Reduction of Schiff-base Macrocyclic Complexes. Stabilisation of Nickel(I) Conjugated Macrocyclic Complexes *via* a Reversible Ligand-to-Metal Electron-transfer Process

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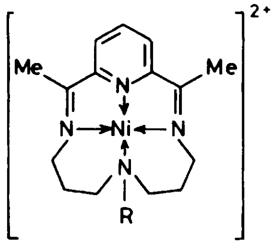
Reductive cyclic voltammetry of two Ni^{II} macrocyclic complexes $[Ni^{II}L]^{2+}$ in acetonitrile each shows two reversible one-electron reduction waves near $^1E_{\frac{1}{2}} = -1.0$ V and $^2E_{\frac{1}{2}} = -1.55$ V. Electrochemical reduction by controlled-potential electrolysis at these potentials and investigation of the reduced products by e.s.r. spectroscopy show the two reduction waves to correspond to the formation of $[Ni^{II}(L^{\bullet-})]^+$ and $[Ni^I(L^{\bullet-})]^0$ respectively. In the presence of axial ligands X = $P(OMe)_3$, PPh_3, or CO, cyclic voltammetry of $[Ni^{II}L]^{2+}$ shows the primary reduction wave to shift to lower negative potentials, the magnitude of $^1E_{\frac{1}{2}}$ increasing in the order $P(OMe)_3 < CO < PPh_3 <$ no ligand added; the magnitude of $^2E_{\frac{1}{2}}$ was found to decrease along this series. Controlled-potential electrolysis of $[Ni^{II}L]^{2+}$ at the primary reduction potential in the presence of these ligands leads to the formation of the metal-reduced nickel(I) complexes, $[Ni^ILX]^+$. Likewise, addition of these ligands to solutions of $[Ni^{II}(L^{\bullet-})]^+$ leads to the stabilisation of the same nickel(I) products. An intramolecular macrocyclic ligand-to-metal electron transfer is thought to be involved in the latter process and in the case of CO this electron transfer is found to be reversible. Reduction of $[Ni^{II}L]^{2+}$ at the secondary reduction potential in the absence or in the presence of CO, PPh_3, or $P(OMe)_3$ leads to the formation of nickel(I) ligand radical species; no nickel(0) products could be isolated.

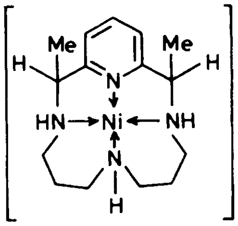
THE preparation of the four-co-ordinate nickel(II) macrocyclic complexes $[Ni^{II}L]^{2+}$, (1) and (2), by a metal template condensation of 2,6-diacetylpyridine with the corresponding triamine is well documented.[1-6] Derivatives of (1) with varying R functions,[7] alkyl chain lengths,[7-11] and with different central metal ions [4,12] have been reported.[13] Di-imino-macrocyclic ligands would be expected to behave as good π acceptors and have been shown to stabilise successfully low-valent transition-metal species.[14-17] However, due to the presence of energetically favourable low-lying π* orbitals of the di-iminopyridine function, reduction of (1) has been shown to give initially a metal-stabilised ligand radical species, $[Ni^{II}(L^{\bullet-})]^+$; [7,18,19] a nickel(I) complex could only be isolated on reduction of (3) where the di-imino-moiety of (1) has been fully reduced with sodium tetrahydroborate.[7,18] Oxidation of (1) yields the corresponding nickel(III) species.[18,19]



(1; R = H)

(2; R = Me)

As part of a continuing study of transition-metal macrocyclic complexes incorporating the 2,6-di-iminopyridine moiety,[20-24] we have investigated the reductive properties of (1) and (2) in the presence of the π-acceptor ligands CO, PPh_3, and $P(OMe)_3$ to determine whether, by the addition of these ligands, the stabilisation of nickel(I) relative to the nickel(II) ligand radical species $[Ni^{II}(L^{\bullet-})]^+$ can be attained, thereby altering the reductive properties of the system. Our interest in the stabilisation of low-valent transition-metal macrocyclic complexes stems from their possible role as catalysts or reagents for organic synthesis. The potential for such reactivity has been recently illustrated by a series of di-iminoiron(0) complexes.[25-27]



