# Complexes of Silver(II) and Silver(III) with Macrocyclic Tetraaza Ligands

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Silver(II) complexes of four macrocyclic tetraaza ligands have been prepared by disproportionation of Ag(I) in the presence of the ligand. Some of these complexes may be oxidized to silver(III) species electrochemically or with NO^+ salts. Spectral and electrochemical properties of the new compounds are reported.

During recent investigations into the coordination chemistry of the ligand in III we attempted to remove Cl^- from

Ia, $R_1 = H$; $R_2 = CH_3$; $n = 2$
b, $n = 3$
IIa, $R_1 = H$; $R_2 = H$; $n = 2$
b, $n = 3$
III, $R_1 = CH_3$; $R_2 = H$; $n = 2$
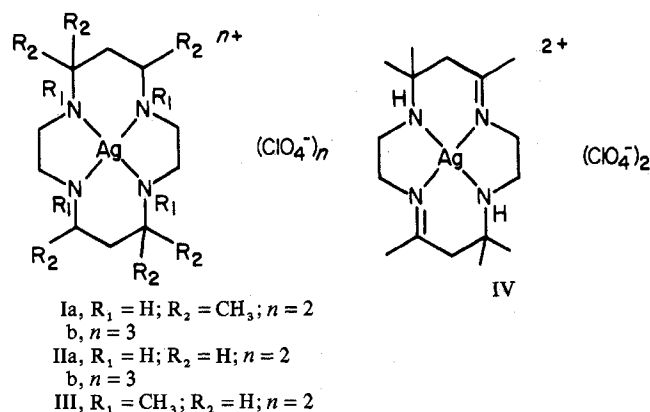
$[NiLCl]ClO_4{}^1$ using Ag^+. When an aqueous solution of the complex was treated with Ag^+ a rapid color change occurred and a silver mirror formed. This behavior could also be observed when aqueous solutions of Ag(I) and the amine were mixed and a crystalline complex of stoichiometry $AgL(ClO_4)_2$ could be isolated from the orange solution after removal of the metallic silver. Further investigation revealed that the general reaction

$$2Ag^+ + L \rightarrow AgL^{2+} + Ag^0$$
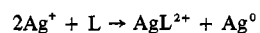
occurred when silver(I) salts react with a variety of macrocyclic amines.[2,3] Some of these silver(II) species have been oxidized both chemically and electrochemically to silver(III) species of substantial stability. Complexes prepared are shown as I–IV. The preparation and properties of these silver(II) and -(III) complexes are the subject of this report.

Experimental Section

Preparation of *meso*-5,5,7,12,12,14-Hexamethyltetraazacyclo-tetradecanesilver(II) Perchlorate (Ia). A solution of 0.83 g of AgClO$_4$ (4 mmol) in 140 ml of reagent grade CH$_3$CN was treated with 0.77 g of ligand (2 mmol as the dihydrate). This solution became deep yellow orange and a silver mirror formed. Stirring was continued for 20 min. The solution was filtered and reduced to a small volume on a rotary evaporator. The yellow solid was collected and was recrystallized from acetonitrile by addition of ether. The solid was collected and washed with ether and dried *in vacuo*: yield 0.7 g of deep yellow crystals. Highly purified acetonitrile[4] did not work

for this reaction. Instead, a white solid results. This was also observed by Kestner and Allred and was characterized as an Ag(I) species.[2]

Preparation of 1,4,8,11-Tetraazacyclotetradecanesilver(II) Perchlorate (IIa). Ligand (1 g, 5 mmol) was added to a stirred solution of 2.1 g of silver perchlorate (10 mmol) in 100 ml of water. A yellow color developed rapidly in the solution and a silver mirror soon formed. After stirring for 1 hr the solution was filtered, acidified to pH 2 with perchloric acid, and concentrated on a rotary evaporator. The orange needles which formed were collected, washed with THF, and dried *in vacuo*: yield 1.4 g.

Preparation of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecanesilver(II) Perchlorate (III). This complex was prepared as above using 1 mmol of ligand and 2 mmol of silver perchlorate in 30 ml of water except the solution was not acidified with perchloric acid before evaporation: yield 0.25 g of dark orange-brown crystals.

