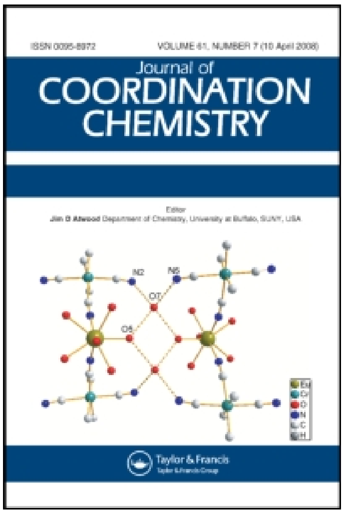

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SYNTHESIS AND MAGNETIC PROPERTIES OF Cu(II)-Mn(II) COMPLEXES WITH *N,N′-BIS* (2-AMINOETHYL)OXAMIDOCOPPER(II)

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Four binuclear complexes have been synthesized, namely $[Cu(oxae)Mn(L)_2](ClO_4)_2$, where oxae is the *N,N′-bis*(2-aminoethyl)oxamido dianion and L denotes 2,2′-bipyridyl (bpy), 4,4′-dimethyl-2,2′-bipyridyl (Me_2bpy), 1,10-phenanthroline (phen) and 5-nitro-1,10-phenanthroline (NO_2-phen). Based on IR, elemental analyses, conductivity measurements and electronic spectra, the complexes are proposed to have extended 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 complexes have been characterized by variable-temperature magnetic susceptibility measurements (4.2–300 K) and the susceptibility data were least-squares fitted to the susceptibility equation derived from the spin Hamiltonian including single-ion zero-field interaction for the manganese(II) ion, $\hat{H} = -2J\hat{S}_1\hat{S}_2 - D\hat{S}_{z1}^2$, where D is the axial zero-field splitting parameter for the manganese(II) ion. The exchange integral, J, was found to be equal to $-29.7\ cm^{-1}$ for bpy, $-31.1\ cm^{-1}$ for phen and $-35.8\ cm^{-1}$ for NO_2-phen. These results are commensurate with antiferromagnetic interactions between adjacent metal ions.

KEYWORDS: Magnetic properties, Cu(II), Mn(II), binuclear complexes, oxamido bridging

INTRODUCTION

Heterobinuclear transition-metal complexes are of current interest due to spin-exchange and charge-transfer properties between metal ions and the domains of metalloenzymes and novel magnetic materials.[1–2] It is known that the mononuclear complex *N,N′-bis*(3-aminopropyl)oxamidocopper(II) [Cu(oxpn)] acts as a bidentate chelating agent toward a second metal ion to form binuclear complexes such as $[Cu(oxpn)M(L)_{1-2}](ClO_4)_2$ (M = Cu, Zn, Ni, Co and Mn, L = bpy, phen and NO_2-phen).[3–7] Recently, we have utilized *N,N′-bis*(2-aminoethyl)oxamido copper(II) [Cu(oxae)] as a bidentate mononuclear fragment to prepare binuclear complexes of the type $[Cu(oxae)M(L)_{1-2}](ClO_4)_2$ (M = Cu and Ni, L = bpy, Me_2bpy, phen and NO_2-phen);[8–9] magnetic properties were studied. As an extension of that investigation, we report the synthesis, characterization and magnetism

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of four new complexes [Cu(oxae)Mn(L)$_2$](ClO$_4$)$_2$, [where oxae = *N,N'-bis*(2-aminoethyl)oxamido dianion, L = 2,2'-bipyridyl (bpy), 4,4'-dimethyl-2,2'-bipyridyl (Me$_2$bpy). 1,10-phenanthroline (phen) and 5-nitro-1,10-phenanthroline (NO$_2$-phen)].

EXPERIMENTAL

[Cu(oxae)Mn(bpy)$_2$](ClO$_4$)$_2$

2,2'-Bipyridyl (bpy), 4,4'-dimethyl-2,2'-bipyridyl (Me$_2$bpy), 1,10-phenanthroline (phen) and 5-nitro-1,10-phenanthroline (NO$_2$-phen) of analytical grade were purchased from Peking Chemical Company. Cu(oxae) was synthesized as previously described.[9–10] [Cu(oxae)Mn(bpy)$_2$](ClO$_4$)$_2$ was prepared as follows.

