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Thermal investigation and stereochemical studies of methylamine, diethanolamine, 2,2′-bipyridyl and 1,10-phenanthroline complexes of nickel(II) in the solid state

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Abstract

Methylamine, diethanolamine, 2,2′-bipyridyl and 1,10-phenanthroline complexes of Ni(II) were synthesized. Thermal investigations were carried out and the stereochemical changes which occurred during the thermal decomposition were studied. The complexes were characterized using elemental and thermal analyses, IR and electronic spectral data, magnetic moment values and conductivity measurement. They were found to have the compositions $[NiL_4(H_2O)_2]X_2 \cdot 2H_2O$, $[NiL'_2X_2] \cdot nH_2O$, $[NiL''_2X_2] \cdot nH_2O$ and $[NiL'''_2(NCS)_2]$ where X is Cl^- or Br^-, L is methylamine (MeA), L′ is 2,2′-bibyridyl (bipy), L″ is 1,10-phenanthroline (phen), L‴ is diethanolamine (DEA), and n varies from 0 to 2.

The configurational changes of the complexes and their intermediates were studied using thermal analysis (TG and DTA), and IR spectral and effective magnetic moment data. All the complexes of Ni(II), except $[NiL'''_2(NCS)_2]$, appeared to possess octahedral structure; $[NiL'''_2(NCS)_2]$ is tetrahedral in structure.

Thermodynamic parameters, the activation energy E_a^*, enthalpy change ΔH, and the entropy change ΔS, for the dehydration and decomposition reactions of the complexes were evaluated using standard methods. A linear correlation was found between the E_a^* and ΔS values for the decomposition reactions of the complexes. Probable decomposition mechanisms are also proposed.

INTRODUCTION

Although the complexes of methylamine, 2,2′-bipyridyl and 1,10-phenanthroline with Ni(II) have been discussed in the literature [1–5], their reported compositions differ from those of the complexes isolated by us. Moreover, detailed thermal investigations and stereochemical studies were not made. The main aim of this work was to synthesize the methylamine,

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diethanolamine, 2,2′-bipyridyl and 1,10-phenanthroline complexes of Ni(II), and to study the stereochemical changes taking place during thermal decomposition. The main aim of selecting the above ligands was to determine the contributions of the inductive and steric effects of the ligands to the stability of the complexes.

When heated under non-isothermal conditions, the complexes decomposed via some stable intermediates. Before and after heating, the bidentate chelating ligands (bipy and phen) appear to coordinate with the central metal ion, nickel(II), at the cis position; this is evident from IR absorption bands. Some thermodynamic parameters, E_a^*, ΔH and ΔS, for the dehydration and decomposition reactions of the complexes in the solid state have been evaluated and the results of the induction and steric effects of the ligands on the thermal stability have been deduced. The probable decomposition pathways are also proposed.

EXPERIMENTAL

Materials and methods

The nickel chloride used was of AR grade and used as-received. Nickel bromide was freshly prepared by neutralizing hydrobromic acid (AR grade) with nickel carbonate (AR grade) and by subsequent crystallization from the filtrates obtained by evaporation. Nickel thiocyanate was freshly prepared by mixing ethanolic solutions of nickel chloride (0.04 mole) and potassium thiocyanate (0.08 mole), with subsequent crystallization from the filtrates obtained by evaporation. Methylamine (Aldrich, USA), diethanolamine (Merck, Germany), 2,2′-bipyridyl (AnalaR) and 1,10-phenanthroline (AnalaR) (both from Glaxo Laboratories Ltd., Bombay) were used as-received. Ethanol and diethylether were dried using standard procedures [6].

Preparation of complexes

$[Ni(MeA)_4(H_2O)_2]Cl_2 \cdot 2H_2O$ (1a) and $[Ni(MeA)_4(H_2O)_2]Br_2 \cdot 2H_2O$ (4a)

Complex (1a) was prepared by adding 10 ml of methylamine (5 mmole) to 30 ml of an ethanolic solution of nickel chloride (1 mmole). After vigorous stirring, a fine blue complex immediately separated out. The complex was collected by filtration, washed with ether, and dried over fused $CaCl_2$ in a desiccator: yield, approx. 70%.

Complex (4a) was prepared in the same way as complex (1a).

$[Ni(bipy)_2Cl_2] \cdot 2H_2O$ (2a) and $[Ni(bipy)_2Br_2] \cdot H_2O$ (5a)

A clear ethanolic solution (15 ml) of 2,2′-bipyridyl (3 mmole) was added dropwise with constant stirring to 25 ml of nickel chloride solution in ethanol (1 mmole). After cooling the resulting mixture in a refrigerator for a few minutes, a fine pink complex separated out. It was filtered, washed with ether and dried over fused calcium chloride in a desiccator: yield, approx. 75%.

Complex (5a) was prepared in a similar manner. However, the resulting mixture of ethanolic solutions of nickel bromide and 2,2'-bipyridyl, was left in a refrigerator overnight and pink pellet-like crystals separated out. The crystals were filtered, washed with ether and dried in a desiccator: yield, approx. 70%.

$[Ni(phen)_2Cl_2]\cdot 2H_2O$ *(3a) and* $[Ni(phen)_2Br_2]$ *(6a)*

Complex (3a) was prepared by adding 10 ml of an ethanolic solution of 1,10-phenanthroline (4 mmole) to 25 ml of an ethanolic solution of nickel chloride (2 mmole) with vigorous stirring. The resulting solution was left in a refrigerator for one week. Pink crystals separated out. The crystals were collected by filtration, washed with ether, and dried over fused calcium chloride in a desiccator: yield, approx. 65%.

Complex $[Ni(phen)_2Br_2]$ (6a) was prepared in a similar manner.

$[Ni(DEA)_2(NCS)_2]$ *(7a)*

This complex was prepared by adding 10 ml of diethanolamine (6 mmole) to 20 ml of an ethanolic solution of $Ni(SCN)_2$ (3 mmole) with constant stirring. The resulting blue solution was left in a refrigerator overnight and blue crystals of the complex settled out. It was filtered, washed with ether and dried over fused calcium chloride in a desiccator: yield, approx. 60%.