Preparation of 5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,8-dienesilver(II) Perchlorate (IV). A suspension of 1 g of the dihydroperchlorate ligand salt and excess freshly prepared silver(I) oxide was shaken for 4 hr in 200 ml of H$_2$O. The solids were removed by filtration and the pale yellow filtrate was acidified with HClO$_4$ and evaporated to a small volume. The yellow crystals were collected, washed with THF, and sucked dry. Conversion to the complex is quite low because of limited solubility of both reagents.

Oxidation of Ia to Ib. Under nitrogen a solution of Ia, 0.6 g (1 mmol), in 50 ml of purified CH$_3$CN was treated with 0.15 g (1 mmol) of NOClO$_4$. After stirring for 1 hr ether was added to crystallize a pale yellow solid. This solid was collected and dried *in vacuo*. It was later found that an identical material could be obtained by the procedure following for oxidation of IIa to IIb. Also, the same complex could be obtained by electrochemical oxidation at a Pt foil electrode. An acetonitrile solution of complex which was 0.1 *M* in purified $(C_2H_5)_4NClO_4$ was contained in a three-compartment cell and electrolyzed with a Par Model 173 potentiostat.

The new complex reacts instantly with water or other basic solvents to yield violet solutions. At room temperature these solutions exhibit no esr signal upon formation. However, a signal slowly grows with time. At the same time the solution lightens in color and finally becomes yellow. The strong esr signal for this solution is typical of the Ag(II) complexes in solution.

Oxidation of IIa to IIb. Oxidation of this material in acetonitrile proved difficult because of the instability of the product complex. However, the oxidation could be conducted in reagent grade acetonitrile containing concentrated perchloric acid. IIa, 0.2 g, dissolved in *ca.* 5 ml of CH$_3$CN containing a few drops of concentrated HClO$_4$ was treated with NOClO$_4$·H$_2$O until the orange color changed to a very pale yellow. A pale yellow solid commenced to form. This suspension was stirred for *ca.* 15 min and the solid collected under a blanket of nitrogen, washed with ether, and dried briefly *in vacuo*. Electrochemical oxidation of this complex could also be performed but conversion to Ag(III) was low because of the competing decomposition to Ag(II).

The diamagnetic complex IIb reacts instantly with water to give deep violet solutions which slowly decay to yellow solutions. These yellow solutions exhibit strong esr signals typical of Ag(II) complexes. Analytical data for the new complexes are contained in Table I.

Esr spectra were obtained with a Varian E9 X-band spectrometer using quartz tubes for solids and a flat solution cell for aqueous and acetonitrile solutions. Flow experiments were performed by gravity feeding solutions of Ag(III) complex in acetonitrile and water in acetonitrile into a Y-shaped mixing device 4–5 cm from the cavity connected to a flat solution cell. Infrared spectra were obtained on Nujol mulls using a Perkin-Elmer 457 spectrophotometer. Nmr spectra were obtained on solutions prepared by dissolving Ag(II) complex in concentrated nitric acid using a Varian A-60A instrument. Evans' meth-

(1) E. K. Barefield and F. Wagner, *Inorg. Chem.*, 12, 2435 (1973).

(2) A single example of such a disproportionation was recently published: M. O. Kestner and A. L. Allred, *J. Amer. Chem. Soc.*, 94, 7189 (1972). The complex prepared by these workers is the same as Ia in this report.

(3) A review of the chemistry of these ligands (other than the N-methylated derivative used in III) has recently appeared: L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, 6, 1 (1971). This reference should be consulted for synthetic details.

(4) Acetonitrile was purified by a modification of the precedure given by E. O. Sherman, Jr., and D. C. Olson, *Anal. Chem.*, 40, 1174 (1968).

Table I. Analytical Data for Silver(II) and Silver(III) Complexes[a]

		Calcd, %					Found, %				
		C	H	N	Ag	Cl	C	H	N	Ag	Cl
Ia	$AgC_{16}H_{36}N_4Cl_2O_8$	32.50	6.14	9.48	18.24		32.76	5.58	9.59	18.44	
IIa	$AgC_{10}H_{24}N_4Cl_2O_8$	23.68	4.77	11.05	21.27		24.02	4.87	11.52	21.12	
III	$AgC_{14}H_{32}N_4Cl_2O_8$	29.85	5.73	9.95	19.15	12.59	29.67	5.87	10.35	17.76	13.06
IV	$AgC_{16}H_{32}N_4Cl_2O_8$	32.72	5.49	9.54	18.37		32.76	5.58	9.59	18.44	
Ib	$AgC_{16}H_{36}N_4Cl_3O_{12}$	27.82	5.25	8.11	15.62	15.4	28.06	5.40	8.18	14.90	14.66
IIb	$AgC_{10}H_{24}N_4Cl_3O_{12}$	19.80	3.99	9.24	17.78		19.25	4.08	9.11	17.10	

[a] Silver analyses tended to be low even when other elemental values were acceptable. Chlorine was particularly difficult for an analyst to do in the presence of silver so these were not routinely performed. Thanks are due to Mr. J. Nemeth and his colleagues for their assistance in the analytical aspects of this work.

