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Formation Equilibrium of a Copper(II)-Binuclear Complex of a New Pyridyl-Containing Tetraoxo Octaaza Macrocyclic Ligand and Its Polarographic Reduction Behavior

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We have studied the complexation reaction of a newly synthesized 26-membered octaaza macrocycle, 3,6,9,17,20,23,29,30-octaazatricyclo[23.3.1.1.^{11,15}]triaconta-1(29),11,13,15(30),25,27-hexaene-2,10,16,24-tetraone (TOBP, L), with a Cu(II) ion by pH-metric titration. It accomodates two copper(II) ions in its macrocyclic cavity with a simultaneous dissociation of the four amide protons to yield a binuclear complex designated as $[\mathrm{Cu_2H_{-4}L}]^\circ$. The formation constant of $[\mathrm{Cu_2H_{-4}L}]^\circ$, $K_{\mathrm{Cu_2H_{-4}L}}$ $(=[\mathrm{Cu_2H_{-4}L^\circ}][\mathrm{H^+}]^4/[\mathrm{Cu^{2+}}]^2[\mathrm{L}])$, was found to be $(3.5\pm0.2)\times10^{-12}$ mol^2 dm^{-6}. At the dropping mercury electrode the Cu(II) binuclear complex gave two reduction steps of equal height in a borate buffer solution, corresponding to the following reduction scheme:

$$\begin{array}{lll}
[\mathrm{Cu_2H_{-4}L}]^\circ + 2\mathrm{H^+} + \mathrm{Hg} + 2e^- \rightleftharpoons \mathrm{Cu(Hg)} + [\mathrm{CuH_{-2}L}]^\circ & & \text{(1st step)} \\
[\mathrm{CuH_{-2}L}]^\circ + 2\mathrm{H^+} \rightleftharpoons \mathrm{CuL^{2+}} & & \text{in a rapid equilibrium} \\
\mathrm{CuL^{2+}} + \mathrm{Hg} + 2e^- \rightleftharpoons \mathrm{Cu(Hg)} + & \begin{array}{l} \mathrm{L} \\ \uparrow\downarrow\ +j\mathrm{H^+} \\ \mathrm{H}_j\mathrm{L}^{j+} \end{array} & \text{(2nd step)}
\end{array}$$

Cyclic tetra- and penta-aminediones possess novel ligand properties of saturated macrocyclic polyamines blended with oligopeptide features.$^{1)}$ They accomodate certain metal ions (e.g. Cu(II), Ni(II), and Co(II) ions) in the polyamine macrocyclic cavities with a simultaneous dissociation of the two amide protons to afford 1:1 ratio complexes, generally designated as $[\mathrm{MH_{-2}L}]^\circ$. In 1982 we reported on a novel cyclic penta-aminedione complex of high-spin nickel(II) ion that possesses a very low E° value of $+0.24_0$ V vs. SCE, and can activate $\mathrm{O_2}$ by 1:1 Ni(II)–$\mathrm{O_2}$ complexation so as to oxygenate benzen into phenol at room temperature.$^{2)}$ We have extended the previous studies on the tetra- and penta-aminedione.$^{3—6)}$ Herein we present systematic studies of the complexation reaction of a newly synthesized pyridyl-containing tetraoxo octaaza macrocyclic ligand (**3**) with a copper(II) ion of the electrochemical behavior of its copper(II) binuclear complex.

Experimental

Reagents. 3,6,9,17,20,23,29,30-octaazatricyclo[23.3.1.1^{11,15}]triaconta-1(29),11,13,15(30),25,27-hexaene-2,10,16,24-tetraone, **3** (TOBP, L). The compound TOBP was prepared as follows (Chart 1). An ethanol solution (200 ml) of diethyl 2,6-pyridinedicarboxylate, **1** (2.33 g, 10 mmol) and bis(2-aminoethyl)amine, **2** (1.03 g, 10 mmol), was refluxed for 4 d. After evaporation of the solvent, the resulting white solid was recrystallized from EtOH to give **3** (510 mg): Mp 250 °C (decomp); IR (KBr pellet) 1670 cm^{-1} (C=O); ^{1}H NMR ($\mathrm{D_2O}$) δ=3.54 (8H, t, J=4.8 Hz), 3.90 (8H, t, J=4.8 Hz), 8.08—8.17 (6H, m); ^{13}C NMR ($\mathrm{D_2O}$) δ=39.3, 49.8, 128.2, 143.0, 150.0, 168.8; MS m/z 468.

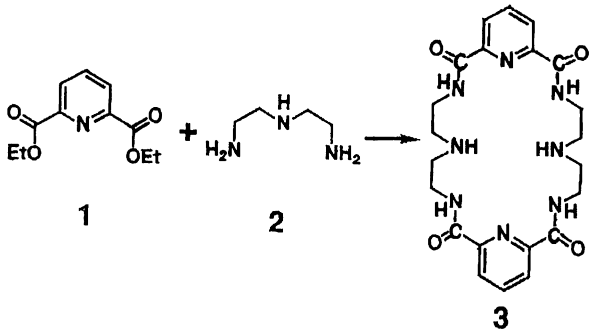

Chart 1.

