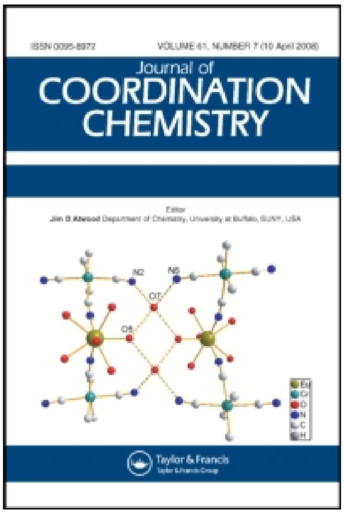

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THE REACTIONS OF SILVER(I) WITH TETRAAZA MACROCYCLIC LIGANDS

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The reactions of silver(I) with 1,4,7,11-tetraazacyclotetradecane (isocyclam), 1,4,8,11-tetraazacyclotetradecane (cyclam) and 1,4,8,12-tetraazacyclopentadecane ([15]aneN_4) resulted in the production of silver and a silver(II) tetraaza macrocyclic complex, AgL^{2+}.

$$2Ag^{1+} + L \longrightarrow AgL^{2+} + Ag$$

The mechanisms of these reactions involve the formation of AgL^{1+} which is oxidized by silver(I) to Ag and AgL^{2+}. However, the reaction of 1,4,7,10-tetraazacyclododecane ([12]aneN_4) with silver(I) resulted in the formation of an unstable complex. Silver(I) did not react with 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane. The most stable Ag(II) complex in aqueous solution with regards to decomposition contains the [15]aneN_4 ligand, while the Ag(II) complex containing [12]aneN_4 is the least stable. Attempts to oxidize benzyl alcohol to benzyl aldehyde using $[Ag(cyclam)](ClO_4)_2$ were unsuccessful.

Keywords: Silver(I)–silver(II) complexes, macrocycles, disproportionations.

INTRODUCTION

It is known that copper(I) is not stable in water and will disproportionate to copper(II) and copper.[1] In contrast, silver(I) is very stable in water and does not readily disproportionate to silver(II) and silver metal.[1] However, silver(I) in the presence of a variety of 14-membered tetraaza-macrocyclic ligands, L, in water disproportionates to Ag and AgL^{2+}.[2–4]

The purpose of this study is to investigate the reaction of silver(I) with tetraaza-macrocycles as a function of the cavity size of the macrocycle and to compare physical properties of the resulting silver(II) complexes. We would also like to explore whether these reactions are ligand-induced disproportionation reactions. Several reaction schemes can be envisioned. Silver(I) may react with the macrocycles in water to form a silver(I) complex, AgL^{1+}. The AgL^{1+} could disproportionate to Ag, AgL^{2+} and L. Another possibility is that AgL^{1+} is oxidized by Ag^{1+} to form elemental silver and AgL^{2+}.

$$AgL^{1+} + Ag^{1+} \longrightarrow Ag + AgL^{2+}$$

In this study we have attempted to determine which of these two mechanisms is occurring.

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EXPERIMENTAL

Basic Chemicals

All silver salts, 1,4,8,11-tetraazacyclotetradecane and 1,4,8,12-tetraazacyclopentadecane were purchased. 1,4,7,10-tetraazacyclododecane, 1,4,7,11-tetraazacyclotetradecane, 1,4,7,10-benzyl-1,4,7,10-tetraazacyclododecane and [Agcyclam]$(ClO_4)_2$ were prepared using published procedures.[3,5-7]

Synthesis of (1,4,8,12-tetraazacyclopentadecane)silver(II) perchlorate hemihydrate

Addition of 0.1 g (0.5 mmol) of 1,4,8,12-tetraazacyclopentadecane to 0.667 g (3 mmol) of $AgClO_4.H_2O$ in 20 cm^3 of water produced an amber solution which then turned grey-green as the reaction proceeded. The solution was stirred for half an hour, filtered, and made acid by the addition of a few drops of perchloric acid. Some product precipitated from solution. The solution was concentrated in vacuum to approximately 2–3 cm^3. The resulting crystals were collected by filtration, washed with several drops of THF, and dried *in vacuo* over P_2O_5. *Anal.*; Calcd. for $AgC_{11}H_{23}N_4Cl_2O_{8.5}$: C, 25.11; N, 10.65; H, 4.41%. Found: C, 25.12; N, 10.58; H, 4.92%.

