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Polarographic Study on the Stabilization of Copper(I) State by Macrocyclic Triamine with an Aid of Monodentate π-Ligand

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Formation equilibria of ternary copper(I)-macrocyclic triamine ([11]aneN_3, [12]aneN_3, iso[12]aneN_3, and [12]-aneN_3S) complexes with monodentate π-ligand (SCN^-, CH_3CN, or imidazole) were studied by the polarographic method. The copper(I)-macrocyclic triamine complexes in solutions containing an excess monodentate π-ligand were found to produce a polarogram consisting of two separate reduction steps of equal height. The chemical equilibria for the formation of the 1 : 1 : 1 ratio copper(I) mixed ligand complexes including macrocyclic triamine and π-ligand were determined by studying the effects of solution pH and concentrations of macrocyclic triamine and π-ligand on the half-wave potential of the 2nd reduction step, which appears at more negative potentials. The eleven-membered macrocyclic triamine, [11]aneN_3, forms the most thermodynamically stable copper(I) mixed ligand complex, $[Cu^IL(A)]^{1-b}$. The formation constants for 1 : 1 : 1 ratio copper(II), macrocyclic triamine, and monodentate π-ligand were determined potentiometrically by studying the effects of SCN^-, CH_3CN, or imidazole concentration on the formation equilibrium of copper(II)-macrocyclic triamine complexes.

There is a growing interest in the chemistry of copper(I) complexes in solution. This stems from the important role of copper(I) in biological systems, in free radical reactions, and in the other essential redox processes. In simple coordination compounds the copper(I) ions are now well documented to show coordination numbers of 2 to 5. In a previous paper,[1] we studied the interaction of copper(I) ion with 2,5,8-trimethyl-2,5,8-triazanonane (pmdien) in CO-saturated or CH_3CN-containing aqueous solutions. The potentially tridentate saturated amine, pmdien, was found to be able to sustain copper(I) state by forming the tetrahedral complex with an aid of monodentate π-ligand, CO or CH_3CN. The extraordinary stability of the copper(I)-pmdien complex in water could be ascribed to the steric and hydrophobic effects of pmdien and also to the coordination of the strong monodentate π-acceptor.

As a continuation of our investigations on the stabilization of copper(I) state by triamine, the reactions of copper(I) ion with macrocyclic triamine which is sterically constrained and has a hydrophobic cavity, in aqueous solutions containing monodentate π-ligand, SCN^-, CH_3CN or imidazole, were studied by employing a conventional d.c. polarographic method. The reaction of copper(II) ions with macrocyclic triamine in aqueous solutions containing SCN^-, CH_3CN or imidazole was also studied using pH-metric titration in this paper.

Experimental

Reagents. Macrocyclic triamine ligands, 1,4,7-triazacyclononane ([9]aneN_3) (**1**), 1,4,7-triazacyclodecane ([10]aneN_3) (**2**), 1,4,8-triazacycloundecane ([11]aneN_3) (**3**), 1,5,9-triazacyclododecane ([12]aneN_3) (**4**), and 1,4,7-triazacyclododecane (iso[12]aneN_3) (**5**) as the HCl or HBr salt were synthesized by the Richmann-Atkins procedure (Chart 1).[2] The sulfur-containing ligand, 1-thia-4,7,10-triazacyclododecane ([12]aneN_3S) (**6**) and macrocyclic tetraamine, 1,4,8,11-tetraazacyclotetradecane ([14]aneN_4 or cyclam) (**7**), were synthesized as described before (Chart 2).[3] The purification method of 2,5,8-trimethyl-2,5,8-triazanonane (pmdien) (**8**) was given in the previous paper.[1] $[Cu^I(CH_3CH)_4]ClO_4$ was prepared as described by Hathaway et al.[4] All other reagents used were of analytical grade.

Apparatus and Measurements. The apparatus and experimental procedures used for the polarographic measurements were as previously used.[5] A voltammetric technique using a rotating disk electrode (RDE) was also applied to the study of the redox behaviors of copper(II) complexes. The variable electrode potential was produced by a dual potentiogalvanostat (DPGS-1) and a functional generator (NFG-3) manufactured by Nikko Keisoku Co., Ltd. In order to rotate the disk electrode at specific rotation rates, a Nikko Keisoku rotating ring(Pt)-disk (glassy carbon) electrode (RRDE-1) coupled with a motor speed controller (SC-5) was used. Rotating disk current–potential curves were recorded with an X–Y recorder, while the potential was scanned at 4 $mV\,s^{-1}$. The pH values of solutions were read with a Hitachi F8-AT digital pH meter with a glass electrode (Horiba Combination Electrode 6327-10C). The apparatus and experimental procedures for the potentiometric study were as previously used.[6] Apparatus and experimental procedures used for the controlled-potential electrolysis were the same as those described previously.[7] All measurements were performed at 25.0±0.1 °C, using test solutions which were adjusted to an ionic strength (I) of 0.20 $mol\,dm^{-3}$by addition of $NaClO_4$. I used borate buffer in this study to keep the solution pH at a desired value ($8.10 < pH < 10.10$), but it had little effect on the polarographic behavior of the copper(II) complexes. Unless otherwise stated, I used 0.030 $mol\,dm^{-3}$ borate buffer solutions for the polarographic