All other chemicals used in this study were of analytical reagent grade and were used without further purification.

Apparatus and Experimental Procedures. The pH-metric titrations were performed with a Mettler Automatic Titrator$^{5,7)}$ under a nitrogen atmosphere at 25±0.10 °C. The apparatus used for the polarographic measurements were as previously used.[5,8] The preparation of the used hanging mercury-drop electrode has been described previously.[9] The apparatus used for the cyclic voltammetric measurements was the same as that applied to a study of Ag(II)-macrocyclic polyamine complexes.[10] The pH values of the test solutions used for the polarographic measurements were determined using a glass-electrode pH meter (a Horiba F8-AT). IR and mass spectral data were recorded on a Shimadzu IR-408 spectrophotometer and a JEOL JMS-01SG-2 mass spectrometer, respectively. Proton and carbon NMR spectra were recorded on a JEOL GX-400 spectrometer (400 MHz, 25 °C). Sodium 3-(trimethylsilyl)propionate-2,2,3,3-d_4 was used as internal standard. All of the experimental conditions and procedures employed for the pH-metric titrations and polarographic measurements have been mentioned previously.[7] The controlled-potential electrolysis was carried out by using a Yanagimoto Controlled Potential Electrolyser (Model VE-8). In the electrolysis the cathode was a mercury-pool electrode, whose surface area was approximately 2.0 cm^2, while the anode was a platinum spiral electrode, which was connected to the electrolytic solution through a salt bridge. A saturated calomel electrode (SCE) was used as a reference electrode, against which the mercury electrode potential was controlled. Twenty milliliters of 2.00 mol dm^{-3} TOBP solution of pH=9.52 containing 4.00 mmol dm^{-3} Cu(II) ions was subjected to controlled-potential electrolysis. The potential of the mercury electrode was kept at -0.52 V vs. SCE, which is in the potential region of the limiting current plateau of the 1st step. In a coulometric study the current through the electrolysis cell during constant-potential electrolysis was automatically recorded with a Toa Electronic Ltd Recorder (FBR-251A) by measuring the i–R drop across a standard 100 Ω resistor inserted between the mercury electrode and the negative terminal of the applied voltage from the constant-potential electrolyser. The quntity of the electricity was determined by a graphical integration of the obtained current–time curve.

When a.c. polarograms were measured, in order to minimize the impeadance of the cell system, a platinum-plate electrode of a large surface area was inserted into the electrolytic solution as the third electrode, which was terminated at the SCE through a 100 μF capacitor.[11]

The values of $-\log[\text{H}^+]$ used to calculate the formation constant were estimated by applying a correction of -0.13 pH unit to the pH meter readings: $-\log[\text{H}^+]=\text{pH}-0.13$.[5,9] Mixed protonation constants ($\log K_i$) of TOBP were determined by titration with a 0.100 mol dm^{-3} carbonate-free tetraethylammonium hydroxide solution using a test solution (50.0 ml) having an ionic strength of 0.200 mol dm^{-3} (NaClO_4) containing 0.500 mmol dm^{-3} fully-protonated ligand (H_4L^{4+}). The $\log K_i$'s determined potentiometrically at 25 °C were 8.53±0.03, 7.63±0.03, 2.0>, 1.7>.

Results and Discussion

Complex Formation Equilibrium. The complex formation equilibria between copper(II) ion and TOBP (L) were analyzed in an identical manner as that previously applied to the macrocyclic dioxo-tetraamine complexes of copper(II) ions.[12] Typical titration curves of H_4L^{4+} solutions are given in Fig. 1. 1 : 1 and 2 : 1 molar-ratio mixtures of copper(II) ion and TOBP (in the form of H_4L^{4+}) gave titration curves with buffer regions at the titration point (a), $5.0>a>2.0$ and $8.0>a>2.0$, respectively (curves B and C). Here, the titration point (a) indicates the number of moles of base added per mole of TOBP present. In considering the small 3rd and 4th protonation constants of TOBP ($2.0>\log K_3$ and $1.7>\log K_4$), these findings clearly indicate that under the present experimental conditions TOBP forms solely the binuclear Cu(II) complex designated as $[\text{Cu}_2\text{H}_{-4}\text{L}]^\circ$. Here, $\text{H}_{-4}\text{L}^{4-}$ denotes the quadriply-deprotonated TOBP anion. Although the detailed results are not shown here, we found that although the 1 : 1 and 2 : 1 molar-ratio mixtures of copper(II) and TOBP gave quite similar visible spectra ($\lambda_{\text{max}}=573$ nm), the molar absorbance of a 1 : 1 molar mixture is exactly half that of a 2 : 1 ratio mixture. This strongly supports the above explanation given for the pH-metric titration. The titration data for the 2 : 1 molar ratio mixture of Cu(II) and H_4L^{4+} were analyzed by assuming the formation of a quadriply-deprotonated binuclear complex, $[\text{Cu}_2\text{H}_{-4}\text{L}]^\circ$. The complex formation and acid-base equilibria involved during titration can be defined by Eqs. 1 and 2.

