the cis stereochemistry, accelerates excited-state dissociation of bromide ligands but not of the smaller chloride ligands.

Acknowledgment. This research was supported by grants from the Danish Natural Science Research Council (to L.H.S.), the National Science Foundation (to D.M.), and the Mellon Foundation (to D.A.S.). The rhodium used in these studies was provided on loan from Johnson Matthey Chemicals Limited. The authors thank Bodil Øby and Tina Pedersen for technical assistance. Preliminary low-temperature emission spectra were measured at the Department of Chemistry and Quantum Institute, University of California, Santa Barbara. We express our gratitude to Professor P. C. Ford for that opportunity and for many instructive discussions.

Registry No. *trans*-$[Rh(tn)_2Cl_2]^+$, 52795-66-1; *trans*-$[Rh(tn)_2Cl_2]Cl$, 92186-50-0; *cis*-$[Rh(tn)_2Cl_2]^+$, 65437-15-2; *trans*-$[Rh(tn)_2(H_2O)Cl]^{2+}$, 92282-21-8; *trans*-$[Rh(tn)_2(H_2O)Cl]S_2O_6$, 92282-23-0; *cis*-$[Rh(tn)_2(H_2O)Cl]^{2+}$, 92186-40-8; *cis*-$[Rh(tn)_2(H_2O)Cl]S_2O_6$, 92186-42-0; *trans*-$[Rh(tn)_2(OH)Cl]^+$, 92186-44-2; *cis*-$[Rh(tn)_2(OH)Cl]^+$, 92282-25-2; *trans*-$[Rh(tn)_2Br_2]^+$, 65394-34-5; *trans*-$[Rh(tn)_2Br_2]Br$, 92186-51-1; *cis*-$[Rh(tn)_2Br_2]^+$, 65437-17-4; *trans*-$[Rh(tn)_2(H_2O)Br]^{2+}$, 92282-22-9; *trans*-$[Rh(tn)_2(H_2O)Br]S_2O_6$, 92282-24-1; *cis*-$[Rh(tn)_2(H_2O)Br]^{2+}$, 92186-41-9; *cis*-$[Rh(tn)_2(H_2O)Br]S_2O_6$, 92186-43-1; *trans*-$[Rh(tn)_2(OH)Br]^+$, 92186-45-3; *cis*-$[Rh(tn)_2(OH)Br]^+$, 92282-26-3; *trans*-$[Rh(tn)_2Cl(OSO_2CF_3)]OSO_2CF_3$, 92186-47-5; *trans*-$[Rh(tn)_2Br(OSO_2CF_3)]OSO_2CF_3$, 92186-49-7.

Contribution from the Department of Physical and Inorganic Chemistry,
University of Western Australia, Nedlands, Western Australia 6009, Australia

Electrochemistry and Photochemistry of Silver(II) Complexes of Macrocyclic Amines

I. J. CLARK and J. MacB. HARROWFIELD*

Received November 10, 1983

Silver(II) complexes of macrocyclic polyamines undergo both thermal and photochemical reduction reactions in a variety of solvents. Cyclic voltammetric and rotating disk electrode studies in acetonitrile have been used to assess the thermodynamics of reduction of silver(I) species and hence the possible use of silver(II) macrocyclic amine complexes in a silver purification process. Preliminary photochemical experiments have shown that photoreduction occurs without ligand decomposition but that quite subtle changes in ligand structure have a marked influence on the photosensitivity of the silver(II) complexes.

The stabilization of metals in high oxidation states by strongly basic ligands is a familiar phenomenon and is exemplified in the readily observed chemistry of silver(II) and silver(III) when coordinated to N-donor ligands.[1-4] However, in the particular case of saturated, macrocyclic tetraamine ligands it appears that this stabilization is only such as to render silver(I) and silver(II) of comparable stability, so that the position of the disproportionation equilibrium

$$2Ag(I) \rightleftharpoons Ag(0) + Ag(II)$$

is significantly solvent dependent.[4,5] This observation suggested to us that macrocyclic amines might well be of practical use in silver recovery and purification through a process closely analogous to one that has been thoroughly investigated for copper.[6] Thus, the equilibrium lies to the right in water but to the left in ethanenitrile (acetonitrile), so that it would appear feasible to dissolve crude silver in a solution of silver(II) in acetonitrile containing a small amount of water and then to remove acetonitrile by distillation until disproportionation occurs.

$$Ag(crude) + Ag^{II}L^{2+} \xrightarrow{CH_3CN/H_2O} 2Ag^I(CH_3CN)_2^+ + L \xrightarrow{H_2O} Ag(pure) + Ag^{II}L^{2+}$$

True utility for such a process would require considerable thermal stability of the complexes with respect to ligand dissociation and possible ligand oxidation[4,7-10] by silver(II). We have chosen to investigate the properties of silver(I) and silver(II) complexes of macrocyclic tetraamines and one macrobicyclic hexaamine through conventional electrochemical methods, including among the ligands species that were expected to differ considerably in their redox stability. As preliminary observations established marked photosensitivity for the various silver(II) compounds, discussion of basic aspects of their photochemistry is included in this report.

Experimental Section

1. Instrumentation. ^1H NMR (60 MHz) and ^{13}C NMR (21.115 MHz) spectra were run on Hitachi R-24B and Bruker WP80 instruments, respectively. All shifts are quoted relative to internal or external tetramethylsilane, 4,4-dimethyl-4-silapentanesulfonate (^1H) and dioxane (^{13}C) being used as internal references in aqueous media. Infrared and UV/visible spectra were recorded on Perkin-Elmer 283 and HP 8450A instruments, while fluorescence excitation and emission spectra were recorded on a Perkin-Elmer 650-40 spectrofluorimeter. EI mass spectra were obtained on an HP 5986 instrument at 70 eV.

ESR spectra were recorded on a Varian 4500-10A spectrometer equipped with an X-band microwave source, a 9-in. magnet, and 100-KHz field modulation. Aqueous solutions of Fremy's salt ($g = 2.0055$) were used as calibrant. The system for electrochemical measurements was constructed from a PAR Model 175 Universal Programmer and Model 173 potentiostat, with a platinum rotating disk electrode, active surface area $(6.162 \pm 0.001) \times 10^{-6}$ m^2, set in Teflon support. Saturated NaCl/calomel (aqueous media) and $Ag/AgNO_3$, 10^{-2} dm^{-3} (dry acetonitrile), were used as reference electrodes.