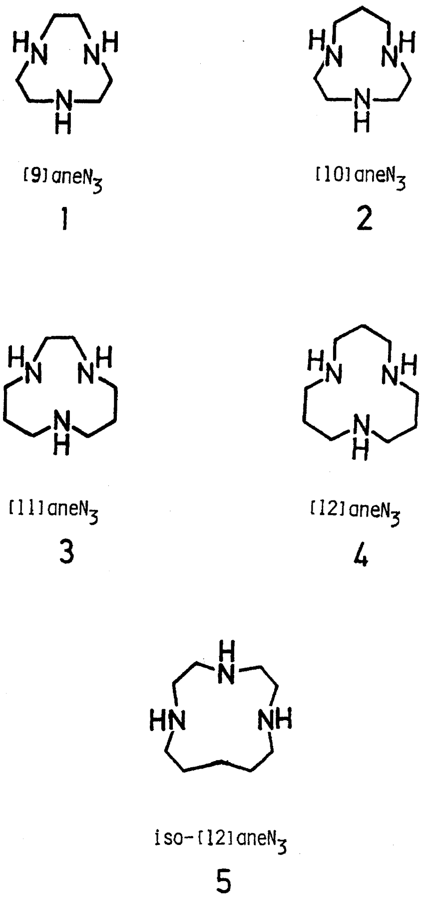

Chart 1.

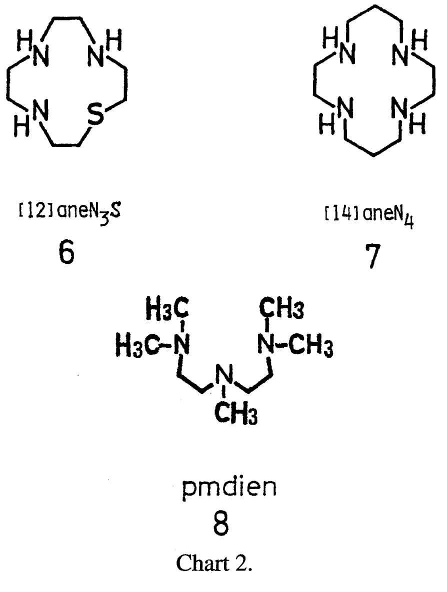

Chart 2.

measurements. Under the experimental conditions employed, the values of $-\log [H^+]$ could be estimated by applying a correction of -0.13 pH unit to the pH meter readings.6) Humidified nitrogen or argon gas free from CO_2 and O_2 was passed over the solution during the pH and voltammetric measurements.

Results and Discussion

Potentiometric Study. The chemical equilibria for the reactions of copper(II)-macrocyclic triamine complexes with a monodentate π-ligand (SCN^-, CH_3CN, or imidazole) were determined first using pH-metric titration. Titrations were conducted using test solutions of macrocyclic triamine in its fully-protonated form, H_3L^{3+}, containing an equimolar copper(II) ion and excess monodentate π-ligand under anaerobic conditions. Therefore, it is natural to consider that the following equilibria takes place in the solution.

$$LH_{i-1}^{(i-1)+} + H^+ = LH_i^{i+}, \quad K_i = [LH_i^{i+}]/[LH_{i-1}^{(i-1)+}][H^+] \tag{1}$$

where i=1, 2, and 3.

$$Cu^{2+} + L = CuL^{2+}, \quad K_{\mathrm{Cu^{II}L}} = [CuL^{2+}]/[Cu^{2+}][L] \tag{2}$$

$$\begin{gathered} CuL^{2+} + jA^{b-} = CuL(A)_j^{2-jb}, \\ K^{jA}_{\mathrm{Cu^{II}L}} = [CuL(A)_j^{2-jb}]/[CuL^{2+}][A^{b-}]^j \end{gathered} \tag{3}$$

where A^{b-} denotes the monodentate π-ligand and

$$\begin{gathered} K^{jA}_{\mathrm{Cu^{II}L}}K_{\mathrm{Cu^{II}L}} = K_{\mathrm{Cu^{II}L(A)_j}} \\ (= [CuL(A)_j^{2-jb}]/[Cu^{2+}][L][A^{b-}]^j). \end{gathered}$$

All the titration curves obtained invariably showed inflection points (pH jumps) at the titration points a=3. Here, a is the number of base added per mole of ligand, L, present. The sum of the concentrations of hydrogen and sodium (from NaOH) ions minus hydroxide ion concentration, α, at the titration point a is given by the relation Eq. 4. The total

$$\begin{aligned} \alpha &= aC_L + [H^+] - [OH^-] \\ &= 3[L] + 2[HL^+] + [H_2L^{2+}] + 3[CuL^{2+}] + 3[CuL(A)^{2-b}] \\ &\quad +3[CuL(A)_2^{2-2b}] + \cdots \end{aligned} \tag{4}$$

concentration of macrocyclic triamine, C_L, and that of copper(II) ion, C_M, are expressed by Eqs. 5 and 6, respectively.

$$C_L = [L]_f + [CuL^{2+}] + [CuL(A)^{2-b}] + [CuL(A)_2^{2-2b}] + \cdots \tag{5}$$

where $[L]_f=[L]+[HL^+]+[H_2L^{2+}]+[H_3L^{3+}]$.

$$C_M = [Cu^{2+}] + [CuL^{2+}] + [CuL(A)^{2-b}] + [CuL(A)_2^{2-2b}] + \cdots \tag{6}$$

Here, I defined the symbols $(\alpha_H)_L$ and β_H as in Eqs. 7 and 8.