ELEMENTAL ANALYSIS, THERMAL INVESTIGATION, IR AND ELECTRONIC SPECTRA, MAGNETIC MOMENT DATA AND CONDUCTIVITY MEASUREMENT

Nickel was estimated gravimetrically using a standard procedure [7]. Carbon, nitrogen and hydrogen were determined using Perkin-Elmer 240C and Carlo Erba 1106 elemental analysers. The results of the elemental analyses are given in Table 1. Thermal investigations (TG and DTA) were carried out on a Shimadzu thermal analyser DT-30 under a dynamic nitrogen atmosphere, with a heating rate of $10°C\ min^{-1}$ and α-alumina as a standard reference substance. The activation energy E_a^* was evaluated from the TG curve using the equation of Horowitz and Metzger [8], and from the DTA curve using the equation of Borchardt and Daniels [9].

The enthalpy change ΔH was evaluated from the DTA curve using the relation [9] $\Delta H = KA$, where K is the heat transfer coefficient (the cell constant or calibration constant; here the cell was a platinum crucible and its constant K was evaluated using indium metal as a calibrant), and A is the total area under the particular DTA curve measured with a compensating planimeter and a Fuji Corona 027 optical tracer. The entropy change ΔS

TABLE 1

Analytical (calculated values in parentheses), magnetic and electronic spectral data

Complexes	Colour	Analysis/%				μ_{eff}/BM	λ_{max}/nm
		Metal	Carbon	Hydrogen	Nitrogen		
(1a) $[NiL_4(H_2O)_2]Cl_2 \cdot 2H_2O$	Light blue	18.03 (18.01)	14.75 (14.73)	8.60 (8.59)	17.20 (17.18)	2.90	–
(1b) $[NiL_4Cl_2]$	Green	23.20 (23.14)	19.00 (18.92)	7.97 (7.88)	22.12 (22.07)	2.97	
(1c) $[NiL_2Cl_2]$	Yellow	30.81 (30.62)	12.72 (12.52)	5.30 (5.22)	14.42 (14.61)		
(2a) $[NiL'_2Cl_2] \cdot 2H_2O$	Pink	12.31 (12.28)	50.21 (50.19)	4.14 (4.18)	11.73 (11.71)	2.96	526
(2b) $[NiL'_2Cl_2]$	Very pale pink	13.34 (13.28)	54.17 (54.29)	3.80 (3.62)	12.60 (12.67)	2.93	
(2c) $[NiL'Cl_2]$	Purple	20.41 (20.53)	42.00 (41.97)	2.68 (2.80)	9.81 (9.79)		
(3a) $[NiL''_2Cl_2] \cdot 2H_2O$	Pink	11.14 (11.16)	54.70 (54.74)	3.82 (3.80)	10.67 (10.64)	3.01	528
(3b) $[NiL''Cl_2]$	Purple	19.10 (18.94)	46.52 (46.47)	2.60 (2.58)	9.21 (9.04)		
(4a) $[NiL_4(H_2O)_2]Br_2 \cdot 2H_2O$	Light blue	14.12 (14.15)	11.54 (11.57)	6.73 (6.75)	13.48 (13.50)	3.29	–
(4b) $[NiL_2Br_2]$	Yellow	21.00 (20.93)	8.63 (8.56)	3.49 (3.57)	10.00 (9.98)		
(5a) $[NiL'_2Br_2] \cdot H_2O$	Pink	10.67 (10.69)	43.70 (43.72)	3.24 (3.27)	10.18 (10.20)	2.92	520
(5b) $[NiL'Br_2]$	Purple	15.71 (15.67)	31.97 (32.03)	2.21 (2.14)	7.50 (7.47)		
(6a) $[NiL''_2Br_2]$	Pink	10.00 (10.14)	49.82 (49.74)	2.73 (2.76)	9.63 (9.67)	2.91	525
(7a) $[NiL'''_2(NCS)_2]$	Deep blue	15.22 (15.26)	31.69 (31.19)	6.00 (5.72)	14.49 (14.56)	3.11	

Key: L is methylamine (MeA), L′ is 2,2′-bipyridyl (bipy), L″ is 1,10-phenanthroline (phen), and L‴ is diethanolamine (DEA).

was calculated from the relation [10] $\Delta S = (\Delta H/T_m)$, T_m being the DTA peak temperature in kelvin. Infrared and far-IR spectra were recorded with Beckman IR 20A and Perkin-Elmer 783 spectrometers in KBr and polythene powder discs. Electronic spectra were recorded using a Beckman DU-6 spectrophotometer, with ethanol, dimethylformamide (DMF) and dimethylsulphoxide (DMSO) as the reference solvents. The effective magnetic moments were evaluated from magnetic susceptibility measurements obtained with an EG and G PAR 155 vibrating-sample magnetometer at room temperature. Conductivity measurements of the complexes in acetonitrile at a concentration of 10^{-3} M were carried out at room temperature with a Systronics (India) conductivity bridge 305, using a dip-type cell.

The solid residues remaining after pyrolyses were identified by qualitative analyses.

RESULTS AND DISCUSSION

$[Ni(MeA)_4(H_2O)_2]Cl_2 \cdot 2H_2O$ (1a)

