Preparation and Properties of Mixed Ligand Dinuclear Copper(II) Complexes Bridged by Deprotonated Oximato and Hydroxo or Acetato

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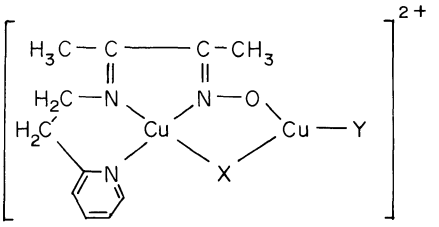
Synopsis. Mixed ligand dinuclear copper(II) complexes bridged by one deprotonated oximato and one hydroxo or two acetato were prepared and characterized according to their magnetic susceptibilities, electric conductivities, visible absorption spectra, and cyclic voltammograms. A very strong antiferromagnetic interaction between two copper(II) ions in hydroxo-bridged complexes has been observed (coupling constants J=−520—−530 cm^{-1}, H=−2$JS_1 \cdot S_2$). Two acetato-containing complexes comprise triply (one deprotonated oximato and two acetato) bridged coppers, which are characterized by J=−130—−235 cm^{-1}.

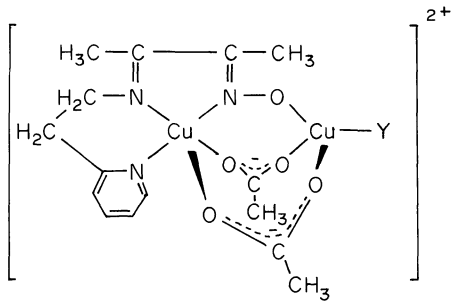
We have recently reported on the preparation, structures and properties of mixed ligand dinuclear copper(II) complexes **1a** and **1b** (structural formula **I**)[1,2] obtained as models for the active site of molluscan oxy-hemocyanin, in which the coordination environment around each copper(II) is non-equivalent to each other.[3,4] As an extension of studies concerning the relationship between the structures and physical properties in these mixed ligand dinuclear copper(II) complexes, the isolation of four copper(II) complexes, **2a**—**2d** (structural formulae **I** and **II**), linked by one deprotonated oximato and one hydroxo or two acetato has been performed. This paper describes the preparation and magnetic, spectroscopic, and electrochemical properties of **2a**—**2d**.



1a (X=N_3^-, Y=bpy[5]), 1b (X=N_3^-, Y=phen[5])

2a (X=OH^-, Y=bpy), 2b (X=OH^-, Y=phen)

I



2c (Y=bpy), 2d (Y=phen)

II

Experimental

Preparation of the Schiff Base L_1 Derived from 2,3-Butanedione-2-oxime and 2-(2-Aminoethyl)pyridine. This ligand was prepared by a method reported in a previous paper.[1]

Preparation of Copper(II) Complexes. $[Cu(L_1)(OH)Cu(bpy)](ClO_4)_2$ (2a) and $[Cu(L_1)(OH)Cu(phen)](ClO_4)_2 \cdot H_2O$(2b). To a mixture of L_1 (0.52 g, 2.5 mmol), 2,2′-bipyridyl (0.39 g, 2.5 mmol) or 1,10-phenanthroline (0.50 g, 2.5 mmol), and $Cu(ClO_4)_2 \cdot 6H_2O$ (1.86 g, 5.0 mmol) in 15 cm^3 of methanol was added sodium hydroxide (0.40 g, 10 mmol). After being stirred at room temperature for 3 h, the reaction mixture was cooled. The obtained brown-green crystalline products were recrystallized from acetone.

2a: Found: C, 35.71; H, 3.46; N, 9.78; Cu, 17.13%. Calcd for $C_{21}H_{23}N_5O_{10}Cl_2Cu_2$: C, 35.85; H, 3.30; N, 9.96; Cu, 18.07%.

2b: Found: C, 37.05; H, 3.38; N, 9.37; Cu, 16.74%. Calcd for $C_{23}H_{23}N_5O_{10}Cl_2Cu_2 \cdot H_2O$: C, 37.05; H, 3.39; N, 9.40; Cu, 17.05%.

$[Cu(L_1)(OAc)_2Cu(bpy)]ClO_4$ (2c). To a mixture of L_1 (0.52 g, 2.5 mmol), 2,2′-bipyridyl (0.39 g, 2.5 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.47 g, 1.25 mmol), and $Cu(OAc)_2 \cdot H_2O$ (0.75 g, 3.75 mmol) in 15 cm^3 of methanol was added sodium hydroxide (0.10 g, 2.5 mmol). The mixture was stirred at room temperature for several hours. After cooling, the resulting precipitate was collected by filtration and recrystallized from acetone. Found: C, 42.98; H, 3.81; N, 9.70; Cu, 17.70%. Calcd for $C_{25}H_{28}N_5O_9ClCu_2$: C, 42.58; H, 4.01; N, 9.93; Cu, 18.03%.