An IL 153 atomic absorption spectrophotometer was used for Ag analyses. C,H,N, analyses were performed by the Canadian Microanalytical Service, Vancouver, BC.

2. Solvent Purification and Basic Chemicals. All aqueous solutions were prepared from deionized, distilled water and, when necessary,

---

(1) Po. H. N. *Coord. Chem. Rev.* **1976**, *20*, 171.
(2) "Gmelin Handbuch der Anorganischen Chemie", 8th ed; Springer Verlag: Weinheim, 1976; Silver Vol. B-7, pp 301–316.
(3) Mertes, K. B. *Inorg. Chem.* **1978**, *17*, 49 and references therein.
(4) Barefield, E. K.; Mocella, M. T. *Inorg. Chem.* **1973**, *12*, 2829.
(5) Kestner, M. O.; Alfred, A. L. *J. Am. Chem. Soc.* **1972**, *94*, 7189.
(6) Parker, A. J. *Search* **1973**, *4*, 426.
(7) Curtis, N. F. *Coord. Chem. Rev.* **1968**, *3*, 3.
(8) Busch, D. H.; Goedken, V. L. *J. Am. Chem. Soc.* **1972**, *94*, 7355.
(9) Busch, D. H.; Hipp, C. J.; Lindoy, L. F. *Inorg. Chem.* **1972**, *11*, 1988.
(10) Keene, F. R.; Ridd, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 5733 and references therein.

0020-1669/84/1323-3740$01.50/0

passed through a Millipore Corp. Milli-Q purifier and deoxygenated by the passage of high-purity nitrogen or argon.

Commercial high-purity acetonitrile, acetone, dimethyl sulfoxide, dimethylformamide, and methanol were purified immediately prior to use by literature methods.[11] Dichloromethane and petroleum ether were distilled at atmospheric pressure to remove involatile contaminants.

Sodium and silver perchlorates (Fluka) were used as received. Anhydrous trifluoromethanesulfonic acid (3M) was distilled under reduced pressure. Cyclam (1,4,8,11-tetraazacyclotetradecane),[12] tetra-*N*-methylcyclam (TMC),[13] *meso*- and *rac*-hexa-*C*-methylcyclam[14] (tet a and tet b, respectively), and tetraethylammonium perchlorate[15] were prepared as in the literature.

3. Ligand Preparations. ***meso*(*C*)-1,4,8,11-Tetraaza-1,4,5,5,7,8,11,12,12,14-decamethylcyclotetradecane (tetra-*N*-methyltet a, TMT A).** tet a (5.68 g, 0.02 mol) was dissolved in dry acetone (150 mL) and the resultant mixture heated to reflux. Anhydrous potassium carbonate (25 g) was added, and then a solution of dimethyl sulfate (8.0 mL, 0.084 mol) in acetone was added dropwise while under reflux over a period of 30 min. The mixture was heated under reflux for a further 3 h and then cooled and the solvent removed under reduced pressure (rotary evaporation). The residue was dissolved in water (200 mL), and 15% NaOH solution was added until the solution pH was greater than 12; it was then extracted with CH_2Cl_2 (5 × 100 mL), dried over magnesium sulfate, filtered, and evaporated to a yellow, viscous oil. This was stirred in boiling petroleum ether (300 mL) for 10 min to extract the product, leaving behind any quaternary ammonium salt, filtered, and taken to dryness to provide crude amine as a white, viscous oil. This was redissolved in hot acetonitrile (150 mL); filtered, and allowed to cool, affording the pure product as large, colorless crystals. A further crop of crystals could be obtained by allowing the solvent to evaporate to approximately 50 mL: yield 2.56 g (38%); mp 62–63 °C. Anal. Calcd for $C_{20}H_{44}N_4$: C, 70.5; H, 13.0; N, 16.5. Found: C, 70.3; H, 13.2; N, 16.5. ^1H NMR ($CDCl_3$) δ 0.88–1.02 (18 H, m, CH_3), 1.20–2.00 (4 H, br m, CH_2), 2.15 (12 H, s, NCH_3), 2.46 (8 H, br s, NCH_2), 2.70–3.06 (2 H, br m, NCH); ^{13}C NMR (broad-band ^1H decoupled spectrum in $CDCl_3$, peaks identified by off-resonance ^1H decoupling) δ 21.52, 24.31, 28.98 (CH_3), 42.36, 48.28, 52.10 (CH_2), 51.30 (CH), 53.18 (C); mass spectrum (parent peak) *m/e* 340.4; IR (CCl_4) no NH stretch.

***rac*(*C*)-1,4,8,11-Tetraaza-1,4,5,5,7,8,11,12,12,14-decamethylcyclotetradecane (tetra-*N*-methyltet b, TMT B).** Substituting tet b for tet a, the same procedure as above was followed. Recrystallization from acetonitrile again provided large, colorless crystals: yield 3.69 g (54%); mp 66–67 °C. Anal. Found: C, 70.3; H, 13.1; N, 16.5. ^1H NMR ($CDCl_3$) δ 0.82–0.96 (18 H, m, CH_3), 1.17–2.00 (4 H, br m, CH_2), 2.13 (12 H, s, NCH_3), 2.25–2.90 (8 H, br m, NCH_2), 3.15–3.35 (2 H, br m, NCH); ^{13}C NMR ($CDCl_3$) δ 21.35, 28.18, and 29.44 (CH_3), 41.34, 44.47, and 48.28 (CH_2), 51.53 (CH), 52.78 (C); mass spectrum (parent peak) *m/e* 340.4; IR (CCl_4) no NH stretch.

