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Nickel(II) Complexes with Dithiooxamide, N,N'-di-methyl- and N,N'-di-hydroxyethyl-dithiooxamide

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Some complexes of Ni^{II} with dithiooxamide (DH_4), N,N'-dimethyldithiooxamide (Met_2DH_2) and N,N'-dihydroxyethyldithiooxamide ($HOEt_2DH_2$) were investigated in the solid state and in solution. The solid complexes $Ni(DH_4)_2(Cl,Br,ClO_4,HSO_4)_2$, $Ni(Met_2DH_2)_2(Cl,Br,ClO_4)_2$ $2H_2O$, $Ni(Met_2DH_2)_2Cl_2$ H_2O . 0.5 EtOH, $Ni(Met_2DH_2)_2(HSO_4)_2$. 0 5 HAc and $Ni(HOEt_2DH_2)_2(ClO_4)_2$ are diamagnetic. Their electronic spectra show a square planar coordination; the splitting parameters Δ_t (cm^{-1}), evaluated for the perchlorate complexes, are in the sequence $DH_4(18420) < HOEt_2DH_2(19060) < Met_2DH_2(19550)$. The compounds $Ni_2(HOEt_2D)_2$ glycol and $Ni_2(HOEt_2DH)_2(SO_4)$ 1.5 glycol are binuclear and polymer complexes containing one diamagnetic square planar and one paramagnetic octahedral nickel atom (μ_{eff} = 3.33 and 3.27 B.M.), as indicated also by their electronic spectra. The complexes investigated in solution by the Job method show that in glacial acetic acid containing HCl or $HClO_4$ the metal: ligand ratio is always 1:2, in methylcellosolve DH_4 and $HOEt_2DH_2$ give with $NiCl_2$ the ratio 1:1 while the stronger ligand Met_2DH_2 still gives the ratio 1:2; with the less competitive perchlorate all the three ligands give the ratio 1:2. The I.R. and far I.R. spectra of the soldis show that DH_4 and Met_2DH_2 are cordinated to the metal through both sulphur and nitrogen atoms. In the NiL_2X_2 complexes this coordination results in a splitting of the ν(CN) band in the region of 1500 cm^{-1} and of the ν(CS) band in the region of 800 cm^{-1} corresponding to the coordinated and uncoordinated halves of the molecules. This spliting is larger for the DH_4- than for the Met_2DH_2-complexes, presumably because of the inductive effect of the methyl group in this latter ligand.

Introduction

Dithiooxamide (DH_4) and N,N'-monosubstituted dithiooxamides generally give, in neutral media, polymeric and insoluble complexes, which, for divalent metals, correspond to a 1:1 stoichiometry. The dithiooxamide, acting as a bridging group, loses a proton from each nitrogen upon complexation.[1] The polymeric chains may have different lengths, depending upon the method of preparation.[2,3] We have demonstrated[4,5] that in strong acid media dithiooxamides can give crystalline and fairly soluble complexes with transition metals without losing protons. Some infrared studies have been performed on the polymeric 1:1 complexes of Ni^{II}, Cu^{II}, Hg^{II}, and Pb^{II} with N,N'-monosubstituted dithiooxamide,[6] on some complexes of the dithiooxamide with $TiCl_4$, $TiBr_4$, and $SnCl_4$[7] and on the complexes CoL_2Cl_2 (L = dithiooxamide or dimethyldithiooxamide).[8]

We have now extended our previous works on the complexes of tetrasubstituted dithiooxamides with transition metals[9,10] to the nickel(II) complexes with dithiooxamide (DH_4), N,N'-dimethyldithiooxamide (Met_2DH_2) and N,N'-dihydroxyethyl-dithiooxamide ($HOEt_2DH_2$), using conductivity and magnetochemical measurements and infrared and electronic spectra.

Experimental Section

For the preparation of the complexes all reagents were of the best commercial grade. Acid used: HAc glacial, HCl (37%), HBr (48%), $HClO_4$ (60%). Most of the complexes were prepared by cooling the warm solution that resulted from mixing the following solutions of the reagents: *$Ni(DH_4)_2Cl_2$*: $NiAc_2 \cdot 4H_2O$ (2 m*M*) in 30 ml HCl to DH_4 (7.5 m*M*) in 50 ml HAc. *$Ni(DH_4)_2Br_2$*: $NiBr_2 \cdot 3H_2O$ (3 m*M*) in 10 ml of HBr to DH_4 (6 m*M*) in 100 ml of HAc. *$Ni(DH_4)_2(ClO_4)_2$*: $Ni(ClO_4)_2 \cdot 6H_2O$ (2 m*M*) in 25 ml HAc to DH_4 (4 m*M*) in 50 ml HAc. *$Ni(DH_4)_2(HSO_4)_2$*: $NiSO_4 \cdot 7H_2O$ (2.5 m*M*) in 6 ml ethylene glycol to DH_4 (5 m*M*) in 60 ml HAc. *$(NiDH_2)_n$*: $NiAc_2 \cdot 4H_2O$ (2 m*M*) in 10 ml HAc to DH_4 (2 m*M*) in 10 ml HAc+20 ml EtOH and warming for 12 hours. *$Ni(Met_2DH_2)_2Cl_2$ $2H_2O$*: $NiAc_2 \cdot 4H_2O$ (4 m*M*) in 40 ml HCl to Met_2DH_2 (8 m*M*) in 80 ml HAc. *$Ni(Met_2DH_2)_2Cl_2$ H_2O 0.25 EtOH*: $NiCl_2 \cdot 6H_2O$ (8 m*M*) in 3 ml H_2O+30 ml HCl

