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Copper(II) Complexes of 6-Amino-5,7-dioxo-1,4,8,11-tetraazacyclotetradecane

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A newly synthesized dioxocyclam ligand, 6-amino-5,7-dioxo-1,4,8,11-tetraazacyclotetradecane, reacts with copper(II) ions and forms a stable binuclear yellow complex, $[\mathrm{Cu_2H_{-2}L}]^{2+}$, as well as a mononuclear pink complex, $[\mathrm{CuH_{-2}L}]^\circ$, in borate buffer solutions. Their formation equilibria were established by the pH-metric titration and spectrophotometric method. At the dropping mercury electrode the yellow copper(II) binuclear complex gave four reduction steps of equal height in a borate buffer solution, corresponding to the following reduction scheme:

$$\begin{array}{ll}
\text{1st step} & [\mathrm{Cu_2H_{-2}L}]^{2+} + e^- \rightleftarrows [\mathrm{Cu^ICu^{II}H_{-2}L}]^+ \\
\text{2nd step} & [\mathrm{Cu^ICu^{II}H_{-2}L}]^+ + e^- + \mathrm{Hg} \rightleftarrows [\mathrm{CuH_{-2}L}]^\circ + \mathrm{Cu(Hg)} \\
\text{3rd step} & [\mathrm{CuH_{-2}L}]^\circ + \mathrm{H}^+ + e^- \rightleftarrows [\mathrm{Cu^IH_{-1}L}]^\circ \\
 & \text{followed by the following rapid protonation;} \\
 & [\mathrm{Cu^IH_{-1}L}]^\circ + \mathrm{H}^+ \rightleftarrows \mathrm{Cu^IL}^\circ \\
\text{4th step} & \mathrm{Cu^IL}^\circ + e^- + \mathrm{Hg} \rightleftarrows \mathrm{Cu(Hg)} + \begin{array}[t]{c} \mathrm{L} \\ \uparrow\downarrow i\mathrm{H}^+ \\ \mathrm{H}_i\mathrm{L}^{i+} \end{array}
\end{array}$$

The structural and redox properties of the copper(II) complexes have received considerable attention over the past decades, because of their occurrence in natural systems: in particular, because of their biological function in protein.[1] Binuclear copper proteins such as hemocyanin, which acts as an oxygen carrier in molluscs and anthropods[2] have attracted a great deal of interest. As a consequence many binuclear copper(II,I) complexes, which mimic such naturally occurring proteins, have been synthesized and studied extensively.

Our earlier studies on the complexation reaction of macromonocyclic polyamines have revealed that the potential quadridentate cyclic dioxotetraamines possessing the ligand functionality of saturated macrocyclic tetraamines blended with oligopeptide features, form stable square planar $\mathrm{N_4}$ complexes, $[\mathrm{MH_{-2}L}]^\circ$, with copper(II) and nickel(II) ions as a result of a double deprotonation of the amides.[3—5] They are capable of stabilizing the Cu(III) state effectively, but are incapable of stabilizing the Cu(I) state in an aqueous solution.[6] We also have synthesized a binuclearing ligand with two identical macrocyclic dioxotetra- and dioxopenta-amines linked with the trimethylene chain and studied the voltammetric behaviors of their copper(II) binuclear complexes.[7] In these systems the cooperative interaction between two metal sites might be very weak; and neither binuclear Cu(I) complex nor a mixed valence Cu(I)–Cu(II) binuclear complex was formed. However, one amino pendant attached dioxocyclam, 6-amino-5,7-dioxo-1,4,8,11-tetraazacyclotetradecane (amino-dioxocyclam, amino-dioxo[14]aneN$_4$), was found to form a 2 : 1 molar ratio as well as 1 : 1 ratio copper(II) complexes and to stabilize the copper(I) oxidation state in a borate buffer, yielding copper(I) and mixed-valence Cu(I)–Cu(II) binuclear complexes in the course of the voltammetric reduction at the dropping mercury electrode (DME).

As a continuation of investigations on the formation equilibria of macrocyclic dioxotetraamine complexes of transition metal ions and in their redox properties, the formation equilibria of copper(II)–amino-dioxocyclam complexes and their voltammetric behavior in aqueous solutions were studied systematically in this paper.

Experimental

Reagents. The synthetic procedures of 6-amino-5,7-dioxo-1,4,8,11-tetraazacyclotetradecane (amino-dioxocyclam) (Fig. 1) were reported in the previous paper.[8] All other chemicals used were of analytical reagent grade (Wakô and Merck).

Apparatus and Experimental Procedures. The pH-metric titrations were performed with a Mettler Automatic Titrator[3,9] under a nitrogen atmosphere at 25 °C. Three titrations were conducted for each system. The apparatus used for the polarographic measurements were as previously used.[3,10] The pH values of the test solutions used for the polarographic measurements were determined using a glass-electrode pH-meter (a Horiba F8-AT). All of the experimental conditions and procedures employed for the pH-metric titrations and polarographic measurements have been described previously.[9] In the polarographic measurements 5.0×10^{-2} mol dm^{-3} $\mathrm{CH_3COOH}$–$\mathrm{CH_3COONa}$, 3.0×10^{-2} mol dm^{-3} phosphate ($\mathrm{KH_2PO_4}$–$\mathrm{Na_2HPO_4}$), or 3.0×10^{-2} mol dm^{-3} borate buffer

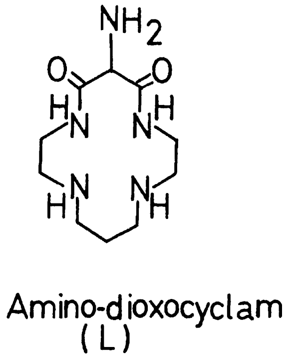

Fig. 1. Amino-pendant dioxocyclam (amino-dioxocyclam) used.

solution was used. They were found to have no effect on the cathodic waves of copper(II) complexes.

