{Me}_2\text{-bpy})_2](\text{ClO}_4)_2$ (2): This complex was obtained as redviolet microcrystals by the same procedure and the same amount of reagents as above but by using $\text{Me}_2\text{-bpy}$ instead of bpy. Yield, 0.759 g (83%); mp, 276.9°C.

Synthesis of $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{Cl-phen})_2](\text{ClO}_4)_2$ (3): This complex was obtained as a brown powder by the same procedure and the same amounts of reagents as above but by using Cl-phen instead of bpy. Yield, 0.839 g (86%); mp, 202.7°C.

Synthesis of $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{Br-phen})_2](\text{ClO}_4)_2$ (4): This red-brown compound was prepared as described for complex (1), except that Br-phen was used instead of bpy. Yield, 0.936 g (88%); mp, 291.4°C.

The chemical analyses confirm the compositions indicated.

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 at the Institute of Physics, Chinese Academy of Sciences, using 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 for all the constituent atoms and effective magnetic moments were calculated by $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms.

RESULTS AND DISCUSSION

Syntheses and coordination environment of the binuclear complexes: A promising method to design and synthesize heterobinuclear complexes is to use a heterobinucleating ligand, which offers either the coordination geometry or the ligand field strength, suitable for dissimilar metal ions [10]. 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 ($H_2dmoxae$) was chosen as the bridging ligand. Simultaneously, 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (Me_2 -bpy); 5-chloro-1,10-phenanthroline (Cl-phen) and 5-bromo-1,10-phenanthroline (Br-phen) were used as terminal ligands, respectively. These binuclear complexes used triethylamine as base of the coordination of the bridging ligand to copper(II) ion through the deprotonated oxamido nitrogen atoms. By adding $Cu(ClO_4)_2 \cdot 6H_2O$ in less than stoichiometric amount, the formation of the binuclear copper(II) complexes is avoided. Indeed, elemental analyses indicate that the reaction of $H_2dmoxae$ with $Cu(ClO_4)_2 \cdot 6H_2O$, $Mn(ClO_4)_2 \cdot 6H_2O$ and L (L = bpy, Me_2 -bpy, Cl-phen, Br-phen) in *ca.* 1:1:1:2 mole ratio yielded the heterobinuclear complexes of the general formula $[Cu(dmoxae)MnL_2](ClO_4)_2$, as expected. These complexes are the first examples of Cu(II)–Mn(II) heterobinuclear complexes bridged by N,N'-bis[2-(dimethylamino)ethyl]oxamido group. On the basis of the molar conductance measurements, spectroscopic characterization and magnetic analysis (*vide infra*) these complexes are presumed to have the coordination environment as shown in Fig. 1.

Molar conductance and some 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 give stable solutions in acetonitrile, DMF and DMSO at room temperature. As solids these complexes are fairly stable in air. For the four Cu(II)–Mn(II) binuclear complexes, the molar conductance ($1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ acetonitrile solution) fall in the expected range for 1:2 electrolytes [11] (see Table 1), indicating that the two perchlorate anions are situated outside the metal coordination sphere. This is consistent with the structure of the complexes shown in Figure 1, further supported by spectroscopic and magnetic studies.

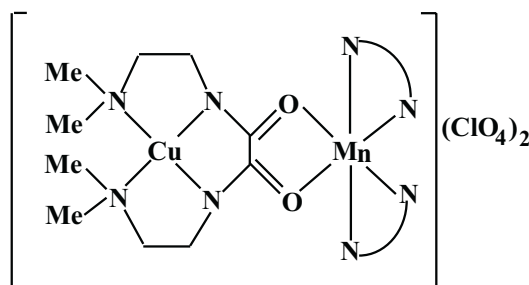


Figure 1. Plausible coordination environments of the complexes ($\overset{\frown}{N}N$ = bpy, Me_2 -bpy, Cl-phen, Br-phen).