This complex has been reported earlier but with a different composition [1]. The presence of the two chloride ions outside the coordination sphere has been confirmed by the conductivity measurements and the molar conductance value was 230 ohm^{-1} cm^2 mol^{-1} [11]. The presence of lattice water as well as coordinated water molecules was confirmed from the IR spectral bands [12] at 3450 and 3080 cm^{-1} for ν(OH), at 1660 and 1615 cm^{-1} for δ(HOH), at 525 cm^{-1} for $\rho_w(H_2O)$, and at 476, 468 and 455 cm^{-1} for ν(M–O) (Table 2). The presence of the amine in the complex has been confirmed by C, H, N analysis (Table 1) and IR spectral data [12] (Table 2). On heating under non-isothermal condition, complex (1a) lost four molecules of water in the temperature range 30–87°C in the TG curve. The corresponding DTA curve (Fig. 1) shows one endothermic peak at 68°C. The intermediate complex $[Ni(MeA)_4Cl_2]$ (1b) indicates that (1a) undergoes a deaquation-anation reaction in which two chloride ions enter into the coordination sphere. This was confirmed by isolating the compound (1b) and measuring its molar conductivity. The molar conductance value in acetonitrile was very low [11]. The colour and magnetic moment [13, 14] of (1a) are light blue and 2.90 BM, respectively, and those of (1b) are green and 2.97 BM, respectively; this also corroborates the octahedral configuration of complexes (1a) and (1b) (Table 1 and Scheme 1). The intermediate complex $[Ni(MeA)_4Cl_2]$ (1b) was isolated by keeping the rate of heating at about 1°C min^{-1} around 87°C and was characterized by elemental analysis, IR spectral data and magnetic moment measurements. This intermediate (1b), on further heating, loses two molecules of ligand in the temperature range 87–173°C and froms $[Ni(MeA)_2Cl_2]$ (1c). The loss of two ligands is also reflected in the corresponding DTA curve, the peak appearing at 140°C

TABLE 2

IR spectral data (in cm^{-1}) for Ni(II) complexes (L is methylamine, L′ is 2,2′-bipyridyl, L″ is 1,10-phenanthroline and L‴ is diethanolamine)

Complexes	$\nu(NH_2)$ [a] $+\nu(OH)$	$\nu(CH_2)$	$\delta(NH_2)$ [a] $+\delta(HOH)$	$\delta(CH_2)$	$\rho_w(CH_2)$	$\tau(NH_2)$ [d] $+\rho_w(CH_2)$ $+\tau(CH_2)$	Stretching vibration of the skeleton $\nu(C-N)$ $+\gamma(C-C)$	$\rho_\gamma(CH_2)$	$\rho_\gamma(NH)$ $+\rho_\gamma(CH_2)$ $+\rho_\gamma(H_2O)$	$\nu(M-O)$	$\nu(M-N)$	$\nu(M-X)$ X is Cl^-, Br^-
(1a) $[NiL_4(H_2O)_2]Cl_2 \cdot 2H_2O$	3450(br) 3080(sr)	2860(w)	1660(sh) 1615(s)	1500(s) 1460(sh)	1410(s)	1258(s)	1004(w)	925(vs)	675(vs)	476(s) 468(sh) 455(sh)	395(sh) 380(s) 375(sh) 360(sh)	
(2a) $[NiL'_2Cl_2] \cdot 2H_2O$	3400(vs, br) 3090(w) 3060(w) 3040(w) 3015(w)	2915(w) 2375(w)	1630(br) 1595(sh) 1590(vs) 1558(s)	1483(s) 1467(vs)	1438(vs)	1309(vs) 1278(ms) 1243(s) 1223(s)	1175(s) 1158(vs) 1100(s) 1060(s)	1013(vvs) 980(sh) 910(s)	775(vvs) 736(vs) 653(s) 634(s)		442(s) 423(s) 360(sh)	282(s) 245(sh) 240(sh) 212(sh) 208(sh)
(3a) $[NiL''_2Cl_2] \cdot 2H_2O$	3405(s, br) 3040(w)	2920(w) 2840(vw)	1620(s) 1600(ms) 1581(s) 1570(sh)	1510(s) 1505(sh) 1490(sh)	1421(vs)	1336(s) 1305(ms) 1255(w) 1221(s)	1195(w) 1144(s) 1102(s)	1050(vvw) 1040(vw) 1000(vw) 910(vw) 870(s) 850(vs) 810(w)	778(s) 729(vs) 648(ms)		432(ms) 308(s)	248(w) 240(w) 230(sh) 220(sh)

(4a) $[NiL_4(H_2O)_2]Br_2 \cdot 2H_2O$	3430(s, br) 3210(w) 3100(w)	2968(w) 2920(w) 2850(w)	1600(s)	1500(s) 1468(w)	1445(w) 1410(s) 1385(w)	1315(w) 1258(w)	1165(w) 1110(w)	1050(w) 1025(s) 1008(w) 930(vs)	785(ms) 745(sh) 675(s, br)	475(w) 463(w)	405(s) 400(sh) 390(sh)	
(5a) $[NiL'_2Br_2] \cdot H_2O$	3460(s,br) 3300(s,br)	3080(w) 3042(w) 3020(w) 2920(w)	1620(sh) 1605(sh) 1600(vs)	1530(s) 1520(sh) 1490(vs) 1470(vs)	1440(vs) 1430(sh) 1380(vs)	1350(sh) 1315(vs) 1285(ms) 1250(s) 1230(s)	1180(s) 1165(vvs) 1125(sh) 1110(s)	1070(vs) 1050(ms) 1022(vvs) 920(vs) 820(sh)	785(vvs) 740(vs) 660(ms) 640(w)		398(sh) 385(sh) 365(w) 349(sh)	290(vs) 275(sh) 260(w)
(6a) $[NiL''_2Br_2]$		2940(s,br)		1520(sh) 1510(sh) 1500(w) 1460(s)	1410(sh) 1380(s) 1340(w)	1320(vvw) 1310(w) 1230(w) 1210(w)	1170(w) 1150(ms) 1105(ms) 1050(w)	970(ms) 920(sh) 870(sh) 850(s)	775(s) 730(vs) 640(w)		308(sh) 300(w)	260(s) 252(w) 235(s) 230(s)
(7a) $[NiL'''_2(NCS)_2]$ [b]	3330(s,br) 3260(ms) 3060(br)	2990(w) 2980(w) 2960(w) 2890(vw) [2050(vs) for ν(C–N)]	1630(br)	1470(s) 1455(ms) 1440(vs) 1430(sh)	1380(sh) 1370(sh)	1350(sh) 1295(vs) 1265(ms) 1220(vs) 1200(vs)	1130(ms) 1100(vs) 1080(vs) 1045(vvs) 1030(s) 980(vs)	940(sh) 905(s) 890(s) 850(s) 810(w)	780(vs) [c] 600(sh) 590(vs) 540(s)		418(ms) 405(w) 370(s) 305(sh)	

Key: v, very; s, strong; m, medium; w, weak; br, broad; and sh, shoulder. [a] Bands due to NH_2 and H_2O vibrations [$\nu(NH_2)/\nu(OH)$; $\delta(NH_2)/\delta(HOH)$] are overlapped; [b] δ(NCS) for (7a) appears at 470 cm^{-1}; [c] ν(CS); [d] NH for diethanolamine; $\rho_w(H_2O)$ for (1a) and (4a) appear at 525 and 540 cm^{-1} respectively.

