Nickel Complexes of the Methyl Esters of Dithiocarbazic and *N*-Substituted Dithiocarbazic Acids

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The nickel complexes of the methyl esters of dithiocarbazic acid $NH_2NHC(=S)SMe$ (L), 2-methyldithiocarbazic acid $NH_2NMeC(=S)SMe$ (MeL), 2-n-butyldithiocarbazic acid, $NH_2NBuC(=S)SMe$ (BuL), 3,3-dimethyldithiocarbazic acid $NMe_2NHC(=S)SMe$ (Me_2L), 3-phenyldithiocarbazic acid $NHPhNHC(=S)SMe$ (PhL), and 3,3-diphenyldithiocarbazic acid $NPh_2NHC(=S)SMe$ (Ph_2L) have been investigated. L, MeL, BuL, and Me_2L can act as neutral ligands giving the high-spin complexes $[NiL_3]X_2$, $[Ni(MeL)_3]X_2$, $[Ni(BuL)_3]X_2$ (X = Cl, Br, or I), and $[Ni(Me_2L)_2Cl_2]$; L and Me_2L can act also in deprotonated form at N(2) giving the low-spin complexes $[Ni(L - H)_2]$ and $[Ni(Me_2L - H)_2]$. PhL and Ph_2L act only in deprotonated form at N(2) giving the low-spin $[Ni(PhL - H)_2]$ and $[Ni(Ph_2L - H)_2]$ respectively. MeL and BuL can be deprotonated at N(3) after co-ordination giving the low-spin complexes $[Ni(MeL - H)_2]$ and $[Ni(BuL - H)_2]$. The complexes have been characterized by their electronic and i.r. spectra.

THE methyl ester of dithiocarbazic acid $NH_2NHC(=S)$-SMe and its N-substituted derivatives have very interesting ligating possibilities because: (*i*) they have four donor atoms, hence they are potentially multidentate ligands; (*ii*) the protons on the N atoms can be lost and complexes with anionic ligands prepared. In recent years, these compounds have received much attention in our laboratory [1] and in other research groups.[2] They have also some biological interest as carcinostatic agents.[1] Here we report the nickel complexes of the following ligands: $NH_2NHC(=S)SMe$ (L), $NH_2NMeC(=S)SMe$ (MeL), $NH_2NBu^nC(=S)SMe$ (BuL), $NMe_2NHC(=S)SMe$ (Me_2L), $NHPhNHC(=S)SMe$ (PhL), and $NPh_2NHC(=S)SMe$ (Ph_2L). In parallel with the investigation of the nickel complexes we also examined the free esters.

EXPERIMENTAL

Materials.—The chemicals were commercial analytical grade reagents and were used without further purification. Nitrogen gas was an ultra-high-purity commercial product. All the compounds were dried *in vacuo* (1 mmHg) † over P_2O_5.

Preparation of the Ligands.—L, MeL, Me_2L, and PhL were prepared as in refs. 3—5.

BuL. A solution of n-butylhydrazine oxalate (50 mmol) in water (25 cm^3) was added to a solution of K[OH] (150 mmol) in ethanol (80 cm^3). The precipitated potassium oxalate was filtered off. Carbon disulphide (25 mmol) was then added at a temperature below 10 °C, followed by CH_3I (125 mmol). At room temperature water (700 cm^3) was added and the white product precipitated (yield 80%), m.p. 43 °C.

Ph_2L. The compound NPh_2NHCS_2H [6] (40 mmol) was dissolved in a solution of K[OH] (40 mmol) in ethanol (250 cm^3). Methyl iodide (40 mmol) was added and after stirring for 5 h the required compound was filtered off (yield 80%), m.p. 150 °C.

