Mixed Complexes of Nickel(II) with *N*-donor Ligands

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High-spin mixed complexes of the type $[Ni(dpt)(L)]X_2$ (where: L = ethylenediamine or propane-1,3-diamine; dpt = 1,5,9-triazanonane; X = Cl, Br, I, and ClO_4) and [Ni(dpt)(L)(NCS)](CNS) have been studied by i.r. and electronic spectroscopy and magnetic techniques. In these complexes the metal probably has a square-pyramidal stereochemistry with exception of the solid $[Ni(dpt)(tn)]I_2$ complex, which seems to have an intermediate configuration between trigonal bipyramidal and square pyramidal. The [Ni(dpt)(L)(NCS)](CNS) complexes have a high-spin six-co-ordinate stereochemistry.

FIVE-CO-ORDINATE nickel(II) complexes are rather unusual and have, as limiting configurations, the square-pyramidal (C_{4v}) or trigonal-bipyramidal (D_{3h}) geometry. In our previously described[1] copper(II) complexes of the type $[Cu(dpt)(L)]X_2$ (where dpt = 1,5,9-triazanonane; L = ethylenediamine (en) or propane-1,3-diamine (tn); X = Cl, Br, I, or ClO_4) the co-ordination takes place through all nitrogen atoms of the ligands, whereas in the compounds of Schlessinger[2] and Curtis[3] dpt seems to be a mono- or bi-dentate ligand, with one or two primary amine groups not bound to the metal.

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[2] G. G. Schlessinger, *Bull. New Jersey Acad. Sci.*, 1967, **12**, 42.

[3] N. F. Curtis, R. W. Raimond, and Y. M. Curtis, *J. Chem. Soc.* (*A*), 1968, 182.

Here we report the preparation and properties of complexes with the general formula $Ni(dpt)(L)X_2$ ($L = en$ or tn; $X = Cl$, Br, I, ClO_4, CNS, or BPh_4). They are micro-crystalline, high-spin, pale violet, and soluble in methanol and, with exception of chloro- and bromo-derivatives, in dimethylformamide (DMF).

All amino-groups of these ligands are clearly bound to the metal, as found for the Cu^{II} complexes.[1] The bands due to the symmetric and antisymmetric stretching of the amino-groups and that due to imino-group of the free ligand are shifted to lower energies on co-ordination.

TABLE 1

Analytical data and physical properties

Compound	M.p. (°C)	Found (%)					Required (%)					μ_{eff} (B.M.) 25 °C ±0·2	Λ_M [a] MeOH	Λ_M [a] DMF
		M	C	H	N	X	M	C	H	N	X			
$[Ni(dpt)(en)]Cl_2$	255 dec.	18·0	29·6	8·0	21·5	22·3	18·3	29·9	7·8	21·8	22·1	2·80	160	
$[Ni(dpt)(en)]Br_2,H_2O$	265 dec.	13·9	22·2	6·4	16·7	37·5	13·7	22·5	6·4	16·4	37·4	2·90	161	
$[Ni(dpt)(en)]I_2$	230	11·4	32·0	6·3	26·8	50·6	11·7	32·1	6·9	26·8	50·4	2·90	149	139
$[Ni(dpt)(en)](ClO_4)_2$	260	13·0	21·2	5·5	15·4	15·5	13·1	21·4	5·6	15·6	15·8	2·80	156	156
$[Ni(dpt)(en)](BPh_4)_2$	178—179	6·2	74·6	7·5			6·6	75·7	7·4					
[Ni(dpt)(en)(NCS)](CNS)	218	16·2	19·0	5·6	14·1		16·0	19·1	5·0	13·9		2·80	70	104
$[Ni(dpt)(tn)]Cl_2,H_2O$	187 dec.	16·6	30·7	7·6	19·6	20·2	16·7	30·6	7·7	19·8	20·1	3·00	165	
$[Ni(dpt)(tn)]Br_2$	255 dec.	14·0	25·3	6·2	16·5	37·6	13·9	25·5	6·4	16·5	37·7	2·91	160	
$[Ni(dpt)(tn)]I_2$	240	11·3	21·5	5·5	13·8	49·3	11·3	20·9	5·3	13·5	49·0	2·90	142	152
$[Ni(dpt)(tn)](ClO_4)_2$	242	12·4	23·1	5·8	15·1	18·5	12·7	23·3	5·9	15·1	18·7	2·80	151	149
$[Ni(dpt)(tn)](BPh_4)_2$	180—181	6·2	75·2	7·5			6·5	75·8	7·5					
[Ni(dpt)(tn)(NCS)](CNS)	191	15·5	34·5	7·3	25·6		15·4	34·7	7·2	25·8		3·00	74	104
$[Ni(dpt)(tn)(NCS)]BPh_4$	221—222	9·1	62·9	7·5			9·2	63·7	7·4					

[a] For 10^{-3}M solutions at 25 °C.

