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The Electrochemical Study of Ag(II) Complexes of Polyaza Macrocycles and Their Acetic Acid Derivatives

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Although an attempt to isolate pure crystallines of Ag(II) complexes failed, we could prepare stable aqueous solutions of the Ag(II) complexes of [15]aneN$_5$, [16]aneN$_5$, and their acetic acid derivatives by disproportionation reactions of Ag(I) induced by these polyaza macrocycles, and have investigated their electrochemical redox behaviors using conventional voltammetric methods. All Ag(II) complexes including the [14]aneN$_4$ (cyclam) complex undergo a reversible two-electron reduction at DME (dropping mercury electrode). From the potential where the $i^2/(i_l - i)$ ratio is unity, the log formation constants were determined to be 43.4, 43.6, 43.3, 39.3, and 42.5 for the cyclam, [15]aneN$_5$, [16]aneN$_5$, cyclam-tetraacetic acid, and [15]aneN$_5$-pentaacetic acid complexes, respectively. Cyclic voltammetric (CV) oxidation scans at the glassy carbon electrode showed a reversible one-electron response (separation of anodic and cathodic peak potentials, $\Delta E_{p'}$=70 mV; the ratio of anodic and cathodic peaks, $(i_p)_{c'}/(i_p)_{a'}$=1), which can be ascribed to a reversible Ag(III)/Ag(II) redox change. Though the acetate groups attached to the nitrogen atoms contribute to the net destabilization of the Ag(II) complexes, they exert a large positive effect on the thermodynamic stability of the Ag(III) state.

The equilibrium constant for the disproportionation reaction of the copper(I) in an aqueous solution is 1.2×10^6.[1] The univalent state copper therefore shows a pronounced tendency to disproportionate according to reaction (A). In sharp contrast to the soluble copper(I) compounds, the equilibrium constant for the formation of silver metal and Ag^{2+} from Ag$^+$ in water, K_d(=[Ag^{2+}]·[Ag^0]/[Ag$^+$]^2), is only 1×10^{-20}.[1] Accordingly, silver(I) in water is stable and shows no tendency to disproportionate. However, in the presence of a variety of tetraaza macrocyclic ligands which can effectively stabilize the divalent oxidation state of silver ion, the Ag(I) compounds disproportionate according to reaction (B). In 1972, Kestner and Allred reported that when AgClO$_4$ or AgNO$_3$ was added to an aqueous suspension or 50% methanolic solution of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, disproportionation of the silver(I) to elemental silver and a silver(II) complex with the ligand occurred.[2] The following year Barfield and Mocella also found that a variety of Ag(II)-tetraaza macrocycle complexes could be made in a similar way.[3] Thus, the reactions of silver(I) ions with tetraaza macrocycles provide a facile process for obtaining silver(II) complexes. Interestingly, the silver(II) complexes of some tetraaza macrocycles, thus prepared, easily undergo one-electron oxidation to form silver(III) species of substantial stability. In this sense, the redox behavior of the Ag(II)-tetraaza macrocycle complex is quite similar to those of nickel(II) analogues,[4,5] or of the copper(II) complexes of dioxo derivatives of tetraaza macrocycles.[6] The silver ions in the presence of some saturated pentaaza macrocycles also disproportionate to the elemental silver and their silver(II) complexes.

$$2\mathrm{Cu}^+ \rightleftarrows \mathrm{Cu}^0 + \mathrm{Cu}^{2+},\ K_a = 1.2\times10^6 \qquad \text{(A)}$$

$$2\mathrm{Ag}^+ + \mathrm{L} \rightleftarrows \mathrm{AgL}^{2+} + \mathrm{Ag}^0 \qquad \text{(B)}$$

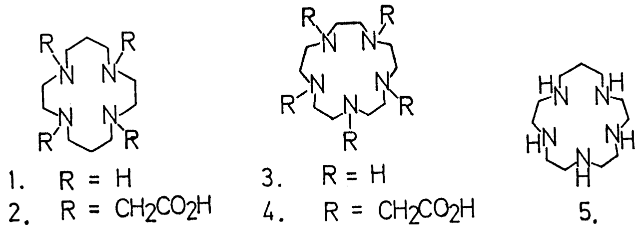
Like other heavy metals such as mercury, lead, and cadmium, silver has long been recognized as one of the most toxic metals.[7] Generally, metal ions exert toxic effects by interacting with the functional groups of biologically important molecules. Soft Lewis acids, silver(I, II) ions, can bind firmly to sulfhydryl groups as well as the nitrogen donors,[8] forming stable complexes, and may exhibit toxic effects. However, not much is known about the precise and specific molecular mechanism underlying these toxic effects.

