Thermally induced isomerisation and decomposition of diethylenetriamine complexes of nickel(II) in the solid state

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Summary

Complexes $[NiL_2]X_2 \cdot nH_2O$ (L = diethylenetriamine; n = 0 when $X = CF_3CO_2$ or CCl_3CO_2; n = 1 when X = Cl or Br, and n = 3 when $X = 0.5SO_4$ or $0.5SeO_4$) and $NiLX_2 \cdot nH_2O$ (n = 1 when X = Cl or Br; n = 3 when $X = 0.5SO_4$ or $0.5SeO_4$) have been synthesised and investigated thermally in the solid state. $NiLSO_4$ was synthesised pyrolytically in the solid state from $[NiL_2]SO_4 \cdot [NiL_2]X_2$ (X = Cl or Br) undergo exothermic irreversible phase transitions (242–282° C and 207–228° C; $\Delta H = -11.3\,kJ\,mol^{-1}$ and $-1.9\,kJ\,mol^{-1}$ for $[NiL_2]Cl_2$ and $[NiL_2]Br_2$, respectively). $[NiL_2](CF_3CO_2)_2$ shows an irreversible thermochromism phenomenon (158–185° C; $\Delta H = 2.0\,kJ\,mol^{-1}$). $NiLX_2 \cdot nH_2O$ (n = 1 or 3) undergo simultaneous deaquation-isomerisation upon heating. All the complexes possess octahedral geometry.

Introduction

Diethylenetriamine (dien or L) complexes of transition metals are well documented in the literature$^{(1-5)}$. All three possible geometric isomers, [unsymmetrical facial, symmetric facial and meridional] of $[CoL_2]^{3+}$ and $[CrL_2]^{3+}$ have been isolated and characterised. Besides the geometrical isomers, the (dien) complexes (both mono- and bis-) exist in different conformational forms which arise due to the two non-planar five-membered chelate rings formed by one diethylenetriamine molecules$^{(2,6)}$.

The structural transformations of coordination complexes upon heating in the solid state have been studied by various workers$^{(7)}$. Recently, we noticed that several solid bis- and tris-diamine complexes of nickel(II) on heating undergo phase transitions, in most cases caused by the conformational changes of the chelate rings$^{(8-15)}$. As diethylenetriamine can be considered to consist of two ethylenediamine moieties, we studied the phase transitions of some nickel(II) diethylenetriamine complexes by analysing the geometry of the complexes and the conformation of the individual chelate rings. We report here the thermal studies of diethylenetriamine complexes of NiX_2 where $X = CF_3CO_2$, CCl_3CO_2, Cl, Br, $0.5SO_4$ or $0.5SeO_4$.

Experimental

All chemicals used were of A.R. grade and high purity diethylenetriamine (L) was purchased from Koch-Light Lab. Ltd. and used as received. The equipment employed for i.r., electronic spectra (mull), magnetic susceptibility, thermal measurements, x-ray diffraction and elemental analysis are as reported earlier$^{(8-15)}$. The enthalpy changes of phase transitions were calculated using a Mettler TA-3000/Shimadzu DT-30 thermal analyser. Table 1 lists the analytical, magnetic, and electronic spectral data. Thermal, i.r. spectra and x-ray powder diffraction data are shown in Tables 2, 3, and 4, respectively.

Table 1. Analytical, magnetic and electronic (mull) spectral data of diethylenetriamine (L) complexes of nickel(II).