Table II. Spectral, Magnetic, and Electrochemical Data for Ag(II) and Ag(III) Complexes I–IV

Complex	Oxidation state	μ_{eff}[a]	λ_{max}[b]	$g_\parallel$[c]	$g_\perp$[c]	Anodic wave[e]	Cathodic wave[e]
I	+2	2.2	348 (7.7)	2.11	2.05_8[d]	0.617 (1)	−0.283 (2)
			280 (3.6)				
	+3	Diamagnetic	g				−0.26 (2)
II	+2	1.95	342 (13.3)	2.09_5	2.03_8	0.71 (1)	
			275 sh (3)				
	+3	Diamagnetic	g				0.68 (1), −0.27 (2)
III	+2	1.81	382 (8.6)	1.99_7	2.07	0.96 (1)	f
			300 (2)				
IV	+2	1.96	338 (6.2)			0.63 (1)	−0.37 (2)
			300 (6.2)				

[a] Faraday measurements. [b] 10^{-3} M complex, 10^{-1} M $(C_2H_5)_4NClO_4$ in CH_3CN; band position in nanometers, molar extinction coefficient $\times 10^{-3}$ in parentheses. [c] Polycrystalline samples at room temperature unless otherwise noted. [d] Doped into Ni(II) complex of corresponding ligand $\sim$5% level. [e] Rotating Pt working electrode, $Ag|0.1$ M Ag^+ in acetonitrile reference electrode, 10^{-3} M complex, 10^{-1} M $(C_2H_5)_4NClO_4$ in CH_3CN; number of electrons given in parentheses. [f] Very poorly defined two-electron wave. [g] No low energy d–d transitions are observed.

od[5] was used to check for paramagnetic species in these solutions using trimethylamine as a standard. Magnetic susceptibility measurements on solids were done by the Faraday method.

Results and Discussion

Reaction of silver(I) with macrocyclic tetraaza ligands is a facile process for forming silver(II) complexes. Although disproportionation is a common process for Cu(I), these represent the first class of Ag complexes to display this behavior. Metallic silver is a by-product in each of these reactions. Kestner and Allred have isolated a silver(I) complex of ligand Ia in acetonitrile under anhydrous conditions.[2] We have also found that white precipitates are formed in purified acetonitrile and that some water is necessary for the disproportionation to occur. All of the silver(II) complexes are yellow to orange and have infrared spectra similar to their nickel analogs. Magnetic moments are in the range 1.9–2.1 BM expected for monomeric d[9] complexes (Table II). These complexes are exceptionally stable compared to previously reported Ag(II) complexes. They are stable in most solvents in which they are soluble (*e.g.*, acetonitrile, water, ethanol) for a considerable time although solutions prepared with reducing solvents such as ethanol form silver mirrors after some time. Previously reported Ag(II) complexes are often quite stable in the solid state. In solution, however, they are powerful oxidants with little stability.[6]

Epr spectra of the silver(II) complexes are typical of a d[9] axial system. In each case $g_\perp$ and $g_\parallel$ are well resolved (Table II). This is expected for a planar d[9] complex.[7] In the case of III, $g_\parallel < g_\perp$ which for a d[9] system indicates that the axial ligand field is greater than the radial field.[7] This would suggest in the present case that the ligand might be folded with coordination of a perchlorate in the solid state as shown below.
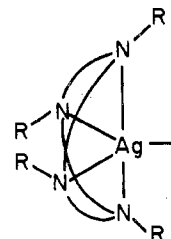
This possibility is neither confirmed nor disproved by the infrared spectrum. Since there are two perchlorate ions, absorptions by an uncoordinated ion can obscure those of one which is weakly coordinating. Resolution of hyperfine coupling to the donor nitrogens was not achieved. The esr spectrum of IIa doped into the corresponding nickel(II) complex at the 5% level also did not show any hyperfine structure.