Preparation of the Complexes.—The compounds $[NiL_3]X_2$, $[Ni(MeL)_3]X_2$, and $[Ni(BuL)_3]X_2$ (X = Cl, Br, or I) were prepared by treating the nickel salts (2 mmol) in ethanol (15 cm^3) with the appropriate esters (6 mmol in 25 cm^3 ethanol). The resulting blue solutions were boiled for a few minutes. The complexes crystallized on standing at room temperature (yield 82%). Treatment of $NiCl_2 \cdot 6H_2O$ with MeL gave $[Ni(MeL)_3]Cl_2 \cdot 3H_2O \cdot 0.5EtOH$.

$[Ni(Me_2L)_2Cl_2]$. A warm solution of Me_2L (3 mmol) in dry ethanol (10 cm^3) was added to a warm solution of $NiCl_2 \cdot 6H_2O$ (1 mmol) in dry ethanol (30 cm^3) acidified with 0.1 N HCl (pH 5). The green solution was evaporated to dryness *in vacuo* (1 mmHg) and the residue crystallized from boiling n-butanol (yield 40%).

$[Ni(MeL)_2X_2] \cdot 0.33EtOH$ (X = Cl *or* Br). The compounds were prepared by treating the appropriate nickel salt (1.5 mmol in 10 cm^3 ethanol) with MeL (4.5 mmol in 20 cm^3 acetone). The green complexes precipitated immediately (yield 35%). The amount of EtOH was determined by thermal gravimetric analysis (t.g.a.).

The complex $[Ni(L - H)_2]$ was prepared as in ref. 7.

$[Ni(Me_2L - H)_2]$. The compound crystallized on treating $NiCl_2 \cdot 6H_2O$ (3.3 mmol) with Me_2L (6.6 mmol) in boiling ethanol (40 cm^3) (yield 90%).

$[Ni(PhL - H)_2]$. The ligand PhL (10 mmol in 60 cm^3 ethanol) was treated with $NiCl_2 \cdot 6H_2O$ (5 mmol in 30 cm^3 ethanol) at room temperature in a N_2 atmosphere. The compound crystallized after stirring for 1 h. It was filtered off and dried in a N_2 atmosphere (yield 10%).

$[Ni(Ph_2L - H)_2]$. The ligand Ph_2L (8 mmol) was dissolved in a solution of K[OH] (8 mmol) in 70% aqueous ethanol (300 cm^3). To the resulting solution, $NiCl_2 \cdot 6H_2O$ (4 mmol) in ethanol (40 cm^3) was added dropwise. The precipitate was filtered off, washed with water and then ethanol, and crystallized from boiling ethanol (yield 80%).

$[Ni(MeL - H)_2]$. The complex $[Ni(MeL)_3]X_2$ (3 mmol) was suspended in 20% aqueous K[OH] (15 cm^3). After stirring for 15 min the required compound was filtered off and washed with water (yield 80%). The compound $[Ni(BuL - H)_2]$ was prepared as above starting from $[Ni(BuL)_3]X_2$ (yield 75%).

Analytical data and room-temperature magnetic moments are in Table 1, i.r. spectra in Supplementary Publication No. SUP 22665 (5 pp.).‡

Physical Measurements.—The visible-reflectance spectra of the finely powdered solids were obtained on a Beckmann DK2 spectrophotometer fitted with a standard reflectance attachment and MgO in the reference beam. Solution

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† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

‡ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

spectra were recorded in ethanol at room temperature on the same instrument (concentration range 10^{-5}—10^{-3} mol dm^{-3}). Infrared spectra were determined (200—4 000 cm^{-1}) on a Perkin-Elmer 621 spectrophotometer as Nujol or poly(chlorotrifluoroethylene) mulls. Magnetic measurements were performed on solid samples with a Gouy balance calibrated with $Hg[Co(SCN)_4]$.