Visible and UV spectra were recorded on a Hitachi spectrometer 124. Apparatus and experimental procedures used for the controlled-potential electrolysis were the same as those described previously.[11)]

Mixed protonation constants (log K_i) of amino-dioxocyclam determined potentiometrically by Kimura et al.[8)] at ionic strength (I) 0.10 mol dm^{-3} were corrected for an ionic strength of 0.20 mol dm^{-3} by using the activity coefficients of the ions derived from the Davies equation[12)] and were used in the calculation. They are 9.70±0.03, 6.00±0.03, and 4.13±0.03. The value of $-\log[\mathrm{H^+}]$ used for the calculation of equilibrium constants were estimated by applying a correction of −0.13 pH unit to pH readings.[3)]

Results and Discussion

Complexation Measurements by Potentiometry. The complex formation equilibria between copper(II) ion and amino-dioxocyclam (L) were analyzed in a manner identical to that previously applied to the macrocyclic dioxopolyamine complexes of copper(II) and mercury(II) ions.[5,13)] An equimolar mixture solution of copper(II) ion and amino-dioxocyclam (in the form of $\mathrm{H_3L^{3+}}$) invariably gave titration curves with two buffer regions at the titration points(a): $4.0>a>0$ ($4.0>\mathrm{pH}>3.2$) and $5.0>a>4.0$ ($9.5>\mathrm{pH}>8.6$) (Fig. 2). Here, the titration point (a) indicates the number of moles of base (tetraethylammonium hydroxide, TEAOH) added per mole of amino-dioxocyclam present. Furthermore, the author found that the equimolar mixture solution of pH higher than 5.0 is pink and displays a visible spectrum quite similar to that of copper(II)–dioxocyclam (5,7-dioxo-1,4,8,11-tetraazacyclotetradecane) complex.[5,6)] The copper(II) complexes of amino-dioxocyclam and parent dioxocyclam gave absorption maxima at wave-lengths of 515 and 505 nm, respectively.[14)] These findings indicate that at the 1st buffer region amino-dioxocyclam forms a 1 : 1 ratio complex designated as $[\mathrm{CuH_{-2}LH}]^+$, where its two amide protons dissociate, but the nitrogen atom of amino pendant moiety remained protonated. At the 2nd buffer region, the protonated pendant amino group, $\mathrm{NH_3}^+$, in the complex dissociates as follows:

$$[\mathrm{CuH_{-2}LH}]^+ = [\mathrm{CuH_{-2}L}]^\circ + \mathrm{H}^+ \qquad (1)$$

The experimental data at the 1st buffer region were analyzed using the theoretical relation applied to the

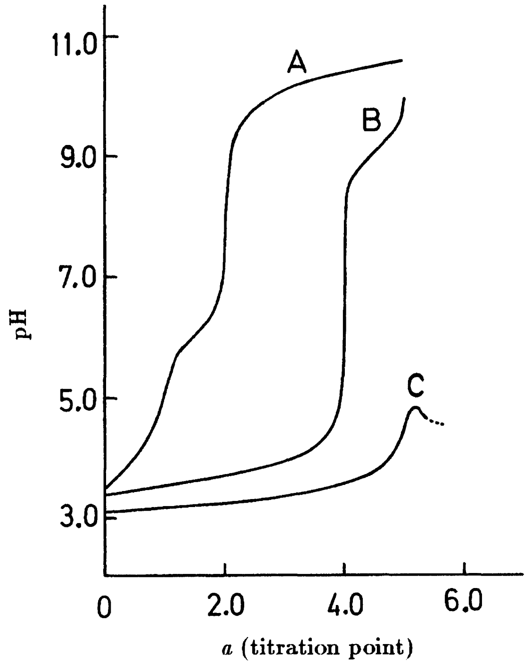

Fig. 2. Titration curves. I=0.20, 25 °C, Amino-dioxocyclam (3HCl salt) 1.00 mmol dm^{-3}. (A) no metal(II) ion, (B) copper(II) 1.00 mmol dm^{-3}, (C) copper(II) 20.0 mmol dm^{-3}.

mercury(II)–dioxo[16]aneN$_6$ complexation.[3)] Although results are not shown here, they fitted well with the following Eq. 2 which can also be applied to the formation of protonated copper(II)–amino-dioxocyclam complex, $[\mathrm{CuH_{-2}LH}]^+$ (Eq. 3).

$$K_{\mathrm{CuH_{-2}LH^+}}(4C_\mathrm{L}-\alpha)^2(\alpha_\mathrm{H})_\mathrm{L}=(\alpha(\alpha_\mathrm{H})_\mathrm{L}-\beta_\mathrm{H}C_\mathrm{L})(4(\alpha_\mathrm{H})_\mathrm{L}-\beta_\mathrm{H})[\mathrm{H^+}] \quad (2)$$

$$\mathrm{Cu^{2+}}+\mathrm{L} \xrightleftharpoons{K_{\mathrm{CuH_{-2}LH^+}}} [\mathrm{CuH_{-2}LH}]^+ + \mathrm{H^+} \qquad (3)$$

Here,

$$\begin{aligned}
\alpha &= aC_\mathrm{L} + [\mathrm{H^+}] - [\mathrm{OH^-}]\\
&= 3[\mathrm{L}] + 2[\mathrm{HL^+}] + [\mathrm{H_2L^{2+}}] + 4[\mathrm{CuH_{-2}LH^+}]\\
&= \frac{\beta_\mathrm{H}}{(\alpha_\mathrm{H})_\mathrm{L}} \times [\mathrm{L}]_\mathrm{f} + 4[\mathrm{CuH_{-2}LH^+}]\\
(\alpha_\mathrm{H})_\mathrm{L} &= 1 + K_1[\mathrm{H^+}] + K_1K_2[\mathrm{H^+}]^2 + K_1K_2K_3[\mathrm{H^+}]^3\\
\beta_\mathrm{H} &= 3 + 2K_1[\mathrm{H^+}] + K_1K_2[\mathrm{H^+}]^2\\
C_\mathrm{M} = C_\mathrm{L} &= [\mathrm{Cu^{2+}}] + [\mathrm{CuH_{-2}LH^+}]\\
&= [\mathrm{L}]_\mathrm{f} + [\mathrm{CuH_{-2}LH^+}]
\end{aligned}$$

C_M and C_L are the analytical concentrations of copper(II) and amino-dioxocyclam, respectively. $[\mathrm{L}]_\mathrm{f}$ and $[\mathrm{Cu^{2+}}]$ denote the concentrations of uncomplexed amino-dioxocyclam and copper(II) ion, respectively. K_i's are protonation constants of amino-dioxocyclam.

From the gradient of the linear relation between $(\alpha(\alpha_\mathrm{H})_\mathrm{L}-\beta_\mathrm{H}C_\mathrm{L})(4(\alpha_\mathrm{H})_\mathrm{L}-\beta_\mathrm{H})[\mathrm{H^+}]$ and $(4C_\mathrm{L}-\alpha)^2(\alpha_\mathrm{H})_\mathrm{L}$ (Fig. 3), the $K_{\mathrm{CuH_{-2}LH^+}}$ ($=[\mathrm{CuL_{-2}LH^+}][\mathrm{H^+}]/[\mathrm{Cu^{2+}}][\mathrm{L}]$) value was estimated to be $(2.3_2\pm0.3_1)\times10^9$.