Synthesis and full structural characterization of the encapsulating ligand, 1,8-diamino-3,6,9,13,16,19-hexaazabicyclo[6.6.6]eicosane (diAMsar), will be described elsewhere.[16]

4. Complex Ion Preparations. $[Ag(cyclam)](ClO_4)_2$, $[Ag(TMC)](ClO_4)_2$, and $[Ag(tet\ a)](ClO_4)_2$ were prepared as described by Barefield and Mocella,[4] and the following preparations are based on their methods.

$[Ag(tet\ b)](ClO_4)_2$. tet b (1.42 g, 0.005 mol) was added to a solution of silver perchlorate hydrate (2.25 g, 0.01 mol) in water (65 mL). The solution was stirred for 20 min and filtered. The filtrate was acidified with concentrated perchloric acid (0.5 mL) and cooled to 5 °C. The resulting yellow-orange crystals were collected, washed with ethanol/water (1/1 v/v) and then recrystallized from water acidified with concentrated perchloric acid to pH 2, affording the pure product as a mixture of yellow and orange crystals, yield 1.57 g (53%, recrystallized). Anal. Calcd for $AgC_{16}H_{36}N_4Cl_2O_8$: C, 32.5; H, 6.1; N, 9.5. Found: C, 31.3; H, 6.1; N, 9.0.

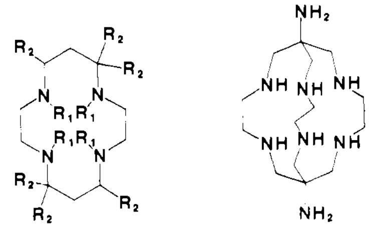

Figure 1. Key to structure on left: $R_1 = R_2 = H$, cyclam; $R_1 = CH_3$ and $R_2 = H$, TMC; $R_1 = H$ and $R_2 = CH_3$, tet a and tet b; $R_1 = R_2 = CH_3$, TMT A and TMT B. Structure on right is diAMsar (diaminosarcophagine).

$[Ag(TMT\ A)](ClO_4)_2$. TMT A (1.70 g, 0.005 mol) was added to a solution of silver perchlorate hydrate (2.25 g, 0.01 mol) in water (150 mL). The solution was stirred for 1 h then filtered. Sodium perchlorate (7 g, 0.05 mol) was added to the filtrate and the solution cooled to 5 °C. The resulting dark red needles were collected, washed with ethanol/water (1/1 v/v), and then recrystallized from water, affording the pure product, yield 1.88 g (58%, recrystallized). Anal. Calcd for $AgC_{20}H_{44}N_4Cl_2O_8$: C, 36.1; H, 7.0; N, 8.4; Ag, 16.2. Found: C, 36.9; H, 6.9; N, 8.7; Ag, 16.3.

$[Ag(TMT\ B)](ClO_4)_2$. Substituting TMT B for TMT A, the above procedure was repeated, yielding dark red crystals of the required complex, yield 1.68 g (52%, recrystallized). Anal. Found: C, 36.2; H, 6.9; N, 8.3.

$[Ag(H_2diAMsar)](ClO_4)_4$. diAMsar (0.31 g, 0.001 mol) was dissolved in water (15 mL). Concentrated perchloric acid (3 drops) was added followed by silver perchlorate hydrate (0.45 g, 0.002 mol), forming a white slurry immediately. The solution was heated gently and stirred for 10 min, during which time the slurry became brown and the solution turned orange. Concentrated perchloric acid (1 mL) was added, and the solution was stirred for a further 5 min to obtain a deep red solution, which was filtered, and a further 5 mL of concentrated perchloric acid added to facilitate crystallization. The solution was cooled to 5 °C for 2 h, and then the deep red plates were collected, washed with ethanol/water (1/1 v/v), and recrystallized in dilute perchloric acid (2 mol dm^{-3}) to afford the pure product, yield 0.23 g (28%, recrystallized). Anal. Calcd for $AgC_{14}H_{36}N_8Cl_4O_{16}$: C, 20.5; H, 4.4; N, 13.6; Ag, 13.1. Found: C, 20.7; H, 4.6; N, 13.7, Ag, 12.7.

$[Ag(H_2diAMsar)](NO_3)_4$. diAMsar (0.16 g, 0.0005 mol) was added to a solution of silver nitrate (0.18 g, 0.001 mol) in water (2 mL). The white paste formed was heated for 30 s on the steam bath, causing transformation to a deep orange solution containing a black precipitate. The precipitate was filtered off and washed with hot water (3 × 1 mL portions) to extract some orange solid. Concentrated nitric acid (1 mL) was added to the combined filtrate and washings, and the solution stood for 2 h at room temperature. The crystalline precipitate formed was collected, washed with ethanol/water (1/1 v/v), and then recrystallized from dilute nitric acid to give deep orange tablets, yield 0.10 g (30%, recrystallized).

All the silver(II) macrocyclic complexes showed a single, broad ESR peak with $g = 2.055 \pm 0.004$. The silver(II) macrobicyclic complex showed a single, very broad ESR peak with $g = 2.073 \pm 0.002$.

5. Electrochemical Measurements. Both cyclic voltammetric (CV) and rotating disk electron (RDE) measurements were made on one system consisting of a Metrohm polarography cell connected via a Luggin capillary to the reference electrode. The cell was thermostated at 25.0 ± 0.1 °C, and all measurements were made under an argon atmosphere with the cell wrapped in aluminum foil to shield out light. Sodium perchlorate was used as the supporting electrolyte in aqueous media and tetraethylammonium perchlorate (TEAP) in acetonitrile. The solvent media and each free ligand were all checked for the existence of electroactive species. For RDE work, the electrode angular velocity could be varied from 1 to 500 rad s^{-1} within ±0.1 rad s^{-1}. Initial scans were conducted between various potential limits, depending on the solution under study, at slow sweep rates (5–20 mV s^{-1}) at an angular velocity of 94 rad s^{-1}. Prior to RDE or CV measurements, the platinum electrode was polished and then cleaned electrochemically in 1 mol dm^{-3} H_2SO_4 by cycling between the onset of proton reduction and platinum oxidation until a constant response was obtained.

6. Photochemistry. The effect of prolonged exposure to natural sunlight was simply investigated by storing samples of the complex

---

(11) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals", 2nd ed.; Pergamon Press: New York, 1980.

