Dithiolene-like Nickel Complexes of the Methyl Ester of Dithiocarbazic Acid and its N^3 Phenyl- and Benzyl-substituted Derivatives. Crystal and Molecular Structure of [Ni{$PhNC_6H_4NNC(S)SMe$}(NCS)]†

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The properties of the complexes [Ni{NHNC(S)SMe}$_2$], [Ni{NPhNC(S)SMe}$_2$], and [Ni{N(CH_2Ph)NC(S)SMe}$_2$] have been investigated. The electronic, i.r., e.s.r., and *X*-ray photoelectron spectra have been studied; electrochemical studies in solution have been performed. The oxidation state of nickel is essentially +2 in all the compounds. The *X*-ray crystal structure of [Ni{$PhNC_6H_4NNC(S)SMe$}(NCS)], which forms on heating [Ni{NPhNC(S)SMe}$_2$], was determined.

Some years ago we reported the results of our investigation on the nickel complexes of the methyl ester of dithiocarbazic acid and its *N*-substituted derivatives.[1–3] We have shown that the ligands co-ordinate through the N and S atoms in neutral or in anionic monodeprotonated forms. Here we report a development of that work dealing with nickel complexes containing the doubly deprotonated ligands. We have already shown that dithiocarbazic esters are able to co-ordinate platinum in the doubly deprotonated form.[4,5] The ligands considered are $NH_2NHC(=S)SMe$ (L), NHPhNHC(=S)SMe (PhL), and $NH(CH_2Ph)NHC(=S)SMe$ ($PhCH_2L$).

Experimental

Materials.—Chemicals were obtained and purified as described previously.[4]

Preparation of the Ligands.—The ligands L, PhL, and $PhCH_2L$ were prepared following reported methods.[4,5]

Preparation of the Complexes.—The complexes [Ni($PhCH_2L$ − H)$_2$] [$PhCH_2L$ − H = $NH(CH_2Ph)N{=}C(S)$-SMe] and [Ni(L − H)$_2$] [L − H = $NH_2N{=}C(S)SMe$] were prepared according to literature procedures.[1]

[Ni(L − 2H)$_2$] [L − 2H = NHNC(S)SMe]. [Ni(L − H)$_2$] (1.3 mmol) was suspended in water (100 cm^3) and stirred. A solution of 37% NH_4OH (4 cm^3) was added followed by 30% aqueous H_2O_2 (10 cm^3). The addition was repeated three times at 1 h intervals. One hour after the last addition the compound was filtered off, washed with water, and dried (yield 26%).

[Ni(PhL − 2H)$_2$] [PhL − 2H = NPhNC(S)SMe]. A solution of $NiCl_2{\cdot}6H_2O$ (1.9 mmol) in water (30 cm^3) was added in an open vessel to a solution of PhL (3.8 mmol) in ethanol (80 cm^3) and water (40 cm^3). After stirring for 5 min 37% NH_4OH (4 cm^3) was added to reach pH 9 and the reaction continued for 20 h. The deep green product was filtered off, washed with diluted ammonia, and dried (yield 30%).

[Ni($PhCH_2L$ − 2H)$_2$] [$PhCH_2L$ − 2H = $N(CH_2Ph)NC$-(S)SMe]. [Ni($PhCH_2L$ − H)$_2$] (1.2 mmol) was suspended in 37% NH_4OH (30 cm^3) and stirred for 16 h in an open vessel. The product was filtered off, washed with ammonia and dried (yield 80%).

[Ni{$PhNC_6H_4NNC(S)SMe$}(NCS)]. [Ni(PhL − 2H)$_2$] (0.4 mmol) was crystallized from boiling CS_2 (50 cm^3). The dark violet crystalline product was filtered off and dried (yield 50%).

Analytical data for the complexes are given in Table 1. Microanalyses were performed by the Microanalytical Service of the Area della Ricerca di Roma del C.N.R.

Table 1. Analytical data for the nickel complexes

Compound	Colour	Analysis (%)*		
		C	H	N
[Ni(L − 2H)$_2$]	Deep blue	16.3 (16.1)	3.0 (2.7)	18.3 (18.7)
[Ni(PhL − 2H)$_2$]	Dark green	42.6 (42.6)	3.4 (3.6)	12.3 (12.4)
[Ni($PhCH_2L$ − H)$_2$]	Grey	45.2 (45.1)	4.3 (4.2)	11.5 (11.7)
[Ni($PhCH_2L$ − 2H)$_2$]	Dark green	45.0 (45.1)	4.1 (4.2)	11.8 (11.7)
[Ni{$PhNC_6H_4NNC(S)$-SMe}](NCS)]	Dark violet	44.5 (44.7)	3.1 (3.0)	13.7 (13.9)

* Calculated values in parentheses.

Physical Measurements.—The u.v.–visible spectra and magnetic moments were measured as in ref. 4. Infrared spectra were recorded with a Perkin-Elmer 983 spectrophotometer.

Electrochemical Measurements.—D.c. polarography and cyclovoltammetry were performed, as reported in ref. 5. All potentials are quoted with respect to a saturated calomel electrode (s.c.e.) with an accuracy of ±5 mV.

Crystal Structure Determination of [Ni{$PhNC_6H_4NNC(S)$-SMe}(NCS)].—*Crystal data.* $C_{15}H_{12}N_4NiS_3$, M = 403.191, monoclinic, space group $P2_1/n$, a = 12.103(2), b = 10.348(2), c = 13.545(3) Å, β = 98.18(2)°, U = 1 679.2(9) Å^3, D_c = 1.595 g cm^{-3}, Z = 4, D_m = 1.60(2) g cm^{-3} (by flotation), Mo-K_α radiation, λ = 0.710 69 Å, μ = 16.8 cm^{-1}, $F(000)$ = 824.

