Binding of Bi- and Tri-valent Nickel by Azophenolates incorporating Thioether/Ether Donor Sites†

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Nickel(II) complexes of tri- and hexa-dentate ligands in which the donors are azo nitrogen, phenolic oxygen and thioether sulfur or ether oxygen have been isolated. Structure determination of three complexes has established the presence of distorted octahedral $NiN_2O_2X_2$ (X = S or O) co-ordination spheres. In dichloromethane solution the nickel(III)–nickel(II) couple is electrochemically observable for the thioether complexes with $E_{\frac{1}{2}}$ in the range 0.65–0.85 V vs. saturated calomel electrode. The blue-violet nickel(III) species can be quantitatively electrogenerated in solution. Upon freezing (77 K) axial EPR spectra ($g_{\parallel} \approx 2.18$, $g_{\perp} \approx 2.06$) compatible with the uncommon hole configuration $(d_{x^2-y^2})^1$ are observed. The ether complexes are more difficult to oxidise and the nickel(III) species are not tractable. This is consistent with the higher strength of nickel–thioether compared to –ether binding.

Synthetic sulfur-ligated nickel complexes displaying trivalent–bivalent metal redox behaviour are of current interest in relation to nickel hydrogenases.[1,2] Only a few such species are known at present, the important ligand types being **1–4**. The case of dithiocarbamates[3,4] **3** has been known for some time and thioethers **2** were utilised by us a few years ago.[5] Subsequently other groups have been used: thiolates **1**,[6] dithiocarbonates **3**[7] and thiocarboxylates **4**.[8] The 1,2-dithiolene type species usually have highly delocalised oxidation levels.[9]
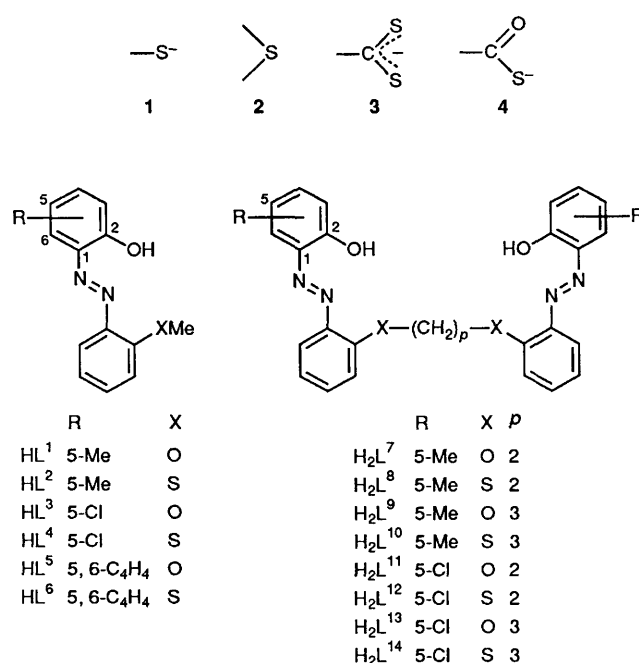
In this work we examine ligation by thioether sulfur present in multidentate configuration with phenolic oxygen and azo nitrogen. Nickel(II) complexes of co-ordination type $NiN_2O_2S_2$ have been isolated and structurally characterised. The nickel(III) congeners are electrogenerated and characterised in solution. The role of sulfur ligation in promotion of metal redox reactions is probed by replacing thioether sulfur with ether oxygen. The $Ni^{II}N_2O_4$ co-ordination sphere thus produced has been authenticated by structure determination. It does not however afford a characterisable nickel(III) analogue.

Results and Discussion

Synthesis of Ligands and Nickel(II) Complexes.—The ligands used in the present work are tridentate HL^{1-6} or hexadentate H_2L^{7-14}. These were synthesised via diazotisation of amines[10] followed by coupling with appropriate phenols.

The dark coloured nickel(II) complexes NiL_2 ($L = L^{1-6}$) and NiL ($L = L^{7-14}$) (Table 1) are formed in excellent yields by stoichiometric reactions between the ligand and nickel(II) acetate tetrahydrate in boiling acetone. They behave as two-electron paramagnets (Table 1). The co-ordination sphere $NiN_2O_2X_2$ is assigned to the entire family on the basis of three structure determinations.

Structures of $[NiL^8]$, $[NiL^{14}]$ *and* $[NiL^5]$.—Views of the three molecules are shown in Figs. 1–3 and selected bond parameters are listed in Table 2. The two thioether complexes will be considered first. In both cases the ligands bind the metal in hexadentate $N_2O_2S_2$ fashion. The co-ordination spheres are severely distorted from octahedral symmetry as can be seen from the angles at the metal centres. The bite angles of the chelate rings incorporating the two sulfur atoms show a large

R	X
HL¹ 5-Me	O
HL² 5-Me	S
HL³ 5-Cl	O
HL⁴ 5-Cl	S
HL⁵ 5,6-C₄H₄	O
HL⁶ 5,6-C₄H₄	S

	R	X	p
H₂L⁷	5-Me	O	2
H₂L⁸	5-Me	S	2
H₂L⁹	5-Me	O	3
H₂L¹⁰	5-Me	S	3
H₂L¹¹	5-Cl	O	2
H₂L¹²	5-Cl	S	2
H₂L¹³	5-Cl	O	3
H₂L¹⁴	5-Cl	S	3

increase with increasing ring size from five- to six-membered: 86.4(1)° in $[NiL^8]$ to 96.7(1)° in $[NiL^{14}]$. In the latter complex the metal ion is located on a crystallographic two-fold axis. The central carbon of the trimethylene bridge is disordered in two orientations (inset in Fig. 2) such that the mean position lies on the same axis.

