Azonaphtholate Ligands for the Nickel(III) Cation: Design, Synthesis and Electrochemical Properties

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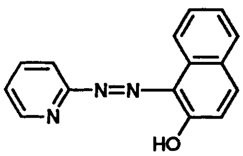
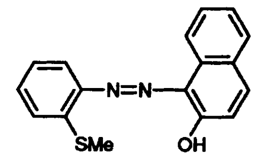
Nickel(II) complexes of tridentate meridionally spanning azonaphtholate ligands, 1-(2-pyridylazo)-2-naphthol (HL[1]) and 1-(2-methylsulfanylphenylazo)-2-naphthol (HL[2]), have been synthesised. The paramagnetic nickel(II) centres are six-co-ordinated, including the donor atoms of the pendant arms. In dichloromethane solution the nickel(III)–nickel(II) redox couple was observed by cyclic voltammetry for both the complexes $[NiL^1_2]$ and $[NiL^2_2]$, $E_{\frac{1}{2}}$ being +0.93 and +0.65 V respectively *versus* saturated calomel electrode. Constant-potential electrolysis generated the nickel(III) complexes in solution. In frozen (77 K) dichloromethane solution the nickel(III) complexes display axial EPR spectra ($g_{\parallel} \approx 2.20$, $g_{\perp} \approx 2.07$) indicating an axial compression and $(d_{x^2-y^2})^1$ ground state. The results demonstrate the significant role of the chelating nature of the ligands and thioether co-ordination in stabilising the trivalent nickel centre.

Interest in sulfur-bound trivalent nickel species[1,2] has grown enormously in recent years[3,4] largely due to the involvement of such species in hydrogenases, enzymes which catalyse the reversible oxidation of hydrogen.[5,6] Physical properties like redox potentials and EPR spectra are very helpful in establishing the nature of different biological nickel sites. Sulfur co-ordination is essential for these centres to be redox active. This characteristic physical property can be modelled by synthetic complexes involving sulfur-containing ligands bonded to nickel in various geometries. Although so far a considerable group of synthetic complexes have been reported, there is no quantitative estimate of the relative stabilisation of trivalent nickel complexes with pyridyl nitrogen or thioether sulfur atoms in the same co-ordination sphere.

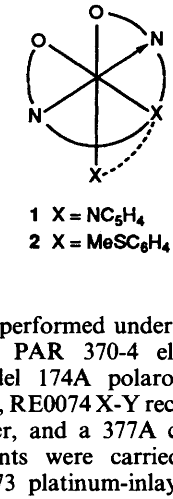
As a part of our ongoing research,[7] in this work we examine the role of pyridyl nitrogen ligation compared to thioether sulfur in generating the trivalent nickel centre. We describe nickel(II) complexes of types NiN_4O_2 **1** and $NiN_2O_2S_2$ **2** utilising substituted azonaphthols HL[1] and HL[2] as the tridentate meridionally spanning ligands. The redox properties of these complexes have been investigated and the one-electron oxidation products characterised in solution. Comparison of metal-centred redox potentials reveals that MeS co-ordination favours metal oxidation relative to 2-pyridyl co-ordination.



HL^1



HL^2



1 X = NC_5H_4
2 X = $MeSC_6H_4$

Experimental

Reagents, Solvents and Starting Materials.—Solvents and reagents were obtained from commercial sources and used without further purification unless otherwise stated. Commercial dichloromethane was purified as before[8,9] for electrochemical and spectroscopic work. Commercial tetraethylammonium bromide was converted into pure tetraethylammonium perchlorate by following an available procedure.[10] Dinitrogen gas was purified by successively bubbling it through alkaline dithionite and concentrated sulfuric acid. 1-(2-Pyridylazo)-2-naphthol (HL[1]) was obtained from Aldrich Chemical Company.

