

## Synthesis, Characterization and Magnetic Studies of $\mu$ -Oxamido-Bridged Cu(II)–Mn(II) Heterobinuclear Complexes

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Four new  $\mu$ -oxamido-bridged copper(II)–manganese(II) heterobinuclear complexes described by the overall formula  $[\text{Cu}(\text{dmoxpn})\text{MnL}_2](\text{ClO}_4)_2$ , where dmoxpn denotes N,N'-bis[3-(dimethylamino)propyl]oxamido dianion, L represents 2,2'-bipyridine (bpy); 4,4'-dimethyl-2,2'-bipyridine ( $\text{Me}_2\text{-bpy}$ ); 5-chloro-1,10-phenanthroline (Cl-phen) or 5-bromo-1,10-phenanthroline (Br-phen), have been synthesized and characterized. Based on elemental analyses, IR and electronic spectra studies and molar conductivity measurements, these complexes are proposed to have oxamido-bridged structures and to consist of the copper(II) ion in a planar environment and the manganese(II) ion in an octahedral environment. The electronic reflectance spectrum indicates the presence of exchange-coupling interaction between bridging copper(II) and manganese(II) ions. The  $[\text{Cu}(\text{dmoxpn})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$  complex has been further characterized by variable temperature susceptibility (4.2–300 K) and the observed data were least-square fitted to the susceptibility equation derived from the spin Hamiltonian,  $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ , giving the exchange integral  $J = -27.8 \text{ cm}^{-1}$ . The results are commensurate with antiferromagnetic interaction between the adjacent manganese(II) and copper(II) ions through the oxamido-bridge within the complex. The influence of structural variation of the bridging ligand on magnetic interactions between the metal ions of this kind of complexes is also discussed.

**Key words:**  $\mu$ -oxamido-bridge, Cu(II)–Mn(II) heterobinuclear complexes, magnetism

Interest in bridged heterobinuclear transition-metal complexes with two different paramagnetic centers has risen considerably in recent years [1–5]. The synthesis, spectroscopic and magnetic investigations of new heterobinuclear complexes are important, not only for gaining some insight into the electronic and geometric structure of metalloproteins and enzymes and thus the correlating structure with biological function, but also for obtaining information about designing and synthesizing molecule magnets and investigating the spin-exchange mechanisms between paramagnetic metal ions. It is known that N,N'-bis(substituent)oxamides could be good candidates in supporting magnetic exchange interactions, because their coordinating ability toward transition-metal ions can be modified and tuned by playing on the na-

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ture of the amide substituents [2], and the remarkable efficiency of the oxamido bridge to transmit electronic effects between the metal ions, and hence this family of ligands has played an important role in molecular magnetism [2–5]. Many polynuclear complexes containing oxamido bridges have been synthesized and their magnetic properties studied [2,5–7]. The effective bridging function of  $\mu$ -oxamido has been revealed by X-ray analysis for some of these complexes [3,4,6]. 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 magnetic interaction of this kind of complexes. Quite recently, we utilized *N,N'*-bis[2-(dimethylamino)ethyl]oxamido dianion as a bridging ligand to prepare the Cu(II)–Mn(II) heterobinuclear complexes and to study their magnetic properties [8]. In order to provide more oxamido-bridged Cu(II)–Mn(II) heterobinuclear complexes to investigate further the structural variation effects upon spin-coupling, in this paper, four new heterometal binuclear complexes,  $[\text{Cu}(\text{dmoxpn})\text{MnL}_2](\text{ClO}_4)_2$  ( $\text{L} = \text{bpy}, \text{Me}_2\text{-bpy}, \text{Cl-phen}, \text{Br-phen}$ ) have been synthesized by using *N,N'*-bis[3-(dimethylamino)propyl]oxamido dianion (abbreviated as *dmoxpn*) as a bridging ligand and the cryomagnetic property of the  $[\text{Cu}(\text{dmoxpn})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$  complex was measured and studied in detail.

