Nickel(II) Complexes with Dithiomalonamide and *NN'*-Diphenyldithiomalonamide

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Dithiomalonamide (HL = Hdtma) and diphenyldithiomalonamide (HL = Hdpma) form diamagnetic planar complexes Ni(dtma)$_2$, Ni(dpma)$_2$, Ni(Hdtma)$_2$X$_2$ (X = Cl, Br, I, or ClO$_4$) and Ni(Hdpma)$_2$X$_2$ (X = I or ClO$_4$) and paramagnetic octahedral complexes Ni(Hdpma)$_3$X$_2$ (X = Cl, Br, or ClO$_4$). NiL$_2$ complexes are non-electrolytes: their electronic spectra in solution and their i.r. spectra in the solid state, both very similar to those of bis(dithioacetylacetonato)nickel(II), the increase in ν(CN), the decrease in ν(CS), and the ν(NiS) frequencies are consistent with a [NiS$_4$] co-ordination. NiL$_2$ form adducts NiL$_2$,*n*A (*n*A = 2 MCS, 2 DMF for Hdtma and DMF, 4 DMF, 2 HAc for Hdpma). The splitting orbital parameter Δ_1 indicates that these anion ligands assume an intermediate position in the spectrochemical series of sulphur donors. Ni(HL)$_2$X$_2$ and Ni(HL)$_3$X$_2$ are *S,N*-co-ordinated, as shown by the splitting of the ν(CN) and ν(CS), by their ν(NiN) and ν(NiS) i.r. bands and by the Δ_1 values, greater for the Ni(HL)$_2$X$_2$ (21 000 cm^{-1}) than for the NiL$_2$ (18 000 cm^{-1}) complexes. The Δ_1 parameters for the Ni(HL)$_2$X$_2$ six-membered ring complexes indicate a ligand strength stronger than in the analogous five-membered ring *S,N*-co-ordinated complexes of the dithio-oxamides. The distorted octahedral Ni(HL)$_3$X$_2$ complexes have *Dq* and *B* values characteristic of [NiS$_3$N$_3$] chromophores.

IN neutral or alkaline solutions dithiomalonamide [Hdtma], like dithio-oxamide, forms complexes with transition metal ions.[1] The existence of diamagnetic compounds Ni(dtma)$_2$,[1] Ni(dpma)$_2$,[2] an dNi(Hdtma)$_2$X$_2$ [3] was reported but these complexes have not been otherwise investigated. Dithiomalonamides are structurally analogous to β-dithioketones and may give metal complexes containing six-membered rings instead of the five-membered rings given by dithio-oxamides.[4,5] Dithiomalonamides offer the advantage, with respect to the β-dithioketones, of being isolable ligands, which can be comparatively studied with their complexes. The nickel(II) complexes of dithiomalonamide and *NN'*-diphenyldithiomalonamide (Hdpma) were investigated in order to compare them with the nickel(II) dithio-oxamide complexes previously studied.[5]

EXPERIMENTAL

Dithiomalonamide was prepared by the method of Taylor and Zoltewicz [6] and *N,N'*-diphenyldithiomalonamide by the method of Barnikow *et al.*[7] The acids were used at the following concentrations: HAc, glacial; HClO$_4$, 60; HCl, 37; HBr, 48; HI, 57%. All reagents were of pure chemical grade.