Reaction of 1,4,7,10-tetraazacyclododecane with silver(I)

Four tenths of a gram (0.0024 mol) of silver nitrate was added to a stirred solution containing 0.20 grams (0.0012 mol) of 1,4,7,10-tetraazacyclododecane, [12]aneN_4, in 20 cm^3 of water. A white precipitate formed immediately. Within 10 minutes a silver mirror began to form on the flask. The white precipitate was either masked by the silver mirror or dissolved. No attempt was made to isolate it. After five additional minutes the solution developed a deep-blue colour which then faded to a colourless solution. Attempts to isolate the blue species by addition of concentrated aqueous $NaClO_4$ solution failed. ESR and electronic spectra were obtained *in situ*.

Reaction of 1,4,7,11-tetraazacyclotetradecane with silver(I)

Addition of 0.02 grams (0.001 mol) of 1,4,7,11-tetraazacyclotetradecane, isocyclam, to 0.34 grams (0.002 mol) of silver nitrate in 20 cm^3 of water produced an immediate colour change from colourless to dark yellow with the simultaneous formation of a silver mirror on the reaction flask. The solution was filtered and then concentrated by removal of solvent in vacuum. Attempts to isolate the yellow species by addition of $NaClO_4$ failed. ESR and electronic spectra were obtained *in situ*.

Attempted oxidation of benzyl alcohol using (1,4,8,11-tetraazacyclotetradecane)-silver(II) perchlorate

(1,4,8,11-Tetraazacyclotetradecane)silver(II) was generated *in situ* by the addition of 1.9 g (8.4 mmol) of $AgClO_4{\cdot}H_2O$ and 0.84 g (4.1 mmol) of 1,4,8,11-tetraazacyclotetradecane to 120 cm^3 of distilled water with stirring. The solution turned yellow then dark green as the silver metal began to precipitate from solution. The solution was stirred for one hour, then filtered. Ten 10 cm^3 portions were pipetted into ten Erlenmeyer flasks. These flasks were placed in either an 80°C oil bath or a 50°C water bath. In all these flasks more silver was deposited and the resulting yellow solutions were filtered again. After the silver stopped precipitating from solution excess benzyl alcohol was added to each flask. At various time intervals (0.5 to 24 hr) the flasks were cooled to room temperature and benzyl alcohol and or benzaldehyde (the expected product of the reaction) was extracted into diethylether. The ether solution was injected into a ten percent diisodecylphthalate column. The column was held at 140°C with a helium flow of 36 $cm^3\ min^{-1}$. Each solution was analyzed by gas chromatography for benzaldehyde. To test the procedure, a similar procedure was employed using Ce(IV) instead of (1,4,8,11-tetraazacyclotetradecane)silver(II). The Ce(IV) oxidizes the benzyl alcohol to benzaldehyde. The benzaldehyde was observed by gas chromatography using the above technique.

Preparation of (1,4,8,11-tetraazacyclotetradecane)silver(II)

(1,4,8,11-tetraazacyclotetradecane)silver(II) was generated *in situ* in the same manner as discussed above except the mole ratio of 1,4,8,11-tetraazacyclotetradecane to silver(I) was varied.

