Redox-induced Reactions of Nickel Maleonitriledithiolate αα'-Di-imine Complexes

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The complex $[Ni^{II}\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$ has been found to undergo one-electron reduction to a species containing Ni^{I}. This species is unstable and disproportionates to the known $[Ni^{II}\{(NC)_2C_2S_2\}_2]^{2-}$ and $[Ni\{(CH_3)_2C_2N_2Ph_2\}_2]$. The complex also reacts upon oxidation to give $[Ni\{(NC)_2C_2S_2\}_2]^{-}$. A similar one-electron reduction of $[Ni(Ph_2C_2S_2)(phen)]$ (phen = 1,10-phenanthroline) has been found to give a stable species with greater delocalisation of the unpaired electron over the ligand.

Transition-metal complexes of the ligand maleonitriledithiolate, $[(NC)_2C_2S_2]^{2-}$ (mnt), show many unusual properties.[1] In particular, the extensive series of redox reactions observed indicate changes in both metal and ligand oxidation state.[2] Recent studies[3] on mixed-ligand complexes of nickel(II) with $[(NC)_2C_2S_2]^{2-}$ and phosphine ligands of the type $[Ni(dppe)\{(NC)_2C_2S_2\}]$ [dppe = 1,2-bis(diphenylphosphino)ethane] have shown that molecules such as this undergo reversible one-electron reductions of Ni^{II}. Previous studies[4] had been made of the analogous four-co-ordinate dithiolene and di-imine complexes of nickel(II).

The complex $[Ni\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$ was reported[4] to undergo a one-electron reduction at a solvent-dependent potential ranging from −0.61 to −0.72 V (*vs.* saturated calomel electrode) and an irreversible oxidation at *ca.* 0.9 V. The reduction couple was chemically reversible and the reduced complexes stable for short periods in solution.

We now report a study of the redox properties of the complex $[Ni\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$ and characterisations of electrochemically produced species and their reaction products by e.s.r. spectroscopy.

Experimental

Complexes $[Ni\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$, $[Ni\{(CH_3)_2C_2N_2Ph_2\}_2]I_2$, and $[Ni(Ph_2C_2S_2)(phen)]$ (phen = 1,10-phenanthroline) were prepared by previously reported methods:[4,5] $[Ni\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$, m.p. 208—210 °C (Found: C, 55.55; H, 4.20; N, 12.45. Calc. for $C_{20}H_{16}N_4NiS_2$: C, 55.2; H, 3.70; N, 13.85%); $[Ni(Ph_2C_2S_2)(phen)]$, m.p. >303 °C (Found: C, 64.25; H, 3.85; N, 5.75. Calc. for $C_{26}H_{18}N_2NiS_2$: C, 64.9; H, 3.75; N, 5.80%).

Electrochemical measurements were performed at a platinum electrode using a PAR 173 potentiostat with PAR 179 digital calorimeter with *iR* compensation and an ECG 175 universal programmer. The reference electrode was Ag-AgCl (saturated LiCl in CH_2Cl_2) separated from the voltammetric cell by a 0.1 mol dm^{-3} NBu_4ClO_4 in CH_2Cl_2 salt bridge. Measurements were carried out in CH_2Cl_2 with NBu_4ClO_4 supporting electrolyte. Potentials are referenced to the ferrocene–ferrocenium couple as reported previously.[3]

X-Band e.s.r. spectra were recorded on a Varian E4 spectrometer. Controlled-potential electrolysis at a platinum electrode was used to generate the oxidised and reduced species *in situ*.

Results and Discussion

The d.c. cyclic voltammogram of $[Ni^{II}\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$ in dichloromethane solvent shows three main features in the potential range −2.0 to +1.6 V. At scan rates of 200 mV s^{-1} these features are an irreversible reduction at E_{pc} = −1.84 V, a quasi-reversible reduction E_0' = −0.73 V (i_p^r/i_p^f = 1.0), and a further irreversible oxidation E_{pa} = +1.14 V [Figure 1(*a*), Table 1]. Miller and Dance[4] assigned these processes to the redox sequences z = $-2 \rightleftharpoons -1$, $-1 \rightleftharpoons 0$, and $0 \rightleftharpoons +1$ for $[Ni\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]^z$. In the reverse scan from −2.0 V, Figure 1(*a*), several smaller anodic peaks are observed above and below 0 V. When a voltammogram is recorded (at 200 mV s^{-1}) sweeping from 0 V to a potential just below that of the quasi-reversible reduction and back to +1.6 V three small