RESULTS AND DISCUSSION

Preparation and Properties of the Nickel Complexes.—All the esters considered react with nickel(II) salts in ethanol giving the high-spin complexes $[NiL_3]X_2$, $[Ni(MeL)_3]X_2$, and $[Ni(BuL)_3]X_2$, and the low-spin complexes $[Ni(Me_2L - H)_2]$ and $[Ni(PhL - H)_2]$; Ph_2L does not react. The different reactivities clearly indicate the influence of the substituents on N(3), which seems to facilitate the anionic deprotonated form of the ligands even in neutral media. To prepare the high-spin $[Ni(Me_2L)_2Cl_2]$ it is necessary to add HCl to the reaction medium to prevent deprotonation of the ligand. The ligand Ph_2L reacts with nickel salts only after addition of K[OH] to the reaction medium, giving $[Ni(Ph_2L - H)_2]$; PhL does not react with nickel salts in acid media. The N(2)-substituted ligands, MeL and BuL, can be deprotonated at the terminal N after co-ordination of the NH_2 group. Thus $[Ni(MeL - H)_2]$ [MeL − H = $^-$NH-NMeC(=S)SMe] can be prepared by treating $[Ni(MeL)_3]X_2$ with aqueous K[OH]. The unstable $[Ni(BuL - H)_2]$ is prepared similarly from $[Ni(BuL)_3]X_2$.

TABLE 1

Analytical data and magnetic moments of nickel complexes

Compound	Colour	Analysis (%) [a] C	H	N	Ni	$\mu_{eff.}$[b]/B.M.
$[NiL_3]Cl_2$	Blue	14.35 (14.5)	4.10 (3.65)	16.7 (16.95)	11.9 (11.85)	3.1_4
$[NiL_3]Br_2$	Blue	12.15 (12.3)	3.00 (3.10)	14.35 (14.35)	10.2 (10.05)	3.1_0
$[NiL_3]I_2$	Blue	10.5 (10.6)	2.60 (2.65)	12.3 (12.35)	8.75 (8.65)	3.1_2
$[Ni(MeL)_3]Cl_2\cdot 3\ H_2O\cdot 0.5\ EtOH$	Blue	19.6 (19.5)	5.20 (5.40)	13.45 (13.65)	10.25 (9.55)	3.1_2
$[Ni(MeL)_3]Br_2$	Blue	17.2 (17.25)	3.60 (3.85)	13.05 (13.4)	9.40 (9.35)	3.1_0
$[Ni(MeL)_3]I_2$	Blue	14.95 (15.0)	3.20 (3.35)	11.4 (11.65)	8.05 (8.15)	3.1_2
$[Ni(BuL)_3]Cl_2$	Blue	32.5 (32.5)	6.50 (6.35)	13.0 (12.65)	8.75 (8.85)	3.2_1
$[Ni(BuL)_3]Br_2$	Blue	28.0 (28.7)	5.35 (5.60)	11.4 (11.15)	8.05 (7.80)	3.1_8
$[Ni(BuL)_3]I_2$	Blue	25.35 (25.6)	4.85 (5.00)	10.1 (9.90)	6.85 (6.95)	3.1_1
$[Ni(Me_2L)_2Cl_2]$	Green	22.55 (22.35)	4.75 (4.70)	13.2 (13.05)	13.55 (13.65)	3.2_8
$[Ni(MeL)_2Cl_2]\cdot 0.33\ EtOH$	Green	19.05 (19.15)	4.25 (4.35)	13.5 (13.45)	14.25 (14.05)	3.2_4
$[Ni(MeL)_2Br_2]\cdot 0.33\ EtOH$	Green	15.85 (15.8)	3.45 (3.60)	11.0 (11.05)	11.55 (11.6)	3.2_6
$[Ni(L - H)_2]$	Greenish	15.8 (15.95)	3.20 (3.35)	18.0 (18.6)	19.2 (19.5)	*c*
$[Ni(Me_2L - H)_2]$	Brown	26.8 (26.9)	4.95 (5.10)	14.85 (15.7)	16.5 (16.45)	*c*
$[Ni(PhL - H)_2]$	Brown	42.1 (42.4)	4.35 (4.00)	12.0 (12.35)	12.9 (12.95)	*c*
$[Ni(Ph_2L - H)_2]$	Brown	55.3 (55.55)	4.25 (4.35)	9.10 (9.25)	9.80 (9.70)	*c*
$[Ni(MeL - H)_2]$	Green	21.55 (21.9)	4.00 (4.30)	17.1 (17.0)	17.9 (17.85)	*c*
$[Ni(BuL - H)_2]$	Green	34.7 (34.85)	5.95 (6.35)	13.35 (13.55)	14.1 (14.2)	*c*
BuL		40.45 (40.4)	7.75 (7.90)	15.65 (15.7)		
Ph_2L		61.35 (61.3)	5.10 (5.15)	10.1 (10.2)		