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Table I. Analytical results.

		Ni	S	Cl	N	C	H_2O	$S_{(SO_4)}$	Color (in transparency)
$Ni(DH_4)_2Cl_2$	calcd.	15.86	34.66	19.16					brown
	found.	15.92	34.89	19.07					
$Ni(DH_4)_2Br_2$	calcd.	12.79	27.95						black-brown
	found	12.71	28.39						
$Ni(DH_4)_2(ClO_4)_2$	calcd.	11.78	25.75	14.24					brown
	found	11.76	25.79	13.99					
$Ni(DH_4)_2(HSO_4)_2$	calcd.	11.90	39.00			9.74		13.00	green
	found	11.99	38.37			9.86		11.10	
$Ni(Met_2DH_2)_2Cl_2 . 2H_2O$	calcd.	12.70	27.75	15.34			7.80		red
	found	12.76	27.87	15.55			9.63		
$Ni(Met_2DH_2)_2Cl_2 . H_2O . 0.25EtOH$	calcd.	12.89		15.57		22.38			red
	found	12.84		15.30		22.44			
$Ni(Met_2DH_2)_2Br_2 . 2H_2O$	calcd.	10.65	23.27						red-violet
	found	10.77	23.82						
$Ni(Met_2DH_2)_2(ClO_4)_2 . 2H_2O$	calcd.	9.94	21.73	12.01			6.10		red-brown
	found	9.74	21.34	11.47			6.44		
$Ni(Met_2DH_2)_2(HSO_4)_2 . 0.5HAc$	calcd.	10.13	33.21		9.67	18.66		11.07	red-violet
	found	9.95	32.81		9.74	18.59		10.28	
$Ni(HOEt_2DH_2)_2(ClO_4)_2$	calcd.	8.71	19.02	10.51					black-red
	found	8.70	18.64	10.22					
$Ni(HOEt_2D) . 0.5Glycol$	calcd.	19.83			9.46	28.40			red
	found	19.81			9.60	28.49			
$Ni_2(HOEt_2DM)_2(SO_4) . 1.5Glycol$	calcd.	16.28	22.23		7.77	24.98			black-blue
	found	16.31	22.54		7.80	24.60			

to Met_2DH_2 (8 m*M*) in 40 EtOH. *$Ni(Met_2DH_2)_2Br_2$ 2-H_2O*: $NiBr_2 \cdot 3H_2O$ (3 m*M*) in 10 ml HBr to Met_2DH_2 (6 m*M*) in 60 ml HAc. *$Ni(Met_2DH_2)_2(ClO_4)_2$ $2H_2O$*: $NiAc_2 \cdot 4H_2O$ (4 m*M*) in 60 HAc+13 ml $HClO_4$ to Met_2DH_2 (8 m*M*) in 70 HAc. *$Ni(Met_2DH_2)_2(HSO_4)_2$ 0.5 HAc*: $NiSO_4 \cdot 7H_2O$ (2.5 m*M*) in 6 ml ethylene glycol to Met_2DH_2 (5 m*M*) in 60 ml HAc. *$(NiMet_2$-$D)_n$*: $NiAc_2 \cdot 4H_2O$ (2 m*M*) in 10 HAc to Met_2DH_2 (2 m*M*) in 10 ml HAc+20 ml EtOH and warming for 12 hours. *$Ni(HOEt_2DH_2)_2(ClO_4)_2$*: $Ni(ClO_4)_2 \cdot$ $6H_2O$ (2.7 m*M*) in 12 ml $HClO_4$ to $HOEt_2DH_2$ (5.4 m*M*) in 15 ml EtOH. *$Ni(HOEt_2D)$ 0.5 glycol*: $NiSO_4 \cdot 7H_2O$ (5 m*M*) in 8 ml glycol to $HOEt_2DH_2$ (5 m*M*) in 12 ml glycol, by adding to the mixture 18 ml EtOH and warming for several hours.