The experimental data at the 2nd buffer region were found to fit well with the theoretical relation (4), which was derived

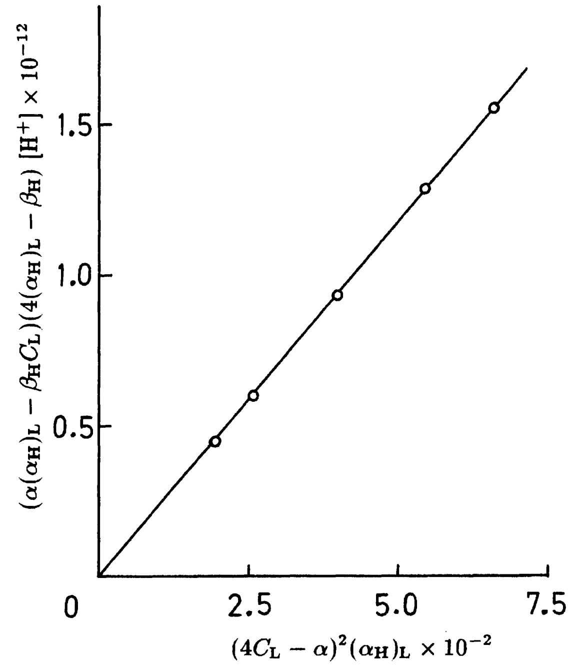

Fig. 3. Determination of $K_{CuH_{-2}LH^+}$ value. I=0.20, 25 °C, Amino-dioxocyclam (3HCl salt) 1.00 mmol dm^{-3}, Copper(II) 1.00 mmol dm^{-3}.

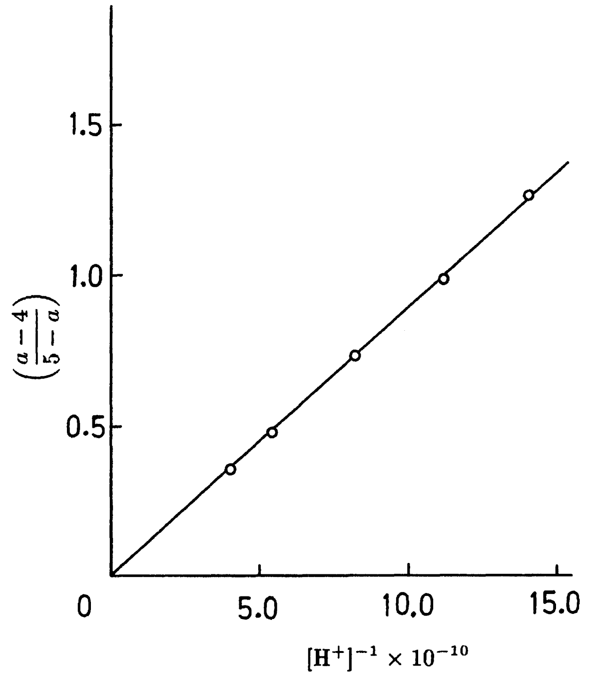

Fig. 4. Determination of K^{-H} value. I=0.20, 25 °C, Amino-dioxocyclam (3HCl salt) 1.00 mmol dm^{-3}, Copper(II) 1.00 mmol dm^{-3}.

in a manner identical to those applied to the copper(II)-15, 15′-trimethylene-bis(1,4,7,10,13-pentaazacyclohexadecane-14,16-dione) (bisdioxo[16]aneN$_5$) complexation[7] for the deprotonation equilibrium (1).

$$K^{-H} = \frac{(a-4)}{(5-a)} \times [H^+] \qquad (4)$$

Here, K^{-H}=[CuH$_{-2}$L°][H$^+$]/[CuH$_{-2}$LH$^+$]. The K^{-H} value could be determined successfully from the slope of a straight line obtained by plotting $(a-4)/(5-a)$ against $[H^+]^{-1}$, which passed through the point of origin (Fig. 4). It was $(8.9_0 \pm 1.4_0) \times 10^{-10}$.

As stated before, the 1 : 1 molar ratio copper(II)–amino-dioxocyclam mixture of pH=10.0 gave quite the same absorption spectrum as that obtained at pH=7.0$_0$. This means that, even when the amino nitrogen of pendant moiety is deprotonated, it does not coordinate to the central copper(II) ion in the complex from the axial position. Furthermore, the copper(II) solution containing an excess amount of amino-dioxocyclam displayed the same visible absorption spectrum as those for the 1 : 1 molar ratio mixture solution (provided that the copper(II) ion concentration is kept constant). This indicates that the copper(II) ion in the solutions containing an excess amount of amino-dioxocyclam exists also as a 1 : 1 ratio complex, [CuH$_{-2}$LH$^+$] or [CuH$_{-2}$L]°.

Contrary to my expectation, the 1.00 mmol dm^{-3} amino-dioxocyclam solution containing 2.00 mmol dm^{-3} copper(II) ion gave no pale blue copper(II) hydroxide precipitates even at pH higher than 8.0, and yielded a yellow solution, which exhibits the absorption spectrum with two absorption maxima at 370 and 660 nm. In this manner the 1.00 mmol dm^{-3} amino-dioxocyclam solution of pH higher than 8.0 gave the Cu(OH)$_2$ precipitates only when the copper(II) concentration is higher than 2.00 mmol dm^{-3}. These findings suggest the high possibility of the formation of the binuclear copper(II)–amino-dioxocyclam complex. The complexation equilibrium between copper(II) ion and amino-dioxocyclam in the solution containing an excess copper(II) ion was also studied pH-metrically. To avoid the intricate calculation in the analysis of experimental data, the titration was carried out by using the amino-dioxocyclam (a 3HCl salt) solution containing a large excess of copper(II) ions. Since copper(II) ions form [Cu(OH)]$^+$ ion or Cu(OH)$_2$ precipitate at pH higher than 4.0, only the experimental data obtained at pH lower than 4.0 were analyzed. The amino-dioxocyclam solution containing an excess amount of copper(II) ion became yellow with the progress of titration and gave a titration curve having a buffer region at the titration point a=5.0 (Fig. 2). This might suggest the formation of binuclear copper(II) complex, [Cu$_2$H$_{-2}$L]$^{2+}$. Experimental data thus obtained at pH lower than 4.0 were found to fit well with Eq. 5, which can be easily derived for the formation of a binuclear complex, [Cu$_2$H$_{-2}$L]$^{2+}$ (Eq. 6).