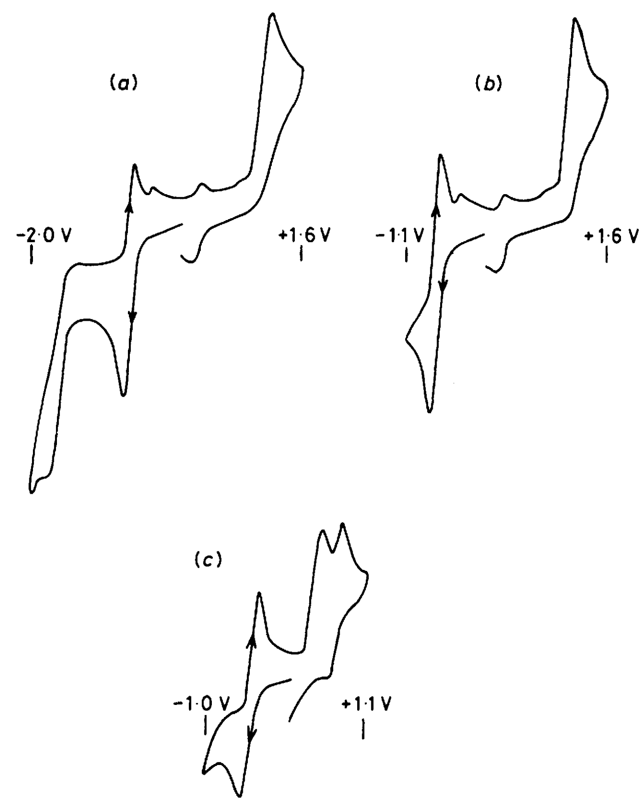

Figure 1. Cyclic voltammogram of $[Ni\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$ at scan rate 200 mV s^{-1} and *ca.* 290 K (CH_2Cl_2 solvent): (*a*) in the range −2.0 to +1.6 V; (*b*) in the range −1.1 to +1.6 V. (*c*) Cyclic voltammogram of $[Ni\{(CH_3)_2C_2N_2Ph_2\}_2]I_2$ in dichloromethane solvent at *ca.* 290 K at scan rate 200 mV s^{-1}

Table 1. Cyclic voltammetry parameters (V) for the complexes $[Ni^{II}\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$ and $[Ni^{II}(Ph_2C_2S_2)(phen)]$ in dichloromethane solvent at *ca.* 290 K

Complex	E_{pc} [a]	E_0' [b]	ΔE_{pp} [a]	E_{pa} [b]	E_0' [b]	ΔE_{pp} [a]
$[Ni\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$ [c]	−1.84	−0.73	0.11	1.14		
$[Ni(Ph_2C_2S_2)(phen)]$		−1.44	0.09		0.30	0.07

[a] At a scan rate of 200 mV s^{-1}. [b] Potential measured halfway between the potentials of the peak cathodic and anodic currents.

Table 2. E.s.r. parameters for reduced complexes in dichloromethane

					$10^4A(^{14}N)/cm^{-1}$		
Complex [a]	g	g_1	g_2	g_3	A_1	A_2	A_3
$[Ni\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]^-$	2.148	2.321	2.119	2.030			8.9
$[Ni(Ph_2C_2S_2)(phen)]^-$	2.056	2.119	2.040	1.998			
$[Cu\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$ [b]	2.068	2.138	2.022	2.022	15.4	9.14	9.14

[a] Frozen-solution data at −160 °C. [b] Ref. 7.