Electrochemical data obtained on these silver(II) complexes are contained in Table II. In each case a one electron quasi-reversible anodic wave was observed at 0.7–0.9 V which indicated that silver(III) complexes might be obtained either by electrochemical or perhaps chemical oxidation. Similar Ni-(II) complexes having oxidation potentials in this range are easily oxidized to the trivalent state.[8] Polarographic data obtained on the Cu(II) complexes analogous to Ia and IVa are available. Perhaps coincidentally both of these complexes have oxidation potentials of ~1.2 V *vs.* the 0.1 M Ag| Ag electrode.[9] As expected, silver, a second row metal, has a lower potential but there also appears to be a dependence on the degree of saturation of the ligand. Unfortunately, only limited data are available so the significance of this observation cannot be assessed. At lower potentials an irrevers-

(5) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(6) J. A. McMillan, *Chem. Rev.*, 62, 65 (1962).
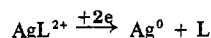(7) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 5, 143 (1970).

(8) (a) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, 8, 1611 (1969); (b) E. K. Barefield and D. H. Busch, *Chem. Commun.*, 522 (1970); (c) N. F. Curtis, *ibid.*, 881 (1966).
(9) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, 10, 463 (1971).

ible two-electron cathodic wave was evident corresponding to the process

$$AgL^{2+} \xrightarrow{+2e} Ag^0 + L$$

After several cathodic scans deposited silver was observed on the Pt electrode.

Since an anodic wave was observed controlled potential oxidation of Ia was attempted. A silver(III) complex with stoichiometry $AgL(ClO_4)_3$ was isolated after the current had decayed *ca.* 85% of the initial value. A more convenient synthesis of this material was achieved by oxidation with $NOClO_4$ in acetonitrile. Electrolysis of IIa proved to be a poor method for obtaining IIb because of the instability of the silver(III) complex which was formed. Nitrosonium perchlorate oxidation of IIa in acetonitrile–perchloric acid medium was successful. Again the composition of the product was $AgL(ClO_4)_3$. Spectral, magnetic, and electrochemical data for these complexes are given in Table II. No attempts were made to oxidize the other silver(II) complexes although their redox potentials suggest that it would be feasible. It is interesting to note that Cu(III) complexes corresponding to Ib and IIb crystallize with two acetonitrile molecules per complex.[9] It is not known whether these are coordinated to the metal ion. Complex Ib is quite stable both in the solid state and in dry, purified acetonitrile. Complex IIb, on the other hand, is very unstable in the solid state and in solution, excepting very pure CH_3CN containing concentrated perchloric acid.

Both complex Ia and IIa dissolve in HNO_3 without decomposition, yielding orange solutions which contain only diamagnetic species judging from their nmr spectra and susceptibility measurements by the Evans technique.[5] This suggests, of course, that nitric acid also oxidizes the silver(II) ion to the 3+ oxidation state. This is the case for the analogous Ni(II) complexes which have similar redox potentials.[8a,c] The nmr spectrum of IIb in concentrated nitric acid is quite similar to that of the analogous nickel complex. The nmr spectrum of Ib (Figure 1) however, differs considerably from that of the corresponding nickel(II) complex.[10] The spectrum of Ib contains only an apparent doublet for the methyl resonances. The axial–equatorial distinction for the *gem*-methyl groups is apparently diminished to the point that they are nearly magnetically equivalent, contrary to the case for the Ni(II) complex where the axial methyls are substantially deshielded compared to the equatorial methyls. Addition of concentrated HCl to HNO_3 solutions containing (initially) Ia produced deep red-orange colors and red-orange needles formed from cold concentrated solutions. These materials appear to contain $[AgLCl_2]^+$ as a mixed nitrate, perchlorate salt. It was not possible to purify them sufficiently for adequate characterization. The behavior of these materials in water is consistent with an Ag(III) formulation.