The ligands bind in two meridional segments of NOS type. Each NiNOS fragment is planar (mean deviation <0.03 Å). The six-membered azophenolate and the five-membered azo-thioether chelate rings are also planar (mean deviation <0.08 Å). The dimethylene bridge in $[NiL^8]$ has a *gauche* configuration as revealed by the torsion angle S(1)–C(14)–C(15)–S(2) −53.4(1)°.

The Ni–S distance in $[NiL^{14}]$ is slightly shorter than those in $[NiL^8]$, but all the observed values fall well within the range (2.39–2.44 Å) that covers most pseudo-octahedral nickel(II) complexes involving thioether co-ordintion.[11]

We now turn to $[NiL^5_2]$. Among the ether complexes prepared by us only this compound afforded X-ray-quality

crystals but even these diffracted relatively weakly. The NiN_2O_4 co-ordination sphere incorporates ether binding. The $NiNO_2$ fragments are planar (mean deviation <0.04 Å) and so are all the chelate rings (mean deviation <0.07 Å). The ether binding is evidently quite weak, the Ni–O(ether) distance being longer than the average Ni–O(phenol) distance by a remarkable 0.2 Å. A similar disparity in Ni–O distances has been observed.[12] In a pseudo-octahedral salicylideneimine nickel(II) complex where phenolato and ether co-ordination coexist.

Thioethers are relatively poor co-ordinating agents[13] and bind nickel only very weakly unless other compelling factors like macrocyclic ligation are present.[11,14] In complexes of the present ligands, thioether co-ordination is strengthened by multiple chelation implicit in tri- and hexa-dentate ligation. The chelate effect is strong enough even to sustain ether co-ordination although ethers are even weaker than thioethers as ligands for transition-metal ions.[15a] This order of binding strength is reflected in the redox behaviour of the complexes (see below).

Table 1 Analytical[a] and magnetic moment data[b]

| Compound | Analysis (%) | | | |
	C	H	N	μ_{eff}
[NiL¹]	62.25 (62.15)	4.75 (4.80)	10.35 (10.35)	3.22
[NiL²]	58.50 (58.65)	4.60 (4.55)	9.80 (9.80)	2.91
[NiL³]	53.70 (53.65)	3.50 (3.45)	9.50 (9.60)	3.17
[NiL⁴]	50.75 (50.85)	3.35 (3.25)	9.20 (9.10)	3.16
[NiL⁵]	66.50 (66.60)	4.20 (4.25)	9.20 (9.15)	3.21
[NiL⁶]	63.25 (63.30)	4.00 (4.05)	8.55 (8.70)	3.11
[NiL⁷]	62.25 (62.35)	4.50 (4.45)	10.25 (10.40)	3.14
[NiL⁸]	59.00 (58.85)	4.30 (4.20)	9.80 (9.80)	3.05
[NiL⁹]	62.80 (62.95)	4.65 (4.70)	10.20 (10.15)	3.14
[NiL¹⁰]	59.40 (59.50)	4.50 (4.45)	9.50 (9.55)	3.05
[NiL¹¹]	53.95 (53.80)	3.10 (3.10)	9.55 (9.65)	3.16
[NiL¹²]	51.15 (51.00)	3.05 (2.95)	9.05 (9.15)	3.04
[NiL¹³]	54.70 (54.35)	3.30 (3.35)	9.40 (8.45)	2.82
[NiL¹⁴]	51.70 (51.80)	3.25 (3.20)	9.05 (8.95)	3.25

[a] Calculated values are in parentheses. [b] In the solid state at 298 K.

Metal Redox Behaviour.—The redox behaviour of the complexes has been examined cyclic voltammetrically in dichloromethane solution. All the complexes with a $NiN_2O_2S_2$ co-ordination sphere display a quasireversible (peak-to-peak separation 150–260 mV) one-electron cyclic response. Representative voltammograms are shown in Fig. 4. All potentials are referred to the saturated calomel electrode (SCE). The $E_{\frac{1}{2}}$ values as well as coulometric data confirming a one-electron stoichiometry are listed in Table 3.

