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Synthesis and Characterization of copper(II) Complexes with 1,4-diamino-3-butanol

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A new binucleating ligand, 1,4-diamino-2-butanol (Hdbl), has been synthesized. Its copper(II) complexes, $Cu(dbl)ClO_4\cdot\frac{1}{4}H_2O$ *and* $Cu(dbl)Cl\cdot\frac{1}{2}H_2O$ *are stable in aqueous solution, keeping the binuclear structure. The measurements of magnetic susceptibilities over the temperature range (300 ~ 80 K) have revealed that the perchlorate complex is binuclear* ($\mu_{eff} = 1.24$, $2J = -336$ cm^{-1}) *in the solid state, but the chloride complex assumes a tetranuclear cubane structure formed by weakly-linked two binuclear units,* ($\mu_{eff} = 1.77$, $\theta = -23.6$ K).

Introduction

In the previous papers we have reported the syntheses of binucleating ligands, 1,5-diamino-3-pentanol (Hdpl) [1] and 1,5-diamino-3-pentanethiol (Hdpet) [2]. These ligands were designed to obtain very stable planar binuclear complexes. In fact, we have confirmed the square planar binuclear structures in M(dpl)X (M = Cu, Ni, Pd) and M(dpet)X (M = Ni, Pd) by X-ray analysis of $Cu(dpl)Cl\cdot H_2O$ [3] and diamagnetism of the Ni(dpl)X and Pd(dpet)X series, where X denotes a mononegative anion [1, 2].

This paper reports the preparation of a new binucleating ligand, 1,4-diamino-2-butanol (Hdbl), and its copper(II) complexes (Fig. 1). Although Hdbl resembles Hdpl and Hdpet, it forms a 5-6 chelate ring system instead of a 6-6 chelate ring system. Such a change will bring about a marked effect on the chemical properties and molecular structure. Thus, we have studied the properties and structures of the dbl copper(II) complexes and discussed this in relation to the dpl complexes.

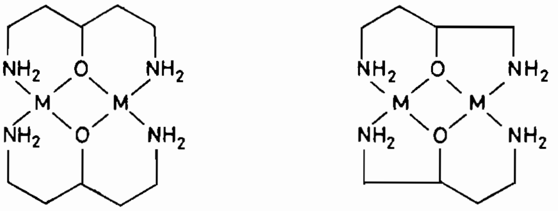

Fig. 1. Chemical structures of $[M_2(dpl)_2]$ (left) and $[M_2(dbl)_2]$ (right).

Experimental

Synthesis

1,4-Diphthaloylamino-2-butanol

A mixture of 1,4-dibromo-2-butanol (12 g, 0.05 mol) and potassium phthalimide (20 g, 0.11 mol) in 70 cm^3 of dry dimethylformamide (DMF) was warmed to 80 °C with stirring for 24 h. Upon cooling the phthalide was precipitated and collected by filtration and washed with water. More phthalide was obtained by evaporating the filtrate under reduced pressure. Yield 17 g (94%). The pure sample was obtained by recrystallization from DMF; m.p. 248–248.5 °C (dec.). *Anal.* Found: C, 65.68; H, 4.59; N, 7.70%. Calcd. for $C_{20}H_{16}N_2O_5$: C, 65.92; H, 4.43; N, 7.69%.

1,4-Diamino-2-butanol dihydrochloride, Hdbl·2HCl

The phthalide (17 g, 0.046 mol) was refluxed for 40 h in a mixture of 50 cm^3 of acetic acid and 30 cm^3 of conc. hydrochloric acid; during which time 10 cm^3 of conc. hydrochloric acid was added three times with 10 h intervals. The resulting phthalic acid was filtered off and the filtrate was concentrated to dryness under reduced pressure. The residue was treated with water, the undissolved material was filtered off, and the filtrate was again concentrated to almost dryness. The residue was treated with a

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large amount of ethanol to obtain a crystalline solid. Yield: 6.5 g (76%). This was recrystallized from methanol and dried at 100 °C under vacuum; m.p. 231 °C (dec.).