$$K_{CuH_{-2}LH^+} + K_{Cu_2H_{-2}L}\left(\frac{5C_L-\alpha}{4C_L-\alpha}\right)\frac{[Cu^{2+}]}{[H^+]} = \frac{(\alpha(\alpha_H)_L - \beta_H C_L)[H^+]}{(4C_L-\alpha)[Cu^{2+}]} \qquad (5)$$

$$[CuH_{-2}LH]^+ + Cu^{2+} = [Cu_2H_{-2}L]^{2+} + H^+ \qquad (6)$$

Here, $\alpha = aC_L + [H^+] - [OH^-] = \frac{\beta_H}{(\alpha_H)_L}[L]_f + 4[CuH_{-2}LH^+] + 5[Cu_2H_{-2}L^{2+}]$ and $K_{Cu_2H_{-2}L}$ (=[Cu$_2$H$_{-2}$L^{2+}][H$^+$]/[CuH$_{-2}$LH$^+$][Cu^{2+}]) in the left-hand side of Eq. 5 is equal to the product, $K^D \times K_{CuH_{-2}LH^+}$. K^D=[Cu$_2H_{-2}$L^{2+}][H$^+$]/[Cu^{2+}]-[CuH$_{-2}LH^+$]. The concentration of uncomplexed copper-

(II) ion, $[\mathrm{Cu}^{2+}]$, in Eq. 5 can be approximated to the total copper(II) concentration under the present experimental conditions. Plots of $(\alpha(\alpha_\mathrm{H})_\mathrm{L}-\beta_\mathrm{H}C_\mathrm{L})[\mathrm{H}^+]/(4C_\mathrm{L}-\alpha)[\mathrm{Cu}^{2+}]$ against $(5C_\mathrm{L}-\alpha)[\mathrm{Cu}^{2+}]/(4C_\mathrm{L}-\alpha)[\mathrm{H}^+]$ yielded a straight line with an intercept which is equal to the $K_{\mathrm{CuH_{-2}LH^+}}$ value. Typical results obtained at copper(II) concentrations of 10.0 and 20.0 mmol dm^{-3} were reproduced in Fig. 5. The straight line in Fig. 5 gave an intercept of $(1.5_3\pm0.3_1)\times10^9$, which is nearly equal to the $K_{\mathrm{CuH_{-2}LH^+}}$ value ($(2.3_2\pm0.3_1)\times10^9$). From the slope of the straight line in Fig. 5, the $K_{\mathrm{Cu_2H_{-2}L}}$ value was evaluated to be $(1.4_5\pm0.2_1)\times10^8$. Thus, one can estimate the K^D value to be $(9.4_8\pm0.8_2)\times10^{-2}$ from the slope and intercept of the above straight line. Theoretical relations for the formations of $[\mathrm{Cu_3(H_{-2}L)_2}]^{2+}$, $[\mathrm{Cu_3(H_{-1}L)_2}]^{4+}$, $[\mathrm{Cu_3L_2}]^{6+}$, and other complexes were also derived. However, the experimental data did not fit the theoretical equations derived for the formations of these complexes. Thus, the experimental evidence collected in the pH-metric titration of the amino-dioxocyclam solution containing an excess amount of copper(II) ions could be explained satisfactorily in terms of the equilibrium (6).

Spectrophotometric Study. The conclusions reached concerning the complexation equilibrium between copper(II) ion and amino-dioxocyclam and the validity of formation constants determined in the pH-metric study were checked by the spectrophotometric method. The absorption spectrum for the 1.00 mmol dm^{-3} amino-dioxocyclam solution of pH=4.41 containing 10.0 mmol dm^{-3} copper(II) ion was recorded and is reproduced in Fig. 6 (Curve C). Using equilibrium constants determined and molar absorbancies for complexes, $[\mathrm{CuH_{-2}LH}]^+$ and $[\mathrm{Cu_2H_{-2}L}]^{2+}$, estimated from the absorption spectra for the 1 : 1 and 2 : 1 molar ratio mixture solutions of copper(II) and amino-dioxocyclam observed at pH=10.0 (Curves A and B, respectively, in Fig. 6), the absorption spectrum for the 1.00 mmol dm^{-3} amino-dioxocyclam solution containing 10.0 mmol dm^{-3} copper(II) ion was simulated at pH=4.41 and compared with the observed one. The simulated absorption spectrum agreed well with the observed one (Fig. 6). As shown in Table 1, absorbances calculated at 370, 515, and 660 nm showed a satisfactory agreement with those observed. Judging from $K_{\mathrm{CuH_{-2}LH^+}}$, $K^{-\mathrm{H}}$, and $K_{\mathrm{Cu_2H_{-2}L}}$ values, amino-dioxocyclam in its 1.00 mmol dm^{-3} solution of pH=10.0 containing an equimolar copper(II) ion and that in the solution containing twice as much copper(II) ions as amino-dioxocyclam are considered to exist as $[\mathrm{CuH_{-2}L}]^\circ$ and $[\mathrm{Cu_2H_{-2}L}]^{2+}$, respectively. Here, it should be mentioned again that the pink complex in the solution of pH=4.41 containing an excess ligand gives the same absorption spectrum as that obtained for the equimolar mixture solution at pH=10.0. In the measurement of spectrum (C) 10.0 mmol dm^{-3} copper(II) solution was used as a reference solution. The above agreement shows that the equilibrium constants are estimated reasonably and the conclusion established in the pH-metric titration is rational.

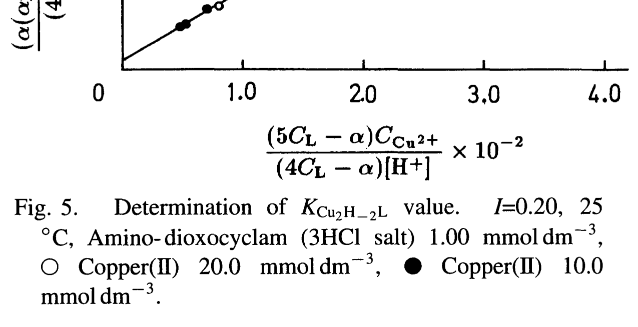

Fig. 5. Determination of $K_{\mathrm{Cu_2H_{-2}L}}$ value. I=0.20, 25 °C, Amino-dioxocyclam (3HCl salt) 1.00 mmol dm^{-3}, ○ Copper(II) 20.0 mmol dm^{-3}, ● Copper(II) 10.0 mmol dm^{-3}.

