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Nickel(II) Complexes with N,N′-Dimethyldithiomalonamide

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From neutral solutions of N,N′-dimethyldithiomalonamide (HL) is formed the neutral diamagnetic planar complex $[NiL_2]$ *while from strong acid media are formed the diamagnetic planar cationic red complexes* $[Ni(HL)_2]X_2$ *(X = Cl, Br, I,* ClO_4*), the paramagnetic octahedral cationic green complexes* $[Ni(HL)_3]X_2$ *(X = Cl,* ClO_4*,* BF_4*), the paramagnetic trans-octahedral green complex* $[Ni(HL)_2Cl_2]$ *and the paramagnetic complexes, presumably* $[Ni(HL)_2][NiX_4]$ *(X = Br, I), containing a planar cation and a tetrahedral anion.* NiL_2 *is* $[S_4]$ *coordinated; its infrared and electronic spectra are very similar to those of the analogous nickel complexes of dithiomalonamide, diphenyldithiomalonamide and dithioacetylacetone. The other complexes are S,N coordinated as shown by the splitting of their ν(CN) and ν(CS) and by the observed ν(NiN) and ν(NiS) infrared bands. The cationic red complex* $[Ni(HL)_2]Cl_2$ *transforms itself into the green complex* $[Ni(HL)_2Cl_2]$ *in the solid state: the transformation occurs in humid air, not in vacuum or dry atmosphere. The solutions of* $[Ni(HL)_2]I_2$ *and* $[Ni(HL)_2][NiI_4]$ *show identical electronic spectra, indicating the formation of very similar complex species by interaction with this solvent. The electronic spectra of the mixtures from which the solid complexes were obtained show that the presence of planar or octahedral complexes in solution depends on the Ni/HL ratio and on the composition of the solution.*

Introduction

Dithiomalonamides are structurally analogous to β-dithioketones, but, while these last ligands must be stabilized by complexation, they are isolable ligands which can be comparatively studied with their complexes. Furthermore, these thioamidic ligands may give metal complexes containing six-membered rings instead of the five-membered rings given by dithiooxamides[1,2]. In a previous work[3] we demonstrated that dithiomalonamide (HDTMA) and N,N′-diphenyldithiomalonamide (HPh_2DTMA) in neutral media give the S,S coordinated neutral complexes $Ni(DTMA)_2$ and $Ni(Ph_2DTMA)_2$ and in acid media the S,N coordinated cationic complexes $Ni(HDTMA)_2X_2$ (X = Cl, Br, I, ClO_4), $Ni(HPh_2DTMA)_2X_2$(X = I, ClO_4) and $Ni(HPh_2DTMA)_3X_2$(X = Cl, Br, ClO_4). The nickel (II) complexes of N,N′-dimethyldithiomalonamide (HMe_2DTMA) have now been prepared in order to investigate the influence of the methyl groups on the composition and the properties of the complexes.

Experimental

N,N′-dimethyldithiomalonamide was prepared by sulphurizing, with P_2S_5, the N,N′-dimethylmalonamide obtained with the method of Backes, West and Witeley[4]. The acids were used at the concentrations: HAc = glacial, HCl = 37%, HBr = 48%, HI = 57%, $HClO_4$ = 60% HBF_4 = 31%. All reagents were of pure chemical grade; $NiAc_2 \cdot 4H_2O$ will be indicated as Niac.

The neutral complex $Ni(Me_2DTMA)_2$ (olive green) was obtained from ethanolic solutions of Niac and of the ligand with molar ratio M:HL = 1:2, its addition compound $Ni(Me_2DTMA)_2 \cdot 1.5DMF$ (olive green) from a concentrated solution of the neutral complex in DMF by adding ethyl ether.

The cationic complexes were prepared by mixing the warm solutions of a nickel salt and of the ligand (HL) in the following ratios and solvents:

$Ni(HMe_2DTMA)_2Cl_2$ (red). HL (4 m*M*) in acetone (12 ml) + HCl (4 ml) to Niac (2 m*M*) in HAc (30 ml); the *red* solution, left to stand at 0° C for 12 h, gives *red* crystals, sparingly soluble in EtOH with green color.