$$(\alpha_H)_L = 1 + K_1[H^+] + K_1K_2[H^+]^2 + K_1K_2K_3[H^+]^3, \tag{7}$$

$$\beta_H = 3 + 2K_1[H^+] + K_1K_2[H^+]^2. \tag{8}$$

As was derived previously for the reaction of cobalt(II) ion with macrocyclic pentaamine and oxatetraamine,8) one can derive the Eq. 9 by appropriate combinations of the above eight equations.

$$\frac{K_{\mathrm{Cu^{II}L}} + K_{\mathrm{Cu^{II}L(A)}}[A^{b-}] + K_{\mathrm{Cu^{II}L(A)_2}}[A^{b-}]^2 + \cdots}{\beta_A^{\mathrm{II}}} = \frac{(3(\alpha_H)_L - \beta_H C_L)(3(\alpha_H)_L - \beta_H)}{(3C_L - \alpha)^2(\alpha_H)_L}, \tag{9}$$

where $\beta_A^{\mathrm{II}}=1+\beta_1^{\mathrm{II}}[A^{b-}]+\beta_2^{\mathrm{II}}[A^{b-}]^2+\cdots$, and β_k^{II} is the k-th overall formation constant of the copper(II)–A^{b-} complex.

Equation 9 indicates that even when the Cu(II)-macrocyclic triamine complex, $\mathrm{CuL^{2+}}$, reacts with a π-ligand and forms a mixed ligand complex, $\mathrm{CuL(A)}_j^{2-jb}$ (j=0, 1, 2, ⋯), the plot of $(\alpha(\alpha_\mathrm{H})_\mathrm{L} - \beta_\mathrm{H}C_\mathrm{L})(3(\alpha_\mathrm{H})_\mathrm{L} - \beta_\mathrm{H})$ against $(3C_\mathrm{L} - \alpha)^2(\alpha_\mathrm{H})_\mathrm{L}$ will give a straight line which passes through the point of origin, but the slope (S) of which increases with an increase in the π-ligand concentration, corresponding to the numerator of the left-hand side of Eq. 9. All the titration data obtained were found to fit the theoretical relation (9). In the $[12]\mathrm{aneN_3}$-, iso$[12]\mathrm{aneN_3}$–, and $[12]\mathrm{aneN_3S}$–$\mathrm{SCN^-}$ systems and $[11]\mathrm{aneN_3}$-imidazole system the $(S\times\beta_\mathrm{A}^\mathrm{II} - K_{\mathrm{Cu^{II}L}})/[\mathrm{A}^{b-}]$ values estimated from the slope (S) of the above linear relation were independent of the concentration of monodentate π-ligand, $[\mathrm{A}^{b-}]$, whereas in the $[11]\mathrm{aneN_3}$– and pmdien–$\mathrm{SCN^-}$ systems, the plot of $(S\times\beta_\mathrm{A}^\mathrm{II} - K_{\mathrm{Cu^{II}L}})/[\mathrm{SCN^-}]$ against $[\mathrm{SCN^-}]$ gave a straight line with an intercept of finite value. A typical straight line obtained for the $[11]\mathrm{aneN_3}$–$\mathrm{SCN^-}$ system is reproduced in Fig. 1. These findings clearly indicate that in the former four systems $\mathrm{CuL^{2+}}$ reacts with a π-ligand and gives solely a 1 : 1 : 1 ratio complex, $\mathrm{CuL(A)}^{2-b}$, but in the latter two systems $\mathrm{CuL^{2+}}$ gives not only $\mathrm{CuL(A)}^{2-b}$ but also $\mathrm{CuL(A)}_2^{2-2b}$. The β_1^II, β_2^II, β_3^II, and β_4^II values used to estimate the $\beta_\mathrm{A}^\mathrm{II}$ value of the $\mathrm{SCN^-}$ system were $5.5_1\times10^1$, $3.4_7\times10^2$, $4.9_0\times10^2$, and $9.7_0\times10^2$, respectively.[9] In the imidazole system, the β_1^II, β_2^II, β_3^II, and β_4^II values of $2.1_4\times10^4$, $7.4_1\times10^7$, $4.9_0\times10^{10}$, and $5.2_5\times10^{12}$ reported by James et al.[10] were used for the estimation of the $\beta_\mathrm{A}^\mathrm{II}$ value. Thus, $K_{\mathrm{Cu^{II}L(A)}}$ values for the $[12]\mathrm{aneN_3}$–, iso$[12]\mathrm{aneN_3}$–, and $[12]\mathrm{aneN_3S}$–$\mathrm{SCN^-}$ systems and that for the $[11]\mathrm{aneN_3}$-imidazole system were estimated from their $(S\times\beta_\mathrm{A}^\mathrm{II} - K_{\mathrm{Cu^{II}L}})/[\mathrm{SCN^-}]$ values. The $K_{\mathrm{Cu^{II}L(A)}}$ and $K_{\mathrm{Cu^{II}L(A)_2}}$ values for the $[11]\mathrm{aneN_3}$– and pmdien–$\mathrm{SCN^-}$ systems were determined from the intercept and slope (S') of the straight line between $(S\times\beta_\mathrm{A}^\mathrm{II} - K_{\mathrm{Cu^{II}L}})/[\mathrm{SCN^-}]$ and $[\mathrm{SCN^-}]$. All the $K_{\mathrm{Cu^{II}L(A)}}/K_{\mathrm{Cu^{II}L}}$ and $K_{\mathrm{Cu^{II}L(A)_2}}/K_{\mathrm{Cu^{II}L}}$ values determined are listed in Table 1, together with the $K_{\mathrm{Cu^{II}L}}$ values reported previously.[1,11,12]