$Ni_2(HOEt_2DH)_2(SO_4)$ 1.5 glycol: $NiSO_4 \cdot 7H_2O$ (2.5 m*M*) in 4 ml ethylene glycol to $HOEt_2DH_2$ (5 m*M*) in 10 ml EtOH, and warming for 1 hour. The color in bulk is black for the DH_4-complexes, black-violet for the Met_2DH_2-complexes, black, black-brown and black-violet for the $HOEt_2DH_2$-complexes in the given sequence.

The compounds were analysed by conventional methods (Table I). The SO_4-ion was determined gravimetrically in the HCl-solution of the complex after filtering the black polymer Ni–DH_4–complex or the ligand Met_2DH_2, which was precipitated by cooling the solution; a little SO_4 is lost especially in the first case. In the case of the polymers (NiL) the precipitation is quantitative and it is sufficient to weigh the precipitate.

Magnetic susceptibilities were measured with the Gouy method at room temperature, or at variable temperature, by using $HgCo(NCS)_4$ as calibrating standard and correcting for diamagnetism with the appropriate Pascal constants. I.R. spectra were recorded on KBr pellets from 4000 to 250 cm^{-1} with a Perkin Elmer 521 spectrophotometer and far I.R. spectra from 400 to 60 cm^{-1}, in nujol mulls, with a Hitachi FIS3 spectrophotometer. Electronic spectra were recorded from 200 to 2000 mμ, on the solids in nujol mulls or on filter paper and on the solutions in quartz cells, with a Beckman DK1A spectrophotometer. Conductivities were measured in acetone with a WTW conductivity bridge. The Job method of continuous variations was applied to the systems indicated in Table VI.

Results and Discussion

The solid complexes having the stoichiometry NiL_2X_2 (L = DH_4, Met_2DH_2, $HOEt_2DH_2$; X = Cl, Br, ClO_4, HSO_4) are diamagnetic. The molar conductivities of the perchlorate complexes in acetone (Λ_m = 178-184 $cm^2\ \Omega^{-1}\ mol^{-1}$) correspond to 1:2 electrolytes. Those of the halide and sulphate complexes could not be measured because of their low solubility.

The complexes $Ni(HOEt_2D) \cdot 0.5$ glycol and $Ni_2(HOEt_2DH)_2(SO_4)$ 1.5 glycol which are microcrystalline and poorly soluble, are probably polymeric. Both are paramagnetic. For one or two paramagnetic nickel atoms the following stoichiometric formulae enable the magnetic moments at 20°C to be calculated from the magnetic susceptibility, correction being made for the diamagnetism of the ligands:

	$Ni_2(HOEt_2D)_2$. glycol	$Ni_2(HOEtDH)_2$ (SO_4)1.5glycol	
for one Ni atom	3.33	3.27	B.M.
for two Ni atoms	2.36	2.31	B.M.

The lower magnetic moments calculated for two nickel atoms are intermediate between the values expected for singlet and triplet ground state. The full temperature range of temperature measurements, between 110 and 330°K, with three different field strengths, was applied to these complexes. The plot $1/\chi_m$ versus T gives straight lines (Figure 1) with an intercept θ {in the formula $\mu_\theta = 2.83\ [\chi_m(T-\theta)]^{1/2}$} of +17°C for $Ni_2(HOEtD)_2 \cdot$ glycol and of +6° for $Ni_2(HOEtDH)_2(SO_4) \cdot 1.5$ glycol.

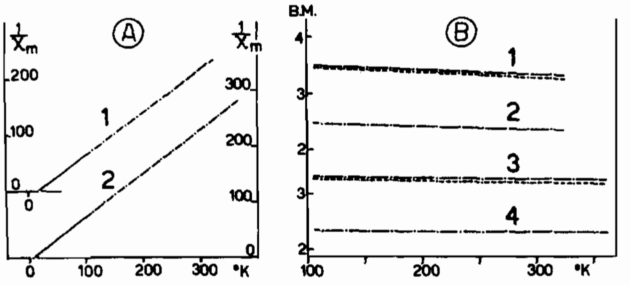
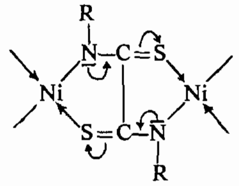


Figure 1. A) Plots of $1/\chi_m$ versus T(°K) and B) Plots of μ_{eff} (B.M.) versus T (°K) for the complexes: $Ni_2(HOEt_2D)_2 \cdot$ glycol: A1, B1 (B.M. calculated for 1Ni) and B2 (B.M. calculated for 2Ni); $Ni_2(HOEt_2DH)_2(SO_4) \cdot 1.5$ glycol: A2, B3 (B.M. calculated for 1Ni) and B4 (B.M. calculated for 2Ni). Dashed lines correspond to the μ_{eff} values corrected for the temperature independent paramagnetism (T.I.P.).