$Ni(HMe_2DTMA)_2Cl_2$ (green). HL (4m*M*) in HAc (15 ml) + HCl (6 ml) to Niac (2 m*M*) in HAc (30 ml): the *red* solution, left to stand at 0° C for 48 h, gives *green* crystals; the same product is obtained by adding $NiCl_2 \cdot 6H_2O$ (2 or 4 m*M*) in EtOH (10 ml) to HL (4 m*M*) in EtOH (12 ml) + HCl (4.5 ml) and cooling the green solution; the green complex is soluble in DMF with green color; when the solutions of Niac (2 m*M*) in HAc (30 ml) and of HL (2 m*M*) in HAc (7 ml) + HCl (4 ml) are mixed the red solution, after 12 h at 0° C, gives a mixture of the red and the green $Ni(HL)_2X_2$ crystals.

$Ni(HMeDTMA)_3Cl_2$ (green). Niac (1 m*M*) in EtOH (6 ml) to HL (4 m*M*) in EtOH (8 ml) + HCl (1.5 ml):

when ethyl ether is added, the green solution gives, green crystals.

$Ni(HMe_2DTMA)_2Br_2$ (red). Niac (1 m*M*) in HAc (15 ml) to HL (2 m*M*) in HAc (15 ml) + HBr (6 ml): when ethyl ether is added, the green solution, after 12 h at 0° C, gives red crystals; the same product is obtained with a metal : ligand ratio = 1 : 4 and by using EtOH instead of HAc.

$Ni(HMe_2DTMA)Br_2$ (dark green). HL (1 m*M*) in HAc (5 ml) + HBr (1 ml) to Niac (2 m*M*) in HAc (15 ml): green solution.

$Ni(HMe_2DTMA)_2I_2$ (red). $NiCO_3 \cdot 2Ni(OH)_2 \cdot 6H_2O$ (2.5 m*M*) in HI (5 ml) + EtOH (15 ml) to HL (5 m*M*) in EtOH (15 ml): black green solution, the same product is obtained with a metal : ligand ratio = 1 : 4.

$Ni(HMe_2DTMA)I_2$ (violet). HL (2 m*M*) in HAc (30 ml) + HI (2 ml) to Niac (4 m*M*) in HAc (35 ml): red solution.

$Ni(HMe_2DTMA)_2(ClO)_2$ (wine red). Niac (2 m*M*) in EtOH (2 ml) + $HClO_4$ (4 ml) to HL (2 m*M*) in EtOH (20 ml): the red solution, after 2 h at 0° C, gives red crystals.

$Ni(HMe_2DTMA)_3(ClO_4)_2$ (green). Niac (1 m*M*) in EtOH (2 ml) + $HClO_4$ (4 ml) to HL (4 m*M*) in EtOH (30 ml): the green solution, after 12 h at 0° C, gives green crystals.

$Ni(HMe_2DTMA)_3(BF_4)_2$ (green). Niac (1 or 4 m*M*) in EtOH (5 ml) + HBF_4 (10 ml) to HL (4 m*M*) in EtOH (25 ml): green solution.

The compounds cannot be recrystallized and were analysed by conventional methods (Table I). Magnetic susceptibilities were measured by the Gouy method at room temperature and corrected with the Pascal constants. Conductivities were measured, when possible, with a WTW bridge at 25° C. Infrared spectra were recorded on the solid complexes in KBr pelletts from 4000 to 250 cm^{-1} and in nujol mulls on polythene from 550 to 250 cm^{-1} with a Perkin Elmer 521 spectrophotometer and in nujol mulls on polythene from 400 to 60 cm^{-1} with a Perkin Elmer FIS3 spectrophotometer. Electronic spectra, in solution or on the solids on filter paper on in nujol mulls, were recorded with a Beckman DK 1A spectrophotometer.

