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Synthesis, Crystal Structures, and Magnetic Properties of Two Heterobinuclear Complexes with a Dissymmetrical Oxamidate Ligand[1]

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Abstract—Two heterobimetallic compounds $\{[CuLMn(H_2O)_3 \cdot 1.75H_2O]_2\}_n$ (**I**) and $\{[CuLCo(H_2O)_3 \cdot 2H_2O]_2\}_n$ (**II**) (H_4L = N-(2,5-dicarboxyl phenyl)-N'-(2-amino propyl)oxamide) have been synthesized and characterized by IR, elemental analysis, single-crystal X-ray diffraction, and magnetic properties. They crystallize in the triclinic system with space group $P\bar{1}$. The structures of the complexes consist of neutral tetranuclear units formed through *syn-anti* carboxylate bridges in ladder-like chains. The magnetic properties of complexes **I** and **II** indicated antiferromagnetic interaction between the metal ions.

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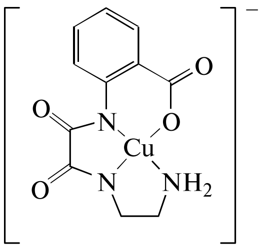
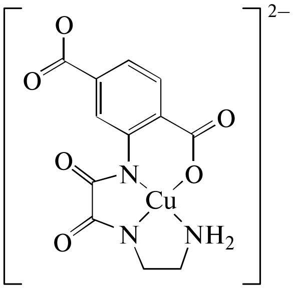
INTRODUCTION

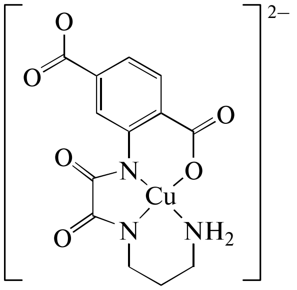
In the past few decades, research on molecular magnetic materials has been of great interest [1–4]. Mixed-metal materials are a major research area for many groups around the world. In order to gain control of both the nuclearity and the topology, a successful strategy is represented by the so-called "complex-as-ligand" approach, utilizing a metal complex as a ligand to coordinate an appropriate additional metal ion [5–9]. Along this line, oxamato copper(II) complexes used for the rational design of heteropolynuclear compounds have received growing attention [10–12]. Recently, we described three mononuclear copper(II) complexes $[CuL]^{n-}$ (L = N-benzoate-N'-(2-aminoethyl)oxamido (Oxbe), 2-(2-(2-aminoethylamino)-2-oxoacetamido)terephthalic acid (Aeoe) and N-(2-aminoterephthalic acid)-N'-(1,3-propanediamine)oxamidate (Aeop):



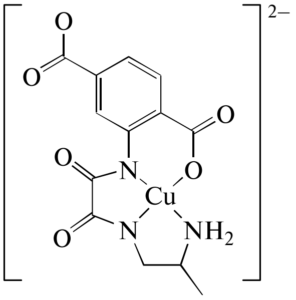
$[Cu(Oxbe)]^-$



$[Cu(Aeoe)]^{2-}$



$[Cu(Aeop)]^{2-}$



$[CuL]^2$

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as precursors for the preparation of both homo- and heterometallic complexes [13–16]. We have now successfully synthesized a new oxamato copper(II) complex CuL (L = N-(2,5-dicarboxyl phenyl)-N'-(2-amido propyl)oxamide) and obtained two new ladder-like chain complexes – $\{[CuLMn(H_2O)_3 \cdot 1.75H_2O]_2\}_n$ (**I**) and $\{[CuLCo(H_2O)_3 \cdot 2H_2O]_2\}_n$ (**II**). The crystal structures and magnetic properties of complexes **I** and **II** have also been investigated.

EXPERIMENTAL

Materials and methods. All reagents were purchased from commercial sources and used without further purification. Elemental analyses for carbon, hydrogen, and nitrogen were performed on a Perkin-Elmer 2400II elemental analyzer. The infrared spectra were recorded on an Avatar-360 spectrometer using KBr pellets in the range of 400–4000 cm^{-1}. Variable temperature magnetic susceptibility data were obtained on microcrystalline samples from 2 to 300 K in a magnetic field of 10 kG, using a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal parameters for all constituent atoms.