In this study we tried to prepare Ag(II) complexes of saturated pentaaza macrocycles, cyclam and their derivatives carrying an acetic acid group on each nitrogen atom by employing a disproportionation reaction of Ag(I) ions; we studied the complexation reactions of Ag(II) ions with these ligands and the redox properties of the Ag(II) complexes through conventional electrochemical methods. The present results concerning the compexation reactions of Ag(II) ions with the polyaza macrocycles and the redox behaviors of their Ag(II) complexes provide useful information concerning the molecular bases of Ag ion toxicity.

Experimental

Ligands. All of the polyaza macrocycles and their derivatives carrying acetic acid groups were prepared according to methods described in the literature[9] (Fig. 1).

Ag(II) Complex Solutions. AgNO$_3$(170 mg, 1.00 mmol) was added to a stirred 15 ml aqueous solution containing 0.40 mmol of 1,4,7,10,13-pentaazacyclopentadecane ([15]aneN$_5$, 86 mg) or 1,4,7,10,13-pentaazacyclohexadecane ([16]aneN$_5$ 92 mg). A dark amber color gradually developed in the solution with a simultaneous formation of a silver mirror on the wall of the reaction vessel. The reaction mixture was then warmed on a steam bath at 55 °C for half an hour, during which time the solution pH was kept constant



Ligands

Fig. 1. Ligands: 1. [14]aneN_4 (Cyclam); 2. [14]aneN_4-tetraacetic acid; 3. [15]aneN_5; 4. [15]aneN_5-pentaacetic acid; 5. [16]aneN_5.

(pH=9.5) by adding a dilute NaOH solution. An attempt to isolate pure Ag(II) complex crystals as perchlorate was made by adding a concentrated $NaClO_4$ solution, but failed. The resulting amber solution was diluted to 50.0 ml with redistilled water and stored in a refrigerater. The Ag(II)-polyaza macrocycle complexes in the aqueous solution were stable for a considerable time, judging from the change in the absorbances and the positions of the absorption maxima in both the visible and UV spectra. Polarographic investigation disclosed that no uncomplexed ligand ([15]aneN_5 or [16]aneN_5 remained in the Ag(II) complex solutions, thus prepared. The concentration of the Ag(II) complex solution was determined as follows: After acidifying with a few drops of concentrated CH_3COOH, 0.50 ml of a 30% H_2O_2 aqueous solution was added dropwise to the 20.0 ml amber solution. To the resulting colorless solution a sufficient amount of sodium thiocyanate crystals were added. The white AgSCN precipitate formed was collected by filteration and weighed to be 26.6 mg. The result suggests the formation of a 1 : 1 ratio Ag(II)-polyaza macrocycle complex. A yellow block form of the Ag(II)-cyclam complex was prepared, as described by Ito et al.,[10] and its aqueous solution was made from redistilled water. The reactions of $AgClO_4$ (or $AgNO_3$) with cyclam-tetraacetic acid and [15]aneN_5-pentaacetic acid also gave a silver mirror and yellowish amber solutions. Since the Ag(II) complexes of these complexone-like ligands are comparatively unstable (the developed yellowish amber color faded to a colorless solution within three or four hours), no attempt was made to isolate the complex crystals.

Reactions of Ag(I) ions with tetraaza and pentaaza macrocycles containing two amide groups such as dioxocyclam,[11] dioxo[15]aneN_5,[12] and dioxo[16]aneN_5[13] also gave silver mirrors and yellow solutions. However the resulting yellow solutions faded immediately to colorless solutions while some turbidity occurred, probably due to a decomposition of the Ag(II) complex.

All of the other chemicals were of reagent-grade and were used without further purification.