X-Ray data collection. The intensities of 1 232 independent reflections having $I \geqslant 3\sigma(I)$ were collected at room temperature on a Nicolet $P2_1$ automated four-circle diffractometer, by the θ–2θ scan technique with graphite-monochromated Mo-K_α radiation. They were corrected for background,

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† Isothiocyanato[methyl 3-(6′-phenyliminocyclohexa-2′,4′-dien-1′-ylidene)dithiocarbazato(1 −)-*S*,N^3,*N*′]nickel(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. units employed: B.M. = 9.27 × 10^{-24} J T^{-1}, eV = 1.6 × 10^{-19} J, Torr ≈ 133 Pa.

Table 2. Final atomic co-ordinates (× 10^4), with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni	2 166(1)	−68(1)	4 595(1)
S(1)	1 712(2)	−878(3)	3 112(2)
S(2)	2 640(2)	−215(3)	1 321(2)
S(3)	−745(2)	−2 208(3)	5 758(2)
N(1)	3 472(6)	716(7)	3 103(5)
N(2)	3 324(6)	707(7)	4 085(5)
N(3)	2 933(6)	569(7)	5 851(4)
N(4)	1 098(6)	−1 032(7)	5 107(5)
C(1)	2 699(6)	−20(9)	2 603(6)
C(2)	4 068(7)	1 351(8)	4 731(6)
C(3)	4 994(7)	2 066(9)	4 494(7)
C(4)	5 678(8)	2 602(9)	5 262(7)
C(5)	5 478(8)	2 485(9)	6 280(7)
C(6)	4 602(7)	1 845(9)	6 526(6)
C(7)	3 841(7)	1 223(8)	5 753(6)
C(8)	2 627(5)	259(6)	6 799(3)
C(9)	3 347(5)	−448(6)	7 492(3)
C(10)	3 024(5)	−778(6)	8 408(3)
C(11)	1 980(5)	−401(6)	8 630(3)
C(12)	1 260(5)	307(6)	7 936(3)
C(13)	1 584(5)	637(6)	7 020(3)
C(14)	344(8)	−1 514(9)	5 368(6)
C(15)	3 802(8)	703(9)	1 029(6)

Table 3. Bond distances (Å) and angles (°), with e.s.d.s in parentheses

Ni–S(1)	2.175(2)	N(2)–C(2)	1.340(10)
Ni–N(2)	1.833(7)	N(3)–C(7)	1.313(9)
Ni–N(3)	1.934(7)	N(3)–C(8)	1.422(7)
Ni–N(4)	1.844(8)	N(4)–C(14)	1.139(9)
S(1)–C(1)	1.711(9)	C(2)–C(3)	1.417(11)
S(2)–C(1)	1.740(8)	C(2)–C(7)	1.456(10)
S(2)–C(15)	1.788(9)	C(3)–C(4)	1.352(11)
S(3)–C(14)	1.653(10)	C(4)–C(5)	1.439(11)
N(1)–N(2)	1.367(8)	C(5)–C(6)	1.332(11)
N(1)–C(1)	1.316(9)	C(6)–C(7)	1.443(11)
S(1)–Ni–N(2)	85.8(2)	Ni–N(4)–C(14)	171.3(8)
S(1)–Ni–N(3)	166.1(2)	S(1)–C(1)–S(2)	114.2(5)
S(1)–Ni–N(4)	92.3(2)	S(1)–C(1)–N(1)	125.4(6)
N(2)–Ni–N(3)	83.4(3)	N(1)–C(1)–S(2)	120.4(6)
N(2)–Ni–N(4)	173.0(3)	N(2)–C(2)–C(7)	112.1(8)
N(3)–Ni–N(4)	97.4(3)	C(7)–C(2)–C(3)	121.7(8)
Ni–S(1)–C(1)	94.2(3)	C(2)–C(3)–C(4)	117.2(9)
C(1)–S(2)–C(15)	103.7(4)	C(3)–C(4)–C(5)	122.4(9)
N(2)–N(1)–C(1)	108.4(7)	C(4)–C(5)–C(6)	121.9(9)
Ni–N(2)–N(1)	125.7(6)	C(5)–C(6)–C(7)	119.3(8)
Ni–N(2)–C(2)	116.7(6)	C(2)–C(7)–N(3)	114.6(8)
Ni–N(3)–C(7)	113.0(5)	C(2)–C(7)–C(6)	117.5(8)
Ni–N(3)–C(8)	124.3(5)	N(4)–C(14)–S(3)	179.4(8)
C(7)–N(3)–C(8)	122.4(6)		

Lorentz, and polarization effects, but no absorption correction was applied in view of the small crystal size (dimensions: 0.3 × 0.1 × 0.05 mm) and absorption coefficient. The cell dimensions were obtained by least-squares refinement of the setting angles of 15 reflections with $2\theta > 25°$.