## EXPERIMENTAL

**Materials:** All of the reagents used in the synthesis were of analytical grade. The hydrated manganese(II) perchlorate and *N,N'*-bis[3-(dimethylamino)propyl]oxamido ( $\text{H}_2\text{dmoxpn}$ ) were prepared by the literature methods [9,10]. *N,N*-Dimethylpropyldiamine, 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 used as commercially.

**Synthesis of  $[\text{Cu}(\text{dmoxpn})\text{MnL}_2](\text{ClO}_4)_2$  ( $\text{L} = \text{bpy}, \text{Me}_2\text{-bpy}, \text{Cl-phen}, \text{Br-phen}$ ):** The methods used to prepare the complexes are virtually identical and are exemplified by the preparation of  $[\text{Cu}(\text{dmoxpn})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$ . To a solution of  $\text{H}_2\text{dmoxpn}$  (0.258 g, 1 mmol) in methanol (20 mL) a solution of piperidine (0.170 g, 2 mmol) in the same solvent (20 mL) was added successively, followed by a solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.352 g, 0.950 mmol) in methanol (10 mL) with stirring at room temperature until the mixture became limpid (about 30 minutes). The resulting solution was then filtered. To the filtrate was added a methanol solution (10 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 (15 mL) under  $\text{N}_2$ . The color of the solution turned from green to pale-red immediately and a small amount of precipitate formed. After stirring for 6 h, the pale-red 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 (1:4) mixture.

Colors, yields and melting points of these complexes are listed in Table 1.

**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. The results of these analyses point on the formulae given in Table 1. IR spectra were recorded with a Nicolet FT-IR 5DX spectrophotometer 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 using a Quantum Design MPMS-5 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms and effective magnetic moments

were calculated by the equation  $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$ , where  $\chi_M$  is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms.

**Table 1.** Data of yields, colors and melting points (M.P.) of the complexes.

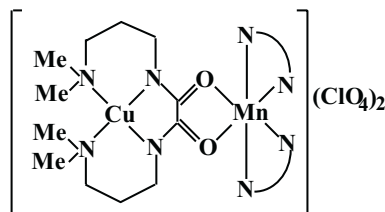
Complex	Empirical Formula (Formula Weight)	Color	Yield (%)	M.P. (°C)
(1)	MnCuC <sub>32</sub> H <sub>40</sub> N <sub>8</sub> O <sub>10</sub> Cl <sub>2</sub> (886.11)	pale-red	61	178.5
(2)	MnCuC <sub>36</sub> H <sub>48</sub> N <sub>8</sub> O <sub>10</sub> Cl <sub>2</sub> (942.21)	violet-red	70	213.8
(3)	MnCuC <sub>36</sub> H <sub>38</sub> N <sub>8</sub> O <sub>10</sub> Cl <sub>4</sub> (1003.04)	purple	85	198.2
(4)	MnCuC <sub>36</sub> H <sub>38</sub> N <sub>8</sub> O <sub>10</sub> Cl <sub>2</sub> Br <sub>2</sub> (1091.94)	purple	80	189.9

(1) = [Cu(dmoxpn)Mn(bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, (2) = [Cu(dmoxpn)Mn(Me<sub>2</sub>-bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>,  
 (3) = [Cu(dmoxpn)Mn(Cl-phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, (4) = [Cu(dmoxpn)Mn(Br-phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.