[a] Calculated values in parentheses. [b] At 290 K; diamagnetic corrections according to Pascal's constants. [c] Diamagnetic.

In the high-spin complex $[Ni(MeL)_3]Cl_2\cdot 3H_2O\cdot 0.5$ EtOH, the solvent molecules have been unequivocally identified by thermoanalytical measurements and by gas chromatography.[8] The H_2O molecules are essential to the existence of the crystalline compound, which cannot be isolated by treating $NiCl_2$ with MeL (mol ratio 1 : 3) in dry ethanol: the green compound $[Ni(MeL)_2Cl_2]$ precipitates from the blue solution. Moreoever, the green compound dissolves in ethanol giving a blue solution showing the electronic spectrum of $[Ni(MeL)_3]Cl_2$. From the ε values its concentration is shown to be two thirds of that expected, in agreement with the equation.

$$3[Ni(MeL)_2Cl_2] \longrightarrow 2[Ni(MeL)_3]Cl_2 + NiCl_2$$

Electronic Spectra.—Ligands (*Table* 2). The electronic spectra of the ligands are very similar and have no absorption bands below 28 200 cm^{-1}. The spectra also do not show significant differences from those reported for esters of dithiocarbamic acids.[9] The electronic spectra of our ligands can be readily interpreted in terms of the four bands (types I—IV following Janssen's classification [10]) present in the spectra of dithiocarbamic acid esters. The low-intensity band I has been assigned to the transition $n \rightarrow \pi^*$ where n is the highest-energy non-bonding orbital mainly localized on the thioxo-sulphur atom and π^* is the lowest-energy antibonding orbital. The band in the spectrum of Me_2L (which is soluble in many solvents) is shifted to higher frequencies with increasing solvent polarity and disappears in concentrated sulphuric acid, in agreement with the assignment. Band II, which is present in all the compounds in which the N atom is conjugated with the C=S group, was not unequivocally assigned. Band III was assigned to a $\pi \rightarrow \pi^*$ transition ' more or less located ' in the C=S group.

High-spin complexes (*Table* 3). The electronic spectra of the high-spin complexes ($\mu_{eff.} \simeq 3.1$ B.M. at room temperature) all show features consistent with octahedral patterns of approximately O_h geometry. The coincident spectra of $[NiL_3]X_2$, $[Ni(MeL)_3]X_2$, and $[Ni(BuL)_3]X_2$ (X = Cl, Br, or I) in the region of the *d-d* transitions suggest that the same chromophore is present in each case, shown to be *trans*-NiN_3S_3 by an *X*-ray determination of $[Ni(MeL)_3]Cl_2\cdot 3H_2O\cdot 0.5EtOH$,[11] the ligands being co-ordinated through the terminal N and

TABLE 2

Electronic spectra (10^3 cm^{-1}) of ligands [a]