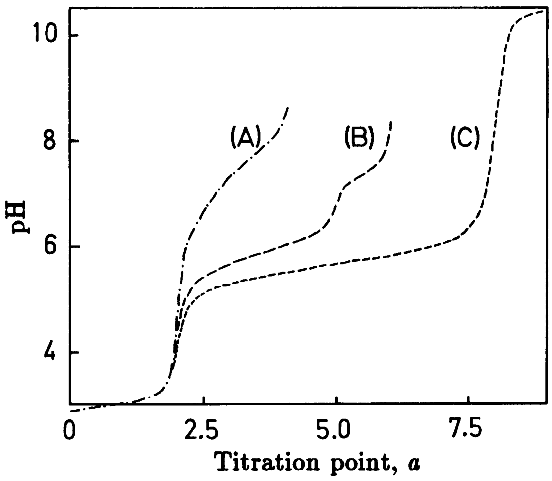

Fig. 1. Titration curves for the copper(II)–TOBP system. Initial concentration of TOBP, C_L, =0.500 mmol dm^{-3}, Initial concentration of HClO_4 =2.00 mmol dm^{-3}, I=0.20 mol dm^{-3}, 25 °C, Volume of test solution=50.0 ml. (A) no copper(II) ion, (B) Initial concentration of copper(II), C_M, =0.500 mmol dm^{-3}, (C) Initial concentration of copper(II), C_M, =1.00 mmol dm^{-3}.

$$2\text{Cu}^{2+}+\text{L}\rightleftharpoons[\text{Cu}_2\text{H}_{-4}\text{L}]^\circ+4\text{H}^+,$$

$$K_{\text{Cu}_2\text{H}_{-4}\text{L}}=\frac{[\text{Cu}_2\text{H}_{-4}\text{L}^\circ][\text{H}^+]^4}{[\text{Cu}^{2+}]^2[\text{L}]} \tag{1}$$

$$\text{H}_{i-1}\text{L}^{(i-1)+}+\text{H}^+\rightleftharpoons\text{H}_i\text{L}^{i+},$$

$$K_i=\frac{[\text{H}_i\text{L}^{i+}]}{[\text{H}_{i-1}\text{L}^{(i-1)+}][\text{H}^+]} \tag{2}$$

The sum of the hydrogen ion and tetraethylammonium ion, $(\text{C}_2\text{H}_5)_4\text{N}^+$, concentrations subtracted by the

OH^- concentration, $[OH^-]$, α, at the titration point a is given by Eq. 4.

$$\begin{aligned}\alpha &= aC_L + [H^+] - [OH^-] \\ &= 4[L] + 3[HL^+] + 2[H_2L^{2+}] + [H_3L^{3+}] + 8[Cu_2H_{-4}L^\circ] \\ &= \frac{\beta_H}{(\alpha_H)_L} \times [L]_f + 8[Cu_2H_{-4}L^\circ] \qquad (3)\end{aligned}$$

Here, $[L]_f$ denotes the concentration of uncomplexed TOBP, and $(\alpha_H)_L$ and β_H are given by Eqs. 4 and 5, respectively.

$$\begin{aligned}(\alpha_H)_L &= 1 + K_1[H^+] + K_1K_2[H^+]^2 + K_1K_2K_3[H^+]^3 \\ &\quad + K_1K_2K_3K_4[H^+]^4 \qquad (4)\end{aligned}$$

$$\beta_H = 4 + 3K_1[H^+] + 2K_1K_2[H^+]^2 + K_1K_2K_3[H^+]^3 \qquad (5)$$

The total concentration of the copper(II) ion and that of TOBP are expressed by Eqs. 6 and 7, respectively.

$$C_M = 2C_L = [Cu^{2+}] + 2[Cu_2H_{-4}L^\circ] \qquad (6)$$

$$C_L = [L]_f + [Cu_2H_{-4}L]^\circ \qquad (7)$$

Here, $[Cu^{2+}]$ means the concentration of uncomplexed copper(II) ions.

By an appropriate combination of Eqs. 1, 2, 3, 4, 5, 6, and 7, one can easily derive relation 8 for the 2 : 1 molar mixture of the Cu(II) ion and H_4L^{4+}.

$$K_{Cu_2H_{-4}L} = \frac{(\alpha(\alpha_H)_L - \beta_H C_L)(8(\alpha_H)_L - \beta_H)^2[H^+]^4}{4(8C_L - \alpha)^3(\alpha_H)_L^2} \qquad (8)$$

At a pH lower than 5.6_3 Eq. 8 can be simplified to Eq. 9, because at this pH region β_H is nearly equal to $2\times(\alpha_H)_L$.

$$K_{Cu_2H_{-4}L}(8C_L - \alpha)^3 = 9(\alpha - 2C_L)(\alpha_H)_L[H^+]^4 \qquad (9)$$

At the titration point $8.0 > a > 2.0$ (pH<5.63) Eq. 9 fitted well with the experimental data; a plot of $(\alpha - 2C_L)\times(\alpha_H)_L[H^+]^4$ against $(8C_L - \alpha)^3$ gave an excellent linear relation which passes through the point of origin (Fig. 2). Thus, the $K_{Cu_2H_{-4}L}$ value of $(3.5\pm0.2)\times10^{-12}$ $mol^2\,dm^{-6}$ could be obtained from the slope of the straight line in Fig. 2.