Physical Measurements.—Solution electrical conductivity and UV/VIS spectra were obtained using a Unitech type UI31C digital conductivity meter and a Shimadzu UV3100 UV/VIS/NIR spectrophotometer respectively. Magnetic susceptibilities in the solid state were measured with a Gouy balance fitted with a Polytronic d.c. power supply. Cyclic voltammetric measurements at 298 K were performed under a pure, dry dinitrogen atmosphere using a PAR 370-4 electrochemistry system incorporating a model 174A polarographic analyser, 175 universal programmer, RE0074 X-Y recorder, 173 potentiostat, 179 digital coulometer, and a 377A 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 the junction contribution. Low-temperature coulometric measurements were made with the help of a Haake F3-k digital cryostat and circulator connected to the jacketed cell bottoms. X-Band EPR spectra were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar flask for measurements at 77 K (liquid dinitrogen). 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 240C elemental analyser. Infrared spectra in the solid state (KBr discs) were recorded on a Perkin-Elmer 883 spectrophotometer.

Synthesis of HL[2].—2-(Methylsulfanyl)aniline was prepared following a reported method.[11] The compound 1-(2-methylsulfanylphenylazo)-2-naphthol (HL^2) was prepared as described previously.[4c]

Synthesis of Complexes.—A general method was used for the synthesis of both the $[NiL^1_2]$ and $[NiL^2_2]$ complexes. Details for $[NiL^1_2]$ are given below.

Bis[1-(2-*pyridylazo*)-2-*naphtholato*]*nickel*(II), $[NiL^1_2]$. An aqueous solution of nickel(II) acetate tetrahydrate (150 mg, 0.602 mmol) was added to a boiling acetone solution of HL^1 (300 mg, 1.200 mmol). The solution changed from orange-red to red-violet. The reaction mixture was heated to reflux for 1.5 h and filtered through a G-4 frit. Upon subsequent concentration of the filtrate on a water-bath the deep red-violet crystalline complex separated. It was washed with water, acetone and hexane and finally dried *in vacuo* over P_4O_{10}. Yield 70%. The complex $[NiL^2_2]$ was prepared similarly from HL^2 (Found: C, 64.80; H, 3.55; N, 15.21; Ni, 10.65. Calc. for $C_{30}H_{20}N_6NiO_2$: C, 64.90; H, 3.60; N, 15.15; Ni, 10.60. Found: C, 63.25; H, 4.00; N, 8.55; Ni, 9.15. Calc. for $C_{34}H_{26}N_4NiO_2S_2$: C, 63.30; H, 4.05; N, 8.70; Ni, 9.10%).

Results and Discussion

Synthesis and Characterisation of Bivalent Nickel Complexes.—The tridentate compounds were synthesised *via* diazotisation of amines[11] followed by coupling with 2-naphthol. The dark red-violet nickel(II) complexes $[NiL_2]$ ($L = L^1$ or L^2) were synthesised in excellent yields by stoichiometric reactions between the naphthols and nickel(II) acetate tetrahydrate in boiling acetone. Selected characterisation data are given in Table 1. The complexes behave as two-electron paramagnets consistent with a d^8 ($S = 1$) ground-state electronic configuration. Solution electrical conductivity measurements revealed non-electrolyte behaviour.

The ligands bind the metal centre in two meridional segments, giving N_4O_2 and $N_2O_2S_2$ octahedral geometries. Although thioether co-ordination occurs in biological systems, under normal circumstances thioether ligands co-ordinate only weakly with the first row transition elements in their usual oxidation states.[12] From the crystal structure[4c] of the methoxy analogue of $[NiL^2_2]$, it is presumed that six-membered azonaphtholate and five-membered azothioether rings are formed after co-ordination, but for $[NiL^1_2]$ both are five membered and pyridine nitrogen has been incorporated in the co-ordination sphere. In $[NiL^2_2]$ the five-membered azothioether ring strengthens the donor ability of the thioether sulfur which is reflected in the redox behaviour of the complexes (see below).