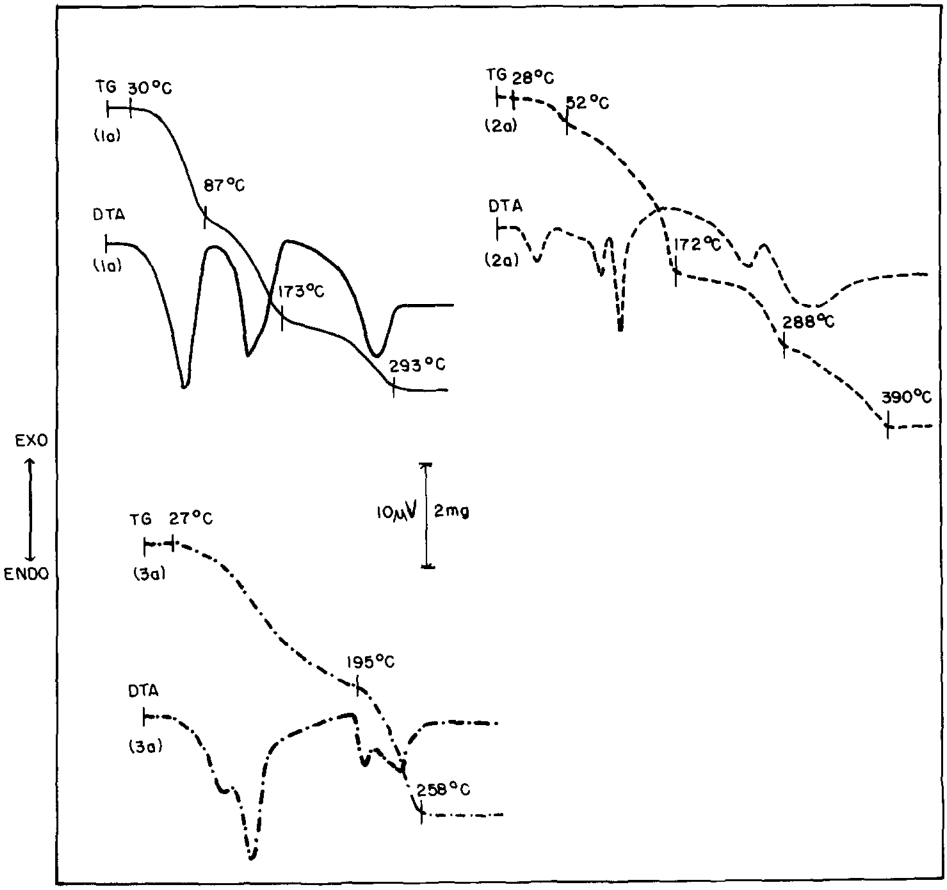
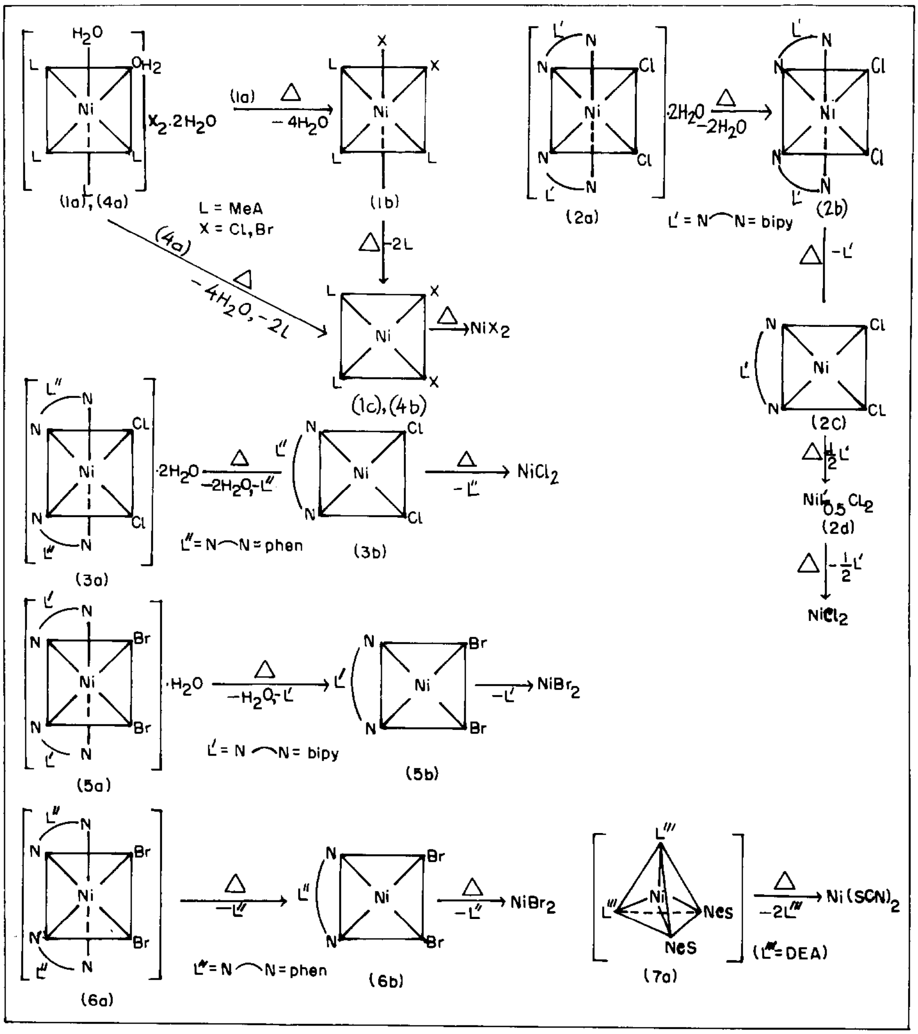


Fig. 1. Thermal curves of ——, complex (1a), $[Ni(MeA)_2(H_2O)_2]Cl_2 \cdot 2H_2O$, sample mass 7.1 mg; – – –, complex (2a), $[Ni(bipy)_2Cl_2] \cdot 2H_2O$, sample mass 7.6 mg; and – · – · –, complex (3a), $[Ni(phen)_2Cl_2] \cdot 2H_2O$, sample mass 11.8 mg.