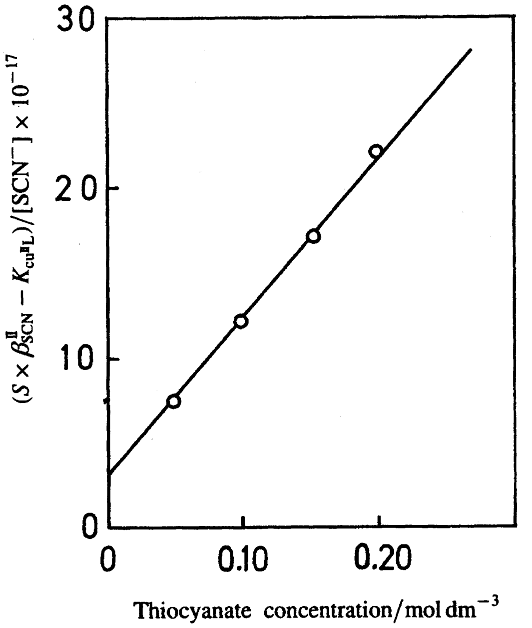

Fig. 1. The plot of $(S\times\beta_\mathrm{SCN}^\mathrm{II} - K_{\mathrm{Cu^{II}L}})/[\mathrm{SCN^-}]$ against $[\mathrm{SCN^-}]$.
Total copper(II) concentration=1.00×10^{-3} mol dm^{-3},
Total $[11]\mathrm{aneN_3}$ concentration=1.00×10^{-3} mo l dm^{-3},
I=0.20 mol dm^{-3}, 25 °C.

Considering the fact that thiocyanate anion, $\mathrm{SCN^-}$, forms $[\mathrm{CuL(SCN)_2}]^0$ as well as $[\mathrm{CuL(SCN)}]^+$, one can not exclude the possibility that the macrocyclic triamine studied acts as a didentate ligand in the complexation reaction with copper(II) ion, because of its strong tendency for the facial coordination and of the preference of the copper(II) ion for meridional coordination.[13]

Polarographic Study. In the aqueous solutions containing only $\mathrm{SCN^-}$,[14,15] $\mathrm{CH_3CN}$, or imidazole[14,16] in high concentration, the copper(II) ions give the polarograms consisting of two separate reduction steps of equal height. The 2nd reduction step which appears at the negative potential has been ascribed to the reversible one-electron reduction of 1 : 2 molar ratio copper(I)–A^{b-} ($\mathrm{SCN^-}$ or imidazole) complex, $[\mathrm{Cu^I(A)_2}]^{1-2b}$ to the metallic copper, Cu(Hg), and its half-wave potential, $(E_{1/2})_2^\mathrm{A}$, is given by Eq. 10.[14]

$$(E_{1/2})_2^\mathrm{A}/\mathrm{V} = E^0_{\mathrm{Cu(I)/Cu(Hg)}}/\mathrm{V} + 0.0591\cdot\log\left(\frac{k_\mathrm{a}}{k_\mathrm{c}}\right) - 0.0591\times\log(\beta_2^\mathrm{I})_\mathrm{A}[\mathrm{A}^{b-}]^2 \qquad (10)$$

where $E^0_{\mathrm{Cu(I)/Cu(Hg)}}$ and $(\beta_2^\mathrm{I})_\mathrm{A}$ denote the apparent standard potential for the Cu(I)/Cu(Hg) couple and the 2nd overall formation constant of copper(I)–A^{b-} complex, respectively. The k_a and k_c in Eq. 10 mean the diffusion current constants (i_l/C) of Cu metal in mercury and of copper(I)–A^{b-} complex in aqueous solution, respectively.[14]

Although no experimental result was given here, the half-

Table 1. $K_{\mathrm{Cu^{II}L(A)}_j}/\mathrm{K_{Cu^{II}L}}$ and $\mathrm{K_{Cu^{II}L}}$ Values for Cu(II)–Triamine Complexes I=0.20 mol dm^{-3}, 25.0 °C.

Ligand	SCN$^-$		Imidazole	
	$K_{\mathrm{Cu^{II}L(SCN)}}/K_{\mathrm{Cu^{II}L}}$	$K_{\mathrm{Cu^{II}L(SCN)_2}}/K_{\mathrm{Cu^{II}L}}$	$K_{\mathrm{Cu^{II}L(imid)}}/K_{\mathrm{Cu^{II}L}}$	$K_{\mathrm{Cu^{II}L}}$
Pmdien	$(4.8\pm0.3)\times10^2$	$(3.2\pm0.2)\times10^3$	—	2.0×10^{12} 1)
$[11]\mathrm{aneN_3}$	$(1.4\pm0.1)\times10^2$	$(4.4\pm0.3)\times10^3$	$(1.6\pm0.1)\times10^2$	2.8×10^{14} 11)
$[12]\mathrm{aneN_3}$	$(1.4\pm0.1)\times10^2$	—	—	4.3×10^{12} 11)
Iso-$[12]\mathrm{aneN_3}$	$(6.5\pm0.4)\times10^1$	—	—	2.4×10^{13} a)
$[12]\mathrm{aneN_3S}$	$(3.6\pm0.4)\times10^1$	—	—	9.5×10^{17} 12)

a) Unpublised datum (determined by the present authors).

wave potential for the 2nd reduction step of copper(II) ion in the aqueous CH_3CN solution was also found to fit well to Eq. 10.