Results and Discussion

From neutral solutions N,N′-dimethyldithiomalonamide forms the neutral diamagnetic planar complex $Ni(Me_2DTMA)_2$, and from strong acid media the diamagnetic planar cationic complexes $Ni(HMe_2DTMA)_2X_2$ (X = Cl, Br, I, ClO_4) (red), the paramagnetic octahedral cationic complexes $Ni(HMe_2DTMA)_3X_2$ (X = Cl, ClO_4, BF_4) (green) and the paramagnetic complexes $Ni(HMe_2DTMA)_2Cl_2$ (green) and $Ni(HMe_2DTMA)X_2$ (X = Br, I). These last two types of complexes do not correspond to any type of complex formed by dithiomalonamide and diphenyldithiomalonamide[3]. The formation of the cationic complexes depends on the equilibrium $HL \rightleftharpoons H^+ + L^-$ which, in strong acid media, is shifted towards the undissociated form of the ligand[3], as in the case of dithiooxamides.[2,5] In the complexes $Ni(HMe_2DTMA)_2Cl_2$ (green) and $Ni(HMe_2DTMA)X_2$ (X = Br, I) too, formed in strong acid media, the ligand is bonded in the undissociated form. These complexes are only very slightly soluble in all the common solvents or readily decompose in their diluted solutions, so that neither conductivity measurements

TABLE I. Analytical data, found % (calcd. %), and magnetic susceptibilities μ_{eff} in Bohr magnetons.

	M.P. (° C)	Ni	S	X	μ_{eff}
$[Ni(Me_2DTMA)_2]$	> 350	15.25(15.40)	33.42(33.65)		dia
$[Ni(Me_2DTMA)_2] \cdot 1.5$ DMF		12.10(11.96)	26.96(26.11)		dia
$[Ni(HMe_2DTMA)_2]Cl_2$	190–2	12.85(12.93)	28.14(28.25)	15.50(15.62)	dia[b]
$[Ni(HMe_2DTMA)_2]Br_2$[a]	227–30	11.15(10.81)		29.14(29.44)	dia
$[Ni(HMe_2DTMA)_2]I_2$	209–12	8.66(9.22)	20.29(20.14)		dia
$[Ni(HMe_2DTMA)_2](ClO_4)_2$	225–8	10.09(10.09)	22.53(22.04)	11.91(12.19)	dia
$[Ni(HMe_2DTMA)_2Cl_2]$	222 dec.	12.79(12.93)	28.92(28.25)	15.64(15.62)	3.12[b]
$[Ni(HMe_2DTMA)_2][NiBr_4]$	224 dec.	15.16(15.42)	17.46(16.84)	42.10(41.98)	3.55(2.51)[c] 3.52[d]
$[Ni(HMe_2DTMA)_2][NiI_4]$	192–5	12.01(12.37)	13.74(13.51)		3.31(2.34)[c] 3.28[d]
$[Ni(HMe_2DTMA)_3]Cl_2$	120 dec.	9.59(9.53)	31.33(31.22)	11.70(11.51)	3.02[e] 2.94[f]
$[Ni(HMe_2DTMA)_3](ClO_4)_2$	184–6	7.68(7.89)	25.82(25.85)	9.10(9.53)	3.00[e] 2.90[f]
$[Ni(HMe_2DTMA)_3](BF_4)_2$	168–71	8.16(8.17)	26.75(26.76)		3.03[e] 2.94[f]

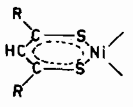
[a] C% = 22.39(22.10). [b] $[Ni(HL)_2]Cl_2$ shows a weak paramagnetism due to the beginning of the formation of $[Ni(HL)_2Cl_2]$; the magnetic susceptibility of $[Ni(HL)_2Cl_2]$ could be corrected only for the Pascal constants. [c] Values referred to one nickel atom and, in brackets, to both nickel atoms; susceptibilities corrected for Pascal constants. [d] Values referred to one nickel atom, corrected for X_{obsd} of $Ni(HL)_2X_2$ + Pascal const. for NiX_2. [e] Values corrected for the Pascal constants. [f] Values corrected for T.I.P.

TABLE II. Electronic spectra ($\mathrm{cm^{-1}}$, log ε) of $\mathrm{Ni(DTAA)_2}$[6,7] in methanol and $\mathrm{Ni(Me_2DTMA)_2}$ in methylcellosolve and their characteristic infrared bands ($\mathrm{cm^{-1}}$) in the solid state.

