Preparation and Properties of the Dinuclear Copper(II) Complexes Bridged by an Alkoxo and an Exogenous Bridging Ligand

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Synopsis. Dinuclear copper(II) complexes, $[Cu_2(L_1)(X)]$, **1**—**4** ($X=N_3^-$, OH^-, OAc^-, pyrazolate(Pz^-)), $[Cu_2(L_2)(X)]$, **5**—**8** ($X=N_3^-$, OH^-, OAc^-, Pz^-), $[Cu_2(L_3)(X)]$, **9**—**12** ($X=N_3^-$, OH^-, OAc^-, Pz^-), and $[Cu_2(L_4)(OH)]$, **13** have been prepared, where H_3L_1 is the Schiff base derived from acetylacetone and 1,3-diamino-2-propanol, H_3L_2 the Schiff base derived from benzoylacetone and 1,3-diamino-2-propanol, H_3L_3 the Schiff base derived from acetylacetone and 1,5-diamino-3-pentanol, and H_3L_4 the Schiff base derived from benzoylacetone and 1,5-diamino-3-pentanol. An azide ion bridges in μ-1,3-fashion for **1** (diamagnetic) and **5** with 6-5-5-6 fused-chelate-rings.¹⁾ On the other hand, a μ-1,1-azide bridge has been observed for **9** (coupling constant, $J=-126$ cm^{-1}, $H=-2JS_1\cdot S_2$) with a 6-6-6-6-fused-chelate ring. The relationship between the various physical properties and the structures of fused-chelate rings is discussed.

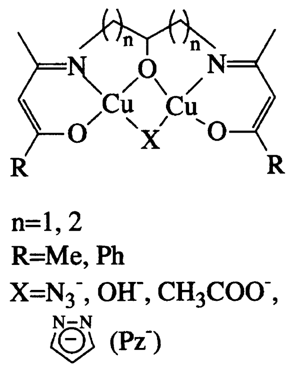
There have been many studies concerning binuclear copper(II) and nickel(II) complexes bridged both by an alkoxo group and by an exogenous bridging ligand, such as the pyrazolate anion.²⁻¹⁶⁾ These investigations were focused on understanding the structure–magnetism relationships and the structural characteristics of the active site in type-3 copper proteins. In this study we prepared a series of copper(II) complexes (structural formula **I**, Chart 1) containing Schiff bases derived from acetylacetone or benzoylacetone and 1,3-diaminopropane-2-ol or 1,5-diaminopentane-3-ol and an exogenous bridging ligand; these were characterized by the magnetic susceptibilities, electronic spectra, and conductivities.

Experimental

Synthesis of Schiff Bases H_3L_1 and H_3L_2 Derived from Acetylacetone or Benzoylacetone and 1,3-Diaminopropane-2-ol. These ligands were prepared according to method described in the literature.⁷⁾

Synthesis of Schiff Bases H_3L_3 and H_3L_4 Derived from Acetylacetone or Benzoylacetone and 1,5-Diaminopentane-3-ol. 1,5-Diaminopentane-3-ol was obtained by the hydrogenation of 1,2-dicyanopropane-2-ol.²⁾ H_3L_3 and H_3L_4 were prepared by a method similar to that described for H_3L_1 and H_3L_2.

Preparation of Copper(II) Complexes. $[Cu_2(L_1)(N_3)]$ (1). To an ethanol solution (10 cm³) of H_3L_1 (0.38 g, 1.5 mmol) were successively added copper(II) perchlorate hexahydrate (1.11 g, 3.0 mmol), sodium azide (0.098 g, 1.5 mmol), and sodium hydroxide (0.18 g, 4.5 mmol). After being stirred at room temperature for several hours, the reaction mixture was cooled. The obtained dark purple products were recrystallized from chloroform. Found: C, 36.99; H, 4.46; N, 16.45%. Calcd for $[Cu_2(C_{13}H_{19}N_2O_3)(N_3)]$: C, 37.13; H, 4.56; N, 16.66%.



I

Chart 1.

$[Cu_2(L_1)(OH)]\cdot 2H_2O$ (2). To an ethanol solution (50 cm³) of H_3L_1 (0.64 g, 2.5 mmol) was added copper(II) hydroxide obtained from copper(II) sulfate pentahydrate (1.3 g, 5.2 mmol) and sodium hydroxide (0.4 g, 10 mmol). The reaction mixture was heated under reflux for 3 h. After it had been filtered, the filtrate was evaporated to dryness in vacuo to give a blue product, which was recrystallized from a water–ethanol mixture. Found: C, 36.23; H, 5.39; N, 6.36%. Calcd for $[Cu_2(C_{13}H_{19}N_2O_3)(OH)]\cdot 2H_2O$: C, 36.27; H, 5.40; N, 6.51%.