Physical measurements

The mass susceptibility in solution was obtained by the Evans method[8] using a Varian A-60 NMR with coaxial cells. The mass susceptibility of the solid at room temperature was determined by the Guoy method. Electronic spectra were measured on a Beckman Acta MIV UV-visible-IR spectrophotometer with 1 cm matched quartz cells. ESR spectra were recorded on a Varian E-4 spectrometer operating at X-band frequencies that were calibrated with diphenylpicrylhydrazyl. Chemical analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

RESULTS AND DISCUSSION

The reaction of $AgClO_4$ with [15]aneN_4, 1,4,8,12-tetraazacyclopentadecane, results in a silver mirror and the isolation of $[Ag[15]aneN_4](ClO_4)_2 1/2H_2O$ from the yellow filtrate. The magnetic moment of $[Ag[15]aneN_4](ClO_4)_2 1/2H_2O$ as determined by the Guoy method is 1.75 μ_B. This magnetic moment is consistent with one unpaired electron and a silver(II) species. The peak maxima at 366 nm ($\varepsilon = 10{,}000$) and 291 nm ($\varepsilon = 5000\ M^{-1}\ cm^{-1}$) found in the electronic spectrum in water is in the range of other silver(II) complexes containing macrocyclic ligands.[2-4]

The reaction of isocyclam, 1,4,7,11-tetraazacyclotetradecane, with $AgNO_3$ also results in a silver mirror and a yellow filtrate. Concentrating the solution and adding $NaClO_4$ did not induce $[Ag(isocyclam)](ClO_4)_2$ to precipitate. Based on the silver mirror and the yellow solution which formed in this reaction, it is highly likely that the yellow solution contains the $[Ag(isocyclam)]^{2+}$ ion. It was possible to measure the magnetic moment of the $[Ag(isocyclam)]^{2+}$ ion in aqueous solution by the Evans method.[8] By calculating the concentration of $[Ag(isocyclam)]^{2+}$ based on the stoichiometry of the reaction the magnetic moment of $[Ag(isocyclam)]^{2+}$ was determined in water to be 1.8 μ_B. This magnetic moment is consistent with a silver(II) complex.[3] Also, the ESR spectrum of this yellow solution possessed a signal which indicates that a paramagnetic species was present. The peak maxima at 370 nm and

275 nm in the electronic spectrum is also consistent with other silver(II) complexes containing macrocyclic ligands.[2-4]

The reaction of $AgClO_4 \cdot H_2O$ with [12]aneN_4 in a two to one mole ratio, respectively, in water resulted in a silver mirror. Within 15 minutes the solution turned blue. The rate of formation of the blue species can be increased by either warming the mixture or by the addition of an oxidizing agent such as potassium peroxydisulfate. Upon standing at room temperature for one to two minutes, the blue colour fades and the solution becomes colourless. The blue colour did not return when additional oxidizing agent was added. We were not able to isolate the blue species due to its rapid rate of decomposition. The electronic spectrum of the blue species has a single band with a maximum absorbance at 545 nm. A signal was observed in the Electron Spin Resonance spectrum for this blue solution. Additional scans were taken at one minute intervals. The ESR scan showed weaker ESR response at longer times. The final scan taken on a colourless solution resulted in no ESR signal. This indicates that no unpaired electrons exist in this solution. However, the observed ESR signal may not be due to the blue species in solution but to an intermediate in a decomposition reaction.

Barefield and Mocella noted that the silver(III) complex $[Agcyclam]^{+3}$ reacted with water to produce a blue solution which turned yellow with time.[3] They suggested that the water reacted with the acidic protons bonded to the coordinated nitrogens (Ag^{3+}–N–H) which resulted in the production of the free radical $[Ag^{2+}N\cdot]$. This free radical is responsible for the blue colour. Barefield and Mocella also suggested that the free radical is diamagnetic because the unpaired electrons, on the nitrogen and on the silver, couple.[3] The $[Ag^{2+}N\cdot]$ species reacts with a hydrogen free radical to produce the yellow paramagnetic solution. A similar reaction sequence may occur in the reaction of [12]aneN_4 with silver(I). A silver(III) complex may be formed, which then reacts with water to form an unstable silver(II) complex. This unstable silver(II) complex decomposes to a colourless diamagnetic species.