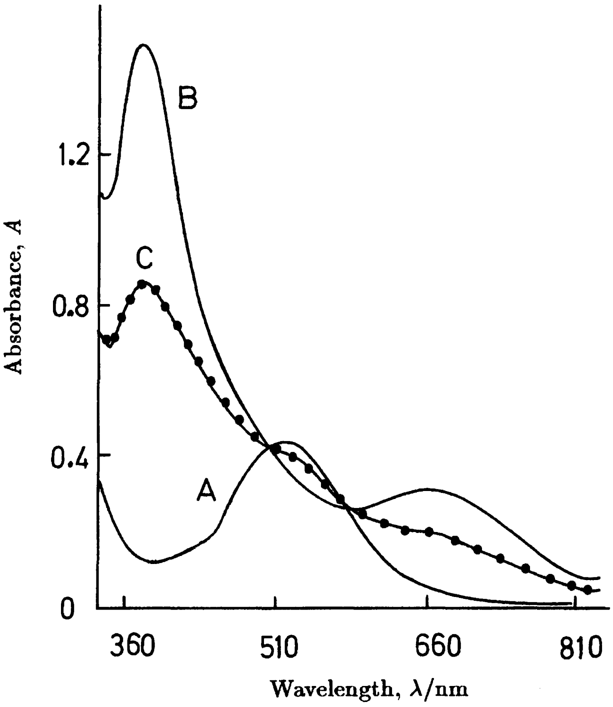

Fig. 6. Absorption spectra of copper(II)–amino-dioxocyclam complexes. I=0.20, 25 °C, Amino-dioxocyclam 1.00 mmol dm^{-3}. (A) copper(II) 1.00 mmol dm^{-3}, pH=7.00, (B) copper(II) 2.00 mmol dm^{-3}, pH=10.0, (C) copper(II) 10.0 mmol dm^{-3}, pH=4.41. solid line: observed, ●: calculated.

Table 1. Absorption Spectral Data I=0.20, 25°C

$[\mathrm{L}]_\mathrm{t}$ [b)	$[\mathrm{Cu(II)}]_\mathrm{t}$ [b)	pH	Absorbance/A		
mmol dm^{-3}	mmol dm^{-3}		370 nm	515 nm	660 nm
1.00	2.00	9.00	1.48_0	0.40_0	0.29_6
1.00	1.00	7.00	0.12_0	0.42_4	0.04_8
1.00	10.00	4.41	0.84_8	0.42_0	0.16_5
			0.85_0 [a)	0.41_1 [a)	0.16_1 [a)

a) Calculated values. b) $[\ ]_\mathrm{t}$ means the total concentration.

The above-mentioned conclusion that amino-dioxocyclam can form a binuclear copper(II) complex could be confirmed by the following experimental facts. The elemental analysis of dark green needles,[14] which were prepared by adding 5.0 ml of 1 mol dm^{-3} NaClO$_4$ solution to 5.0 ml solution of pH=7.0 containing 1.00 mmol Cu(ClO$_4$)$_2$·6H$_2$O and 0.50 mmol amino-dioxocyclam and by evaporating the resulting mixture solution slowly, revealed that it might be given by Cu$_2$H$_{-2}$L(ClO$_4$)$_2$·H$_2$O (C$_{10}$H$_{21}$N$_5$O$_{11}$Cl$_2$Cu$_2$, molecular weight=585.3).[15] This dark green needle gave yellow solutions at pH higher than 8.0. The 10.0 ml yellow solution of pH=10.0 containing 5.9 mg of dark green needles exhibited an identical absorption spectrum with that for the 1.00 mmol dm^{-3} amino-dioxocyclam solution of pH=10.0 containing 2.00 mmol dm^{-3} copper(II) ions. This clearly indicates that 5.9 mg dark green needles correspond to 1.0×10^{-2} mmol 2 : 1 molar ratio copper(II)–amino-dioxocyclam complex having a molecular weight of 585, and hence gives a strong support to the conclusion obtained by the elemental analysis.

Furthermore, the solution prepared by dissolving 3.2 mg of dark green needles into 25 ml of 0.10 mol dm^{-3} NaNO$_3$ solution and adjusting the solution pH to 1.46 gave a well-defined single cathodic wave, due to the reduction of copper(II) ion to the copper amalgam, Cu(Hg), at the dropping mercury electrode (DME). Its limiting current at −0.20 V vs. SCE was found to be 2.57 μA, corresponding to 0.437 mmol dm^{-3} copper(II) ion. This finding indubitably indicates that the dark green needles contain 21.7% copper, corresponding to the formula, Cu$_2$H$_{-2}$L(ClO$_4$)$_2$·H$_2$O. All these experimental results support the conclusion that amino-dioxocyclam can form a binuclear copper(II) complex, [Cu$_2$H$_{-2}$L]$^{2+}$, under the experimental conditions employed.

Polarographic Reduction. The polarographic reduction behaviors of copper(II)–amino-dioxocyclam complexes were studied in acetate and borate buffer solutions.

Pink Mononuclear Copper(II)–Amino-dioxocyclam Complex. Copper(II) ions in acetate buffer solutions containing an excess amount of amino-dioxocyclam ligand gave a single well-defined cathodic wave having a diffusion-controlled nature at DME, and its limiting current, i_l, was proportional to the bulk copper(II) ion concentration. Plots of log ($i/(i_l-i)$) against the d.c. potential, E, invariably gave a straight line with a reciprocal slope falling in the range of −31 to −35 mV, corresponding to the reversible two-electron reduction. Here, i means the cathodic current at E. The half-wave potential shifted to the more negative potentials along with an increase in the solution pH obeying the relation (7), and also with an increase in the concentration of amino-dioxocyclam, [L]$_f$, obeying the relation (8) (Table 2).

$$\frac{\Delta E_{1/2}}{\Delta \log(\alpha_H)_L[H^+]} = +29.6\ \mathrm{mV} \tag{7}$$

$$\frac{\Delta E_{1/2}}{\Delta \log[L]_f} = -29.6\ \mathrm{mV} \tag{8}$$

Table 2. Effects of pH and Ligand Concentration, [L]$_f$, on the Half-Wave Potential, $E_{1/2}$
[Cu(II)]$_t$=0.30 mmol dm^{-3}, I=0.20, 25 °C, Acetate buffer=5.0$_0$×10^{-2} mol dm^{-3}

pH	[L]$_f$	$E_{1/2}$	$\Delta E_{1/2}$/mV	
	mmol dm^{-3}	V vs. SCE	Calcd	Obsd
3.94	5.00	-0.230_0	0	0
4.48	5.00	-0.283_1	$-55._1$	$-53._1$
4.93	5.00	-0.326_1	$-97._4$ $(+9._0)$	$-96._1$ $(+9._9)$
4.93	10.00	-0.336_2	(0)	(0)
4.93	20.00	-0.348_3	$-11._9$	$-12._1$

( ): The effect of ligand concentration.