(12) Barefield, E. K.; Wagner, F.; Herlinger, A. W.; Dahl, A. R. *Inorg. Synth.* **1976**, *16*, 220.

(13) Barefield, E. K.; Wagner, F. *Inorg. Chem.* **1973**, *12*, 2435.

(14) Busch, D. H.; Tait, A. M. *Inorg. Synth.* **1978**, *18*, Parts 1 & 2.

(15) Lo, S. T. D.; Swaddle, T. W. *Inorg. Chem.* **1976**, *15*, 1881.

(16) Engelhardt, L. M.; Harrowfield, J. M.; Sargeson, A. M.; White, A. H., to be submitted for publication.

Table I. Electronic Spectra of Silver(II) Complexes in Water

complexes	wavelength/ nm	$10^{-3}\epsilon$/mol^{-1} dm^3 cm^{-1}
$[Ag(cyclam)](ClO_4)_2$	278 ± 1	2.7 ± 0.1
	340 ± 1	4.7 ± 0.1
$[Ag(TMC)](ClO_4)_2$	290 ± 1	2.4 ± 0.1
	400 ± 2	8.8 ± 0.2
$[Ag(tet\ a)](ClO_4)_2$	272 ± 1	3.0 ± 0.1
	345 ± 1	11.5 ± 0.2
$[Ag(tet\ b)](ClO_4)_2$	283 ± 1	2.7 ± 0.1
	357 ± 1	7.5 ± 0.2
$[Ag(TMT\ A)](ClO_4)_2$	278 ± 1	1.0 ± 0.1
	400 ± 2	10.9 ± 0.2
$[Ag(TMT\ B)](ClO_4)_2$	282 ± 1	1.3 ± 0.1
	425 ± 2	9.6 ± 0.2
$[Ag(H_2diAMsar)](ClO_4)_4$	307 ± 1	5.86 ± 0.05
	408 ± 2	3.41 ± 0.03

ions in acetonitrile solution in stoppered flasks under nitrogen or air. For short-term irradiation and in ESR experiments, a 1000-W mercury vapor lamp was employed.

Results and Discussion

1. Ligand and Complex Ion Characterization. Structures of the ligands used in this study are represented in Figure 1.

With the exception of the tetra-*N*-methyl derivatives of tet a and tet b and diaminosarcophagine, these are well-known and well-characterized species.[12-14,17,18] Full characterization of diAMsar and several of its dipositive metal ion complexes will be reported elsewhere.[16,19] Tetra-*N*-methyl tet a and tet b have, in fact, also been synthesized by others,[20] and their preparation is unremarkable, though tetramethylation of tet a and tet b could, in principle, give rise to several structural isomers and it should be noted that the materials presently obtained behaved as uncharged species in basic solution, demonstrating the absence of quaternary ammonium centers. Attempts to avoid even the possibility of quaternization, by use of the Eschweiler–Clarke reaction successfully employed in the synthesis of tetra-*N*-methylcyclam,[13] were thwarted by the production of intractable brown gums from both tet a and tet b.

Silver(II) complexes of macrocyclic tetraamines are well characterized both structurally and spectroscopically,[3-5] though the possibility of diastereoisomerism arising from different N-donor atom configurations has not been thoroughly investigated. All our efforts to detect such isomerism have, however, been unsuccessful except in the case of $Ag(tet\ b)^{2+}$, and it appears that in all other instances a single species is present. We have assumed on the basis of the gross structural similarity of $Ag(tet\ a)^{2+}$ to first transition series divalent metal complexes of tet a and tet b[21] that the isomeric form of $Ag(TMC)^{2+}$ is probably the same as that of $Ni(TMC)^{2+}$ when derived from nickel(II) and the free ligand, but in all cases some ambiguity remains with respect to structural details. In a sense, the particular isomeric form of a complex is irrelevant if its application is successful, but it is also true that reactivity differences seen between the presently described macrocyclic complexes may well be indices of different N-donor atom configurations.

2. Spectroscopy. (a) Electronic Absorption and Emission Spectra. Characteristics of the absorption spectra of the complexes in an aqueous solution are summarized in Table I. Although all the complexes can be described as yellow-orange solids, there is obviously considerable variation in the position of the maximum for the band giving rise to their color and it is noteworthy that the longest wavelengths are associated with the complexes containing tertiary N-donor ligands. Since these ligands are more readily oxidized than those with secondary N donors (see below), it is plausible to assign the absorption band as due to ligand-to-metal charge transfer. This is also consistent with the moderately high band intensities, which would appear to exclude assignment as d–d transitions, though it is possible that there is overlap of d–d and LMCT bands.

The fluorescence–excitation spectra closely matched the absorption spectra, suggesting that there is rapid relaxation from upper to lower excited states. In acetonitrile and aqueous solutions all the complexes showed a weak, broad emission centered between 495 and 500 nm, indicating a Stokes shift possibly as large as 9500 cm^{-1} in the extreme case ($Ag(cyclam)^{2+}$).

(b) ^{1}H NMR Spectra. Somewhat surprisingly, the macromonocyclic ligand complexes showed well-resolved ^{1}H NMR spectra, with resonances apparently little shifted from those of diamagnetic analogues. As the macromonocyclic complexes are presumably close to planar ions, it is possible that all protons may lie close to a nodal surface of the dipolar field, whereas this could not occur in octahedral $Ag(H_2diAMsar)^{4+}$. The lack of resolution in the $Ag(H_2diAMsar)^{4+}$ resonances may reflect the relative proximity of the protons to the silver(II) center, a supposition that has been tested by a structure determination on the nitrate salt.[19]

3. Electrochemistry. Qualitative investigations were initially made of the reactions of the silver(II) complexes with high-purity silver powder in a number of solvents. Reduction was not observed in acetone or methanol but was observed to different degrees in DMF, Me_2SO, and acetonitrile, with the order of reactivity being DMF << Me_2SO < acetonitrile. The nature of the macrocyclic ligand also significantly influenced the extent of reduction, the secondary amine species as a group being less reactive than the tertiary amine group, where the order of activity was TMT A < TMT B << TMC. Even for TMC, however, cycling through the steps

$$Ag^{II}L + Ag \rightarrow 2Ag(I) + L \rightarrow Ag^{II}L + Ag$$

proved to be of low efficiency (only approximately 50% of the original silver(II) was regenerated after a single reduction in acetonitrile/water followed by distillation to remove the acetonitrile). In an attempt to discover the reasons for this, a detailed study was made of the electrochemistry of the silver(II) complexes in pure acetonitrile solvent. Note that in pure water and water/acetonitrile mixtures the current response in CV and RDE measurements was so degraded as to make useful quantitative information almost impossible to obtain. As photodecomposition of the solid complexes had been observed in several instances, all electrochemical measurements were made with solutions shielded as completely as possible from light.