A recent study conducted by I. Murase et al. revealed that the binuclear copper(II) complex of the tricyclic octaaza ligand reacts with various anion (F^-, Cl^-, Br^-, and N_3^-) to form an anion-bridged complex.[13] We therefore also investigated the effect of the chloride anion on the complexation equilibrium of the copper(II) ion with TOBP. The slopes of the straight lines between $(\alpha - 2C_L)(\alpha_H)_L[H^+]^4$ and $(8C_L - \alpha)^3$ divided by 9 (Eq. 9) determined at varied concentrations of chloride anions are listed in Table 1. The result evidently shows that that the $[Cu_2H_{-4}L]^\circ$ complex does not combine with the chloride ion at concentrations lower than 0.10 $mol\,dm^{-3}$, but at higher concentrations it may combine with chloride ion, yielding a binuclear mixed ligand complex. The bromide anion at concentrations lower than 0.10 $mol\,dm^{-3}$ was also found to exert little effect on the above complexation reaction of the copper(II) ion with TOBP. The above collected evidence clearly shows that in the lower halide-ion concentration TOBP accomodates two copper(II) ions in its macrocyclic cavity to afford the copper(II) binuclear complex designated as $[Cu_2H_{-4}L]^\circ$ with a simultaneous dissociation of the four amide protons. In general, as was observed in the binuclear copper(II) complex of hexaaza macrocycle, 3,6,9,17,20,23-hexaazatricyclo[23,3.1.1^{11,15}]triaconta-1(29),11(30),12,14,25(26),27-hexaene,[14] the coordination of anionic groups to the metal(II) ion would minimize the electrostatic repulsion between two metal(II) ion centers, and can stabilize the binuclear complex. Thus, the deprotonation of amide groups of TOBP would be effective in stabilizing the binuclear copper(II)-TOBP complex. On the other hand, the neutral TOBP molecule is likely to accomodate only one copper(II) ion in its cavity

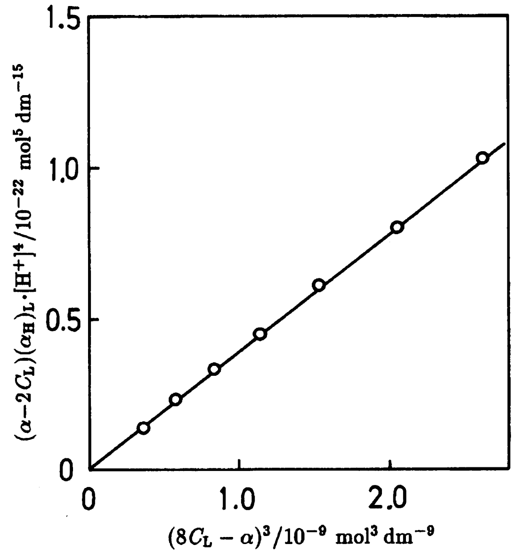

Fig. 2. Plots of $(\alpha - 2C_L)(\alpha_H)_L[H^+]^4$ against $(8C_L - \alpha)^3$ Copper(II)–TOBP system. Initial concentration of TOBP, C_L, =0.500 $mmol\,dm^{-3}$, Initial concentration of $HClO_4$ =2.00 $mmol\,dm^{-3}$, Initial concentration of copper(II), C_M, =1.00 $mmol\,dm^{-3}$, I=0.20 $mol\,dm^{-3}$, 25 °C.

Table 1. Effect of Cl^- Concentration on the Slope of the Linear Relation between $(\alpha - 2C_1)(\alpha_H)_L[H^+]^4$ and $(8C_L - \alpha)^3$
Initial Concentration of TOBP, C_L, =0.500 $mmol\,dm^{-3}$, Initial Concentration of $HClO_4$ =2.00 $mmol\,dm^{-3}$, Initial Concentration of Copper(II), C_M, =1.00 $mmol\,dm^{-3}$, I=0.20 $mol\,dm^{-3}$, 25 °C

$[Cl^-]$/mol dm^{-3}	Slope/10^{-13} $mol^2\,dm^{-6}$ ($10^{12}K_{Cu_2H_{-4}L}$)
0	3.9±0.2 (3.5±0.2)
0.050	4.1±0.2 (3.7±0.2)
0.100	4.0±0.2 (3.6±0.2)
0.150	4.6±0.2 (4.1±0.2)
0.200	5.2±0.3 (4.7±0.3)

hole on account of the electrostatic repulsion between two copper(II) ion centers.

The d–d transition of a copper(II) binuclear complex in an aqueous solution occurs at 573 nm ($\lambda_{\max}$). This may lend support to the assignment of a slightly disordered square-planar configuration to the two copper(II) centers in the complex, $[Cu_2H_{-4}L]^{\circ}$. In order fully to confirm the structure of a binuclear copper(II) complex by an X-ray crystal analysis, we attempted to isolate pure crystals of the complex, but failed.