To Cu(oxae) (94.2 mg, 0.4 mmol) stirred in ethanol (5 cm^3) was successively added a solution of Mn(ClO$_4$)$_2\cdot$6H$_2$O (144.8 mg, 0.4 mmol) in ethanol (10 cm^3) and a solution of bpy (125 mg, 0.8 mmol) in ethanol (10 cm^3). After stirring for 5 h, the solution was filtered. Violet-red microcrystals were obtained, washed several times with absolute ethanol and diethyl ether and dried *in vacuo*. Anal., calcd. for $C_{26}H_{28}N_8O_{10}Cl_2CuMn$: C, 38.9; H, 3.5; N, 14.0; Cu, 7.9; Mn, 6.8%. Found: C, 39.0; H, 3.5; N, 14.3; Cu, 7.6; Mn, 6.9%.

[Cu(oxae)Mn(Me$_2$bpy)$_2$](ClO$_4$)$_2$

This complex was obtained as violet-red microcrystals by the same procedure but using Me$_2$bpy instead of bpy. Anal., calc. for $C_{30}H_{36}N_8O_{10}Cl_2CuMn$: C, 42.0; H, 4.2; N, 13.1; Cu 7.4; Mn, 6.4%. Found: C, 41.9; H, 4.3; N, 13.2; Cu, 7.5; Mn, 6.5%.

[Cu(oxae)Mn(phen)$_2$](ClO$_4$)$_2$

This complex was prepared in the same way by using phen instead of bpy. Violet-red microcrystals were obtained. Anal., calc. for $C_{30}H_{28}N_8O_{10}Cl_2CuMn$: C, 42.4; H, 3.3; N, 13.2; Cu, 7.5; Mn, 6.5%. Found: C, 42.6; H, 3.3; N, 13.3; Cu, 7.3; Mn, 6.4%.

[Cu(oxae)Mn(NO$_2$-phen)$_2$](ClO$_4$)$_2$

This complex was prepared in the same way by replacing bpy with NO$_2$-phen. Violet-red microcrystals were obtained. Anal., calc. $C_{30}H_{26}N_{10}O_{14}Cl_2CuMn$: C, 38.3; H, 2.8; N, 14.9; Cu, 6.8; Mn, 5.8%. Found: C, 38.6; H, 2.9; N, 15.0; Cu, 6.9; Mn, 5.6%.

Measurements

Elemental analyses for carbon, hydrogen and nitrogen were carried out with a Perkin-Elmer elemental analyser, Model 240. Metal contents were determined by EDTA titration. IR spectra were measured on a Shimadzu IR spectrophotometer, Model 408, using KBr pellets, and the electronic spectra (AcCN solution) were measured on a Hitachi-240 spectrophotometer. The molar conductances were measured with a DDS-11A conductometer. Variable temperature magnetic susceptibilities were measured on a vibrating sample magnetometer, Model CF-1. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms, and the magnetic moments were calculated using the equation $\mu = 2.828(\chi_M T)^{1/2}$

RESULTS AND DISCUSSION

Composition and Coordination Environment

Elemental analyses indicate that the reaction of Cu(oxae) with $Mn(ClO_4)_2 \cdot 6H_2O$ and L (bpy, Me_2bpy, phen or NO_2-phen) yields the heterobinuclear complexes $[Cu(oxae)Mn(L)_2](ClO_4)_2$. For the four complexes, the molar conductance values (see Table 1) fall in the expected range for 1:2 electrolytes,[11] indicating that the two perchlorate anions are situated outside the metal coordination sphere. The significant bands from the IR spectra of the complexes are given in Table 1. It is noted that the carbonyl stretching vibration at 1615 cm^{-1} for the mononuclear fragment Cu(oxae) was considerably shifted towards higher frequencies (*ca* 20–25 cm^{-1}) in their binuclear complexes. Therefore, in general, when the deprotonated amide nitrogen is coordinated to the metal ion, its amide I band shifts considerably towards lower wavenumbers. 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). Although the amide I band is due to a composite N—C=O vibration, it can essentially be seen as $\nu_{C=O}$; it is likely that the bond order of C=O in the binuclear complexes is higher than in its corresponding mononuclear complex. This shift has often been used as definite proof of an oxamide-bridge.[3] On the other hand, the $-NH_2$ vibration at 3250 cm^{-1} for Cu(oxae) was present for all complexes and a broad, intense band was observed at 1085 cm^{-1}, which is typical for a non-coordinated perchlorate ion.[12] This is consistent with the measured conductance data. The electronic absorption spectral data for these complexes (AcCN solution) are given in Table 1. A broad band in the visible range can be observed, attributed to the d—d transitions of copper(II). The absorption bands in the short wavelength range (see Table 1) may be attributed to a charge transfer band. Further investigation of these and similar systems is still required in order to obtain a detailed assignment for charge transfer. The coordination environment of manganese(II) in the complex is most likely a

Table 1 Physical data for the complexes.