Apparatus and Measurements. Cyclic voltammetry (CV) was performed with a three-electrode system comprising a glassy carbon working electrode (a 3 mm glassy carbon rod, Grade GC-20, Tokai Electrode Company), a Pt-wire auxiliary electrode, and a saturated calomel reference electrode (SCE). Voltammograms were generated using a solid-state potentiostat and a potential scanner constructed in this laboratory (following the design of Itabashi and Oikawa[14]) and recorded on a Rika Denki RW-11 X-Y recorder. The visible and UV spectra were recorded on a Hitachi U-3210 spectrophotometer with 1 cm matched quarz cells. The polarographic apparatus and experimental procedures were identical to those described previously.[9,10] The pH values were read with a Horiba F8-AT digital pH meter with a glass electrode. All the measurements were performed at 25.00±0.05 °C and an ionic strength(I) of 0.20 mol dm^{-3}. Under these experimental conditions the values of $-\log[H^+]$ could be estimated by applying a correction of −0.13 pH unit to the pH meter readings.[15] Humidified N_2 gas free from CO_2 and O_2 was passed over the solution during the voltammetric and pH measurements.

Results and Discussion

Spectroscopy. Typical absorption spectra of the Ag(II) complexes are shown in Fig. 2; their characteristics are summarized in Table 1. Although all of the complex solutions can be described as yellowish amber, there are obviously considerable differences in the position and intensity of the maximum. It is plausible to assign these absorption bands to the ligand to a metal-charge transfer in the Ag(II) com-

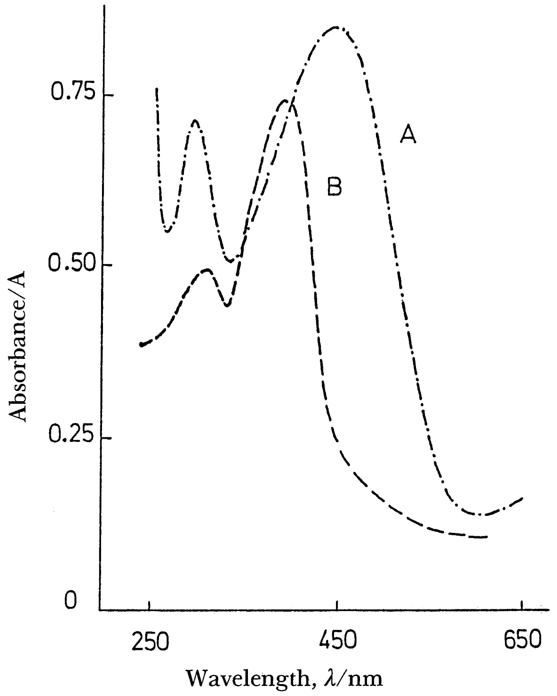


Fig. 2. Absorption spectra: A. Ag(II)-[15]aneN_5 complex; 0.202 mM. B. Ag(II)-[16]aneN_5 complex; 0.200 mM. I=0.20 M ($NaNO_3$). (M=mol dm^{-3}).

Table 1. Spectral Data for the Ag(II) Complexes

Ligand	λ_{max}/nm (log ε)	
[14]aneN_4 (1)[a]	348 (3.67)	280 (3.43)
[14]aneN_4-tetraacetic acid (2)	380 (3.48)	290 (3.28)
[15]aneN_5 (3)	445 (3.62)	300 (3.44)
[15]aneN_5-pentaacetic acid (4)	417 (~3.3)	300 (~3.2)
[16]aneN_5 (5)	380 (3.56)	305 (3.38)

a) Ref. 16.

plex. This is also consistent with the moderately high band intensities (molar extinction coefficients). All two peak maxima found in the electronic spectra of the Ag(II) complexes in water were in the range of silver(II) complexes containing polyaza macrocycles.[16] The absorption spectra of the cyclamtetraacetic acid and [15]aneN$_5$-pentaacetic acid complexes were measured immediately after sample fixation at pH=9.5. The spectra changed rapidly with a decrease in the intensity and faded to a colorless solution after one hour.

Polarography. Since the anodic dissolution of mercury, due to the free polyaza macrocycle, takes place at potentials where its Ag(II) complex undergoes a reduction at DME, and, hence, interferes with the accurate determination of cathodic current ascribable to the reduction of the Ag(II) complex, all of the polarographic measurements were made in buffer solutions containing no free macrocycles.