The Polarographic Reduction. All of the polarographic measurements were made in solutions containing no free ligand, because of its low solubility in a borate buffer solution. Furthermore, it is surface-active and often retards the electrode-reduction process of the copper(II) binuclear complex at the dropping mercury electrode (DME). In the borate buffer solutions the copper(II)-TOBP complex gave two well-defined reduction steps of equal height. A typical current-voltage curve obtained at DME is reproduced in Fig. 3. The wave-heights of both steps were found to be exactly proportional to the square-root of the effective mercury pressure on the DME. Furthermore, we found that the wave-heights of 1st and 2nd reduction steps for the borate buffer solutions containing 0.20 mmol dm^{-3} TOBP and 0.40 mmol dm^{-3} copper(II) ions were nearly equal to the height of the reduction wave of 0.20 mmol dm^{-3} copper(II) ions in a 0.20 mol dm^{-3} KCl solution.

The number of electrons involved in the electrode reaction of the 1st step was estimated coulometrically by a controlled-potential electrolysis. It was calculated from the following relation:[15]

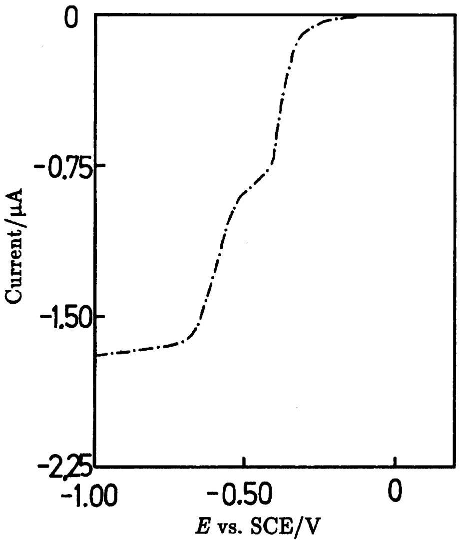

Fig. 3. d.c. Polarogram of copper(II)–TOBP complex, $[Cu_2H_{-4}L]^{\circ}$. Concentration of $[Cu_2H_{-4}L]^{\circ}$, $[Cu_2H_{-4}L^{\circ}]$, $=0.200$ mmol dm^{-3}, Concentration of borate, [borate], $=0.030$ mol dm^{-3}, $I=0.20$ mol dm^{-3}, 25 °C, pH=9.45.

$$n=\frac{Q}{FM}\times\frac{(i_1)_{\circ}}{(i_1)_{\circ}-(i_1)}, \tag{10}$$

where Q is the quantity of electricity required for the electrolysis expressed in Coulombs, F Faraday's constant, M the initial amount of Cu(II)-TOBP complex present in the solution expressed in moles, and $(i_1)_{\circ}$ and (i_1) are the limiting currents of the 1st step before and after the controlled-potential electrolysis, respectively. The Q value was estimated by subtracting the quantity of electricity measured with the supporting electrolyte solution under the same experimental conditions of actual electrolysis from that measured with the test solution. In a determination of the Q value a controlled-potential electrolysis was carried out for about 30 min. The Q, $(i_1)_{\circ}$, and (i_1) values determined were 2.56 Coulombs, 14.30 μA and 9.50 μA, respectively. Using these data the n value was estimated to be 1.9_8. Plots of $\log(i^2/(i_1-i))$ against the d.c. potential (E) of two steps gave straight lines with reciprocal slopes of ca. −30 mV. Here, i_1 and i denote the limiting current and the current at potential E, respectively. All of these findings can be interpreted as indicating a reversible two-electron reduction for both steps. The reversible nature of the electrode processes was also confirmed by the conventional ac polarographic method.[16]

In order to determine whether the reduction product of the 1st step for the binuclear Cu(II) complex is contained in the solution or in the mercury of the electrode as a copper amalgam, the mercury electrode used in the coulometric study was separated from the solution, carefully washed with redistilled water, and then treated with 50 ml of a 5 mol dm^{-3} warm HNO_3 solution to completely dissolve the mercury. After adjusting the pH of the resulting clear solution to 0.3, a slow current of H_2S gas was introduced into it. Black metal(II) sulfides obtained were filtered off and washed with hot distilled water. The metal(II) sulfides were then gently boiled with 10.0 ml of a 3.0 mol dm^{-3} HNO_3 solution in a porcelain dish. After boiling for 3 min., undissolved sulfides were filtered off. The filtrate was then evaporated to a syrup on the steam bath. The residue was dissolved in distilled water, and subjected to an ac polarographic analysis of copper. From the a.c. peak-height of the copper(II) ions in a 0.20 mol dm^{-3} KCl solution (20 ml) the copper content was determined. The amount of copper found in the mercury electrode was 1.27×10^{-2} mmol, corresponding to a 96% recovery of the reduced copper. We also studied the redox behavior of the copper(II)-TOBP complex in a borate buffer solution at the hanging mercury-drop electrode (HMDE). The d.c. current–voltage curve of the copper(II)-TOBP complex was measured by scanning the HMDE potential in the anodic direction at a constant rate of 3.0 mV s^{-1} in stirred test solutions. Although the results are not shown here, the potential excursion from −0.53 V vs. SCE always gave an anodic current–voltage curve ascribable to the anodic dissolution of copper metal formed during the initial stage of potential excursion.