TABLE 2

I.r. absorption bands (4000—150 cm^{-1})

$[Ni(dpt)(en)]Cl_2$	3320sh, 3290vw, 3230vw, 3160m, 2730w, 1600sh, 1590vs, 1330s, 1275vs, 1158vs, 1100s, 1078m, 1025vs, 985m, 665vs, 525vs, 500m, 405sh, 402m, 320vs, 233ms, 210vw
$[Ni(dpt)(en)]Br_2,H_2O$	3480m, 3430w, 3340sh, 3280sh, 3230m, 3190w, 3160m, 2730w, 1630m, 1605sh, 1590s, 1340vw, 1330s, 1275s, 1255s, 1165m, 1150s, 1132w, 1108s, 1090m, 1070m, 1030vs, 975s, 945s, 905m, 888w, 865w, 845vw, 808w, 670vw, 652m, 600m, 520vs, 498m, 405sh, 401mw, 392mw, 345mw, 316vs, 227ms, 205vw
$[Ni(dpt)(en)]I_2$	3340w, 3270w, 3230m, 3210sh, 3120m, 2725vw, 1600sh, 1585m, 1340s, 1320w, 1275vs, 1260m, 1232w, 1228w, 1160vs, 1125s, 1100s, 1090w, 1070s, 1035vs, 1015m, 975vs, 920vs, 890s, 870w, 815w, 800s, 660m, 630s, 502s, 410m, 394mw, 355mw, 318vs, 233ms, 210vw, 204vw
$[Ni(dpt)(en)](ClO_4)_2$	3350vs, 3338m, 3290m, 3180m, 2730m, 1595vs, 1340m, 1320w, 1278vs, 1260w, 1160w, 1080br, 1020s, 975s, 920s, 900vw, 882s, 815vw, 798s, 622vs, 600m, 560w, 510sh, 409ms, 397mw, 358w, 330m, 235ms, 205vw
[Ni(dpt)(en)(NCS)](CNS)	3340m, 3290w, 3248m, 3210m, 3160w, 2730w, 2098s, 2070s, 1580m, 1325w, 1315w, 1285w, 1270w, 1255m, 1210m, 1155s, 1125s, 1100m, 1072w, 1050vw, 1020vs, 980w, 950m, 920m, 900s, 860sh, 880w, 780m, 770m, 645m, 600m, 510m, 500w, 470w, 418sh, 416ms, 366mw, 332m, 314m, 253m, 228ms, 213vw
$[Ni(dpt)(tn)]Cl_2,H_2O$	3460m, 3325w, 3280m, 3230m, 3160m, 2730m, 1640m, 1600vs, 1350m, 1340m, 1320s, 1280m, 1260m, 1170s, 1145s, 1135m, 1115s, 1098m, 1075s, 1030m, 1020s, 980s, 930s, 915m, 905m, 900sh, 880w, 870w, 810m, 800w, 640m, 615w, 498m, 480sh, 420sh, 412ms, 377mw, 351m, 332m, 315ms, 230vs, 214vw
$[Ni(dpt)(tn)]Br_2$	3360w, 3280m, 3230m, 3160s, 2730w, 1580s, 1360vw, 1340m, 1320m, 1280m, 1260m, 1250w, 1160s, 1110s, 1075vs, 1025vs, 985s, 930s, 910s, 895w, 880w, 810m, 640s, 505m, 480sh, 430vw, 417m, 355m, 330m, 311mw, 233ms, 214vw
$[Ni(dpt)(tn)]I_2$	3340sh, 3270m, 3230m, 3160s, 2722w, 1575m, 1330m, 1310w, 1275w, 1260m, 1242m, 1175w, 1152s, 1135vw, 1120m, 1090m, 1070s, 1020vs, 1000sh, 980s, 925w, 905m, 880w, 870w, 810m, 798vw, 625s, 518sh, 500m, 414m, 386w, 355m, 339ms, 300ms, 231ms, 214m
$[Ni(dpt)(tn)](ClO_4)_2$	3330s, 3295s, 3180m, 2730w, 1596vs, 1340s, 1320m, 1280s, 1260m, 1240w, 1160m, 1070br, 1020m, 970m, 920s, 880s, 815vw, 798vs, 620vs, 560s, 520sh, 510sh, 500s, 409s, 358w, 325ms, 233ms, 211vw, 206vw
[Ni(dpt)(tn)(NCS)](CNS)	3320sh, 3280m, 3220m, 3160m, 2720m, 2095vs, 2070vs, 1610w, 1580m, 1318m, 1280m, 1260vw, 1250w, 1225w, 1155s, 1125s, 1100m, 1080m, 1020m, 1005w, 975w, 915s, 900sh, 890w, 870w, 800w, 780m, 770w, 640m, 560w, 535w, 500sh, 490m, 465w, 411vs, 359vs, 330vs, 304m, 291m, 229vs, 206vw