In acetate (0.050 mol dm^{-3}), Tris. (0.050 mol dm^{-3}), and borate (0.030 mol dm^{-3}) buffer solutions, Ag(II)-cyclam, -[15]aneN$_5$ and -[16]aneN$_5$ complexes gave well defined cathodic waves at DME. Typical polarograms obtained for the cyclam and [15]aneN$_5$ complexes are reproduced in Fig. 3. The diffusion current constant k_{AgL}'s (defined by the Ilkovic equation as $607\cdot n\cdot D^{1/2}\cdot m^{2/3}\cdot t_d^{1/6}$ at 25 °C), for the reduction of the Ag(II)-polyaza macrocycle complexes were almost the same as those for the anodic dissolution wave due to the free polyaza macrocycles ($Hg+L \rightleftarrows HgL^{2+}+2e^-$); plots of $\log(i^2/(i_l-i))$ against dc potential, E, invariably gave straight lines having reciprocal gradients of ca. −30 mV over the entire pH range covered, suggesting a two-electron reversible reduction (Fig. 4). Here, i_l and i denote the limiting current and the current at potential E, respectively. The reversible nature of the electrode processes was also confirmed by the ac polarographic method.[17] The potential, E^0 (defined as the value of DME potential where the $[i^2/(i_l-i)]$ is unity), shifted to more negative potentials upon increasing the solution pH and the log concentration of the Ag(II) complex, C_{AgL}, obeying the following the relations; however, it was independent of the concentration of the buffer reagent. Typical results obtained in the polarography of the Ag(II)-[15]aneN$_5$ complex are shown in Table 2. The SO$_4^{2-}$

$$\frac{\Delta E^0}{\Delta \log(\alpha_H)_L} = 30\ \text{mV} \tag{1}$$

$$\frac{\Delta E^0}{\Delta \log C_{AgL}} = -30\ \text{mV} \tag{2}$$

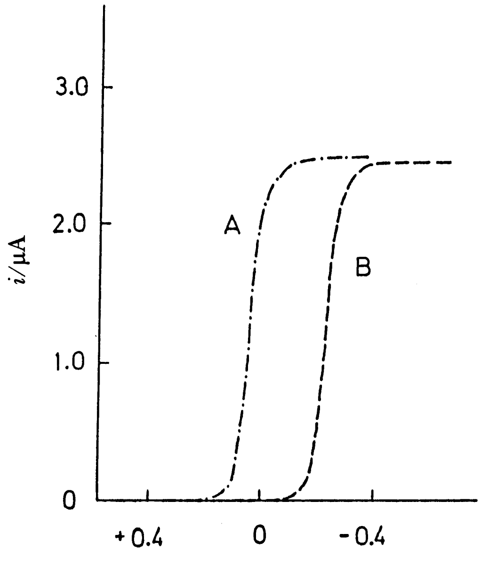


Fig. 3. Dc polarograms: A. Ag(II)-[14]aneN$_4$ complex; 0.40 mM. B. Ag(II)-[15]aneN$_5$ complex; 0.40 mM. pH=9.19, [borate]=0.030 M, I=0.20 M, 25 °C.

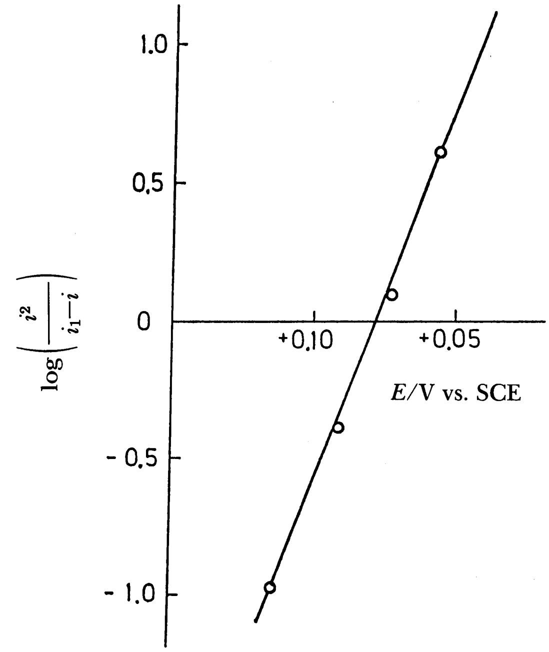


Fig. 4. $\log(i^2/(i_l-i))$ against E plot: Ag(II)-[14]aneN$_4$ complex; 0.40 mM, pH=4.90, [OAc$^-$]=0.050 M, [SO$_4^{2-}$]=0.20 M, 25 °C.