As shown by the polarograms in Fig. 2, the copper(II)-macrocyclic triamine ([11]aneN_3) complex in solution not containing a monodentate π-ligand, SCN^-, produced by all appearances a single wave which might correspond to its direct two-electron reduction to the metallic state,[1] whereas in the solution containing an excess SCN^- copper(II)-macrocyclic triamine complex gave a polarogram consisting of two separate reduction steps of equal height, which is exactly one-half of the wave-height for the copper(II)-macrocyclic triamine complex in the absence of SCN^-. A similar well-shaped current-voltage curve consisting of two separate steps of equal height also could be obtained in the voltammetric reduction of the copper(II)-macrocyclic triamine complex in the SCN^- solution at a rotating disk electrode (glassy carbon).

The wave-height of two reduction steps observed at the dropping mercury electrode (DME) were exactly proportional to the square-root of effective pressure on DME. Furthermore, the plot of $\log(i/(i_1-i))$ against the d.c. potential, E, for both steps gave a straight line with a reciprocal slope falling in the range from −58 to −64 mV, corresponding to the reversible one-electron reduction process. Here, i_1 means the limiting current and i the current at E. Although no detailed result was 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 complex.[7] The electrolysis was carried out at the potential where the limiting current of the 1st step can be observed. 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 controlled-potential electrolysis was 0.93. Furthermore, the solution obtained by treating the mercury metal used for the electrolysis with nitric acid was analyzed for the copper(II) ions by the polarographic method. However, no copper(II) ion could be detected. The copper(I) solution containing excess macrocyclic triamine and monodentate π-ligand (SCN^-, CH_3CN, or imidazole), which was prepared by dissolving $[Cu^I(NCCH_3)_4]ClO_4$ crystal[4] into the deaerated borate buffer solution containing excess macrocyclic triamine and π-ligand, always gave composite anodic and cathodic waves of equal height. The anodic and cathodic waves exactly appear at potentials where the 1st and 2nd reduction steps for the copper(II) complex occur. All these findings collected clearly imply that the 1st step at the positive potential is ascribable to the reversible one-electron reduction of copper(II) complex to the copper(I) complex and the 2nd step to the reversible one-electron reduction of the resulted copper(I) complex to the metallic copper, Cu(Hg). Although no quantitative determination of copper metal in the mercury cathode was made, the copper amalgam formation at the 2nd reduction step was evidenced by recording the current–voltage curve in the 0.10 mol dm^{-3} KNO_3 solution at the hanging mercury drop electrode,[17] which was used in the controlled-potential electrolysis conducted at the potential where the 2nd reduction step gives its limiting current.

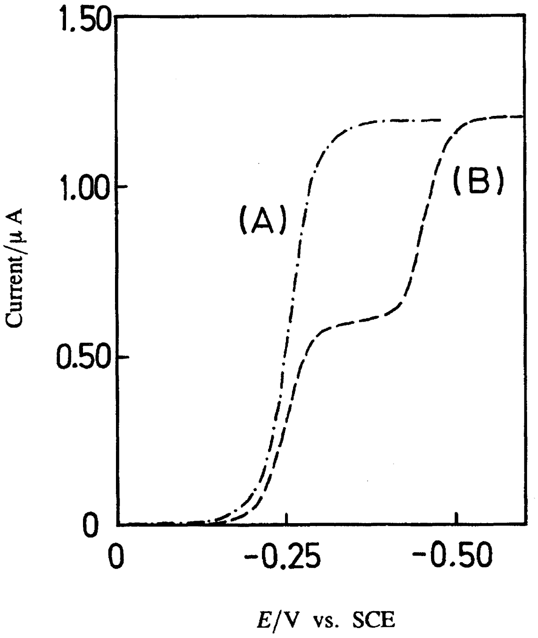

Fig. 2. Polarograms of copper(II)–[11]aneN_3 complexes. Total copper(II) concentration=2.0×10^{-4} mol dm^{-3}, Total [11]aneN_3 concentration=2.00×10^{-3} mol dm^{-3}, [borate]=0.030 mol dm^{-3}, pH=9.75, I=0.20 mol dm^{-3}, 25 °C.
(A) no SCN^-, (B) Total SCN^- concentration=4.00×10^{-2} mol dm^{-3}.

In order to determine the stoichiometric composition of the copper(I) complexes formed at the electrode surface and their formation constants, I have investigated thoroughly the effects of the solution pH and the concentrations of uncomplexed SCN^- and macrocyclic triamine ([11]aneN_3), $[L]_f$, on the half-wave potential of the 2nd reduction step at the negative potential. Its half-wave potential, $(E_{1/2})_2^{\mathrm{L,SCN}}$ was found to shift to the more negative potentials with increases in the solution pH and of the concentrations of uncomplexed SCN^- and macrocyclic triamine, $[L]_f$. Under the present experimental conditions, the initial concentrations of SCN^- and macrocyclic triamine used were always in large excess over that of copper(II) ion. Therefore, $[SCN^-]$ and $[L]_f$ can be regarded as practically equal to the initial concentrations of SCN^- and macrocyclic triamine. In considering that the most popular coordination number exhibited by copper(I) ion is tetrahedral or pseudo-tetrahedral four,[1,18] it is natural to assume the electrode reaction (11) for the 2nd reduction step where the 1 : 1 : 1 molar ratio (I)–[11]aneN_3–SCN^- complex formed at the electrode surface as a result of the one-electron reduction of copper(II)–[11]aneN_3 complex in the SCN^- solution is in a rapid equilibrium with $[Cu^I(SCN)_2]^-$. The half-wave potential then is expressed as in Eq. 12.

