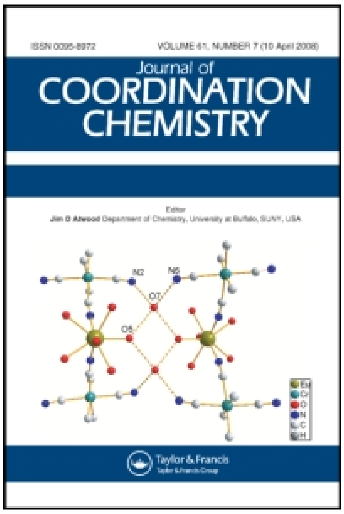

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CYCLIC VOLTAMMETRIC STUDIES OF AXIALLY SUBSTITUTED NICKEL(II) COMPLEXES CONTAINING A MACROCYCLIC SCHIFF-BASE LIGAND

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The 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 nickel(II)$[Ni(L)(H_2O)_2][PF_6]_2$ which is used as a starting material for cyclic voltammetric studies of a series of seven-coordinate nickel(II) complexes $[Ni(L)X_2]^{2+}$ (X = 4-substituted pyridines, imidazole, 1-methylimidazole, 2-methylimidazole, 1,2-dimethylimidazole, pyrazine, thiazole, triphenylphosphite, dimethylsulfoxide and dabco). Cyclic voltammetry of the complexes in acetonitrile shows a reversible one-electron reduction wave in the range of −1.08 to −1.46 V vs a Ag/$AgBF_4$ reference electrode.

Keywords: Schiff-base; nickel; cyclic voltammetry; macrocycle

INTRODUCTION

Macrocycles providing an essentially planar environment for any central metal ion are prone to axial ligation of the coordinatively unsaturated metal. This can change the redox chemistry of the macrocyclic complex either by simply changing the redox potential or by altering the site of reduction. Solution electrochemistry provides an excellent method for studying the redox chemistry of such systems.

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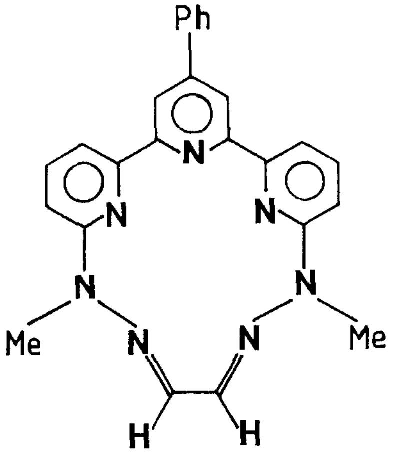

FIGURE 1 Structure of the ligand L.

Structural[1] and electrochemical[2] studies on transition metal complexes of pentadentate macrocycles incorporating 2,2′-bypyridyl or 1,10-phenanthroline units have been made. The stabilization of low valent metal species in these systems has been correlated with the π-acceptor properties and stereochemical requirements of the diimine macrocyclic ligand. It has been demonstrated that similar π-acceptor properties are shown by higher diimine chelates such as terpyridyl.[3]

The reduction of transition metal complexes of potential π-acceptor macrocyclic ligands such as L (Figure 1) is of interest because of the possibility of forming either metal-reduced species or metal-stabilized ligand radical species in which the electron resides mainly on the macrocyclic ligand. As previously shown,[4–13] the redox properties of macrocyclic complexes may be highly dependent on axial ligation. We have carried out studies on the redox chemistry of nickel(II) complexes of L in the presence of a series of axial ligands to determine whether variations in redox properties might be observed. The choice of axial substituent was made considering that charged axial ligands such as thiocyanate or halides normally resulted in very insoluble species. For this reason, neutral ligands such as N-donor heterocyclic species were employed in this work.