	$\mathrm{Ni(DTAA)_2}$		$\mathrm{Ni(Me_2DTMA)_2}$
	calcd. energy	obs. max.	obs. max.
d–d transition:			
$^1A_g \rightarrow {}^1B_{1g}(x^2-y^2 \rightarrow xy)$	17580	14890sh(2.52)	15150sh(2.43)
$^1A_g \rightarrow {}^1B_{3g}(xz \rightarrow xy)$	18630	18120 (3.45)	18020 (2.91)
M→L charge transfer:			
$^1A_g \rightarrow {}^1B_{2u}(xz \rightarrow L(\pi^*))$	19120	18120 (3.45)	23530sh(3.31)
$^1A_g \rightarrow {}^1B_{3u}(yz \rightarrow L(\pi^*))$	24360	25510sh(3.62)	26320sh(3.94)
L→M charge transfer:			
$^1A_g \rightarrow {}^1B_{2u}, {}^1B_{3u}(L(\pi) \rightarrow xy)$	34040	35460sh(4.59)	
$^1A_g \rightarrow {}^1B_{2u}, {}^1B_{3u}(L(\sigma) \rightarrow xy)$	43800	41150 (4.23)	40530 (4.61)
L→L*			
$^1A_g \rightarrow {}^1B_{2u}$	29040	29670 (4.33)	30960 (4.62)
$^1A_g \rightarrow {}^1B_{1u}$	35490	36500 (4.66)	37630 (4.72)
$\mathrm{HMe_2DTMA}$ = 29330(2.33), 37810(4.33)			
$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$			1510vsb
$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C}) + \delta(\mathrm{C{-}H})$		1488	(1418m)
$\delta(\mathrm{C{-}H}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$		1313	1333m
$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$		1292	(1233vs)
$\pi(\mathrm{C{-}H})$		831	778s
$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$		705	650m
$\nu(\mathrm{Ni{-}S})$		390	329m
		371	(282sh)
ring def.		[160]	163vs
[calcd.]			

could be taken nor electronic spectra recorded on their solutions. Their magnetic properties will be discussed with their I.R. and electronic spectra.

The neutral complex $\mathrm{Ni(Me_2DTMA)_2}$ has an $\mathrm{S_4}$-coordination, like the $\mathrm{Ni(DTMA)_2}$ and $\mathrm{Ni(Ph_2DTMA)_2}$ complexes[3], as shown by the remarkable analogies of the I.R. and electronic spectra (Table II) of these complexes with those of the nickel(II) dithioacetylacetonate, $\mathrm{Ni(DTAA)_2}$[6,7]. When a proton of the $\mathrm{CH_2}$ group is removed, the six-membered ring acquires a pseudo-aromatic character, common to all these complexes.



($\mathrm{R = CH_3NH, PhNH, NH_2\ CH_3}$)

The observed ν(CS) and ν(NiS) frequencies are comparable to those observed in other neutral complexes.[3,8,9]

The electronic spectrum of the neutral complex is essentially the same in the solid state as it is in solutions of methylcellosolve, dimethylformamide or of the strongly coordinating pyridine. This indicates that, in this $[\mathrm{S_4}]$ planar complex too, the axial σ interactions are negligible. The orbital parameter Δ_1[10], calculated from the $^1A_g \rightarrow {}^1B_{1g}(x^2-y^2 \rightarrow xy)$ in plane transition by assuming a correction factor (11) ($F_2 = 10 \times F_4 = 800$) of 2800 $\mathrm{cm^{-1}}$ (7), is (17950 $\mathrm{cm^{-1}}$), i.e. equal to those of the $\mathrm{Ni(DTMA)_2}$ and $\mathrm{Ni(Ph_2DTMA)_2}$ complexes in solution, and, in the spectrochemical series of sulphur donors[7,12,13], place these ligand anions in an intermediate position near dithioacetylacetonates.