These facts indicate that the electrode process for the reduction of 1 : 1 ratio pink complex in an acetate buffer is expressed as:

$$\begin{array}{l} [\mathrm{CuH_{-2}LH}]^+ + \mathrm{H}^+ + \mathrm{Hg} + 2e^- \rightleftarrows \mathrm{Cu(Hg)} + \ \mathrm{L} \\ \hphantom{[\mathrm{CuH_{-2}LH}]^+ + \mathrm{H}^+ + \mathrm{Hg} + 2e^- \rightleftarrows \mathrm{Cu(Hg)} + \ } \uparrow\downarrow +i\mathrm{H}^+ \\ \hphantom{[\mathrm{CuH_{-2}LH}]^+ + \mathrm{H}^+ + \mathrm{Hg} + 2e^- \rightleftarrows \mathrm{Cu(Hg)} + \ } \mathrm{H}_i\mathrm{L}^{i+} \end{array}$$

On the other hand, in borate buffer solutions it gave two well-defined reduction steps of equal height, which is exactly one half of the limiting current obtained in an acetate buffer solution (at a given bulk copper(II) concentration) (Fig. 7). Plots of log ($i/(i_l-i)$) against the d.c. potential, E, for both steps gave invariably straight lines with reciprocal slopes of ca. −60 mV, corresponding to the one-electron reversible reduction. The half-wave potential of the 1st step which occurs at more positive potentials was independent of the amino-dioxocyclam (at a given pH), but shifted to more negative potentials along with an increase in the solution pH,

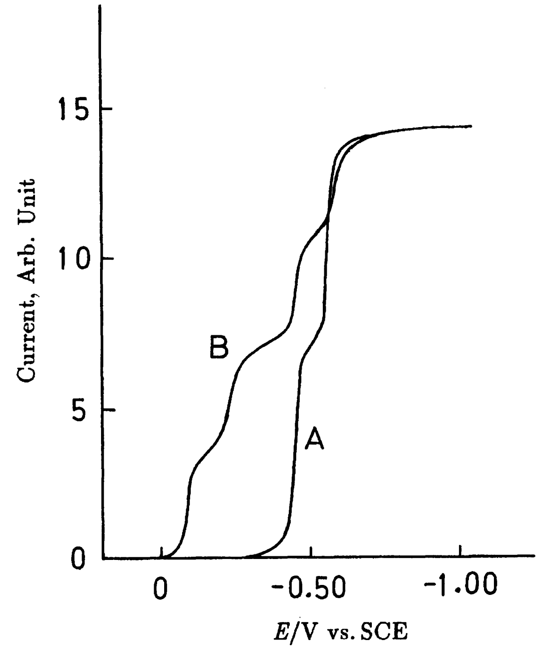

Fig. 7. Polarograms of copper(II)–amino-dioxocyclam complexes in borate buffer solutions. I=0.20, 25 °C, pH=10.0, Amino-dioxocyclam 0.30 mmol dm^{-3}. (A) copper(II) 0.30 mmol dm^{-3}, (B) copper(II) 0.60 mmol dm^{-3}.

obeying the following Eq. 9 (Table 3):

$$\frac{\Delta E_{1/2}}{\Delta \log\left(\dfrac{[\mathrm{H}^+]}{1+[\mathrm{H}^+]}\right)} = 59.1\ \mathrm{mV} \qquad (9)$$

In considering the fact that the uncomplexed amino-dioxocyclam gave no cathodic wave at potentials where the copper(II) complex is reduced at DME, these findings are considered to be consistent with the following one-electron reduction (10):

$$\left.\begin{array}{c}[\mathrm{CuH}_{-2}\mathrm{L}]^\circ \\ \uparrow\downarrow \qquad +\mathrm{H}^+ \\ [\mathrm{CuH}_{-2}\mathrm{LH}]^+\end{array}\right\} + \mathrm{H}^+ + \mathrm{e}^- \rightleftarrows [\mathrm{Cu^IH}_{-1}\mathrm{L}]^\circ \qquad (10)$$

The half-wave potential of the 2nd step occurring at more negative potentials shifted to more negative potentials along with increases in solution pH and the concentration of amino-dioxocyclam obeying the relations (11) and (12), respectively. These two findings suggest the reduction mechanism (13) for the 2nd step (Table 4).

$$\frac{\varDelta E_{1/2}}{\varDelta\ \log(\alpha_\mathrm{H})_\mathrm{L}} = 59.1\ \mathrm{mV}\ (\text{at a given } [\mathrm{L}]_\mathrm{f}) \qquad (11)$$

$$\frac{\varDelta E_{1/2}}{\varDelta\ \log[\mathrm{L}]_\mathrm{f}} = -59.1\ \mathrm{mV}\ (\text{at a given pH}) \qquad (12)$$

$$[\mathrm{Cu^IL}]^\circ + \mathrm{Hg} + \mathrm{e}^- \rightleftarrows \mathrm{Cu(Hg)} + \begin{array}{l}\mathrm{L} \\ \uparrow\downarrow +\mathrm{H}^+ \\ \mathrm{H}_j\mathrm{L}^{j+}\end{array} \qquad (13)$$

Table 3. The Effect of pH on the Half-Wave Potential of the First Step, $E_{1/2}$, at a Given Ligand Concentration, $[\mathrm{L}]_\mathrm{f}$ $[\mathrm{Cu(II)}]_\mathrm{t}$=0.30 mmol dm^{-3}, I=0.20, 25 °C, $[\mathrm{L}]_\mathrm{f}$=10.00 mmol dm^{-3}, Borate buffer=0.030 mol dm^{-3}

pH	$\log\left(\dfrac{[\mathrm{H}^+]}{1+[\mathrm{H}^+]/K^{-\mathrm{H}}}\right)$	$E_{1/2}$	$\Delta E_{1/2}$/mV	
		V vs. SCE	Calcd	Obsd
7.39$^{\mathrm{a)}}$	-9.059_4	-0.464_0	0	0
8.35	-9.129_0	-0.469_1	$-4._1$	$-5._1$
9.25	-9.462_1	-0.489_2	$-23._8$	$-25._2$
10.13	-10.165_0	-0.532_0	$-65._3$	$-68._0$

a) Phosphate buffer: 0.050 mol dm^{-3}.