The electrode reaction is assigned to metal redox behaviour (EPR evidence, see below) and can be represented as in equations (1) and (2). The $E_{\frac{1}{2}}$ values of the couples lie in the

$$[NiL^{1-6}_2] \longrightarrow [NiL^{1-6}_2]^+ + e \qquad (1)$$

$$[NiL^{7-14}] \longrightarrow [NiL^{7-14}]^+ + e \qquad (2)$$
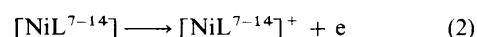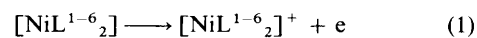
range 0.65–0.85 V. For a given R group the $E_{\frac{1}{2}}$ values show no large variation between the two series of complexes. The R substituents electronically affect the formal potential in the expected manner. Thus R = Me significantly lowers the potential compared to R = Cl.

Nickel(III)–nickel(II) reduction potential data are now available for a few complexes involving thioether co-ordination. These span the range 0.6–0.8 V.[5,15] Potentials lower than these are observed for complexes of the anionic ligand types **1**, **3** and **4**.[6–8] In nickel hydrogenases the potential lies below −0.4 V.[1,2]

The electrochemical behaviour of the ether complexes is quite different from that of the thioether species (Fig. 4). The anodic current begins to increase progressively above ≈0.7 V and there are signs of a very ill defined anodic response near 1 V not associated with a cathodic counterpart on scan reversal. If the anodic current is at all due to metal oxidation the oxidised complex must be very unstable. In any case it is clear that the nickel(III)–nickel(II) $E_{\frac{1}{2}}$ values for the ether complexes must lie higher than those of the thioether congeners.

The $E_{\frac{1}{2}}$ of a couple depends on several enthalpy and entropy terms. Among similarly constituted molecules a number of these terms remain more or less invariant, affording equation (3).[16]
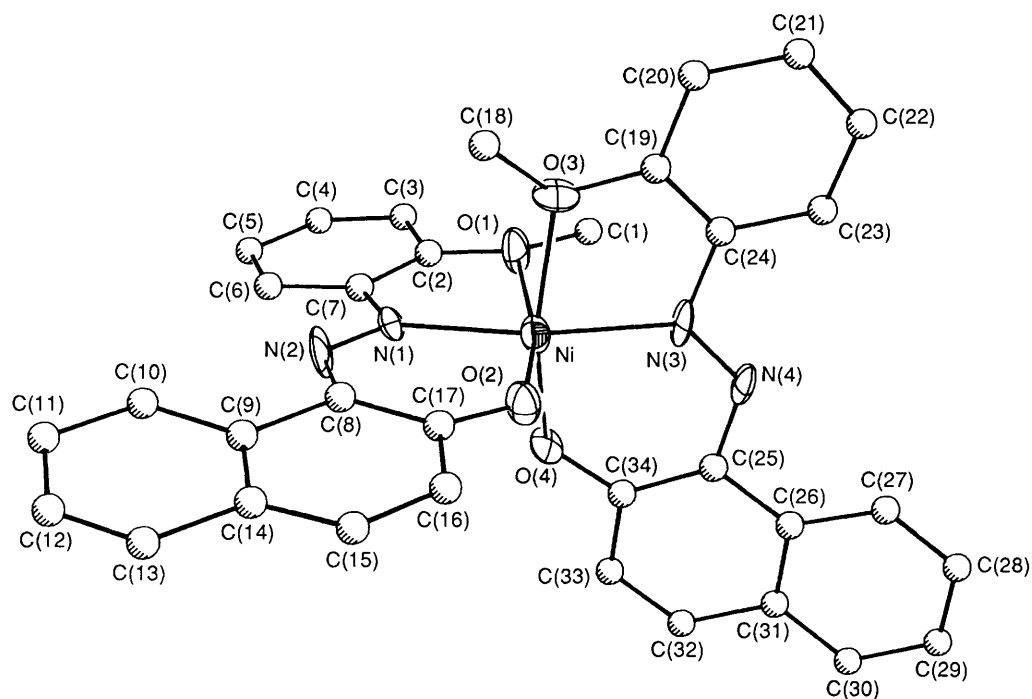
$$E_{\frac{1}{2}} = -\Delta H_f^{\circ}/F + k \qquad (3)$$
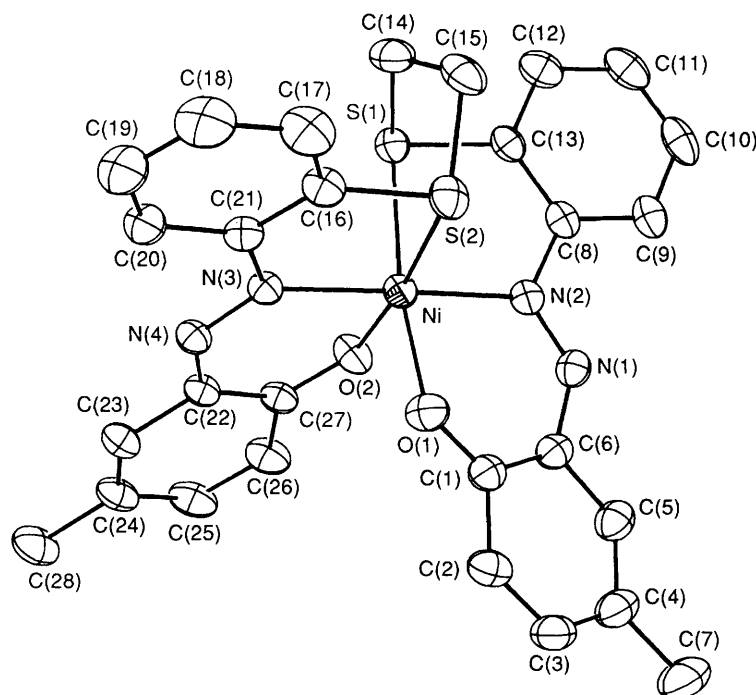
Fig. 1 Perspective view and atom labelling scheme of [NiL⁸]. Atoms are shown as 50% thermal probability ellipsoids
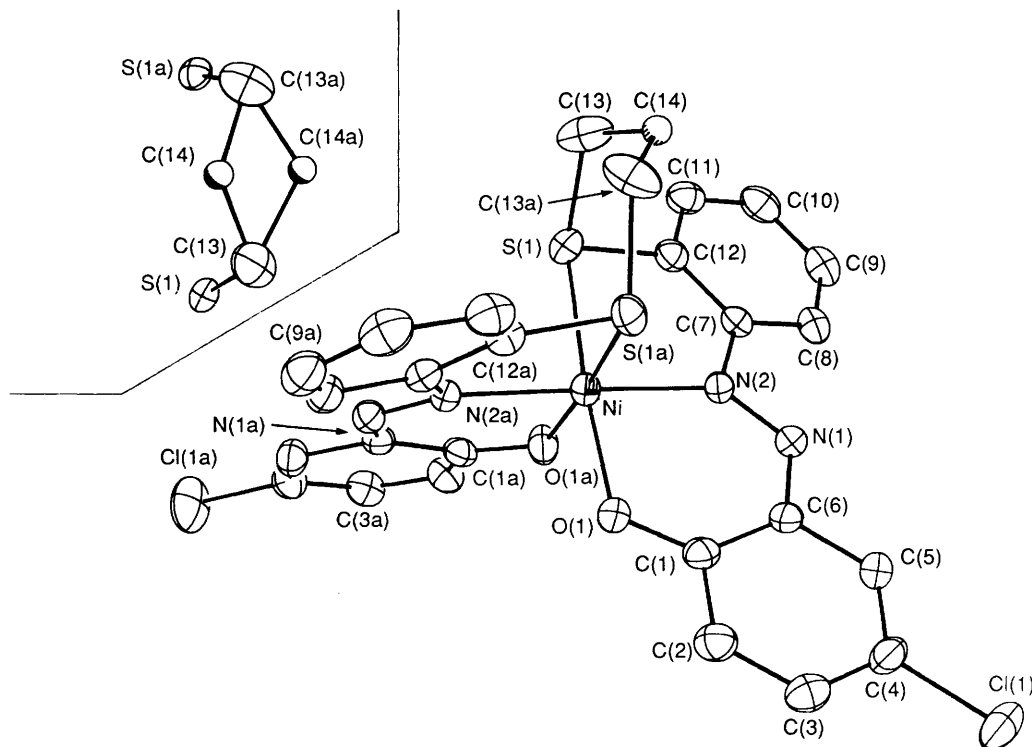
Fig. 2 Perspective view and atom labelling scheme of [NiL^{14}]. Atoms are shown as 50% thermal probability ellipsoids except for the disordered C(14) whose two orientations are shown in the inset