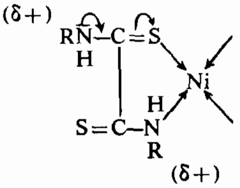
For both complexes the plot of $\mu_{eff} = 2.83\ [\chi_m \cdot T]^{1/2}$ versus T gives, a straight line in all cases, whether calculated for 1Ni or for 2Ni atoms (Figure 1), with a slight negative slope even if corrected for T.I.P. The magnetic susceptibilities obey the Curie-Weiss law and the magnetic moments μ_{eff} are sufficiently independent of the temperature and of the field strength to preclude the possibilities of spin-state isomerism and of cooperative interactions in the crystal. Therefore, in these complexes only one nickel atom may be considered paramagnetic with a presumably octahedral coordination, while the other one is diamagnetic with a presumably square planar coordination in a binuclear structure. The presence of an octahedral nickel. ion in these complexes is shown by the bands at 10750 and 10150 cm^{-1} in their electronic spectra. This case is analogous to that of the S, S'-0-xylyl-2, 3-pentanedionebis (mercaptoethylimine) nickel(II) dibromide[11] (magnetic moment = 1.5 B.M.) in which octahedral dibromo molecules may coexist with either the square-pyramidal monobromo complex or the square-planar dibromide, in the ratio of approximately one paramagnetic complex to three diamagnetic entities. Similar is the case of the bis (C, C'-diphenylethylendiamine) nickel(II) dichloroacetate[12] in which the unit cell contains both octahedral nickel ions and square-planar nickel ion in the ratio 2:1, with a paramagnetism of 2.5 B.M.

I.R. Spectra

Met_2DH_2-complexes (*Table II*). The very strong thioamide I band of the ligand (1528 cm^{-1}), having a high ν(CN) contribution,[9,13] is practically unaltered in the (Ni · Met_2D) complex (1521 cm^{-1}), in which both sulphur and both nitrogen atoms are symmetrically bonded to nickel atoms in the polymeric structure:



In the $Ni(Met_2DH_2)_2X_2$ (X = Cl, Br, ClO_4, HSO_4) complexes this band is split into two very strong bands at 1590-1600 cm^{-1} and 1480-1490 cm^{-1}, corresponding to an increase and a decrease of the (CN) double bond character of the metal-sulphur-bonded and of the metal-nitrogen-bonded half of the molecule, respectively, in a structure such as:



(A)

Similarly the very strong thioamide IV band of the ligand (867 cm^{-1}) having a high ν(CS) contribution,[9,13] has practically the same value in the polymer (862 cm^{-1}), with a second weaker band at 883 cm^{-1} due to the uncomplexated terminal groups of the polymer chaines. This band is split in the other complexes into a strong band at 870 cm^{-1} and into a second band at 800 cm^{-1} for the Br- and ClO_4-complexes, or at 847 cm^{-1} for the Cl- and HSO_4-complexes; this corresponds to an increase and a decrease of the (CS) double bond character of the metal-nitrogen-bonded and of the metal-sulphur-bonded half of the molecule, respectively, in the structure (A).

The very weak thioamide VI band of the ligand (462 cm^{-1}), corresponding to a (CS) deformation mode,[13] may be masked by the strong bands appearing in the complexes at 450-490 cm^{-1}; in context of the other far infrared bands these may be attributed to a metal-ligand bond.

The new bands observed in the complexes at 403-406 and 382-386 cm^{-1} may be assigned to a ν(NiS) mode analogously to the bands observed at 340 cm^{-1} in the nickel complex of quinazoline (1H, 3H)-2,4-dithione,[14] and at 351-383 cm^{-1} in the Ni-xanthates.[15] A predominantly ν(MS) mode was also assigned to the bands at 295-410 cm^{-1} in the Ni-dimercaptoethylene complex.[16]

Since no other new bands appear in the far I.R. spectra of the complexes, their strong bands at 450-490 cm^{-1} may be assigned to a ν(NiN) mode, like those observed at 510 cm^{-1} for the nickel complex of quinazoline (1H, 3H)-2,4-dithione,[14] at 494 cm^{-1} for the nicekl-bis-dimethylglyoximate[17] and at 435

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Table II. Infrared spectra (cm^{-1}) of Ni^{II} complexes of Met$_2$D H$_2$ (L)