(a) Complexes of Macrocycles with Secondary N-Donor Atoms. Major differences in the electroactivity of the free ligands make it convenient to discuss the electrochemistry of the complex ions under groupings depending on whether the N-donor atoms are secondary or tertiary. Both CV and RDE scans of the free ligands cyclam, tet a, and tet b in acetonitrile containing 0.1 mol dm^{-3} tetraethylammonium perchlorate showed the absence of any electroactive species in the range −1.0 to +1.0 V (relative to 0.01 mol dm^{-3} silver nitrate in acetonitrile). The CV for cyclam is shown in Figure 2a along with that of $Ag(cyclam)^{2+}$. RDE data for the complex are shown in Figure 2b. These data typify those for the other

---

[17] Melson, G. A., Ed. "Coordination Chemistry of Macrocyclic Compounds"; Plenum Press: New York, 1979.

[18] Izatt, R. M.; Christensen, J. J., Eds. "Synthetic Multidentate Macrocyclic Compounds"; Academic Press: New York, 1978.

[19] The structure of the Ag(II) complex of diAMsar will be reported as part of an extensive structural investigation of M^{2+} (M = Mg, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Hg) complexes of this ligand: Englehardt, L. M.; Harrowfield, J. M.; Sargeson, A. M.; White, A. H., paper in preparation.

[20] Kepert, D. L., private communication.

[21] Curtis, N. F. In "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1979; pp 222–241.

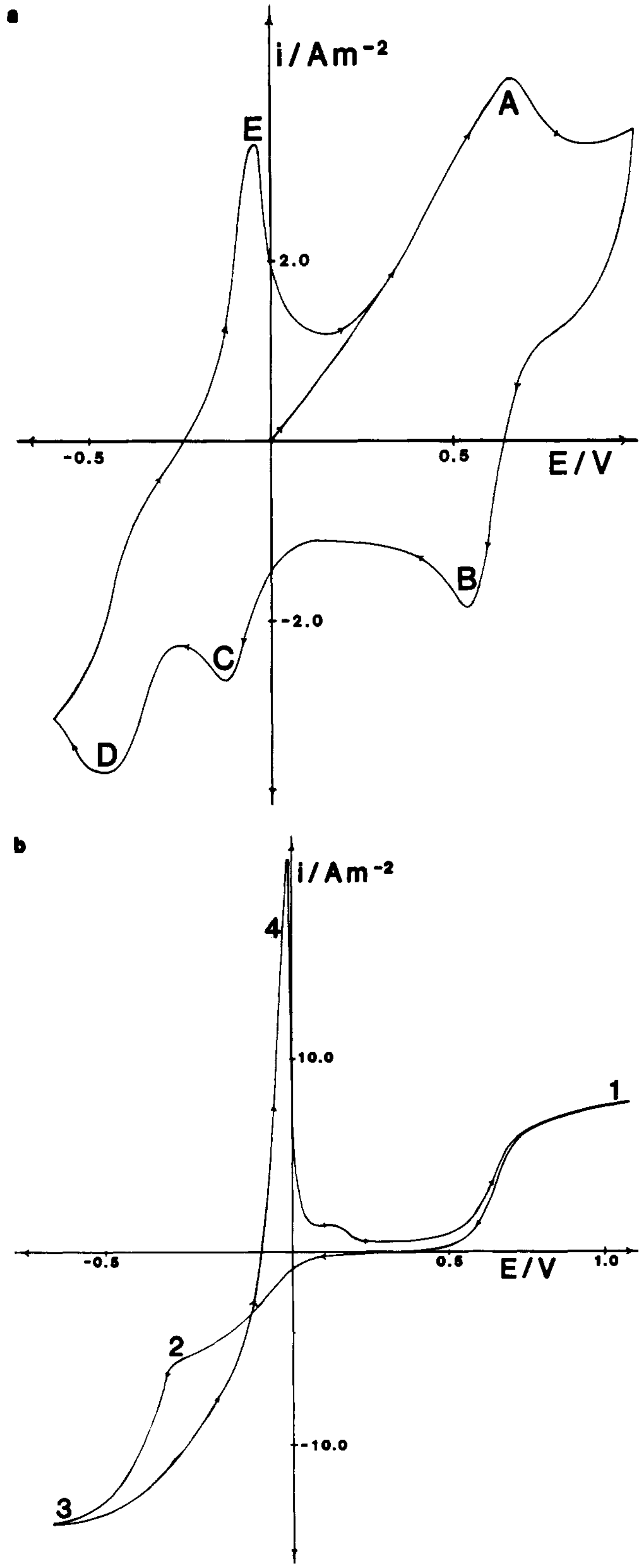

Figure 2. (a) Cyclic voltammogram of $[Ag(cyclam)](ClO_4)_2$ (v = 200 mV s^{-1}, on Pt in 0.1 mol dm^{-3} TEAP). (b) RDE scan of $[Ag(cyclam)](ClO_4)_2$ (ω = 94 rad s^{-1}, v = 200 mV s^{-1}, on Pt in 0.1 mol dm^{-3} TEAP).

secondary N-donor atom complexes, though some unique features for each are discussed below.