I.r., u.v., and visible spetroscopic, conductivity, and magnetic data led us to believe that stereochemistry other than five-co-ordinate would be unlikely for the metal complexes when $X = Cl$, Br, I, or ClO_4, while the thiocyanate derivatives are octahedral. Analytical data for the compounds and their physical characteristics are reported in Table 1. The i.r. bands (4000—150 cm^{-1}) are listed in Table 2.

The bands which in the perchlorate derivatives occur at 1080—1070 and 622—620 cm^{-1} are due to the ν_3 and ν_4 modes respectively, while the strong Raman-active bands at 920 cm^{-1} could be due to the ν_1 vibration mode. These values are typical for a non-bonded perchlorate group.[4-6]

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The medium absorption bands present in the range 3480—3460 cm^{-1}, ν(OH), and 1640—1630 cm^{-1}, δ(HOH), in [Ni(dpt)(en)]Br_2,H_2O and [Ni(dpt)(tn)]Cl_2,H_2O respectively, clearly confirm the presence of water of crystallisation. Moreover starting with [Ni(dpt)(L)]X_2 (L = en or tn; X = Cl, Br, I, or ClO_4) we have obtained only the two compounds [Ni(dpt)(L)]$(BPh_4)_2$ by reaction with $NaBPh_4$, thus confirming the presence of non-co-ordinated halide atoms in the complexes.

Metal–halogen absorption, usually found in the range 250—210 cm^{-1},[7,8] is absent in the far-i.r. spectra of the complexes [Ni(dpt)(L)]X_2 (X = Cl, Br, or I).

The molar conductivity values (Table 1) of [Ni(dpt)(L)]X_2 type derivatives are typical of 1 : 2 electrolytes.[9]

TABLE 3

Electronic spectra (cm^{-1}) [a]

[Ni(dpt)(en)]Cl_2	Solid	7100, 8300, 11,200, 18,500, 29,400
	Methanol	11,300 (6·9), 12,700sh, 18,500 (5·7), 29,000 (6·4)
[Ni(dpt)(en)]Br_2,H_2O	Solid	7100, 8300, 11,500, 18,400, 29,400
	Methanol	11,100 (5·4), 12,700sh, 18,200 (5·7), 28,400 (6·0)
[Ni(dpt)(en)]I_2	Solid	7050, 8300, 10,500, 17,500, 27,800
	DMF	6800 (1·3), 10,600 (6·1), 17,500 (7·1), 28,200 (9·4)
	Methanol	11,100 (5·3), 12,600sh, 18,000 (6·0), 28,300 (7·8)
[Ni(dpt)(en)]$(ClO_4)_2$	Solid	7200, 8300, 11,100, 17,900, 28,600
	DMF	7400, 10,800 (2·3), 17,900 (4·1), 28,600 (8·1)
	Methanol	10,650 (4·4), 17,700 (5·8), 28,200 (8·2)
[Ni(dpt)(en)(NCS)](CNS)	Solid	10,600, 17,350, 29,250
	DMF	10,650 (6·1), 17,700 (7·1), 27,800 (9·2)
	Methanol	10,600 (10·4), 12,500sh, 17,400 (10·4), 28,200 (8·9)
[Ni(dpt)(tn)]Cl_2,H_2O	Solid	7100, 8300, 10,200, 17,500, 28,600
	Methanol	9750 (4·4), 17,400 (9·8), 27,600 (15·5)
[Ni(dpt)(tn)]Br_2	Solid	7100, 8300, 10,000, 17,500, 27,800
	Methanol	9700 (4·3), 17,600 (10·0), 27,600 (15·8)
[Ni(dpt)(tn)]I_2	Solid	8300, 9300, 17,200, 27,800
	DMF	10,200 (2·3), 17,500 (6·6), 28,200 (11·4)
	Methanol	10,100 (4·1), 17,500 (9·8), 28,300sh
[Ni(dpt)(tn)]$(ClO_4)_2$	Solid	7200, 8300, 10,900, 17,900, 28,200
	DMF	7400 (0·4), 10,900 (4·1), 17,900 (8·1), 28,600 (10·2)
	Methanol	10,900 (8·0), 17,700 (13·6), 27,900 (14·3)
[Ni(dpt)(tn)(NCS)](CNS)	Solid	10,900, 18,000, 29,150
	DMF	10,650 (6·1), 17,700 (7·1), 27,800 (9·2)
	Methanol	10,600 (8·4), 12,300sh, 17,500 (8·9), 27,900 (12·7)

[a] ε molar for solutions in parentheses.