Compound	Found (Calcd.)% Ni	C	H	N	μ_{eff} (B.M.)	λ_{max} (nm)
$[NiL_2]Cl_2 \cdot H_2O$ *(1)*	16.4(16.6)	27.0(27.1)	7.8(7.9)	23.6(23.7)	3.2	530, 350
$[NiL_2]Cl_2$ *(1a)*	17.6(17.5)	29.0(28.6)	7.5(7.7)	24.8(25.0)	3.3	550, 355
$[NiL_2]Cl_2$ *(1b)*	17.4(17.5)	28.4(28.6)	8.0(7.7)	25.1(25.0)	3.2	550, 360
$NiLCl_2 \cdot H_2O$ *(1c)*	23.5(23.4)	19.3(19.1)	6.2(6.0)	17.2(16.7)	3.1	600, 370
$NiLCl_2$ *(1d)*	25.3(25.2)	20.2(20.6)	5.5(5.7)	17.9(18.0)	3.2	610, 375
$[NiL_2]Br_2 \cdot H_2O$ *(2)*	13.6(13.3)	21.6(21.7)	6.1(6.3)	19.1(19.0)	3.2	538, 350
$[NiL_2]Br_2$ *(2a)*	13.2(13.8)	22.8(22.6)	6.0(6.1)	19.8(19.8)	3.1	552, 368
$[NiL_2]Br_2$ *(2b)*	13.8(13.8)	22.6(22.6)	6.2(6.1)	19.5(19.8)	3.1	550, 367
$NiLBr_2 \cdot H_2O$ *(2c)*	17.2(17.3)	13.9(14.1)	3.8(4.4)	12.3(12.4)	3.2	610, 380
$NiLBr_2$ *(2d)*	18.3(18.2)	14.8(14.9)	4.1(4.0)	12.9(13.0)	3.3	620, 370
$[NiL_2](CF_3CO_2)_2$ *(3)*	11.7(11.9)	28.7(29.3)	4.9(5.3)	17.2(17.1)	3.2	530, 345
$[NiL_2](CF_3CO_2)_2$ *(3a)*	12.0(11.9)	29.1(29.3)	5.1(5.3)	17.1(17.1)	3.2	503, 337
$[NiL_2](CCl_3CO_2)_2$ *(4)*	10.2(9.9)	24.1(24.4)	4.6(4.4)	14.3(14.2)	3.3	503, 335
$[NiL_2]SO_4 \cdot 3H_2O$ *(5)*	14.5(14.1)	23.3(23.1)	7.5(7.7)	20.1(20.2)	3.2	541, 349
$NiLSO_4 \cdot 3H_2O$ *(5b)*	19.1(18.8)	15.7(15.4)	6.2(6.1)	13.6(13.5)	3.1	590, 355
$NiLSO_4$ *(5c)*	23.2(22.8)	18.6(18.6)	4.9(5.0)	15.9(16.3)	3.2	600, 380
$[NiL_2]SeO_4 \cdot 3H_2O$ *(6)*	13.0(12.7)	21.0(20.8)	6.8(6.9)	17.9(18.2)	3.1	592, 355
$NiLSeO_4 \cdot 3H_2O$ *(6b)*	15.9(16.4)	13.5(13.4)	5.4(5.3)	12.1(11.7)	3.2	595, 358
$NiLSeO_4$ *(6c)*	20.0(19.3)	15.5(15.7)	4.1(4.3)	13.9(13.8)	3.1	607, 370

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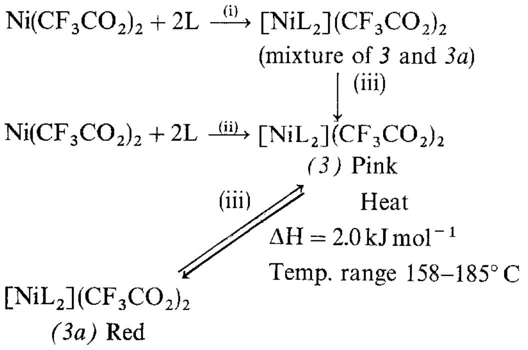

Scheme 1. (i) MeOH/EtOH/*i*-PrOH; (ii) MeCN; (iii) Crystallisation from MeCN.

Synthesis of the complexes

$[NiL_2]Cl_2\cdot H_2O$ *(1)*, $[NiL_2]Br_2\cdot H_2O$ *(2)*, $NiLCl_2\cdot H_2O$ *(1c)* and $NiLBr_2\cdot H_2O$ *(2c)* were prepared by the methods reported earlier$^{(3)}$.

$[NiL_2]$ $(CF_3CO_2]_2$ *(3)* was prepared by adding diethylenetriamine (2–3 mmol) dropwise to the metal salts (1 mmol) dissolved in EtOH (10 cm^3). The complex, which separated immediately, was filtered and washed with EtOH.

$[NiL_2]$ $(CF_3CO_2)_2$ thus prepared was admixed with its post-phase isomer *(3a)*. The impure species was dissolved in hot (*ca.* 50° C) MeCN, filtered and then the filtrate was allowed to cool at ice temperature when pink crystals of *(3)* separated out. These were filtered and washed with cold (*ca.* 10° C) MeCN and dried. Note here that the reaction of $Ni(CF_3CO_2)_2$ with diethylenetriamine in MeOH/EtOH/*i*-PrOH yields a mixture of pink *(3)* and red *(3a)* isomers of $[NiL_2]$ $(CF_3CO_2)_2$ but a pure pre-phase product *(3)* (pink) is obtained if MeCN is used as the reaction medium (Scheme 1).

$[NiL_2]$ $(CCl_3CO_2)_2$ *(4)* was prepared by adding (dien) (2–3 mmol) dropwise to the metal salts (1 mmol) dissolved in EtOH (10 cm^3). The complexes which separated immediately were filtered and washed with EtOH and dried.