Structure solution and refinement. The structure was solved by conventional Patterson and Fourier methods. The refinement of 200 parameters (six observations per parameter) was accomplished by full-matrix least squares, using anisotropic thermal parameters for non-hydrogen atoms and a fixed isotropic thermal parameter of 4.5 Å^2 for hydrogen atoms, included at calculated positions. A regular hexagon with a C–C distance of 1.395 Å was fitted to the C(8)—C(13) phenyl carbon atoms which was then refined as a rigid group. The final residual *R* and weighted *R′*, defined as $R = \Sigma|\Delta F|/\Sigma|F_o|$ and $R' = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{\frac{1}{2}}$, were 0.047 and 0.042 respectively, the weighting factor being $w = 1/[\sigma^2(F_o) + 0.0003\, F_o^2]$.

Calculations were carried out on an IBM 4361/4 computer using the SHELX 76 program system.[6]

Neutral-atom scattering factors (f' and f'' values) were taken from ref. 7. Final atomic co-ordinates for non-hydrogen atoms are given in Table 2, interatomic distances and angles in Table 3. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

X-Ray Photoelectron Spectra.—The spectra were recorded on the VG ESCA 3Mk II of the ESCA Service of the Area della Ricerca di Roma del C.N.R. The exciting source was provided by the unmonochromatized Al-K_α radiation (1 486.6 eV). The vacuum in the analyzer was 10^{-3} Torr. The samples were dusted on a double-sided Scotch tape. The experiments were performed at *ca.* 300 K and replicated at the temperature of liquid nitrogen in order to check if, under *X*-ray irradiation, any change occurred in both the peak positions and shapes: no appreciable difference was revealed between the two conditions. The binding energy (b.e.) values result from the average of three independent sample depositions. The reproducibility was within ±0.2 eV. Curve peak-fitting was carried out by means of a Du Pont 310 curve resolver using a Gaussian shape fit.

E.S.R. Measurements.—E.s.r. spectra were measured at the *X*- or *Q*-band frequency using a Varian E-9 spectrometer equipped with a standard variable-temperature accessory, a Systron-Donner 6246 frequency counter, and a Bruker BNM-20 gaussmeter. The reduced species were generated and measured *in situ* using a home-built electrolytic cell[8] connected to the electrochemical apparatus used for the electrochemical measurements.

Results and Discussion

Preparation and Properties of the Nickel Complexes.—All the nickel complexes containing the monodeprotonated ligands $[Ni(L - H)_2]$, $[Ni(PhL - H)_2]$, and $[Ni(PhCH_2L - H)_2]$ react readily in strongly basic (NH_4OH) aqueous ethanol in air giving the deeply coloured compounds $[Ni(L - 2H)_2]$, $[Ni(PhL - 2H)_2]$, and $[Ni(PhCH_2L - 2H)_2]$ containing the doubly deprotonated ligands. All the compounds are stable in the solid state and dissolve in many organic solvents, in which they more or less rapidly decompose. However, in CH_2Cl_2 the compounds are stable for at least 3 h and accurate measurements could be performed. The complexes $[Ni(L - 2H)_2]$ and $[Ni(PhCH_2L - 2H)_2]$ are diamagnetic while $[Ni(PhL - 2H)_2]$ is paramagnetic at room temperature ($\mu_{eff.} = 1.5$ B.M.). This compound shows peculiar behaviour when crystallized from CS_2: the compound formally loses one mole of MeSH giving a new species of formula $C_{15}H_{12}N_4NiS_3$, $[Ni\{PhNC_6H_4NNC(S)SMe\}(NCS)]$ whose structure was determined by *X*-ray crystallography.

Description of the Structure of $[Ni\{PhNC_6H_4NNC(S)SMe\}(NCS)]$.—In Figure 1 the chemical unit, together with the atomic labelling, is presented.

As shown in Figure 2, the four complex units present in the unit cell are not sterically independent: they are coupled, two by two, through a centre of symmetry in such a way that the metal atom is surrounded by five neighbours in a tetragonally-distorted square-pyramidal geometry.

The basal plane is formed by the sulphur and nitrogen atoms, S(1), N(2), N(3), belonging to the tridentate ligand, and by the nitrogen atom, N(4), of the thiocyanato group. The Ni–S(1) distance of 2.175(2) Å falls in the range 2.16 – 2.18 Å already discussed for analogous nickel–thio complexes containing five-

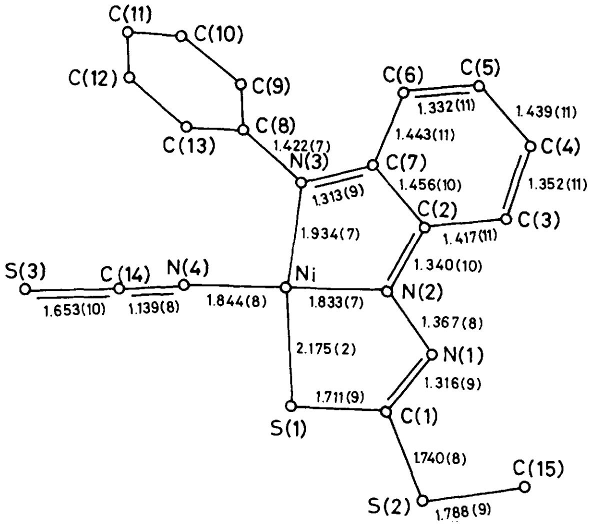

Figure 1. Scheme of the chemical unit of [Ni{PhNC$_6$H$_4$NNC(S)SMe}(NCS)] showing the atom labelling and the system of double bonds as deduced from the bond distances