Synthesis of the ligand H_4L. A 5 mmol (0.682 g) portion of ethyl oxalyl chloride in 10 mL of THF (THF = tetrahydrofuran) was added dropwise to 40 mL of a THF solution of 5 mmol (0.93 g) of 2-aminoherephthalic acid. After one hour, the mixture was added dropwise into a solution which contained 30 mL of absolute ethanol and 4.5 mL of 1,2-propanediamine at 0°C. The resulting solution was stirred for 3 h, and H_4L was precipitated as a white powder, washed with ethanol and dried under vacuum. The yield was 1.1 g (71%).

For $C_{13}H_{15}N_3O_6$

anal. calcd., %:	C, 50.49;	H, 4.89;	N, 13.59.
Found, %:	C, 50.43;	H, 4.83;	N, 13.66.

Synthesis of the copper(II) precursor (CuL). A 5 mmol (1.546 g) amount of H_4L and 20 mmol (0.8 g) of NaOH were dissolved in 100 mL of water. Then 5 mmol (0.7623 g) of $CuCl_2 \cdot 2H_2O$ was added. The resulting violet-red solution was filtered and concentrated to 20 mL. Then ethanol was added slowly into the filtrate, and $Na_2[CuL] \cdot H_2O$ precipitated as a red polycrystalline powder and was washed with ethanol and dried under vacuum at room temperature. The yield was 2.2 g (89%).

For $C_{13}H_{13}N_3O_7Na_2Cu$

anal. calcd., %:	C, 36.08;	H, 3.03;	N, 9.71.
Found, %:	C, 36.03;	H, 3.01;	N, 9.77.

Synthesis of $\{[CuLMn(H_2O)_3 \cdot 1.75H_2O]_2\}_n$ (I). A 0.1 mmol (0.044 g) amount of $Na_2[CuL] \cdot H_2O$ was dissolved in 15 mL of water, and 15 mL of a DMF solution containing 0.1 mmol (0.0244 g) $Mn(CH_3COO)_2 \cdot 4H_2O$ was added under constant stirring. The resulting blue-violet solution was filtered, and single crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of the solution. The yield was 0.036 g (70%).

For $C_{13}H_{20.50}N_3O_{10.75}MnCu$

anal. calcd., %:	C, 30.66;	H, 4.06;	N, 8.25.
Found, %:	C, 30.72;	H, 4.01;	N, 8.21.

Synthesis of $\{[CuLCo(H_2O)_3 \cdot 2H_2O]_2\}_n$ (II). Complex **II** was prepared in a similar way as **I** except for $CoCl_2 \cdot 6H_2O$ being used instead of $Mn(CH_3COO)_2 \cdot 4H_2O$. The yield was 0.032 g (62%).

For $C_{13}H_{21}N_3O_{11}CuCo$

anal. calcd., %:	C, 30.15;	H, 4.09;	N, 8.11.
Found, %:	C, 30.22;	H, 4.04;	N, 8.07.

X-ray crystallography. The single crystals used for data collection of compounds **I** and **II** were mounted on a Bruker Smart APEX diffractometer with a CCD detector using graphite monochromated MoK_α radiation (λ = 0.71073 Å). Lorentz and polarization factors were applied for the intensity data and absorption corrections were performed using the SADABS program [17]. The crystal structures were solved using the SHELXL program and refined using full matrix least-squares [18]. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with the attached carbons. Crystal data collection and refinement parameters are given in Table 1.