$[Cu(L_1)(OAc)_2Cu(phen)]ClO_4$ (2d). Schiff base L_1 (0.52 g, 2.5 mmol), 1,10-phenanthroline (0.50 g, 2.5 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.47 g, 1.25 mmol), and $Cu(OAc)_2 \cdot H_2O$ (0.75 g, 3.75 mmol) were dissolved in methanol (15 cm^3). To the reaction mixture was added sodium hydroxide (0.10 g, 2.5 mmol); the resulting mixture was stirred for several hours at room temperature. After removing the precipitate, the filtrate was evaporated to give a brown-green microcrystalline product, which was washed with ether. Found: C, 43.54; H, 3.89; N, 9.30; Cu, 17.06%. Calcd for $C_{27}H_{28}N_5O_9ClCu_2 \cdot H_2O$: C, 43.40; H, 4.06; N, 9.38; Cu, 17.01%.

Measurements. Magnetic susceptibility, conductivity, and infrared absorption spectra measurements were carried out as described in a previous paper.[1] The visible absorption spectra

Table 1. Physical Properties of the Complexes

	Complex	μ_{eff}[a]	λ_{max}[b]	Λ[b]
		BM	nm (ε)	S cm^2 mol^{-1}
2a	$[Cu(L_1)(OH)Cu(bpy)](ClO_4)_2$	0.47	605(197), 371(2520)[c]	140
2b	$[Cu(L_1)(OH)Cu(phen)](ClO_4)_2 \cdot H_2O$	0.53	615(204), 370(2780)[c]	142
2c	$[Cu(L_1)(OAc)_2Cu(bpy)]ClO_4$	1.52	654(163), 386(1060)[c]	71
2d	$[Cu(L_1)(OAc)_2Cu(phen)]ClO_4$	1.12	665(169), 387(970)[c]	83

a) Room temperature. b) DMF solutions. c) Shoulder.

were recorded on a Hitachi U-3410 spectrophotometer. Cyclic and steady-state voltammetric measurements were performed with an assembly comprising a Huso HECS 972 microelectrode potentiostat and a Hokuto Denko function generator (HB-104). The working electrode used for the cyclic voltammetry was a glassy carbon disk electrode (B. A. S. 11-2012). Steady-state voltammetry was carried out using a platinum microdisk of 30 μm diameter made by one of us (A. I.). All of the electrochemical measurements were carried out in *N,N*-dimethylformamide (DMF) at 25 °C under a nitrogen atmosphere, tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}) was used as the supporting electrolyte.

Results and Discussion

The magnetic moments at room temperature, visible absorption spectral and electric conductance data for the complexes **2a**—**2d** are given in Table 1. The magnetic moments of complexes **2a** and **2b** at room temperature were lower than those (0.99—1.01 BM) of the corresponding azido bridged dinuclear copper(II) complexes, **1a** and **1b**. In addition, the magnetic susceptibilities of **2a**—**2d** were measured over the temperature range 77—300 K. The temperature dependences of all the complexes obey the following modified Bleaney-Bowers equation:[6]

$$\chi_A = \frac{Ng^2\beta^2}{kT} \frac{1}{3+\exp(-2J/kT)}(1-p) + \frac{Ng^2\beta^2}{4kT} \cdot p + N\alpha \quad (1)$$

Here, g, J, $N\alpha$, and p are, respectively, the g factor, the exchange integral, T.I.P. and the percentage of impure species. A typical example of the data is shown in Fig. 1, which indicates that the experimental data fit the theoretical expression given above. Table 2 gives the main parameters estimated from the variable-temperature data of **2a**—**2d**. The strongly antiferromagnetic coupling that was found for complexes **2a** and **2b** is explained as follows: (i) the N–O$^-$ bridging groups of L_1 and OH$^-$ have excellent superexchange properties; (ii) although complexes **2a** and **2b** have not been structurally characterized by X-ray crystallography, we consider that the N–O$^-$ and OH$^-$ bridges lie in the equatorial plane of the tetragonal copper(II) centers, judging from the structure of the corresponding complex **1a**.[2] Antiferromagnetic exchange interactions are also present in complexes **2c** and **2d** (Table 2). In the IR spectrum of complex **2c**, the ν_{as}(COO) and ν_s(COO) bands are at 1580 cm^{-1} and 1410 cm^{-1}, respectively. Likewise, these bands are also observed for **2d** (1575 and 1415 cm^{-1}). The splittings between ν_{as}(COO) and ν_s(COO) in these complexes are 160—170 cm^{-1}, indicating that two acetato groups are in the familiar bidentate bridging mode in **2c** and **2d**.[7,8] From these magnetic susceptibilities, the IR