Table 2. Typical Data of the Effects of C_{AgL} and pH on the E^0 Values of the Ag(II)-[15]aneN$_5$ Complex, I=0.20 M, 25 °C

pH	C_{AgL}	$(\alpha_H)_L$	E^0	ΔE^0/mV	
	mM		V vs. SCE	Obsd	Calcd[a]
7.11	0.40	2.06×10^6	−0.0906	+115.1	+120.0
8.63	0.40	1.90×10^3	−0.1762	+29.5	+30.3
9.19	0.40	1.79×10^2	−0.2057	0	0
9.45	0.40	6.59×10^1	−0.2192	−13.5	−12.8
9.80	0.40	2.02×10^1	−0.2328	−27.1	−28.0
10.21	0.40	6.44	−0.2460	−40.3	−42.6
9.19	0.20	1.79×10^2	−0.1970	+8.9	+8.7[b]
9.19	1.20	1.79×10^2	−0.2200	−14.1	−14.3[b]

a) $29.6\times\Delta\log(\alpha_H)_L$. b) $-29.6\times\Delta\log C_{AgL}$.

anions in the solution had little effect on the E^0 value. This indicates that SO_4^{2-} anions do not react with Ag(II) complexes under the present experimental conditions. Therefore, all of the above findings are evidently consistent with the following theoretical equation derived for the reversible two-electron reduction of the Ag(II) complex at DME ($AgL^{2+}+Hg+2e \rightleftarrows Ag(Hg)+L$).

$$E^0=(E_{1/2})_{Ag^{2+}}-0.0296\log\left(\frac{K_{Ag^{II}L}}{(\alpha_H)_L}\right)+0.0296\log k_{AgL} \quad (3)$$

Here, $(E_{1/2})_{Ag^{2+}}$ is the half-wave potential of the reversible reduction of Ag^{2+} ions at DME ($Ag^{2+}+Hg+2e^- \rightleftarrows Ag(Hg)$), $K_{Ag^{II}L}$ the formation constant of the Ag(II) complex ($=[Ag^{II}L]/[Ag^{2+}]\cdot L]$), $(\alpha_H)_L$, $1+[H^+]\times K_1+[H^+]^2\times K_1K_2+...$, K_i, the protonation constant of L, and $k_{AgL}=i_l/C_{AgL}$.

Theoretically, $(E_{1/2})_{Ag^{2+}}$ can be related to the standard potential, ε^0, for the Ag^{2+}/Ag^0 redox couple by the following relation.[18]

$$(E_{1/2})_{Ag^{2+}}=\varepsilon^0+E_S+0.0296\log C_{sat}\cdot f_{sat} \quad (4)$$

E_S in Eq. 4 is the emf of the cell, Ag (s)/Ag^{2+}/Ag(Hg), C_{sat}, the saturated concentration of Ag in its amalgam, and f_{sat}, the activity coefficient of Ag in the amalgam. From the ε^0, E_S, and C_{sat} values reported the $(E_{1/2})_{Ag^{2+}}$ value could be estimated to be 1.09 V vs. SCE (1.34 V vs. NHE) at 25 °C, using the f_{sat} value of 1. E_S value was estimated from the half-wave potential of the reduction of 1×10^{-4} mol dm^{-3} $[Ag(CN)_2]^-$ at DME[19] using the $K_{Ag(CN)_2}$ value ($=[Ag(CN)_2^-]/[Ag^+]\cdot[CN^-]^2$) of $10^{21.1}$[20] to be −0.01 V vs. SCE. ε^0 is the algebraic average of standard potentials for the Ag^+/Ag^0 and Ag^{2+}/Ag^+ redox couples (1.140 V vs. SCE).[21] C_{sat} value of 6.07×10^{-2} mol dm^{-3}[22] was used in the estimation of the $(E_{1/2})_{Ag^{2+}}$ value.

With the aid of Eq. 3 the formation constants, $K_{Ag^{II}L}$'s were determined from the measured E^0 values using a k_{AgL} value of 3.87×10^{-3} (μA mol^{-1} dm^3) and listed in Table 3. Using the $K_{Ag^{II}L}$ values in Table 3, the apparent formation constants, $K_{ap}(=K_d\cdot K_{Ag^{II}L}/(\alpha_H)_L)$, at pH=9.5 for reaction (B) were calculated to be 3.4×10^{20}, 7.2×10^{21}, 7.0×10^{21}, 2.3×10^{17}, and 3.9×10^{20} for the cyclam, [15]aneN_5, [16]aneN_5, cyclam-tetraacetic acid, and [15]aneN_5-pentaacetic acid systems, respectively. These large apparent formation constants made the attainment of the Ag(II) state more easy, offering a useful method for the preparation of Ag(II) complex solutions in all cases studied. As shown by the $K_{Ag^{II}L}$ values in Table 3, the fifth nitrogen donors of [15]aneN_5 and [16]aneN_5 contribute little to the thermodynamic stability of Ag(II) complexes. Taking account of the fact that sulfate anions do not react with the Ag(II)-polyaza macrocycle complexes, this finding may suggest that these pentaaza macrocycles coordinate to Ag(II) ions most likely with four nitrogen atoms.