Supplementary material for structures **I** and **II** has been deposited with the Cambridge Crystallographic Data Centre (no. 730894 (**I**), 730895 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

X-ray single crystal structures analyses have revealed that complexes **I** and **II** crystallize in the triclinic system, space group $P\overline{1}$. They are similar in structure and both consist of binuclear neutral molecule and three coordinated water and a solvate water molecules, as shown in Fig. 1. The structural parameters of the CuL fragment in **I** and **II** are almost the same. The Cu ion is in a distorted square pyramidal CuN_3O_2 surrounding. It is coordinated by one oxygen atom and three nitrogen atoms from oxamidate bridges, and the apical position is occupied by another carboxylic oxygen atom with a bond length of 2.554 Å for **I** and 2.516 Å for **II**. These bonds are longer than those in other complexes reported by us [13, 14]. The Cu–N bond lengths range between 1.901(3) and 2.017(3) Å in **I**, 1.894(3) and 2.015(3) Å in **II**. They are comparable with the range found in the literature [13]. Mn(II), and Co(II) are both coordinated by two oxygen atoms from one oxamido ligand, three oxygen atoms from water molecules and one oxygen atom from another carboxylic group. The distances from copper to manganese for **I**, copper to cobalt for **II** are 5.471 and 5.359 Å, respectively. The Mn–O bond lengths are in the range of 2.154(3)–2.233(3) Å, the Co–O bond lengths are 2.086(3)–2.143(3) Å, similar to values reported previously [13, 14].

In complex **I**, as an example, the binuclear molecules are linked by coordinative bonds between carboxylic oxygen atoms and Mn ions to give tetranuclear neutral loops. These tetranuclear neutral loops are further associated by coordinative bonds between carboxylic oxygen atoms and Cu ions to form a new ladder-like chain structure (Fig. 2). Selected bond lengths and angles are listed in Table 2.

The ligand H_4L exhibits a ν(C=O) vibration band of the oxamidate group at ~1636 cm^{-1} [19], a ν_{as}(COO) (ν(COOH)) vibration band at ~1673 cm^{-1} [20], and the bands of the ν(N–H) group (oxamidate group) at ~2986 and 3110 cm^{-1}. These bands are all missing in the spectrum of the three complexes because of loss of the protons of both the COOH and N–H (oxamidate group) groups. The new sharp strong band observed in complexes **I** (1652 cm^{-1}) and **II** (1653 cm^{-1}) is the result of an overlap between ν_{as}(COO) of the ionized carboxylate group and the vibration of the oxamidate group (ν(C=O)) acting in bidendate mode. In addition, the $-NH_2$ vibration for H_4L was present for all complexes and with a small shift from 3426 cm^{-1} for complex **I** and 3422 cm^{-1} for **II**. Such a red shift indicates that the nitrogen atom of $-NH_2$ coordinates to the copper ion.

The magnetic susceptibility of complex **I** has been measured in the range of 2–300 K. At room temperature, the μ_{eff} value of **I** is 5.98 μ_B. Upon cooling, it decreases regularly, approaching a minimum around 2 K with $\mu_{eff} = 4.81\ \mu_B$.

There are two main kinds of magnetic interactions for the present systems, namely: (i) Cu(1)–Mn(1) and $Cu(1)^{\#1}$–$Mn(1)^{\#1}$ through a *cis*-oxamidate bridge; (ii) Cu(1)–$Mn(1)^{\#3}$ and $Mn(1)^{\#1}$–$Cu(1)^{\#2}$ through the *cis-anti* carboxylate oxygen bridge, as shown in Fig. 2.

The interaction (i) in complex **I** is well-known to favor an exceptionally strong antiferromagnetic interaction [21]. For (ii), it is evident that copper(II) orbitals are mismatched for interaction to take place through the *syn-anti* carboxylate group, since the exchange pathway Cu(II)–O–C–O–Mn(II) involves an axial position in the Cu(1) (d_{z^2}) direction [22]. This fact should cause a weak magnetic interaction.