EXPERIMENTAL

Materials

Published methods were used to prepare $H_2L[PF_6]_2$ by template condensation of bis-6,6″-(α-methylhydrazino)-4′-phenyl-2,2′:6″,2′-terpyridine with glyoxal about Cr(III) or $SnMe_2Cl_2$.[14–16] 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 $[Ni(L)(H_2O)_2][PF_6]_2$

The free macrocycle $H_2L[PF_6]_2$ (0.04 mmol) and Ni(II) acetate tetrahydrate (0.1 mmol) in 50 mL of dry methanol were heated to reflux under nitrogen. The mixture was refluxed until a clear solution was obtained, then a methanolic solution of $[NH_4][PF_6]$ was added to the hot solution which was allowed to cool slowly and the Ni(II) complex was obtained as a yellow precipitate.

Physical Measurements

The infrared (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 M of tetrabutylammonium 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 auxiliary and working electrodes and a $Ag/AgBF_4$ reference electrode with sample concentrations of 10^{-3}–10^{-4} M. The EPR spectrum was measured at 77 K on a Varian E109 Model Spectrophotometer (X band) and was calibrated with diphenylpicrylhydrazyl (dpph; $g = 2.0037$).

RESULTS AND DISCUSSION

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 proceeded in a satisfactory way with manganese(II) as the template. However, the isolation of the metal-free macrocyclic ligand L as its dication may be done from template condensations in which the transient template ions chromium(III) or $[SnMe_2]^{2+}$ are used.[16] The elemental analyses and some physical properties of $H_2(L)[PF_6]_2$ and its coordination complex $[Ni(L)(H_2O)_2][PF_6]_2$ are given in Table I. Molar conductivity of 10^{-3} M solutions in $MeNO_2$, MeCN or DMSO at 22°C fall in the range expected for 1 : 2 electrolytes.[17] These conclusions are supported by the IR spectra where two bands at 840 and 557 cm^{-1} characteristic of the hexafluorophosphate anion not coordinated to the metal are present.

Pertinent IR data for the different compounds are given in Table II. The spectra of the complexes show similarities to one another and reveal the absorptions for L. The bands assigned to the pyridine ring vibrations are 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 IR spectrum of L is devoid of 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 wavenumber relative to the ligand results from a decrease in the C=N double bond character owing to the coordination. In all compounds the

TABLE I The elemental analyses[a] and molar conductance of the ligand H_2L^{2+} and the nickel complexes

Compounds	*C* (%)	*H* (%)	*N* (%)	Λ_M[b]		
				$MeNO_2$	*MeCN*	*DMSO*
$H_2L[PF_6]_2$	42.5 (42.2)	3.6 (3.2)	13.4 (13.8)	168	263	57
$[Ni(L)(H_2O)_2][PF_6]_2$	36.5 (36.7)	3.3 (3.6)	11.9 (12.1)	140	264	49
$[Ni(L)(NC\text{-}py)_2][PF_6]_2 \cdot 3H_2O$	43.3 (43.1)	3.1 (3.4)	14.9 (14.9)	138	252	52
$[Ni(L)(Me_2N\text{-}py)_2][PF_6]_2 \cdot 4H_2O$	43.2 (43.2)	4.3 (4.5)	14.2 (14.2)	153	263	45
$[Ni(L)(NH_2\text{-}py)_2][PF_6]_2 \cdot 2H_2O$	42.6 (42.3)	3.7 (3.6)	15.8 (15.4)	144	271	47
$[Ni(L)(Me\text{-}Im)_2][PF_6]_2 \cdot 4H_2O$	39.4 (39.4)	4.1 (4.1)	15.1 (15.3)	157	258	52
$[Ni(L)(py)_2][PF_6]_2 \cdot 2H_2O$	41.9 (41.8)	3.5 (3.5)	13.0 (13.0)	136	265	53

[a]Calculated values are given in parenthesis.
[b]Molar conductivity units are $ohm^{-1}\,cm^2\,mol^{-1}$.