The complexes were prepared as follows: Ni(dtma)$_2$ and Ni(dpma)$_2$ from ethanolic solutions of the ligands and nickel(II) acetate with molar ratio M : L = 1 : 2; Ni(dtma)$_2$,2 DMF and Ni(dpma)$_2$,DMF by adding diethyl ether to a solution of the NiL$_2$ complexes in dimethylformamide; Ni(dpma)$_2$,4 DMF from a solution of NiL$_2$ in DMF by adding a little diethyl ether and cooling at 5 °C for 24 h. The other complexes were prepared by mixing warm solutions of nickel acetate [Ni(ac)] and of the ligand (HL) in the following ratios and solvents. Ni(Hdtma)$_2$Cl$_2$: Ni(ac) (2 mmol) in EtOH (25 ml) to HL (4 mmol) in EtOH (125 ml) + HCl (15 ml). Ni(Hdtma)$_2$Br$_2$: Ni(ac) (4 mmol) in EtOH (30 ml) + HBr (10 ml) to HL (8 mmol) in EtOH (250 ml) + HBr (15 ml). Ni(Hdtma)$_2$I$_2$: Ni(ac) (4 mmol) in EtOH (30 ml) + HI (5 ml) to HL (8 mmol) in EtOH (230 ml) + HI (6 ml); Ni(Hdtma)$_2$(ClO$_4$)$_2$: Ni(ac) (0·6 mmol) in HAc (30 ml) + HClO$_4$ (3 ml) to HL (0·3 mmol) in HAc (60 ml) + HClO$_4$ (6 ml). Ni(dpma)$_2$,2 HAc- Ni(ac) (2 mmol) in HAc (30 ml) to HL (4 mmol) in HAc (100 ml); Ni(Hdpma)$_3$Cl$_2$: Ni(ac) (0·7 mmol) in EtOH (6 ml) + HCl (6 ml) to HL (2 mmol) in EtOH (48 ml); Ni(Hdpma)$_3$Br$_2$: Ni(ac) (2 mmol) in EtOH (20 ml) + HBr (15 ml) to HL (4 mmol) in EtOH (110 ml); Ni(Hdpma)$_2$I$_2$: Ni(ac) (2 mmol) in EtOH (20 ml) + HI (15 ml) to HL (5 mmol) in EtOH (110 ml); Ni(Hdpma)$_2$(ClO$_4$)$_2$: Ni(ac) (1 mmol) in HAc (2·5 ml) + HClO$_4$ (2·5 ml) to HL (2 mmol) in HAc (40 ml); Ni(Hdpma)$_3$(ClO$_4$)$_2$: (a) by adding Ni(ac) (2 mmol) in cold EtOH (20 ml) + HClO$_4$ (15 ml) to HL (8 mmol) in EtOH (130 ml); a mixture of Ni(HL)$_2$(ClO$_4$)$_2$ (red) and Ni(HL)$_3$(ClO$_4$)$_2$ (green) was obtained; (b) by suspending these filtered red and green crystals in a hot solution of HL (250 mg) in EtOH (15 ml) and adding HClO$_4$ the red complex turned rapidly into the green complex which was filtered whilst still warm to avoid the precipitation of the ligand; (c) by mixing the warmed solutions (a), filtering the precipitate whilst still warm and cooling the filtered warm solution, only the complex Ni(Hdpma)$_3$(ClO$_4$)$_2$ (green) was formed. The compounds cannot be recrystallized and were analysed by conventional methods. Magnetic susceptibilities were measured by the Gouy method and corrected with the Pascal constants. Conductivities were measured with a WTW bridge at 25 °C.

I.r. spectra were recorded with a Perkin-Elmer 521 spectrophotometer on the solids in KBr pellets (4000—250 cm^{-1}), and in Nujol mulls on Polythene (550—250 cm^{-1}), and with a Perkin-Elmer FIS3 spectrophotometer in Nujol mulls on Polythene (400—60 cm^{-1}). Electronic spectra, in solution and on the solids on filter paper or in Nujol mulls, were recorded with a Beckman DK1A spectrophotometer.[8]

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RESULTS AND DISCUSSION

Dithiomalonamide forms diamagnetic planar complexes Ni(dtma)$_2$, Ni(dtma)$_2$,2 A (A=MCS,*DMF) and Ni(Hdtma)$_2$·X$_2$ (X = Cl, Br, I, or ClO$_4$). Diphenyldithiomalonamide forms diamagnetic planar complexes Ni(dpma)$_2$, Ni(dpma)$_2$,*n*A (*n*A=DMF, 4 DMF, 2 HAc) and Ni(Hdpma)$_2$,X$_2$ (X = I or ClO$_4$) and paramagnetic octahedral complexes Ni(Hdpma)$_3$,X$_2$ (X = Cl, Br, or ClO$_4$). The formation of cationic complexes Ni(HL)$_2$X$_2$ or Ni(HL)$_3$X$_2$ depends on the fact that in strong acid media the equilibrium $\mathrm{HL} \rightleftharpoons \mathrm{H}^+ + \mathrm{L}^-$ is shifted towards the undissociated form of the ligand, as in the case of dithio-oxamides.[4,5] The molar conductivities of all the perchlorato-complexes in DMF and MeNO$_2$, are typical of 1 : 2 electrolytes. In these solvents few other complexes have solubilities suitable for conductivity measurements. The lower conductivity of Ni(Hdpma)$_2$I$_2$ and Ni(Hdpma)$_3$Br$_2$ seems to indicate an interaction of the halide ion with the complex in DMF solution. Ni(dtma)$_2$, Ni(dpma)$_2$, and Ni(dpma)$_2$,2 HAc behave as non-electrolytes. The very low conductivity of this last compound and its i.r. and electronic spectra (see below) enable it to be considered as an adduct rather than as a cationic complex Ni(Hdpma)$_2$,Ac$_2$. An HAc adduct was already found as in the nickel(II) complex, Ni(*NN'*-dimethyldithio-oxamide)$_2$(HSO$_4$)$_2$,0·5 HAc.[5]