Table 4. Effects of pH and Ligand Concentration, $[\mathrm{L}]_\mathrm{f}$, on the Half-Wave Potential of the Second Step, $E_{1/2}$ $[\mathrm{Cu(II)}]_\mathrm{t}$=0.30 mmol dm^{-3}, 25 °C, I=0.20, Borate buffer=0.030 mol dm^{-3}

pH	$[\mathrm{L}]_\mathrm{f}$	$E_{1/2}$	$\Delta E_{1/2}$/mV	
	mmol dm^{-3}	V vs. SCE	Calcd	Obsd
7.39$^{\mathrm{b)}}$	10.00	-0.548_1	$+56._9$	$+54._0$
8.35	10.00	-0.602_1	0 (0)$^{\mathrm{b)}}$	0 (0)$^{\mathrm{b)}}$
9.25	10.00	-0.645_0	$-47._0$	$-42._9$
10.13	10.00	-0.675_6	$-74._1$	$-73._5$
8.35	25.00	-0.626_2	$(-23._5)^{\mathrm{b)}}$	$(-24._1)^{\mathrm{b)}}$

a) ( ): The effect of ligand concentration. b) Phosphate buffer 0.050 mol dm^{-3}.

Furthermore, it was found that the concentration of copper(II) complex produced no effect on the $E_{1/2}$ values of either step. In order to check whether the Cu(I) state really intervenes, the polarographic behavior of copper(I) ion in borate buffer solutions containing an excess amino-dioxocyclam was also studied. The copper(I) ion in the above solutions invariably gave composite anodic and cathodic waves of equal height,[15] which appear at potentials where the 1st and 2nd reduction steps for the copper(II) complex occur. This clearly indicates that the Cu(I) complex can really exist as a reduction intermediate. The finding that the normal 1 : 1 molar ratio copper(I)–amino-dioxocyclam, $[\mathrm{Cu^IL}]^\circ$, is the reacting species at the 2nd step might imply that the reduction reaction (10) is followed by a subsequent rapid protonation reaction (14).

$$[\mathrm{CuH}_{-1}\mathrm{L}]^\circ + \mathrm{H}^+ = [\mathrm{Cu^IL}]^\circ \qquad (14)$$

In considering that the d^{10} metal ion such as Zn^{2+} can not promote the dissociation of the amide group in its complexation reaction with dioxopolyazamacrocycles,[7] the d^{10} Cu(I) complex, $[\mathrm{CuH}_{-1}\mathrm{L}]^\circ$, might be unstable under the usual experimental conditions. Therefore, it would react rapidly with a proton to yield the stable Cu(I) complex, $[\mathrm{Cu^IL}]^\circ$. Irrespective of the solution pH, the copper(II) complex of the parent dioxocyclam gives exclusively a single two-electron reduction wave. Hence, the pendant nitrogen donor of coordinated amino-dioxocyclam molecule is considered to play a decisive role in stabilizing and holding the Cu(I) ion. This is also the reason why the Cu(I)–amino-dioxocyclam complex is stable in a borate buffer but not in an acetate buffer.

The polarographic behavior of 1 : 1 ratio pink complex was also studied using the 1 : 1 molar ratio mixture solution at pH higher than 8.10 (borate buffer). Copper(II) ion in the solution containing an equimolar amino-dioxocyclam also gave two well-defined steps of equal height. Plots of $\log(i/(i_\mathrm{l}-i))$ against the dc potential for the 1st step also gave a straight line with a reciprocal slope of ca. −60 mV, suggesting a reversible one-electron reduction. Its half-wave potential shifted to more negative potentials with an increase in pH obeying the relation (9), and was independent of the concentration of the complex, as in the solution containing an excess amino-dioxocyclam. The 2nd step occurring at the more negative potentials gave a straight line with a reciprocal slope of ca. −60 mV only when the $\log(i^2/(i_\mathrm{l}-i))$ value was plotted against E. The potential at $(i^2/(i_\mathrm{l}-i))=1$, E°, was independent of the concentration of copper(II) complex, but shifted to more negative potentials with an increase in solution pH, obeying faithfully relation (11). All of the above experimental findings collected in the 1 : 1 molar ratio mixture system also can be explained in terms of (10), (14), and (13). The Cu(I)–amino-dioxocyclam complex, $[\mathrm{Cu^IL}]^\circ$, is assumed to adapt a tetrahedral structure.[16,17]

Yellow Binuclear Copper(II)–Amino-dioxocyclam Complex. The polarographic behavior of yellow binuclear copper(II) complex was studied using the 2 : 1 molar ratio mixture solution of copper(II) ion and amino-dioxocyclam at pH from 8.10 to 10.10 (borate buffer solution).

As illustrated by the polarogram reproduced in Fig. 7, the yellow binuclear copper(II) complex in borate buffer solutions gave four well-defined reversible reduction steps of equal height, each corresponding to one one-electron reduction. Of course, the wave-heights of these steps were exactly proportional to the square-root of the effective mercury pressure and the concentration of binuclear copper(II) complex. The 1st step which appears at about −0.10 V vs. SCE displayed a linear relation having the reciprocal slope of ca. −60 mV when $\log(i/(i_l - i))$ in place of $\log(i^2/(i_l - i))$ was plotted against the dc potential, E. This suggests the formation of a mixed valence Cu(I)–Cu(II) binuclear complex as a reduction intermediate. Although the detailed results were not shown here, the number of electrons involved in the 1st reduction step was determined coulometrically by employing the controlled-potential electrolysis using apparatus and experimental procedures similar to those used in the copper(II)–TOBP (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) complex.[11] The number of electrons estimated from the quantity of electricity required for the electrolysis and the decrease in the limiting current of the 1st step by the electrolysis was 0.92. By employing the controlled-potential electrolysis I tried to prepare and isolate the mixed valence Cu(I)–Cu(II) binuclear amino-dioxocyclam complex, but failed. This failure implies that the mixed valence Cu(I)–Cu(II) binuclear complex is not so stable that it can be isolated from the reaction mixture, but it can exist only as a reaction intermediate in the polarographic reduction. Furthermore, the solution obtained by treating the mercury metal used for the electrolysis with nitric acid was analyzed for the copper(II) ion by polarographic and spectrophotometric methods. However, no copper(II) ion could be detected. The controlled-potential electrolysis was, of course, done at the potentials where the limiting current of the 1st reduction can be observed.