The i.r., far-i.r., and conductivity measurements exclude both tetrahedral and octahedral formulations for these derivatives and suggest a five-co-ordinate stereochemistry. Their electronic spectra are consistent with such a formulation, being similar to those of known five-co-ordinate nickel complexes.[10-12]

We propose that all the compounds are five-co-ordinated with square pyramidal geometry in the solid state, except the case of [Ni(dpt)(tn)]I_2 complex, which seems to have an intermediate configuration between trigonal bipyramidal and square pyramidal.[13] The spectra (Table 3) are in good agreement with those reported [14,15] for square-pyramidal high-spin *N*-bonded complexes.

In methanol or DMF solution all compounds seem to have a square-pyramidal geometry.

As far as the thiocyanate derivatives are concerned, our experiments show that these compounds have high-spin six-co-ordinate structures. The free thiocyanate ion has three fundamental i.r. absorption frequencies: a strong band due to the CN stretching, a weak band due to the CS stretching, and a weak band due to NCS bending.

In our complexes all three absorption bands are split into two peaks: ν(CN) at 2098—2095 and 2070 cm^{-1}; ν(C–S) at 780 and 770 cm^{-1}; δ(NCS) at 470—465 and 490 cm^{-1}.

These compounds show the three fundamental bands of the free thiocyanate ion, while the value of ν(CS) stretching frequency, at 780 cm^{-1} is diagnostic of a *N*-bonded thiocyanato-group. Furthermore this fact is supported by the NCS bending frequency found in our complexes at 490 cm^{-1} indicating that the thiocyanate is *N*-bonded (400—440 cm^{-1} for *S*-bonded thiocyanate complexes). This is in very good agree-

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ment with the available literature data[16-21] and is consistent with the conductivity measurements (Table 1), which show 1 : 1 electrolyte behaviour.[22]

The absorption bands found at 253 and 291 cm^{-1} for L = en and tn respectively can be assigned to a metal–nitrogen stretching mode involving the nitrogen of the thiocyanate anion.[23] By reaction with $NaBPh_4$ only one NCS group was substituted.

The electronic spectra of the two compounds are similar. They are typical of an octahedral stereochemistry of Ni^{II} paramagnetic complexes and show the three bands characteristic of such a configuration, with a shoulder in the range 12,300—12,500 cm^{-1}. These bands can be assigned to the transitions: $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ ν_1; $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$ ν_2; $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$ ν_3 (Table 4), while the shoulder could be assigned to the $^3A_{2g}(F) \longrightarrow {}^1E_g(D)$.

TABLE 4

Ligand-field parameters (cm^{-1}) [a]

		$^3A_{2g}(F) \xrightarrow{\nu_3} {}^3T_{1g}(P)$	$^3A_{2g}(F) \xrightarrow{\nu_2} {}^3T_{1g}(F)$	$^3A_{2g}(F) \xrightarrow{\nu_1} {}^3T_{2g}(F)$	Dq	B'	β
[Ni(dpt)(en)(NCS)](CNS)	Solid	29,250	17,350	10,600	1060	990	0·95
	methanol	28,200	17,400	10,600	1060	920	0·88
[Ni(dpt)(tn)(NCS)](CNS)	Solid	29,150	18,000	10,900	1090	960	0·92
	methanol	27,900	17,500	10,600	1060	910	0·87

[a] B (free ion) 1041 cm^{-1} (L. Sacconi, *Transition Metal Chem.*, 1968, **4**, 199).

On the assumption of O_h symmetry, D_q values, B', and β values were calculated.

These results are consistent with an approximately octahedral environment and are in good agreement with those obtained by Farago and her co-workers[5] for *N*-bonded Ni^{II} complexes.

The high-spin behaviour of these compounds is expected for strongly electronegative donor atoms, such as oxygen or nitrogen.

The magnetic susceptibility values (see Table 1) of five-co-ordinate complexes follow the Curie–Weiss law; the μ values are lower than those expected for high-spin nickel(II) complexes. It is possible, however, to exclude the existence of a spin-free–spin-paired equilibrium, because the values found are practically constant over the temperature range −160 to +80 °C with a zero Weiss constant. This could be interpreted by admitting that the magnitude of the orbital contribution to the magnetic moment is rather small and that the predominant contribution to the magnetic susceptibility is given by the spin-only term.