Fig. 3 Perspective view and atom labelling scheme of [NiL$^5_2$]. Non-carbon atoms are shown with 50% thermal probability ellipsoids

Here F is the Faraday constant, k a constant and ΔH_f° the difference between the enthalpies of formation of the reduced and oxidised complexes. Since the enthalpy of formation of the oxidised complex will generally be more negative, ΔH_f° is expected to be positive (endothermic), the more so when bonds are stronger. The observed trend $E_{\frac{1}{2}}(\text{NiN}_2\text{O}_2\text{S}_2) < E_{\frac{1}{2}}(\text{NiN}_2\text{O}_4)$ is qualitatively consistent with the binding strength Ni–S(thioether) > Ni–O(ether).

Electrogeneration and EPR Spectra of Nickel(III) *Species.*— Blue-violet solutions of thioether nickel(III) species are pro-

duced upon coulometric oxidation (Table 3) of the corresponding nickel(II) complexes in dichloromethane solution. The tridentate nickel(III) complexes are thermally less stable and for these coulometry was performed at 258 K. The hexadentate complexes were generated at 298 K without decomposition. Upon one-electron reduction of the oxidised solutions the original nickel(II) species are regenerated. None of the nickel(III) species as salts has been isolated so far.

Frozen solutions (77 K) of the nickel(III) complexes display axial EPR spectra. A representative spectrum is shown in Fig. 5 and g values are listed in Table 3. The g values lie considerably

Table 2 Selected bond distances (Å) and angles (°)[a]

(i) [NiL⁸]

Ni–S(1)	2.436(2)	Ni–S(2)	2.418(2)
Ni–N(2)	2.031(4)	Ni–N(3)	2.027(4)
Ni–O(1)	1.986(4)	Ni–O(2)	1.972(4)
S(1)–Ni–S(2)	86.4(1)	S(1)–Ni–N(2)	83.3(1)
S(1)–Ni–N(3)	97.3(1)	S(1)–Ni–O(1)	171.9(1)
S(1)–Ni–O(2)	92.0(1)	S(2)–Ni–N(2)	97.6(1)
S(2)–Ni–N(3)	84.7(1)	S(2)–Ni–O(1)	90.0(1)
S(2)–Ni–O(2)	174.5(1)	N(2)–Ni–N(3)	177.6(1)
N(2)–Ni–O(1)	90.0(1)	N(2)–Ni–O(2)	87.3(1)
N(3)–Ni–O(1)	89.5(1)	N(3)–Ni–O(2)	90.3(1)
O(1)–Ni–O(2)	92.3(1)		

(ii) [NiL¹⁴][b]

Ni–S(1)	2.396(2)	Ni–N(2)	2.038(3)
Ni–O(1)	1.973(4)		
S(1)–Ni–S(1a)	96.7(1)	S(1)–Ni–N(2)	84.8(1)
S(1)–Ni–N(2a)	96.4(1)	S(1)–Ni–O(1)	175.1(1)
S(1)–Ni–O(1a)	84.3(1)	N(2)–Ni–N(2a)	178.2(2)
N(2)–Ni–O(1)	90.4(1)	N(2)–Ni–O(1a)	88.4(1)
O(1)–Ni–O(1a)	95.2(2)		

(iii) [NiL⁵₂]

Ni–N(1)	2.005(11)	Ni–N(3)	1.999(13)
Ni–O(1)	2.164(8)	Ni–O(2)	1.967(10)
Ni–O(3)	2.158(11)	Ni–O(4)	1.978(10)
O(1)–Ni–O(2)	166.0(4)	O(1)–Ni–O(3)	86.4(4)
O(1)–Ni–O(4)	89.6(4)	O(1)–Ni–N(1)	78.5(4)
O(1)–Ni–N(3)	95.1(4)	O(2)–Ni–O(3)	88.7(4)
O(2)–Ni–O(4)	97.8(4)	O(2)–Ni–N(1)	89.0(4)
O(2)–Ni–N(3)	96.7(4)	O(3)–Ni–O(4)	167.2(4)
O(3)–Ni–N(1)	95.5(5)	O(3)–Ni–N(3)	78.7(5)
O(4)–Ni–N(1)	95.5(4)	O(4)–Ni–N(3)	89.6(5)
N(1)–Ni–N(3)	171.7(5)		

[a] Estimated standard deviations of the least significant digits are given in parentheses. [b] S(1a), N(2a) and O(1a) are the symmetry equivalents of S(1), N(2) and O(1) respectively.
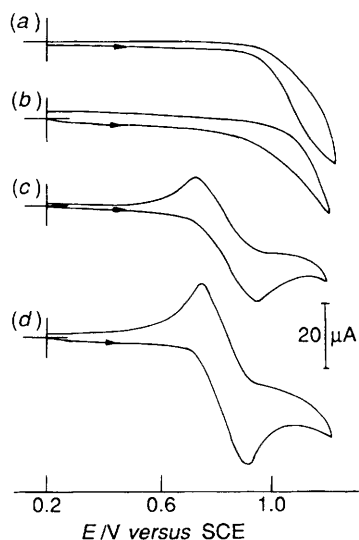

Fig. 4 Cyclic voltammograms (scan rate 50 mV s⁻¹) of $\approx 10^{-3}$ mol dm⁻³ solutions of (a) [NiL³₂], (b) [NiL¹³], (c) [NiL⁴₂] and (d) [NiL¹⁴] in dichloromethane (0.1 mol dm⁻³ NEt₄ClO₄) at a platinum electrode at 298 K

Table 3 Electrochemical data[a] and EPR g values[b]

	Ni^{III}–Ni^{II} couple		
Compound	$E_{\frac{1}{2}}{}^{c}/V(n)^{d}$	$g_{\parallel}$	$g_{\perp}$
[NiL²₂]ᶻ	0.70 (0.97)	2.187	2.070
[NiL⁴₂]ᶻ	0.84 (0.99)	2.185	2.073
[NiL⁶₂]ᶻ	0.65 (1.03)	2.202	2.083
[NiL⁸]ᶻ	0.71 (1.05)	2.183	2.063
[NiL¹⁰]ᶻ	0.65 (0.98)	2.184	2.070
[NiL¹²]ᶻ	0.80 (0.97)	2.180	2.060
[NiL¹⁴]ᶻ	0.82 (0.98)	2.180	2.064