The complexes are soluble in dichloromethane, chloroform, dimethylformamide or Me_2SO. Several studies of the kinetics of chelation of nickel(II) by pyridylazo ligands in solution have appeared,[13] but little is known about the stoichiometry and composition of the compounds isolated in the solid state. The simple 1-(phenylazo)-2-naphthol ligand[14] forms a diamagnetic bis(chelate) complex with nickel(II) which has no ability to expand its co-ordination sphere through adduct formation with neutral nitrogen-donor ligands, *e.g.* pyridine and imidazole. Formation of tris(chelate) species with another bidentate ligand is also not possible. However if a pyridine ring is incorporated within the azonaphthol framework it can co-ordinate the metal centre. Such a modification of the ligand design helps us to synthesise a six co-ordinated paramagnetic nickel(II) compound which is otherwise difficult to obtain.

Absorption Spectra.—The UV/VIS spectral data for the synthesised complexes in dichloromethane solutions are given in Table 1. In dichloromethane solution $[NiL^1_2]$ and $[NiL^2_2]$ display several bands and shoulders in the 900–300 nm region. The spectrum of $[NiL^1_2]$ is shown in Fig. 1. The ligands themselves have strong absorption bands in the visible region and the nickel(II) ligand-field transitions could not be identified with confidence. However the octahedral ν_1 band appears as a shoulder in the region 800–750 nm.

Redox Behaviour of the Complexes.—Cyclic voltammetry has been used to study the redox behaviour in dichloromethane for both complexes. An initial anodic scan in dichloromethane solution reveals a well defined cyclic response due to the nickel(III)–nickel(II) couple which can be represented as in equations (1) and (2). The $E_{\frac{1}{2}}$ values, calculated from the

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

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

average of the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials, are 0.93 and 0.65 V *vs.* SCE respectively. At a scan rate of 50 mV s^{-1} the separations between the anodic and cathodic peak potentials (ΔE_p) are 260 and 160 mV for the $[NiL^1_2]$ and $[NiL^2_2]$ 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 results of the electrochemical studies collected in Table 2 also provide support for chemical reversibility on the cyclic voltammetric time-scale.

For both complexes, coulometric oxidations at +1.26 and +0.93 V respectively resulted in the passage of an average of 0.98 and 1.03 F (94555 C) of charge per mol of complex. Electrochemical measurements on nickel(III)–nickel(II) systems have commonly employed dichloromethane as solvent, since it permits a wide range of potentials to be covered without

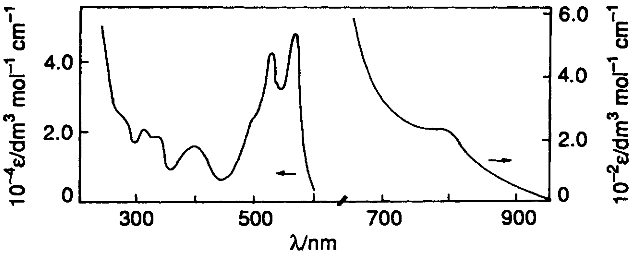


Fig. 1 Electronic spectrum of $[NiL^1_2]$ in dichloromethane at 298 K

Table 1 Magnetic moments,[a] electronic absorption[b] and infrared[c] spectral data

Compound	Colour	μ_{eff}/μ_B	λ/nm (ε/dm³ mol⁻¹ cm⁻¹)	$\tilde{\nu}$(N=N)/cm⁻¹
$[NiL^1_2]$	Dark brown	3.01	790 (240) (sh), 570 (48 000), 530 (41 800), 395 (15 190), 340 (18 570), 315 (19 830)	1345, 1360
$[NiL^2_2]$	Red-violet	3.11	815 (240) (sh), 650 (920) (sh), 540 (29 005) (sh), 510 (31 120), 375 (16 615), 320 (16 920) (sh)	1345, 1365

[a] In the solid state at 298 K; $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}. [b] Solvent dichloromethane; sh = shoulder. [c] In KBr discs.