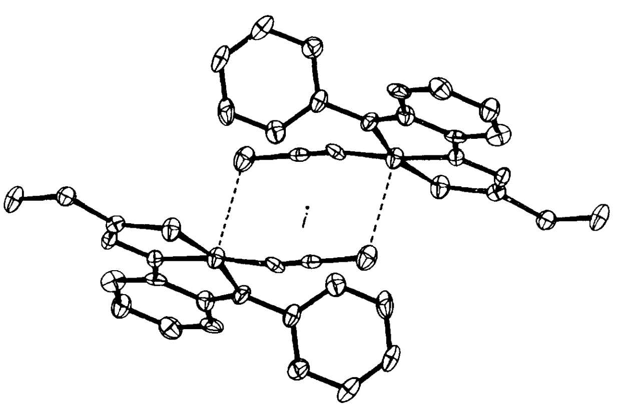

Figure 2. Perspective view of two complex units coupled through Ni–S intermolecular interactions. Anisotropic thermal ellipsoids are given at 30% probability level

membered rings;[9] lengthening of Ni–N(3) with respect to Ni–N(2) and Ni–N(4) distances [1.934(7), 1.833(7), and 1.844(8) Å respectively] is observed, due to the *trans* effect of the sulphur atom, but the distances are all consistent with the literature data.[10]

The fifth, apical, position is occupied by a sulphur atom, S(3′), from the symmetry-related thiocyanato group: the nickel atom is displaced from the basal plane by 0.144 Å towards S(3′) at a distance of 2.92(1) Å. Apart from the phenyl ring which is rotated by 63° around the N(3)–C(8) bond, the ligand molecule, including the NCS group, is planar, the maximum deviation being 0.14 Å for the S(3) atom which is involved in the interaction with the centrosymmetric Ni′ atom.

The analysis of the interatomic distances within the tridentate ligand indicates that there is a lack of extensive conjugation in favour of a system of localised single and double bonds (Figure 1). The bonds shown as single bonds are in fact significantly longer than the analogous ones shown as double bonds (see Table 3): C–C distances range between 1.417(11) and 1.456(10) Å, while C=C values are 1.332(11) and 1.352(11) Å; similarly C=N bond distances range from 1.313(9) to 1.340(10) Å *versus* a N(3)–C(8) single bond of 1.422(7) Å.

Infrared Spectra.—Data are given in Table 4. For the complex [Ni(PhCH$_2$L – H)$_2$], the absorption assigned to ν(N–H) of the ligand deprotonated at N^2 (3 116 cm^{-1}) is observed at lower wavenumber than for the free ligand (3 243 and 3 143 cm^{-1}), indicating co-ordination through N^3. The absorption at 1 527 cm^{-1} is assigned to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ of a partial double bond. The strong bands at 3 177 and 3 255 cm^{-1} in the spectrum of [Ni(L – 2H)$_2$], which are shifted to 2 220 and 2 310 cm^{-1} upon deuteriation, are assigned to ν(N–H). No bands attributable to ν(N–H) appear in the spectra of [Ni(PhL – 2H)$_2$], [Ni(PhCH$_2$L – 2H)$_2$], and [Ni{PhNC$_6$H$_4$NNC(S)SMe}(NCS)], confirming complete deprotonation of the ligands.

The shift to higher wavenumbers of the ν(C–N) absorption observed for [Ni{PhNC$_6$H$_4$NNC(S)SMe}(NCS)] relative to the other complexes (Table 4) is in agreement with the higher double-bond character evidenced by the crystal structure.

The i.r. spectrum of [Ni(PhL – 2H)$_2$] shows features similar to that of the square-planar complex [Pt(PhL – 2H)$_2$][4] but the absorptions are clearly split suggesting a lower symmetry for the nickel complex according to its magnetic moment. In the spectrum of [Ni(L – 2H)$_2$] absorptions attributable to ν(Ni–N) are found at 496 and 426 cm^{-1} (shifted by deuteriation to 488 and 410 cm^{-1}) and bands attributable to ν(Ni–S) are found at 372 and 324 cm^{-1} (unaffected by deuteriation).

The ν(Ni–N) and ν(Ni–S) bands are found in the spectral regions 490—412 cm^{-1} and 383—315 cm^{-1}, respectively, for [Ni(PhCH$_2$L – 2H)$_2$] and [Ni(PhL – 2H)$_2$].

The spectrum of [Ni{PhNC$_6$H$_4$NNC(S)SMe}(NCS)] shows a very strong band at 2 106 cm^{-1} attributable to ν(C–N) of the NCS group.

Electronic Spectra.—Data are given in Table 5 and spectra are reported in Figures 3 and 4. The electronic spectrum of [Ni(PhCH$_2$L – H)$_2$] is consistent with a square-planar D_{2h} geometry with the first absorption bands corresponding to the three spin-allowed transitions, $^1A_{1g} \longrightarrow {}^1A_{2g}$, $^1B_{1g}$, ^1E_g, in accord with the spectra of Ni$^{\mathrm{II}}$ complexes of monodeprotonated dithiocarbazic esters already reported.[1] When the ligand is deprotonated at both nitrogen atoms the spectrum changes markedly with the appearance of a very intense band at 12.8×10^3 cm^{-1} (log ε = 4.19) (Figure 3) which is characteristic of dithiolene-like complexes.[11]