## RESULTS AND DISCUSSION

**Composition and coordination environment of the binuclear complexes:** In this study, the synthetic strategy for preparing heterobinuclear complexes is to use heterobinucleating ligand, which offers either the coordination geometry or the ligand field strength suitable for dissimilar metal ions [11]. As “heterobinucleating ligand” we have selected N,N'-bis[3-(dimethylamino)propyl]oxamido (H<sub>2</sub>dmoxpn), simultaneously, 2,2'-bipyridine (bpy); 4,4'-dimethyl-2,2'-bipyridine (Me<sub>2</sub>-bpy); 5-chloro-1,10-phenanthroline (Cl-phen) and 5-bromo-1,10-phenanthroline (Br-phen) were used as terminal ligands. In the course of preparing of these binuclear complexes the use of piperidine as base makes the bridging ligand coordinate to copper(II) ion through the deprotonated oxamido nitrogen atoms. By adding Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in less than stoichiometric amount, the formation of the binuclear copper(II) complexes is avoided. Indeed, elemental analyses indicate that the reaction of H<sub>2</sub>dmoxpn with Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and L (L = bpy, Me<sub>2</sub>-bpy, Cl-phen, Br-phen) in *ca.* 1:1:1:2 mole ratio have yielded the heterobinuclear complexes of the general formula [Cu(dmoxpn)MnL<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, as expected. These complexes are the first examples of Cu(II)–Mn(II) heterobinuclear complexes bridged by N,N'-bis[3-(dimethylamino)propyl]oxamido group. On the basis of the stoichiometric determinations, spectroscopic characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Figure 1.

**General properties of the binuclear complexes:** All the Cu(II)–Mn(II) binuclear complexes are sparingly soluble in water, methanol, 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 the complexes are fairly stable in air so as to facilitate physical measurements. For the four



**Figure 1.** Plausible coordination environment of the complexes ( $\overset{\curvearrowright}{\text{N}}\text{N} = \text{bpy}, \text{Me}_2\text{-bpy}, \text{Cl-phen}, \text{Br-phen}$ ).

Cu(II)–Mn(II) binuclear complexes, the molar conductance values ( $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$  acetonitrile solution) fall in the expected range for 1:2 electrolytes [12] (see Table 2), indicating that the two perchlorate anions are situated outside the metal coordination sphere and in accord with the presumed structure of the complexes shown in Figure 1. The structure of the binuclear complexes was further supported by the following spectroscopic characterization and magnetic studies.

**Infrared spectra:** The IR spectra taken in the region  $4000\text{--}400 \text{ cm}^{-1}$  provide some information regarding the mode of coordination in the complexes and were analyzed in a careful comparison with that of the free ligand ( $\text{H}_2\text{dmoxpn}$ ). The most relevant IR absorption bands from the IR spectra of the complexes, along with their assignments, are shown in Table 2. We will only discuss here the selected infrared bands. The IR spectrum of the free ligand ( $\text{H}_2\text{dmoxpn}$ ) shows a sharp distinct band at  $3320 \text{ cm}^{-1}$ , 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  $475\text{--}480 \text{ cm}^{-1}$  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 ( $\text{C=O}$ ) stretching vibration for the free ligand remains at *ca.*  $1630 \text{ cm}^{-1}$  in the IR spectra of the four binuclear complexes, which is similar to the band exhibited by an analogous complex [8]. This observation means that the carbonyl oxygen atoms of the ligand are coordinated with manganese(II) ion and are indicative of the oxamido-bridged structures. Because the deprotonated amide nitrogen is coordinated with the metal ion to form mononuclear complex, its amide I band shifts considerably towards lower wave numbers, however, in the case of an oxamide dianion coordinated to two metal ions as a bridging ligands, the amide I band reverts to near its original position (in the protonated species) [2,5]. Although the amide I band is the result of a composite  $\text{N-C=O}$  vibration, it can essentially be seen as  $\nu(\text{C=O})$ . It is likely that the bond order of  $\text{C=O}$  in binuclear complexes is higher than in its corresponding mononuclear complex. Thus, this shift has often been used as definite proof of an oxamido-bridge [2]. The facts that the  $\text{C=O}$  deformation at  $725 \text{ cm}^{-1}$  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  $\text{-N=C-}$  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 2), suggesting that the N atoms of the terminal ligands are coordinated with the Mn(II)