Infrared Spectra.—The i.r. assignments given for Hdtma by Jensen and Nielsen [9] were used for the tentative interpretation of the spectra of the complexes. The complete i.r. spectra are deposited as Supplementary Publication No. 20644 (5 pp.).†

The diamagnetic inner complexes Ni(dtma)$_2$ and Ni(dpma)$_2$ show some characteristic and very similar bands (Table 1) which indicate the same co-ordination for both complexes. The increase of the ν(CN) and the decrease of the ν(CS) frequencies with respect to the ligand and the existence of two ν(NiS) bands are consistent with a [NiS$_4$] square planar co-ordination.[10,11] By removal of a proton from the CH$_2$ group the six-membered ring acquires an aromatic character as in acetylacetonates, monothioacetylacetonates, and dithioacetylacetonates. The i.r. bands for the two complexes are very similar to those observed and calculated by Siiman and Fresco for the thioacetonates.[11,12] The observed ν(NiS) frequencies agree very well with those found in other [NiS$_4$] complexes like nickel xanthates (350—380 cm^{-1}) and dithiolates (330—430 cm^{-1}).[13] The observed ν(CS) frequencies are comparable with those observed in other inner complexes like Pt(S$_2$CNH$_2$)$_2$ (622 cm^{-1}) [13] and Ni(thiosemicarbazide)$_2$ (678 cm^{-1}).[14]

TABLE 1

Characteristic i.r. bands of the complexes

	Ni-(dtma)$_2$	Ni-(dpma)$_2$	Ni-(dpma)$_2$,-2HAc	Ni-(dpma)$_2$,-DMF
ν(C–N)	1529vsb	1528vs	1520vsb	1532sh
$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C}) + \delta(\mathrm{C{-}H})$	1435m	(1450m)	(1440m)	(1442m)
$\delta(\mathrm{C{-}H}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$	(1328vsb)	1316sb	(1310m)	(1312m)
$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$	1249ms	1250vs	1265s	1258sb
π(C–H)	793vs	796s	811m	808ms
$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	649s	647vs	647m	657ms
ν(Ni–S)	400m	366s	359m	365s
	352sb	326ms	350sh	326ms
ring def.	188ms	166w	164b	166vw

The adducts NiL$_2$,*n*A (A = DMF,HAc) give the i.r. spectra of NiL$_2$ + A. Ni(dtma)$_2$,2 MCS completely loses MCS when it is included in a KBr pellet under vacuum. The i.r. spectra of Ni(dpma)$_2$ and Ni(dpma)$_2$,-*n*A (*n*A = 2HAc,DMF) are very similar (Table 1) and show that HAc is present in the crystal in the acid form, hydrogen-bonded to the ligand molecules of the complex, as shown by the ν(CO) bands (1757 and 1695 cm^{-1}) intermediate between the values observed in the vapour and in liquid HAc,[15–17] but greater than the values of the CO$_2^-$ ion.[18]

