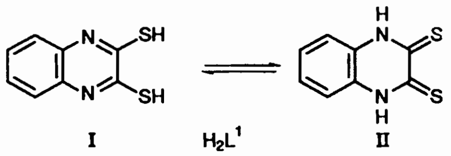
Nickel-(II) and -(III) Complexes with NiS_4 Environments: Electron Paramagnetic Resonance and Electrochemical Studies

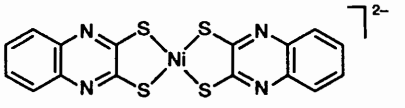
Sami Mukhopadhyay and Debashis Ray *
Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

A group of nickel(II) complexes having a square-planar NiS_4 co-ordination sphere have been synthesised using the bidentate quinoxaline-2,3-dithiol ligand (H_2L^1). In dimethylformamide solution the nickel(III)–nickel(II) couple is electrochemically observable for both the thiolate $[NiL^1_2]^{2-}$ and thione $[Ni(H_2L^1)_2]^{2+}$ complexes with $E_{\frac{1}{2}}$ values of +0.12 and +0.32 V respectively *vs.* saturated calomel electrode. The nickel(III) species can be electrogenerated in solution. Upon freezing (77 K) rhombic EPR spectra ($g_{xx} \approx 2.30$, $g_{yy} \approx 2.05$, $g_{zz} \approx 2.03$) compatible with the uncommon configuration $d_{xy}{}^1$ ($g_{\parallel} > g_{\perp}$) are observed. The fact that the thione (neutral sulfur) complexes are more difficult to oxidise is consistent with the effectiveness of the polarisable sulfur atoms in the thiolate complex, resulting in the stabilisation of Ni^{III} and the observation of relatively low values for the Ni^{II}–Ni^{III} potential.

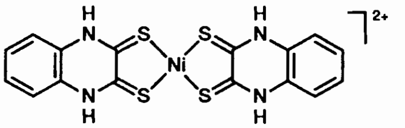
Nickel extended X-ray absorption fine structure (EXAFS) studies of numerous hydrogenase enzymes suggest that the nickel ion is co-ordinated to approximately four sulfur atoms in either a distorted octahedral or square-pyramidal array.[1] These nickel sites are characterised by low Ni^{III}–Ni^{II} redox potentials and exhibit characteristic rhombic EPR spectra assigned to a nickel(III) centre.[2] Herein we report the ligating behaviour of quinoxaline-2,3-dithiol (H_2L^1) towards the stabilisation of the trivalent state of nickel. Nickel(II) complexes of both the dithiolate and dithioamide forms of the ligand have been synthesised. These complexes undergo metal-centred oxidations to afford products that are meaningfully formulated as trivalent nickel complexes. Comparison of metal redox potentials, reveals that dithioamide co-ordination disfavours metal oxidation relative to dithiolate co-ordination.



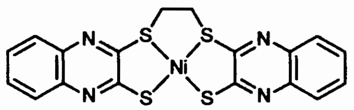
I H_2L^1 II



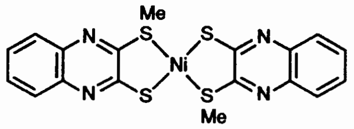
$[NiL^1_2]^{2-}$



$[Ni(H_2L^1)_2]^{2+}$



$[NiL^2]$



$[NiL^3_2]$

Experimental

Chemicals and Starting Materials.—Solvents and reagents were obtained from commercial sources and used without further purification unless otherwise stated. Dimethylformamide (dmf) was dried over solid potassium hydroxide before a final reflux and distillation.[3] Commercial tetraethylammonium bromide was converted to pure tetraethylammonium perchlorate by following an available procedure.[4] The dithiol ligand H_2L^1 was prepared as described previously.[5]

Physical Measurements.—Solution electrical conductivity and UV/VIS spectra were obtained using a Uniitech type UI 31C digital conductivity meter and a Shimadzu UV 3100 UV/VIS/near-IR spectrophotometer respectively. Magnetic susceptibility in the solid state was measured with a Gouy balance. Cyclic voltammetric measurements at 298 K were performed under a pure and dry dinitrogen atmosphere using PAR 370-4 electrochemistry system incorporating a model 174A polarographic analyser, model 175 universal programmer, model RE0074 X-Y recorder, model 173 potentiostat, model 179 digital coulometer, and a model 377 A cell system. The three-electrode measurements were carried out with a planar Beckman model 39273 platinum inlay working electrode, a platinum wire auxiliary electrode, and an aqueous saturated calomel (SCE) reference electrode. A platinum-wire-gauze working electrode was used in coulometric experiments. The reported potentials are uncorrected for junction contribution. X-Band EPR spectra were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar flask for measurements at 77 K (liquid nitrogen). The spectra were calibrated with diphenylpicrylhydrazyl (dpph) ($g = 2.0037$). The microwave power level was maintained at *ca.* 0.2 mW. Microanalytical data (C,H,N) were obtained with a Perkin Elmer model 240 C elemental analyser.

