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Preparation and electrochemical study of a silver(I) complex of a heptaaza quinquedentate macrocyclic ligand

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Abstract—The quinquedentate ligand L, prepared by template condensation of bis-6,6″-(α-methylhydrazino)-4′-phenyl-2,2′ : 6″,2′-terpyridine with glyoxal, forms a stable crystalline complex of silver(I) $[Ag(L)(H_2O)_2][PF_6]$. Oxidative cyclic voltammetry of this complex in acetonitrile shows a reversible one-electron oxidation wave at +0.75 V, *vs* a $Ag/AgBF_4$ reference electrode. Electrochemical oxidation by controlled potential electrolysis of such a solution and investigation of the oxidized product by EPR and IR spectroscopy, elemental analysis and conductivity, shows that the oxidation wave could correspond to the formation of a ligand–radical cation. © 1997 Elsevier Science Ltd

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One dominant characteristic of synthetic macrocyclic ligands is the stability which they impart to the resulting complexes, an example of which is the increased occurrence in these compounds of metal ions in unusual oxidation states. The technique of solution electrochemistry provides an excellent method for studying the redox chemistry of such systems and when combined with appropriate spectroscopic methods it is possible to assign the redox site unambiguously.

In early studies the redox chemistry of tetraazamacrocyclic complexes was carried out in which the factors influencing the generation of both oxidized and reduced metal species were investigated [1–3]. The degree of stabilization was, as expected, found to be very dependent on the structure of the macrocyclic involved. In particular, it was demonstrated that the overall redox properties of a given system are influenced by macrocyclic ring size, the charge on the ligand, the nature of ligand substituents and the extent and type of ligand unsaturation. The degree of ring strain undoubtedly influences the redox behaviour and the stronger the in-plane ligand field the more readily oxidation occurs due to the strong equatorial interactions.

Owing to the propensity of divalent silver to act as an oxidizing agent, silver(II) complexes have been rare and stable only when formed with ligands which could survive the strong oxidizing capabilities of silver(II). For the most part these ligands have been nitrogen-containing unsaturated heterocycles, such as pyridines and related compounds. Thus, in the presence of a saturated tetraaza macrocycle such as cyclam (1,4,8,11-tetraazacyclotetradecane), disproportionation of silver(I) occurs to produce a silver mirror and a stable silver(II) complex of the macrocycle [4–6]. In some cases the silver(II) complexes thus formed may then be oxidized further to silver(III) species either electrochemically or chemically using nitrosyl $(NO)^+$ salts. Open-chain complexes containing the terpyridine moiety have also been prepared. Morgan and Burstall [7] described the silver(II) complexes $Ag(terpy)X_2$ ($X = NO_3$, ClO_4, 0.5 S_2O_6, 0.5 S_2O_8) of unknown structures. These complexes were unstable in aqueous solution and gave rise to the corresponding silver(I) complexes [8]. PES spectra of these and other octahedral $[Ag(terpy)X]^{2+}$ (X = pyridine mono and dicarboxilic acids) species have been reported [9–12]. Salts of $[Ag(terpy)_2]^{2+}$ were obtained by electrochemical oxidation of silver(I) in the presence of terpyridine [13,14].

The electrochemical study of a silver(I) complex

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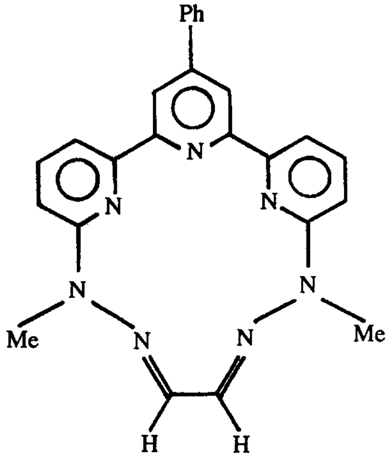

L

Scheme 1.

based on a quinquedentate macrocyclic ligand L incorporating a 2,2′:6′,2″-terpyridyl moiety is the subject of the present work.

EXPERIMENTAL

Materials

Published methods were used to prepare $H_2L(PF_6)_2$ by the template condensation of bis-6,6″-(α-methylhydrazino)-4′-phenyl-2,2′:6″,2′-terpyridine with glyoxal in the presence of Cr^{III} or $SnMe_2Cl_2$ [15–17]. Solvents used for synthetic and spectroscopic work were distilled over appropriate drying agents prior to use. All other chemicals for synthetic experiments were of analytical grade, available commercially. Unless otherwise stated the reactions were carried out under dry nitrogen.