The infrared spectra of the other complexes (Table III) containing the ligand in the undissociated form, are very similar and show the splitting of the ν(CN) band of the ligand (1550 $\mathrm{cm^{-1}}$) into two bands at higher (1570–1590 $\mathrm{cm^{-1}}$) and lower (1460–1480 $\mathrm{cm^{-1}}$) frequencies, and of the ν(CS) band of the ligand (893 $\mathrm{cm^{-1}}$) into two bands at higher (890–920 $\mathrm{cm^{-1}}$) and lower (between 640 and 880 $\mathrm{cm^{-1}}$) frequencies. This splitting is typical for an S,N-coordination of the ligand to the metal.[2,3] Furthermore, new bands in the far infrared region can be assigned to ν(NiN) and to ν(NiS) frequencies. Table III gives the new bands appearing in

TABLE III. More relevant i.r. bands (cm^{-1}) for the complexes $Ni(HL)_2X_2$ (X = Cl, Br, I, ClO_4, $NiBr_4$, NiI_4), $[Ni(HL)_2Cl_2]$ and $Ni(HL)_3X_2$ (X = ClO_4, BF_4, Cl).

	ν(CN)			ν(CS)			ν(NiN)			ν(NiS)	
HMe_2DTMA		1550vs			893s						
$Ni(HL)_2Cl_2$	1580vs		1483ms	908ms	815msb	700ms	489ms	471s	414mb	360s	297m
$Ni(HL)_2Br_2$	1590vs	1510m	1475m	913m	876mb	658m	486sh		420sh	356ms	297ms
$Ni(HL)_2I_2$	1580vs	1550m	1465m	895m	850mb	672w	486sh		408mb	354ms	295ms
$Ni(HL)_2(ClO_4)_2$[a]	1590vs		1480ms	910w	775mb	692m	497sh		409vw	359ms	284ms
$Ni(HL)_3Cl_2$	1565vs		1470s	905m	780mb	732ms 714ms	486m	454w		312s	
$Ni(HL)_3(ClO_4)_2$[b]	1570vs		1469s	900m	757ms	671mb	476w		427ms	310vsb	282sh
$Ni(HL)_3(BF_4)_2$[c]	1567vs		1467s	901m	805sh	692sh	498w	482sh	427mb	316sb	
$[Ni(HL)_2Cl_2]$[d]	1586vs	1573sh	1480vs	918ms	783ms	717sb	509sh	454vs		321ms	296sb
$Ni(HL)_2 \cdot NiBr_4$[e]	1580vs		1470vs	890ms	718s	641s	469m	456sh		349vs	278ms
$Ni(HL)_2 \cdot NiI_4$[f]	1578vsb	1553vsb	1461ms	900s	737vs	660sb	490w			352m	

[a] ClO_4^- bands: 1095vsb, 927w, 630vs, 467m. [b] ClO_4^- bands: 1096vsb, 927–917w, 627sb, 451m. [c] BF_4^- bands: 1050s, 994ms, 740vsb, 473s, 348vw. [d] ν(NiCl): 182 vsb. [e] $NiBr_4^{2-}$ bands: 235s, 114s. [f] NiI_4^{2-} bands: 179s.

TABLE IV. Electronic spectra of the complexes (kK), ε in brackets.