Similar spectra are observed for [Ni(L – 2H)$_2$], [Ni(PhCH$_2$L – 2H)$_2$] (Figure 3), and [Ni{PhNC$_6$H$_4$NNC(S)SMe}(NCS)] (Figure 4). It is worth noting that the spectra of diamagnetic [Ni(L – 2H)$_2$] and [Ni(PhCH$_2$L – 2H)$_2$] show close similarity to the published[5] spectra for the diamagnetic Pt$^{\mathrm{II}}$ complexes with the same ligands, whereas the spectrum of the paramagnetic complex [Ni(PhL – 2H)$_2$] is very similar to that of [Ni{PhNNC(S)NEt$_2$}$_2$], which contains the pseudo-tetrahedral chromophore NiN$_2$S$_2$, but has been described as diamagnetic.[10] The intense long wavelength bands are assigned to charge-transfer bands according to reported assignments for platinum and nickel dithiolene-like complexes.[5,11]

Electrochemical Measurements.—The electrochemical behaviour of [Ni(L – 2H)$_2$], [Ni(PhL – 2H)$_2$], [Ni(PhCH$_2$L – 2H)$_2$], and [Ni{PhNC$_6$H$_4$NNC(S)SMe}(NCS)] in CH$_2$Cl$_2$ solution shows electron-transfer properties as already found for other dithiolene-like nickel complexes with a five-membered delocalized N–S chelate ring.[11] They have been investigated by means of d.c. and cyclic voltammetry; data are reported in Tables 6 and 7. The voltage range +0.100 to –2.000 V was explored for the reduction step. All the compounds show one well defined polarographic wave corresponding to the one-step reduction $[\mathrm{Ni(L-2H)_2}]^0 \underset{-e}{\overset{+e}{\rightleftharpoons}} [\mathrm{Ni(L-2H)_2}]^-$.

Table 4. I.r. spectra (cm^{-1}) of the nickel complexes

[Ni(PhCH$_2$L − H)$_2$]	[Ni(PhCH$_2$L − 2H)$_2$]	[Ni(L − 2H)$_2$]	[Ni(PhL − 2H)$_2$]	[Ni{PhNC$_6$H$_4$NNC(S)-SMe}(NCS)]	Tentative assignment (prevalent contribution)
3 116s		3 255vs			ν(N–H)
		3 177vs			
				2 106vs	ν(C–N) of NCS$^-$
3 028m	3 058vw		3 069vw	3 060vw	benzene ring modes
	3 028vw		2 989vw		
1 602vw	1 598w		1 588m	1 599w	benzene ring modes
1 527s					ν(C$\overset{\cdots}{-}$N)
1 584vw	1 584vw		1 565vw	1 576w	benzene ring modes
	1 451m	1 442m	1 450s	1 507m	ν(C$\overset{\cdots}{-}$N)
1 492w	1 490m		1 481s	1 477m	benzene ring modes
1 080m	1 071m	1 061s	1 094m	1 099m	ν(C–S) + ν(N–N)
1 002s	1 029w	970w	1 048m	1 081s	
971m	997w	959m	1 032w	1 031s	
940s	958m		1 019w	977vw	
913s	948m		993s	964vw	
	917w		968vw	943vw	
			943vw	918w	
			926w	904w	
			914vw		
492w	460w	496m	490m	484vw	ν(Ni–N)
441w	417m	426w	466m	470vw	
			434w	461vw	
			416vw	436w	
384vw	380w	372w	383m	365m	ν(Ni–S)
339w	330w	324w	372w	315w	
			341w		
			315vw		

Table 5. Electronic spectra (ν) of the nickel complexes in CH$_2$Cl$_2$

Compound	Chromophore	$10^{-3}\ \nu^a$/cm^{-1}
[Ni(PhCH$_2$L − H)$_2$]		16.4 (1.87), 22.5 (2.31), 31.6 (3.95), 37.9 (4.34)
[Ni(PhCH$_2$L − 2H)$_2$]		12.8 (4.19), 20.0 (3.38), [27.8] (3.77), 35.7 (4.48)
[Ni(L − 2H)$_2$]		13.7 (4.22), 20.3 (2.69), [26.3] (3.39), [31.6] (3.89), 37.8 (4.56)
[Ni(PhL − 2H)$_2$]		12.7 (3.54), 18.9 (3.80), 25.0 (3.97), [26.3] (3.92), [35.97] (4.30), 38.5 (4.37)
[Ni{PhNC$_6$H$_4$NNC(S)-SMe}(NCS)]	NiN$_3$S^b	9.9 (3.12), 16.5 (3.77), [19.5] (4.01), 21.4 (4.07), 30.3 (3.94), [41.7] (4.33)
[Ni{PhNNC(S)NEt$_2$}$_2$]^c	NiN$_2$S$_2$	11.9 (3.37), 17.4 (4.07), [19.6] (3.90), 23.5 (4.08), 31.3 (4.43), [33.9] (4.34)

^{a} log (ε/dm^3 mol^{-1} cm^{-1}) in parentheses; shoulders in square brackets. ^{b} See text. ^{c} See ref. 11.