Table 1. Crystallographic data and refinement parameters for complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	509.30	517.80
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.3093(17)	9.2330(10)
b, Å	9.6018(18)	9.4977(10)
c, Å	11.285(2)	11.2446(12)
α, deg	81.693(3)	82.633(2)
β, deg	72.698(3)	73.036(2)
γ, deg	82.159(3)	82.067(2)
V, $Å^3$	948.3(3)	930.10(17)
Z	2	2
ρ_{calcd}, g cm^{-3}	1.784	1.849
$\mu(MoK_\alpha)$, mm^{-1}	1.850	2.101
T, K	293(2)	293(2)
λ, Å	0.71073	0.71073
Index ranges	$-11 \le h \le 8$, $-11 \le k \le 11$, $-13 \le l \le 12$	$-10 \le h \le 10$, $-11 \le k \le 11$, $-13 \le l \le 7$
Reflections collected	4898	4630
Independent reflection (R_{int})	3320 (0.0151)	3255 (0.0165)
Reflections with $I \ge 2\sigma(I)$	2672	2548
Parameters	271	271
Goodness-of-fit	1.077	1.201
R_1, wR_2 ($I \ge 2\sigma(I)$)*	0.0419, 0.1129	0.0410, 0.1094
R_1, wR_2 (all data)*	0.0545, 0.1190	0.0565, 0.1153
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* $Å^{-3}$	0.552/–0.412	0.400/–0.484

$* R_1 = \sum||F_o| - |F_c||/\sum|F_o|,\ wR_2 = \left[\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o^2)^2\right]^{1/2}$.

On the basis of these considerations, we take the system as an isolated binuclear moiety with (i) Cu(1)–Mn(1) and $Cu(1)^{\#1}$–$Mn(1)^{\#1}$ through a *cis*-oxamidate bridge and take (ii) into account as interactions between these binuclear moieties. The magnetic analysis was then carried out by using the theoretical expression of the magnetic susceptibility deduced from the spin Hamiltonian $\hat{H} = -2J\hat{S}_{Cu(1)}\hat{S}_{Mn(1)}$.

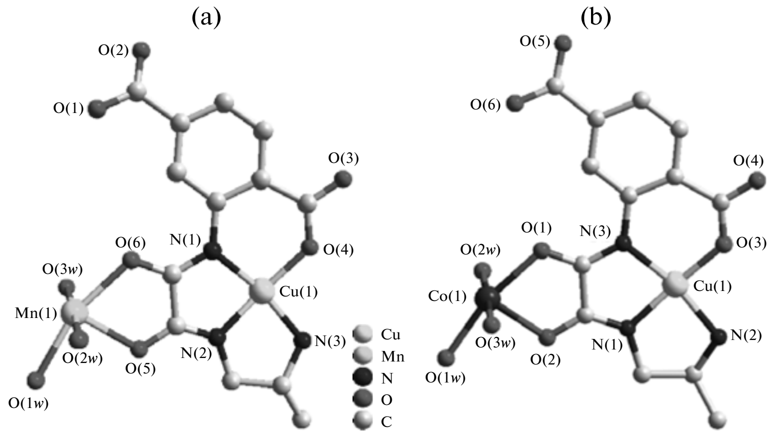

Fig. 1. Molecular structures of complexes **I** (a) and **II** (b). The hydrogen atoms and solvent water molecules are omitted for clarity.