(Fig. 1). Complex (1c) is yellow in colour [13, 14] and diamagnetic in nature, which indicates its square-planar configuration (Scheme 1). Complex (1c) was also characterized as for (1a) and (1b). On further heating, complex (1c) is then converted to $NiCl_2$, losing two ligands between 173 and 293°C with an endothermic DTA peak at 280°C (Fig. 1).

The E_a^* values for the conversions complex (1a) → (1b) and (1b) → (1c) were found to be 87 and 80 kJ mol^{-1} from TG, and 102 and 81 kJ mol^{-1} from DTA curves, respectively. The values of ΔH for the steps (1a) → (1b), (1b) → (1c), and (1c) → $NiCl_2$ were 80, 69 and 43 kJ mol^{-1}, and the corresponding ΔS values were 235, 167 and 78 J K^{-1} mol^{-1}, respectively. The probable decomposition path and the structures of the complexes (1a), (1b) and (1c) are shown in Scheme 1.



Scheme 1.

$[Ni(bipy)_2Cl_2]\cdot 2H_2O$ (2a)

This complex has been described [1–5] but its thermodynamic properties and stereochemical changes have not been reported. The pink colour, the magnetic moment value [13, 14] (2.98 BM) and λ_{max} value (Table 1) show that complex (2a) has an octahedral configuration. The presence of lattice water is confirmed by the IR bands [12] at 3400, 3090 and 3060 cm^{-1} for $\nu(OH)$, and at 1630, 1595 and 1590 cm^{-1} for $\delta(HCH)$ (Table 2). Furthermore, the mass loss in the TG curve of (2a) in the temperature range 28–52°C corresponds to two molecules of water (Table 3). An endothermic peak in the DTA curve is observed at 50°C (Fig. 1).

TABLE 3

Thermal parameters of methylamine (L), 2,2′-bipyridyl (L′), 1,10-phenanthroline (L″) and diethanolamine (L‴) of Ni(II)

	Decomposition reactions	Temperature range/°C	DTA peak temperature/°C		E_a^*/kJ mol^{-1} [a]		Enthalpy change [a] ΔH/kJ mol^{-1}	Entropy change [a] ΔS/J K^{-1} mol^{-1}
			Endo	Exo	TG	DTA		
1(a)	$[NiL_4(H_2O)_2]Cl_2 \cdot 2H_2O \longrightarrow [NiL_4Cl_2]$	30–87	68	–	87	102	80	235
(b)	$[NiL_4Cl_2] \longrightarrow [NiL_2Cl_2]$	87–173	140	–	80	81	69	167
(c)	$[NiL_2Cl_2] \longrightarrow NiCl_2$	173–293	280	–	–	–	43	78
2(a)	$[NiL'_2Cl_2] \cdot 2H_2O \longrightarrow [NiL'_2Cl_2]$	28–52	50	–	–	–	14	43
(b)	$[NiL'_2Cl_2] \longrightarrow [NiL'Cl_2]$	52–172	120 [b], 138	–	75	86	60	153
(c)	$[NiL'Cl_2] \longrightarrow [NiL'_{0.5}Cl_2]$	172–288	280	–	–	–	18	33
(d)	$[NiL'_{0.5}Cl_2] \longrightarrow NiCl_2$	288–390	–	–	–	–	–	–
3(a)	$[NiL''_2Cl_2] \cdot 2H_2O \longrightarrow [NiL''Cl_2]$	27–195	70, 102 [b]	–	40	54	110	293
(b)	$[NiL''Cl_2] \longrightarrow NiCl_2$	195–258	217, 255 [b]	–	137	–	20	38
4(a)	$[NiL_4(H_2O)_2]Br_2 \cdot 2H_2O \longrightarrow [NiL_2Br_2]$	24–175	45, 125 [b]	–	50	61	117	294
(b)	$[NiL_2Br_2] \longrightarrow NiBr_2$	175–250	232	–	–	211	51	101
5(a)	$[NiL'_2Br_2] \cdot H_2O \longrightarrow [NiL'Br_2]$	28–147	110	–	39	36	87	227
(b)	$[NiL'Br_2] \longrightarrow NiBr_2$	147–256	245	–	237	–	22	42
6(a)	$[NiL''_2Br_2] \longrightarrow [NiL''Br_2]$	30–233	80	–	–	34	62	176
(b)	$[NiL''Br_2] \longrightarrow NiBr_2$	233–337	292	–	101	108	21	37
7(a)	$[NiL'''_2(NCS)_2] \xrightarrow[\text{change}]{\text{Phase}} [NiL'''_2(NCS)_2]$	140–214	185	–	–	–	–	–
(b)	$[NiL'''_2(NCS)_2] \longrightarrow Ni(SCN)_2$	214–344	–	255 [b]	104	39	131	248

[a] In some cases thermodynamic parameters are not possible to evaluate due to irregular nature of the TG and DTA curves. [b] The peak temperature used for the evaluation of entropy changes.

The presence of chloride ion inside the co-ordination sphere is confirmed by the appearance of bands for ν(NiCl) at 283, 245, 240, 212 and 208 cm^{-1} in the far IR range [12] (Table 2). Furthermore, the presence of two chloride ions at the cis position is confirmed by the appearance of additional infrared-active bands [12] as mentioned above (Table 2). The anhydrous complex $[Ni(bipy)_2Cl_2]$ (2b) is converted in $[Ni(bipy)Cl_2]$ (2c) on the loss of one molecule of 2,2′-bipyridyl in the temperature range 52–172°C. The corresponding DTA curve has two sharp endothermic peaks at 120 and 138°C. The compound (2c) is purple and diamagnetic [13, 14] which supports its square-planar configuration. On heating, complex $[Ni(bipy)Cl_2]$ (2c) is converted into $NiCl_2$ in two steps 2(c) and 2(d) in the ranges 172–288 and 288–390°C respectively. The intermediate complex $[Ni(bipy)_{0.5}Cl_2]$ (2d) is unstable and could not be isolated.