	(L)		$^1A_g \rightarrow {}^3B_{1g}$ or $^3B_{3g} \rightarrow$		$^1B_{1g}$	$\rightarrow {}^1B_{3g}$	C.T.		
A) Solids:									
$Ni(Me_2DTMA)_2$	6.76		10.53sh		15.38	18.02sh		25.32	
			$^1A_g \rightarrow {}^3B_{1g}$ or $^3B_{3g}$			$\rightarrow {}^1B_{1g}$			
$Ni(HMe_2DTMA)_2Cl_2$	6.76		11.11sh			17.70sh	21.50	27.03	
$Ni(HMe_2DTMA)_2Br_2$	6.45		10.26sh			18.02	21.28	27.40	
$Ni(HMe_2DTMA)_2I_2$	6.45		10.53sh			17.70	20.83sh	27.78	
$Ni(HMe_2DTMA)_2(ClO_4)_2$			10.75sh			17.95	21.19	27.40	
					$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	$\rightarrow {}^3T_{1g}(F)$			B
$Ni(HMe_2DTMA)_3Cl_2$	6.64		8.45sh		10.05	15.75	22.07sh		0.72
$Ni(HMe_2DTMA)_3(ClO_4)_2$	6.54		8.40sh		10.00	16.13	21.74sh		0.85
$Ni(HMe_2DTMA)_3(BF_4)_2$	6.54		8.47sh		9.76	15.62	21.74sh		0.79
$[Ni(HMe_2DTMA)_2Cl_2]$	7.02		9.90		13.79	17.54sh	23.26sh		
$Ni(HMe_2DTMA)_2[NiBr_4]$	6.45	7.94	10.41	13.51	17.03	20.75sh	27.03		
$Ni(HMe_2DTMA)_2[NiI_4]$		7.41		11.43	18.18sh	21.05sh	27.78		
B) Solutions:						d–d bands			
$Ni(HMe_2DTMA)_2I_2$ in acetone			8.40sh[70]		9.26[110]		12.27sh[70]	14.49[216]	
$Ni(HMe_2DTMA)_2[NiI_4]$ in acetone			8.40sh[83]		9.22[132]		12.27sh[95]	14.28[290]	
a) $NiCl_2$ + 2HL in EtOH + HCl (green)			8.47sh[17]		9.71[26]		13.89[19]	15.87[37]	
b) $NiAc_2$ + 2HL in HAc + HCl (red)			8.47sh[3]		9.52[4]			17.61[217]	
c) $NiAc_2$ + 2HL in HAc + Acet. + HCl (green)			8.47sh[13]		9.52[19]			17.36[144]	
d) $NiAc_2$ + 2HL in EtOH + HBr (green)			8.33sh[13]		9.57[22]			16.00[47]	
e) $2NiAc_2$ + HL in HAc + HBr (green)			7.07[45]		7.72[39]		12.99[39]		
f) $NiAc_2$ + HL in EtOH + $HClO_4$ (red)			9.35[7]		9.57[10]			17.70[50]	
g) $NiAc_2$ + 4HL in EtOH + $HClO_4$ (green)			8.47 [23]		9.71[46]			16.00[64]	

the I.R. spectra of the complexes in the range of the ν(NiN) and ν(NiS) frequencies observed for other nickel(II) complexes.[2,3,14]

In these HMe_2DTMA complexes a strong deformation of the ν(NH) bands is consistent with an S,N coordination; the perchlorate and fluoborate ions are not coordinated.

The electronic spectra (Table IV) of the solid cationic diamagnetic complexes $Ni(HMe_2DTMA)_2X_2$ (X = Cl, Br, I, ClO_4) show a weak band, appearing at 6.5–7.0 kK in all the solid complexes, which is ascribable to the ligand, and a weak shoulder at 10.3–11.1 kK which may be assigned to a spin-forbidden transition $^1A_g \rightarrow {}^3B_{1g}$ or $^3B_{3g}$. Only one d–d band is recognizable in these solid complexes at 17.7–18.0 kK ($^1A_g \rightarrow {}^1B_{1g}$), the other d–d band lying under the charge transfer bands as in other complexes.[3] The energies of this band are very similar in all these solid complexes and do not seem to be influenced by the change of the anion. The corrected splitting parameters Δ_1, calculated from the $^1A_g \rightarrow {}^1B_{1g}$ ($x^2–y^2 \rightarrow xy$) transition of the cationic complexes are significantly greater (20.5–20.8 kK) than that of the neutral complex NiL_2 (17.95 kK). This confirms an $[S_2N_2]$ coordination for the cationic and an $[S_4]$ coordination for the neutral complexes. The Δ_1 value for the $Ni(HL)_2X_2$ complexes places dimethyldithiomalonamide and the dithiooxamides[2] in the following S,N-donor spectrochemical series: dithiooxamide(18.42)<N,N'-dihydroxyethyldithiooxamide(19.06) < N,N'-dimethyldithiooxamide(19.55) < dimethyldithiomalonamide (20.5–20.8<dithiomalonamide(21.0) < diphenyldithiomalonamide(21.3).