$$\begin{array}{l}[\mathrm{Cu^IL(SCN)}]^0+\mathrm{e}^-+\mathrm{Hg}\rightleftharpoons \mathrm{Cu(Hg)}+\mathrm{L}+\mathrm{SCN}^-\\ \qquad\downarrow\!\uparrow\ +\mathrm{L}-\mathrm{SCN}^-\\ [\mathrm{Cu^I(SCN)_2}]^-\end{array}\tag{11}$$

$$\begin{aligned}(E_{1/2})_2^{\mathrm{L,SCN}}/\mathrm{V} &= E^0_{\mathrm{Cu(I)/Cu(Hg)}}/\mathrm{V}+0.0591\cdot\log\left(\frac{k_\mathrm{a}}{k_\mathrm{c}}\right)\\ &-0.0591\cdot\log\left[(\beta_2^\mathrm{I})_{\mathrm{SCN}}[\mathrm{SCN}^-]^2+\frac{K_{\mathrm{CuI_{L(SCN)}}}[\mathrm{L}]_\mathrm{f}[\mathrm{SCN}^-]}{(\alpha_\mathrm{H})_\mathrm{L}}\right]\end{aligned}\tag{12}$$

From Eqs. 10 and 12 one can easily derive Eq. 13 on the assumption that all the diffusion current constants, *k*, are identical. The $(\Delta E_{1/2})_2$ value in Eq. 13 means the difference in the half-wave potential of the 2nd reduction step between the copper(II) ions in the SCN$^-$ solution and those in the SCN$^-$–[11]aneN$_3$ mixture solution.

$$\left[\mathrm{antilog}\left(\frac{(\Delta E_{1/2})_2}{0.0591}\right)-1\right](\beta_2^\mathrm{I})_{\mathrm{SCN}}[\mathrm{SCN}^-]^2 = \frac{K_{\mathrm{CuI_{L(SCN)}}}[\mathrm{L}]_\mathrm{f}[\mathrm{SCN}^-]}{(\alpha_\mathrm{H})_\mathrm{L}}\tag{13}$$

The experimental data obtained were all found to fit well to the above theoretical equation, Eq. 13; the $[\mathrm{Antilog}((\Delta E_{1/2})_2/0.0591)-1]\cdot(\alpha_\mathrm{H})_\mathrm{L}$ value (A_1) estimated from the $(\Delta E_{1/2})_2$ value at given concentrations of [11]aneN$_3$ and SCN$^-$, the $[\mathrm{Antilog}((\Delta E_{1/2})_2/0.0591)-1]/[\mathrm{L}]_\mathrm{f}$ value (A_2) at given concentrations of hydrogen ion and SCN$^-$, and the $[\mathrm{Antilog}((\Delta E_{1/2})_2-1]\cdot[\mathrm{SCN}^-]$ value (A_3) at given concentrations of hydrogen ion and [11]aneN$_3$ were constant. All these findings give good support for the formation of $[\mathrm{Cu^IL(SCN)}]^0$. A typical result obtained was given in Table 2.

Thus, the $K_{\mathrm{CuI_{L(SCN)}}}$ $(=[\mathrm{Cu^IL(SCN)}^0]/[\mathrm{Cu}^+][\mathrm{L}][\mathrm{SCN}^-])$ value was determined by applying the Eq. 13 to the $(\Delta E_{1/2})_2$ value obtained experimentally. In the above estimation $(\beta_2^\mathrm{I})_{\mathrm{SCN}}$ value of 1.00×10^{11}[19] was used. Other $K_{\mathrm{CuI_{L(SCN)}}}$ values were determined in an identical manner to the ways applied to the [11]aneN$_3$ system were determined. All the $K_{\mathrm{CuI_{L(SCN)}}}$ values determined are listed in Table 3.

The copper(II)-macrocyclic triamine complexes in solutions containing CH$_3$CN or imidazole also gave polarograms consisting of two separate reduction steps of equal height, suggesting the formation of copper(I) mixed ligand complexes including CH$_3$CN or imidazole. The polarographic behaviors of the copper(II)-macrocyclic triamine complexes in CH$_3$CN or imidazole solution were studied thoroughly and the formation constants of the copper(I) mixed macro-

Table 2. Effects of pH, [11]aneN$_3$ Concentration, $[\mathrm{L}]_\mathrm{f}$, and Thiocyanate Concentration, [SCN$^-$] on the Half-Wave Potential of 2nd Reduction Step
Total copper(II) concentration=2.0×10^{-4} mol dm^{-3}, I=0.20 mol dm^{-3}, 25 °C.