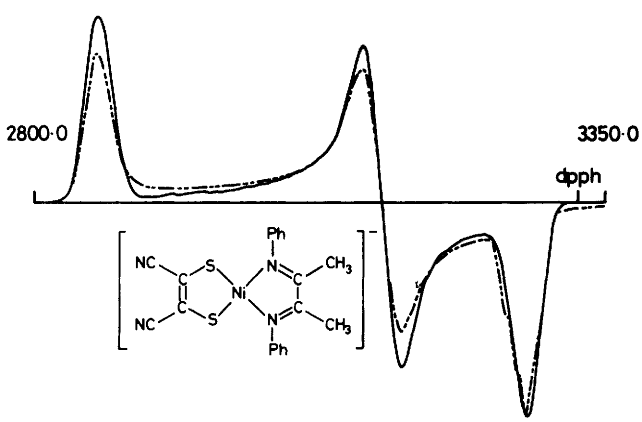

Figure 2. Frozen-solution e.s.r. spectrum (— · · —) of $[Ni^{I}\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]^-$ in dichloromethane solvent at −160 °C and spectrum simulated with $g_1 = 2.321$, $g_2 = 2.119$, $g_3 = 2.030$, $\sigma_z = 13$, $\sigma_x = 13$, and $\sigma_y = 12$ G (——). Magnetic field given in G (G = 10^{-4} T); dpph = diphenylpicrylhydrazyl

peaks are discerned on the anodic sweep, at $E_{pa} = -0.39$, +0.21, and +0.76 V, Figure 1(*b*). The peak at $E_{pa} = +0.21$ V has a cathodic return peak corresponding to the one-electron oxidation of $[Ni\{(NC)_2C_2S_2\}_2]^{2-}$.[2]

To identify the other peaks in the voltammogram, $[Ni^{II}\{(CH_3)_2C_2N_2Ph_2\}_2]I_2$, a four-co-ordinate complex containing unco-ordinated iodide, was studied in dichloromethane. A reversible reduction at $E_0' = -0.45$ V and two irreversible oxidation peaks $E_{pa} = +0.36$ and +0.76 V (200 mV s^{-1}) were observed, Figure 1(*c*). The peak at +0.36 V corresponds to the irreversible oxidation of the free iodide ion. The process at $E_0' = -0.45$ V corresponds to the two-electron process (1).[5] The peaks in the return sweep of the voltammogram, at

$$[Ni\{(CH_3)_2C_2N_2Ph_2\}_2]^{2+} \underset{-2e^-}{\overset{+2e^-}{\rightleftharpoons}} [Ni\{(CH_3)_2C_2N_2Ph_2\}_2] \quad (1)$$

$E_{pa} = -0.39$ to 0.76 V, Figure 1(*b*), are then identified as due to the species $[Ni\{(CH_3)_2C_2N_2Ph_2\}_2]^z$.

The appearance of the species $[Ni\{(NC)_2C_2S_2\}_2]^{2-}$ and $[Ni\{(CH_3)_2C_2N_2Ph_2\}_2]$ upon one-electron reduction of the mixed-ligand complex implies the reduced product is unstable to a 'symmetrisation' reaction to the bis(chelates). This behaviour has recently been observed in reduced mixed-ligand complexes of nickel(II) such as $[Ni(dppe)(R_2NCS_2)]^+$ which upon reduction disproportionates into $[Ni^{II}(R_2NCS_2)_2]$ and $[Ni^0(dppe)_2]$.[3] A similar disproportionation reaction is found here, Figure 3, although the detailed mechanism is at present unknown.

An *in situ* electrolysis of $[Ni^{II}\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$ at a potential below that of the first one-electron reduction at −60 °C gave a paramagnetic species. The e.s.r. spectrum in solution was a single line at $g = 2.148$. The frozen solution at −160 °C gave a rhombic spectrum, Figure 2. The component corresponding to g_3, Table 2, showed superhyperfine splitting due to two equivalent ($I = 1$) nitrogen nuclei. An estimate of the coupling constant $A_3(^{14}N)$ of 8.9×10^{-4} cm^{-1} was made from a direct measurement of the lines in the spectrum. The e.s.r. parameters of the frozen-solution spectrum are listed in Table 2. The anisotropic g values were obtained by comparison with simulated spectra. The anisotropy in the g values is greater in magnitude than those previously found for $[Ni^{I}(R_2NCS_2)_2]^-$ and nickel(I) phosphine(dithiolate) complexes [3] and is in agreement with the formulation of the initial one-electron reduction product as a nickel(I) complex [equation (2)].

$$[Ni^{II}\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}] \xrightarrow{+e^-} [Ni^{I}\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]^- \quad (2)$$

The isoelectronic complex $[Cu^{II}\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$ has been studied by e.s.r. spectroscopy.[6,7] A covalency parameter of $\alpha^2 = 0.57$ determined from the spin-Hamiltonian parameters indicated that the unpaired electron was extensively delocalised from the central copper atom onto the maleonitriledithiolate ligand. A comparison of the g values for the copper and nickel complexes, Table 2, indicates an anisotropy for the formally nickel(I) complex greater than observed for the copper(II) complex.