TABLE II Important IR absorptions frequencies (cm^{-1}) of the ligand H_2L^{2+} and its nickel complex

Compounds	*C=N*	*Pyridine*			*Monosubstituted benzene*	*PF_6*	
$H_2L[PF_6]_2$	1610	1544	1471	1476	740	838	558
$[Ni(L)(H_2O)_2][PF_6]_2$	1604	1575	1490	1449	740	840	558

IR band assigned to the monosubstituted benzene falls in the range 740–730 cm^{-1}. The spectrum for the aquo complex showed in addition to the 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.[18] The IR spectra of the compounds were consistent with the absence of the bands associated with amine and carbonyl groups. The solid complex showed IR spectral bands characteristic of coordinated water and is, therefore, formulated as $[Ni(L)(H_2O)_2][PF_6]_2$ in the solid state.

The magnetic moment measurement was made in the solid state at room temperature. The nickel(II) complex $[Ni(L)(H_2O)_2][PF_6]_2$ has a magnetic moment value of 3.06 BM a typical value for high-spin d^8 systems with two unpaired electrons. The EPR spectrum of $[Ni(L)(H_2O)_2][PF_6]_2$ powder shown in Figure 2, has a small band at low field ($g_{\parallel} = 4.33$) and a broad band at higher field ($g_{\perp} = 2.00$). No observable hyperfine splitting attributable to ^{61}Ni (1.25% natural abundance, nuclear spin $I = 3/2$) was observed. Attempts to record EPR signals in acetonitrile glass were unsuccessful. Most of the EPR studies of nickel(II) complexes have been carried out in host lattices and since the spins of ^{58}Ni and ^{60}Ni are zero and ^{61}Ni is present in small percentage, metal hyperfine splitting has only rarely been observed.

The electronic spectra were recorded for the $[Ni(L)(H_2O)_2]^{2+}$ complexes in acetonitrile, dimethylsulfoxide and nitromethane solutions.

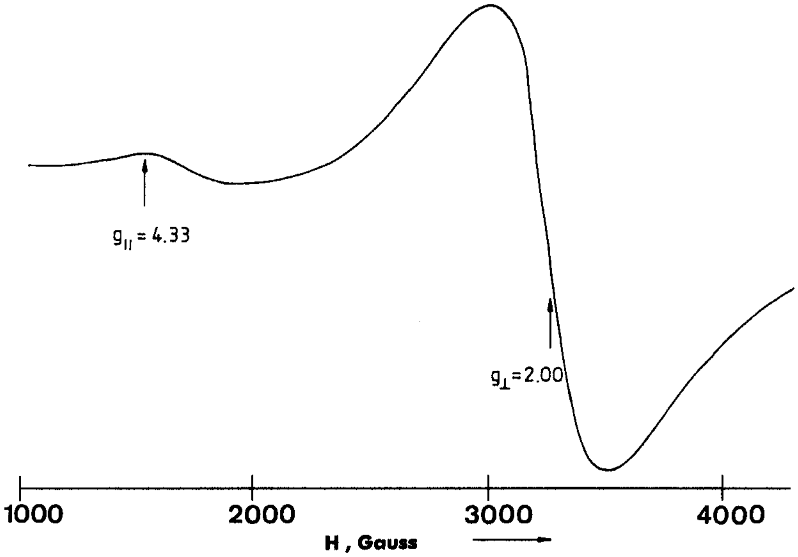

FIGURE 2 EPR spectrum of $[Ni(L)(H_2O)_2][PF_6]_2$ powder at 77 K.

Multicomponent bands in acetonitrile and dimethylsulfoxide were observed between 26 000 and 50 000 cm^{-1}, and two of them at 28 000 and 38 000 cm^{-1} are very intense UV absorption bands which also occur in the spectra of the analogous macrocycle metal complexes[19] although at slightly different energies. These have been assigned to metal ligand charge transfer transitions which normally have very high extinction coefficients. In nitromethane the complex has a strong band at 25 400 cm^{-1} which has also been assigned as a charge transfer transition and three bands below 24 000 cm^{-1} (23 150, 21 830 and 20 330 cm^{-1}) which parallel the results found for a nickel(II) complex of pentadentate N_3O_2 open ligand.[20] These bands could be assigned within the complete spin-triplet basis, ($^3P + {}^3F$) of the d^8 configuration for nickel(II).