$[Cu_2(L_2)(N_3)]$ (5) and $[Cu_2(L_2)(OH)]$ (6). These were prepared in the same way as described for the corresponding copper(II) complexes, **1** and **2**, respectively. $[Cu_2(L_2)(N_3)]$, **5**: C, 50.60; H, 4.28; N, 12.91%. Calcd for $[Cu_2(C_{23}H_{23}N_2O_3)(N_3)]$: C, 50.72; H, 4.27; N, 12.86%. $[Cu_2(L_2)(OH)]$, **6**: C, 53.42; H, 4.58; N, 5.49%. Calcd for $[Cu_2(C_{23}H_{23}N_2O_3)(OH)]$: C, 53.16; H, 4.67; N, 5.39%.

$[Cu_2(L_2)(Pz)]$ (8). To an ethanol solution (30 cm³) of H_3L_2 (0.76 g, 2.0 mmol) were added copper(II) perchlorate hexahydrate (1.48 g, 4.0 mmol), pyrazole (0.14 g, 2.0 mmol), and sodium hydroxide (0.32 g, 8.0 mmol). The solution was stirred at room temperature for several hours. The resulting grey-violet precipitate was collected by filtration, and washed with ethanol, dichloromethane, and acetone. Found: C, 53.83; H, 4.58; N, 9.88%. Calcd for $[Cu_2(C_{23}H_{23}N_2O_3)$-

(Pz)]·1/2H_2O: C, 53.96; H, 4.71; N, 9.68%.

$[Cu_2(L_3)(N_3)]$ (9). This complex was also prepared by a similar method as that described for complex **1**. The obtained dark-green products were recrystallized from chloroform–ether. Found: C, 40.02; H, 5.09; N, 15.76%. Calcd for $[Cu_2(C_{15}H_{23}N_2O_3)(N_3)]$: C, 40.16; H, 5.18; N, 15.62%.

$[Cu_2(L_3)(OAc)]$ (11). Schiff base H_3L_3 (1.0 g, 3.5 mmol) was dissolved in methanol (20 cm^3). To this solution was added copper(II) acetate monohydrate (1.4 g, 7.0 mmol) and triethylamine (1.4 g, 14 mmol); the reaction mixture was stirred for several hours at room temperature. After it had been filtered off, the grey-violet material was washed with methanol. Found: C, 41.46; H, 5.88; N, 5.87%. Calcd for $[Cu_2(C_{15}H_{23}N_2O_3)(C_2H_3O_2)]\cdot 1.5H_2O$: C, 41.46; H, 5.93; N, 5.69%.

$[Cu_2(L_4)(OH)]$ (13). Almost the same procedure as that described for **2** was applied. After filtration of the reaction mixture, the filtrate was concentrated to about one-half of the volume and allowed to set for a few hours in a refrigerator. The dark-blue crystalline products were collected by filtration and washed with ethanol. Found: C, 55.48; H, 5.47; N, 4.99%. Calcd for $[Cu_2(C_{25}H_{27}N_2O_3)(OH)]$: C, 54.83; H, 5.16; N, 5.12%.

Compounds **3**, **4**, **7**, **10**, and **12** have been described elsewhere.5,6,8,11)

Measurements. The magnetic susceptibility, conductivity, infrared and visible absorption spectra, and ESR spectra were carried out as described in a previous paper.17)

Table 1. Physical Properties of the Complexes

Complex		μ_{eff} a)	λ_{max} (ε/Cu) b)
		BM	nm
1	$[Cu_2(L_1)(N_3)]$	0.20	558(810), 352(4610)
2	$[Cu_2(L_1)(OH)]\cdot 2H_2O$	1.46	612(118)
3	$[Cu_2(L_1)(OAc)]\cdot H_2O$ 8)	1.64 8)	607(200)
	$[Cu_2(L_1)(OAc)]$ 6)	1.92 6)	608(198)
4	$[Cu_2(L_1)(pz)]$ 5)	1.49 5)	560(273) 5)
5	$[Cu_2(L_2)(N_3)]$	0.4	574(266) c)
6	$[Cu_2(L_2)(OH)]$ d)	1.32	614(— e))
7	$[Cu_2(L_2)(OAc)]$ 8)	1.70	611(230)
8	$[Cu_2(L_2)(pz)]\cdot 0.5H_2O$	1.45	551(— e))
9	$[Cu_2(L_3)(N_3)]$	1.46	565(96), 436(1600)
10	$[Cu_2(L_3)(OH)]$ 11)	1.27	560(86)
11	$[Cu_2(L_3)(OAc)]\cdot 1.5H_2O$	0.86	565(166)
12	$[Cu_2(L_3)(pz)]$ 5,11)	0.64 5)	583(105)
13	$[Cu_2(L_4)(OH)]$	0.88	565(102)

a) Room temperature. b) $CHCl_3$ solutions. c) CH_2Cl_2 solution. d) The temperature dependence of the magnetic susceptibility of this complex obeys the Bleaney–Bowers equation.20) The magnetic parameters are estimated as $g=2.28$, $N\alpha=60\times10^{-6}$ cgs emu mol^{-1}, and $J=-198$ cm^{-1} from the best fit of the χ_A values to the Bleaney–Bowers equation. e) No ε value is available owing to the poor solubility of the complex.