[a] Unless otherwise stated, the meaning of the symbols is as in the text. Solvent, dichloromethane; supporting electrolyte, NEt₄ClO₄ (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 dichloromethane (77 K). [c] Cyclic voltammetric data on $z = 0$ 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.
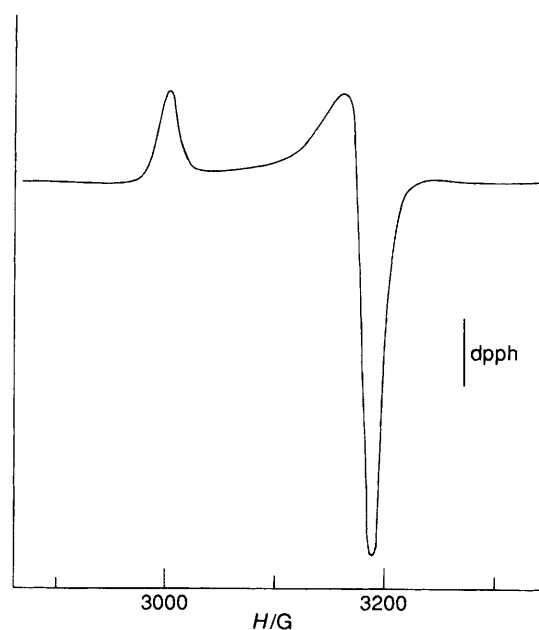
Fig. 5 X-Band (9.105 GHz) EPR spectrum of [NiL⁸]⁺ in frozen (77 K) dichloromethane; G = 10⁻⁴ T

compression and a $(d_{x^2-y^2})^1$ ground state.[17] This type is very uncommon among nickel(III) complexes which are usually axially elongated $[g_{\perp} > g_{\parallel}, (d_{z^2})^1$ ground state].[6c,15] The nickel hydrogenases also belong to the latter type.[1,2] For example, the Ni–C form of the *Desulfovibrio gigas* hydrogenase has $g_{\perp}$ components at 2.19, 2.16 and $g_{\parallel} = 2.02$.[18]

Conclusion

The main findings of this research are that stable Ni^{II}N₂O₂X₂ (X = O or S) complexes incorporating thioether/ether co-ordination have been obtained. The thioether complexes alone undergo facile electrooxidation affording EPR characterisable Ni^{III}N₂O₂S₂ species which have the uncommon $(d_{x^2-y^2})^1$ ground state. The efficacy of thioether as opposed to ether binding in promotion of metal oxidation is in line with the binding order Ni–S(thioether) > Ni–O(ether).

above 2, and the unpaired electron is evidently located in a predominantly metal [nickel(III), low-spin d^7] orbital. The spectrum belong to the $g_{\parallel} > g_{\perp}$ type corresponding to axial