Five peaks, A–E, are apparent in the cyclic voltammogram of $Ag(cyclam)^{2+}$. Study of silver perchlorate in acetonitrile showed peak E to be associated with the process $Ag \rightarrow Ag(CH_3CN)_2^+$, and peaks A and B have previously been assigned to the $Ag^{II}L \leftrightarrow Ag^{III}L$ interconversion. As the free ligand is electroinactive, peaks C and D were therefore associated with the reduction processes $Ag(cyclam)^{2+} \xrightarrow{e^-} Ag(cyclam)^+$ (peak C; –0.1 V) and $Ag(cyclam)^+ \xrightarrow{e^-} Ag$ + cyclam (peak D; –0.5 V). The RDE data can be similarly interpreted; plateau 1 corresponds to the $Ag(II) \leftrightarrow Ag(III)$ process, peak 2 to the $Ag(II) \rightarrow Ag(I)$ process, and peak 3 to the $Ag(I) \rightarrow Ag(0)$ electron transfer, while peak 4 is ascribed to dissolution of the metallic silver layer on the platinum electrode. The observation that, for negative potentials, the anodic sweep current was greater than that in the cathodic sweep was taken to be indicative of autocatalysis in silver deposition (i.e., that silver is more readily deposited on silver than on platinum).

The separation of peaks A and B is large (>100 mV) even at very low sweep rates and was increased considerably when anhydrous trifluoromethanesulfonic acid was added to the solution. This is consistent with some change in conformation involving inversion (via deprotonation) at donor nitrogen in the conversion between silver(II) and silver(III) species. Further indication of a slow chemical step preceding charge transfer was obtained from negative deviations from linearity in the plot of peak current vs. the square root of the sweep rate for high sweep rates. A large peak separation was also seen for $Ag(tet\ b)^{2+}$, but for $Ag(tet\ a)^{2+}$ it was very close to the reversible value of 59 mV, indicating that the silver(II) and silver(III) species here may have a common diastereoisomeric form. $Ag(tet\ a)^{2+}$ showed, however, rather complex reduction behavior in that peaks C and D were combined and reoxidation showed at least three solid products had been formed. The collapse of peaks C and D was also observed when solutions of $Ag(cyclam)^{2+}$ were acidified, but this is presumably merely indicative of acid assistance of ligand removal. The only unique feature of the electrochemistry of $Ag(tet\ b)^{2+}$ was the presence of slight shoulders on peaks A and B of its CV scan. This was taken as consistent with the presence of a mixture of diastereoisomers in this complex. Overall, the electrochemistry of silver complexes of secondary N-donor macrocyclic tetraamines is remarkably similar to that of silver complexes of porphyrin ligands.[2,22-24]

(b) Complexes of Macrocycles with Tertiary N-Donor Atoms. The free ligands TMC, TMT A, and TMT B all underwent irreversible oxidation in acetonitrile at potentials (0.6–0.7 V) similar to those at which silver(II) complexes of the secondary N-donor ligands underwent oxidation to silver(III) species. Hence, formation of silver(III) complexes of appreciable lifetime was not observed with tertiary N ligands. As is seen in "typical" results for $Ag(TMT\ A)^{2+}$ (Figure 3), however, the CV and RDE data for the tertiary N-donor complexes were even more complicated than that for the secondary N-donor species.

The peaks labeled A–E were assigned as follows: (i) wave A (–0.1 V) corresponds to the process $Ag(TMT\ A)^{2+} \xrightarrow{e^-} Ag(TMT\ A)^+$. (ii) Wave B (–0.34 V) corresponds to the process $Ag(CH_3CN)_2^+ \xrightarrow{e^-} Ag$. (iii) Wave C (–0.68 V) corresponds to the process $Ag(TMT\ A)^+ \xrightarrow{e^-} Ag$ + TMT A. (iv) Wave D (–0.05 V) corresponds to the process $Ag \rightarrow Ag(CH_3CN)_2^+ + e^-$. (v) Wave E (0.0 V) corresponds to the process $Ag(TMT\ A)^+ \rightarrow Ag(TMT\ A)^{2+} + e^-$.

Identification of waves B and D was, of course, readily achieved by independent measurements. Both waves C and E were diminished (and wave D enhanced) in intensity at low sweep rates, suggesting that the species involved must have been undergoing a relatively slow decomposition reaction. Since $Ag(TMT\ A)^{2+}$ is inert to substitution in acetonitrile,

---

(22) Giraudeau, A.; Louati, A.; Callot, H. J.; Gross, M. *Inorg. Chem.* **1981**, *20*, 769.

(23) Kumar, A.; Neta, P. *J. Phys. Chem.* **1981**, *85*, 2830.

(24) Rapid demetalation of an Ag(I) porphyrin has been observed by: Krishnamurthy, M. *Inorg. Chem.* **1978**, *17*, 2242.

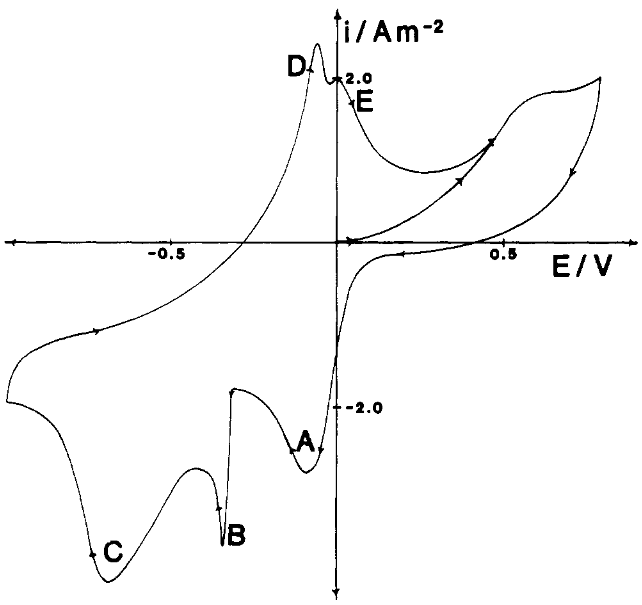

Figure 3. Cyclic voltammogram of $[Ag(TMT\ A)](ClO_4)_2$ (v = 200 mV s^{-1}, on Pt in 0.1 mol dm^{-3} TEAP).

waves C and E were therefore most simply associated with an unstable $Ag(TMT\ A)^+$ species. Solutions of silver perchlorate and ligand in dry acetonitrile (from which supposed silver(I) macrocycle complexes have been isolated[4,5]) show, as expected on this basis, two reduction waves (waves B and C).