		L	(NiL)$_n$	NiL$_2$Cl$_2$.2H$_2$O	NiL$_2$Br$_2$.2H$_2$O	NiL$_2$(ClO$_4$)$_2$.2H$_2$O	NiL$_2$(HSO$_4$)$_2$.0.5HAc	
		3180vs		3255ms	3230s	3260s	3225s	
	ν(NH)	3120sh		3150ms	3160ms	3165ms	3155m	
		3076vw		3120sh	3105ms	3130m	3105m	
				1604vs	1595vs	1588vsb	1603vsb	
I	ν(CN)	1528vs	1521vs	1555s	1510w	1520w	1520m	
				1480vs	1478vs	1478vs	1478vs	
	δ(CH$_3$)	1426ms	1440w	1440ms	1438ms	1435s	1434s	
II	δ(NH)+ν(CS)+ν(CN)	1345vs	1392s	1383vs	1383vs	1380vs	1382vs	
			1264vs 1230sh	1212vs	1214vs	1217vs	1214vs	ν(RN)
	ρ(CH$_3$)	1154w						
			1126s	1100vs	1100vs	1090vsb	1096s	ν(RN)?
				1064w	1062ms	1065sh	1073w	
III	ν(CS)+ν(RN)	1016vs	1032vs	1020s	1020ms	1020vs	1016vs	
	ν(CC)+def(CH$_3$)							
IV	ν(CS)	867vs	883w	872s	870s	870s	872vs	
			862m	847vs	803vs	802m	846m	
V	π(NH)	693vs	680w	620vs	625vs	620vsb	625vs	
		604m		584m	587m	592sh	582ms	
VI	def(CS)	462vw	476m	481s	479s	487s	459s	ν(MN)
			458s		452s		420sh	
			406s	403wb	405s	406ms	404m	ν(MS)
					386w	384m	382w	
		284sb	306mb	286s	284s	282mb	284s	
				238sh				
		210s		206sb		183m	220s	
		90s				124sb		

Table III. Infrared spectra (cm^{-1}) of Ni^{II} complexes of DH$_4$ (L).

		L	(NiL)$_n$	NiL$_2$Cl$_2$	NiL$_2$Br$_2$	NiL$_2$(ClO$_4$)$_2$	NiL$_2$(HSO$_4$)$_2$	
		3370sh	3425vs	3360m	3360s	3360s	3360m	
	ν(NH$_2$)	3295s	3260s	3280sh	3280sh	3290s	3290sh	
		3212s			3200sh	3170s	3200sh	
		3140s			3130sh	3000sb	3000sb	
				1675vs	1660s	1662vs	1665s	
	δ(NH$_2$)	1580vs	1590w	1640w	1626s	1640m	1629m	
				1592s	1560w		1585w	
I	ν(CN)	1423vs	1490vs	1475vsb	1468vsb	1485vs	1480vsb	
			1285w	1275vsb	1255s		1283s	
II	ν(CC)+ρ(NH$_2$)+ν(CS)	1327w	1348w	1310sh	1300ms	1300ms	1310sh	
III	ρ(NH$_2$)+ν(CS)	1193s		1213m	1212m	1220w	1230sh	
			1112s					
			1015w					
		890vw	865sh	865w	860w	870w		
			825s					
				1005vs	996vs	1000w	1002s	
IV	ν(CS)	832vs				980w		
			764vs	773s	748vsb	750s	753sb	
V	ω(NH$_2$)	700vs		700sh	650m	654m	650mb	
	τ(NH$_2$)	640vs	582m	602vs	602vs	605vs	606vs	
VI		472m		506w	505w		508w	
		407m	410s	435s	428s	451s	418s	ν(MN)
		393w		374m	371m	374m	374m	ν(MS)
			352s	355w	353sh	358sh	355w	
		293m	290w	279m	278m	273m	278m	
				195m	150m	150m	176m	
		90m		166m	115m	125m		

cm^{-1} in the bis(glycinato) nickel(II).[18] The same bands at 476-458 and 406 cm^{-1} are shown by the polymer in which Ni–N and Ni–S bonds are certainly present.

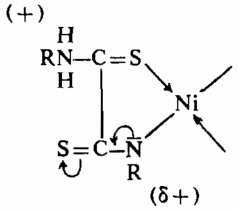
A Ni–N(amidic) bond stronger than the Ni–S bond may be questionable and requires further comment. The very strong band observed at 1264 cm^{-1} for the polymer and at 1212-1217 cm^{-1} for the other complexes is very similar to the strong band observed in the region of 1200 cm^{-1} by Desseyn *et al.*[6] in the polymeric 1:1 complexes of Cu^{II} and Ni^{II} with N,N′ substituted dithiooxamides. This band was assigned to R–N vibrations; the increase of the polarity of the R–N bond, subsequent to complexation, resulted in an increase in intensity. For this reason Cu^{II} and Ni^{II} were considered by these authors as being linked mainly to nitrogen, while Hg^{II} and Pb^{II}, which in their complexes, like the ligand, give practically no absorption in this region, were considered as being linked mainly to sulphur. Similarly the presence of a strong

Table IV. I.R. spectra (cm^{-1}) of the ClO_4^- and HSO_4^- ions in the NiL_2X_2 complexes. The values in parenthesis correspond to superimposed bands.