$[NiL_2]SO_4\cdot 3H_2O$ *(5)*, $[NiL_2]SeO_4\cdot 3H_2O$ *(6)*, $NiLSO_4\cdot 3H_2O$ *(5b)*, and $NiLSeO_4\cdot 3H_2O$ *(6b)* were prepared by adding (dien) (1 mmol for mono- and 2–3 mmol for bis-species) dropwise to the metal salts (1 mmol) dissolved in a minimum quantity of H_2O (5 cm^3) with stirring. EtOH was added dropwise until a slight turbidity appeared. An excess of EtOH was added with stirring until shiny crystals separated. The crystals were filtered, washed with EtOH and dried.

$NiLSO_4$ *(5c)* was prepared thermally in the solid state from complex *(5)* (Table 2). $[NiL_2]Cl_2$ *(1a)*, $[NiL_2]Br_2$ *(2a)*, $[NiL_2]Cl_2$ *(1b)*, $[NiL_2]Br_2$ *(2b)*, $[NiL_2](CF_3CO_2)_2$ *(3a)*, $NiLCl_2$ *(1d)*, $NiLBr_2$ *(2d)*, $NiLSeO_4$ *(6c)* were prepared in the solid state by the temperature-arrest technique from their respective parent complexes (Table 2).

$[NiL_2]Cl_2$ *(4a ≡ 1a)* was synthesised by thermal decomposition in the solid state of *(4)* and was purified by washing with EtOH.

Results and discussion

Bis-(dien) complexes of nickel(II)

We report here six bis-(dien) complexes. The complex, $[NiL_2]$ $(CF_3CO_2)_2$ *(3)* is thermochromic and the complexes $[NiL_2]Cl_2\cdot H_2O$ *(1)* and $[NiL_2)Br_2\cdot H_2O$ *(2)* undergo exothermic phase transitions after deaquation. The other complexes $[NiL_2]SO_4\cdot 3H_2O$ *(5)*,

Table 2. Thermal parameters of the nickel(II) diethylenetriamine (L) complexes.

Decompositions	Temp. range (°C)	D.t.a. peak temp. (°C) Endo.	Exo.	ΔH (kJ mol^{-1})
$[NiL_2]Cl_2\cdot H_2O$ *(1)* → $[NiL_2]Cl_2$ *(1a)*	109–170	162	–	–
$[NiL_2]Cl_2$ *(1a)* → $[NiL_2]Cl_2$ *(1b)*	242–282	–	258	−11.3^b
$[NiL_2]Cl_2$ *(1b)* → $NiLCl_2$ *(1d)*	284–355	336	331	–
$NiLCl_2$ *(1d)* → $NiCl_2$	355–390	351	343, 368	–
$NiLCl_2\cdot H_2O$ *(1c)* → $NiLCl_2$ *(1d)*	70–127	90	–	–
$NiLCl_2$ *(1d)* → $NiCl_2$	285–380	338	315, 378	–
$[NiL_2]Br_2\cdot H_2O$ *(2)* → $[NiL_2]Br_2$ *(2a)*	88–157	144	–	–
$[NiL_2]Br_2$ *(2a)* → $[NiL_2]Br_2$ *(2b)*	207–228	–	218	−1.9^b
$[NiL_2]Br_2$ *(2b)* → $NiBr_2$	302–410	342	320, 358, 375	–
$NiLBr_2\cdot H_2O$ *(2c)* → $NiLBr_2$ *(2d)*	118–195	140	–	–
$NiLBr_2$ *(2d)* → $NiBr_2$	312–415	335	320, 352, 365	–
$[NiL_2](CF_3CO_2)_2$ *(3)* → $[NiL_2](CF_3CO_2)_2$ *(3a)*	158–185	163	–	2.0
$[NiL_2](CF_3CO_2)_2$ *(3a)* → NiO	218–260	215, 227, 240	221	–
$[NiL_2](CCl_3CO_2)_2$ *(4)* → $[NiL_2]Cl_2$ *(4a)*^{a}	129–138	–	138	–
$[NiL_2]SO_4\cdot 3H_2O$ *(5)* → $[NiL_2]SO_4$ *(5a)*	58–103	93	–	–
$[NiL_2]SO_4$ *(5a)* → $NiLSO_4$ *(5c)*	290–350	346	–	–
$NiLSO_4$ *(5c)* → $NiSO_4$	378–430	397	382	–
$NiLSO_4\cdot 3H_2O$ *(5b)* → $NiLSO_4$ *(5c)*	92–132	101, 123	–	–
$NiLSO_4$ *(5c)* → $NiSO_4$	331–435	380	364	–
$[NiL_2]SeO_4\cdot 3H_2O$ *(6)* → $[NiL_2]SeO_4$ *(6a)*	48–101	88	–	–
$[NiL_2]SeO_4$ *(6a)* → $NiSeO_4$	260–315	–	305	–
$NiSeO_4\cdot 3H_2O$ *(6b)* → $NiLSeO_4$ *(6c)*	165–200	191	–	–
$NiLSeO_4$ *(6c)* → $NiSeO_4$	290–320	–	310	–

^{a}On purification this compound shows identical behaviour to *(1b)*; ^{b}Enthalpy change calculated from d.t.a. peaks.