Table 1 Electronic absorption spectral[a] and molar conductivity[b] data

Compound	Colour	λ/nm (ε/dm^3 mol^{-1} cm^{-1})	Λ_M/ohm^{-1} cm^2 mol^{-1}
$Na_2[NiL^1{}_2]$	Dark red	562 (3302), 520 (4623), 482 (4953), 317 (24 636), 262 (19 260)	135
$K_2[NiL^1{}_2]$	Dark red	558 (3115), 530 (3445), 358 (4210) (sh), 314 (25 510), 263 (21 980)	155
$[Ni(H_2L^1)_2]Cl_2$	Bluish green	658 (2480), 600 (2540), 472 (4580) (sh), 360 (5005) (sh), 313 (22 580), 264 (19 260)	175
$[Ni(H_2L^1)_2][ClO_4]_2$	Green	660 (2035), 605 (2105), 410 (3710), 315 (18 765), 261 (15 285)	130
$[NiL^2]$	Brown	562 (5132), 527 (5570), 448 (4530) (sh), 314 (27 020), 263 (21 690)	Non-electrolyte
$[NiL^3{}_2]$	Brown	530 (4840), 408 (4230), 330 (13 455), 344 (13 560), 263 (17 940)	Non-electrolyte

[a] Solvent dmf; sh = shoulder. [b] In dmf solution, 2:1 and 1:2 electrolytes have Λ_M in the range 130–170 ohm^{-1} cm^2 mol^{-1}.

Syntheses of Complexes.—A general method was used for the synthesis of all $[NiL^1{}_2]^{2-}$ and $[Ni(H_2L^1)_2]^{2+}$ complexes. The complexes $[NiL^2]$ and $[NiL^3{}_2]$ were synthesised by treating $[NiL^1{}_2]^{2-}$ with 1,2-dibromoethane and iodomethane respectively in stoichiometric ratios. Details are given below for representative examples of each class.

*Sodium bis(quinoxaline-*2,3*-dithiolato)nickelate*(II), $Na_2[NiL^1{}_2]$. An ethanolic solution of nickel(II) chloride hexahydrate (310 mg, 1.3 mmol) was added to a warm ethanolic solution of Na_2L^1 (550 mg, 2.6 mmol), prepared from H_2L^1 and sodium metal in dry ethanol. The reaction mixture was heated to reflux for 1 h, then cooled and filtered through a G-4 frit. Upon subsequent concentration of the filtrate on a water-bath a deep red compound separated which was washed with diethyl ether and hexane and finally dried *in vacuo* over P_4O_{10}. Yield 85%. The potassium salt was prepared similarly from K_2L^1 {Found: C, 39.35; H, 1.70; N, 11.50; Ni, 12.10. Calc. for $Na_2[NiL^1{}_2]$, $C_{16}H_8N_4Na_2NiS_4$: C, 39.30; H, 1.65; N, 11.45; Ni, 12.00. Found: C, 37.00; H, 1.55; N, 10.70; Ni, 11.30. Calc. for $K_2[NiL^1{}_2]$, $C_{16}H_8K_2N_4NiS_4$: C, 36.85; H, 1.55; N, 10.75; Ni, 11.25%}.