Table 3. Log $K_{Ag^{II}L}$ and $E_{1/2}$ Values, I=0.20 M, 25 °C

Ligand	Log $K_{Ag^{II}L}$	$E_{1/2}$ V vs. SCE
[14]aneN_4 (1)	43.4±0.2	+0.600
[14]aneN_4-tetraacetic acid (2)	39.3±0.2	+0.230
[15]aneN_5 (3)	43.6±0.2	+0.265
[15]aneN_5-pentaacetic acid (4)	42.5±0.2	+0.200
[16]aneN_5 (5)	43.3±0.2	+0.150

Cyclic Voltammetry. Figure 5 shows typical cyclic voltammograms at a scan rate of 100 mV sec^{-1} for the Ag(II)-[15]aneN_5, -[16]aneN_5 and -cyclam complexes (1.5×10^{-3} mol dm^{-3}, pH=9.5). The separation of anodic and cathodic peak potentials, ΔE_p, was 70—80 mV in all cases and the peak-height ratio nearly unity. Both peak-heights were proportional to the square root of the scan rate, $V^{1/2}$. Slight variations (±3 mV) of peak potential separation with different scan rates (from 25 mV sec^{-1} to 400 mV sec^{-1}) were also observed. These features are indicative of quasi-reversible (one-electron) electrochemical behavior; hence, the midpoint between two peak potentials should be a reasonable estimate of the electrode potential corresponding to the polarographic half-wave potential.[23] In all cases at pH's higher than 8.0 the half-wave potentials obtained from the midpoint between two CV peak potentials were found to be independent of the solution pH and of the concentration of uncomplexed ligand. Meyerstein et al.[24] reported that SO_4^{2-} anions bind strongly to a Ni(III)-cyclam complex in an aqueous solution, making considerably easier the attainment of the trivalent state of nickel in a sulfate solution. The silver(II)-cyclam complex investigated here also displayed a similar behavior. Figure 6

