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SYNTHESES AND MAGNETISM OF TRINUCLEAR COPPER(II) 1,2-ETHYLENEBIS(OXAMIDO) COMPLEXES

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Abstract—Four novel trinuclear copper(II) complexes have been synthesized, namely $\{[Cu(ebo)][Cu(L)]_2\}(ClO_4)_2$, where ebo denotes 1,2-ethylenebis(oxamido) and L is 2,2′-bipyridyl (bpy), 4,4′-dimethyl-2,2′-bipyridyl (Me_2 bpy), 1,10-phenanthroline (phen) or 5-nitro-1,10-phenanthroline (NO_2-phen). Based on IR, elemental analyses, conductivity measurements and electronic spectra these complexes are proposed to have oxamido-bridged structures and to consist of three copper(II) ions in which each metal ion has a square planar environment. The temperature dependence of the magnetic susceptibility of $\{[Cu(ebo)][Cu(NO_2\text{-phen})]_2\}(ClO_4)_2 \cdot 2H_2O$ has been studied in the 4–200 K range, giving the exchange integral $J = -80.9$ cm^{-1}. The result revealed the operation of an antiferromagnetic spin-exchange interaction between the adjacent copper ions.

The study of bridged polynuclear complexes is an active field of coordination chemistry.[1,2] This research work would be helpful for understanding the structure and chemical features governing electronic exchange coupling through multiatom bridging ligands. Although there are some difficulties in synthesizing trinuclear complexes, some trinuclear copper(II) complexes have been prepared and characterized.[3–13] In order to provide more examples of this kind with a new bridging group, we used a "metal complex as ligand" technique[14] to synthesize four trinuclear copper(II) complexes, $\{[Cu(ebo)][Cu(L)]_2\}(ClO_4)_2$ [L = 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)], where ebo stands for the 1,2-ethylenebis(oxamido).

EXPERIMENTAL

Materials

All starting materials were purchased from the Peking Chemical Company and were of reagent grade. Although Nonoyama *et al.*[15] described the procedure for synthesis of copper(II) mononuclear dianion $[Cu(ebo)]^{2-}$, the pure $Na_2[Cu(ebo)]$ could not be obtained. We have used a modification of this procedure in our study.

$Cu(NO_3)_2 \cdot 3H_2O$ (1.2 g, 5 mmol) and 1,2-ethylenebis(oxamate) (1 g, 5 mmol) were stirred in DMSO (100 cm^3). An aqueous solution (10 cm^3) of NaOH (0.24 g, 6 mmol) was added dropwise with stirring. After *ca* 2 h, the rose–red precipitate thus formed was filtered off and washed several times with absolute ethanol. Violet–red microcrystals of $Na_2[Cu(ebo)] \cdot 2H_2O$ can be recrystallized from water (pH = 11). Found: C, 21.1; H, 2.8; N, 16.2. Calc. for $C_6H_6N_4O_4Na_2Cu \cdot 2H_2O$: C, 21.0; H, 2.9; N, 16.3%.

Preparation of $\{[Cu(ebo)][Cu(bpy)]_2\}(ClO_4)_2 \cdot 2H_2O$

To $Na_2[Cu(ebo)] \cdot 2H_2O$ (137.4 mg, 0.4 mmol) stirred in absolute 2-propanol (5 cm^3) in presence of ethyl orthoformate was successively added a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (296.4 mg, 0.8 mmol) in absolute 2-propanol (10 cm^3) and bpy (124.9 mg, 0.8 mmol) in absolute 2-propanol (10 cm^3). After stirring for 3 h at 60°C the green microcrystals thus

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formed were filtered off, washed several times with absolute methanol and diethyl ether and dried *in vacuo*. Found: C, 33.2; H, 2.7; N, 11.9; Cu, 20.2. Calc. for $C_{26}H_{22}N_8O_{12}Cl_2Cu_3 \cdot 2H_2O$: C, 33.4, H, 2.8; N, 12.0; Cu, 20.4%.

Preparation of $\{[Cu(ebo)][Cu(Me_2bpy)]_2\}(ClO_4)_2 \cdot 3H_2O$

This complex was obtained as green microcrystals by the same procedure but using Me_2bpy instead of bpy. Found: C, 35.5; H, 3.7; N, 11.0; Cu, 18.7. Calc. for $C_{30}H_{30}N_8O_{12}Cl_2Cu_3 \cdot 3H_2O$: C, 35.7; H, 3.6; N, 11.1; Cu, 18.8%.

Preparation of $\{[Cu(ebo)][Cu(phen)]_2\}(ClO_4)_2 \cdot 2H_2O$

This complex was prepared in the same way but using phen instead of bpy and methanol instead of 2-propanol. Green microcrystals were obtained. Found: C, 36.5; H, 2.5; N, 11.6; Cu, 19.6. Calc. for $C_{30}H_{22}N_8O_{12}Cl_2Cu_3 \cdot 2H_2O$: C, 36.6; H, 2.7; N, 11.4; Cu, 19.5%.