Experimental

Materials.—All chemicals used for synthesis were of com-

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Table 4 Atomic coordinates ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
(a) [NiL⁸]							
Ni	3440(1)	1258(1)	3466(1)	C(11)	7121(3)	4937(3)	8066(2)
S(1)	5196(1)	1451(1)	5250(1)	C(12)	6790(3)	3692(3)	7316(2)
S(2)	5652(1)	1813(1)	2853(1)	C(13)	5625(3)	3058(2)	6199(2)
N(1)	2681(2)	3541(2)	4552(2)	C(14)	6919(3)	1460(3)	4800(2)
N(2)	3623(2)	2997(2)	4665(2)	C(15)	7246(3)	2220(2)	4171(3)
N(3)	3169(2)	−505(2)	2276(2)	C(16)	5484(3)	269(2)	1854(2)
N(4)	1992(2)	−1487(2)	1860(2)	C(17)	6536(3)	85(3)	1226(3)
O(1)	2162(2)	1353(2)	2107(1)	C(18)	6422(3)	−1086(3)	421(3)
O(2)	1658(2)	650(2)	3923(1)	C(19)	5266(3)	−2084(3)	254(3)
C(1)	1381(3)	2069(2)	2285(2)	C(20)	4208(3)	−1920(2)	868(2)
C(2)	276(3)	1907(2)	1258(2)	C(21)	4284(2)	−733(2)	1665(2)
C(3)	−545(3)	2662(3)	1371(3)	C(22)	769(2)	−1453(2)	2290(2)
C(4)	−375(3)	3648(3)	2509(3)	C(23)	−459(3)	−2612(2)	1667(2)
C(5)	675(3)	3836(2)	3520(3)	C(24)	−1794(3)	−2778(2)	1936(2)
C(6)	1583(3)	3086(2)	3452(2)	C(25)	−1942(3)	−1751(3)	2869(3)
C(7)	−1288(4)	4486(3)	2601(3)	C(26)	−807(3)	−628(3)	3492(2)
C(8)	4767(3)	3668(2)	5838(2)	C(27)	620(2)	−414(2)	3259(2)
C(9)	5099(3)	4923(2)	6620(2)	C(28)	−3107(3)	−3998(3)	1271(3)
C(10)	6272(3)	5541(2)	7719(2)				
(b) [NiL¹⁴]							
Ni	5000	3594(1)	2500	C(5)	3231(3)	2382(3)	−2019(4)
Cl(1)	2988(1)	1423(1)	−4026(1)	C(6)	3775(3)	2726(2)	−640(4)
S(1)	4435(1)	4643(1)	3243(1)	C(7)	2834(3)	3997(3)	603(4)
O(1)	5348(2)	2717(2)	1740(3)	C(8)	1821(3)	3900(3)	−532(4)
N(1)	3187(2)	3206(2)	−522(3)	C(9)	1161(3)	4313(3)	−494(5)
N(2)	3561(2)	3573(2)	654(3)	C(10)	1478(3)	4820(3)	641(5)
C(1)	4799(3)	2502(3)	434(4)	C(11)	2472(3)	4917(3)	1774(5)
C(2)	5209(3)	1980(3)	5(5)	C(12)	3155(3)	4508(3)	1762(4)
C(3)	4664(3)	1679(3)	−1335(5)	C(13)	4581(4)	5800(3)	3040(6)
C(4)	3667(4)	1874(3)	−2345(4)	C(14)	4546(7)	6030(6)	1873(9)
(c) [NiL⁵₂]							
Ni	1965(2)	4090(2)	2483(1)	C(14)	5006(12)	1229(13)	2127(8)
N(1)	1827(9)	3103(10)	1574(6)	C(15)	5396(13)	1784(13)	2821(9)
N(2)	2421(10)	2380(11)	1436(6)	C(16)	4845(12)	2477(13)	3105(9)
N(3)	1901(9)	4995(11)	3382(7)	C(17)	3790(12)	2771(14)	2675(9)
N(4)	2260(8)	5966(12)	3604(5)	C(18)	1467(15)	1667(16)	3055(10)
O(1)	385(7)	4367(8)	1821(5)	C(19)	1268(11)	3278(14)	3767(9)
O(2)	3347(7)	3484(9)	2955(5)	C(20)	911(11)	2653(14)	4270(8)
O(3)	1400(8)	2853(9)	3110(5)	C(21)	818(12)	3175(13)	4915(9)
O(4)	2350(8)	5467(8)	2032(5)	C(22)	1033(10)	4297(13)	5060(8)
C(1)	−237(12)	5222(14)	1995(9)	C(23)	1347(9)	4924(13)	4542(7)
C(2)	144(11)	3938(13)	1096(8)	C(24)	1493(10)	4414(12)	3894(7)
C(3)	−763(11)	4167(14)	536(8)	C(25)	2674(10)	6637(13)	3163(7)
C(4)	−946(12)	3694(13)	−187(9)	C(26)	3084(10)	7712(12)	3500(7)
C(5)	−236(12)	2995(14)	−325(9)	C(27)	3151(10)	7952(13)	4255(8)
C(6)	684(12)	2772(13)	241(8)	C(28)	3543(11)	8963(15)	4571(8)
C(7)	900(11)	3254(12)	967(8)	C(29)	3862(11)	9790(14)	4147(8)
C(8)	3359(11)	2192(12)	1962(8)	C(30)	3830(11)	9563(13)	3418(8)
C(9)	3989(11)	1379(11)	1686(8)	C(31)	3419(12)	8505(14)	3085(8)
C(10)	3559(12)	756(13)	1004(8)	C(32)	3414(12)	8232(14)	2330(9)
C(11)	4195(13)	10(15)	757(9)	C(33)	3046(10)	7262(14)	2004(8)
C(12)	5184(14)	−83(15)	1184(9)	C(34)	2660(11)	6392(13)	2403(8)
C(13)	5609(13)	483(13)	1825(9)				

mercial reagent grade and were employed without further purification. The preparation of tetraethylammonium perchlorate and purification of dichloromethane for electrochemical/spectroscopic work were done as before.[19a]

Physical Measurements.—Microanalytical data (C, H, N) were obtained with a Perkin-Elmer model 240C elemental analyser. Electrochemical measurements were done using the PAR model 370-4 electrochemistry system as before.[19b] The EPR spectra were recorded in the X-band with a Varian E-109C spectrometer fitted with a quartz Dewar flask for measurements at 77 K (liquid nitrogen), and calibrated with diphenylpicrylhydrazyl (dpph) ($g = 2.0037$).

Synthesis of Ligands.—2-(Methylthio)aniline, 1,2-bis(2-aminophenylthio)ethane, 1,3-bis(2-aminophenylthio)propane, 1,2-bis(2-aminophenoxy)ethane and 1,3-bis(2-aminophenoxy)propane were prepared following reported methods.[10] All the ligands were synthesised using the same general method. The details for one representative preparation are given below.

1,2-*Bis*[o-(2-*hydroxy*-5-*methylphenylazo*)*phenylthio*]*ethane*, H_2L^8. 1,2-Bis(2-aminophenylthio)ethane (3.50 g) in concentrated HCl (8 cm³) and water (8 cm³) was diazotised at 0 °C with NaNO₂ (2.50 g) in water (10 cm³). Separately, p-cresol (2.80 g) was dissolved in 20% NaOH (20 cm³) at 0 °C. The diazotised solution was then slowly added to the cold alkaline solution of p-cresol with vigorous stirring. Stirring

was continued for 30 min after the addition was complete. The whole mixture was then kept under refrigeration for 1 h. The precipitated ligand was collected by filtration, washed thoroughly with water and dried *in vacuo* over P_4O_{10}. It was then recrystallised from 90% ethanol. Yield 4.30 g (Found: C, 65.30; H, 5.00; N, 10.70. Calc. for $C_{28}H_{26}N_4O_2S_2$: C, 65.35; H, 5.05; N, 10.90%).