One feature of the CV scan of $[Ag(TMC)](ClO_4)_2$ that deserves special mention is that the waves corresponding to A and E in $Ag(TMT\ A)^{2+}$ reduction are shifted some 200 mV to more anodic potentials. This is consistent with the observation that $[Ag(TMC)](ClO_4)_2$ is much more easily reduced by silver in acetonitrile than any of the other complexes.

(c) Silver Complexes with the Encapsulating Ligand diAMsar. The complex $Ag(H_2diAMsar)^{4+}$ was originally prepared in the hope that simple redox chemistry involving only complexed silver(I), silver(II), and silver(III) would be observed and thereby simplify analysis of the behavior of the macromonocyclic complexes. However, reversible oxidation of a silver(III) species was not observed below potentials sufficient for oxidation of the free ligand, and reduction of the stable silver(II) complex occurred as a 2e process to give silver and free ligand (Figure 4). This behavior is completely analogous to that of the copper(II) complex.[25] It does indicate that the steric requirements of silver(I) are remarkably stringent in that apparently neither the macrocyclic or macrobicyclic ligands can adopt a form sufficiently close to the commonly observed linear or tetrahedral donor atom geometries[26] for silver(I) to allow a silver(I) complex to have more than a fleeting existence.

4. Photochemistry. Initial attempts to record visible absorption spectra of solutions of the silver(II) complexes showed photobleaching to occur in natural light, though with considerable variation in time scale from hours ($Ag(cyclam)^{2+}$) to weeks ($Ag(H_2diAMsar)^{4+}$). Prolonged or high-intensity irradiation led in all cases to the deposition of metallic silver, but again a distinction could be drawn between secondary and tertiary N-donor ligands in that with the latter group a relatively stable intermediate-state solution containing $Ag(CH_3CN)_2^+$ and partly protonated ligand could be far more readily generated. A presumed silver(I) complex could nevertheless be isolated by photoreduction of $Ag(cyclam)^{2+}$ in

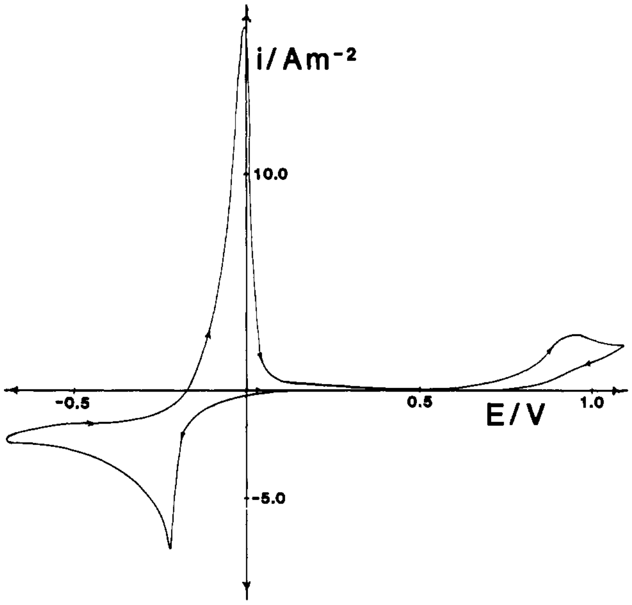

Figure 4. Cyclic voltammogram of $[Ag(H_2diAMsar)](ClO_4)_4$ (v = 200 mV s^{-1}, on Pt in 0.1 mol dm^{-3} TEAP).

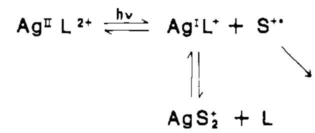

Figure 5. Key: L = macrocyclic tetramine (axial coordination possible); S = solvent.

acetonitrile. White crystals that were very sensitive to air and water precipitated from the reaction mixture during the early stages of irradiation, and these could be dissolved in water to regenerate some $Ag(cyclam)^{2+}$.

While $Ag(CH_3CN)_2^+$ and silver metal were obvious reduction products of the photoreaction, identification of the oxidation product(s) proved difficult. Recovery of macrocyclic ligands as their hydrochloride salts showed that at least 98% of reaction left the ligands unaffected, so that presumably the major oxidation products were solvent derived. ESR experiments in which solutions of the silver(II) complexes in acetonitrile were irradiated with a high-intensity UV/visible lamp showed essentially immediate loss of the broad ESR signal of silver(II), but resonances of (intermediate) ligand and/or solvent-derived radicals were not observed in its place. Preliminary spin-trapping experiments have indicated that a radical product may be isolated, but its identity remains to be established. GC–MS examination of the reaction mixture, after removal of ionic materials by ion exchange, indicated the presence of several materials at trace level, but they could not be identified with "obvious" possible products of solvent oxidation such as $NCCH_2CH_2CN$.

Given that the position of the lowest energy electronic absorption band in the silver(II) complexes is significantly solvent dependent, it is possible that the transition has a significant charge transfer from solvent component, so that a plausible rationale for all the present observations is the reaction scheme[27] shown in Figure 5.

Reversibility of the photoinduced electron transfer is suggested by the fact that the overall reaction is faster in the presence of oxygen (rather than argon or nitrogen), although

---

(25) Creaser, I. I.; Lawrance, G. A.; Sargeson, A. M., to be submitted for publication.

(26) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; pp 968–972.

(27) This is essentially a simplified version of that proposed to describe the photochemistry of Cu(II) complexes of tet a and tet b: Muralidharan, S.; Ferraudi, G. *Inorg. Chem.* **1981**, *20*, 2306. In this study, ligand photooxidation was observed to compete with that of solvent in aqueous but not in nonaqueous media.

the yield of identifiable products (AgS_2^+ and L) is unchanged.