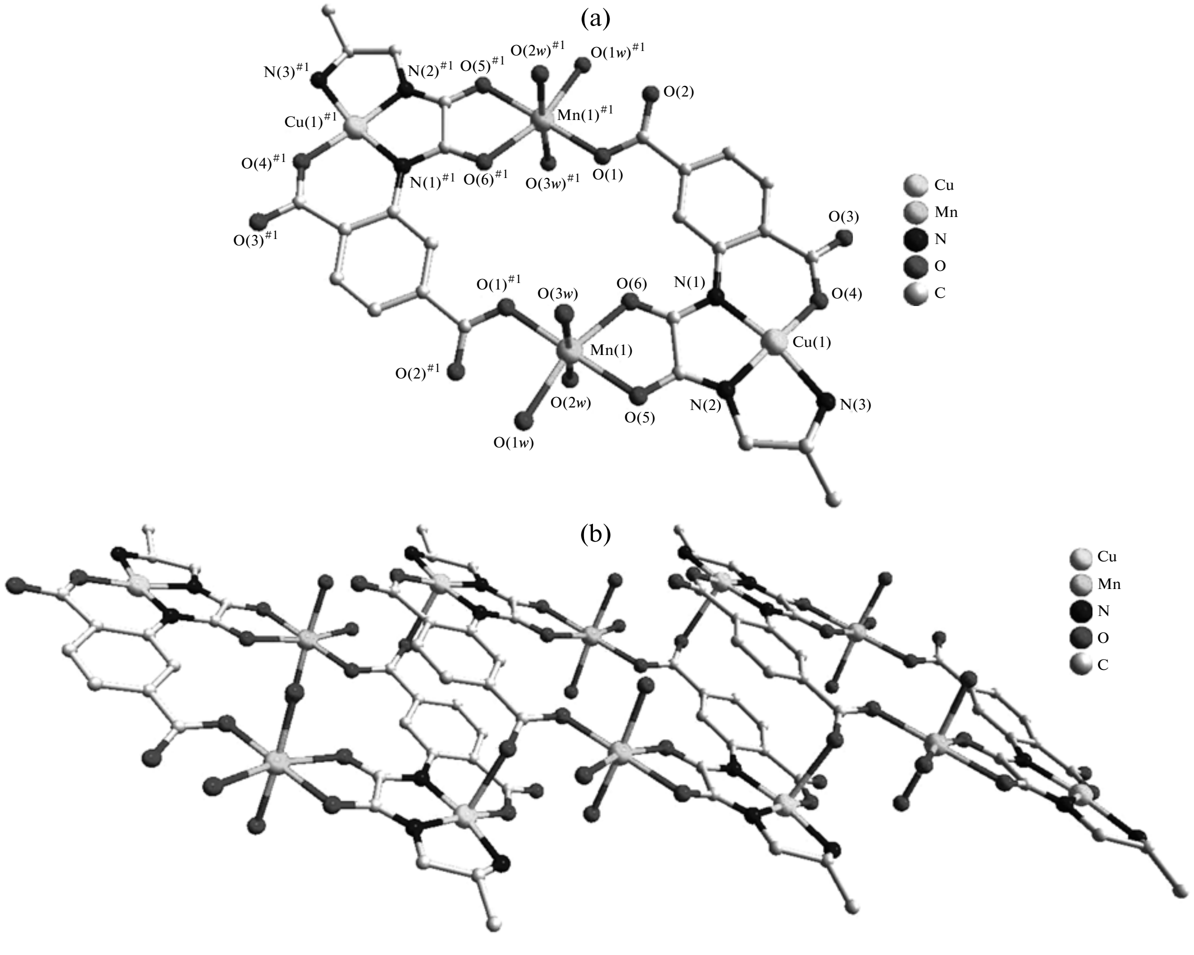

Fig. 2. The tetranuclear unit structure of complex (a) **I**; 1D ladder-like chain structure of complex **I** (b). The hydrogen atoms and solvent water molecules are omitted for clarity. Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x + 2, -y, -z$.