Thom, Hosken and Hancock[9] have shown through molecular mechanics calculations and equilibrium studies that [12]aneN_4 should be a stronger field ligand than the larger macrocycles such as cyclam when complexed to heavier metal ions such as mercury(II) or lead(II). Therefore, [12]aneN_4 would be expected to function as a stronger field ligand to silver(I) than cyclam, isocyclam or [15]aneN_4. The net effect of bonding a strong field ligand to silver(I) would be to raise the energy of the highest occupied antibonding molecular orbital containing the d electrons to such a high level that electrons are readily removed. This may explain why only the [12]aneN_4 will interact with silver(I) to possibly produce a silver(III) species. Because the [12]aneN_4 is not likely to bond to silver(II) in a planar manner, $[Ag([12]aneN_4)]^{2+}$ should be susceptible to decomposition.

All attempts to effect a reaction between 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane with silver(I) in water failed.

It can be concluded that the reaction of Ag(I) with either a 14 or 15 membered tetraaza-macrocycle results in the production of a yellow AgL^{+2} species and silver metal. In contrast, the reaction of [12]aneN_4 with silver(I) in water results in an unstable paramagnetic blue solution while the tetra-*N*-benzyl derivative of [12]aneN_4 did not react with silver(I) at all.

The silver(II) complexes containing tetraaza-macrocyclic ligands are relatively poor oxidizing agents. For example, $[Ag(cyclam)](ClO_4)_2$ could not oxidize benzyl alcohol to benzaldehyde. In contrast, Ag^{2+} is a very strong oxidizing agent. The AgL^{2+} complexes are also relatively stable in solution with regards to decomposition. The approximate half life for the decomposition of $[Ag([15]ane)N_4)](ClO_4)_2 \cdot 1/2H_2O$ and $[Ag(cyclam)](ClO_4)_2$ in water at 20°C is 132 hours and 23 hours, respectively (the decay in the optical density at the peak maximum was followed as a function of time).

The band maxima listed in Table I, with the possible exception of $[Ag[12]aneN_4]^{2+}$, are likely to involve ligand to metal charge transfer transitions. The basis for assigning these bands as charge transfer transitions is their high extinction coefficients. Clark and Harrowfield observed that band maxima at the highest wavelengths were found for Ag(II) complexes containing tertiary *N* donors such as tetra-*N*-methyl-1,4,8,11-tetraazacyclotetradecane.[4] Tertiary amines are more easily oxidized than secondary amines. On this basis they concluded that these bands are ligand to metal charge transfer transitions.[4] Since the peak maxima that were observed for the complexes prepared in this study are in the same range as that found by Clark and Harrowfield, and since ligand field transitions for silver(II) complexes are usually found at lower energies,[10] all the maxima listed in Table I except for $[Ag[12]aneN_4]^{2+}$ have been assigned to ligand to metal transitions. The relatively large differences in the band maxima observed among silver(II) complexes containing secondary amines can be related to the Ag^{2+}–N bond energy. The electrons involved in weaker Ag^{2+}–N bonding should be in higher energy bonding orbitals than electrons involved in stronger Ag^{+2}–N bonding. The antibonding molecular orbitals associated with weaker bonding molecular orbitals should be at lower energies compared to stronger bonds. As a result the silver(II) complexes containing the more strained silver to nitrogen bonds should result in ligand to metal transitions at lower energies. On this basis it would appear that the unsymmetrical 14-membered ring, isocyclam, and the 15-membered ring, $[15]aneN_4$, result in more strained and weaker Ag to N bonds than the symmetrical 14-membered ring, cyclam, or tet a (Table I). This relative ordering of ligand to metal bond strain as a function of the ligand cavity size of the macrocyclic ligand is consistent with reported data on the relative ligand field strength of these ligands.[11-13] Both [15]ane and isocyclam are usually weaker field ligands than the symmetrical $[14]aneN_4$ ligands.