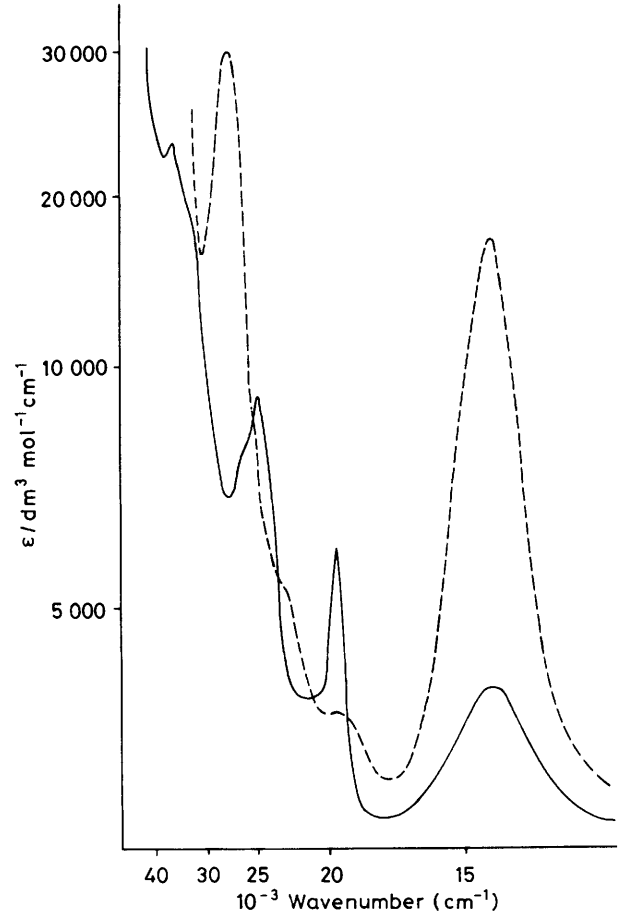

Figure 3. Electronic spectra of [Ni(PhL − 2H)$_2$] (——) and [Ni(PhCH$_2$L − 2H)$_2$] (– – –) in CH$_2$Cl$_2$

The process is electrochemically quasi-reversible and monoelectronic as suggested by the cyclovoltammetric *i*(cat)/*i*(an) and ΔE_p values (Table 6) and by the values of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ in d.c. polarography (Table 7). A second non-reversible wave suggests a second reduction step corresponding to the formation of highly unstable species.

E.S.R. Measurements.—Among the neutral complexes reported above, [Ni(PhCH$_2$L − 2H)$_2$] and [Ni(L − 2H)$_2$] are fully diamagnetic, whereas [Ni(PhL − 2H)$_2$] shows a room temperature magnetic moment of 1.5 B.M. suggesting that a single unpaired electron is present.

In agreement with this, the two former complexes are e.s.r. silent, whereas [Ni(PhL − 2H)$_2$] exhibits a spectrum both in

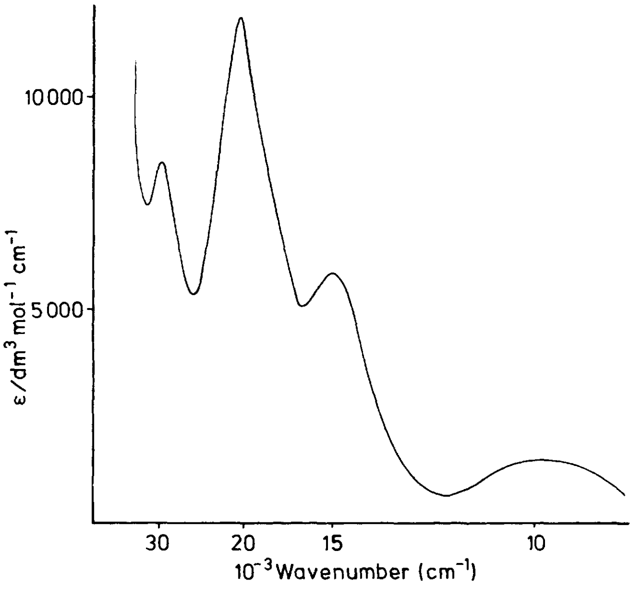

Figure 4. Electronic spectrum of [Ni{$PhNC_6H_4NNC(S)SMe$}(NCS)] in CH_2Cl_2

Table 6. Cyclic voltammetric data for nickel complexes in CH_2Cl_2 solution (1 × 10^{-3} mol dm^{-3})

Compound	E_p(cat)/V	ΔE_p*/V	i(cat)/i(an)
[Ni(L − $2H)_2$]	−0.165	0.07	1.4
[Ni(PhL − $2H)_2$]	−0.120	0.10	1.0
[Ni($PhCH_2L$ − $2H)_2$]	−0.294	0.10	1.0
[Ni{$PhNC_6H_4NNC(S)SMe$}(NCS)]	+0.045	0.08	1.2

* Cathodic to anodic peak potential separation.

Table 7. D.c. voltammetric data for the reduction at a pulsing platinum electrode of nickel complexes in CH_2Cl_2 solution (1 × 10^{-3} mol dm^{-3})[a]

Compound	$E_{\frac{1}{2}}$/V	i/μA	Slope[b]/V
[Ni(L − $2H)_2$]	−0.135	1.36	0.060
[Ni(PhL − $2H)_2$]	−0.055	2.20	0.050
[Ni($PhCH_2L$ − $2H)_2$]	−0.244	2.00	0.070
[Ni{$PhNC_6H_4NNC(S)SMe$}(NCS)]	+0.075	0.88	0.050

[a] Containing 0.1 mol dm^{-3} NBu_4BF_4; pulsing time t_p = 2 s, T = 20 °C. [b] Calculated using $E_{\frac{3}{4}} - E_{\frac{1}{4}}$.