Complex	Colour	Λ_M ($\Omega^{-1}cm^2$ mol^{-1}) in AcCN	IR (cm^{-1}) -NH_2	C=O	ClO_4^-	UV (10^3 cm^{-1}) d-d(ε mol^{-1}cm^{-1}L)	CT[a]	
Cu(oxac)	violet		3250	1615		18.7		
$[Cu(oxae)Mn(bpy)_2](ClO_4)_2$	violet-red	299	3250	1640	1085	19.4 (173)	23.6	27.9
$[Cu(oxae)Mn(Me_2bpy)_2(ClO_4)_2$	violet-red	294	3250	1635	1085	19.6 (168)	23.6	27.9
$[Cu(oxae)Mn(phen)_2](ClO_4)_2$	violet-red	299	3250	1635	1085	19.0 (140)	23.7	28.0
$[Cu(oxae)Mn(NO_2\text{-phen})_2](ClO_4)_2$	violet-red	299	3250	1640	1085	19.2 (389)	24.2	28.6

[a] $\varepsilon > 10^3$ mol^{-1} cm^{-1}L

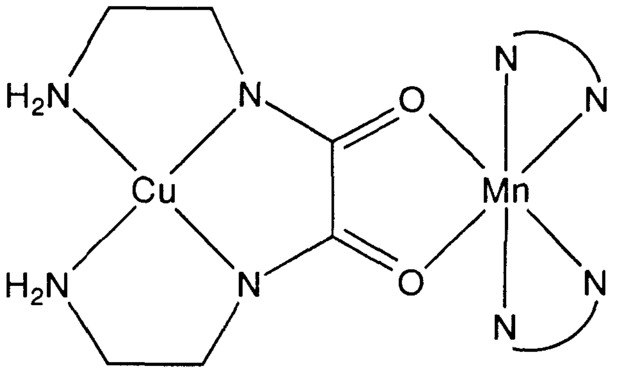

Figure 1 Supposed structure of $[Cu(oxae)Mn(L)_2]^{2+}$ (L = bpy, Me_2bpy, phen or NO_2-phen).

distorted octahedron owing to the fact that the two bidentate ligands (bpy, 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 d-d transitions of manganese(II) ($^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^4T_{2g}(G)$, $^4A_{1g}$ . . .) are spin-forbidden, in the spectra of the Cu(II)-Mn(II) complexes no characteristic band for manganese(II) was found. Based on the composition of these complexes, IR, electronic spectra and conductivity measurements, the complexes are proposed to have an oxamido-bridged structure, as shown in Figure 1.

Spin-Exchange Interactions in Cu(II)-Mn(II) Complexes

The temperature dependences of the susceptibilities and magnetic moments are shown in Figures 2–4. The moments decrease steadily with decreasing temperature, implying the existance of an antiferromagnetic spin-exchange interaction within each molecule. Based on the Heisenberg model, the data for Cu(II)-Mn(II) binuclear

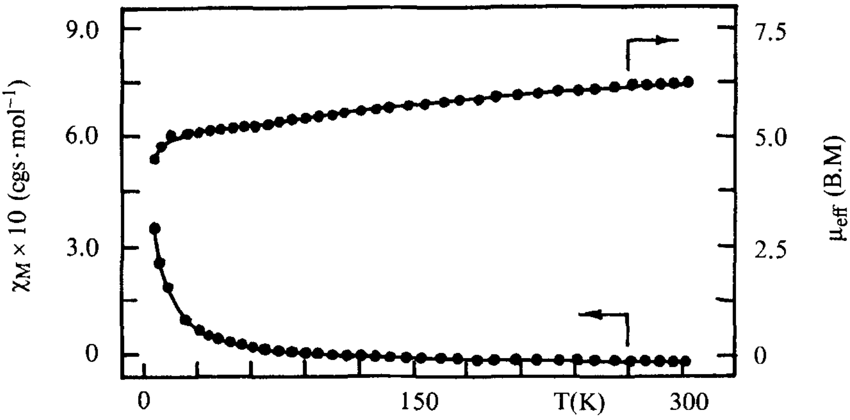

Figure 2 Temperature variation of the magnetic susceptibility and magnetic moment of $[Cu(oxae)Mn(bpy)_2](ClO_4)_2$. This curve was calculated using equation (*3*).