(3)

RESULTS AND DISCUSSION

The macrocyclic complex $[Ni^{II}L]^{2+}$, (1), has been reported to undergo two reversible reductions in acetonitrile under the conditions of cyclic voltammetry at a platinum microsphere.[7,18] Coulometric measurements confirm that these reductions are each one-electron processes.[7] Chemical and electrochemical reductions of (1) have shown that the two reduction waves correspond to the initial formation of a nickel(II) ligand radical species $[Ni^{II}(L^{\bullet-})]^+$ followed by reduction to $[Ni^I(L^{\bullet-})]^0$, a nickel(I) ligand radical complex.[3,7,18] We have measured the cyclic voltammograms for the complexes (1) and (2) in acetonitrile in the presence and in the absence of the π-acceptor ligands CO, PPh_3, and $P(OMe)_3$. Under these conditions the complexes all show two reversible or quasi-reversible reduction waves as listed in Table 1. Solutions of (1) and (2) in acetonitrile were reduced by controlled-potential electrolysis in the presence and in the absence of CO, PPh_3, and $P(OMe)_3$ at the reduction potentials as indicated in Table 1. The electron spin resonance spectral data of the reduced species are listed in Table 2 and the spectra are reproduced in Figure 1.

Table 1

Cyclic voltammetric data * for the reduction of complexes (1) and (2) in acetonitrile at 25 °C with 0.1 mol dm^{-3} [NBu$^n_4$][BF$_4$] as base electrolyte in the presence of π-acceptor ligands

Complex	Ligand	1st Reduction wave $^1E_{\frac{1}{2}}$/V	2nd Reduction wave $^2E_{\frac{1}{2}}$/V
(1)		−0.97	−1.54
	PPh$_3$	−0.96	−1.56
	CO	−0.95	−1.60
	P(OMe)$_3$	−0.82	−1.68
(2)		−0.99	−1.53
	PPh$_3$	−0.98	−1.54
	CO	−0.96	−1.61
	P(OMe)$_3$	−0.85	−1.68

* $E_{\frac{1}{2}}$ values relative to Ag–AgNO$_3$ standard electrode. $E_{\frac{1}{2}}$ (ferrocene–ferrocinium) = +0.19 V. Cyclic voltammograms run on 10^{-3}—10^{-4} mol dm^{-3} solutions.

Reduction of (1) or (2) at −1.0 V in acetonitrile by controlled-potential electrolysis yielded a dark green solution, the e.s.r. spectrum of which at 77 K as an acetonitrile glass showed a single isotropic line at $g = 2.002$ indicating the formation of a nickel(II)-stabilised ligand radical species, [Ni^{II}(L$^{\bullet -}$)]$^+$; no nickel(I) products could be detected by e.s.r. spectroscopy. This is in agreement with the previously reported work on the one-electron reduction of (1), the electron residing mostly on the unsaturated part of the macrocyclic ligand,[7,18] either delocalised over the di-iminopyridine moiety or localised on one of the imine bonds. Neither (1) nor (2) showed clearly defined e.s.r. spectra at 77 K as acetonitrile glasses.

Table 2

E.s.r. spectral data [a] of products formed by reduction of complexes (1) and (2) at the first reduction potential in the presence of π-acceptor ligands

Complex	Ligand	E.s.r. spectrum $g_{\parallel}$	$g_{\perp}$	Assignment
(1)		2.002 [b]		[Ni^{II}(L$^{\bullet -}$)]$^+$
	CO	2.211	2.050	[Ni^{I}L]$^+$
	PPh$_3$ [c]	2.206	2.068	[Ni^{I}L]$^+$
	P(OMe)$_3$	2.190	2.065	[Ni^{I}L]$^+$
(2)		2.002 [b]		[Ni^{II}(L$^{\bullet -}$)]$^+$
	CO	2.146	2.031	[Ni^{I}L]$^+$
	PPh$_3$ [c]	2.145	2.053	[Ni^{I}L]$^+$
	P(OMe)$_3$	2.137	2.040	[Ni^{I}L]$^+$

[a] Measured in acetonitrile at 77 K. [b] $g_{av.}$ (isotropic). [c] Excess of PPh$_3$ was required.