Both of the Ag(III) complexes which we isolated in pure crystalline form react instantly with water to form violet solutions. The color of these solutions slowly changes to yellow upon standing. The paramagnetic nature of the Ag-(II) complex species produced precluded detailed studies of the products by nmr spectroscopy. However, the infrared spectrum of the complex products from the decomposition of Ib in water showed no band near 1660 cm^{-1} as would be expected for coordinated imine in the macrocycle. Thus,
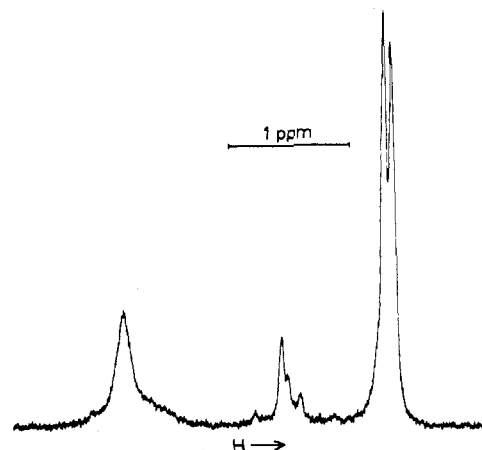
Figure 1. Nmr spectrum at 60 MHz of the silver(III) complex Ib in concentrated HNO_3, prepared by dissolving the silver(II) complex in the concentrated acid.

no ligand oxidation appears to occur in the course of this Ag(III) → Ag(II) reduction. The violet species was generated in a flow system for esr measurements by mixing an acetonitrile solution of Ib with a 25:75 H_2O–CH_3CN mixture. No signal could be detected immediately after formation of the violet species. When the flow was stopped an isotropic signal at $g = 2.05$ slowly grew. This is the same signal observed for the Ag(II) complex of this ligand in the same medium. The general behavior observed here is the same as that observed for the decomposition of the corresponding Ni-(III) complex.[11] We found the following processes occurred in this case.

$$Ni^{III}-\overset{/}{N}-H + base \rightarrow Ni^{II}-\overset{/}{N}\cdot$$
$$\phantom{Ni^{III}-N-H}\underset{A}{} \underset{B}{}$$

$$Ni^{II}-\overset{/}{N}\cdot \xrightarrow{H\cdot} Ni^{II}-\overset{/}{N}-H$$
$$\phantom{Ni^{II}-N \xrightarrow{H} Ni^{II}-N}\underset{C}{}$$

In the present case species B would be $[Ag^{II}L\cdot]^{2+}$ and in contrast to the Ni system might be expected to be diamagnetic since there are two unpaired spins which could couple. In one experiment we observed an esr signal which we could attribute to the triplet species but this result could not be duplicated. The nature of this species is under further investigation. Hydrogen atoms for trapping species B came from decomposed complex in the Ni(III) decompositions. We assume a similar path for $[Ag^{II}L\cdot]^{2+}$ although this fact has not been experimentally proven.

In conclusion, the formation of these novel complexes further illustrates the effect of the exceptionally strong ligand field exerted by macrocyclic tetraaza ligands. This serves to raise antibonding levels (d orbitals) in the species of lower oxidation state to such high energy that electrons are easily removed. In the present case Ag^+ is a sufficiently strong oxidizing agent to remove the antibonding electron from AgL^+ with formation of AgL^{2+}. Even more surprising is the removal of a second electron by NO^+ to yield Ag(III). These results could suggest that silver is in fact quite similar to gold as well as to copper in its chemistry.

(10) L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4092 (1969). The nmr spectrum of this complex cannot be obtained in nitric acid since oxidation to Ni(III) takes place. The nmr spectrum obtained on a trifluoroacetic acid solution is essentially the same as the one shown in this reference.
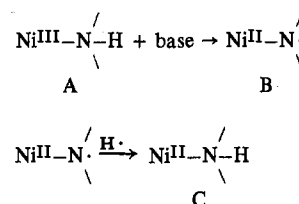
(11) E. K. Barefield and M. T. Mocella, Abstracts, 165th National Meeting of American Chemical Society, Dallas, Texas, April 1973, No. INOR 139; submitted for publication.

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Kinetics of Silver(III) Complexation by Periodate and Tellurate Ions

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The tetrahydroxoargentate(III) ion has been prepared in sodium hydroxide media by anodic oxidation of silver metal. The kinetics of Ag(III) complex formation with periodate and tellurate ions has been studied by the stopped-flow method at an ionic strength of 1.2 M. Both reactions result in a rate law attributable to stepwise formation of the bis complex. At 25° the second-order rate constants for formation of the mono- and bis(periodato)argentate(III) complex are 4.5×10^4 and $9.3 \times 10^3 \ M^{-1} \ \sec^{-1}$. The corresponding values for tellurate complexation are 2.72×10^3 and $1.0 \times 10^4 \ M^{-1} \ \sec^{-1}$ although the order of this assignment is less certain. Activation parameters have been determined and are consistent with the associative-type mechanisms common to other square-planar low-spin d^8 metal ions.