The electronic spectra of the solid high-spin, octahedral complexes $Ni(HMe_2DTMA)_3X_2$ (X = Cl, ClO_4, BF_4) (Table IV) are similar to those of thc analogous HPh_2DTMA-complexes[3] and of other S_3N_3 chromophores like Ni(thiosemicarbazide)$_3{}^{2+}$ [15] or Ni(thiocarbohydrazide)$_3{}^{2+}$, thus confirming an S,N coordination. The splitting of the first spin-allowed transition, not due to overtone of the ligand, indicates a tetragonal distortion.[15]

The green $Ni(HMe_2DTMA)_2Cl_2$ complex has, at room temperature, a magnetic moment (3.12 B.M.) in the range 2.9–3.3 B.M. usually observed for octahedral nickel(II) compounds. Its electronic spectrum in the solid state (Table IV) shows four bands in the range 7–18 kK which may be d–d in character and correspond to the splitting of the ν_1 ($^3A_{2g} \rightarrow {}^3T_{2g}(F)$) and ν_2 ($^3A_{2g} \rightarrow {}^3T_{1g}(F)$) bands in a complex of D_{4h} *trans*-octahedral symmetry $[Ni(HMe_2DTMA)_2Cl_2]$. The first band at 7 kK could contain the ligand band observed at 6.5–6.7 kK in the other complexes. Such a splitting was observed for the $Ni(pyridine)_4Cl_2$ [16] and for the $Ni(thiazole)_4Cl_2$ [17] complexes at least for the ν_1 band. The green $[Ni(HMe_2DTMA)_2Cl_2]$ complex can be directly prepared by the methods described in the experimental part, but it can also be obtained by a spontaneous transformation of the planar red $[Ni(HMe_2DTMA)_2]Cl_2$ complex by standing in humid air or instaneously by contact with water. This transformation does not occur in vacuum or in a dry atmosphere. When the transformation occurs slowly the red and the green crystals can be distinguished in the mixture under the microscope and in the electronic spectrum (Figure 1D).

The $Ni(HMe_2DTMA)X_2$ (X = Br, I) complexes are paramagnetic with magnetic moments at room temperature either of 2.51 and 2.34 B.M., calculated for the stoichiometric formula, or of 3.55 and 3.31 P.M., calculated for one nickel atom in the formula $[Ni(HMe_2DTMA)_2][NiX_4]$ containing a diamagnetic planar cation $Ni(HL)_2{}^{2+}$ and a paramagnetic tetrahedral anion

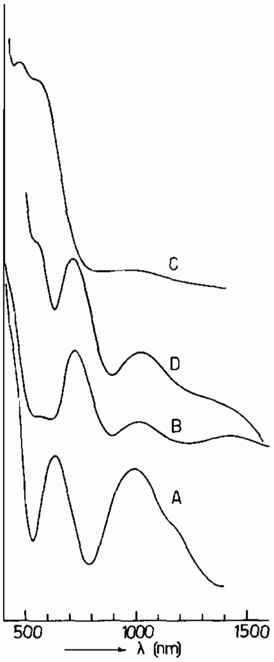


Figure 1. Electronic spectra of the solid complexes: (A) octahedral $[Ni(HL)_3]Cl_2$; (B) *trans*-octahedral, green $[Ni(HL)_2Cl_2]$; (C) planar, red $[Ni(HL)_2]Cl_2$; (D) *trans*-octahedral, green $[Ni(HL)_2Cl_2]$ complex obtained by the spontaneous transformation of the planar, red $[Ni(HL)_2]Cl_2$ complex still present in small amounts.

$[NiX_4]^{2-}$. The magnetic moments of 2.51 and 2.34 B.M. are too high for low-spin five-coordinated complexes[18] and too low for high-spin five-coordinated complexes (3.2–3.4 B.M.).[19] The magnetic moments of 3.55 and 3.31 B.M. are somewhat lower than those observed at 300° K for $(Et_4N)_2[NiBr_4]$ (3.80 B.M.) and for $(Et_4N)_2[NiI_4]$ (3.44 B.M.)[20] but some deforming influences of the cationic complex $Ni(HMe_2DTMA)_2{}^{2+}$ on the $[NiX_4]^{2-}$ complex may be responsible for the lowering of its magnetic moment. The low magnetic moment (3.47 B.M. at 300° K) for Ni^{II} in $[n\text{-}Bu_4N]_2[NiI_4]$ was attributed by Goodgame, Goodgame and Cotton[21] to a distortion of the $[NiI_4]^{2-}$ complex in the crystal causing considerable splitting and separation of the ground-state multiplet. Some $NiX_4{}^{2-}$ bands can be observed in the far infrared spectra of these complexes (Table III).