Preparation of $[Ag(L)(H_2O)_2][PF_6]$

The free macrocycle $H_2L(PF_6)_2$ (0.04 mmol) and Ag(OAc) (0.1 mmol) in dry methanol (50 dm^3) were heated to reflux under nitrogen. The mixture was refluxed until a clear solution has been obtained, then a methanolic solution of $(NH_4)(PF_6)$ was added to the hot solution, which was allowed to cool slowly and the silver(I) complex was obtained as a yellow precipitate.

Physical measurements

The IR spectra were recorded on a Perkin–Elmer model 983 spectrophotometer and obtained by the KBr pellet method. The spectra were calibrated against the 1603 cm^{-1} band of polystyrene. Conductance measurements were made using a Wayne Kerr Universal Bridge. The conductivity cell was calibrated with aqueous KCl. Microanalyses were performed by the Cambridge University Chemistry Department Microanalytical service. Electrochemical measurements were recorded on a Model 170 electrochemistry system (Princeton Applied Research). All readings were taken using a three-electrode potentiostatic system in acetonitrile with 0.1 mol dm^{-3} on *n*-butyl ammonium tetrafluoroborate present as supporting electrolyte. The potentials are referenced against a saturated calomel electrode (SCE). Cyclic voltammetric studies were carried out using platinum wires as auxilliary and working electrodes and a Ag–$AgBF_4$ reference electrode with sample concentrations of 10^{-3}–10^{-4} mol dm^{-3}. Alternating (a.c.) voltammetry, typically 10 mV and 200 Hz, was carried out using commercially available cells. Controlled potential electrolysis experiments were carried out using a platinum gauze as the working electrode. The EPR spectrum was measured as a glass in acetonitrile at 77 K on a Varian E109 model spectrophotometer (X band) and was calibrated with diphenylpicrylhydrazyl (dpph; $g = 2.0037$).

RESULTS AND DISCUSSIONS

Although complexes of 6,6″-bis(α-methylhydrazino)-4′-phenyl-2,2′:6′,2″-terpyridine have been prepared with a wide range of transition metal and main group metal ions, the condensation with glyoxal only proceeded in a satisfactory way with nickel(II) or manganese(II) as the template. However, the isolation of the metal-free macrocyclic ligand L may be obtained as its dication from template condensations in which the transient template ions such as chromium(III) or $[SnMe_2]^{2+}$ are used [17]. The elemental analyses and some physical properties of $H_2(L)(PF_6)_2$ and its coordination complexes $[Ag(L)(H_2O)_2][PF_6]$ and $[Ag(L)(CH_3CN)][BF_4]_2$ are given in Table 1. Molar conductivities of the protonated ligand and the $[Ag(L)(CH_3CN)][BF_4]_2$ complex in acetonitrile fall in the range for 2:1 electrolytes, while the conductivity of the silver(I) complex in the same solvent falls in the range for a 1:1 electrolyte. The results show that the ligand coordinates to silver ions with molar ratio 1:1. All compounds are stable in air.

Electrochemistry

The redox behaviour of the silver(I) complex was preliminarily examined by cyclic voltammetry. Unlike first-row transition metal complexes $[M(L)(H_2O)_2][PF_6]_2$ ($M = Mn^{II}$, Ni^{II}, Co^{II}, Fe^{II} and Cu^{II}), $[Ag(L)(H_2O)_2][PF_6]$ is found to have a well-defined anodic voltammetric response [18]. Figure 1 shows a portion of the cyclic voltammetric response exhibited by the silver(I) complex in a deareated acetonitrile solution, along with the symmetric wave obtained using a.c. polarography. One oxidation peak occurs at +0.75 V with a directly associated reduction

Table 1. The elemental analyses[a] and molar conductance of the ligand H_2L^{2+} and its silver complexes

Compounds	Colour	C (%)	H (%)	N (%)	Λ_M (Ω^{-1} cm^2 M^{-1})
$H_2L(PF_6)_2$	Orange	42.5	3.6	13.4	263
		(42.2)	(3.2)	(13.8)	
$[Ag(L)(H_2O)_2]PF_6$	Yellow	42.2	3.5	13.9	158
		(42.4)	(3.5)	(13.8)	
$[Ag(L)(CH_3CN)][BF_4]_2$	Orange	43.8	3.4	15.1	273
		(43.7)	(3.2)	(15.1)	

[a] Calculated values are given in parentheses.