Introduction

The existence of silver in the 3+ oxidation state both in solid compounds and as soluble species has been well documented. In addition to the oxide $Ag^IAg^{III}O_2$ (formally AgO),[1] several oxy salts and tetrafluoroargentates are described in the literature.[2] Silver(I) nitrate can be oxidized to Ag(III) in the presence of complexing agents, such as periodate or tellurate, either by peroxydisulfate[3] or by electrolysis[4] in alkaline solutions. From these solutions, compounds of the general formula $M_7Ag(IO_6)_2 \cdot nH_2O$ and $M_9Ag(TeO_6)_2 \cdot nH_2O$, where M is Na, K, or H, can be crystallized out. The same compounds have also been obtained by direct reaction of the appropriate ligand with alkaline solutions saturated with AgO.[5] Organic ligands such as biguanidine[6a] and its derivatives[6b] also stabilize Ag(III) as has been confirmed by photoelectron spectroscopy.[6c] The stabilizing effect of the porphyrin ring has been indicated by esr measurements.[7]

All silver(III) compounds, for which magnetic susceptibility has been measured, are diamagnetic.[1-3,6-8] This is consistent with the tendency of Ag(III) to coordinate in the square-planar configuration found for the analogous spin-paired d^8 systems Au(III), Cu(III), Pt(II), Ni(II), and Pd(II).

The simplest species of Ag(III) to be prepared in solution has been reported by Cohen and Atkinson.[9] They found that when a smooth strip of silver is anodically oxidized in concentrated KOH solutions (1.2–12 M) a yellow solution results that contains silver in the 3+ oxidation state only. They identified the silver species present as the tetrahydroxoargentate(III) ion. The $Ag(OH)_4^-$ ion shows a single broad absorption band in the ultraviolet spectrum with the reported maximum at 271 nm. Addition of potassium periodate or potassium tellurate results in solutions whose electronic spectra are identical with those obtained by dissolving solid bis(periodato)argentate(III) or bis(tellurato)-argentate(III) salts in water.[9,10] Punkies, *et al.*,[11] have identified a silver(III) species produced in pulse radiolysis studies on Ag^+ in neutral solution. The absorption spectrum of this species closely matches that of the $Ag(OH)_4^-$ ion having a single broad peak with a maximum at 270 nm.

The tetrahydroxoargentate(III) ion is metastable; the silver(III) is reduced to AgO, presumably by the solvent, with a half-life ranging from about 100 min in 1.2 M KOH to approximately 240 min in 12 M KOH at 27.2°.[10] Cohen[10] was unable to prepare $Ag(OH)_4^-$ by electrolysis of silver in 12 M sodium hydroxide.

In this paper we report on the stoichiometry and kinetics of the ligand-exchange reaction between the OH⁻ ligands of the tetrahydroxoargentate(III) ion and periodate and tellurate, respectively. These reactions are rapid, necessitating the use of the stopped-flow technique. We also report on the preparation of $Ag(OH)_4^-$ in NaOH solution by an electrolytic technique somewhat different from that of Cohen and Atkinson.[9]

Experimental Section

Preparation of Tetrahydroxoargentate(III) Solutions. Approximately 200 ml of 1.2 M NaOH solution was placed in a 250-ml polyethylene beaker with cover. The cover was equipped with appropriate ports to accommodate the anode, the cathode compartment with cathode, and a glass capillary. The anode consisted of a 1 cm wide strip of silver foil (Handy and Harman) dipped into the solution to a depth of 5 cm giving a nominal surface area for electrolysis of 10 cm². The surface area of the silver foil, determined by a double-

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(1) J. A. McMillan, *J. Inorg. Nucl. Chem.*, **13**, 28 (1960).

(2) J. A. McMillan, *Chem. Rev.*, **62**, 65 (1962).

(3) L. Malatesta, *Gazz. Chim. Ital.*, **71**, 467 (1941).

(4) L. Jensovsky and M. Skala, *Z. Anorg. Allg. Chem.*, **312**, 26 (1961).

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(6) (a) D. Sen, *J. Chem. Soc. A*, 1304 (1969); (b) D. Sen and K. Chakravarty, *J. Indian Chem. Soc.*, **21**, 47 (1944); (c) D. A. Zatko and M. L. Simms, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR 41.

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