

Binuclear Copper(II) Complex Containing Two N₄-Macrocyclic Rings

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Binuclear copper(II) complexes can be classified into two groups, namely the complexes whose coordination units are nearly in a plane (group A) and the complexes whose coordination units face to each other (group B), (*cf.*, Fig. 1). Most binuclear copper complexes so far reported belong to group A, and have been extensively studied from various aspects, especially from the view point of magnetochemistry. On the other hand, complexes of group B reported thus far were only limited to copper acetate type compounds until several years ago. Recently, some face-to-face diporphyrins [1] and the bis-tren cryptate [2] were reported. Kida *et al.*, have reported the binuclear copper(II) complex containing two planar N₂O₂ coordination sites very recently [3].

We have started to study the complexes of group B, since the mechanism of interaction between the copper ions should be quite different from that of the group A complexes. In addition to this reason, the group B binuclear copper complexes have become important from the biological point of view, *i.e.*, they

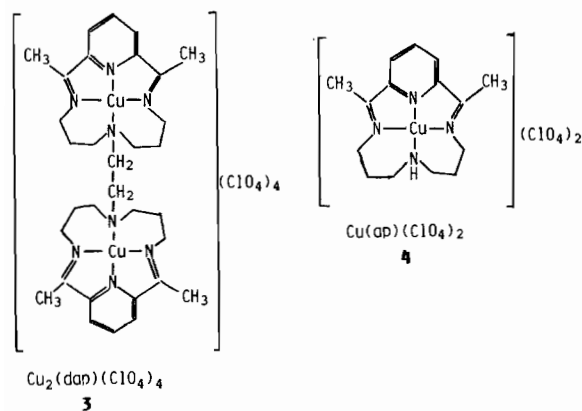


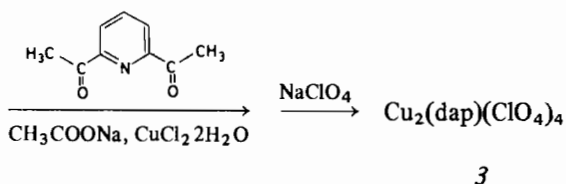
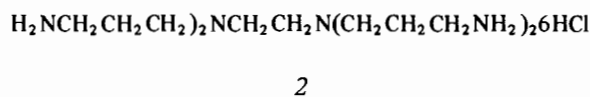
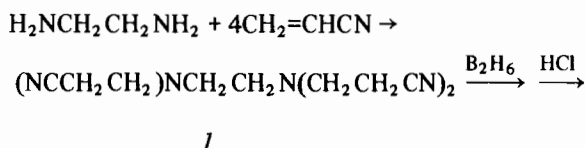
Fig. 1. Chemical Structure of the Complexes.

might provide models for type III copper in enzyme systems [4].

In this paper we report the synthesis and characterization of a copper(II) binuclear complex which contains two N₄-macrocyclic coordination units connected with an ethylene chain probably in a face-to-face fashion.

Experimental

The synthesis of the complex was carried out in the following scheme.



N,N,N',N'-tetrakis(3-aminopropyl)-1,2-diaminoethane (2)

N,N,N',N'-Tetrakis(2-cyanoethyl)-1,2-diaminoethane (1) [5] (11.4 g, 0.04 mol) was dissolved in 100 ml of THF. While this solution was mechanically stirred, diborane which was generated by the reaction of NaBH₄ (8.2 g, 0.22 mol) and BF₃·O(C₂H₅)₂ (42 g, 0.30 mol) in diglyme was introduced into this solution with a nitrogen stream. The reaction took place at room temperature for one hour. The solution soon became turbid and gradually viscous. The reaction mixture was then refluxed for 3 h with stirring. After cooling to room temperature, methanol was added dropwise to the reaction mixture to decompose unreacted diborane until hydrogen was no longer evolved. When the mechanical stirring was being continued, the mixture soon became a homogeneous solution. To this solution concentrated hydrochloric acid was added little by little. This procedure was accompanied by the violent generation of hydrogen. When the evolution of H₂ became gentle, the solu-

tion was heated on a water bath, and hydrochloric acid was added until H_2 was no longer generated. The solution was filtered and the filtrate was evaporated under reduced pressure. Methanol and a small amount of hydrochloric acid were added to the residue, and evaporated under reduced pressure. This procedure was repeated for five times in order to remove boric acid as methyl borate. The viscous residue was washed with a small amount of ethanol for several times, and dried in a vacuum desiccator over P_2O_5 . The white solid thus obtained was so hygroscopic that no further purification was made, and used for the synthesis of the complex.