Compound	Solvent	I $n\rightarrow\pi^*$	II $\pi\rightarrow\pi^*$	III $\pi\rightarrow\pi^*$ (C=S)	IV
L	Reflectance	[28.2]	30.3	38.8	42.9
	MeOH			37.1 (4.26)	46.5 (4.30)
MeL	Reflectance	[28.2]	29.9 [31.2]	41.5	
	MeOH		36.9 (4.28)	39.0 (4.20)	46.5 (4.30)
BuL	Reflectance	[28.2]	30.3 31.1	38.1	
	MeOH	[31.0] (2.39)	36.5 (4.18)	39.1 (4.09)	
Me_2L	Reflectance	[28.2]	30.7 [31.7]	[39.4]	43.1
	MeOH	[30.6] (1.96)	36.0 (4.05)	40.3 (3.85)	
	n-Hexane	30.3 (1.85)	35.7 (4.00)	40.3 (3.90)	46.1 (4.15)
	0.1 N aqueous Na[OH]			[42.0] (4.03)	44.6 (4.08)
	98% H_2SO_4				44.6 (4.01)
PhL	Reflectance		30.9	37.6 [b]	42.6 [b]
	MeOH		35.9 (4.14)	41.7 (4.18) [b]	
Ph_2L	Reflectance		[30.3] 33.3	37.0 [b]	
	MeOH		36.2 (4.28)	42.0 (4.14) [b]	

[a] log ε in parentheses, shoulders in square brackets. [b] Containing Ph components.

the non-methylated S atom. The same value of $\nu_1 = \Delta = 11\,600$ cm^{-1} for all the compounds indicates that the substituents on N(2) do not affect the ligating behaviour of the dithio-esters considered.

The complexes $[Ni(MeL)_2Cl_2]$ and $[Ni(MeL)_2Br_2]$ show the first spin-allowed band at lower energies than the corresponding band in $[Ni(MeL)_3]X_2$ (X = Cl or Br), suggesting that they have the chromophores $NiN_2S_2Cl_2$ and $NiN_2S_2Br_2$, respectively, the lowering of Δ being a consequence of the substitution by weaker ligands in the co-ordination sphere. The complex $[Ni(Me_2L)_2Cl_2]$ shows $\nu_1 = \Delta = 8\,700$ cm^{-1} lower than that ($\Delta = 9\,700$ cm^{-1}) found for $[Ni(MeL)_2Cl_2]$. This lowering is due to a decrease of electron density at N(3) caused by the methyl groups, and has recently been confirmed *via* molecular-orbital (m.o.) calculations in this laboratory.[12]

Low-spin complexes (*Table* 3). The low-spin complexes $[Ni(L-H)_2]$, $[Ni(MeL-H)_2]$, $[Ni(BuL-H)_2]$, $[Ni(Me_2L-H)_2]$, $[Ni(PhL-H)_2]$, and $[Ni(Ph_2L-H)_2]$ show electronic spectra consistent with square-planar, D_{2h}, geometry. Apart from a presumably almost constant correction for interelectron repulsion, the first spin-allowed transition, in the range 15 500—17 400 cm^{-1}, gives the ligand-field strength Δ, the value of which can give information on the co-ordinating behaviour of the ligands considered. The nearly coincident values of ν_1 for $[Ni\{NH_2N{=}C(S)NH_2\}_2]$ with a *trans*-NiN_2S_2 chromophore [13] and for $[Ni(L-H)_2]$ suggest the same chromophore for both compounds, L — H being co-ordinated through terminal N and non-methylated S atoms.

The complex $[Ni(Me_2L-H)_2]$, with ligand co-ordinated through terminal N and non-methylated S atoms,[14] shows ν_1 (15 800 cm^{-1}), at lower energy than that (at ν_1 17 400 cm^{-1}) of $[Ni(L-H)_2]$, as is also observed in the high-spin complexes with the same ligands. The same trend was observed for $[Ni(NMe_2CH_2CH_2S)_2]$ compared to $[Ni(NH_2CH_2CH_2S)_2]$.[15] The complexes $[Ni(PhL-H)_2]$, $[Ni(MeL-H)_2]$, and $[Ni(BuL-H)_2]$ show ν_1 at lower energies than the corresponding band of $[Ni(L-H)_2]$, which suggests that these compounds also have *trans*-NiN_2S_2 configurations (a *cis*-NiN_2S_2 configuration gives bands at higher