Table 2 Electrochemical data and EPR *g* values

(*a*) Electrochemical data[a]

Couple	$E_{\frac{1}{2}}{}^{b}$/V	$\Delta E_p{}^c$/mV	n^d	E^e/V
$[NiL^1{}_2]^+ + e \rightleftharpoons [NiL^1{}_2]$	0.93	260	0.98	1.26
$[NiL^2{}_2]^+ + e \rightleftharpoons [NiL^2{}_2]$	0.65	160	1.03	0.93

(*b*) EPR *g* values[f]

Compound	$g_{\parallel}$	$g_{\perp}$	g_{av}
$[NiL^1{}_2]^+$	2.198	2.073	2.115
$[NiL^2{}_2]^+$	2.202	2.083	2.123

[a] Unless otherwise stated, the meaning of the symbols is as in the text. Solvent, dichloromethane; supporting electrolyte, NEt_4ClO_4 (0.1 mol dm^{-3}); working electrode, platinum; reference electrode, SCE; solute concentration ≈ 10^{-3} mol dm^{-3}. [b] Cyclic voltammetric data at 298 K at a scan rate of 50 mV s^{-1}: $E_{\frac{1}{2}}$ calculated as the average of the anodic and cathodic peak potentials. [c] Peak-to-peak separation. [d] Constant-potential coulometric data: $n = Q/Q'$, where Q is the observed coulomb count and Q' the calculated coulomb count for a one-electron transfer. [e] Potential used for coulometry at 258 K. [f] In frozen (77 K) dichloromethane solution.

decomposition and because the trivalent states are generally stable for longer periods in the anhydrous solvent medium.[15a] For $[NiL^1{}_2]$ another reductive response is observable at $E_{\frac{1}{2}}$ −1.14 V (ΔE_p, 260 mV, E_{pc} −1.27 and E_{pa} −1.01 V) presumably due to reduction of the metal-bonded azo group. The type of quasi-reversibility observed here has been shown to be a feature of several nickel(III) systems.[15b] The most marked feature of these data (Table 2) is the moderately strong oxidising nature of the $[NiL^1{}_2]^+$ species, indicating its usefulness as a one-electron oxidant.

Substitution of the pyridine ring of HL^1 by the methylsulfanylphenyl group of HL^2 in the chelate ring results in a shift in the nickel(III)–nickel(II) reduction potential by about 140 mV. The overall difference (280 mV) in the reduction potentials of $[NiL^1{}_2]^{+/0}$ and $[NiL^2{}_2]^{+/0}$ having NiN_4O_2 and $NiN_2O_2S_2$ co-ordination spheres arises mainly from the presence of the less-polarisable pyridine nitrogen atoms in the former. Low potentials are observed when the nickel centre is bonded to neutral less-electronegative but more-polarisable soft donor atoms. Therefore basicity (σ-donor ability) is not the only criterion in judging the suitability of any donor atom towards the stabilisation of high oxidation states of metal ions. The pyridine nitrogen atom has good σ-basic and weak π-acidic character, yet stabilises lower oxidation states compared to thioether sulfur. The thioether sulfur atom in $[NiL^2{}_2]$ can use its more basic sp^3 lone pair for binding the metal, whereas in $[NiL^1{}_2]$ the available lone-pair orbital on the pyridine nitrogen is less basic, sp^2.

Electrochemical Synthesis of Nickel(III) *Complexes and EPR Spectra*.—The unequivocal existence of nickel(III) complexes rather than nickel(II)–radical systems was confirmed from the EPR data. Nickel(III) complexes are produced in dichloromethane solution upon one-electron coulometric oxidation (Table 2) of the corresponding nickel(II) complexes. The oxidised complexes are thermally less stable at 300 K and therefore coulometry was performed at 258 K. Solutions of $[NiL^1{}_2]^+$ and $[NiL^2{}_2]^+$ are blue-violet. The original nickel(II) complex can be generated upon one-electron reduction of the oxidised solutions. We are currently trying to isolate the nickel(III) species in the solid state for further study.