**Table 2.** Physical data for the ligand and the Cu(II)-Mn(II) heterobinuclear complexes.

Compound	$\Lambda_M$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	IR ( $\text{cm}^{-1}$ )				$\nu(\text{ClO}_4^-)$	${}^6A_1 \rightarrow {}^4A_1 + {}^4E$	UV (nm)		
		$\nu(\text{C}=\text{O})$	$\nu(\text{Cu}-\text{N})$	$\nu(\text{Mn}-\text{O})$	$\nu(\text{N}=\text{C})$				$\nu(\text{Mn}-\text{N})$	${}^2B_1 \rightarrow {}^2A_1$
H <sub>2</sub> dmoxpn		1630								
(1)	275	1630	475	452	1528	430	1100, 630	420	520	260
(2)	280	1630	480	455	1535	435	1090, 628	421	524	262
(3)	272	1630	478	453	1542	428	1095, 630	420	521	265
(4)	288	1630	476	450	1530	434	1098, 630	422	525	270

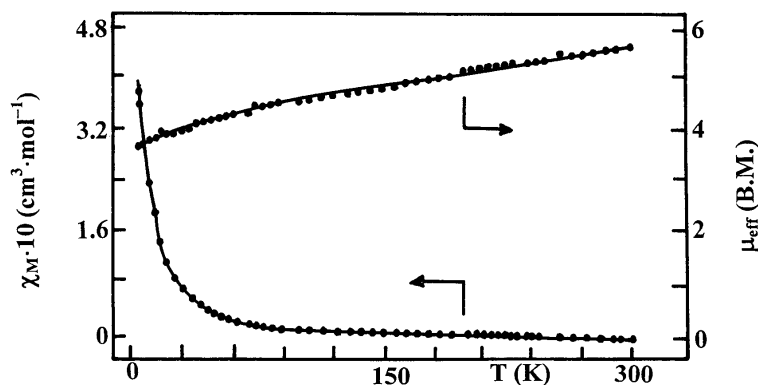
(1): [Cu(dmoxpn)Mn(bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>,  
(2): [Cu(dmoxpn)Mn(Me<sub>2</sub>-bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>,  
(3): [Cu(dmoxpn)Mn(Cl-phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>,  
(4): [Cu(dmoxpn)Mn(Br-phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.

ion. The additional band observed at around 435–428  $\text{cm}^{-1}$  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 [13], 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 2. 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 2). The band observed at 520–525 nm is characteristic of copper(II) in a square-planar environment [14], 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 an exchange-coupling interaction existing between copper(II) and manganese(II) ions. It is characteristic of the transition [15] 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. In addition, a stronger absorption in the short wavelength range (see Table 2) may be attributable to the charge-transfer absorption band, which may be due to the spin-exchange interaction between the copper(II) and manganese(II) ions through the  $\pi$ -path orbital set up by an oxamido bridge [2]. Further investigations of these and similar systems are required in order to obtain more detailed assignment for charge transfer.

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. It should be pointed out that the most direct and forceful evidence for the above assumption may come from X-ray crystallographic studies. Unfortunately, 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, the plausible binuclear structure is further proved by the following magnetic study.

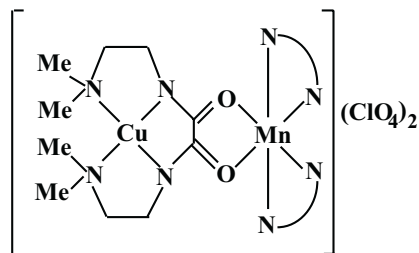
**Magnetic studies of  $[\text{Cu}(\text{dmoxpn})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$ :** From the above discussion of electronic spectra of these complexes, it follows that a spin-coupled interaction exists between copper(II) and manganese(II) ions. In order to understand quantitatively the magnitude of the spin-exchange interaction, variable-temperature molar magnetic susceptibility (4.2–300 K) data were collected for complex  $[\text{Cu}(\text{dmoxpn})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$  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 ( $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ ,  $S_1 = 1/2$ ,  $S_2 = 5/2$ ):



**Figure 2.** Temperature variation of  $\chi_M$  (lower curve) and  $\mu_{\text{eff}}$  (upper curve) for the complex  $[\text{Cu}(\text{dmoxp})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$ . The curves are based on equation (1) using the parameters given in the text. (•), experimental data; (—), calculated curves as described in the text.