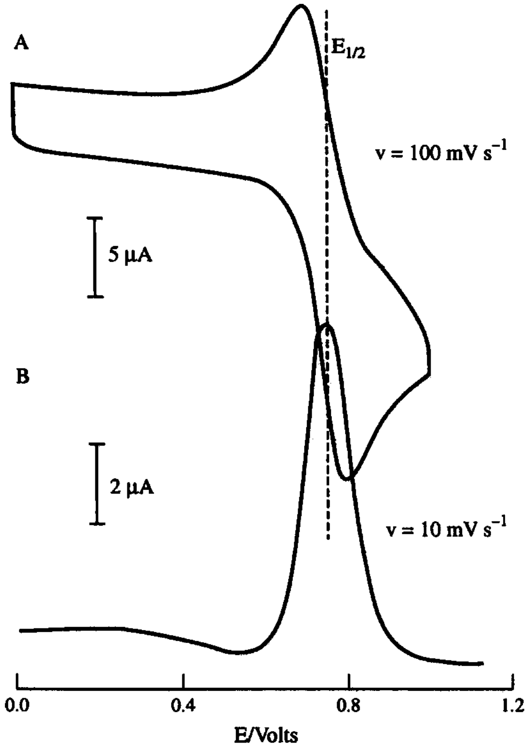

Fig. 1. (A) Cyclic voltammetric response of a CH_3CN solution containing $[Ag(L)(H_2O)_2]^+$ and $[NBu_4][NH_4]$ (0.1 mol dm^{-3}). Scan rate 100 mV s^{-1}. (B) Alternating current polarography of the above solution. Scan rate 10 mV s^{-1}, ω = 200 Hz.

peak in the reverse scan. A second irreversible oxidation was also noted at +1.34 V *vs* Ag/$AgBF_4$ reference electrode, lacking a directly associated response in the reverse scan. The less positive oxidation wave has been assigned to the Ag^{II}/Ag^{I} couple. The most positive oxidation wave can correspond to successive oxidation leading to Ag^{III} species formed by a subsequent chemical reaction at the electrode. Coulometric measurements confirm that these oxidations are one-electron processes.

The electron transfer at +0.75 V was confirmed to be reversible by a.c. polarography over the a.c. frequency range 20–1000 Hz, showing linear dependence of Ip with $\omega^{1/2}$. Similarly, the cyclic voltammetric behaviour indicates full reversibility for scan rates in the range 20 mV s^{-1}–20 V s^{-1}, showing linear dependence of Ip *vs* $v^{1/2}$. Furthermore, in the case of reversible electron transfer the potential Ep, corresponding to maximum current on a.c. polarography, coincides with $E_{1/2}$, the average of the potentials of the cathodic and anodic peaks, on cyclic voltammetry (Fig. 1).

Controlled potential electrolysis of $[Ag(L)(H_2O)_2][PF_6]$ in acetonitrile at +1.0 V leads to a change in colour of the solution from yellow to orange. The orange solution was transferred by syringe to a Schlenk tube and the silver species was isolated as the orange product $[Ag(L)(CH_3CN)][BF_4]_2$ by the addition of dry, oxygen-free diethyl ether. The hexafluorophosphate anion from the starting material was changed for tetrafluoroborate anion from the supporting electrolyte.

IR spectroscopy

IR spectra show similarities with other metal(II) complexes of L [18]. Pertinent IR data of the different compounds are given in Table 2. The spectra of the complexes show similarities to one another and reveal the absorptions for structure L. The bands assigned to the pyridine ring vibrations were shifted to lower frequencies, which is a good indication of the coordination of the heterocyclic nitrogen atom. However, major significance must be attached to the fact that the L IR spectrum is devoid of any evidence for the presence of either a ketonic carbonyl (1700 cm^{-1}) or primary amine groups (3300, 3200 cm^{-1}). This and the presence of a strong C=N stretching band in the range 1580–1610 cm^{-1} provide assurance that the required Schiff base linkages have formed. The shifting of the C=N absorption band to lower wave numbers relative to the ligand results from a decrease in the C=N double-bond character owing to the coordination. In all compounds the IR band assigned to the mono-substituted benzene falls in the range 740–780 cm^{-1}. The $[Ag(L)(H_2O)_2][PF_6]$ compound presents a P—F stretching frequency quite broad, centred around 840 cm^{-1}, and is typical of compounds having hexafluorophosphate counter-ions. The spectrum for this hydrated complex showed in addition to the

Table 2. Important IR absorptions frequencies (cm^{-1}) of the ligand H_2L^{2+} and its silver complexes