X	L						
ClO_4^-	DH_4	1120s	1095vs	922m		618s	469m
	Met_2DH_2	1137vs	(1090vsb)	917s	726sb	(620vsb)	466m
HSO_4^-	DH_4	1172vsb	1068s	(886s)	(851s)	568vs	438m
	Met_2DH_2	1166sb	1050ms	(783mb)	(693mb)	564ms	446m

ν(RN) band could mean that also in these complexes the Ni–N is stronger than the Ni–S bond.

In the polymeric 1:1 complex the negative charge of both nitrogen atoms is enhanced by removing the protons. In the case of the $Ni(Met_2DH_2)_2X_2$ complexes the negative charge of the nitrogen atom bonded to the metal may be enhanced either if the proton of the complexated HNR groups is involved in an hydrogen bridge removing the (δ+) chafge, or through a tautomeric structure such as:



(B)

in which the free HNR group is protonated. The (B) structure may also account for the splitting of the ν(CN) and ν(CS) bands.

The very strong ν(NH) band of the ligand (3180 cm^{-1}), which obviously disappears in the 1:1 polymer, is substituted in the other complexes by three strong or medium bands at 3230-3260, 3150-3165, and 3100-3130 cm^{-1}, observed on mulls in hexachlorobutadiene. Two ν(NH) bands could be ascribed, in the structure (A), to the different situation of the two, bonded and not bonded, RHN- groups. But, considering (a) that three ν(NH) bands are observed in the I.R. spectrum of DH_4 (Table III) at 3295, 3212 and 3140 cm^{-1}, (b) that the absorptions of the NH_2^+ groups are similar to those of the primary amines and (c) that the N–H stretching frequencies are lower in the former case,[19] the appearance of three ν(NH) bands in these complexes could be due to the presence of a RNH_2^+ group, as in structure (B).

Structure (B), in which only one hydrogen atom has been substituted by the metal, as in the 1:1 polymeric complex, could also explain the fact that a protonation of the other nitrogen atom by strong acids, which cuts the polymeric sequence, allows the formation of these crystalline and soluble 1:2 complexes instead of the insoluble 1:1 polymer obtained in neutral media.

The spectra of the perchlorate and sulphate ions (Table IV) correspond to a deformation of these ions from the Td symmetry,[20,22] obvious for the sulphate ion, by assuming it to be present as a HSO_4^- ion. The perchlorate ion deformation can be explained only by an interaction with the molecule of the complex.

It is, however, very likely that this interaction also takes place for the other anions, HSO_4^-, Cl^-, Br^-, since the I.R. and electronic spectra of the four complexes are very similar.

The possibility of a coordinative axial interaction taking place between the anion and the metal should be excluded from their elctronic spectra, which indicate a planar symmetry of these diamagnetic complexes. A purely electrostatic axial interaction with the metal could, however, justify the rather high difference (about 45 cm^{-1}) of the lower ν(CS) frequencies between the complexes of the more electronegative Cl^- and HSO_4^- ions (847 cm^{-1}) and the complexes of the less electronegative Br^- and ClO_4^- ions (803 cm^{-1}), in the sense that a more electronegative ion pointing on the metal in the structure (A) could induce a mesomeric backshift resulting in a higher double bond character of the (CS) group bonded to the metal. Another interaction of the ions could, however, take place on the hydrogen atom of the positively charged groups RNH(δ+) bonded to the metal in the structure (A), enhancing the Ni–N bond and weakening the Ni–S bond.

The infrared spectrum of $Ni(Met_2DH_2)_2Cl_2 \cdot H_2O \cdot 0.25\ EtOH$ is identical to that of $Ni(Met_2DH_2)_2Cl_2 \cdot 2H_2O$ excepting the presence of several bands of EtOH which may be observed on samples preserved in dessicator for some months.

DH_4-complexes (Table III). The greater difference between the I.R. spectra of the DH_4-complexes seems to be due to the absence of the screening or stabilizing effect of the methyl groups and to the consequently greater sensitivity of the DH_4 molecule toward the environment.