The more relevant i.r. bands of the cationic complexes Ni(HL)$_2$X$_2$ and Ni(Hdpma)$_3$X$_2$, which are new or different with respect to the ligand, are reported in Table 2. In some cases a choice between two close bands was impossible. The bands assignable to ν(CN) and ν(CS), as main contribution, are split. As in other complexes of thioamidic polyfunctional ligands the higher ν(CN) and the lower ν(CS) frequencies may correspond to that half of the molecule *S*-bonded to the metal; the lower ν(CN) and the higher ν(CS) frequencies to the half of the molecule *N*-bonded to the metal. The ν(CN) and ν(CS) frequencies of Hdtma and its complexes lie in the range of those of the dithio-oxamide and its cationic nickel complexes.[5] The ν(NiN) and ν(NiS) frequencies lie in the range of the values found for the nickel(II) complexes of other thioamidic ligands like dithio-oxamides [5] [ν(NiN) 420—490 cm^{-1}; ν(NiS) 350—400 cm^{-1}] or quinazoline (1*H*,3*H*)-2,4-dithione [19] [ν(NiN) 510 cm^{-1}; ν(NiS) 340 cm^{-1}]. Also the strong deformation of the ν(NH) bands in these complexes support an *S*,*N*-co-ordination of the metal. The perchlorate ion is not deformed.

Electronic Spectra.—The electronic spectra of the non-electrolyte, diamagnetic NiL$_2$ complexes, and their adducts with MCS and DMF are essentially the same in the solid state (Table 3) and in MCS solution (Table 4)

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* MCS, methylcellusolve, 2-methoxyethanol.

† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20, items less than 10 pp. are supplied as full size copies).

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TABLE 2

Properties of the complexes $Ni(HL)_2X_2$ and $Ni(HL)_3X_2$

	I.r. bands [a]					Λ_M [c]	
	ν(CN)	ν(CS)	ν(NiN)	ν(NiS)	μ_{eff} [b]	DMF	MeCN
Hdtma	1440vs	800ms					
$Ni(Hdtma)_2Cl_2$	1473vs, 1402w, 1328s	928w, 810sb, 685s	427ms	385m, 331ms	*d*		
$Ni(Hdtma)_2Br_2$	1473vs, 1405w, 1320s	929m, 768s, 700ms	425s	381m, 330m	*d*		
$Ni(Hdtma)_2I_2$	1460vs, 1401w, 1300vs	927m, 718vs, 683m	421s	378m, 326m	*d*		
$Ni(Hdtma)_2(ClO_4)_2$	1473vsb, 1410vw, 1320vs	934m, 772s, 703s	421s	383m, 332m	*d*		167
Hdpma	1513vs	680vs					
$Ni(Hdpma)_2I_2$	1544s, 1508w, 1433vsb	684vs, 638m	477m	354w, 320w, 303m	*d*	116	
$Ni(Hdpma)_2(ClO_4)_2$	1550vs, 1440vsb	685vs, 647m	487m, 479sh	354vw, 322vw, 303m	*d*	153	145
$Ni(Hdpma)_3Cl_2$	1545s, 1534w, 1446s	688vs, 640sh		354m, 322vw, 302w	2·86		
$Ni(Hdpma)_3Br_2$	1528sb, 1437s	687vs, 639w	486w, 477sh	352w, 319m, 303m	2·99	125	
$Ni(Hdpma)_3(ClO_4)_2$	1523sb, 1430sb	691vs, 648vw	(462vw)	348w, 307m	3·10	153	152

[a] Relevant bands in cm^{-1}. [b] In B.M. [c] In Ω^{-1} cm^2 mol^{-1} from 10^{-3}M solution in dimethylformamide and nitromethane. [d] Diamagnetic.

TABLE 3

Electronic spectra (in cm^{-1}) of the solid complexes

	$^1A_g \rightarrow$	$^1B_{1g}$	$\rightarrow {}^1B_{3g}$	C.T.				
$Ni(dtma)_2$		14 930sh	18 020		25 320			
$Ni(dtma)_2$,2DMF		14 930sh	18 180		25 640			
$Ni(dpma)_2$		15 500	17 540sh	20 830sh	24 390			
$Ni(dpma)_2$,DMF		15 870	18 520sh	21 280	22 990			
$Ni(dpma)_2$,2HAc		15 220sh	17 610sh	21 500sh	23 260sh			
	$^1A_g \rightarrow$	$^3B_{1g}$ or $^3B_{3g}$	$\rightarrow {}^1B_{1g}$					
$Ni(Hdtma)_2Cl_2$			18 180	21 050sh	27 030			
$Ni(Hdtma)_2Br_2$			18 180	21 050sh	25 970			
$Ni(Ndtma)_2I_2$			17 860	20 620sh	25 640			
$Ni(Hdtma)_2(ClO_4)_2$			18 180	21 740	27 400			
$Ni(Hdpma)_2I_2$		11 110sh	17 700	22 990sh				
$Ni(Hdpma)_2(ClO_4)_2$		11 110sh	18 520	23 530	25 000			
	$^3A_{2g} \rightarrow$	$^3T_{2g}(F)$	$\rightarrow {}^3T_{1g}(F)$				*Dq*	*B*
$Ni(Hdpma)_3Cl_2$	8300sh	10 100	15 870	21 280	23 810	26 320	1010	720
$Ni(Hdpma)_3Br_2$	8300sh	10 000	16 050	20 410		25 000	1000	820
$Ni(Hdpma)_3(ClO_4)_2$	8300sh	10 280	16 390	19 800	22 990	28 990	1030	810