*Bis(quinoxaline-*2,3*-dithione)nickel*(II) *chloride*, $[Ni(H_2L^1)_2]Cl_2$. To a solution of $Na_2[NiL^1{}_2]$ (400 mg, 0.818 mmol) in dry ethanol (40 cm^3) was added dilute HCl (HCl : water, 1 : 1) dropwise under magnetic stirring until the solution was strongly acidic. Thin needles precipitated immediately from the green solution. Stirring was continued for 30 min after the addition of acid was complete. The precipitated complex was collected by filtration, washed thoroughly with water and ethanol and dried *in vacuo* over P_4O_{10}. Yield 70%. The corresponding perchlorate salt was prepared from $Na_2[NiL^1{}_2]$ and $HClO_4$ {Found: C, 37.00; H, 2.35; N, 10.75; Ni, 11.40. Calc. for $[Ni(H_2L^1)_2]Cl_2$, $C_{16}H_{12}Cl_2N_4NiS_4$: C, 37.10; H, 2.30; N, 10.80; Ni, 11.35. Found: C, 29.80; H, 1.90; N, 8.70; Ni, 9.10. Calc. for $[Ni(H_2L^1)_2][ClO_4]_2$, $C_{16}H_{12}Cl_2N_4NiO_8S_4$: C, 29.75; H, 1.85; N, 8.65; Ni, 9.10%}. **CAUTION**: While we encountered no accidents with $[Ni(H_2L^1)_2][ClO_4]_2$, perchlorate salts of metal complexes with organic ligands are potentially explosive.[6] Care should be exercised in their handling.

[(3,3′*-Ethylenedithio)diquinoxaline-*2*-thiolato*]*nickel*(II) $[NiL^2]$. An ethanolic solution of 1,2-dibromoethane (100 mg, 0.532 mmol) was added to an ethanolic solution of $Na_2[NiL^1{}_2]$ (200 mg, 0.409 mmol) and heated to reflux for 1.5 h during which time the solution changed from red to brown. After cooling the solution was filtered through a G-4 frit and on concentration a dark brown compound separated which was washed thoroughly with water and ethanol and finally dried *in vacuo* over P_4O_{10}. Yield 70%. The complex $[NiL^3{}_2]$ containing the monomethylated derivative of H_2L^1 was prepared similarly from iodomethane {Found: C, 45.85; H, 2.55; N, 11.90; Ni, 12.50. Calc. for $[NiL^2]$, $C_{18}H_{12}N_4NiS_4$: C, 45.90; H, 2.55; N, 11.90; Ni, 12.45. Found: C, 45.75; H, 3.00; N, 11.80; Ni, 12.45. Calc. for $[NiL^3{}_2]$, $C_{18}H_{14}N_4NiS_4$: C, 45.70; H, 2.95; N, 11.85; Ni, 12.40%}.

Results and Discussion

Syntheses.—The dark red anionic $[NiL^1{}_2]^{2-}$ and blue-green cationic $[Ni(H_2L^1)_2]^{2+}$ complexes (Table 1) were synthesised in excellent yields by stoichiometric reactions between H_2L^1 and appropriate nickel(II) salts in boiling ethanol with or without added ethanolic hydroxides. Acidification of $[NiL^1{}_2]^{2-}$ complexes with dilute acids also gives rise to $[Ni(H_2L^1)_2]^{2+}$ complexes. The anion $[NiL^1{}_2]^{2-}$ is already known[7] and can also be isolated as the tetrabutylammonium salt. We have also prepared the neutral complexes $[NiL^2]$ and $[NiL^3{}_2]$ according to equations (1) and (2) in ethanol. The

$$[NiL^1{}_2]^{2-} + BrCH_2CH_2Br \longrightarrow [NiL^2] + 2Br^- \qquad (1)$$

$$[NiL^1{}_2]^{2-} + 2MeI \longrightarrow [NiL^3{}_2] + 2I^- \qquad (2)$$

complexes are moderately soluble in chloroform, dmf or dmso and are stable for several days in solution in the presence of air and moisture. The tetrabutylammonium salt $[NBu_4]_2[NiL^1{}_2]$, however, is quite soluble in acetonitrile, dmf and dichloromethane. In protic solvents no oligomerisation occurs, in contrast to most nickel(II) thiolates.[8] Solution electrical conductivity measurements show the expected pattern. Magnetic moments in the solid state are consistent with a $d^8(S = 0)$ electronic configuration for the complexes.

Electronic Spectra.—The UV/VIS spectral data for the prepared complexes in dmf solution are given in Table 1. The very intense absorption bands in the visible region of these complexes are charge-transfer in nature and the expected d–d transitions are obscured. In planar bis(dithiolate) complexes of nickel(II), several d–d bands are found in the ranges 635–530 and 480–430 nm in ethanol.[8,9] The UV/VIS spectra of $Na_2[NiL^1{}_2]$ and $K_2[NiL^1{}_2]$ (Fig. 1) are similar and remain unchanged over several hours in dmf. All the cationic and anionic complexes have almost identical electronic spectra in solution pointing to the same type of co-ordination in each as opposed to six-co-ordinated nickel(II) complexes for cationic species of H_2L^1 reported earlier.[7a] This is also corroborated by the analytical and magnetic data (see above).