The ν(CN) band of the ligand (1423 cm^{-1}) is raised in the complexes to 1470-1485 cm^{-1}, corresponding to the $(\overset{\frown}{N}\!-\!C\!=\!\overset{\frown}{S}\rightarrow)$ group, which is sulphur-bonded to the metal. The lower ν(CN) frequency, corresponding to the $(S=C-N\rightarrow)$ group, which is nitrogen-bonded to the metal, could be identified in the strong band at 1255-1285 cm^{-1} in three of the $Ni(DH_4)_2X_2$ complex. Jensen and Nielsen[8] considered the 1280 and 1330 cm^{-1} bands of the complex $Co(DH_4)_2Cl_2$ as corresponding to the 1199 cm^{-1} band of DH_4. The assignement of the strong band at 1260-1280 cm^{-1} to a ν(CN) mode seems, however, to be likely, although it is about 150 cm^{-1} lower than that of the ligand. In both structures (A) and (B) a lone pair of the nitrogen atom is involved in the M–N bond without the compensation due to the inductive effect of the methyl groups that occurs in the Met_2DH_2–complexes, in which this ν(CN)

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Table V. Electronic spectra (cm^{-1}) of the solid complexes.

		$^1A_g \rightarrow {}^1B_{1g}$	$\rightarrow {}^1B_{3g}$	$\rightarrow {}^1Ag$ or C.T.	C.T.
$Ni(DH_4)_2Cl_2$		15380	17090	18870	23260
$Ni(DH_4)_2Br_2$		15620	17090	18690	24390
$Ni(DH_4)_2(ClO_4)_2$		15620	17240	18870	24390
$Ni(DH_4)_2(HSO_4)_2$		15080	17090	18350	
$Ni(Met_2DH_2)_2Cl_2 . 2H_2O$		16450	17860	19230	23810
$Ni(Met_2DH_2)_2Br_2 . 2H_2O$		16530	18180	19800	
$Ni(Met_2DH_2)_2(ClO_4)_2 . 2H_2O$		16750	18280	19610	23810
$Ni(Met_2DH_2)_2(HSO_4)_2 . 0.5HAc$		16640	18180	19120	
$Ni(HOEt_2DH_2)_2(ClO_4)_2$		16260	17700	18690	23530
$Ni(HOEt_2D)$. 0.5 Glycol	10750	16390		19530	
$Ni_2(HOEt_2DH)_2SO_4$. 1.5 Glycol	10150	15920	16810	18690	25000

Table VI. Nickel: Ligand ratio obtained by the Job method and electronic spectra (cm^{-1}) of the complexes in solution (extinctions in parenthesis).

Solution		Job	DH_4		Job	Met_2DH_2		Job	$HOEt_2DH_2$	
$NiAc_2$ in HAc+HCl	(9:1)	1:2	15620(269)	18020(123)	1:2	16810(360)	18870(335)	1:2	16260(739)	18450(684)
$NiAc_2$ in $HAc+HClO_4$	(9:1)	1:2	15620(683)	17790(490)	1:2	16670(453)	18870(540)	1:2	16450(91)	18660(87)
$NiCl_2$ in MCS		1:1	15150(46)	20320(81)	1:2	16180(17)	20410*(71)	1:1	15500(22)	21740(40)
$Ni(ClO_4)_2$ in MCS		1:2	17540*(370)	19120(560)	1:2	15870(93)	19880(288)	1:2	15620(51)	19800(120)
$NiAc_2$ in HAc		1:1	14920	16393*						

* Shoulder.

frequency is only 40-50 cm^{-1} lower. Furthermore, it may be observed that ν(CN) frequencies of pure single (CN) bonds, as in tertiary amines and simple amides, are at about 1000-1230 cm^{-1}.[19]

The ν(CS) band of the ligand (832 cm—^{1}) is lowered in the complexs to 750-770 cm^{-1} and corresponds to the $(\overset{\frown}{N}\dot{-}C\overset{\frown}{=}S\rightarrow)$ group. The higher ν(CS) frequency, corresponding to the $(S=C-N\rightarrow)$ groups, could be identified in the strong band at about 1000 cm^{-1} and is shown by three of the complexes. It is worthy of note that the perchlorate complex does not show the lower ν(CN) band and only a weak higher ν(CS) band at 980-1000 cm^{-1}. Similarly, the symmetrically complexated polymer shows only weak bands at 1285 and 1015 cm^{-1}, probably due to irregularities in the polymer itself, or to the presence of uncomplexated terminal groups in the polymer chains. The strong thioamide V band of the ligand (700 cm^{-1}), mainly ω(NH$_2$), might correspond to the band at 825-865 cm^{-1} in the complexes as was proposed by Jensen and Nielsen[8] for the $Co(DH_4)_2Cl_2$ complex, but it seems more likely that it corresponds to those at 650-700 cm^{-1}.