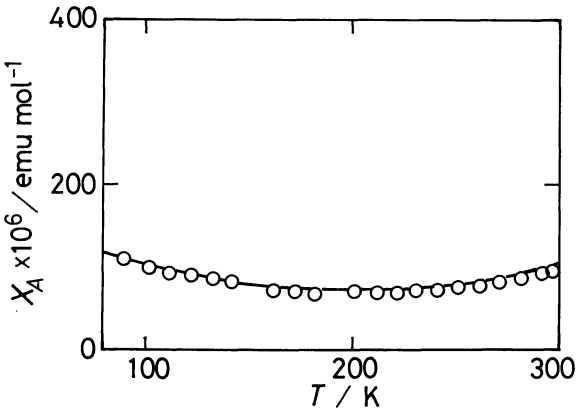


Fig. 1. Temperature dependence of the magnetic susceptibility of **2a**. The open circles indicate the observed susceptibility. The solid line shows the theoretical susceptibility calculated by the modified Bleaney–Bowers equation (Eq. 1)[6] with g, $2J$, and $N\alpha$ values described in Table 2.

Table 2. Magnetic Parameters of Copper(II) Complexes

Complex	g	$2J$	$N\alpha \times 10^{-6}$	p
		cm^{-1}	emu mol^{-1}	
2a	2.09	−1040	60	0.007
2b	2.00	−1060	60	0.027
2c	2.11	−260	60	0.057
2d	2.11	−470	60	0.009

spectra and the analytical data, we estimate that compounds **2c** and **2d** are dimeric complexes bridged by one deprotonated oximato and two acetato groups having the structures represented as **II**. The molar conductances (Table 1) of complexes **2a** and **2b** reveal that they are 1 : 2 electrolytes in DMF solution.[9] On the other hand, two acetato complexes, **2c** and **2d**, are 1 : 1 electrolytes in DMF (Table 1).[9]

Figures 2 and 3 give cyclic voltammograms of compounds **2a**, **2b** and **2d**. The $E_{p,c}$ values of complexes **2a** and **2b** were observed at −480 and −470 mV, respectively. On the reverse scan no appreciable reoxidation peak corresponding to the cathodic peak appeared; an oxidation peak was observed at a more positive potential (+0.3 V for **2a**, +0.1 V for **2b**), indicating that the redox reactions are chemically irreversible. On the other hand, $\Delta E_p(E_{p,a}-E_{p,c})$ in acetato complex **2d** is 140 mV ($E_{1/2}$=−790 mV). Accordingly, the redox system of **2d**

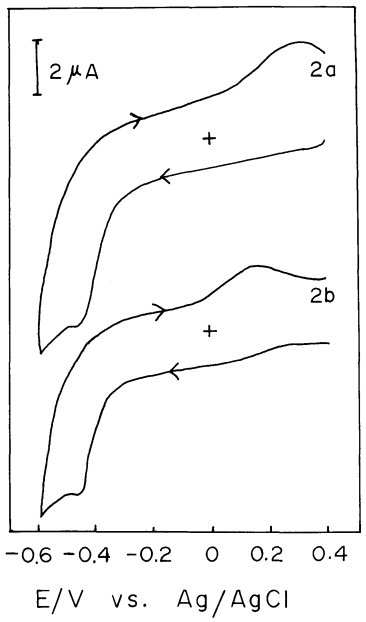


Fig. 2. Cyclic voltammograms of **2a** and **2b** in DMF at a scan rate of 100 mV s^{-1}.

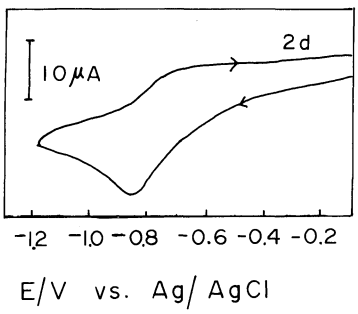


Fig. 3. Cyclic voltammogram of **2d** in DMF at a scan rate of 100 mV s^{-1}.

in DMF is quasi-reversible. In order to elucidate the number of electrons involved in the redox process of **2a, 2b,** and **2d** we carried out steady state voltammetry and controlled-potential coulometry in DMF. These attempts were, however, unsuccessful, since adsorption on the working electrode of the material produced by electrolysis occurs. Nevertheless, we suppose that the reduction of **2a** and **2b** at −480—−470 mV is the following two-electron process:

$$Cu^{2+}(L_1)\text{–}Cu^{2+}(\text{bpy or phen}) \xrightarrow{2e^-} Cu^{+}(L_1)\text{–}Cu^{+}(\text{bpy or phen}).$$

The estimate described above is based on data for the controlled-potential coulometry of similar complex $[Cu(L_1)(N_3)Cu(pmdt)](ClO_4)_2$ (pmdt; *N,N,N′,N″,N″*-pentamethyldiethylenetriamine), in which an one-step, two-electron transfer (Cu^{2+}–Cu^{2+} ⟶ Cu^{+}–Cu^{+}) takes place.[1] We consider that the same type of two-electron transfer in an acetato complex **2d** probably occurs. These electrochemical behaviors are identical with type-3 copper protein centers.[10]

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