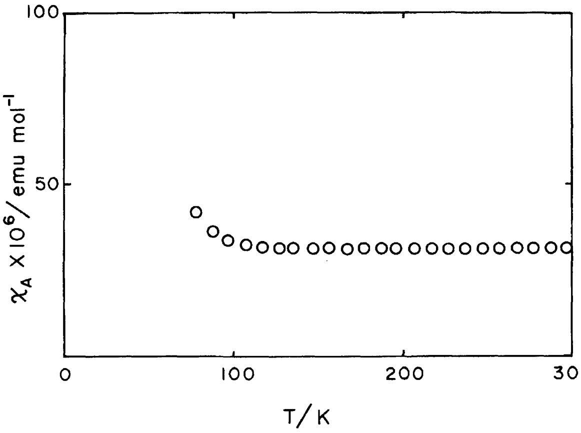


Fig. 1. The temperature-dependence of magnetic susceptibility of the complex **1**.

Results and Discussion

The magnetic moments and visible absorption spectral data for compounds **1**—**13** are given in Table 1. All of the complexes are non-electrolytes; this was confirmed by conductivity measurements in *N*,*N*-dimethylformamide (DMF) solutions. The IR spectra of azido-containing complexes **1** and **5** show a strong ν_{asym} (N_3^-) band at 2020 cm^{-1}, indicating that an azide ion bridges two copper(II) ions with an μ-1,3 type.17) Complexes **1** and **5** are essentially diamagnetic based on the μ_{eff} values (Table 1) at room temperature and the temperature-dependences of the magnetic susceptibilities (an example is given in Fig. 1). These are also ESR-silent in both solid and chloroform solution. Mc'Kee et al. have reported a diamagnetic dinuclear copper(II) complex $[Cu_2(L\text{-}Et)\ (N_3)]\ (BF_4)_2$ bridged by an azido and an alkoxo, where HL-Et represents *N*,*N*,*N*′,*N*′-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-propanediamine.18) The diamagnetism of this complex arises from the fact that each copper(II) approximates a square-pyramidal geometry, and thus the alkoxo and μ-1,3-azido, having good super-exchange properties, bridge the two coordination planes, resulting in their coplanarity.18) Accordingly, we consider that diamagnetic complexes **1** and **5** have a bridging mode that is similar to that in $[Cu_2(L\text{-}Et)(N_3)](BF_4)_2$. On the other hand, the azide ion in **9** links two copper(II) ions in μ-1,1-fashion ($\nu_{asym}(N_3)$: 2100 cm^{-1}).19) The magnetic susceptibility of **9** was measured over the temperature range 77—300 K.14) The magnetic parameters were estimated to be $g=2.08$, $N\alpha=60\times10^{-6}$ cgs emu mol^{-1}, and $2J=-252$ cm^{-1} from the best fit of the χ_A values to the Bleaney–Bowers equation.20) The antiferromagnetic exchange interaction in **9** is much weaker than those of complexes **1** and **5**. This is attributable to differences in the bridging mode of the azide ion and the geometry around copper(II). In the IR spectrum of complex **11**, the ν_{as}(COO) and ν_s(COO) bands are at 1570 and 1400 cm^{-1}, respectively. The splitting between ν_{as}(COO) and ν_s(COO) in **11** is 170 cm^{-1}, indicating that the carboxylate group bridges between two copper(II) ions as Cu–O–C–O–Cu.21) This familiar bridging mode has been confirmed by the X-ray crystallography to the acetato complex **3**.6,8) From a comparison of the magnetic moments between **2** and **10**, **3** and **11**, or **4** and **12** (Table 1), it may be concluded that the antiferromagnetic interaction in the complexes having the 6-5-5-6-fused-chelate-ring structure is weaker than that in the complexes with 6-6-6-6-fused-chelate-ring structures. However, these results differ from that in the azido-bridged complexes described above. Detailed structure information, such as the crystal structures will be necessary in order to discuss the structure–magnetism relationship in more detail.

As is clear from Table 1, the d–d absorption bands of the hydroxo- or acetato-bridged complexes were observed at a shorter wavelength in **10**, **11**, and **13** than in **2**, **3**, and **6**. This fact suggests that the copper(II) complexes which consist of 6-5-5-6-fused-chelate-ring systems are less stable than the 6-6-6-6-fused-chelate-ring containing complexes. In addition, these results may be correlated to the strength of the antiferromagnetic interaction between two copper(II) in these complexes, as mentioned above. It is noteworthy that the visible absorption band of azido-bridged complex **1** has an exceptionally high ε value (Table 1), which is close to those of metazidohemocyanin (ε, ca. 600 at $\lambda_{\max}\approx 500$ nm)[22] and oxyhemocyanin (ε, ca. 1000 at $\lambda_{\max}=580$ nm).[23]

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References

1) Such notations are used throughout the text to express arrangement and size of the individual rings involved in the fused-chelate ring system.

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