In order to establish the reduction mechanism of the Cu(II)-TOBP complex, we first explored the hydrogen-ion concentration effect on the d.c. potential (E°) at which $\log(i^2/(i_1-i))$ is zero. The E° values for the 1st and 2nd steps were found to shift to more negative potentials along with an increase in the solution pH, obeying relations (11) and (12), respectively. The results are given in Tables 2 and 3

$$\frac{\Delta E_1^\circ}{\Delta \log[\mathrm{H}^+]^2} = +30\ \mathrm{mV} \qquad (11)$$

$$\frac{\Delta E_2^\circ}{\Delta \log(\alpha_\mathrm{H})_\mathrm{L}} = +30\ \mathrm{mV} \qquad (12)$$

Table 2. Effect of Solution pH on E_1°
Concentration of $[\mathrm{Cu_2H_{-4}L}]^\circ$, $[\mathrm{Cu_2H_{-4}L^\circ}]$, = 0.200 mmol dm^{-3}, Concentration of Borate, [borate], =0.030 mol dm^{-3}, I=0.20 mol dm^{-3}, 25 °C

pH	E_1° vs. SCE/V	ΔE_1°/mV	
		Calcd[a)]	Obsd
8.40	−0.2995	+62.1	+65.0
9.04	−0.3395	+24.2	+25.0
9.45	−0.3645	0	0
9.82	−0.3872	−21.9	−22.7
10.20	−0.4110	−44.3	−46.5

a) Calculated by using Eq. 11.

Table 3. Effect of Solution pH on E_2°
Concentration of $[\mathrm{Cu_2H_{-4}L}]^\circ$, $[\mathrm{Cu_2H_{-4}L^\circ}]$, = 0.200 mmol dm^{-3}, Concentration of Borate, [borate], =0.030 mol dm^{-3}, I=0.20 mol dm^{-3}, 25 °C

pH	$(\alpha_\mathrm{H})_\mathrm{L}$	E_2° vs. SCE/V	ΔE_2°/mV	
			Calcd[a)]	Obsd
8.40	2.55	−0.5660	+10.5	+10.0
9.04	1.36	−0.5730	+ 2.5	+ 3.0
9.45	1.12	−0.5760	0	0
9.82	1.05	−0.5760	− 0.8	0
10.20	1.02	−0.5774	− 1.2	− 1.4

a) Calculated by using Eq. 12.

Here, E_1° is the E° value for the 1st step which appears at more positive potentials; E_2° is that for the 2nd steps at more negative potentials. We also found that the concentrations of the copper(II) complex and of borate buffer produced no effect on the E_1° and E_2° values. The fact that $\Delta E_1^\circ/\Delta\log[\mathrm{H}^+]^2$ is 30 mV indicates that two protons are involved in the electrode process of the 1st step. On the other hand, the experimental fact that E_2° shifted to more negative potentials obeying relation (12) clearly suggests that the electroactive species for the second step is the normal 1 : 1 ratio complex, $\mathrm{CuL^{2+}}$. In considering that the $\mathrm{H_{-2}L^{2-}}$ ion can not exist in a free state in an aqueous solution, it can safely be concluded that all of the above findings are evidently consistent with the following step-wise two-electron reduction, corresponding to the E_1° and E_2° values given by Eqs. 16 and 17, respectively. 1st step:

$$[\mathrm{Cu_2H_{-4}L}]^\circ + 2\mathrm{H^+} + 2\mathrm{e^-} + \mathrm{Hg} \rightleftharpoons \mathrm{Cu(Hg)} + [\mathrm{CuH_{-2}L}]^\circ \qquad (13)$$

which is followed by a rapid protonation of $[\mathrm{CuH_{-2}L}]^\circ$, (14)

$$[\mathrm{CuH_{-2}L}]^\circ + 2\mathrm{H^+} \rightleftharpoons \mathrm{CuL^{2+}} \qquad (14)$$

2nd step:

$$\mathrm{CuL^{2+}} + 2\mathrm{e^-} + \mathrm{Hg} \rightleftharpoons \mathrm{Cu(Hg)} + \begin{array}{c} \mathrm{L} \\ \upharpoonleft\downharpoonright\ +j\mathrm{H^+} \\ \mathrm{H}_j\mathrm{L}^{j+} \end{array} \qquad (15)$$

$$E_1^\circ = \varepsilon_\circ' + 0.0296\ \mathrm{V} \times \log[\mathrm{H^+}]^2 - 0.0296\ \mathrm{V} \times \log K_{\mathrm{CuH_{-2}L}}^{\mathrm{Cu_2H_{-4}L}} \qquad (16)$$

where $\varepsilon_\circ' = \varepsilon^\circ{}_{\mathrm{Cu(II)/Cu(Hg)}} + 0.0296\ \mathrm{V} \times \log(k_\mathrm{a} k_{\mathrm{CuH_{-2}L}}/k_{\mathrm{Cu_2H_{-4}L}})$, $K_{\mathrm{CuH_{-2}L}}^{\mathrm{Cu_2H_{-4}L}} = [\mathrm{Cu_2H_{-4}L^\circ}][\mathrm{H^+}]^2/[\mathrm{CuH_{-2}L^\circ}]$-$[\mathrm{Cu^{2+}}]$, and $\varepsilon^\circ{}_{\mathrm{Cu(II)/Cu(Hg)}}$ is the formal potential for $\mathrm{Cu^{2+}} + 2\mathrm{e^-} + \mathrm{Hg} \rightleftharpoons \mathrm{Cu(Hg)}$.

