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Template Synthesis of a Macrocyclic Tetracopper(II) Complex with Two Bridging Hydroxide Ions in Face-to-face Manner

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The reaction of 2,6-diformyl-4-methylphenol, triethylenetetramine, and copper(II) perchlorate hexahydrate in the 2:2:4 molar ratio formed a macrocyclic tetracopper(II) complex $[Cu_4(L)(OH)_2](ClO_4)_4$ where H_2L denotes the macrocycle formed by two molecules of 2,6-diformyl-4-methylphenol and two molecules of triethylenetetramine. The two hydroxide groups, each bridging a pair of copper(II) ions, are facing each other in a close distance so as to be replaced by an azide ion, affording $[Cu_4(L)(N_3)](ClO_4)_5$.

The oxidation of water to dioxygen in photosystem II (PS II) of green plants has been shown to proceed at an active site comprising four manganese ions.1) A mechanistic scheme that invokes the conversion of two water molecules (or two hydroxide or oxide ions) to bridging peroxide as a precursor to the release of dioxygen has been proposed.2) In this scheme two oxygen atoms must be in a close proximity to each other to provide a stereochemical pathway for O-O bond formation. Some tetranuclear manganese complexes have been obtained as models3) but complexes with two molecules of H_2O, OH^-, or O^{2-} in vicinal position are very few.4) In this communication we report the synthesis of a tetracopper(II) complex of a macrocycle, in which two hydroxide groups, each bridging a pair of copper(II) ions, are facing each other so as to be replaced by a bridging azide ion.

The macrocyclic tetracopper(II) complex $[Cu_4(L)(OH)_2](ClO_4)_4$ (**1**) was obtained as green crystals by a reaction of 2,6-diformyl-4-methylphenol (328 mg, 2 mmol), triethylenetetramine (293 mg, 2 mmol), and copper(II) perchlorate hexahydrate (1,480 mg, 4 mmol) in methanol, where H_2L denotes the macrocycle derived from the 2:2 condensation of 2,6-diformyl-4-methylphenol and triethylenetetramine.5) The yield was ca. 70%. The most

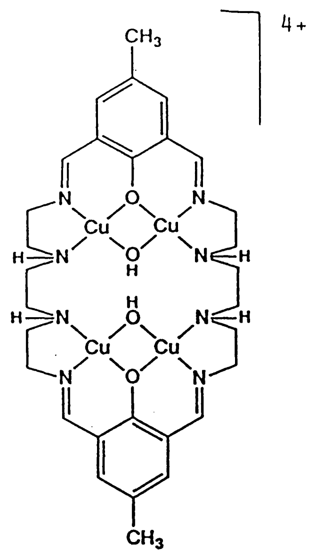

Fig. 1.

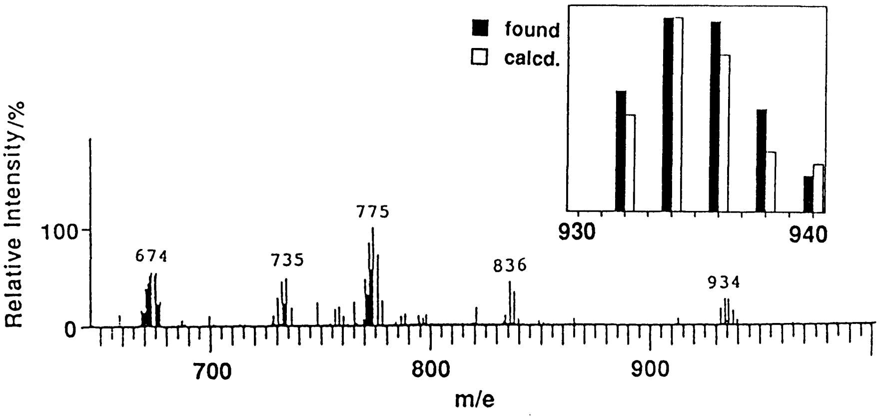

Fig. 2. FAB mass spectrum of **1**.

probable structure of the complex **1** is shown in Fig. 1.

The complex **1** (100 mg), NaN_3 (6.3 mg), and $NaClO_4$ (12 mg) were dissolved in N,N-dimethylformamide (10 cm^3), and the solution was refluxed for one hour to give $[Cu_4(L)(N_3)](ClO_4)_5$ (**2**) as green microcrystals.[6] The yield was 38%.

The formation of the macrocyclic complex **1** was evidenced by FAB mass spectrum (Fig. 2) which showed a group of peaks from (m/e) 932 to 940 assignable to $Cu_4(L)(OH)_2(ClO_4)^+$. The appearence of many peaks is due to the presence of isotopic masses for Cl and Cu (^{35}Cl 75.53, ^{37}Cl 24.47%; ^{63}Cu 69.1, ^{65}Cu 30.9%) as indicated by the simulation given in the insert. The spectrum also shows peaks at (m/e) 834-840, 771-779, 731-737, and 669-678 which are assigned to $Cu_4(L)(OH)_2^+$, $Cu_3(L)(OH)_2^+$, $Cu_3(L)^+$, and $Cu_2(L)^+$, respectively.

Some geometrical isomers are considered for **1** with respect to the configurations of the amino nitrogens on the lateral chains. Based on cyclic voltammograms described later we presume that one of the isomers is preferentially formed, though the structure of the isomer is unkown at this stage.