Anal. Found: C, 26.97; H, 7.97; N, 15.77%. Calcd for $C_4H_{12}N_2O\cdot 2HCl$: C, 27.13; H, 7.98; N, 15.82%.

Cu(dbl)Cl·½H₂O

To a warm solution of Hdbl·2HCl (0.9 g, 5 mmol) and anhydrous copper(II) chloride (700 mg, 5 mmol) in 50 cm^3 of methanol was added dropwise triethylamine until blue precipitates appeared. They were collected by filtration, washed with ethanol, and recrystallized from diluted ethanol to give pale blue fine needles.

Anal. Found: C, 22.60; H, 5.74; N, 13.10; Cu, 29.9%. Calcd for $C_8H_{24}N_4O_3Cu_2Cl_2$: C, 22.75; H, 5.74; N, 13.27; Cu, 30.09%.

Cu(dbl)ClO₄·¼H₂O

The ligand hydrochloride, Hdbl·2HCl (0.36 g, 2 mmol) was dissolved in 20 cm^3 of water and to this was added silver perchlorate until no more precipitates were resulted and the solution was filtered. Copper(II) perchlorate hexahydrate (0.72 g, 2 mmol) was added to the filtrate and the solution was heated on a water bath. The pH of the solution was adjusted to 9 by the addition of triethylamine, and the deep blue solution thus formed was concentrated under reduced pressure. The resulting blue crystals were collected and recrystallized from water and dried under vacuum at room temperature.

Anal. Found: C, 17.76; H, 4.30; N, 10.41; Cu, 23.5%. Calcd for $C_{16}H_{46}N_8O_{21}Cu_4Cl_4$: C, 17.75; H, 4.28; N, 10.35; Cu, 23.48%.

Measurements

The electronic spectra were recorded on Shimadzu MPS-5000 and UV-240 spectrophotometers. Magnetic susceptibilities were measured by the Faraday method. The apparatus was calibrated by the use of $[Ni(en)_3]S_2O_3$. The susceptibilities were corrected for the diamagnetism of the constituting atoms by the use of Pascal's constants. The electric conductivity was measured with a Yanagimoto conductivity apparatus Model MY7.

Results and Discussion

The effective magnetic moments of $Cu(dbl)ClO_4\cdot \frac{1}{4}H_2O$ *1* and $Cu(dbl)Cl\cdot \frac{1}{2}H_2O$ *2* at room temperature were found to be 1.24 and 1.77, respectively. The magnetic susceptibilities of the former complex in the 100–300 K range are best simulated by the Bleaney-Bowers equation, [4]

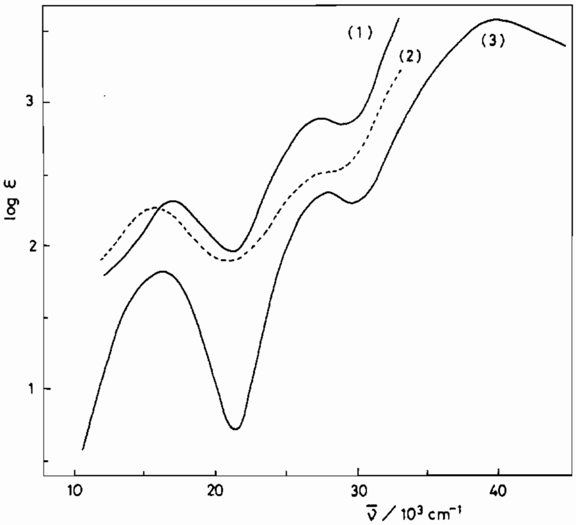

Fig. 2. Electronic spectra of (1) $Cu(dbl)Cl\cdot \frac{1}{2}H_2O$ (nujol mull), (2) $Cu(dbl)ClO_4\cdot \frac{1}{4}H_2O$ (nujol mull), and (3) $Cu(dbl)ClO_4\cdot \frac{1}{4}H_2O$ (in water). Absorbances for (1) and (2) are in arbitrary scale.

$$\chi_A = \frac{N\beta^2 g^2}{3kT}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1} + N\alpha$$

with $2J = -336$ cm^{-1}, $g = 2.02$ and $N\alpha = 65 \times 10^{-6}$ c.g.s. e.m.u., assuming 1.0% paramagnetic impurity, where χ_A, N, g, J, β and $N\alpha$ denote the usual meanings. This result indicates that the complex is binuclear and has a structure as shown in Fig. 1.