Synthesis of Complexes.—The same general procedure was followed for all the complexes. Details for one representative case are given below.

[NiL^8]. An aqueous solution of nickel(II) acetate tetrahydrate (150 mg, 0.602 mmol) was added to a warm acetone solution of H_2L^8 (310 mg, 0.603 mmol). The reaction mixture was heated to reflux for 1 h. Upon subsequent concentration the deep red-violet crystalline complex separated, was washed with ethanol and hexane and dried *in vacuo* over P_4O_{10}. Yield 65%.

X-Ray Structure Determinations.—Single crystals of all three compounds were grown by slow diffusion of hexane into dichloromethane solutions.

Crystal data. [NiL^8], $C_{28}H_{24}N_4NiO_2S_2$, $M = 571.3$, triclinic, space group $P\bar{1}$, $a = 9.544(2)$, $b = 12.607(3)$, $c = 12.735(3)$ Å, $\alpha = 114.78(2)$, $\beta = 103.97(2)$, $\gamma = 99.98(2)°$, $U = 1283.0(5)$ Å^3 (by least-squares refinement of diffractometer centred reflections), $Z = 2$, $D_c = 1.486$ g cm^{-3}, dark parallelopiped ($0.68 \times 0.20 \times 0.20$ mm), μ(Mo-Kα) = 9.52 cm^{-1}, $\lambda = 0.710\ 73$ Å, $F(000) = 592$.

[NiL^{14}], $C_{27}H_{20}Cl_2N_4NiO_2S_2$, $M = 626.2$, monoclinic, space group $C2/c$, $a = 18.106(6)$, $b = 15.212(5)$, $c = 12.687(4)$ Å, $\beta = 131.59(2)°$, $U = 2613(1)$ Å^3 (by least-squares refinement of diffractometer angles for 25 automatically centred reflections), $Z = 4$, $D_c = 1.590$ g cm^{-3}, red prism ($0.24 \times 0.30 \times 0.20$ mm), μ(Mo-Kα) = 11.38 cm^{-1}, $\lambda = 0.710\ 73$ Å, $F(000) = 1280$.

[$NiL^5{}_2$], $C_{34}H_{26}N_4NiO_4$, $M = 613.3$, monoclinic, space group $P2/a$, $a = 13.796(6)$, $b = 11.845(4)$, $c = 18.446(7)$ Å, $\beta = 108.25(3)°$, $U = 2863(2)$ Å^3 (by least-squares refinement of diffractometer angles for 25 automatically centred reflections), $Z = 4$, $D_c = 1.423$ g cm^{-3}, green prism ($0.14 \times 0.04 \times 0.22$ mm), μ(Mo-Kα) = 7.24 cm^{-1}, $\lambda = 0.710\ 73$ Å, $F(000) = 1272$.

Data collection and processing. Nicolet R3m/V diffractometer, θ–2θ scan method for [NiL^8] ($2 \leqslant 2\theta \leqslant 55°$), ω-scan method for [NiL^{14}] ($2 \leqslant 2\theta \leqslant 55°$) and [$NiL^5{}_2$] ($2 \leqslant 2\theta \leqslant 45°$), graphite-monochromated Mo-Kα radiation. 5519 Independent {4169 observed [$I > 3\sigma(I)$]} reflections for [NiL^8], 2992 {1595} for [NiL^{14}], 4813 {1318} for [$NiL^5{}_2$]. Corrected for Lorentz and polarisation factors in each case; semiempirical absorption correction (transmission 0.7511–0.9160, 0.7181–0.7404 and 0.8852–0.9434 respectively). Two standard reflections, monitored in each case, showed no significant variations.

Solution and refinement. The structures were solved by using direct methods and refined by full-matrix least-squares procedures. All non-hydrogen atoms for [NiL^8] and [NiL^{14}] (except the disordered carbon atom in the latter) were refined anisotropically. In the case of [$NiL^5{}_2$] only the atoms other than carbon and hydrogen were made anisotropic due to the limited number of observed data. Hydrogen atoms were included at calculated positions with isotropic thermal parameters (0.08 Å^2). The final residuals R and R' were 0.0306 and 0.0404, 0.0397 and 0.0452, and 0.0682 and 0.0699 respectively. The function minimised was $\Sigma w(|F| - |F_c|)^2$ with weights $w = 1/[\sigma^2(F) + 0.0007(F)^2]$, $1/[\sigma^2(F) + 0.0002(F)^2]$ and $1/[\sigma^2(F) + 0.0005(F)^2]$ respectively. The maximum and

minimum residual electron densities in the final ΔF map were 0.27 and -0.12, 0.31 and -0.35, and 0.45 and -0.66 e Å^{-3}. Positional parameters for the non-hydrogen atoms are collected in Table 4. Computations were carried out on a MicroVAX II computer using the SHELXTL-PLUS program system.[20]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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