Compounds	C═N		Pyridine		Benzene monosubstituted	PF_6	BF_4
$H_2L(PF_6)_2$	1610	1544	1471	1476	740	838, 558	
$[Ag(L)(H_2O)_2][PF_6]$	1580	1540	1440	1430	765	840, 560	
$[Ag(L)(CH_3CN)][BF_4]_2$	1590	1540	1460	1440	780		1080

O—H stretching vibration at 3500–3400 cm^{-1} a broad band of moderate intensity at 605 cm^{-1}, which is usually assigned to wagging or rocking modes of coordinated water. The IR spectrum of the orange product $[Ag(L)(CH_3CN)][BF_4]_2$ showed characteristic bands for the tetrafluoroborate anion at 1080 cm^{-1} and the C≡N stretching vibration from CH_3CN at 2235 cm^{-1}. The IR spectrum of the starting material $[Ag(L)(H_2O)_2][PF_6]$ resembles in general that of the product $[Ag(L)(CH_3CN)][BF_4]_2$.

EPR spectroscopy

The paramagnetic nature of the $[Ag(L)(CH_3CN)][BF_4]_2$ complex species produced precluded detailed studies of the product by NMR spectroscopy. The starting material $[Ag(L)(H_2O)_2][PF_6]$ does not yield an EPR spectrum, however, its oxidation was followed by EPR spectroscopy, which showed the gradual gain of the signal assigned to the oxidized product; on completion of the oxidation a EPR signal could be detected. The EPR of the orange product as an acetonitrile glass at 77 K is shown in Fig. 2, where the g values are 2.13 and 2.08 for parallel and perpendicular tensors, respectively. These values coincide with other reported values for silver(II) complexes [4,5,19] but the hyperfine doublet structure characteristic of the nuclear spin and the superhyperfine couplings due to ^{14}N nuclei were not observed. On the other hand, an isotropic EPR espectrum with no hyperfine splitting and a g value very nearly equal to the free electron value (2.0023) should be expected in the case of a metal-stabilized ligand radical species. Since the EPR spectral data for the $[Ag(L)(CH_3CN)][BF_4]_2$ complex do not provide firm evidence that it is an Ag^{II} species, the oxidized product could be regarded as a ligand–radical cation.

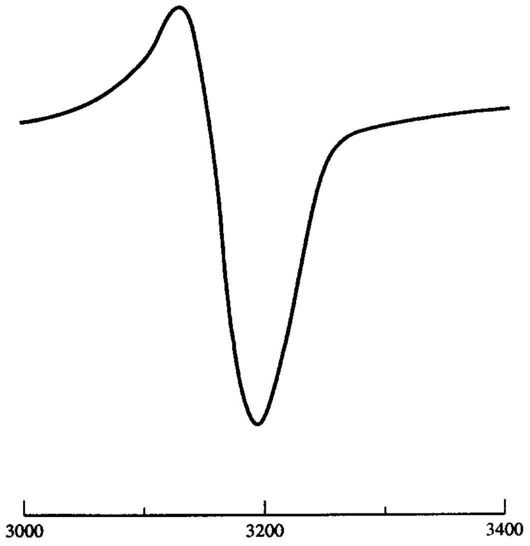

Fig. 2. EPR spectrum of electrogenerated $[Ag(L)(MeCN)]^{2+}$ in frozen acetonitrile solvent at 77 K.

In the absence of information such as the silver hyperfine coupling constant it is not possible to estimate the extent of delocalization of the unpaired electron onto the macrocyclic ligand. However, Kivelson and Neimann [20] have shown that for an ionic environment $g_\parallel$ is normally >2.3 and for a covalent environment it is <2.3. In the present case, $g_\parallel < 2.3$ is indicative of the covalent nature of the complex. The G parameter obtained by the expression $(g_\parallel - 2)/(g_\perp - 2)$ has the value 1.63, suggesting that there is not considerable exchange interaction between silver centres ($G < 4$) [21].

Finally, it should be pointed out that a comparison of the IR spectra data of the silver complexes with those from manganese(II), copper(II), cobalt(II) and nickel(II) complexes of L, the crystal structure of which proves conclusively that a macrocycle is present [17,18], provides strong support for the presence of the monomeric products with silver ions. The ligand is potentially quinquedentate since steric restraints will not permit the two nitrogens with methyl groups attached to coordinate to a metal contained in the ligand cavity. It is proposed that the silver compound has pentagonal bipyramidal structure in which the axial sites are occupied by solvent and/or water molecules, but these structures must be regarded as speculative in the absence of crystallographic evidence.

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