In the case of the chloride complex *2* whose magnetic moment is almost normal, magnetic susceptibility obeyed the Curie-Weiss law with $\theta = -23.6$ K in the 100–300 K range. This behavior is typical of type C-a complexes of Nishida and Kida's classification [5] (or Tetr-1A of Nieminen's classification) [6] for alkoxo-bridged copper(II) complexes. According to Nishida and Kida [5, 7] (and/or Nieminen [6]), complexes of this type take a tetranuclear cubane structure in which two binuclear units (Fig. 1) are linked to copper atoms of another binuclear unit *via* the axial coordination but this linkage is not so strong as to completely quench the antiferromagnetic interaction between the two copper(II) ions [6]. In the present complex the chlorine atoms are probably weakly coordinated to copper atoms.

The electronic spectra of *1* and *2* obtained in nujol mulls (Fig. 2) show that the d–d band of *2* is substantially red–shifted relative to that of *1*. The bands attributable to the CT transition from the bridging oxygen pπ to the metal dσ orbital [8] were observed at about 28×10^3 cm^{-1} for both compounds, but the intensity of this CT bands of *2* is much lower than that of *1*. This spectral feature suggests that *2* is a typical type C-a complex [5].

TABLE I. Magnetic Data and Band Maxima (10^3 cm^{-1}) (ϵ) of Electronic Spectra.

		$Cu(dbl)ClO_4 \cdot \frac{1}{4}H_2O$ *1*	$Cu(dbl)Cl \cdot \frac{1}{2}H_2O$ *2*	$Cu(dpl)ClO_4$	$Cu(dpl)Cl \cdot \frac{1}{2}H_2O$
μ_{eff}		1.24	1.77	0.22	0.72
$-2J$ (cm^{-1})		360		>1000	640
θ (K)			−23.6		
d–d	H_2O	16.3(66.7)	16.4(66.7)	17.7(76.6)	17.7(76.6)
	EtOH	16.5(63.0)	16.4(62.3)	18.0(56.5)	18.0(59.0)
	nujol	17.0	16.0	19.0	17.5, 16.5(sh)
CT	H_2O	28.1(239)	28.0(239)	28.4(1300)	28.4(1300)
	EtOH	28.2(552)	28.1(592)	28.6(1610)	28.4(1300)
	nujol	27.6	27.8	27	27

In aqueous solution the spectra of *1* and *2* are practically the same. The spectra of methanol solution are very similar to those of aqueous solution, the band positions being almost unchanged and the intensities only slightly changed (*cf.* Table I). These results indicate that both *1* and *2* dissociate into binuclear complex cations and simple anions in aqueous and methanol solutions, and are in good agreement with the results of the electric conductivity measurement of *2* in methanol (166 ohm^{-1} cm^{-2} mol^{-1}) which falls in the range for 1:2 electrolytes in methanol [9].

Table I lists the magnetic and spectral data of the dbl and dpl complexes. The d–d bands of the dbl complexes are substantially lower in frequency than are those of the dpl complexes, presumably due to the increased strain in the chelate ring system on going from dpl to dbl complexes.

In contrast to the facile formation of 1:1 copper(II) dbl complexes, attempts to prepare the corresponding nickel(II) complexes have not been successful. The blue solution obtained by mixing Hdbl, a nickel(II) salt and triethylamine in methanol yielded only an amorphous precipitate. This is again attributable to the strain in the chelate ring system which hinders the rigid planar coordination.

Thus, we conclude that dbl does not form a planar binuclear structure with metal(II) ions as easily as dpl does.

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