The enthalpy ΔH and entropy ΔS changes for the conversion (2a) → (2b) were 14 kJ mol^{-1} and 43 J K^{-1} mol^{-1} respectively (Table 3). The activation energy for the conversion (2a) → (2c) was 75 from TG and 86 kJ mol^{-1} from the DTA curves. The enthalpy and entropy changes for steps 2(b) and 2(c) were calculated and are shown in Table 3. The probable decomposition mechanism is shown in the scheme.

$[Ni(phen)_2Cl_2] \cdot 2H_2O$ (3a)

This complex has been described earlier [1–5] but its thermal investigation and decomposition path have not been reported. It is pink in colour. The IR and electronic spectra, and magnetic data (Table 2) suggest that the organic ligands are chelated and that complex (3a) possesses octahedral configuration. It has a magnetic moment value of 3.01 BM.

The presence of lattice water was confirmed by the IR spectral bands [12] which appear at 3405 and 3040 cm^{-1} for ν(OH) and at 1620, 1600, 1581 and 1570 cm^{-1} for δ(HOH) (Table 2). The presence of chloride ions inside the coordination sphere was confirmed by the appearance of far-infrared-active bands [12] at 248, 240, 230 and 220 cm^{-1} for ν(Ni–Cl). Because the number of infrared-active bands is greater than one, the two chloride ions might occupy the cis position [12]. The presence and coordination of 1,10-phenanthroline in complex (3a) was confirmed by the elemental analysis (Table 1) and characteristic infrared-active bands [12] (Table 2). The mass loss in the TG curve between 27 and 195°C (Fig. 1) corresponds to two molecules of lattice water and one molecule of 1,10-phenanthroline and indicates the formation of an intermediate complex $[Ni(phen)Cl_2]$ (3b). The corresponding DTA peaks appear at 70 and 102°C and are endothermic in nature. The complex (3b) was isolated and characterized by elemental analysis, IR spectral data and magnetic moment measurement. The purple colour and diamagnetic nature of the complex $[Ni(phen)Cl_2]$ (3b) indicate its square-planar configuration.

On further heating, complex (3b) undergoes decomposition to $NiCl_2$ in the temperature range 195–258°C. The corresponding DTA curve shows two endothermic peaks at 217 and 255°C. The activation energy E_a^* for the conversion of $[Ni(phen)_2Cl_2] \cdot 2H_2O$ (3a) → $[Ni(phen)Cl_2]$ (3b) was found to be 40 and 54 kJ mol^{-1} from the TG and DTA curves, respectively. The corresponding enthalpy ΔH and entropy ΔS changes were 110 kJ mol^{-1} and 293 J K^{-1} mol^{-1} respectively. The E_a^*, ΔH and ΔS values for the step $[Ni(phen)Cl_2] \rightarrow NiCl_2$ were 137 kJ mol^{-1} (from TG), 20 kJ mol^{-1} and 38 J K^{-1} mol^{-1}, respectively (Table 3). The probable decomposition mechanism is shown in the scheme.

$[Ni(MeA)_4(H_2O)_2]Br_2 \cdot 2H_2O$ (4a)

This complex has been reported earlier [1] but with a composition that is different from the present compound; the thermal behaviour and stereochemical changes were not studied. It is light blue in colour and has a magnetic moment value of 3.29 BM (Table 1). The presence of coordinated and lattice water molecules was confirmed by the IR spectral bands [12] which appear at 3430, 3210 and 3100 cm^{-1} for $\nu(OH)$, at 1600 cm^{-1} for $\delta(HOH)$, at 675 cm^{-1} for $\rho_\gamma(H_2O)$, at 540 cm^{-1} for $\rho_w(H_2O)$, and at 475 and 463 cm^{-1} for $\nu(Ni–O)$ (Table 2). When complex (4a) is heated under non-isothermal condition, the mass loss in the TG curve in the range 24–175°C and the appearance of two endothermic DTA peaks at 45 and 125°C (Fig. 2) indicate the elimination of four molecules of water and two ligands. On heating, the complex $[Ni(MeA)_4(H_2O)_2]Br_2 \cdot 2H_2O$ (4a), undergoes a deaquation-anation-deamination reaction giving the complex $[Ni(MeA)_2Br_2]$ (4b) (Scheme 1).

Complex (4b) was isolated by pyrolysis and characterized by elemental analysis, IR spectra, magnetic moment data and conductivity measurement. It is yellow in colour and diamagnetic. This supports its square-planar configuration as well as the presence of two Br^- ions inside the coordination sphere. On further heating, complex (4b) loses the two amine ligands between 175 and 250°C, which is confirmed by the mass loss from the TG curve. The corresponding DTA curve shows one endotherm with a peak at 232°C.

The value of E_a^* for the conversion (4a) → (4b) was computed from the TG curve and found to be 50 kJ mol^{-1}, and for the conversions (4a) → (4b) and (4b) → $NiBr_2$, the values of E_a^* from the DTA curve were 61 and 211 kJ mol^{-1}, respectively. The enthalpy and entropy changes for the conversions (4a) → (4b) and (4b) → $NiBr_2$ were evaluated and found to be 117 and 51 kJ mol^{-1}, and 294 and 101 J K^{-1} mol^{-1}, respectively. The decomposition pathway is shown in the scheme.

$[Ni(bipy)_2Br_2] \cdot H_2O$ (5a)

Although this compound has been reported earlier [1–5] its thermal investigation and stereochemical changes in the solid state are not known.