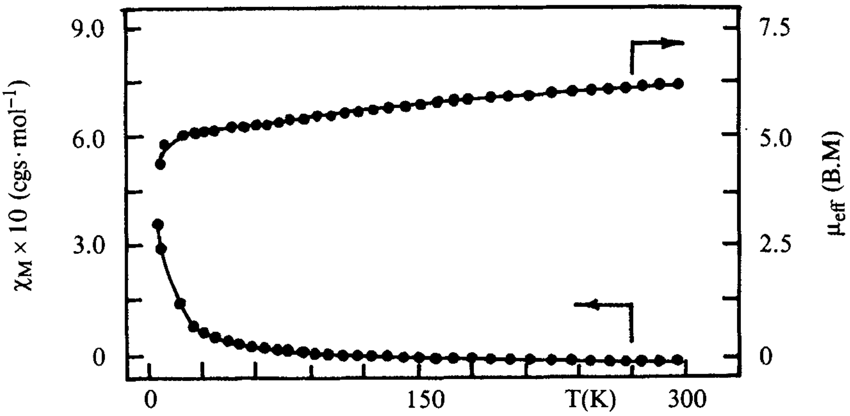

Figure 3 Temperature variation of the magnetic susceptibility and magnetic moment of $[Cu(oxae)Mn(phen)_2](ClO_4)_2$. This curve was calculated using equation (*3*).

complexes were initially analysed by equation (*1*) with an equal g value and equation (*2*) with two different g values,

$$\chi_M = \frac{Ng^2\beta^2}{kT}\left[\frac{10\exp(-6J/kT) + 28}{5\exp(-6J/kT) + 7}\right] \qquad (1)$$

$$\chi_M = \frac{2N\beta^2}{kT}\left[\frac{5g_2^2 + 14g_3^2\exp(6J/kT)}{5 + 7\exp(6J/kT)}\right] \qquad (2)$$

where g_3 and g_2 are g factors associated with the $S = 3$ and 2 states and may be related to the local g_{Cu} and g_{Mn} values,[2,13] $g_2 = (7g_{Mn} - g_{Cu})/6$ and $g_3 = (5g_{Mn} - g_{Cu})/6$.

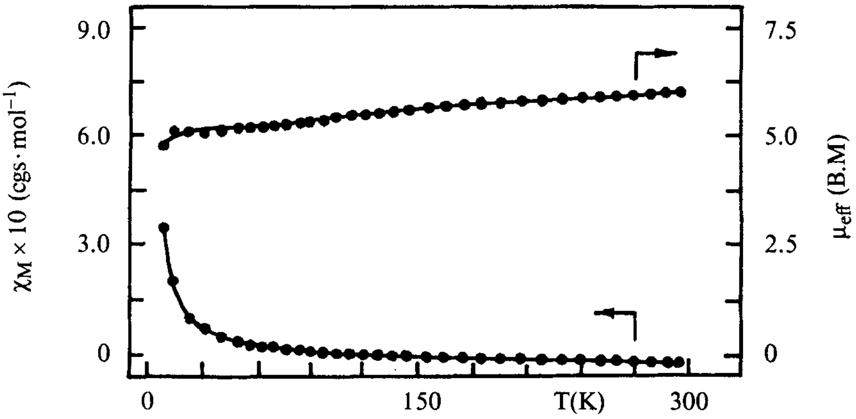

Figure 4 Temperature variation of the magnetic susceptibility and magnetic moment of $[Cu(oxae)Mn(NO_2\text{-}phen)_2](ClO_4)_2$. This curve was calculated using equation (*3*).