TABLE 4

Electronic spectra (in cm^{-1}, log ε in parentheses) of $Ni(dtaa)_2$ in methanol and of $Ni(dtma)_2$, $Ni(dpma)_2$, Hdtma and Hdpma in methylcellusolve [a]

	$Ni(dtaa)_2$ [b]		$Ni(dtma)_2$	$Ni(dpma)_2$
Transition [b]	Calcd. energy	Obs. max.	obs. max.	obs. max.
d–d				
$^1A_g \rightarrow {}^1B_{1g}(x^2-y^2 \rightarrow xy)$	17 580	14 890sh (2·52)	15 150 (1·51)	15 150 (1·90)
$^1A_g \rightarrow {}^1B_{3g}(xz \rightarrow xy)$	18 630	18 120 (3·45)	18 180sh (1·94)	17 540sh (2·33)
M → L charge transfer				
$^1A_g \rightarrow {}^1B_{2u}(xz \rightarrow L(\pi^*))$	19 120	18 120 (3·45)	22 730sh (3·15)	23 260sh (4·22)
$^1A_g \rightarrow {}^1B_{3u}(yz \rightarrow L(\pi^*))$	24 360	25 510sh (3·62)	25 640sh (3·85)	
L → M charge transfer				
$^1A_g \rightarrow {}^1B_{2u}, {}^1B_{3u}(L(\pi) \rightarrow xy)$	34 040	35 460sh (4·59)		34 600 (4·62)
$^1A_g \rightarrow {}^1B_{2u}, {}^1B_{3u}(L(\sigma) \rightarrow xy)$	43 800	41 150 (4·23)	39 680 (4·75	42 550 (4·43)
L → L*				
$^1A_g \rightarrow {}^1B_{2u}$	29 040	29 670 (4·33)	31 250 (4·56)	28 990 (4·78)
$^1A_g \rightarrow {}^1B_{1u}$	35 490	36 500 (4·66)	36 630 (4·81)	38 170 (4·51)

Hdtma = 28 330 (2·59), 37 310 (4·35). Hdpma = 21 740sh (1·79), 26 320sh (2·69), 32 900 (4·40), 45 460 (4·40).

[a] The frequencies of the last four bands of the complex $Ni(dpma)_2$ well agree with those calculated for the $[NiS_2C_2C]$ ring of the $Ni(dtaa)_2$ complex. As Hdpma shows two bands at 32 900 and 45 460 cm^{-1}, the bands of the complex at 34 600 and 42 550 cm^{-1} could be assigned to L → L* transitions and those at 28 990 and 38 170 cm^{-1} to L → M charge transfer transitions. The HPhN groups bonded to the ring could be responsible of this inversion. [b] From ref. 18.

or other solvents such as acetone, dimethylformamide, or the strongly co-ordinating pyridine. This shows that they are very stable square-planar complexes in which axial σ interaction is negligible, the metal p_z valence orbital being involved in an extensive π-orbital with a consequent planar symmetry stabilization. Their spectra in MCS solution are compared in Table 4 with the very similar spectrum of bis(dithioacetylacetonato)-nickel(II), $\mathrm{Ni(dtaa)_2}$, for which a complete energy level scheme has been given by Siiman and Fresco.[20] This similarity supports an $[\mathrm{S_4}]$ co-ordination for these inner complexes of the dithiomalonamides. The electronic spectrum of the solid complex $\mathrm{Ni(dpma)_2}$,2 HAc, which is very similar to those of the neutral inner complexes $\mathrm{NiL_2}$ and of their adducts with DMF, confirms that this compound is an adduct of the neutral complex $\mathrm{NiL_2}$.