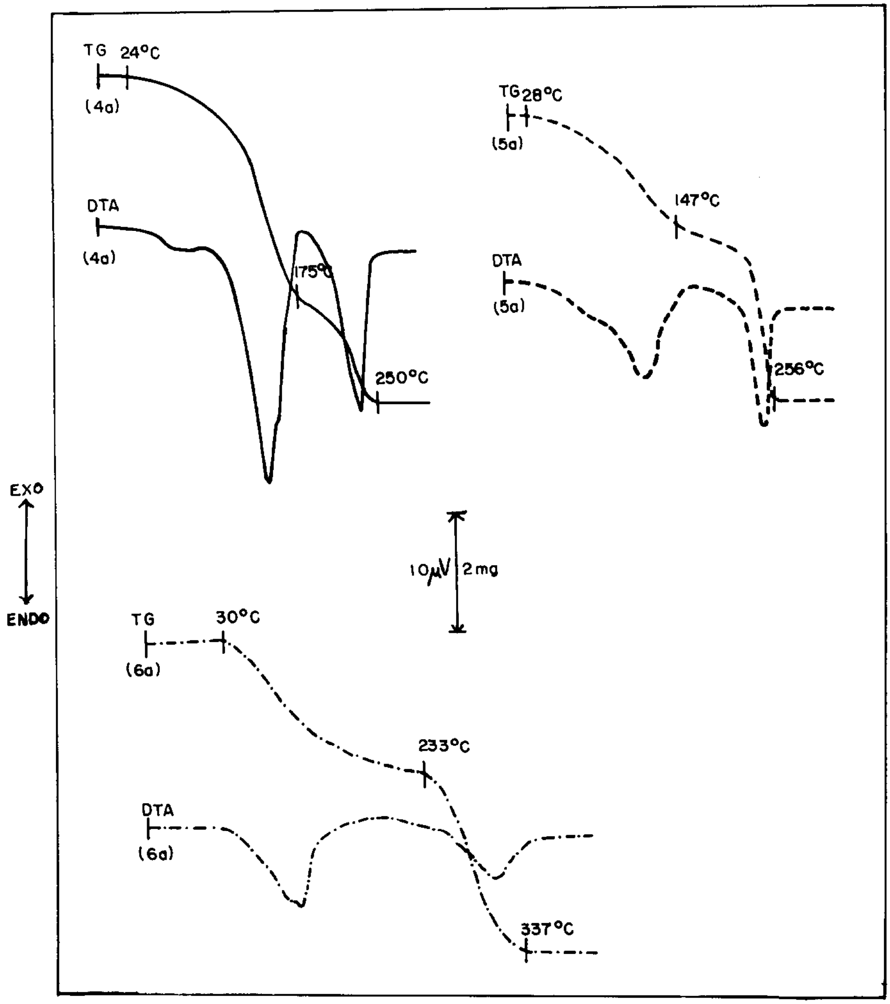


Fig. 2. Thermal curves of ——, complex (4a), $[Ni(MeA)_4(H_2O)_2]Br_2 \cdot 2H_2O$ sample mass 12.8 mg; – – –, complex (5a), $[Ni(bipy)_2Br_2] \cdot H_2O$, sample mass 14.6 mg; and – · – · –, complex (6a), $[Ni(phen)_2Br_2]$, sample mass 15.5 mg.

Complex (5a) possesses octahedral configuration, as is evident from IR, electronic and magnetic moment data (Tables 1 and 2). It is pink in colour and has a magnetic moment value of 2.92 BM. The presence of lattice water was confirmed by the appearance of IR spectral bands [12] at 3460 and 3300 cm^{-1} for $\nu(OH)$, and at 1620, 1605, and 1600 cm^{-1} for $\delta(HOH)$. The presence of Br^- ion inside the coordination sphere was confirmed by far-IR spectra [12] and the $\nu(Ni-Br)$ bands appearing at 290, 275 and 260 cm^{-1}. The presence of additional infrared-active bands for $\nu(Ni-Br)$ indicates that the two Br^- ions are in the cis position [12].

The mass loss in the TG curve in the temperature range 28–147°C corresponds to one molecule of lattice water along with one molecule of the organic ligand. The corresponding DTA peak appears at 110°C (Fig. 2). The complex [Ni(bipy)Br_2] (5b) was isolated at around 145–147°C by keeping the rate of heating at 1°C min^{-1}. It was then characterized by elemental analysis, IR spectra and magnetic moment measurement. It was purple in colour and with a zero value for the magnetic moment, indicating its square-planar configuration (Scheme 1). On further heating, the complex [Ni(bipy)Br_2] (5b) was converted into $NiBr_2$ in one step in the range 147–256°C. The corresponding DTA peak appeared at 245°C and was endothermic in nature. The activation energy E_a^* for the conversions (5a)–(5b) and (5b) → $NiBr_2$ were computed and found to be 39 (from TG) and 36 (from DTA) kJ mol^{-1} for the first step and 237 kJ mol^{-1} (from TG) for the conversion of (5b) → $NiBr_2$. The corresponding enthalpy and entropy changes were also evaluated and were found to be 87 kJ mol^{-1} and 227 J K^{-1} mol^{-1} for (5a) → (5b), and 22 kJ mol^{-1} and 42 J K^{-1} mol^{-1} for (5b) → $NiBr_2$.

[Ni(phen)$_2$Br$_2$] (6a)

This complex has been reported earlier [1–5] but its thermal behaviour and stereochemical changes were not studied. The IR, electronic and magnetic moment data (Tables 1 and 2) support its octahedral configuration. It is pink in colour and has a magnetic moment value of 2.91 BM. The presence of bromide ions inside the coordination sphere was confirmed by far-IR data [12]. The infrared-active bands for ν(Ni–Br) appeared at 260, 252, 235 and 230 cm^{-1}. The appearance of additional infrared-active bands indicates the presence of two bromide ions at the cis position [12].

On heating, complex (6a) lost one molecule of organic ligand (1,10-phenanthroline) in the temperature range 30–233°C to give [Ni(phen)Br_2] (6b) (Fig. 2). The DTA peak for the corresponding step appears at 80°C and is endothermic in nature. The purple colour and diamagnetic nature of complex (6b) supports its square-planar configuration (Scheme 1). On further heating, complex (6b) was converted into $NiBr_2$ in the temperature range 233–337°C and the corresponding DTA peak showed one endothermic peak at 292°C (Fig. 2). The activation energy for the conversion of (6a) → (6b) was 34 kJ mol^{-1} from the DTA curve, and for the conversion of (6b) → $NiBr_2$ was 101 and 108 kJ mol^{-1} from the TG and DTA curves, respectively (Table 3). The enthalpy ΔH and entropy ΔS changes for the above two steps were also evaluated and the values were 62 and 21 kJ mol^{-1}, and 176 and 37 J K^{-1} mol^{-1} respectively.