TABLE I

Electronic spectral maxima of Ag(II) complexes in water.

$[Agcyclam]^{+2}$	345 nm
$[Ag[15]aneN_4]^{+2}$	366 nm
$[Ag[isocyclam]^{+2}$	370 nm
$[Ag(TMC)]^{+2}$	400 nm[4]
$[Ag(teta)]^{+2}$	345 nm[4]
$[Ag[12]aneN_4]^{+2}$	545 nm

TMC = tetra-*N*-methyl-1,4,8,11-tetraazacyclotetradecane; teta = 1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethylcyclotetradecane.

The electronic spectrum of the product of the reaction of silver(I) with $[12]aneN_4$ is most interesting. If we assume that the band at 545 nm is due only to $[Ag([12]aneN_4)]^{2+}$, then we must conclude that $[Ag([12]aneN_4)]^{2+}$ contains the most strained metal to nitrogen bonds. This is also consistent with data obtained with other metal ions.[11-13] However, this band cannot be assigned to a single species with certainty.

To determine whether these reactions involve the oxidation of AgL^{1+} by Ag^{1+} we carried out reactions using excess L in order to reduce the concentration of free silver(I). (Cyclam was used in these reactions because of its commercial availability.) The relative yield of $[Ag(cyclam)]^{2+}$ obtained under the conditions of excess cyclam were compared with the yield of $[Ag(cyclam)]^{2+}$ resulting from the reaction of silver(I) with cyclam in a two to one mole ratio. Reacting silver nitrate with cyclam in a mole ratio of two to one (10 mmol to 5 mmol in 100 cm^3 of water) results in a silver mirror and a filtrate having a peak maximum at 350 nm with an extinction coefficient of 5300 M^{-1} cm^{-1} (all the extinction coefficients were calculated on the basis that half the number of moles of silver(I) were stoichiometrically converted to $[Ag(cyclam)]^{2+}$). The pH of this filtrate was 7.4. Employing a one to 1.9 mole ratio of silver nitrate to cyclam (2.93 mmol to 5.65 mmol) resulted in the production of silver metal and a filtrate with a band at 330 nm and an extinction coefficient of 746 M^{-1} cm^{-1}. The extinction coefficient at 350 nm, where no peak exists, was calculated to be 629 M^{-1} cm^{-1}. The pH of this solution was 11.4. If triethylamine or cyclam is added to the solution prepared using a 2 to 1 Ag(I) to cyclam mole ratio, so as to change the pH from 7.4 to 11.4, the peak observed at 350 nm disappears and a new band is found at 330 nm. The calculated extinction coefficient at 330 nm is 4204 while at 350 nm it is 3600 M^{-1} cm^{-1}. We can conclude that under basic conditions $[Ag(cyclam)]^{+2}$ is not stable and will decompose. Even after taking into account the instability of $[Ag(cyclam)]^{2+}$ in basic solution, it is evident that less $[Ag(cyclam)]^{2+}$ is produced when Ag(I) is reacted with excess cyclam than when silver(I) reacts with cyclam in a two to one mole ratio. Therefore, it is concluded that the yield of Ag and $[Ag(cyclam)]^{2+}$ in aqueous solution depends on the relative concentration of Ag^{1+}. Silver(I) is likely to function as the oxidizing agent in these reactions.

In order to eliminate the possibility that dioxygen from the air or the counter-anions, nitrate or perchlorate, could function as the oxidizing agent for $[Ag(cyclam)]^{1+}$, the reactions were carried out under argon and using $AgBF_4$ instead of $AgNO_3$ or $AgClO_4$. Treating $AgBF_4$ with cyclam under argon in a two to one mole ratio, resulted in a silver mirror and a filtrate with an extinction coefficient of 5835 M^{-1} cm^{-1} at 350 nm. Therefore we conclude that $NO_3{}^{1-}$, $ClO_4{}^{1-}$ and O_2 are not active participants in these reactions.

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