Table 2. Selected bond lengths (Å) and angles (deg) for complex **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
		I	
Cu(1)–O(4)	1.892(3)	Cu(1)–N(2)	1.901(3)
Cu(1)–N(1)	1.967(3)	Cu(1)–N(3)	2.017(3)
Mn(1)–O(1)$^{\#1}$	2.154(3)	Mn(1)–O(2*w*)	2.167(3)
Mn(1)–O(6)	2.182(3)	Mn(1)–O(5)	2.190(3)
Mn(1)–O(3*w*)	2.195(4)	Mn(1)–O(1*w*)	2.233(3)
		II	
Cu(1)–O(3)	1.886(3)	Cu(1)–N(1)	1.894(3)
Cu(1)–N(3)	1.971(3)	Cu(1)–N(2)	2.015(3)
Co(1)–O(3*w*)	2.086(3)	Co(1)–O(2)	2.091(3)
Co(1)–O(6)$^{\#1}$	2.092(3)	Co(1)–O(1)	2.111(3)
Co(1)–O(2*w*)	2.116(3)	Co(1)–O(1*w*)	2.143(3)
Angle	ω, deg	Angle	ω, deg
		I	
O(4)Cu(1)N(1)	95.47(12)	N(2)Cu(1)N(1)	85.15(13)
O(4)Cu(1)N(3)	94.99(12)	N(2)Cu(1)N(3)	83.84(13)
N(1)Cu(1)N(3)	168.40(13)	O(1)$^{\#1}$Mn(1)O(2*w*)	89.42(12)
O(1)$^{\#1}$Mn(1)O(6)	102.96(10)	O(2*w*)Mn(1)O(6)	90.85(12)
O(1)$^{\#1}$Mn(1)O(5)	178.52(11)	O(2*w*)Mn(1)O(5)	89.96(12)
O(6)Mn(1)O(5)	75.70(10)	O(1)$^{\#1}$Mn(1)O(3*w*)	86.44(16)
O(2*w*)Mn(1)O(3*w*)	175.86(14)	O(6)Mn(1)O(3*w*)	90.09(13)
O(5)Mn(1)O(3*w*)	94.17(15)	O(1)$^{\#1}$Mn(1)O(1*w*)	94.22(11)
O(2*w*)Mn(1)O(1*w*)	86.80(12)	O(6)Mn(1)O(1*w*)	162.64(10)
O(5)Mn(1)O(1*w*)	87.09(10)	O(3*w*)Mn(1)O(1*w*)	93.50(13)
		II	
O(3)Cu(1)N(3)	95.69(12)	N(1)Cu(1)N(3)	85.09(13)
O(3)Cu(1)N(2)	94.85(12)	N(1)Cu(1)N(2)	83.65(13)
N(3)Cu(1)N(2)	167.83(13)	O(3*w*)Co(1)O(2)	89.76(11)
O(3*w*)Co(1)O(6)$^{\#1}$	90.67(11)	O(2)Co(1)O(6)$^{\#1}$	178.07(11)
O(3*w*)Co(1)O(1)	91.30(11)	O(2)Co(1)O(1)	79.17(10)
O(6)$^{\#1}$Co(1)O(1)	98.94(10)	O(3*w*)Co(1)O(2*w*)	178.66(13)
O(2)Co(1)O(2*w*)	91.57(13)	O(6)$^{\#1}$Co(1)O(2*w*)	87.99(14)
O(1)Co(1)O(2*w*)	88.80(13)	O(3*w*)Co(1)O(1*w*)	87.39(12)
O(2)Co(1)O(1*w*)	87.84(10)	O(6)$^{\#1}$Co(1)O(1*w*)	94.05(11)
O(1)Co(1)O(1*w*)	166.95(11)	O(2*w*)Co(1)O(1*w*)	92.81(13)

* Symmetry codes: $^{\#1}$ $-x + 2, -y, -z$ for **I**; $^{\#1}$ $-x + 2, -y + 1, -z + 1$ for **II**.