Table 8. E.s.r. data of nickel complexes in fluid and frozen CH_2Cl_2

		T = 300 K		T = 110 K	
Compound		g_{iso}	A_{iso}[a]	$g_{\parallel}$	$g_{\perp}$
[Ni(PhL − 2H)(PhL − 3H)]	X-band	2.031	0.88	2.050	2.016
	Q-band	2.029		2.053	2.018
[Ni($PhCH_2L$ − $2H)_2]^-$[b]	X-band	2.034			
[Ni(PhL − 2H)(PhL − 3H)]$^-$[c]	X-band	2.005			

[a] In mT. [b] Electrochemically reduced at −0.400 V. [c] Electrochemically reduced at −0.220 V.

fluid and frozen solution typical of a spin-doublet ground state. Important features of the spectrum (see Table 8 and Figure 5) are the small g tensor anisotropy and the presence of ligand hyperfine splitting. This latter, which could be measured only in the isotropic spectrum, gives rise to a partly resolved triplet with a lineshape unequivocally suggesting interaction of the unpaired electron with a single nitrogen nucleus.

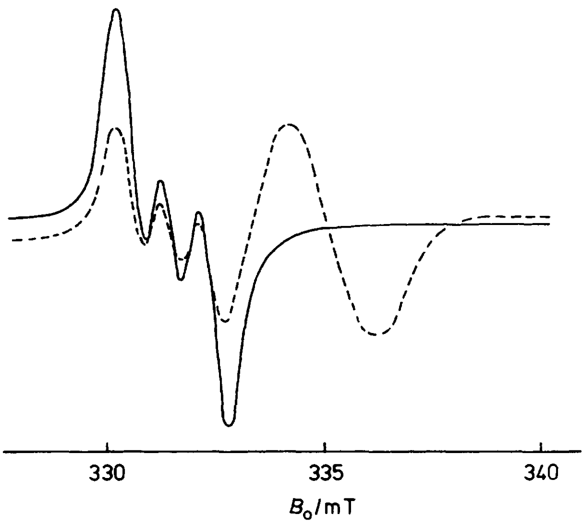

Figure 5. Room temperature X-band e.s.r. solution spectrum of [Ni(PhL − $2H)_2$] in CH_2Cl_2, before (——) and after (– – – –) one-electron electrochemical reduction

Dithiolene-like complexes containing related ligands, such as the thiosemicarbazides, have been reported.[11] On the basis of their spectroscopic properties they were described as M^{II} bis-chelate derivatives of the doubly deprotonated ligand in its radical, monoanionic form. Depending on the nature of the central metal ion these compounds can be diamagnetic, weakly, or fully paramagnetic. Open d-shell metal ions favour extensive spin–spin coupling and hence diamagnetic or weakly paramagnetic compounds, if low-lying excited states are present. Similar spin–spin interactions are absent or negligible for complexes of closed-shell d ions, which therefore behave as true biradicals, with two weakly interacting unpaired electrons and spin-triplet ground state.

The above picture, which explains the magnetic properties of dithiolene-like complexes containing an even number of electrons, cannot account for the $S = \frac{1}{2}$ ground state of [Ni(PhL − $2H)_2$]. In this case we must assume that one of the two ligand molecules is in a different protonation state, and since i.r. spectroscopy clearly rules out the presence of the singly deprotonated molecule, PhL − H, we believe that cleavage of a further hydrogen has occurred to give the diamagnetic monoanionic ligand PhL − 3H. The complex, reformulated as [Ni(PhL − 2H)(PhL − 3H)] contains a single unpaired electron. According to the e.s.r. results, namely the g tensor anisotropy and the absolute value of the ligand hyperfine splitting, such an electron is largely localized on the doubly deprotonated ligand, which thus behaves as a radical monoanion.

The above explanation, although tentative, is attractive in that it allows an easy rationalization of the unique chemical reactivity of [Ni(PhL − 2H)(PhL − 3H)]. Cleavage of the carbon–hydrogen bond in the phenyl *ortho* position appears to be a necessary step for the formation of the carbon–nitrogen bond and transformation of the original complex into [Ni{$PhNC_6H_4NNC(S)SMe$}(NCS)].

As discussed elsewhere in this paper the complexes [Ni(L − $2H)_2$], [Ni($PhCH_2L$ − $2H)_2$], and [Ni(PhL − 2H)(PhL − 3H)] are the central members of a three electron-transfer series and can be easily reduced electrochemically to give the corresponding monoanions. Therefore, in order to support the

Table 9. N 1*s*, S 2*p*, Ni $2p_{\frac{3}{2}}$ Binding energy values (eV) for the ligands and the nickel complexes after curve fitting

Compound	N^2	N^3	S	SMe	Ni $2p_{\frac{3}{2}}$
L	400.9	399.6	163.4	164.7	
PhL	401.0	400.0	163.1	164.5	
$PhCH_2L$	401.3	400.3	163.3	164.9	
$[Ni(L - H)_2]$	398.8	400.4	162.4	164.1	854.3
$[Ni(L - 2H)_2]$	398.7	399.7	162.9	164.1	854.5
$[Ni(PhL - H)_2]$	399.2	400.6	162.3	164.0	855.1
$[Ni(PhL - 2H)_2]$	399.3	400.1	162.8	164.3	855.3
$[Ni(PhCH_2L - H)_2]$	399.1	400.7	162.8	164.3	855.0
$[Ni(PhCH_2L - 2H)_2]$	399.2	400.0	162.8	164.3	855.2

	N(1)	N(2)	N(3)	N(4)	S(1)	S(2)	S(3)	Ni $2p_{\frac{3}{2}}$
$[Ni\{PhNC_6H_4NNC(S)SMe\}(NCS)]$ *	398.6	399.9	400.7	399.4	162.6	164.5	163.5	855.6

* See Figure 2.

above discussion, we decided to examine the e.s.r. behaviour of diamagnetic $[Ni(PhCH_2L - 2H)_2]$ and paramagnetic $[Ni(PhL - 2H)(PhL - 3H)]$ upon electrochemical reduction *in situ*.