IR Spectra.—Dithiolate and dithione resonances for the bound ligands L^1 and H_2L^1 in the nickel(II) complexes may be confirmed from IR spectral data. Bands for the free ligand H_2L^1 in the region 810–830 cm^{-1} assigned to $\nu_{C=S}$ modes are shifted to lower frequencies (790–800 cm^{-1}) for $[Ni(H_2L^1)_2]Cl_2$ and $[Ni(H_2L^1)_2][ClO_4]_2$. This indicates co-ordination of the ligand to the metal through sulfur which diminishes the double bond character of C=S. The presence of a ν_{NH} band (3130–3150 cm^{-1}) indicates the thione form (**II**) of the ligand in the cationic complexes; bands at these frequencies are absent in the thiolate form of the ligand in the anionic $[NiL^1{}_2]^{2-}$ species.

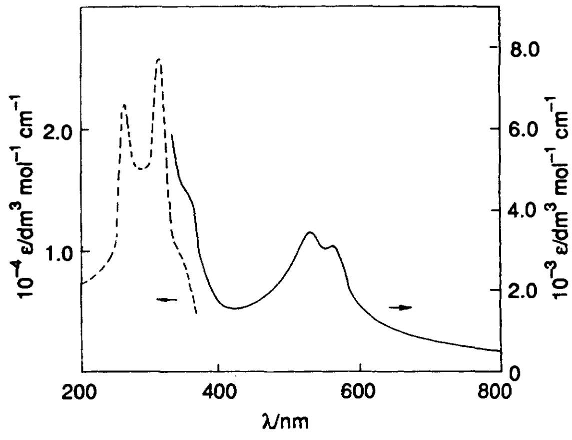


Fig. 1 Electronic spectra of $K_2[NiL^1{}_2]$ in dmf at 298 K

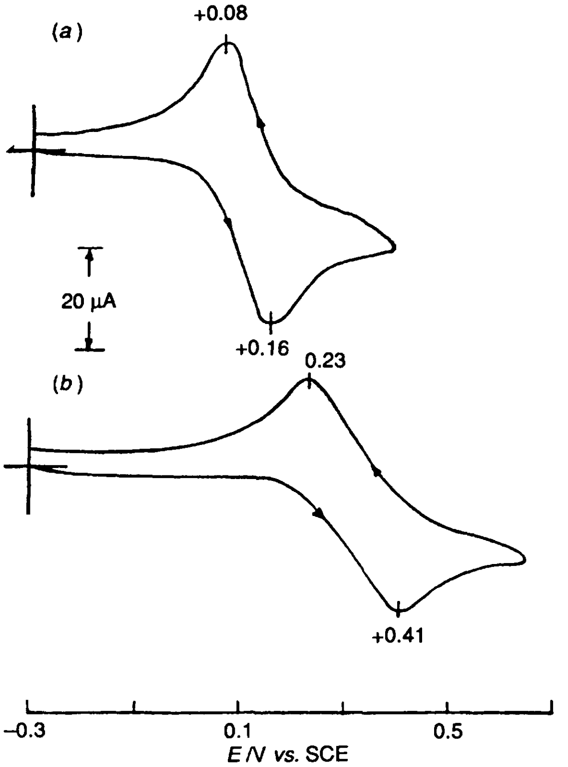


Fig. 2 Cyclic voltammograms (scan rate 50 mV s^{-1}) of 10^{-3} mol dm^{-3} solutions of (*a*) $Na_2[NiL^1{}_2]$, and (*b*) $[Ni(H_2L^1)_2]Cl_2$ in dmf (0.1 mol dm^{-3} NEt_4ClO_4) at a platinum electrode at 298 K

Table 2 Electrochemical data[a] and EPR *g* values[b]

	Ni^{III}–Ni^{II} couple				
Compound	$E_{\frac{1}{2}}{}^{c}$/V(n^d)	ΔE_p/mV	g_{xx}	g_{yy}	g_{zz}
$\{Na_2[NiL^1{}_2]\}^z$	0.12 (0.98)	80	2.299	2.054	2.036
$\{[Ni(H_2L^1)_2]Cl_2\}^z$	0.32 (1.03)	180	2.295	2.050	2.031