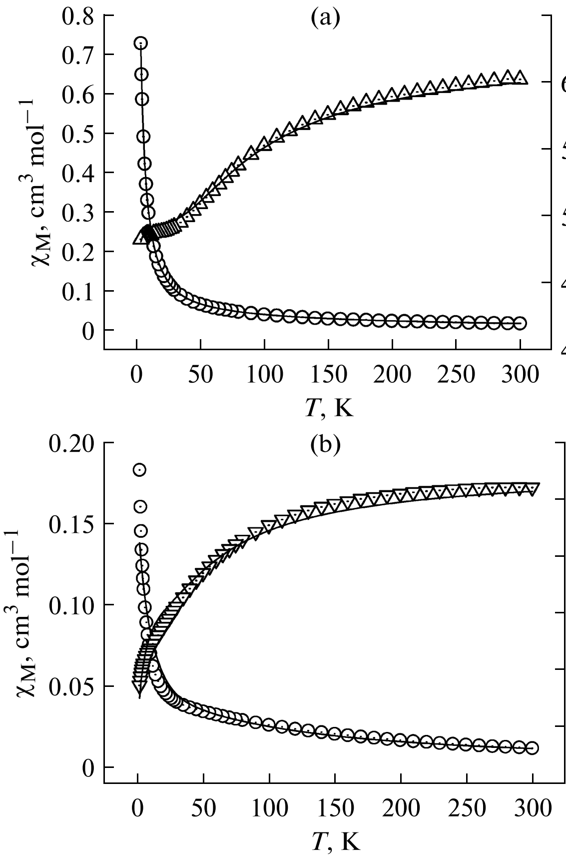

Fig. 3. χ_M and μ_{eff} versus T plots for complexes **I** (a) and **II** (b).

The expression of the magnetic susceptibility for a Cu–Mn system is

$$\chi_M = \frac{Ng^2\beta^2}{KT}\left[\frac{10\exp(-6J/KT) + 28}{5\exp(-6J/KT) + 7}\right] + N_\alpha,$$
$$N_\alpha = 200 \times 10^{-6}\ \text{cm}^3\ \text{mol}^{-1}.$$

And further using molecular field approximation to deal with magnetic exchange interactions between the binuclear systems

$$\chi'_M = \frac{\chi_M}{1 - (2zj'/Ng^2\beta^2)\chi_M},$$

where J is the exchange integral between Cu and Mn ions within the binuclear moiety, zj' is the magnetic interactions between binuclear systems. N_α is the temperature independent paramagnetism. The best fitting for the experimental data gives $J = -17.7$ cm^{-1}, $g = 2.03$, $zj' = -0.05$ cm^{-1}. The agreement factor $R = \sum(\chi_{obsd} - \chi_{calcd})^2/\sum\chi^2_{obsd}$ is 9.56×10^{-5}, which corresponds to a good match as can be seen in Fig. 3a. The negative J value suggests that the interactions between Cu and Mn ions are antiferromagnetic.

The magnetic behavior of complex **II** was measured in the temperature range 2–300 K and is indicative of an overall antiferromagnetic coupling, as shown in Fig. 3b. The room temperature value for μ_{eff} is 5.19 μ_B. Upon cooling the μ_{eff} value decreases regularly, approaching a minimum around 2 K with $\mu_{eff} = 1.71$ μ_B.

The principle of the theory model about the Cu–Co system is similar to the Cu–Mn system described above. We also think approximately the system also as an isolated binuclear moiety. The magnetic analysis was then carried out by using the theoretical expression of the magnetic susceptibility deduced from the spin Hamiltonian $\hat{H} = -2J\hat{S}_{Cu1}\hat{S}_{Co1}$. The expression of the magnetic susceptibility is

$$\chi_M = \frac{Ng^2\beta^2}{KT}\left[\frac{10 + 2\exp(-4J/KT)}{5 + 3\exp(-4J/KT)}\right] + N_\alpha,$$
$$N_\alpha = 200 \times 10^{-6}\ \text{cm}^3\ \text{mol}^{-1}.$$

And further using molecular field approximation to deal with magnetic exchange interactions between the binuclear units

$$\chi'_M = \frac{\chi_M}{1 - (2zj'/Ng^2\beta^2)\chi_M},$$

where J is the magnetic exchange interaction transferred through the *cis*-oxamidate bridge between Cu and Co ions, zj' is the magnetic interactions between binuclear systems. N_α is the temperature independent paramagnetism. The best-fit parameters are $J = -19.7$ cm^{-1}, $g = 2.61$, $zJ' = -4.1$ cm^{-1}. Agreement factor $R = \sum(\chi_{obsd} - \chi_{calcd})^2/\sum\chi^2_{obsd}$ is 6.33×10^{-3}. The negative J value suggests that the interactions between Cu^{2+} and Co^{2+} ions are antiferromagnetic.

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