$$E_2^\circ = \varepsilon_\circ'' + 0.0296\ \mathrm{V} \times \log(\alpha_\mathrm{H})_\mathrm{L} - 0.0296\ \mathrm{V} \times \log K_{\mathrm{CuL}}, \qquad (17)$$

where $\varepsilon_\circ'' = \varepsilon^\circ{}_{\mathrm{Cu(II)/Cu(Hg)}} + 0.0296\ \mathrm{V} \times \log(k_\mathrm{a} k_\mathrm{L}/k_{\mathrm{CuL}})$ and $K_{\mathrm{CuL}} = [\mathrm{CuL^{2+}}]/[\mathrm{Cu^{2+}}][\mathrm{L}]$. Here k_a, k_{CuL}, $k_{\mathrm{CuH_{-2}L}}$, $k_{\mathrm{Cu_2H_{-4}L}}$ and k_L in the above equations are the diffusion-current coefficients of copper metal in mercury, $\mathrm{CuL^{2+}}$, $[\mathrm{CuH_{-2}L}]^\circ$, $[\mathrm{Cu_2H_{-4}L}]^\circ$ and L in an aqueous solution.[10,17)]

If the reduction product for the 1st step is a stable binuclear Cu(I) complex, $[\mathrm{Cu_2^IH_{-2}L}]^\circ$, and hence the electrode process is given by Eq. 18, plots of $\log(i/(i_1-i))$ vs. E should give a straight line with a reciprocal slope of 29.6 mV.

$$[\mathrm{Cu_2H_{-4}L}]^\circ + 2\mathrm{H^+} + 2\mathrm{e^-} \rightleftharpoons [\mathrm{Cu_2^IH_{-2}L}]^\circ \qquad (18)$$

However, the plot of $\log(i/(i_1-i))$ against E did not give a straight line having a reciprocal slope of 29.6 mV. In considering the facts obtained by the controlled-potential electrolysis and the voltammetric measurement at the HMDE, the above log-plot examination completely excludes the possibility of the formation of a binuclear copper(I)-TOBP complex.

If the complex, $[\mathrm{CuH_{-2}L}]^\circ$, formed at the first reduction step is stable enough to undergo a reversible two-electron reduction directly, that is, the electrode process for the second step is expressed as Eq. 19, the ratio $\Delta E_2^\circ/\Delta\log(\alpha_\mathrm{H})_\mathrm{L}[\mathrm{H^+}]^2$,

$$[\mathrm{CuH_{-2}L}]^\circ + 2\mathrm{H^+} + 2\mathrm{e^-} + \mathrm{Hg} \rightleftharpoons \mathrm{Cu(Hg)} + \begin{array}{c} \mathrm{L} \\ -j\mathrm{H^+}\ \upharpoonleft\downharpoonright \\ \mathrm{H}_j\mathrm{L}^{j+} \end{array} \qquad (19)$$

in place of $\Delta E_2^\circ/\Delta\log(\alpha_\mathrm{H})_\mathrm{L}$, should be equal to ca. 30 mV. On the other hand, if the mononuclear complex, $[\mathrm{CuH_{-2}L}]^\circ$, is in a rapid equilibrium with $\mathrm{CuL^{2+}}$, and the electrode process for the second step is expressed as Eq. 20, E_2° is given by Eq. 21.

$$\left.\begin{array}{l}[\mathrm{CuH_{-2}L}]^\circ \\ \upharpoonleft\!\downharpoonright\ \ 2\mathrm{H}^+ \\ \mathrm{CuL}^{2+}\end{array}\right\} + 2\mathrm{e}^- + \mathrm{Hg} \rightleftharpoons \mathrm{Cu(Hg)} + \begin{array}{l}\mathrm{L} \\ \upharpoonleft\!\downharpoonright\ \ j\mathrm{H}^+ \\ \mathrm{H}_j\mathrm{L}^{j+}\end{array} \qquad (20)$$

$$\begin{aligned} E_2^\circ = \varepsilon_\mathrm{o}'' &+ 0.0296\log(\alpha_\mathrm{H})_\mathrm{L} \\ &-0.0296\log[K_\mathrm{CuL}(1+K^{-2\mathrm{H}}/[\mathrm{H}^+]^2)] \qquad (21)\end{aligned}$$