	ν_3(Ni–X) stretching	ν_4(X–Ni–X) bending
$(Et_4N)_2[NiBr_4]$ (22)	231sh 224s	83m
$(n\text{-}Pr_4N)_2[NiBr_4]$ (22)	228sh 219s	71(?)m
$(n\text{-}Pr_4N)_2[NiI_4]$ (22)	189s	
$Ni(HMe_2DTMA)_2[NiBr_4]$ (this w.)	235s	114(?)s
$Ni(HMe_2DTMA)_2[NiI_4]$ (this w.)	179s	

The electronic spectra (Table IV) of the $[Ni(HL)_2][NiX_4]$ complexes arise from the superposition of the spectra of the squareplanar cationic and tetrahedral anionic complexes. It has been demonstrated[21] that the electronic spectra of the tetrahalo $[NiX_4]^{2-}$ ions are also very sensitive to the evironment of the complex species and that in nitromethane solution solvent-containing species like $[NiX_3(solvent)]^-$ are likely to be formed. The electronic spectra of the $[Ni(HMe_2DTMA)_2][NiX_4]$ complexes show some similarities with those of the $[(C_6H_5)_4P]_2[NiBr_4]$ and $(n\text{-}Bu_4N)_2[NiI_4]$ complexes[21] in the solid state or in nitromethane solution:

$[(C_6H_5)_4P]_2[NiBr_4]$[21]	
in C_4Cl_6 mull	7040, 10500sh, 12900, 14100, 15000sh, 18200
in MeCN solution	8098, 8620, 13500sh, 14180, 15380, 16300sh, 19230sh
in $MeNO_2$ solution	6993, 8475, 13300, 14290, 15380, 16500sh
$[Ni(HMe_2DTMA)_2][NiBr_4]$	
solid state	7937sb, 10410vw, 13514vs, 17035vs
$(n\text{-}Bu_4N)_2[NiI_4]$ (21)	
in C_4Cl_6mull	6954, 11250, 12050, 13640, 14810, 19230
in $MeNO_2$	8300, 14180, 18870
$[Ni(HMe_2DTMA)_2][NiI_4]$	
solid state	7407mb, 11429sb, (18182sh)

In the electronic spectra of the $[Ni(HMe_2DTMA)_2][NiX_4]$ complexes the bands at 17–18 kK seem to be due to the planar cation, while the bands between 7.4 and 13.5 kK are similar to those of the $[NiX_4]^{2-}$ ions, especially in solution. These similarities with the spectra of the $[NiX_4]^{2-}$ in solution could be due to a deformation of the $[NiX_4]^{2-}$ ion in the solid $(Ni(HL)_2)(NiX_4)$ complex or perhaps also to the formation of a different tetrahedral complex $[NiX_3L]^-$ by the substitution of one halide ion with one of the free (N or S) atoms of the ligand of the cationic complex. This last hypothesis also affords a better explanation of the low magnetic moments since the "mixed" tetrahedral nickel complexes generally have lower magnetic moments: e.g. $(Et_4N)[Ni(Ph_3P)Br_3]$ = 3.60 B.M., $[Ni(Ph_3P)_2Br_2]$ = 3.27 B.M. (20).

Table IV presents the electronic spectra in solution. The complexes $[Ni(HL)_2]I_2$ and $[Ni(HL)_2][NiI_4]$ in acetone are identical, showing that both complexes interact with solvent to give very similar complex species in solution. The solutions a)→g) reproduce the media from which the different solid complexes were obtained. Species appear to prevail as follows: in the solutions b) c) f), the planar $[Ni(HL)_2]^{2+}$ species; in the solutions a) d) g), an octahedral species of undefined composition; in the solution e), the tetrahedral species $[NiBr_4]^{2-}$ due to the excess of nickel in HBr. It is remarkable that from the red HAc + HCl solution in which a planar complex species is prevalent the green *trans*-octahedral complex $[Ni(HL)_2Cl_2]$ is obtained, while from the red–green HAc + Acetone + HCl solution, in which an octahedral complex is prevalent the red planar complex $[Ni(HL)_2]Cl_2$ is obtained.

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