The orbital parameter Δ_1[21] was calculated from the ${}^1A_g \longrightarrow {}^1B_{1g}$ ($x^2 - y^2 \longrightarrow xy$) in plane transition, by assuming a correction factor[22] ($F_2 = 10$, $F_4 = 800$) of 2800 cm^{-1}.[20] The calculated Δ_1 values of 17 950 cm^{-1} for $\mathrm{Ni(dtma)_2}$ and $\mathrm{Ni(dpma)_2}$ in solution place these ligand anions in the spectrochemical series of sulphur donors[20,23,24] in an intermediate position near dithioacetylacetonate, as follows: maleonitriledithiolate-(14 490) < diethyldithiophosphate(17 300) < dithioacethylacetonate(17 690) < dithiomalonamide anion-(17 950) = diphenyldithiomalonamide anion(17 950) < ethylxanthate(18 300) < diethyldithiocarbamate-(18 600) < 2,3-dimercaptopropanol anion(19 000) < dithiomalonate(20 200) < dithio-oxalate(20 500).

The electronic spectra of the solid high-spin, octahedral complexes $\mathrm{Ni(Hdpma)_3X_2}$ (X = Cl, Br, or $\mathrm{ClO_4}$) (Table 3) are similar to those of $\mathrm{NiS_3N_3}$ chromophores like $\mathrm{Ni(thiosemicarbazide)_3^{2+}}$[25] or $\mathrm{Ni(thiocarbohydrazide)_3^{2+}}$[26] supporting an *S,N*-co-ordination for these complexes. The splittings of the first spin-allowed transition, not due to i.r. overtone of the ligand, indicate a tetragonal distortion.[25] The third spin-allowed transition, calculated at 26 500 cm^{-1}, is masked by the very intense charge-transfer bands occurring at 20 000—26 000 cm^{-1}.

The electronic spectra of the solid diamagnetic complexes $\mathrm{Ni(Hdtma)_2X_2}$ (X = Cl, Br, I, or $\mathrm{ClO_4}$) and $\mathrm{Ni(Hdpma)_2X_2}$ (X = I or $\mathrm{ClO_4}$) show only one *d–d* band (${}^1A_g \longrightarrow {}^1B_{1g}$) *ca.* 18 000 cm^{-1}, the other *d–d* bands lying under the stronger charge transfer bands, as in the case of the bis(salicylaldiminato)nickel(II) complex.[27] The band energies for the solid Hdtma complexes are very similar and do not seem to be influenced by the change of the anion. A little greater difference is shown by the complexes $\mathrm{Ni(Hdpma)_2I_2}$ (17 700 cm^{-1}) and $\mathrm{Ni(Hdpma)_2(ClO_4)_2}$ (18 520 cm^{-1}). These last complexes also show a very low intensity band at 1100 cm^{-1} which may be assigned to a spin-forbidden transition ${}^1A_g \longrightarrow {}^3B_{1g}$ or ${}^3B_{3g}$.

The corrected splitting parameter Δ_1, calculated from the ${}^1A_g \longrightarrow {}^1B_{1g}$ ($x^2 - y^2 \longrightarrow xy$) transition of the cationic complexes $\mathrm{Ni(Hdtma)_2(ClO_4)_2}$ and $\mathrm{Ni(Hdpma)_2(ClO_4)_2}$ are significantly greater (21 000 cm^{-1}) than those (18 000 cm^{-1}) of the inner complexes $\mathrm{NiL_2}$. This confirms an $[\mathrm{S_2N_2}]$ co-ordination for the former and an $[\mathrm{S_4}]$ co-ordination for the latter complexes. The Δ_1 values for the $\mathrm{Ni(HL)_2X_2}$ complexes place dithiomalonamide and diphenyldithiomalonamide and the dithio-oxamides[5] in the following *S,N*-donor spectrochemical series dithio-oxamide(18 420) < *NN'*-dihydroxyethyldithio-oxamide (19 060) < *NN'*-dimethyldithio-oxamide-(19 550) < dithiomalonamide(21 000) < diphenyldithiomalonamide(21 300 cm^{-1}).

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