A particularly noteworthy feature of the seven-coordinate nickel(II) complexes is the appearance of a band in the near IR region (below 10 000 cm^{-1}). The spectra in acetonitrile and dimethylsulfoxide show these low energy bands at 5848 and 6944 cm^{-1}, respectively, and they correspond with the moderate intensity band at 6500 cm^{-1}, assigned to a ^3E ^3A transition, also observed with the pentadentate N_3O_2 ligand.[21]

Electrochemical Studies

The axially-substituted nickel(II) macrocycle complexes $[Ni(L)(X_2)][PF_6]_2$ were readily prepared from the aquo species in methanol by direct reaction with the ligand to be incorporated. Isolation was achieved by the addition of a precipitating counterion or by precipitation with diethyl ether. Alternatively the compounds could simply be left to crystallize. Unfortunately some of these compounds could not be studied in the electrochemical cell because of the solvolyzing power of acetonitrile which readily replaces the axial ligand, giving similar voltammograms to the diaquo species in this solvent. Therefore, the axially-substituted adducts of L-complexes were prepared by adding an excess of the neutral ligand to the electrochemical cell. In acetonitrile (MeCN) solution an equilibrium between the solvated species $[Ni(L)(MeCN)_n]^{2+}$ and the species incorporating the axial X substituent $[Ni(L)(X)_2]^{2+}$ should be expected. ($X = 4$-substituted pyridines, imidazole, 1-methylimidazole, 2-methylimidazole, 1,2-dimethylimidazole, pyrazine, thiazole, triphenylphosphite, dimethylsulfoxide and dabco).

Electrolyte concentrations of 0.1 M were used in all electrochemical experiments and all solutions were degassed with argon prior to use and kept under an argon atmosphere throughout the experiment.

For the nickel(II) systems, the degree of reversibility of the reduction wave varies widely, and the half-wave potential $E_{1/2} = -1.08$ V remains constant to within a small degree. Only the π-donor ligands imidazole and 1-methylimidazole give more negative $E_{1/2}$ values (−1.40 and −1.46 V, respectively) suggesting a more difficult reduction. The π-acceptor ligand trimethylphosphite was also investigated as an axial ligand for the nickel(II) complex. No significant shifts were observed in the half-wave potential at −1.08 V of the parent aquo complex when an excess of triphenylphosphite was added to the electrochemical cell containing $[Ni(L)(H_2O)_2][PF_6]_2$. The electrochemical data for the entire series of nickel(II) macrocyclic complexes are presented in Table III and a current–potential curve for $[Ni(L)(H_2O)_2]^{2+}$ in the presence of 1-methylimidazole is shown in Figure 3. All the complexes studied gave very well defined polarographic reduction curves due to the electron transfer process to either metal or ligand which can schematically be represented by:

$$[Ni(II)(L)]^{2+} + e^- \longrightarrow [Ni(I)(L)]^+$$

or

$$[Ni(II)(L)]^{2+} + e^- \longrightarrow [Ni(II)(L^-)]^+.$$

The complexes having $E_{1/2}$ values close to the aquo complex indicate a metal-centered process while the complexes with more negative reduction potentials probably exhibit a ligand-centered process. The high negative reduction potential shows that the metal ion is highly stabilized by the

TABLE III Cyclic voltammetry data for the axially-substituted nickel(II) macrocycles