$Cu_2(2-dap)(ClO_4)_4$ (3)

One half gram (0.0003 mol) of 2,6-diacetylpyridine and 0.5 g of copper(II) chloride dihydrate (0.03 mol) were dissolved in 300 ml of methanol-water (1:1) solution. To this solution was added a methanol-water (1:1) solution containing 1.5 g of 2 and 2 g of sodium acetate, and the resulting bluish-green solution was stirred for 2 h at 60 °C and then left standing at room temperature for 24 h. The solution became violet. It was filtered and the filtrate was concentrated to about 50 ml under reduced pressure. To this solution was added a saturated aqueous sodium perchlorate. The violet fine crystals separated were recrystallized from water and desiccated over P_2O_5 . Yield 0.3 g. *Anal.* Found: C, 35.86; H, 4.49; N, 10.46%. Calcd for $Cu_2(dap)(ClO_4)_4$: C, 36.00; H, 4.35; N, 10.50%.

Results and Discussion

Lindoy *et al.* [6] prepared a copper(II) complex, $Cu(ap)(ClO_4)_2$ (4) with a macrocyclic ligand derived from the reaction of 2,6-diacetylpyridine and 1,5,9-triazanonane. As readily seen in Fig. 1, our compound (3) is only different from the compound (4) in that each molecule is connected with the $-CH_2-CH_2-$ chain. The IR spectrum of the compound (4) showed bands at 1619 and 1590 cm^{-1} which were assigned to $\nu(C=N)$ and a skeletal vibration of pyridine ring, respectively. Similar bands were also observed in the same positions in our compound (3). The broad intense band at about 1100 cm^{-1} due to ClO_4^- shows no remarkable splitting, indicating practically no coordination of ClO_4^- .

The visible absorption spectra of $Cu_2(dap)(ClO_4)_4$ and $Cu(ap)(ClO_4)_2$ are very similar to each other, both showing a broad band due to the d-d transitions with a maximum at $18.5 \times 10^3 cm^{-1}$. This is compatible with the essentially square planar coordination. All the above facts support the chemical structure (3) as illustrated in Fig. 1.

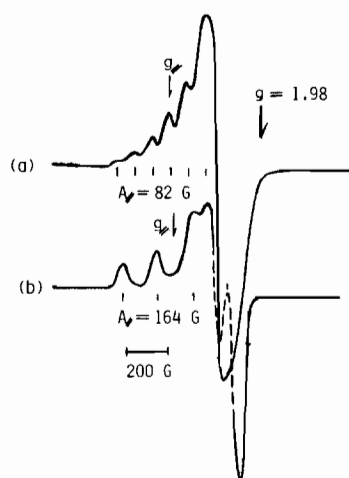


Fig. 2. X-band ESR Spectra of $Cu_2(dap)(ClO_4)_4$ (a) and $Cu(ap)(ClO_4)_4$ (b) in DMF Glass at 77 K.

The effective magnetic moment of this compound (for one copper atom) is 1.76 B.M. at room temperature and 1.67 B.M. at 87.4 K. The magnetic susceptibilities over the temperature range 290–87 K obey the Curie-Weiss law with $\theta = -14$ K. Since the ground state is orbitally singlet, this result suggests that some antiferromagnetic interaction is operative between the two copper(II) ions.

The existence of such interaction is definitely demonstrated by the ESR spectrum. As seen in Fig. 2, ESR spectra of $Cu_2(dap)(ClO_4)_4$ and $Cu(ap)(ClO_4)_2$ in DMF glass both show an axial pattern, but in the spectrum of the former complex at least six hyperfine peaks can be observed in the g_{\parallel} region, with $A_{\parallel} = 82$ G, which is a half of that of $Cu(ap)(ClO_4)_2$. This clearly indicates that there is an appreciable interaction between the two copper(II) ions in the complex (3), since it is theoretically established that the coupling of two copper nucleus ($I = 3/2$) brings about two sets of seven hyperfine lines whose separation (A_{\parallel}) is one half of that of hyperfine lines of the mononuclear species constituting the binuclear complex [7]. In this case, it is likely that the two sets are overlapping each other, because the g_{\parallel} value (2.230) of Fig. 3a is nearly the same as that (2.263) of Fig. 3b.

Thus, considering the above facts and the chemical structure (3 in Fig. 1) we presume that in the complex the two coordination units face to each other forming a kind of strati-binuclear complex.

We are undertaking the synthesis and characterization of the complexes having an extended carbon chain (3 ~ 6) between the two macrocycles.

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