[a] Unless otherwise stated, the meaning of the symbols is as in the text. Solvent, dmf; supporting electrolyte, NEt_4ClO_4 (0.1 mol dm^{-3}); working electrode, platinum; reference electrode, SCE; solute concentration $\approx 10^{-3}$ mol dm^{-3}. [b] Measurements on electrogenerated $z = +1$ complexes in frozen dmf–toluene (1:1) (77 K). [c] Cyclic voltammetric data of $z = 0$ complexes at scan rate 50 mV s^{-1}: $E_{\frac{1}{2}}$ calculated as the average of anodic and cathodic peak potentials. [d] Constant potential coulometric data: $n = Q/Q'$, where Q is the observed coulomb count and Q' the calculated coulomb count for one-electron transfer.

Metal Redox Behaviour.—In order to investigate the suitability of the quinoxaline-2,3-dithiol ligand in stabilisation of the nickel(III) oxidation state towards reduction, and to explore the possibility of isolating the corresponding trivalent species, electrochemical studies were performed. The redox behaviour of the complexes has been examined by cyclic voltammetry in acetonitrile and dmf solutions.

An initial anodic scan in dmf solution reveals a well defined cyclic response (Fig. 2) due to the Ni^{III}–Ni^{II} couple for both $Na_2[NiL^1{}_2]$ and $[Ni(H_2L^1)_2]Cl_2$ [equations (3) and (4)]. The

$$[Ni^{III}L^1{}_2]^- + e \rightleftharpoons [Ni^{II}L^1{}_2]^{2-} \qquad (3)$$

$$[Ni^{III}(H_2L^1)_2]^{3+} + e \rightleftharpoons [Ni^{II}(H_2L^1)_2]^{2+} \qquad (4)$$

$E_{\frac{1}{2}}$ values, calculated from the average of the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials, are at 0.12 and 0.32 V *vs.* SCE respectively. At a scan rate of 50 mV s^{-1} the anodic and cathodic peak potential separations (ΔE_p) are 80 and 180 mV for the thiolate and thione complexes respectively, suggesting quasi-reversible one-electron processes (peak current function $i_p/v^{\frac{1}{2}}$ is dependent upon v, $i_{pa}/i_{pc} \approx 1$ at all scan rates). The $E_{\frac{1}{2}}$ values as well as coulometric data confirming one-electron stoichiometries are listed in Table 2. The electrode reactions are assigned to metal redox behaviour (EPR evidence, see below) and can be represented as in equations (3) and (4). No solvent dependent shifts in $E_{\frac{1}{2}}$ values were observed, with cyclic voltammetric data in acetonitrile essentially the same as in dmf. The excellent reversibility of voltammetric interconversions of oxidation states is a very strong indication that the nature and the geometry of the co-ordination sphere is conserved in the redox process.

For $[NiL^1{}_2]^{2-}$ coulometric oxidation at +0.32 V resulted in the passage of an average of 0.98 F (94555 C) of charge (three determinations) per mole of complex. Reduction at 0.08 V caused transfer of 95% of the charge passed in oxidation, indicating very little, if any, decay of the oxidised species over the 25 min period of the experiment. Thus, couples (3) and (4) are electrochemically quasi-reversible, chemically reversible processes in dmf solution.

The observed potential values are considerably lower than those generally found for non-biological nickel complexes, a situation consistent with the observation that thiolates stabilise metals in high formal oxidation states.[9,10] Indeed the lowest Ni^{II}–Ni^{III} potential has been found for bis(bicyclo[2.2.1]heptane-1,2-dithiolato)nickel(II), which undergoes metal-based oxidation to the trivalent state at $E_{\frac{1}{2}} = -0.76$ V *vs.* SCE in dmf.[9a]

The difference in reduction potentials (0.20 V) of $[NiL^1{}_2]^{-/2-}$ and $[Ni(H_2L^1{}_2]^{3+/2+}$, both of which have a planar NiS_4 group, arises mainly from the effects of less basic sulfur atoms in the latter. Low potentials are observed when the nickel centre is bonded to the anionic dithiolate form of the ligand compared to the dithione form. The observed trend $E_{\frac{1}{2}}([NiL_2]^{-/2-}) < E_{\frac{1}{2}}([Ni(H_2L^1)_2]^{3+/2+})$ is qualitatively consistent with the binding strength Ni–S (thiolate) > Ni–S (thione).[11] As more polarisable ligands are added to the nickel co-ordination sphere, the positive charge density on the nickel atom decreases, resulting in easier oxidation.