Preparation of $\{[Cu(ebo)][Cu(NO_2\text{-phen})]_2\}(ClO_4)_2 \cdot 2H_2O$

This complex was obtained in the same way but replacing bpy with NO_2-phen and 2-propanol with methanol. Green microcrystals were obtained. Found: C, 33.6; H, 2.2; N, 13.0; Cu, 17.7. Calc. for $C_{30}H_{20}N_{10}O_{16}Cl_2Cu_3 \cdot 2H_2O$: C, 33.5; H, 2.3; N, 13.1; Cu, 17.8%.

Measurements

Elemental analyses of carbon, hydrogen and nitrogen were performed with a Perkin–Elmer Model 240 elemental analyser. Metal contents were determined by EDTA titration. IR spectra were measured on a Shimadzu Model 480 IR spectrophotometer, using KBr pellets, and the electronic spectra (DMF) were measured on a Hitachi-240 spectrophotometer. Reflectance spectra were measured on a Hitachi Model 340 spectrophotometer. The molar conductance was measured with a DDS-11A conductometer. Variable temperature magnetic susceptibility was 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 $\mu_{eff} = 2.828(XT)^{1/2}$. ESR spectra were measured with a JES-FEIXG ESR apparatus using the X-band.

RESULTS AND DISCUSSION

General characterization

Elemental analyses indicated that the reaction of $Na_2[Cu(ebo)] \cdot 2H_2O$ with $Cu(ClO_4)_2 \cdot 6H_2O$ and bpy, Me_2bpy, phen or NO_2-phen yielded the trinuclear complexes, the molar conductance values (see Table 1) falling in the expected range for 1 : 2 electrolytes,[16] indicating that the two perchlorate anions are outside the coordination sphere. The significant bands in the IR spectra of these complexes are given in Table 1. Bands at 1590–1620 cm^{-1} may be attributable to the central bridging oxamido ligand (vs broad).[17] A broad intense band

Table 1. Physical data for complexes

			IR (cm^{-1})			UV		
		Λ_M	—OH	C=O		λ (nm)/ε_{max} (M^{-1} cm^{-1})		μ/B.M.
Complex[a]	Colour	(Ω^{-1} cm^2 mol^{-1})	—NH	C=N	ClO_4^-	*d–d*	CT	(*T*/K)
1	green	141	3400	1600	1100	590	226	1.52
						(324)	(18670)	(293.4)
2	green	145	3400	1600	1100	594	262	1.51
						(360)	(15630)	(293.2)
3	green	146	3400	1600	1100	596	270	1.49
						(322)	(34530)	(293.2)
4	green	140	3400	1600	1100	597	263	1.47
						(320)	(25210)	(293.3)

[a] **1** $\{[Cu(ebo)][Cu(bpy)]_2\}(ClO_4)_2 \cdot 2H_2O$; **2** $\{[Cu(ebo)][Cu(Me_2bpy)]_2\}(ClO_4)_2 \cdot 3H_2O$; **3** $\{[Cu(ebo)][Cu(phen)]_2\}(ClO_4)_2 \cdot 2H_2O$; **4** $\{[Cu(ebo)][Cu(NO_2\text{-phen})]_2\}(ClO_4)_2 \cdot 2H_2O$.

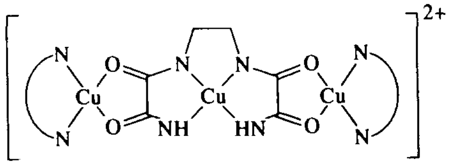

Fig. 1. Proposed chemical structure of [Cu(ebo)(CuL)$_2$]$^{2+}$ (L = bpy, Me$_2$bpy, phen and NO$_2$-phen).

at 1100 cm^{-1} and a sharper one at 610 cm^{-1} were also observed. The lack of any splitting suggests the presence of non-coordinated tetrahedral ClO_4^-. In addition, a broad absorption band of the complexes at *ca* 3400 cm^{-1} indicates the presence of lattice water, and a single absorption of medium intensity is observed at 3340 cm^{-1} [ν(N—H) stretching band] for all complexes, revealing the existence of N—H amide groups. The electronic absorption spectral data (DMF solution) for these complexes are given in Table 1, which are essentially similar to the reflectance spectra in solid state. This suggests that these complexes do not dissociate into their component parts in DMF. As shown in Table 1, a strong absorption in the UV range and a weak absorption in the visible range can be observed. The former may be attributed to the charge-transfer absorption bands which may be due to the spin exchange interaction between the copper(II) ions through the π-path orbital set up by the oxamide bridge. This requires more detailed study.[18] The latter may be attributed to the *d–d* transition of the copper(II) ions which is consistent with a square-planar environment. Based on the discussion above these complexes are proposed to have an extended oxamido-bridged structure and to contain three copper(II) ions in which each copper(II) ion situated in a planar environment,[18] as shown in Fig. 1. The X-band powder ESR spectra at room temperature for these complexes exhibit a similar band and the g values obtained are summarized in Table 2.