Frozen (77 K) solutions of the nickel(III) complexes display axial EPR spectra with $g_{av} > 2.1$. A representative spectrum is shown in Fig. 2 and *g* values are listed in Table 2. The *g* values are considerably greater than 2, and the unpaired electron is evidently located in a predominantly metal [nickel(III), low-spin d^7] orbital. The oxidation (loss of electron density) involves an orbital that is largely localised on the metal. For a low-spin d^7 tetragonally distorted octahedral ion values of $g_{\parallel} \approx 2.20$ and $g_{\perp} \approx 2.07$ are consistent with the axially symmetric systems.[16] If the electron were delocalised into the ligand systems a *g* value close to 2.00 would be expected[17,18] for the (principally carbon-centred) paramagnetic species.

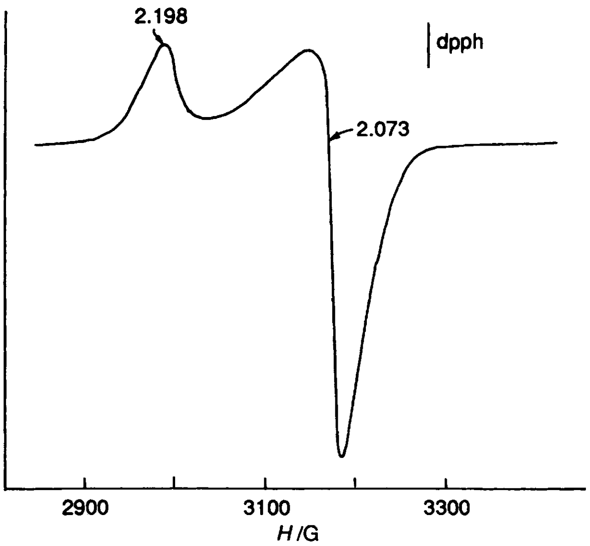


Fig. 2 The X-band (9.095 GHz) EPR spectrum of $[NiL^1{}_2]^+$ in frozen (77 K) dichloromethane; G = 10^{-4} T

No nitrogen hyperfine splitting in any of the $g_{\parallel}$ and $g_{\perp}$ components of the spectrum is observed indicating no interaction of the unpaired electron with the nitrogen donor atoms around the metal centre. The nature of the EPR spectra of $[NiL^1{}_2]^+$ and $[NiL^2{}_2]^+$ is similar. The oxidised complexes exhibit Jahn–Teller distortion with a local symmetry of D_{4h} around the nickel. They belong to the $g_{\parallel} > g_{\perp}$ class consistent with a tetragonally distorted octahedral nickel(III) complex in which the unpaired electron is in the $d_{x^2-y^2}$ (^2E_g ground state) rather than the d_{z^2} orbital. This is consistent with tetragonal compression $[(\pi d)^6(\sigma d)^1 \equiv t^6{}_{2g}\, e^1{}_g]$. The $g_{\parallel} > g_{\perp}$ type of EPR spectrum is very uncommon among nickel(III) complexes which are usually elongated $[g_{\perp} > g_{\parallel}, (d_{z^2})^1$ ground state].[4a,7,19–21]

Conclusion

The presence of tridentate chelate rings is no doubt of crucial importance for the synthesis of six-co-ordinated paramagnetic neutral nickel(II) chelates. The pendant pyridyl arm in the azonaphthol backbone of the ligand can influence the metal redox behaviour in contrast to the methylsulfanyl arm. It is clear that pyridyl ligands disfavour the trivalent state. In a nitrogen (pyridine) environment the trivalent complexes so synthesised could be useful as high-potential one-electron oxidants. The greater covalency of the Ni–S bond leads to a decrease in $E_{\frac{1}{2}}$ values. Metal-centred oxidations are verified from the observed *g* anisotropy in the EPR spectra of the oxidised complexes in solution. The presence of aromatic heterocyclic nitrogens and thioether sulfurs in the first co-ordination sphere of nickel in $[NiL^1{}_2]$ and $[NiL^2{}_2]$ provides different stability towards nickel oxidation states. It is also apparent that the meridional chelating ability of the ligand system has a marked effect upon the generation and stability of the trivalent nickel centre.