Here, $K^{-2\mathrm{H}} = [\mathrm{CuH_{-2}L^\circ}][\mathrm{H}^+]^2/[\mathrm{CuL}^{2+}]$. Therefore, plots of antilog$[(\varepsilon_\mathrm{o}''-E_2^\circ)/0.0296+\log(\alpha_\mathrm{H})_\mathrm{L}]$ vs. $[\mathrm{H}^+]^{-2}$ should give a straight line with an intercept of finite value, corresponding to the K_CuL value. This theoretical relation, however, did not fit to the experimental data of the 2nd step (Fig. 4). The antilog$[(\varepsilon_\mathrm{o}''-E_2^\circ)/0.0296+\log(\alpha_\mathrm{H})_\mathrm{L}]$ value was almost independent of the H^+ concentration. Thus, all of the experimental evidence found can be satisfactorily interpreted in terms of the reaction mechanism, which consists of three reaction pathway ((13), (14), and (15)). For this reason, the K_CuL value can be equated with the antilog$[(\varepsilon_\mathrm{o}''-E_2^\circ)/0.0296+\log(\alpha_\mathrm{H})_\mathrm{L}]$. The estimated K_CuL value was $(1.7\pm0.2)\times10^{20}$ $\mathrm{mol^{-1}\,dm^3}$.

Copper(II) ions also form 2 : 1 ratio complexes, designated as $[\mathrm{Cu_2H_{-4}L}]^\circ$, with propylene-bridged bisdioxo-[14]aneN$_4$ and -[16]aneN$_5$.[18] However, the Cu(II)–propylene-bridged bisdioxocyclic polyamine complexes gave only one cathodic step, consisting of a total four-electron reduction process. This may suggest that the two Cu(II) centers in the binuclear TOBP complex weakly interact with each other, or have slightly different coordination geometries, making a sharp contrast to those in the propylene-bridged bisdioxo-cyclic polyamine complexes. The cyclic voltammetric study also revealed that two Cu(II) centers of the TOBP complex undergo electro-oxidation at different electrode potentials. A typical cyclic voltammogram obtained at a scan rate of 100 $\mathrm{mV\,s^{-1}}$ using a glassy carbon rod as a working electrode is reproduced in Fig. 5. The peak splitting (ΔE_p) for the two cyclic voltammograms was in the range from 60 to 70 mV, which is indicative of a quasireversible one-electron electrochemical behavior, suggesting the formation of a binuclear Cu(III) complex.

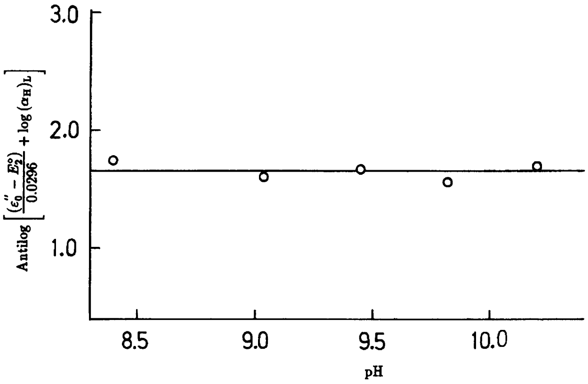

Fig. 4. Plots of antilog$[(\varepsilon_\mathrm{o}''-E_2^\circ)/0.0296+\log(\alpha_\mathrm{H})_\mathrm{L}]$ against pH. Concentration of $[\mathrm{Cu_2H_{-4}L}]^\circ$, $[\mathrm{Cu_2H_{-4}L^\circ}]$, $=0.200$ $\mathrm{mmol\,dm^{-3}}$, Concentration of borate, [borate], $=0.030$ $\mathrm{mol\,dm^{-3}}$, $I=0.20$ $\mathrm{mol\,dm^{-3}}$, 25 °C.

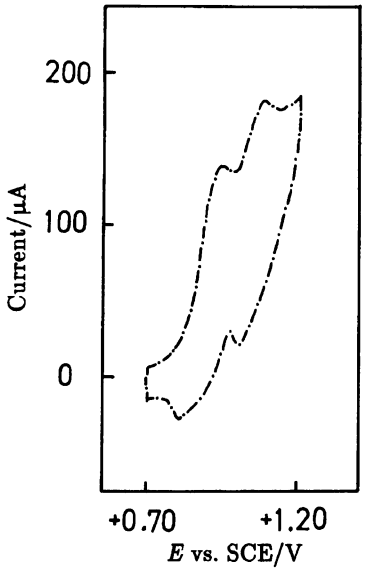

Fig. 5. Cyclic voltammogram of the copper(II)–TOBP complex at glassy carbon working electrode. Concentration of $[\mathrm{Cu_2H_{-4}L}]^\circ$, $[\mathrm{Cu_2H_{-4}L^\circ}]$, $=0.500$ $\mathrm{mmol\,dm^{-3}}$, Concentration of sodium sulfate, $[\mathrm{Na_2SO_4}]$, $=0.50$ $\mathrm{mol\,dm^{-3}}$, Scan rate$=100$ $\mathrm{mV\,s^{-1}}$, pH$=9.70$.

As stated above, we found the 1 : 1 ratio normal copper(II) complex, CuL^{2+}, only as an intermediate in the polarographic reduction of $[\mathrm{Cu_2H_{-4}L}]^\circ$. This might suggest that the first Cu(II) ion already bound to the neutral ligand molecule (L) would effectively promote the dissociation of amide protons. Thus, a subsequent attack of the second Cu(II) ion gives a stable binuclear complex, $[\mathrm{Cu_2H_{-4}L}]^\circ$.

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