TABLE 3

Electronic (reflectance) spectra (10^3 cm^{-1}) of nickel(II) complexes [a]

Compound	Chromophore		ν_1	ν_2	ν_3	
(*a*) High-spin [b]						
$[Ni(MeL)_3]Cl_2\cdot3\,H_2O\cdot0.5\,EtOH$ [c]	*trans*-NiN_3S_3	[10.5]	11.6	17.9	[26.7]	30.7, 40.0
		[10.3] (1.46) [d]	11.1 (1.59) [d]	17.7 (1.35) [d]	27.4 (1.12) [d]	36.9 (4.68), [39.1] (4.59), 46.1 (4.57) [d]
$[Ni(MeL)_2Cl_2]\cdot0.33\,EtOH$			9.7 [11.1]	16.0	[26.6]	[29.4], 32.6, 35.1, [38.5], 42.6
$[Ni(MeL)_2Br_2]\cdot0.33\,EtOH$			10.0 [10.8]	15.9	[26.3]	31.4, 37.7, 42.4
$[Ni(Me_2L)_2Cl_2]$			8.7	14.6	24.4	30.0, [31.0]
(*b*) Low-spin [e]						
$[Ni(L-H)_2]$			17.4		23.3	29.9, 34.7, 42.4
$[Ni(MeL-H)_2]$			16.0	[21.0]		27.8, [33.3], 41.7
$[Ni(BuL-H)_2]$			14.8 [f]		26.3 [f]	
$[Ni(Me_2L-H)_2]$	*trans*-NiN_2S_2		15.8	[20.2] 21.7		[30.0], 30.8, 40.3
			15.9 (1.55) [d]	21.5 (1.99) [d]		31.0 (3.98), 37.5 (4.37) [d]
$[Ni(Ph_2L-H)_2]$			15.5	21.5	23.8	28.2, 34.0
$[Ni(PhL-H)_2]$			16.1	[22.5]		30.1, [33.8], 44.4
$[Ni\{NH_2N{=}C(S)NH_2\}_2]$	*trans*-NiN_2S_2		17.5	22.2	25.6	34.5
$[Ni\{NH_2NHC({=}S)NH_2\}_2][NO_3]_2$	*cis*-NiN_2S_2		19.0	22.7		28.5, 33.7

[a] log ε in parentheses, shoulders in square brackets. [b] ν_1, ν_2, and ν_3 correspond to the three spin-allowed *d–d* transitions $^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$, $^3T_{1g}(F)$, and $^3T_{1g}(P)$; higher frequencies are charge-transfer or ligand absorptions. [c] The same visible-reflectance and solution spectrum is obtained for $[NiL_3]X_2$, $[Ni(BuL)_3]X_2$ (X = Cl, Br, or I), and $[Ni(MeL)_3]X_2$ (X = Br or I). [d] In MeOH. [e] ν_1, ν_2, and ν_3 correspond probably to the three spin-allowed *d-d* transitions $^1A_{1g}\rightarrow{}^1A_{2g}$, $^1B_{1g}$ and ^1E_g; higher frequencies are charge-transfer or ligand absorptions. [f] Registration of the u.v. spectrum is not possible because of decomposition.

energies, *e.g.* $[Ni\{NH_2NHC(=S)NH_2\}_2][NO_3]_2$ shows[16] ν_1 at 19 000 cm^{-1}). The lower values of ν_1 may be related to steric and electronic effects of Ph on N(3) in the first case, and to deprotonated N(3) in the other cases (see i.r. spectra in text).