Cyclic voltammetric measurements of (1) and (2) in acetonitrile in the presence of excess of P(OMe)$_3$, PPh$_3$, or CO showed shifts in the primary reduction wave to lower negative potentials, the magnitude of $^1E_{\frac{1}{2}}$ increasing in the order P(OMe)$_3$ < CO < PPh$_3$ < no ligand added. The magnitude of $^2E_{\frac{1}{2}}$ for the secondary reduction wave was found to decrease along this series. The variation in the primary reduction wave of (1) was measured in the presence of various concentrations of P(OMe)$_3$. On addition of P(OMe)$_3$, $^1E_{\frac{1}{2}}$ was found to shift to lower negative potentials, reaching a minimum on the addition of approximately a 15-fold excess of P(OMe)$_3$; addition of further aliquots of P(OMe)$_3$ had no effect on the value of $^1E_{\frac{1}{2}}$. These results are consistent with the co-ordination of at least one P(OMe)$_3$ ligand to (1), in equilibrium in acetonitrile with non-solvated and solvated forms of (1). Scheme 1 represents some of the possible equilibria set up in solution. Solvation of (1) to give paramagnetic six- and five-co-ordinate complexes is well known to occur.[6]

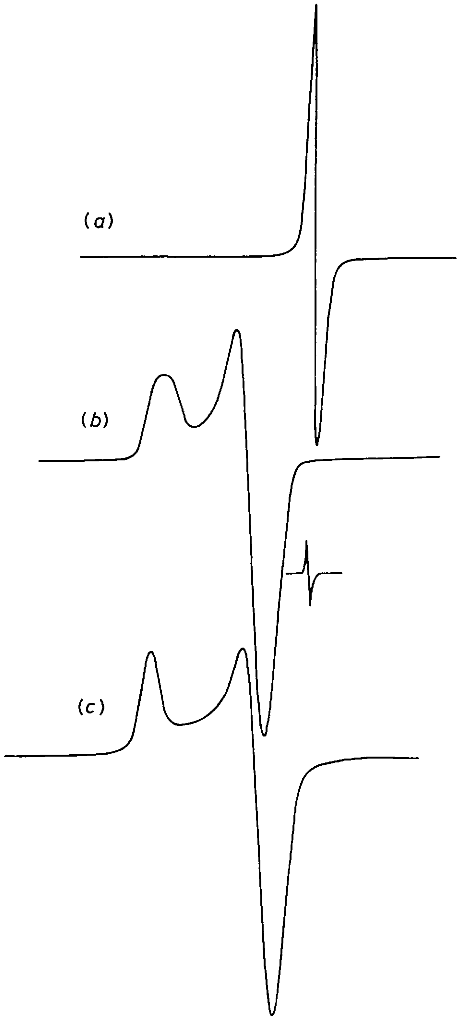


Figure 1 E.s.r. spectra of derivatives of complex (1): (a) [Ni^{II}(L$^{\bullet -}$)]$^+$, (b) [Ni^{I}L{P(OMe)$_3$}]$^+$, and (c) [Ni^{I}L(CO)]$^+$ in acetonitrile at 77 K

Determination of the stability constants for complex formation in (1) and (2) and in other di-iminonickel(II) macrocyclic systems is now under active investigation in our laboratories.

Coulometric measurements have confirmed that (1) undergoes two one-electron reductions;[7] comparison of the line shape and i values for the cyclic voltammograms of (1) and (2) with those obtained in the presence of P(OMe)$_3$ (Figure 2), PPh$_3$, and CO indicates that the same numbers of electrons are involved in the reductions involving these axial ligands.