pH	$10^3[\mathrm{L}]_\mathrm{f}$ / mol dm^{-3}	$10^2[\mathrm{SCN}^-]$ / mol dm^{-3}	$10^{-2}(\alpha_\mathrm{H})_\mathrm{L}$	$(E_{1/2})_2^{\mathrm{L,SCN}}$ / V vs. SCE	$(\Delta E_{1/2})_2$ / mV	$10^{-2}A_1$[a)]	$10^{-3}A_2$[b)]	10^1A_3[c)]
9.25	2.00	4.00	4.89	-0.426_0	$20._0$	5.76	—	—
9.46	2.00	4.00	3.00	-0.433_3	$27._3$	5.68	—	—
9.75	2.00	4.00	1.53	-0.446_0	$40._0$	5.76	—	—
9.94	2.00	4.00	0.979	-0.456_0 (-0.406_0)[d)]	$50._0$	5.89	3.01	2.41
9.94	4.00	4.00	—	-0.472_4	$66._4$	—	3.05	—
9.94	8.00	4.00	—	-0.489_0	$83._3$	—	3.05	—
9.94	2.00	8.00	—	-0.477_0 (-0.441_4)[d)]	$35._6$	—	—	2.40
9.94	2.00	12.00	—	-0.491_2 (-0.463_0)[d)]	$26._2$	—	—	2.40

a) $A_1=[\mathrm{Antilog}((\Delta E_{1/2})_2/0.0591-1](\alpha_\mathrm{H})_\mathrm{L}$. b) $A_2=[\mathrm{Antilog}((\Delta E_{1/2})_2/0.0591)-1]/[\mathrm{L}]_\mathrm{f}$. c) $A_3=[\mathrm{Antilog}((\Delta E_{1/2})_2/0.0591-1][\mathrm{SCN}^-]$. d) $E_{1/2}$ in solution not containing [11]aneN$_3$ ($(E_{1/2})_2^{\mathrm{SCN}}$).

Table 3. Formation Constants of Cu(I) Mixed Ligand Complexes and Zn(II)-Cyclic Triamine Complexes
I=0.20 mol dm^{-3}, 25.0 °C.

Ligand	$K_{\mathrm{CuI_{L(A)}}}$			K_{ZnL}
	SCN$^-$	Imidazole	CH$_3$CN	
Pmdien	$(1.5\pm0.2)\times10^{12}$	—	—	—
[11]aneN$_3$	$(8.8\pm0.6)\times10^{14}$	$(7.6\pm0.7)\times10^{13}$	$(3.0\pm0.3)\times10^{14}$	2.6×10^{10} [24)]
[12]aneN$_3$	$(3.2\pm0.3)\times10^{14}$	—	—	2.6×10^{8} [24)]
Iso-[12]aneN$_3$	$(3.8\pm0.4)\times10^{13}$	—	$(5.3\pm0.6)\times10^{12}$	1.0×10^{7} [24)]
[12]aneN$_3$	$(6.6\pm0.6)\times10^{13}$	—	$(2.2\pm0.2)\times10^{13}$	—
[9]aneN$_3$	—	—	—	4.2×10^{11} [11)]
[10]aneN$_3$	—	—	—	1.9×10^{11} [11)]

cyclic triamine complexes including CH_3CN or imidazole, $K_{Cu^IL(SCN)}$ (=$[Cu^IL(A)^+]/[Cu^+][L][A^0]$), were determined in the same way as those applied to the SCN^- system. The $K_{Cu^IL(A)}$ values thus determined were also listed in Table 3. In the calculation of $K_{Cu^IL(SCN)}$ values $(\beta_2^I)_A$ values of $2.2_4\times10^4$ and $2.7_5\times10^{10}$ were used for the CH_3CN[20] and imidazole complexes.[10] The copper(II)–[12]aneN_3 and –iso-[12]aneN_3 complexes in the imidazole solution also gave two reduction steps, but the half-wave potential difference between two reduction steps is not large enough to determine the cathodic current of the 2nd step at the negative potential accurately. Hence, the $K_{Cu^IL(A)}$ values for these complexes could not be estimated.

In order to see whether other macrocyclic polyamine can sustain the copper(I) state with the acid of monodentate π-ligand similar extensive studies on the polarographic behaviors of the copper(II) complexes of smaller ring macrocyclic triamine, [9]aneN_3 and [10]aneN_3, and of tetraamine, [14]aneN_4 (cyclam), were carried out in the solutions containing an excess amount of SCN^-. But no confirmative evidence for the formation of the copper(I) mixed ligand complexes involving these macrocyclic polyamines could be obtained. I also investigated the polarographic behaviors of copper(II)–[11]aneN_3, –[12]aneN_3, –iso[12]aneN_3, and –[12]aneN_3S complexes in solutions of NH_3 or sulfur-containing ligand, mercaptoethanol. Making a sharp contrast to thiocyanate anion, these non-π-ligands could not stabilize the copper(I) state, because they seem incapable of reducing the negative charge in the central copper(I) ion.

Riedeo and Kaden mentioned in their potentiometric study on the complexation reactions of copper(II) ions macrocyclic triamines that they can form 1 : 2 ratio complex, CuL_2^{2+}, as well as 1 : 1 ratio complex, CuL^{2+}.[21] However, this pH-metric study revealed that under the present experimental conditions the equilibrium concentration of CuL_2^{2+} is negligibly small as compared with those of CuL^{2+} and mixed ligand complexes.

The half-wave potential of the 1st reduction step was found to shift to the more negative potentials with decreases in hydrogen ion and π-ligand concentrations, and with an increase in the macrocyclic triamine concentration, obeying accurately relation (14), which was derived for the reversible one-electron reduction process (15) as has been done in the copper(II)-amine complex.[14]

$$(E_{1/2})_1/\mathrm{V} = \mathrm{const.} - 0.0591 \times \log\left[\frac{\frac{K_{Cu^{II}L}}{(\alpha_H)_L}[L]_f(1+K^{A}_{Cu^{II}L}[A^{b-}]+K^{2A}_{Cu^{II}L}[A^{b-}]^2)}{(\beta_2^I)_A[A^{b-}]^2+\frac{K_{Cu^IL(A)}}{(\alpha_H)_L}[L]_f[A^{b-}]}\right] \tag{14}$$