Magnetic properties

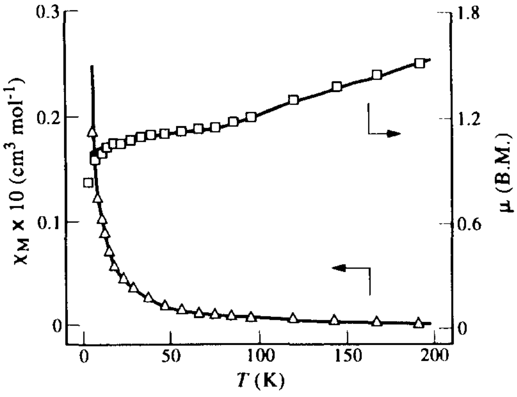

Fig. 2. Temperature variation of the magnetic susceptibility and magnetic moment for {[Cu(ebo)][Cu(NO$_2$-phen)]$_2$}(ClO$_4$)$_2\cdot$2H$_2$O. The curve is drawn based on eq. (1) using the magnetic parameter given in the text.

The observed magnetic moment per mole copper(II) atom for the trinuclear complexes at room temperature (see Table 1) is 1.52, 1.51, 1.49 and 1.47 B.M. for (**1**)–(**4**), respectively, which are lower than the spin-only value (1.73 B.M.), implying the operation of an antiferromagnetic spin exchange interaction. The slight difference among magnetic data at room temperature shows that similar structural terminal ligands have little effect on the magnetic behaviour of these complexes. In order to understand quantitatively the magnitudes of spin-exchange interaction, the temperature dependence of magnetic susceptibility for {[Cu(ebo)][Cu(NO$_2$-phen)]$_2$}(ClO$_4$)$_2\cdot$H$_2$O were measured and are shown in Fig. 2. The magnetic analysis was performed by using the susceptibility equation based on the spin Hamiltonian, $\hat{H} = -2J(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_2\cdot\hat{S}_3) - 2J'\hat{S}_1\cdot\hat{S}_3$, assuming that J represents the exchange integrals between the neighbouring copper ions ($J_{12} = J_{23} = J$) and J' describes the integral between the terminal copper nuclei within the trinuclear complex ($J' = J_{13}$).[18–20] The susceptibility equation for the trinuclear copper(II) system ($S_1 = S_2 = S_3 = 1/2$) is given by[22,23]

$$X_A = \frac{Ng^2\beta^2}{12K(T-\theta)}\ -$$

Table 2. ESR data for trinuclear complexes at room temperature

Complex	g	g	g
1 {[Cu(ebo)][Cu(bpy)]$_2$}(ClO$_4$)$_2\cdot$2H$_2$O	2.09	2.04	2.06
2 {[Cu(ebo)][Cu(Me$_2$bpy)]$_2$}(ClO$_4$)$_2\cdot$3H$_2$O	2.12	2.04	2.07
3 {[Cu(ebo)][Cu(phen)]$_2$}(ClO$_4$)$_2\cdot$2H$_2$O	2.08	2.05	2.06
4 {[Cu(ebo)][Cu(NO$_2$-phen)]$_2$}(ClO$_4$)$_2\cdot$2H$_2$O	2.10	2.04	2.06

$$\times\left[\frac{10\exp(J/KT)+\exp(-2J/KT)+\exp(-2J'/KT)}{2\exp(J/KT)+\exp(-2J/KT)+\exp(-2J'/KT)}\right]$$

$$\times(1-\rho)+\rho\frac{Ng^2\beta^2}{4KT}+N\alpha$$

where X_A is the magnetic susceptibility per copper(II) ion, J is the exchange integral between the adjacent copper ions, θ is the Curie–Weiss parameter, $N\alpha$ $(=180\times10^{-6}\ \mathrm{cm}^3\ \mathrm{mol}^{-1})$ is the temperature-independent paramagnetism, ρ is the fraction of monomeric copper(II) impurity and other symbols have their conventional meanings. In order to avoid a risk of overparameterizing, we used the g $(=2.06)$ value obtained from ESR measurement. As shown in Fig. 2, a good fit to the experimental data was obtained for $J=-80.9$ cm^{-1}, $J'=-6.18$ cm^{-1}, $\theta=-1.16$ K, $\rho=0.001$. The agreement factor F defined here as $F=\Sigma[(X_M)_{obs.}-(X_M)_{calc.}]^2/\Sigma(X_M)_{obs.}$ is then equal to 1.48×10^{-3}. The result indicates that the complex shows antiferromagnetic spin-exchange interaction within the trinuclear unit.

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