Reduction of [Ni^{II}L]$^{2+}$ in acetonitrile in the presence of CO, PPh$_3$, or P(OMe)$_3$ by controlled-potential

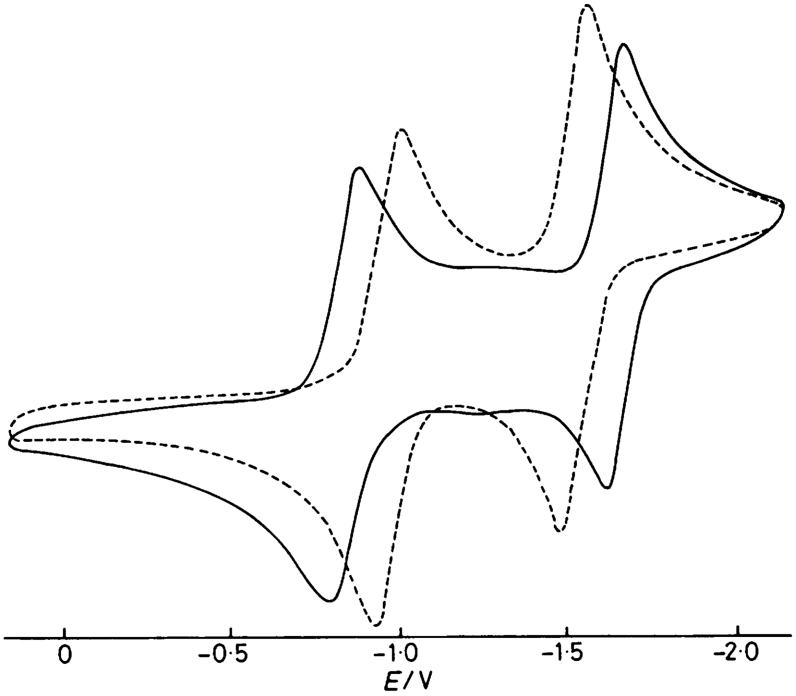


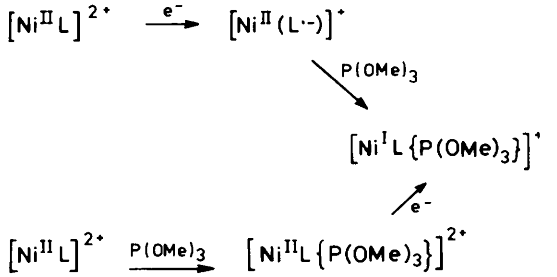
FIGURE 2 Cyclic voltammograms of complexes (1) (– – – –) and (1) in the presence of P(OMe)$_3$ (——) measured in 0.1 mol dm^{-3} [NBu$^n{}_4$][BF$_4$] in acetonitrile at a platinum microsphere relative to a Ag–AgNO$_3$ reference electrode

electrolysis at the primary reductive potentials each showed by e.s.r. the presence of d^9 nickel(I) species (Table 2, Figure 1). Under these conditions, the nickel(II) ligand radical complex [Ni^{II}(L$^{\bullet -}$)]$^+$ was detected only as an intermediate product which decayed to give the corresponding nickel(I) species (Scheme 2). The visible spectra of these reduced solutions all show bands near 500 nm (ε = 2 900) partially obscured by u.v. bands tailing into the visible absorption spectrum. We tentatively assign these as nickel(I)$\rightarrow$macrocyclic ligand charge-transfer bands.