In the far infrared spectra of the complexes the strong band at 410-450 cm^{-1} may be assigned to a ν(MN) frequency, while the bands at 350-375 cm^{-1} may correspond to ν(MS) frequencies. These bands are lower in the DH_4—complexes than the corresponding bands of the Met_2DH_2—complexes, since, as a result of the inductive effect of the methyl groups, Met_2DH_2 is a stronger ligand than DH_4. The inductive effect of the CH_3 groups is clearly shown by the fact that the ν(CN) mode of Met_2DH_2 (1528 cm^{-1}) is greater than that of DH_4 (1423 cm^{-1}). The ν(CS) frequency is greater in Met_2DH_2 (867 cm^{-1}) than in DH_4 (832 cm^{-1}) because in DH_4 the sulphur atom is hydrogen-bonded to a NH_2 group of another molecule[23] and consequently the C=S double bond character is reduced.

The δ(NH$_2$) band of DH_4 (1580 cm^{-1}) still present in the polymer as a weak band (1590 cm^{-1}) due to uncomplexated terminal groups of the polymer chains, is shifted to higher frequencies and split in the complexes as a result of the different situation of the complexated and uncomplexated NH_2 groups, as in the structure (A).

In the DH_4—complexes the ClO_4^- and SO_4^{2-} ions also show a multiplicity of bands (Table IV) corresponding to an interaction of these ions with the complex, as in the Met_2DH_2—complexes.

$HOEt_2DH_2$—complexes. The I.R. spectra of the $HOEt_2DH_2$—complexes are much more complicated; only the perchlorate complex has the same stoichiometry as that the other two ligands, but no valuable information can be obtained from its I.R. spectrum.

Electronic spectra. The electronic spectra of the solid complexes (Table V) show three bands which may be considered as d-d in character because they are at greater energy in the Met_2DH_2 complexes than in the DH_4—complexes; this is in agreement with the fact, already observed for the ν(MN) frequencies, that Met_2DH_2 is a stronger ligand than DH_4.

These planar complexes may be considered as having a D_{2h} symmetry because of the presence of two symmetrical M—S bonds and two symmetrical M—N bonds. Some L(π) interaction with the Z axis of the metal may be expected, as in other sulphur coordinated complexes. This situation may be compared with that of the [bis(maleonitriledithiolato)Ni^{II}]$^{n-}$[24] and that of the bis(dithioacetylacetonato) Ni^{II},[25] in which the ligands were assumed to point to the metal

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in four directions intermediate to the XY axes.

With a similar orientation of the ligands to the XY axes the first two bands at 15000-16000 and at 17000-18000 cm^{-1} may be assigned to $^1A_g \rightarrow {}^1B_{1g}$ and $\rightarrow {}^1B_{3g}$ transitions, respectively, while the third, observable only in the solid spectra at 18300-19800 cm^{-1}, may be due to a $^1A_g \rightarrow {}^1A_g$ transition or to C.T. transition. The constancy of these bands in all the complexes of the same ligand, irrespective of the anions, seems to confirm that the anions are not coordinatively bonded to the metal in axial position, even if a pure electrostatic interaction may be admitted, as previously discussed.

With the coordinate system rotated 45° from the system used in square planar tetrahalides and other similar complexes, the splitting parameter Δ_1[26] is the reverse of the one–electron transition for the latter complexes. A correction factor[27] ($F_2 = 10F_4 = 800$ cm^{-1}) of 2800 cm^{-1},[25] gives Δ_1 for the perchlorate complexes of the three ligands in the sequence DH_4 (18420) < $HOEt_2DH_2$(19060) < Met_2DH_2(19550).

The complexes $Ni(HOEt_2D) \cdot 0.5$ glycol and $Ni_2(HOEt_2DH)_2 \cdot SO_4 \cdot 1.5$ glycol show a band at 10750 and 10150 cm^{-1} attributable to an octahedral nickel ion while the other d–d band corresponds to a planar nickel ion present in a binuclear structure.

The complexes existing in the solutions of the systems investigated (Table VI) by the Job method show that in HAc containing strong mineral acids (HCl or $HClO_4$) the metal: ligand ratio is always 1:2, while in the neutral solutions of $NiCl_2$ in methylcellosolve (MCS) the competitive action of the chloride ion is strong enough to reduce the ratio to 1:1 for the weaker ligands DH_4 and $HOEt_2DH_2$ but not for the stronger Met_2DH_2 which gives the ratio 1:2. In the solutions of $Ni(ClO_4)_2$ in methylcellosolve, in the absence of a competitive action of the perchlorate ion, all the three ligands give a ratio 1:2. Also, the solutions of DH_4 in pure HAc only give the 1:1 complex, due to the competitive action of the Ac^- ion and/or to a partial polymerization.

The influence of strong acids on the formation of the 1:2 complex, in solution and in the solid state, may be ascribed to the protonation of one nitrogen atom of the dithiooxamides which prevents polymerization.

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