Infrared Spectra.—ν (NH) bands, which are present in the region 3 100—3 200 cm^{-1} of the i.r. spectra of the esters L, Me_2L, PhL, and Ph_2L, are absent in the spectra of $[Ni(L - H)_2]$, $[Ni(Me_2L - H)_2]$, $[Ni(PhL - H)_2]$, and $[Ni(Ph_2L - H)_2]$, suggesting deprotonation of the ligands at N(2) in the complexes. $\nu(NH_2)$ bands are shifted to lower frequencies and $\delta(NH_2)$ bands to higher frequencies with respect to the free ligands in the spectra of high-spin complexes, which is diagnostic of co-ordination of the NH_2 group. The complexes $[Ni(MeL - H)_2]$ and $[Ni(BuL - H)_2]$ show i.r. spectra lacking the $\delta(NH_2)$ band; this, according to n.m.r. studies,[17] confirms that the terminal N is deprotonated. $\nu(NH^-)$ bands are at frequencies higher than the ν(NH) bands of neutral co-ordinated ligands, suggesting strengthening of the linkage between the charged N atom and the proton.

The Me_2L ligand exhibits medium-intensity bands between 2 760 and 2 820 cm^{-1} attributable to a CH stretching vibration of the Me_2N group correlated with the presence of a lone pair on the N atom.[18] The lack of these bands in the spectrum of $[Ni(Me_2L - H)_2]$ and of $[Ni(Me_2L)_2Cl_2]$ indicates that a bond between nickel and the Me_2N group is formed.

With the exception of MeL, the spectra of the esters show bands at *ca.* 1 500 cm^{-1} assignable to a C–N stretching mode coupled with δ(NH); the contribution of the latter is more important, as confirmed for example in the case of PhL, the i.r. spectrum of which lacks the band at 1 500 cm^{-1} after deuteriation. In the same region new bands appear in the spectra of $[Ni(L - H)_2]$, $[Ni(MeL - H)_2]$, $[Ni(PhL - H)_2]$, and $[Ni(Me_2L - H)_2]$ at 1 510, 1 575, 1 550, and 1 545 cm^{-1}, respectively, attributable to a C–N stretching mode with partial double-bond character. The band at 1 575 cm^{-1} in the spectrum of $[Ni(MeL - H)_2]$ is not shifted on deuteriation, confirming this assignment. It is to be noted that the higher values of ν(CN) bands in the spectra of $[Ni(Me_2L)_2Cl_2]$, $[Ni(Me_2L - H)_2]$, $[Ni(MeL - H)_2]$, and $[Ni(BuL - H)_2]$ can be tentatively explained by admitting a higher electron drainage from non-methylated S atoms to metal, which enhances the double-bond character of the C–N as confirmed by calculation.[12] The higher electron drainage can be caused by lowering of the ligating ability of N(3) by methyl groups in complexes of Me_2L and by deprotonation in complexes of MeL − H and BuL − H. The deprotonation can lead to different hybridization of N orbitals, modifying the ligating behaviour, as already suggested from the electronic spectra.

The spectrum of $[Ni(Ph_2L - H)_2]$ does not show bands above 1 400 cm^{-1} attributable to C–N; this indicates co-ordination *via* N(2), because it would be expected that the electron drainage from N(2) to metal would weaken the C–N bond.

Co-ordination of non-methylated S atoms is confirmed by the lowering of ν(C=S) with respect to that in the free ligands for the high-spin complexes and by the lowering of ν_{sym} and ν_{asym} of the $C(S^-)SCH_3$ group for the low-spin complexes. The Cl co-ordination in $[Ni(MeL)_2Cl_2]\cdot 0.33$ EtOH is confirmed by the presence of a band attributable to ν(Ni–Cl) at 280 cm^{-1}, which is absent in the spectrum of $[Ni(MeL)_2Br_2]\cdot 0.33$ EtOH. In the spectra of the high-spin complexes new bands appear in the ranges 470—490 cm^{-1} and 360—370 cm^{-1} attributable to ν(Ni–N) and ν(Ni–S), respectively.[19]

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