$$\left.\begin{array}{c}[Cu^{II}L(A)_2]^{2-2b}\\ \upharpoonleft\downharpoonright\\ [Cu^{II}L(A)]^{2-b}\\ \upharpoonleft\downharpoonright\\ Cu^{II}L^{2+}\end{array}\right\}\begin{array}{c}+e^- + jSCN^- \rightleftharpoons\\ \\ j=0,\ 1\ \mathrm{or}\ -1\end{array}\left\{\begin{array}{l}[Cu^IL(A)]^{1-b}\\ \quad\upharpoonleft\downharpoonright\\ [Cu^I(A)_2]^{1-2b}+L\\ \qquad\qquad\upharpoonleft\downharpoonright\\ \qquad\qquad H_iL^{i+}\end{array}\right. \tag{15}$$

Here, $K^{A}_{Cu^{II}L}$ and $K^{2A}_{Cu^{II}L}$ in Eq. 14 are defined by Eq. 3. The results obtained in the [11]aneN_3 system are given in Table 4. The $K_{Cu^IL(A)}$ value in the Eq. 14 used for the calculation if the shift of half-wave potential, $(\Delta E_{1/2})_1$, in Table 4 was the one that was determined by the above-mentioned polarographic investigation of the nature of the 2nd reduction step. The agreement between the calculated and observed $(\Delta E_{1/2})_1$ values also supports the conclusion drawn from the systematic study of the 2nd reduction step. In order to ascertain the formation of $[Cu^IL(SCN)]^0$, by employing the controlled-potential electrolysis using apparatus and experimental procedures similar to those applied to the copper(II)–TOBP complex,[7] I tried to prepare and isolate the ternary copper(I) complex of SCN^- and macrocyclic triamine, $[Cu^IL(SCN)]^0$. However, this attempt has not been successful as yet.

Among the coordination number of 2 to 5 exhibited by the copper(I) ion in the simple coordination compounds, the most popular one is the tetrahedral or pseudo-tetrahedral four.[18] Since macrocyclic triamines are sterically constrained to facial coordination,[22] it is natural to consider that the mixed ligand complexes, $[Cu^IL(A)]^{1-b}$ observed in this study are tetrahedral in nature, as was concluded in th copper(I)–pmdien–CO mixed ligand complex.[1] Dreiding molecular model examination also confirmed the above conclusion. The severe constraint of the smaller ring ligands causes the direction of the nitrogen lone-pair orbitals to be shifted away from the copper(I) orbitals. Thus, the smaller ring macrocyclic triamine, [9]aneN_3 and [10]aneN_3, can not stabilize effectively the copper(I) state even with an acid of π-ligand, SCN^-. In the case of the 14-membered macrocyclic tetraamine, [14]aneN_4, it has the stronger preference for the square-planar coordination[23] and, hence, is judged to be incapable of adapting a conformation enforced by the bonding demands of the copper(I) ion. This might be the main reason for [14]aneN_4 being incapable of stabilizing effectively the copper(I) state. The $K_{Cu^IL(A)}$ values in Table 3 clearly point out that the macrocyclic triamines are much more effective in stabilizing the copper(I) state than the methylated open-chain triamine, pmdien. This would be attributed to the stronger preference of the macrocyclic triamine for the tetrahedral

Table 4. Effects of Concentrations of Hydrogen Ion, Thiocyanate Ion, and [11]aneN_3 on the Half-Wave Potential of the 1st Reduction Step
I=0.20 mol dm^{-3}, 25 °C.

pH	$10^3[SCN^-]$ mol dm^{-3}	$10^3[L]_f$ mol dm^{-3}	$E_{1/2}$ V vs. SCE	$(\Delta E_{1/2})$/mV calcd	$(\Delta E_{1/2})$/mV obsd
9.25	40.0	2.00	-0.242_9	$+11._9$	$+12._1$
9.46	40.0	2.00	-0.243_5	$+11._5$	$+11._5$
9.75	40.0	2.00	-0.255_0	0	0
9.97	40.0	2.00	-0.257_7	$-2._8$	$-2._7$
9.75	80.0	2.00	-0.246_5	$+7._9$	$+8._5$
9.75	120.0	2.00	-0.241_5	$+13._4$	$+13._5$
9.75	40.0	4.00	-0.259_0	$-3._6$	$-4._0$
9.75	40.0	8.00	-0.261_0	$-5._5$	$-6._0$

coordination, which is required by copper(I) ion, and also to the hydrophobicity of the cyclic cavity. Among the 9- to 12-membered macrocyclic triamines, [9]aneN_3 forms the most thermodynamically stable complex with a small d^{10} metal ion, Zn^{2+}[11,24] (Table 3). However, a large d^{10} copper(I) ion would be expected to form a stable complex only with the larger ring macrocyclic triamine. This trend undoubtedly reflects the largest $K_{\mathrm{Cu^I L(A)}}$ values for the [11]aneN_3 system.

In this study I found that the α-donor, sulfur, of mercaptoethanol and that of [12]aneN_3S do not stabilize the copper(I) state, while the π-acceptors, SCN^-, CH_3CN, and imidazole can effectively. In the π-bond formation, the π-ligand usually act as a Lewis acid and accepts electrons from the filled t_{2g} orbital of the metal ion,[1] so it reduces effectively the negative charge in the central metal ion. In this manner, the presence of the π-ligand strengthens the copper(I)-ligand bond and contributes to the stability of the tetrahedral copper(I) complex.

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