The probable decomposition pathway is shown in the scheme.

[Ni(DEA)$_2$(NCS)$_2$] (7a)

Complex (7a) has not been reported earlier. It is deep blue in colour and its magnetic moment value is 3.11 BM. The IR (Table 2), magnetic moment

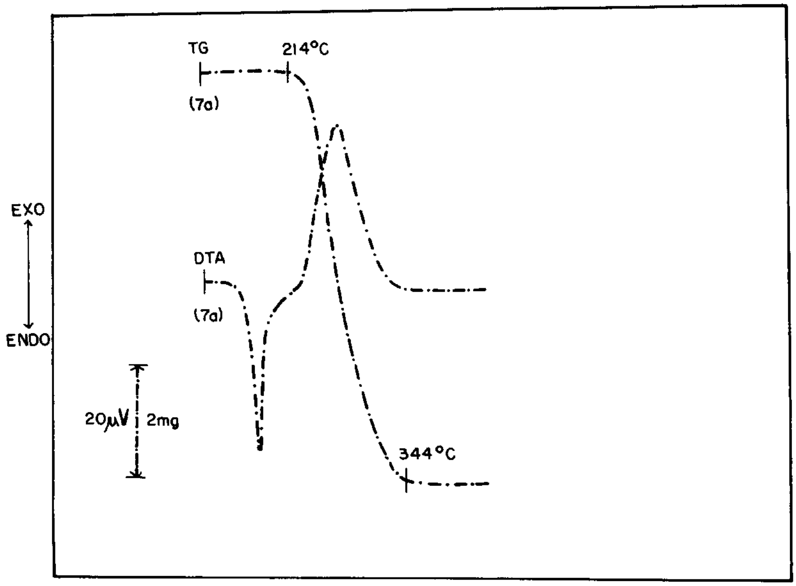


Fig. 3. Thermal curves of complex (7a), $[Ni(DEA)_2(NCS)_2]$, sample mass 14.5 mg.

and electronic spectral data (Table 1) suggest a tetrahedral configuration. In the IR spectra, the appearance of ν(CN) at 2050 cm^{-1}, ν(CS) at 780 cm^{-1} and δ(NCS) at 470 cm^{-1} suggest the coordination of the –NCS group through the nitrogen [12].

On heating under non-isothermal conditions, complex (7a) first undergoes melting, producing an endothermic peak which appears at 185°C on the DTA trace. This was also visually confirmed in a melting-point bath. After melting, complex (7b) is converted into $Ni(SCN)_2$ by losing two molecules of diethanolamine in the temperature range 214–344°C (Fig. 3). The corresponding DTA peak is exothermic and appears at 255°C (Fig. 3). The activation energy values evaluated from TG and DTA curves for the conversion of $[Ni(DEA)_2(NCS)_2]$ (7b) $\rightarrow Ni(SCN)_2$ were found to be 104 and 39 kJ mol^{-1}, respectively. The values of the enthalpy and entropy changes are 131 kJ mol^{-1} and 248 J K^{-1} mol^{-1} respectively. The probable decomposition path is shown in the scheme.

In each case, except complex (7a), the solid residue obtained after pyrolysis was $NiCl_2$, as confirmed by qualitative analysis. But for complex (7a), the residue after pyrolysis was $Ni(SCN)_2$ which was also confirmed by qualitative analysis.

A linear correlation obtained by plotting E_a^* versus ΔS values (Fig. 4) shows that a system having a higher entropy change ΔS will require less energy E_a^* for its thermal decomposition [10].

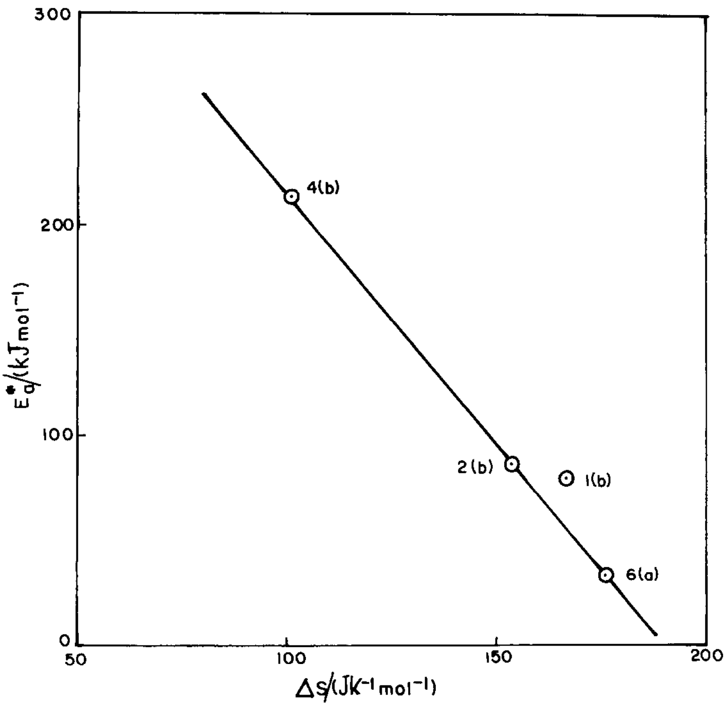


Fig. 4. Plots of the values of E_a^* versus ΔS for the conversions of 1(b), $[Ni(MeA)_4Cl_2] \rightarrow [Ni(MeA)_2Cl_2]$; 2(b), $[Ni(bipy)_2Cl_2] \rightarrow [Ni(bipy)Cl_2]$; 4(b), $[Ni(MeA)_2Br_2] \rightarrow NiBr_2$; and 6(a), $[Ni(phen)_2Br_2] \rightarrow [Ni(phen)Br_2]$.

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