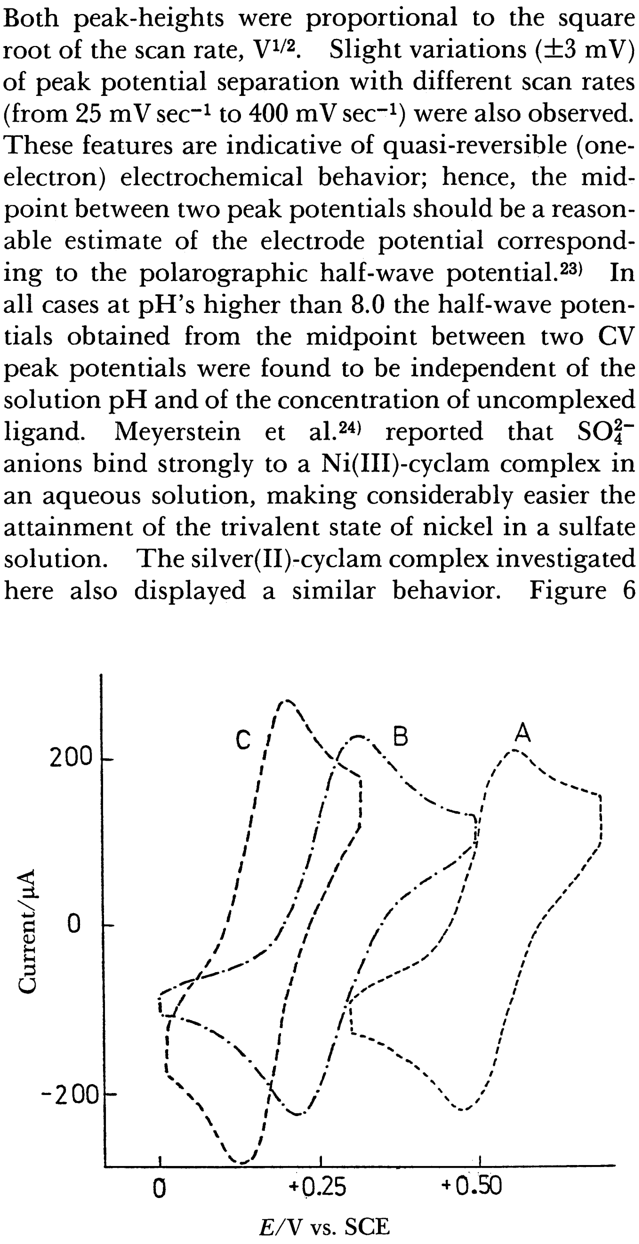


Fig. 5. Cyclic voltammograms: A. [Ag(II)-[14]aneN_4]=1.0 mM, B. [Ag(II)-[15]aneN_5]=1.0 mM, C. [Ag(II)-[16]aneN_5]=1.0 mM, [borate]=0.030 M, pH=9.10, scan rate, V=200 mV sec^{-1}.

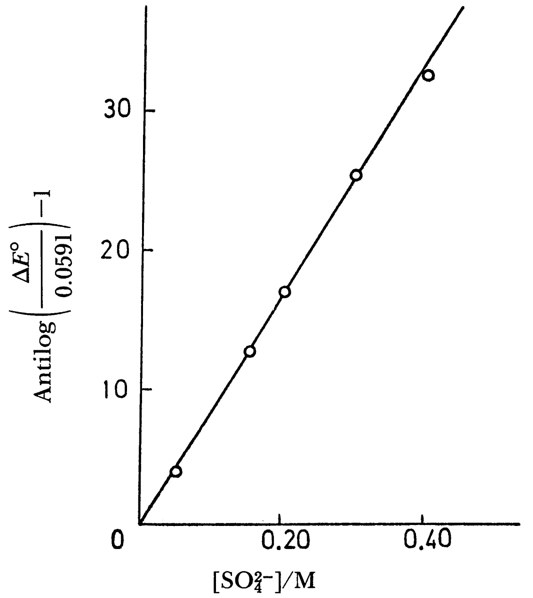


Fig. 6. Dependence of E° on the concentration of SO_4^{2-}, [Ag(II)-[14]aneN$_4$]=1.50 mM, [OAc$^-$]=0.050 M, pH=3.84, 25 °C.

shows plots of antilog $(E_{1/2}/0.0591)-1$ against the sulfate concentration, $C_{SO_4^{2-}}$. Here, $\Delta E_{1/2}$ means the $E_{1/2}$ shift due to SO_4^{2-} ions. A straight line passing through the origin could be obtained. This behavior is consistent with the following electrode process; the half-wave potential, $E_{1/2}$, can be expressed in the form of relation (6). The formation constant, where $E^0_{Ag^{3+}/Ag^{2+}}$ denotes the standard potential for the Ag^{3+}/Ag^{2+} redox couple.

$$\begin{array}{l} AgL^{2+} + SO_4^{2-} \rightleftarrows AgL(SO_4)^+ + e^- \\ \qquad\qquad\quad \uparrow\downarrow +SO_4^{2-} \\ \qquad\qquad\quad AgL^{3+} \end{array} \tag{5}$$

$$E_{1/2} = E^0_{Ag^{3+}/Ag^{2+}} - 0.0591\log\left[\frac{K_{Ag^{III}L}(1+K_m\cdot C_{SO_4^{2-}})}{K_{Ag^{II}L}}\right] \tag{6}$$

$K_m(=[AgL(SO_4)^+]/[AgL^{3+}]\cdot[SO_4^{2-}])$, of mixed ligand complex, $[AgL(SO_4)]^+$, can be estimated from the slope of the above straight line to be 83, which is slightly less than that reported by Maria Pravento et al.[25] The half-wave potentials, $E_{1/2}$'s, for the other systems investigated in this report underwent little SO_4^{2-} effect within the concentration range of 0.050 to 0.400 mol dm^{-3}, suggesting that SO_4^{2-} anions do not react with the Ag(III) complexes of [15]aneN$_5$, [16]aneN$_5$, and polyaza macrocycles carrying acetic acid groups on nitrogen atoms. Therefore, in all of the systems except for the cyclam complex in a sulfate solution, the electrode reaction (5) and the theoretical relation (6) for the half-wave potential can be simplified to (7) and (8), respectively. A rearrangement of Eq. 8 gives the relative ease of oxidation of Ag(II)

$$AgL^{2-n} = AgL^{3-n} + e^- \tag{7}$$

$$E_{1/2} = E^0_{Ag^{3+}/Ag^{2+}} - 0.0591\log\frac{K_{Ag^{III}L}}{K_{Ag^{II}L}} \tag{8}$$

to Ag(III),R, expressed by Eq. 9. It is, however, impossible to estimate the R value using Eq. 9, since the $E^0_{Ag^{3+}/Ag^{2+}}$ value is lacking.