SCHEME 1

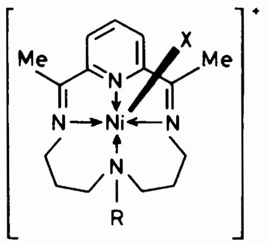
The i.r. spectrum of the solid product obtained from the reduction of (1) or (2) in the presence of CO, however, showed no bands assignable to a carbonyl-stretching vibration. Weak bands near 2 300 cm^{-1} indicated the presence of co-ordinated acetonitrile. The e.s.r. spectrum of the product redissolved in acetonitrile showed a single isotropic signal, g = 2.002, assigned to the nickel(II) ligand radical species, [Ni^{II}(L$^{\bullet -}$)]$^+$. It is of interest to note here that the i.r. spectrum of [Ni^{II}(L$^{\bullet -}$)]$^+$ showed weaker bands near 1 620 cm^{-1} assigned to the C=N stretching vibration, ν(C=N), than the starting materials (1) or (2). A similar loss of intensity of the imine stretching vibration has been recently noted for other ligand radical species of di-imino-complexes[28] and is ascribed to weaker C=N bond strength due to net occupation of the imine π* orbitals. On bubbling CO gas through a solution of [Ni^{II}(L$^{\bullet -}$)]$^+$ however, the nickel(I) e.s.r. spectrum reappeared and the solution i.r. spectrum showed a band at 1 995 cm^{-1} which we assign to the ν(C≡O) stretching vibration of metal-co-ordinated CO. These results indicate that CO is reversibly bound to the nickel(I) centre and on loss of CO an intramolecular electron transfer from metal to ligand occurs to give the corresponding nickel(II) ligand radical species [equation (i)]. Addition of P(OMe)$_3$, PPh$_3$, or CO to solutions of

$$[\mathrm{Ni^{II}(L^{\bullet -})}]^+ \underset{-\mathrm{CO}}{\overset{+\mathrm{CO}}{\rightleftharpoons}} [\mathrm{Ni^{I}L(CO)}]^+ \qquad (i)$$



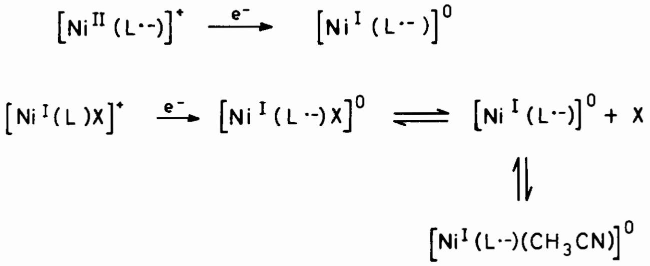
SCHEME 2

$[\mathrm{Ni^{II}}(\mathrm{L}^{\bullet-})]^+$ prepared directly from (1) or (2) yielded the corresponding nickel(I) species. Electrochemical reduction of (1) or (2) in the presence of one equivalent of $\mathrm{P(OMe)_3}$ led to the formation, detected by e.s.r. spectroscopy, of the phosphite nickel(I) complex; no ligand radical species could be detected. Addition of a second equivalent of $\mathrm{P(OMe)_3}$ had no effect on the nickel(I) spectrum. On this basis we assume the formation of a five-co-ordinate intermediate for the structure of the nickel(I) products described herein. This may be represented by (4) which is consistent with the proposed structures for other nickel(I) complexes.[19,29]



(4 ; R = H or Me)

Complexes (1) and (2) were reduced in acetonitrile by controlled-potential electrolysis in the absence and in the presence of CO, $\mathrm{P(OMe)_3}$, and $\mathrm{PPh_3}$ at the secondary reduction potentials as indicated in Table 1. The e.s.r. spectra of the reduced solutions as acetonitrile glasses at 77 K are rather complex probably due to coupling between the two paramagnetic centres in the product, but indicate the formation of nickel(I) ligand radical complexes $[\mathrm{Ni^{I}}(\mathrm{L}^{\bullet-})]^0$ in the absence of axial ligands ($g_{\mathrm{av.}} = 2.188$, $g_{\mathrm{iso.}} = 2.002$) and $[\mathrm{Ni^{I}}(\mathrm{L}^{\bullet-})\mathrm{X}]^0$ {X = CO, $\mathrm{P(OMe)_3}$, or $\mathrm{PPh_3}$; $g_{\mathrm{av.}} = 2.180$, $g_{\mathrm{iso.}} = 2.002$ for $[\mathrm{Ni^{I}}(\mathrm{L}^{\bullet-})(\mathrm{PPh_3})]^0$}. In addition, equilibria may be set up in solution (Scheme 3) thus complicating the e.s.r. spectra further. The presence of such equilibria is supported by cyclic voltammetric measurements on the secondary reduction potential, the value of ${}^2E_{\frac{1}{2}}$ being found to reach a maximum on the addition of approximately 10 equivalents of $\mathrm{P(OMe)_3}$. Addition of further aliquots of $\mathrm{P(OMe)_3}$ had no effect on ${}^2E_{\frac{1}{2}}$. No evidence was obtained for the stabilisation of nickel(0) species in these reduction experiments. This is not surprising since the preferred tetrahedral co-ordination geometry of nickel(0) complexes is not possible for the di-iminopyridine macrocyclic ligand.