Complex	$E_{1/2}$ (V)	$(E_{pa} - E_{pc})$ mV
$[Ni(L)(H_2O)_2]^{2+}$	−1.08	150
$[Ni(L)(py)_2]^{2+}$	−1.20	90
$[Ni(L)(4\text{-}NC\text{-}py)_2]^{2+}$	−1.06	160
$[Ni(L)(4\text{-}NH_2\text{-}py)_2]^{2+}$	−1.32	120
$[Ni(L)(4\text{-}Me_2N\text{-}py)_2]^{2+}$	−1.30	120
$[Ni(L)(pyrazine)_2]^{2+}$	−1.22	230
$[Ni(L)(thiazole)_2]^{2+}$	−1.18	140
$[Ni(L)(Im)_2]^{2+}$	−1.40	90
$[Ni(L)(1\text{-}Me\text{-}Im)_2]^{2+}$	−1.46	80
$[Ni(L)(2\text{-}Me\text{-}Im)_2]^{2+}$	−1.27	200
$[Ni(L)(1,2\text{-}diMe\text{-}Im)_2]^{2+}$	−1.10	60
$[Ni(L)(Ph_3P)_2]^{2+}$	−1.16	170
$[Ni(L)(dmso)_2]^{2+}$	−1.20	80
$[Ni(L)(dabco)_2]^{2+}$	−1.10	110

All potentials are relative to a $Ag/AgBF_4$ electrode at room temperature in a *tetra-n*-butylammonium tetrafluoroborate–acetonitrile solution. Scan rate 100 mV s^{-1}.

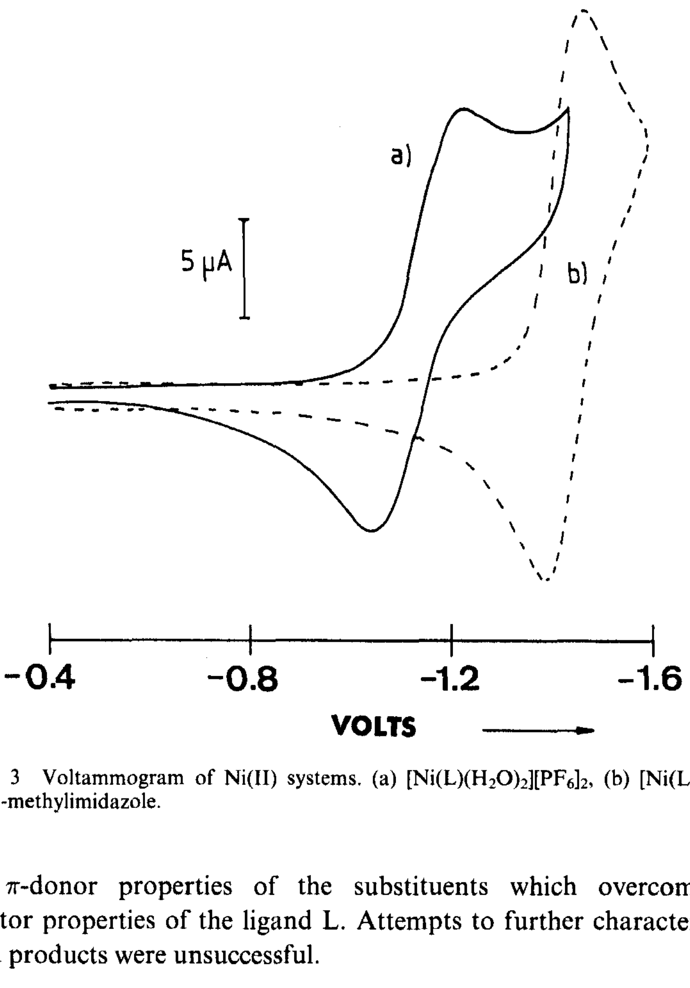

FIGURE 3 Voltammogram of Ni(II) systems. (a) $[Ni(L)(H_2O)_2][PF_6]_2$, (b) $[Ni(L)(H_2O)_2][PF_6]_2$ + 1-methylimidazole.

strong π-donor properties of the substituents which overcomes the π-acceptor properties of the ligand L. Attempts to further characterize the reduced products were unsuccessful.

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