However, the data below *ca* 38K did not satisfactorily fit equations (*1*) and (*2*). This may be attributed to the single ion zero-field interaction of the manganese(II) ion.[14] We therefore adopted a susceptibility equation based on the modified Heisenberg operator, $\hat{H} = -2J\hat{S}_1\hat{S}_2 - D\hat{S}_{z1}{}^2$, where D is the axial zero-field splitting parameter for the Mn(II) ion.[14–15] The expression for the susceptibility χ_M is given by equation (*3*).

$$\chi_M = \frac{(Ng^2\beta^2/kT)[18\exp(A) + 8\exp(B) + 2\exp(C) + 8\exp(E) + 2\exp(F)]}{[2\exp(A) + 2\exp(B) + 2\exp(C) + \exp(D) + 2\exp(E) + 2\exp(F) + \exp(G)]}$$

$$\begin{aligned} A &= (12J + 25D/4)/(kT) \\ B &= [9J + 17D/4 + (9J^2 - 8DJ + 4D^2)^{1/2}]/(kT) \\ C &= [9J + 5D/4 + (9J^2 - 2DJ + D^2)^{1/2}]/(kT) \\ D &= (12J + D/4)/(kT) \\ E &= [9J + 17D/4 - (9J^2 - 8DJ + 4D^2)^{1/2}]/(kT) \\ F &= [9J + 5D/4 - (9J^2 - 2DJ + D^2)^{1/2}]/(kT) \\ G &= (6J + D/4)/(kT) \end{aligned} \qquad (3)$$

As shown in Figures 2–4, good least-squares fits to the experimental data were attained with equation (*3*). The magnetic parameters thus determined are $J = -29.7\ cm^{-1}$, $g = 2.16$, $D = -0.71\ cm^{-1}$ for bpy; $J = -31.1\ cm^{-1}$, $g = 2.16$, $D = -0.71\ cm^{-1}$ for phen; $J = -35.8\ cm^{-1}$, $g = 2.14$, $D = -0.47\ cm^{-1}$ for NO_2-phen. The agreement factors F defined here as $F = \Sigma[(\chi_M)_{obs.} - (\chi_M)_{calc.}]^2/\Sigma(\chi_M)_{obs.}$ are then equal to 5.3×10^{-5} (bpy), 2.8×10^{-4} (phen) and 8.3×10^{-5} (NO_2-phen), respectively. This result also indicates that the complexes $[Cu(oxae)Mn(L)_2]\ (ClO_4)_2$ (L = bpy, phen and NO_2-phen) possess an antiferromagnetic spin-exchange interaction between the metal ions.

To describe the mechanism of the exchange interaction, several models have been proposed.[16–18] According to these models, strict orbital orthogonality results in ferromagnetism ($J > 0$), otherwise an antiferromagnetic coupling ($J < 0$) should be involved in the system. For the present complexes, if the whole molecular symmetry is considered to be C_{2v}, the 3d metallic orbitals of Cu(II) and Mn(II) ions transform[19] as $a_1(d_{z2}$ and $d_{x2-y2})$, $a_2(d_{yz})$, $b_1(d_{xy})$ and $b_2(d_{zx})$. Around the Cu(II) ion, there is just one unpaired electron which occupies the b_1 orbital and around Mn(II) there are five unpaired electrons which populate the a_1, a_2, b_1 and b_2 orbitals. Because there is no orthogonality between b_1(Cu) and b_1(Mn), namely $S = \langle b_1(Cu)|b_1(Mn)\rangle \neq 0$, antiferromagnetic exchange interactions should be observed in these complexes.

We have previously investigated the magnetic behaviour of $[Cu(oxpn)Mn(L)_2]$ $(ClO_4]_2$[7] (where oxpn = *N,N′-bis*(3-aminopropyl)oxamido, L = bpy, phen and NO_2-phen), and obtained the following results for the magnetic interaction: $[Cu(oxae)Mn(bpy)_2](ClO_4)_2$ ($J = -29.7\ cm^{-1}$) > $[Cu(oxpn)Mn(bpy)_2](ClO_4)_2$ ($J = -10.7\ cm^{-1}$); $[Cu(oxae)Mn(phen)_2](ClO_4)_2$ ($J = -31.1\ cm^{-1}$) > $[Cu(oxpn)Mn(phen)_2](ClO_4)_2$ ($J = -15.3\ cm^{-1}$; $[Cu(oxae)Mn(NO_2 \cdot phen)_2](ClO_4)_2$ ($-35.8\ cm^{-1}$) > $[Cu(oxpn)Mn(NO_2\text{-}phen)_2](ClO_4)_2$ ($J = -15.4\ cm^{-1}$).

Acknowledgements

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