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References

1 J. R. Lancaster, jun. (Editor), *The Bioinorganic Chemistry of Nickel*, VCH, New York, 1988.

2 R. Cammack, *Adv. Inorg. Chem.*, 1988, **32**, 297.

3 D. Ray, S. Pal and A. Chakravorty, *Inorg. Chem.*, 1986, **25**, 2674.

4 (*a*) H.-J. Krüger and R. H. Holm, *J. Am. Chem. Soc.*, 1990, **112**, 2955; (*b*) N. Baidya, M. M. Olmstead and P. K. Mascharak, *J. Am. Chem. Soc.*, 1992, **114**, 9666; (*c*) S. Bhanja Choudhury, D. Ray and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1992, 107.

5 A. E. Przybyla, J. Robbins, N. Menon and H. D. Peck, jun., *FEMS Microbiol. Rev.*, 1992, **88**, 109; R. P. Hausinger, *Microbiol. Rev.*, 1987, **51**, 22; C. T. Walsh and W. H. Orme-Johnson, *Biochemistry*, 1987, **26**, 4901.

6 G. Fauque, H. D. Peck, jun., J. J. G. Moura, B. H. Huynh, Y. Berlier, D. V. DerVartanian, M. Teixeira, A. E. Przybyla, P. A. Lespinat, I. Moura and J. LeGall, *FEMS Microbiol. Rev.*, 1988, **54**, 299; J. J. G. Moura, M. Teixeira and I. Moura, *J. Mol. Catal.*, 1984, **23**, 303.

7 S. Mukhopadhyay and D. Ray, *J. Chem. Soc., Dalton Trans.*, 1993, 1159.

8 G. K. Lahiri, S. Bhattacharya, B. K. Ghosh and A. Chakravorty, *Inorg. Chem.*, 1987, **26**, 4324.

9 D. D. Perrin, W. L. F. Armango and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 1980.

10 D. T. Sawyer and J. L. Roberts, jun., *Experimental Electrochemistry for Chemists*, Wiley, New York, 1974, pp. 167–215.

11 F. P. Dwyer, N. S. Gill, S. C. Gyartas and F. Lions, *J. Am. Chem. Soc.*, 1954, **76**, 383.

12 S. G. Murrey and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 365; S. R. Cooper and S. C. Rawle, *Struct. Bonding (Berlin)*, 1990, **72**, 1; A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 1990, **35**, 1.

13 R. L. Reeves, G. S. Calabrese and S. A. Harkaway, *Inorg. Chem.*, 1983, **22**, 3076; C. D. Hubbard and D. Pacheco, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1373; R. L. Reeves, M. S. Maggio and S. A. Harkaway, *J. Phys. Chem.*, 1979, **83**, 2359.

14 S. Mukhopadhyay and D. Ray, unpublished work.

15 (*a*) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, 1969, **8**, 1611; (*b*) F. P. Bossu and D. W. Margerum, *J. Am. Chem. Soc.*, 1976, **98**, 4003.

16 A. G. Lappin, C. K. Murray and D. W. Margerum, *Inorg. Chem.*, 1978, **17**, 1630.

17 A. L. Balch, F. Rohrscheid and R. H. Holm, *J. Am. Chem. Soc.*, 1965, **87**, 2301.

18 E. I. Steifel, J. H. Waters, E. Billing and H. B. Gray, *J. Am. Chem. Soc.*, 1965, **87**, 3016.

19 K. Nag and A. Chakravorty, *Coord. Chem. Rev.*, 1980, **33**, 87.

20 S. Bhattacharya, R. N. Mukherjee and A. Chakravorty, *Inorg. Chem.*, 1986, **25**, 3448.

21 S. A. Jacobs and D. W. Margerum, *Inorg. Chem.*, 1984, **23**, 1195.

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