A cyclic voltammogram of $[Ni\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$ sweeping from 0 to +1.6 V (a potential past that of the irreversible oxidation) and returning to 0 V gave a cathodic peak $E_{pc} = 0.11$ V (at 200 mV s^{-1}) due to the one-electron reduction of $[Ni\{(NC)_2C_2S_2\}_2]^-$ to $[Ni\{(NC)_2C_2S_2\}_2]^{2-}$. No evidence could be found for the complex $[Ni\{(CH_3)_2C_2N_2Ph_2\}_2]^{2+}$. An *in situ* electrolysis at a potential greater than the irreversible oxidation potential gave a species with an e.s.r. spectrum centred at $g = 2.062$. On freezing the solution to −160 °C a rhombic spectrum identical to that reported

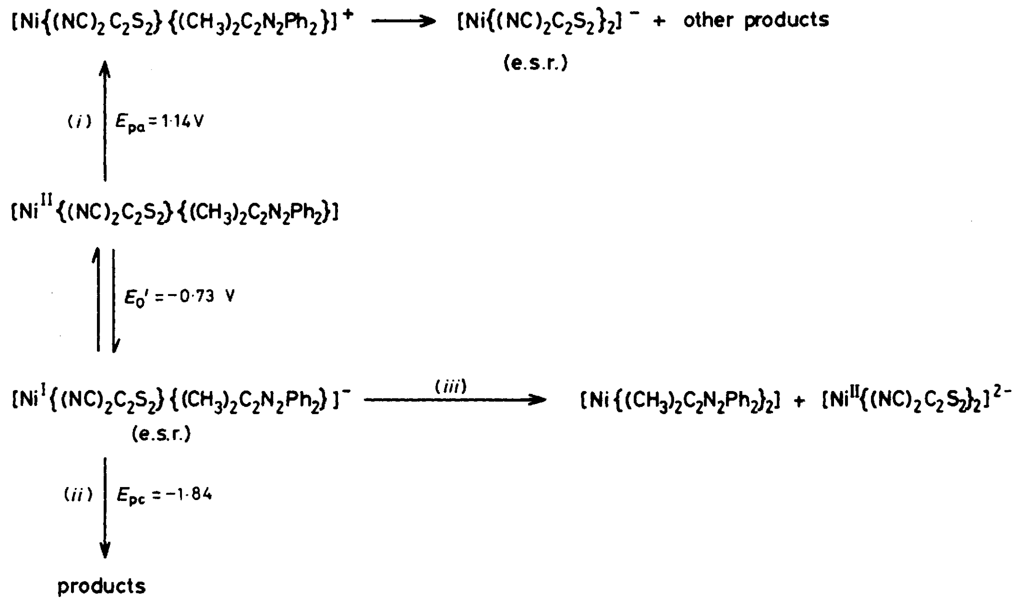

Figure 3. Reaction scheme for the electrochemistry of $[Ni^{II}\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$. Potentials measured at scan rate 200 mV s^{-1}. (*i*) Irreversible oxidation; (*ii*) irreversible reduction; (*iii*) disproportionation reaction with ligand exchange

for $[Ni\{(NC)_2C_2S_2\}_2]^-$ ($g_1 = 2.140$, $g_2 = 2.043$, $g_3 = 1.996$) was observed confirming the identity of this species.[8]

The initial reduction product of $[Ni\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]$ to a nickel(I) species may be compared with the analogous $[Ni(Ph_2C_2S_2)(phen)]$. This complex was shown to undergo two electrochemical processes in the potential range −2.0 to +1.0 V in dichloromethane. A reversible one-electron reduction occurs at −1.44 V.[4] An e.s.r. spectrum of the reduction product at 0 °C gave a single peak which split on freezing to give a rhombic pattern, Table 2. The *g*-value anisotropy is considerably smaller than shown for $[Ni^I\{(NC)_2C_2S_2\}\{(CH_3)_2C_2N_2Ph_2\}]^-$ indicating a greater delocalisation of the unpaired electron onto the 1,10-phenanthroline relative to the di-imine ligand. A comparable delocalisation has been found in $[Ni(Ph_2C_2S_2)_2]^-$.[9]

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