The values found for the six-co-ordinate CNS-derivatives (2·90—3·00 B.M.) are consistent with an octahedral environment for nickel(II).[24]

Unfortunately these complexes are not soluble in less polar or less co-ordinating solvents, *e.g.* nitrobenzene, nitromethane, and 1,2-dichloroethane. However we think that the ionisation cannot be due to the methanol or DMF because this fact would contrast with all the other experimental results for the chloro-, bromo-, iodo-, and ClO_4-derivatives. Furthermore, no evidence is found of any metal–halogen vibration (Table 2) in both the series of complexes. The unique bands present are anion-independent and are due to ν(Ni–N) and δ(N–Ni–N). These stretching and deforming modes have the same wavenumbers both in [Ni(dpt)(L)]X_2 (X = Cl, Br, I, or ClO_4) and in [Ni(dpt)(L)(NCS)]CNS derivatives, these compounds having the same C_{4v} symmetry.

EXPERIMENTAL

Ethylenediamine, propane-1,3-diamine, 1,5,9-triazanonane (dpt), $NiSO_4,7H_2O$, and $NiCl_2,6H_2O$ were commercially available. $NiBr_2$ and $Ni(ClO_4)_2,6H_2O$ were made according to literature methods.

Preparation of [Ni(dpt)(L)]Cl_2, [Ni(dpt)(L)]Br_2 *and* [Ni(dpt)(L)]$(ClO_4)_2$.—A solution of dpt (260 mmol), was mixed with a hot solution of $NiCl_2,6H_2O$ [or $NiBr_2$ or $Ni(ClO_4)_2,6H_2O$] (200 mmol) and this mixture was then added to ethylenediamine or propane-1,3-diamine (260 mmol) dissolved in methanol.

The resulting solution was concentrated and cooled. The complex, so obtained, was recrystallised from methanol.

Preparation of [Ni(dpt)(L)]I_2.—The ligand dpt (70 mmol) and ethylenediamine or propane-1,3-diamine (70 mmol) were added to a hot water–ethanol solution of $NiCl_2,6H_2O$ (50 mmol). A warm aqueous alcoholic solution of KI (100 mmol) was then added to the hot mixture. The solution was filtered and the filtrate heated to boiling and allowed to cool. The crude product was filtered off, washed with ethanol, and twice recrystallised from ethanol.

Preparation of [Ni(dpt)(L)(NCS)](CNS).—The ligand dpt (75 mmol) and ethylenediamine or propane-1,3-diamine (75 mmol) were added to an aqueous solution of $Ni(SO_4)$,$7H_2O$ (50 mmol). A warm solution of $Ba(SCN)_2$ (50 mmol) was added to this mixture and the precipitate of $BaSO_4$ was digested on a steam-bath for *ca.* 1 h. The complex obtained on cooling the filtrate after addition of ethanol, was crystallised from aqueous ethanol.

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Analyses.—Nickel was determined by ethylenediaminetetra-acetic acid, halogens by Volhard's method; perchlorates were reduced to chlorides in a Wurzschmitt Universal Bomb with Na_2O_2 and ethylene glycol; C, H, and N were determined with a Perkin-Elmer 240 Analyser.

Visible and U.v. Spectra.—Absorption solution spectra were recorded in the range 7000—30,000 cm^{-1} at room temperature with a Beckman DK2-A spectrophotometer. The same instrument was used for recording solid-state spectra by Venanzi's method.[25]

I.r. Measurements.—The i.r. spectra were recorded in the range 4000—150 cm^{-1} with Perkin-Elmer spectrophotometers, models 457 and 225, and with an Hitachi–Perkin-Elmer FIS3 spectrophotometer. Atmospheric water was removed from the spectrophotometer housing with a stream of dry nitrogen. The spectra in the range 4000—400 were measured for KBr discs and for Nujol mulls. Far-i.r. spectra were measured for Nujol mulls supported between polyethylene sheets.

Conductivity Measurements.—The measurements were carried out at 25 ± 0·1 °C with a WTW model LBR/B conductivity bridge for *ca.* 10^{-3}M solution in methanol or DMF.

Magnetic Susceptibility Measurements.—Magnetic measurements between -160 and $+80$ °C were carried out by Gouy's method using a Newport Instrument and the molecular susceptibilities were corrected for the diamagnetism of the component atoms by use of Pascal's constants.[26]

The Gouy tube was calibrated with twice distilled water and $[Ni(en)_3]S_2O_3$.

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