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

where  $\chi_M$  denotes the susceptibility per binuclear complex and the remaining symbols have their usual meaning. As shown in Figure 2, good least-square fits to the experimental data were attained with equation (1). 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  $7.8 \times 10^{-4}$ . The magnetic parameters thus determined are  $J = -27.8 \text{ cm}^{-1}$ ,  $g = 2.03$ ,  $\theta = 1.2 \text{ K}$ . The 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 [16]. 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 [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  $b_2(d_{zx})$  [17]. 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  $S = \langle b_1(\text{Cu}) | b_1(\text{Mn}) \rangle \neq 0$ , hence, the antiferromagnetic exchange interaction should be observed in the complex.



**Figure 3.** Coordination environment of  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$ .

We have previously investigated the magnetic behavior of the analogous  $\mu$ -oxamido heterobinuclear copper(II)-manganese(II) complex [8]  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$ , where dmoxae denotes the N,N'-bis[2-(dimethylamino)ethyl]oxamido dianion and obtained the following results for the magnetic interactions:  $[\text{Cu}(\text{dmoxpn})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$  ( $J = -27.8 \text{ cm}^{-1}$ ) <  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$  ( $J = -36.9 \text{ cm}^{-1}$ ). In fact, the two complexes have essentially the same skeletal structure and the same terminal ligand, thus, their IR and electronic spectra are also similar. The only difference between  $[\text{Cu}(\text{dmoxpn})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$  and  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$  is that the chelate ring around the copper(II) consists 6-5-6 members in  $[\text{Cu}(\text{dmoxpn})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$  (see Figure 1) and 5-5-5 members in  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$  (see Figure 3). It is known that the relative stabilities of copper(II) complexes consisting of 6-5-6 member fused chelates are always higher than those of the 5-5-5 complexes [18]. Ojima and Nonoyama [2] pointed out, the higher the relative stability of the chelate ring arrangement, the less extensive is the delocalization of the  $\pi$  electrons in the oxamido bridge [2]. In other words, lower relative stability of the ligand field in an oxamido dimer molecule makes the magnetic interaction through the oxamido bridge stronger [2]. Therefore, the  $|J|$  value of  $[\text{Cu}(\text{dmoxae})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$  should be larger than that of  $[\text{Cu}(\text{dmoxpn})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$ .

**Conclusion:** The goal of this paper is to investigate the influence of structural variation of the bridging ligand on magnetic interactions in  $\text{Mn}^{\text{II}}\text{Cu}^{\text{II}}$  bimetallic species. In view of the effective bridging function of oxamido groups, we selected N,N'-bis[3-(dimethylamino)propyl]oxamido ( $\text{H}_2\text{dmoxpn}$ ) as a bridging ligand to synthesize four new  $\mu$ -oxamido-bridged copper(II)-manganese(II) heterobinuclear complexes and to study their magnetic properties. The main feature of the spectrum is a sharp and intense band corresponding to the  ${}^6\text{A}_1 \rightarrow {}^4\text{A}_1 + {}^4\text{E}$  spin-forbidden transition for manganese(II) activated by an exchange mechanism, which is characteristic of the presence of exchange-coupling interaction between bridging copper(II) and manganese(II) ions. The temperature dependence of the magnetic susceptibility of the  $[\text{Cu}(\text{dmoxpn})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2$  complex has been investigated in the 4~300 K range and has revealed a ground quintet-excited septet energy gap of  $3J = -83.4 \text{ cm}^{-1}$ . It has also indicated that the magnitude of the spin-exchange interaction between



Mn(II) and Cu(II) ions has to do with the relative stability of the chelate ring arrangement around copper(II), that is, lower relative stability of the ligand field in an oxamido dimer molecule makes the magnetic interaction through the oxamido bridge stronger. The results have confirmed that in this system the magnetic interactions may be tuned by playing the nature of the bridging ligands, and this strategy opens vast perspectives.

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