$$R = \frac{K_{Ag^{III}L}}{K_{Ag^{II}L}} = \text{Antilog}\left(\frac{E^0_{Ag^{3+}/Ag^{2+}} - E_{1/2}}{0.0591}\right) \tag{9}$$

In spite of this obstacle, it is safely concluded that the more thermodynamically stable is the Ag(III) complex, the more negative the half-wave potential for the oxidation of the Ag(II) complex becomes. The half-wave potentials in solutions containing no sulfate anion determined from the CV measurements are listed in Table 3.

As judged from the $K_{Ag^{II}L}$ values in Table 3, an acetic acid group attached to the secondary amine, rather, contributes to the net destabilization of the Ag(II) complexes, whose magnitude tends to vary with the macrocyclic ring size. These acetic acid groups may pose a severe steric hindrance to the reaction of the ligand with Ag(II) ions by blocking access of the nitrogen donors. On the other hand, they exert a great positive effect on the thermodynamic stability of the Ag(III) state. This would be explained as the incorporation of negatively charged acetate carbonyl in the complexation with Ag(III) ions. Thus, it is not totally correct to consider that the Ag(III) ions do form square planar complexes with polyaza macrocycles, simply because the Ag(III) is d^8 ion, even though the common geometry of the d^8 Cu(III) is square planar.[25] The finding that the $E_{1/2}$ values for the pentaaza macrocycle complexes are considerably smaller than that for the cyclam complex suggests the additive coordination of the 5-th nitrogen donor of pentaaza macrocycles, and also lends strong support to the above conclusion that the Ag(III) ion forms polyaza macrocycle complexes with coordination numbers greater than four.

Rotating Disk Electrode Study. A rotating-disk electrode (glassy carbon) study also disclosed a well-shaped cathodic step at about −0.15 V vs. SCE in the

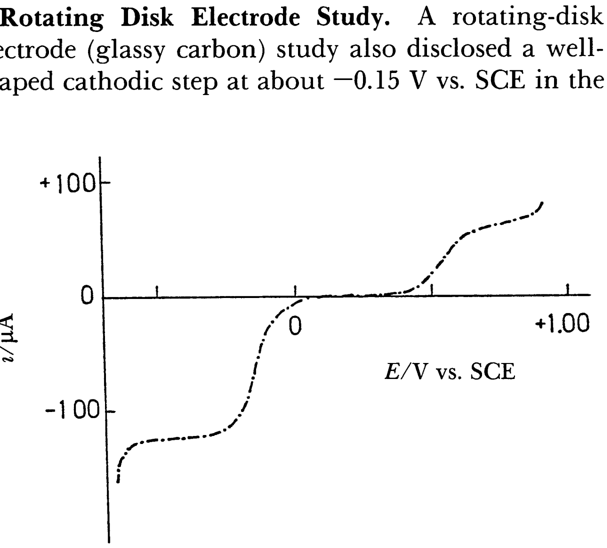


Fig. 7. Voltammogram of the Ag(II)-[14]aneN$_4$ complex at RDE: [Ag(II)-[14]aneN$_4$]=1.5 mM, [OAc$^-$]=0.050 M, 25 °C, pH=4.91, rotation velocity=1000 rpm.

reduction scan (followed by an anodic stripping peak in the reverse scan). On the other hand, in the oxidation scan a reversible step could be observed at a potential which nearly equals the midpoint between the anodic and cathodic peak potentials of the cyclic voltammogram (Fig. 7). The height ratio between the cathodic and anodic steps was almost two, lending strong support to the conclusions reached by dc polarography and cyclic voltammetry, that Ag(II) complexes easily undergo two-electron reduction at the DME (dc polarography) and one-electron oxidation at the glassy carbon electrode (cyclic voltammetry).

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