Conclusion

The very different coordination proclivities of silver(I) and silver(II) would appear to preclude the possibility of strong coordination of one multidentate, saturated amine ligand in both oxidation states. This is a somewhat preplexing conclusion, since it is not entirely obvious that macrocyclic or macrobicyclic polyamines as studied in the present work should not be able to adopt a configuration suited to, say, linear, trigonal, or tetrahedral coordination of silver(I). It is also obscure as to why open-chain polyamines, even ammonia itself, do not give rise to readily accessible silver(II) complexes although there is, of course, much empirical evidence of marked differences between the properties of macrocyclic ligands and their open-chain analogues.[28]

The development of a silver purification procedure based on silver(II) complexes of macrocyclic amines does not require that the silver(I) species produced by reduction in acetonitrile be a strong macrocyclic complex. Hence, it might be presumed that the cyclic process for silver purification outlined previously would be feasible provided photoreduction and acid generation leading to consumption of macrocyclic amine could be avoided. In a practical sense, however, it would seem that the purpose of sophisticated (and expensive) ligand design is at least partly defeated if the ligand is not then involved in a robust and simple system. More specifically, the complex $Ag(TMC)^{2+}$ found to undergo most facile reduction by silver metal incorporates the least readily accessible ligand and is one of the most sensitive to photoreduction. It is therefore unlikely that an $Ag(TMC)^{2+}$-based process could effectively compete with any such as AgCl purification through chloro complex formation in nonaqueous solvents based on less exotic procedures.

Whatever value the silver(II) complexes discussed herein may have as thermal oxidants, their photoredox behavior warrants further examination. The apparent lack of any ligand decomposition during their photoreactions in acetonitrile obviously suggests some potential for use in photoelectrochemical devices. Our current research is directed toward development of a more detailed understanding of the nature of the reactive excited state and a quantitative description of its redox kinetics.

Acknowledgment. This work was initiated from discussions with the late Professor A. J. Parker. I. G. Smith is thanked for the preliminary development. Financial support was received from the Australian Research Grants Scheme.

Registry No. TMT A, 92216-10-9; TMT B, 92216-11-0; tet a, 10368-90-8; tet b, 10368-91-9; $[Ag(cyclam)](ClO_4)_2$, 41777-41-7; $[Ag(TMC)](ClO_4)_2$, 41777-42-8; $[Ag(tet\ a)](ClO_4)_2$, 41777-44-0; $[Ag(tet\ b)](ClO_4)_2$, 38596-53-1; $[Ag(TMT\ A)](ClO_4)_2$, 92096-40-7; $[Ag(TMT\ B)](ClO_4)_2$, 92216-13-2; $[Ag(H_2diAMsar)](ClO_4)_4$, 92096-43-0; $[Ag(H_2diAMsar)](NO_3)_4$, 92096-45-2; Ag, 7440-22-4; $AgNO_3$, 7761-88-8; dimethyl sulfate, 77-78-1; silver perchlorate, 7783-93-9.

---

(28) Lamb, J. D.; Izatt, R. M.; Christensen, J. J.; Eatough, D. J. In "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1979; Chapter 3.

Contribution from the Institut für Physikalische und Theoretische Chemie,
Universität Regensburg, D-8400 Regensburg, Federal Republic of Germany

Effect of High Pressure on the Emission Spectrum of $[Ru(bpy)_3](PF_6)_2$ Single Crystals

HARTMUT YERSIN* and ERICH GALLHUBER

Received March 28, 1984

Investigations of the emission of $[Ru(bpy)_3](PF_6)_2$ single crystals under high pressure are reported for the first time. The spectra are recorded at room temperature up to 52 kbar. The following pressure effects are observed: a very small red shift, a distinct sharpening of emission spectra, and a considerable decrease in emission intensity. Model conceptions are presented to account for the experimental results.

Introduction

During the past decade, the photophysical as well as the photochemical properties of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) have attracted widespread interest.[1-3] Most investigations of the excited states of $[Ru(bpy)_3]^{2+}$ were confined to fluid solutions,[4,5] glassy matrices,[6-8] or mixed crystals.[9-11] That is why only little is known about the spectroscopic properties of pure single crystals.[12,13] It has been demonstrated that polarized spectroscopy with emphasis on the emission spectroscopy of single crystals is an especially effective technique for the investigation of excited-state properties.[14]

The existing theoretical models for the excited states of $[Ru(bpy)_3]^{2+}$ and related compounds are controversial. The Crosby model,[15] constructed to explain the emission behavior of $[Ru(bpy)_3]^{2+}$ at low temperature, has been contradicted recently by the electronic structure models of Kober and Meyer[16] and of Ferguson and Herren.[17] But the latter models are still too coarse to be capable of explaining the data obtained from emission spectroscopy. Moreover, there is disagreement concerning the symmetry of the complexes in their lowest exited states, which may be reduced from the D_3 ground-state symmetry to C_2.[8,18,19] So further theoretical and experimental investigations have to be undertaken to come to a better un-

---

(1) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83.
(2) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.
(3) Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834.
(4) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853.
(5) Allsopp, S. R.; Cox, A.; Kemp, T. J.; Reed, W. J. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1275.
(6) Fujita, I.; Kobayashi, H. *Inorg. Chem.* **1973**, *12*, 2758.
(7) Elfring, W. H.; Crosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 2683.
(8) Carlin, C. M.; DeArmond, M. K. *Chem. Phys. Lett.* **1982**, *89*, 297.
(9) Hipps, K. W. *Inorg. Chem.* **1980**, *19*, 1390.
(10) Felix, F.; Ferguson, J.; Güdel, H. U.; Ludi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4096.
(11) Ferguson, J.; Herren, F. *Chem. Phys. Lett.* **1982**, *89*, 371.
(12) Yersin, H.; Gallhuber, E.; Vogler, A.; Kunkely, H. *J. Am. Chem. Soc.* **1983**, *105*, 4155.
(13) Gallhuber, E. Diplomarbeit, Universität Regensburg, 1983.
(14) Yersin, H.; Gliemann, G. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 539.
(15) Hipps, K. W.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7042.
(16) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3967.
(17) Ferguson, J.; Herren, F. *Chem. Phys.* **1983**, *76*, 45.
(18) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441.
(19) Braterman, P. S.; Harriman, A.; Heath, G. A.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1801.

0020-1669/84/1323-3745$01.50/0