Electrogeneration and EPR Spectra of Nickel(III) *Species.*—Nickel(III) species are produced upon coulometric oxidation (Table 2) of the corresponding nickel(II) complexes in dmf solution. Solutions of $[NiL^1{}_2]^-$ and $[Ni(H_2L^1)_2]^{3+}$ are brown and greenish-brown. Upon one-electron reduction of the oxidised solutions the original nickel(II) species are regenerated. So far neither of the nickel(III) species has been isolated as the solid salt.

Frozen (77 K) solutions of the nickel(III) complexes display nearly axial EPR spectra with $g_{av} = 2.129$. A representative spectrum is shown in Fig. 3 and *g* values are listed in Table 2.

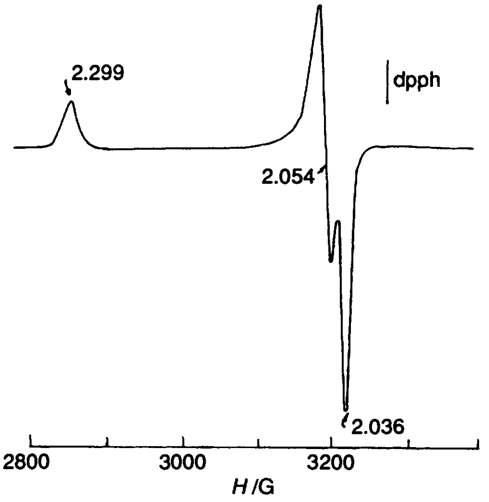
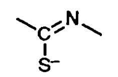


Fig. 3 X-Band (9.095 GHz) EPR spectrum of $[\mathrm{NiL^1}_2]^-$ in frozen (77 K) dmf–toluene (1 : 1); G = 10^{-4} T

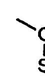
The g values lie considerably above 2, and the unpaired electron is evidently located in a predominantly metal [nickel(III), low-spin d^7] orbital. The large anisotropies and $g_{av} \gg 2$ demonstrate the nickel(III) formulation.

No nitrogen hyperfine structure is observed indicating non-co-ordination of solvent dmf molecules to the nickel centre. The nature of the EPR spectra of $[\mathrm{NiL^1}_2]^-$ and $[\mathrm{Ni(H_2L^1)_2}]^{3+}$ are similar. The two EPR resonances at higher fields are relatively closely spaced and can be considered as components of $g_\perp$. In this idealisation the oxidised complexes belong to the $g_\parallel > g_\perp$ class consistent with a square-planar nickel(III) complex in which the unpaired electron is in the d_{xy} orbital [$^2B_{2g}$ ground state].[12] The cumulative EPR spectral evidence is consistent with the formulation of the oxidised products as $[\mathrm{NiL_2}]^-$ and $[\mathrm{Ni(H_2L^1)_2}]^{3+}$ and the absence of axial ligands. The $g_\parallel > g_\perp$ type of EPR spectrum is very uncommon among nickel(III) complexes which are usually axially elongated [$g_\perp > g_\parallel$, $(d_{z^2})^1$ ground state].[9a,13] Obviously there is no direct correspondence between the observed g values for the present system and for the various spectra for hydrogenase enzymes.[2a,14]

Relative stabilisation of Ni^{III} by $>$C=S$\rightarrow$$>$C–S$^-$ replacement such as that reflected by the different $E_{\frac{1}{2}}$ values for the Ni^{III}–Ni^{II} couples of the cationic and anionic complexes reported here has not been observed previously for square-planar complexes of similar ligands. Stabilisation of Ni^{III} by $>$O(ether)$\rightarrow$$>$S(thioether) replacement has been observed previously for octahedral complexes.[11,15] The metal centred nature of the oxidation is due to a decrease in the electron donating properties of type **III** sulfurs *vs.* alkane thiolates[16] and is comparable to thiocarboxylate sulfurs of type **IV**.[10b] The presence of an imino function attached to the sulfur donor centre greatly affects the average ligand hardness.[17] The role of thiolate ligation in the promotion of metal redox reactions compared to thione co-ordination is thus established.



III



IV

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