The half-wave potential of the 1st step, $(E_{1/2})_1$, was found to be independent of the solution pH and the concentration of binuclear complex (Table 5). In considering the fact that plots of $\log(i/(i_l - i))$ against E gave a straight line having a reciprocal slope of ca. −60 mV and those collected by the controlled-potential electrolysis, these facts can be explained reasonably by assuming the following electrode process for the 1st reduction step:

$$[\mathrm{Cu}_2^{\mathrm{II}}\mathrm{H}_{-2}\mathrm{L}]^{2+} + \mathrm{e}^- \rightleftarrows [\mathrm{Cu}^{\mathrm{I}}\mathrm{Cu}^{\mathrm{II}}\mathrm{H}_{-2}\mathrm{L}]^+ \qquad (15)$$

On the other hand, the 2nd step which appears at about −0.25 V vs. SCE gave a straight line with a reciprocal slope of ca. −60 mV when the $\log(i^2/(i_l - i))$ value in place of $\log(i/(i_l - i))$ was plotted against E. In order to establish the reduction mechanism for the 2nd step, the effects of concentrations of hydrogen ion and of complex on the potential where $(i^2/(i_l - i))$ is unity, $E°$ were studied. The $E°$ value was found to be independent of both hydrogen ion and complex concentrations, corresponding to the following reaction mechanism (Table 5). Although no detailed result is given here, copper amalgam formation at the 2nd reduction step was confirmed by the controlled-potential electrolysis using a mercury pool electrode. As in the case of copper(II)–TOBP complex,[11] the solution obtained by treating the mercury metal used for the electrolysis with nitric acid was analyzed for the copper(II) ion by the polarographic method. Ninety per cent of the copper metal estimated from the decrease in the limiting current of the 2nd step by the controlled-potential electrolysis was detected. If the binuclear Cu(I) complex, $[\mathrm{Cu}_2^{\mathrm{I}}\mathrm{H}_{-2}\mathrm{L}]°$, is the reduction product, and hence, no copper amalgam is formed, plots of $\log(i/(i_l - i))$ against E should give a straight line with a reciprocal slope of −59.1 mV. However, plots of $\log(i/(i_l - i))$ against E for the 2nd step gave no straight line with a reciprocal slope of −59.1 mV.

Table 5. Effects of pH and Concentration of Binuclear Copper(II) Complex on the $E_{1/2}$ (1st Step) and $E°$ (2nd Step) Values
I=0.20 mol dm^{-3}, 25 °C, Borate buffer=0.030 mol dm^{-3}

pH	$[\mathrm{Cu(II)}]_t$	$E_{1/2}$	$E°$
	mmol dm^{-3}	V vs. SCE	V vs. SCE
8.17	0.30	-0.094_0	-0.213_0
9.13	0.30	-0.093_7	-0.213_2
10.15	0.30	-0.093_8	-0.213_4
9.13	0.15	-0.093_7	-0.213_0
9.13	0.50	-0.094_0	-0.213_5

$$[\mathrm{Cu}^{\mathrm{I}}\mathrm{Cu}^{\mathrm{II}}\mathrm{H}_{-2}\mathrm{L}]^+ + \mathrm{e}^- + \mathrm{Hg} \rightleftarrows \mathrm{Cu(Hg)} + [\mathrm{Cu}^{\mathrm{II}}\mathrm{H}_{-2}\mathrm{L}]° \qquad (16)$$

Provided that all the experimental conditions are kept constant, the potentials where last two reduction steps appear exactly coincide with those of the 1st and 2nd reduction steps for the 1 : 1 molar ratio mixture solution of copper(II) ion and amino-dioxocyclam at pH's higher than 8.10. Furthermore, these steps exhibited the same polarographic behavior as those of the two reduction steps observed in the above 1 : 1 molar ratio mixture solution. The half-wave potential for the 3rd step appearing at about −0.45 V vs. SCE shifted to more negative potentials with an increase in the solution pH, obeying relation (9), but was independent of copper(II) complex concentration. The $E°$ value for the 4th step at about −0.58 V vs. SCE, where $\log(i^2/(i_l - i))$ value is zero, also shifted to more negative potentials with an increase in the solution pH, obeying relation (11), but was independent of the concentration of copper(II) complex. These findings show that the reaction process for the 3rd step at about −0.45 V vs. SCE is given by Eq. 10, which is followed by the rapid protonation of the reduction product Eq. 14, and that for the 4th step at about −0.58 V vs. SCE by Eq. 13.

Almost all the cyclic binucleating ligands studied recently are large-sized polyazamacrocyclic molecules containing two identical ligating moieties separated by (ligating or non-ligating) linkages and those prepared by bridging the two small-sized cyclic rings possessing the ligand functionality.[18—22] For this reason, it is somewhat surprising that the smaller ligand, amino-dioxocyclam, can act as

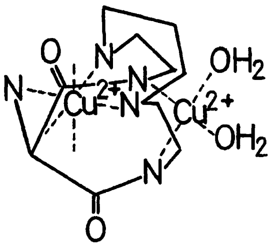

Fig. 8. Proposed model for the binuclear complex.

a binucleating ligand in the reaction with copper(II) ion and form the mixed valence binuclear Cu(I)–Cu(II) complex as a reduction intermediate. It is generally believed that the desirable features of the ligand which can effectively stabilize the unusual oxidation states (Cu(I), Cu(III) etc.) of metal centers are sufficient flexibility to allow the proper metal–metal spatial relationships and the metal coordination geometries to vary easily from one which stabilizes one oxidation state to the other stabilizing the other oxidation state. The donor sets capable of stabilizing these unusual oxidation states effectively are also required.

Although detailed crystal structure of the dark green needle has not been determined yet, the distance between two copper centers in the above binuclear copper complex is so short that two copper centers probably can take positions appropriate for their mutual influence and cooperative interaction, and hence, the Cu(I)–Cu(II) mixed valence state may be effectively stabilized. The model shown in Fig. 8 may be useful in understanding of the above explanation offered for the structure of the binuclear copper complex. An X-ray crystallographic investigation on the structure of the dark green binuclear copper(II)–amino-dioxocyclam complex is now under way.

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