In the case of $[Ni(PhCH_2L - 2H)_2]$ formation of the monoanion is accompanied by the expected appearance of an isotropic e.s.r. line which, although lacking any hyperfine structure, shows almost the same *g* values as the neutral $[Ni(PhL - 2H)(PhL - 3H)]$ compound. This suggests that in both cases the additional unpaired electron resides in a molecular orbital which is essentially ligand based.

In contrast, reduction of $[Ni(PhL - 2H)(PhL - 3H)]$ does not give the expected diamagnetic monoanion. In fact, the decrease in intensity of the e.s.r. triplet typical of the neutral compound is paralleled by the appearance of a novel, featureless e.s.r. absorption with an almost free-electron *g* value (2.005) (Figure 5). Apparently the diamagnetic $[Ni(PhL - 2H)(PhL - 3H)]$ is not stable and undergoes further electrochemical or chemical rearrangement to an ill defined, possibly organic paramagnetic species.

X-Ray Photoelectron Spectra.—In Table 9 binding energy values (in eV) of the title compounds and of some methyl esters are reported.

The Ni $2p_{\frac{3}{2}}$ binding energy values in these compounds are characteristic of the nickel atoms in their formal oxidation state +2. Analysis of the shape of the photoelectronic spectra (Figure 6) shows sharp peaks for the diamagnetic compounds while the high-spin complex exhibits a broader peak with high intensity satellites, in agreement with the magnetic measurements and with literature data.[12–14] The data for the S 2*p* binding energies of the SMe group show the same value for all the complexes and the free ligands, whilst for the co-ordinated sulphur atom the binding energy is lower in the complexes than in the free ligands. This effect can derive from conjugation between the N–C–S atoms.

The binding energy values of N^2 and N^3 are quite similar in all the free ligands, the value of N^2 being higher than that of N^3 in agreement with literature data.[12] These results can be attributed to the electron-withdrawing influence of the –C(S)SMe group on N^2, while the electron effects of the substituents influence the N^3 binding energy values.[13,15,16]

Significant changes in the binding energy values of the N^2 and N^3 atoms are observed when the esters are co-ordinated in the monodeprotonated form. Monodeprotonation induces an increase of the electronic charge density on N^2 while the little increase of the binding energy value of N^3 (400.4—400.7 eV) which is now higher than that of N^2, can be correlated to a decrease of the electronic charge on the atom due to co-ordination and relative back donation. In the doubly deprotonated compounds the binding energy values of N^3 are lower than in the monodeprotonated species, as a result of the new double bond. The substituent effects on the binding energy values of N^3 agree well with previous results.[12,13]

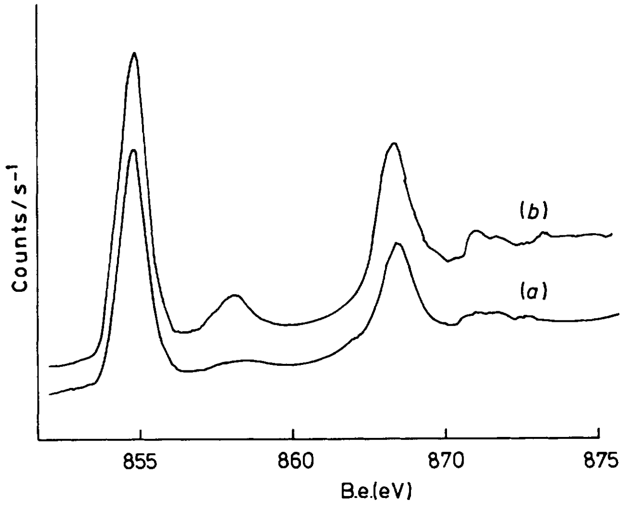

Figure 6. *X*-Ray photoelectron spectra of the Ni $2p_{\frac{3}{2}}$ level for diamagnetic $[Ni(PhCH_2L - 2H)_2]$ (*a*) and paramagnetic $[Ni(PhL - 2H)_2]$ (*b*) complexes

The increase of the binding energy value on going from unsubstituted ligand nickel complexes (854.5 eV) to the N^3 substituted ligands (855.1—855.3 eV) reflects the decrease of the electronic charge density on the metal atom, due to a greater metal to ligand back-donation promoted by the electron-withdrawing groups.

Curve fitting of the photoelectronic spectra of $[Ni\{PhNC_6H_4NNC(S)SMe\}(NCS)]$ shows four and three components for N 1*s* and S 2*p*, respectively (Table 9).

Of the four components of the N 1*s* spectrum, the one at 398.6 eV, similar to the value for N(2) in the doubly deprotonated compounds, can be attributed to atom N(1) (Figure 2); the other two at 399.9 and 400.7 eV, to N(2) and N(3) (Figure 2) respectively.

The two components of the S 2*p* spectrum at 162.6 and 164.5 eV can be assigned to the S(1) atom co-ordinated to the nickel and to the –SMe group, respectively, by analogy with the other compounds (Table 9).

The N 1s (399.4 eV) and the S 2p (163.5 eV) binding energy values can be attributed to the nitrogen and sulphur of the –SCN group.

The difference (Δ = 236 eV) between the binding energy values of N 1s and S 2p shows that the SCN group is bound by the nitrogen atom in agreement with empirical rules reported in the literature.[17]

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