SCHEME 3

The results described in this paper indicate that in the macrocyclic complexes (1) and (2), and in other conjugated macrocyclic systems where reduction leads to the initial formation of a metal-stabilised ligand radical species, addition of a π-acceptor axial ligand(s) may lead to a preferred reduction at the metal centre thus successfully stabilising the low-oxidation-state metal species. We have recently found such a stabilisation of a cobalt(I) macrocyclic system by the addition of $\mathrm{P(OMe)_3}$ [30] and low-valent complexes of tetra-aza-macrocyclic ligands have been likewise stabilised by the addition of CO.[29,31,32] It should be noted that the reduction potentials at which nickel(I) products are formed from (1) are particularly favourable when compared with other *N*-donor macrocyclic [3,18,19] and non-macrocyclic systems.[33,34] This reflects the strong π-acceptor properties of the di-iminopyridine moiety and the enhanced stabilisation achieved by the axial ligand.

EXPERIMENTAL

Infrared spectra were measured as Nujol mulls between KBr discs or in acetonitrile in KBr solution cells (over the range 250 ⟶ 4 000 $\mathrm{cm^{-1}}$) using Perkin-Elmer 257 and 457 spectrometers. Visible and ultraviolet spectra were measured in quartz cells using a Pye Unicam SP 8-100 spectrophotometer.

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 $\mathrm{dm^{-3}}$ of $[\mathrm{NBu^n_4}][\mathrm{BF_4}]$ present as supporting electrolyte. Cyclic voltammetric studies were carried out using platinum wires as auxillary and working electrodes and a Ag–$\mathrm{AgNO_3}$ reference electrode with sample concentrations of 10^{-3} to 10^{-4} mol $\mathrm{dm^{-3}}$. Controlled-potential electrolysis experiments were carried out using a platinum gauze as the working electrode, a salt bridge being incorporated to separate oxidised and reduced species. E.s.r. spectra were measured as glasses in acetonitrile at 77 K. All solvents used were distilled, dried, and degassed before use and all compounds were handled under a nitrogen atmosphere using Schlenk-tube techniques.

Preparation of Complexes (1) *and* (2).[1,6,7]—The preparation of the tetrafluoroborate salt of (1) is typical.

Nickel dichloride hexahydrate (2.4 g, 0.1 mol $\mathrm{dm^{-3}}$), 2,6-diacetylpyridine (1.6 g, 0.1 mol $\mathrm{dm^{-3}}$), and 3,3′-iminobis(propylamine) (1.3 g, 0.1 mol $\mathrm{dm^{-3}}$) were refluxed together in 50% aqueous ethanol (200 $\mathrm{cm^3}$) for 36 h. Excess of sodium tetrafluoroborate was added and the reaction mixture evaporated to dryness. The macrocyclic complex was taken up in acetonitrile to remove excess of sodium tetrafluoroborate and the solution evaporated to dryness. The dark brown complex was recrystallised twice from methanol–diethyl ether to give a bright orange product.

Complex (1) as its $\mathrm{BF_4^-}$ or $\mathrm{PF_6^-}$ salt was dissolved in acetonitrile containing 0.1 mol $\mathrm{dm^{-3}}$ of $[\mathrm{NBu^n_4}][\mathrm{BF_4}]$ as base electrolyte and reduced by controlled-potential electrolysis at −1.0 V under a constant stream of argon gas. The reduced solution was transferred by syringe to a Schlenk tube and the nickel(II) ligand radical species was precipitated by the addition of diethyl ether.

Addition of $\mathrm{P(OMe)_3}$, $\mathrm{PPh_3}$, or CO to the above reduced solution yielded the corresponding nickel(I) complexes.

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