Infrared spectra: IR spectra taken between 4000–400 cm^{-1} provide some information regarding the mode of coordination in the complexes and were analyzed in a careful comparison with that of the free ligand (H_2dmoxae). The most relevant IR absorption bands of the complexes, along with their assignments are shown in Table 1. We will only discuss here some selected infrared bands. The IR spectrum of the free ligand (H_2dmoxae) shows a sharp distinct band at 3280 cm^{-1} , which is attributed to $\nu(\text{N-H})$ stretching vibration band. However, in the IR spectra of all complexes this band had disappeared, accompanied by the appearance of a strong band in the 470–475 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 (C=O) stretching vibration for the free ligand remains at *ca.* 1650 cm^{-1} in the IR spectra of the four dinuclear complexes. This might be due to the following reasons: If 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 oxamide dianion, coordinated to two metal ions as a bridging ligands, the amide I band reverts near to its original position (in the protonated species) [2,5]. Although the amide I band results from a composite N-C=O vibration, it can essentially be seen as $\nu(\text{C=O})$. It is likely that the bond order of C=O in binuclear complexes is higher than in its corresponding mononuclear complex. This shift has often been used as a definite proof of an oxamido-bridge [2]. Thus, the above observations mean that the carbonyl oxygen atoms of the ligand are coordinated with manganese(II) ion and are indicative of the oxamido-bridged structures. The facts that the C=O deformation at 728 cm^{-1} of the ligand had disappeared, and accompanied by the appearance of a new band at *ca.* 450 cm^{-1} due to $\nu(\text{Mn-O})$, further confirm the coordinated nature of the carbonyl oxygens in these binuclear complexes. Furthermore, the $-\text{N=C}-$ stretching vibration for the terminal ligands (bpy, $\text{Me}_2\text{-bpy}$, Cl-phen, Br-phen) were found in the corresponding binuclear complexes (see Table 1), suggesting the coordination of N atoms of the terminal ligands with the Mn(II) ion. The additional band, observed at around 430–425 cm^{-1} due to $\nu(\text{Mn-N})$, further supports this view. In addition, a broad and intense band, centered at *ca.* 1100 cm^{-1} and a strong sharp band at *ca.* 630 cm^{-1} , typical for a non-coordinated perchlorate group [12], 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, three absorption bands are observed (see Table 1). The band observed at 540~545 nm may be attributed to the d-d transition of copper(II) in a square-planar environment, while the band at *ca.* 420 nm is due to the exchange-coupling interaction, existing between copper(II) and manganese(II) ions and is characteristic of the transition between the low-lying pair state $S = 2$ and the excited pair state $S^* = 2$ (abbreviated as $S_L \rightarrow S^*_E$) [13], which displays a coupling band in the electronic spectrum, in accord with the

following magnetic study. In addition, a stronger absorption in the short wavelength range (see Table 1) may be attributed to the charge-transfer absorption bands, which may be due to the spin-exchange interaction between the copper(II) and manganese(II) ions through the π -path orbital set up by an oxamido bridge [2]. Further investigations of these and similar systems are required in order to obtain a more detailed assignment for charge transfer. Failure to observe any d-d bands may be due to the weakness of the absorption. The coordination environment of manganese(II) in these complexes is most likely a distorted octahedron, owing to the fact that two bidentate terminal ligands (bpy, Me₂-bpy, Cl-phen, Br-phen) coordinate with Mn(II). Thus, according to ligand field theory, and assuming O_h symmetry, the ground state of manganese(II) is ⁶A_{1g}. Because the d-d transitions of manganese(II) [⁶A_{1g} → ⁴T_{1g}(G), ⁴T_{2g}(G), ⁴A_{1g}, ...] are both Laporte and spin-forbidden, no characteristic manganese(II) band was found in the spectra of the binuclear Cu(II)–Mn(II) complexes [14].

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

Compound	Λ_M ($\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$)	IR (cm^{-1})						UV (nm)		
		$\nu(\text{C}=\text{O})$	$\nu(\text{Cu}-\text{N})$	$\nu(\text{Mn}-\text{O})$	$\nu(\text{N}=\text{C})$	$\nu(\text{Mn}-\text{N})$	$\nu(\text{ClO}_4^-)$	$S_L \rightarrow S^*_E$	d-d	CT
H ₂ dmoxae		1650								
(1)	246	1650	470	450	1520	430	1100, 630	420	542	260
(2)	248	1652	475	458	1528	425	1085, 628	421	540	262
(3)	242	1655	472	452	1530	428	1100, 626	420	543	261
(4)	251	1650	473	456	1532	420	1098, 625	422	545	260

(1): [Cu(dmoxae)Mn(bpy)₂](ClO₄)₂,
 (3): [Cu(dmoxae)Mn(Cl-phen)₂](ClO₄)₂,

(2): [Cu(dmoxae)Mn(Me₂-bpy)₂](ClO₄)₂,
 (4): [Cu(dmoxae)Mn(Br-phen)₂](ClO₄)₂.