The infrared spectrum of **1** shows a sharp band at 3600 cm^{-1} attributable to the ν(O-H) mode of bridging OH^- group. A weak band at 3240 cm^{-1} is assigned to the ν(N-H) of the secondary amine. The vibrations due to primary amine and carbonyl group are absent. Instead, the ν(C=N) stretch appears at 1650 cm^{-1}. The perchlorate vibration near 1100 cm^{-1} is seen as aplit bands (1140, 1110, and 1090 cm^{-1}), suggesting a weak coordination of the perchlorate to copper(II) ion. Molar electric conductance of **1** in N,N-dimethylformamide is 340 S $cm^2 mol^{-1}$ in infinite dilution, indi-

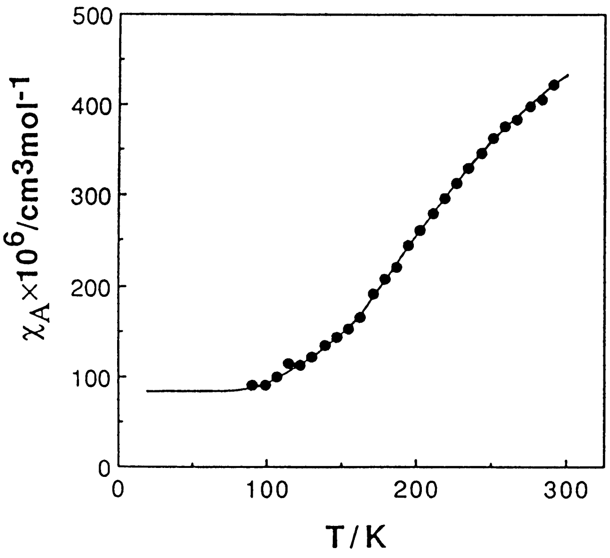

Fig. 3. χ_A vs. T curve of 1.

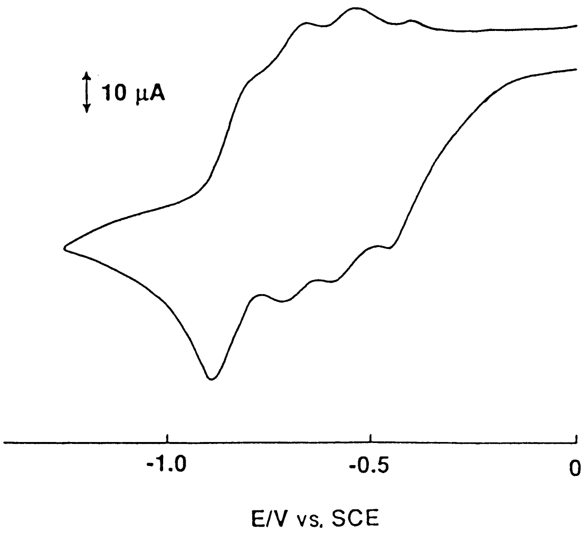

Fig. 4. Cyclic Voltammogram of **1**: in dmf, glassy carbon electrode, scan rate 100 mV s^{-1}.

cating that **1** behaves as a 4:1 electrolyte in solution.[7)]

The magnetic susceptibility of **1** was measured in the temperature range 90-300 K. The result is given in Fig. 3. The magnetic moment per one copper is 0.99 μ_B at room temperature and decreases with lowering of temperature down to 0.26 μ_B at 90 K, suggesting the operation of an antiferromagnetic interaction within a molecule. The magnetic behavior can be well simulated based on the Bleaney-Bowers equation,[8)]

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

where each symbol has its usual meaning. The magnetic parameters determined by the least-squares fitting are as follows: g=2.1, J=-270 cm^{-1}, and $N\alpha=87\times10^{-6}$ cm^3mol^{-1}. The result indicates that two dicopper(II) units in a molecule are magnetically independent of each other and a significant antiferromagnetic spin-coupling operates within each dicopper(II) unit. The exchange integral (J=-270 cm^{-1}) is comparable to those of binuclear copper(II) complexes of Schiff bases derived from the 1:2 condensation of 2,6-diformyl-4-methylphenol and N,N-disubstituted ethylenediamine.[9)]

The electrochemical property of **1** has been examined by cyclic voltammetry in N,N-dimethylformamide using a glassy carbon working electrode (Fig. 4). Four redox couples appear in the region -0.4 – -0.9 V. Since the controlled-potential electrolysis at -0.7 V indicates the transfer of three electrons, the four couples can be assigned to the step-wise electron transfers: Cu_4(II,II,II,II) Cu_4(I,II,II,II) Cu_4(I,I,II,II) Cu_4(I,I,I,II) Cu_4(I,I,I,I). Thus, the complex **1** functions as a four-electron mediator relevant to the Kok's four-photon scheme of PS II.$^{10)}$

The complex **2** shows no IR band due to bridging OH^- in the region 3600–3500 cm^{-1}. Instead, **2** shows two bands at 2085 and 2045 cm^{-1} attributable to N_3^- ion. The magnetic moment of **2** also decreases with lowering of temperature (1.50 μ_B at 300 K and 0.69 μ_B at 80 K) but does not obey the Bleaney-Bowers equation. This is probably because the magnetic interaction operates among four copper(II) ions through the azide bridge. Thus, the macrocyclic complex **1** bears the two bridging OH^- groups in face-to-face manner so as to be replaced by an azide ion.

Studies on macrocyclic tetranuclear complexes of other metal ions are in progress in our laboratory.

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5) Recrystallized from a dmf-ether mixture. Found: C, 31.41; H, 4.11; N, 8.55; Cu, 19.4%. Calcd for $[Cu_4(L)(OH)_2](ClO_4)_4$·ether: C, 31.35; H, 3.87; N, 8.60; Cu, 19.5%.

6) Recrystallized from a dmf-ether mixture. Found: C, 32.75; H, 4.79; N, 10.91; Cu, 16.0%. Calcd for $[Cu_4(L)(N_3)](ClO_4)_5$·dmf·2.5ether: C, 32.64; H, 4.71; N, 10.62; Cu, 16.1%.

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