All our efforts to grow crystals of these copper(II)–manganese(II) binuclear complexes, suitable for X-ray structure determination, have been so far 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 [6], 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 Figure 1. The plausible binuclear structure is proved by the following magnetic study.

Magnetic susceptibility of [Cu(dmoxae)Mn(bpy)₂](ClO₄)₂: The above discussion has shown that a spin-coupled interaction exists between copper(II) and manganese(II) ions. In order to understand quantitatively the spin-exchange interaction, variable-temperature molar magnetic susceptibility (4.2–300 K) data were collected for complex [Cu(dmoxae)Mn(bpy)₂](ClO₄)₂. The magnetic analysis was also performed using (1), which includes a parameter θ to correct 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 χ_M denotes the susceptibility per binuclear complex and the remaining symbols have their usual meaning. As shown in Figure 2, good least-square fits to the experimental data were attained with (1). The magnetic parameters, thus determined, are $J = -36.9 \text{ cm}^{-1}$, $g = 2.02$, $\theta = 1.7 \text{ K}$. The agreement factor F , defined here as $F = \Sigma[(\chi_M)_{\text{obs.}} - (\chi_M)_{\text{calc.}}]^2 / \Sigma(\chi_M)_{\text{obs.}}$, is then equal to 1.28×10^{-5} . This result has 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 molecule may be explained by several models, which have so far been proposed [15]. According to these models, a 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 [6], 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 $a_1(d_{z^2}$ and $d_{x^2-y^2})$, $a_2(d_{yz})$, $b_1(d_{xy})$ and $b_2(d_{zx})$ [16]. Around the copper(II) ion, there is just one unpaired electron which occupies the b_1 orbital and

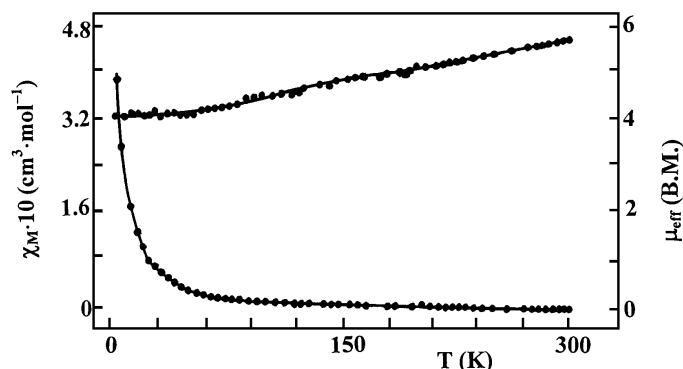


Figure 2. Temperature variation of χ_M (lower curve) and μ_{eff} (upper curve) for the complex [Cu(dmoxae)Mn(bpy)₂](ClO₄)₂. The curves are based on equation (1) using the parameters given in the text. (•), experimental data; (—), calculation curves as described in the text.

around manganese(II) ion there are five unpaired electrons, which populate the a_1 , a_2 , b_2 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 $S = \langle b_1(\text{Cu}) | b_1(\text{Mn}) \rangle \neq 0$, hence, the antiferromagnetic exchange interaction should be observed in the complex.

If we compare the J value with that previously reported for the analogous μ -oxamido heterobinuclear copper(II)–manganese(II) complex [17] $[\text{Cu}(\text{oxae})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$ [where oxae denotes the N,N' -bis(2-aminoethyl)oxamido dianion], we obtained the following results for the magnetic interactions: $[\text{Cu}(\text{oxae})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$ ($J = -29.7 \text{ cm}^{-1}$) < $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$ ($J = -36.9 \text{ cm}^{-1}$). In fact, these complexes have similar bridging ligands and the same terminal ligand. The only difference between $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$ and $[\text{Cu}(\text{oxae})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$ is that four methyl ($-\text{CH}_3$) 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 bridged atom orbital [18]. 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 [19] 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. Such investigation is in progress in our laboratory.

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