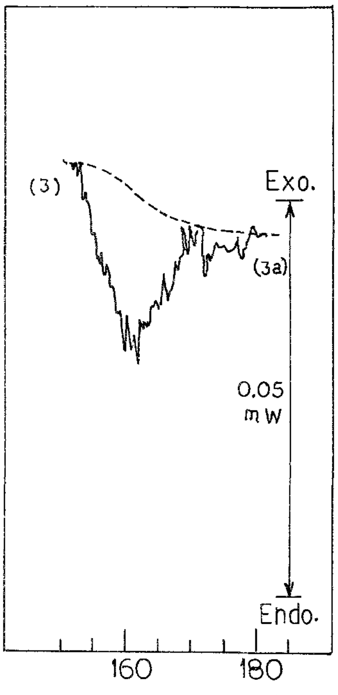

Figure 1. D.s.c. curve of [NiL_2] $(CF_3CO_2)_2$ *(3)* (wt. taken = 3.07 mg) (——), the line (----) denote the base line (both the lines drawn through averaging device from the built-in computer).

[NiL_2]$SeO_4 \cdot 3H_2O$ *(6)*, and [NiL_2] $(CCl_3CO_2)_2$ *(4)* do not undergo any type of transition. These are discussed below.

Thermochromism in [NiL_2] $(CF_3CO_2)_2$ (3)

The complex [NiL_2] $(CF_3CO_2)_2$ *(3)* undergoes an irreversible endothermic phase transition (158–185° C; $\Delta H = 2.0\,kJ\,mol^{-1}$) (Figure 1) associated with a colour change from pink to red. The red isomer is stable in the atmosphere and in a desiccator. However, it reverts to the pink isomer when crystallised from MeCN (Scheme 1). Both isomers possess octahedral geometry as is evident from the magnetic moment and electronic spectra (Table 1). The electronic spectra (mull) of the two isomers are similar except for a shift of the peaks of red isomer to the longer wave length region (Table 1). It is significant that both *(3)* and *(3a)* show identical electronic spectra (λ_{max} = 650 nm and 410 nm) in MeOH, EtOH, *i*-PrOH, MeCN, and CH_2Cl_2. The differences in λ_{max} values are observed only in the solid state. The i.r. spectra (Table 3) and the x-ray powder diffraction patterns (Table 4) of the two isomers differ appreciably from each other.

Either geometrical isomerisation or conformational changes of the five-membered chelate rings formed by the (dien) molecules are likely to be responsible for these differences. Bis-complexes with the flexible tri-dentate ligand diethylenetriamine can exist as three geometric isomers which are designated as *s-fac*, *u-fac* and *mer*$^{(1)}$. All three isomers of [ML_2]$^{3+}$ [M = cobalt(III) or chromium(III)] are documented in the literature$^{(1-5)}$. Searle and House$^{(1)}$ have characterised these isomers using i.r. spectra in the regions 750–950 cm^{-1} and 1550–1600 cm^{-1}. We have observed similar i.r. spectra for pink *(3)* and red *(3a)* isomers in the regions 750–950 cm^{-1} and 1550–1600 cm^{-1} (Table 3) and these spectral patterns are characteristic of the *mer* isomer. Paoletti *et al.*$^{(16)}$ showed [NiL_2]$Cl_2 \cdot H_2O$ to possess a *mer* geometry by x-ray single crystal analysis. The i.r. spectrum of [NiL_2]$Cl_2 \cdot H_2O$ *(1)* is similar to those of the red *(3a)* and pink *(3)*, particularly in the above mentioned regions. This eliminates the possibility of geometrical isomerisation occurring in *(3)* → *(3a)* transition. Consequently, conformational changes in the chelate rings are likely to be responsible for the phase transition$^{(8-15,18-20)}$ and these two (pink and red) are probably conformers. The i.r. spectra of the pink and red form differ appreciably in the regions (3300–3150 cm^{-1}, 3000–2850 cm^{-1}, 1350–

Table 3. I.r. spectral data (cm^{-1}) for the isomers *(3)* and *(3a)* in KBr.

Isomer [NiL_2]$(CF_3CO_2)_2$	$\nu(NH_2)$	$\nu(CH_2)$	$\delta(NH_2)$	$\rho_r(NH_2)$	$\rho_w(CH_2) + \rho_w(NH_2)$ + stretching vibration of skeleton $\nu(C{-}N) + \nu(C{-}C)$	$\rho_r(CH_2)$
(3)	3340w, 3320m, 3280mbr, 3260m, 3185s, 3175s	2942m, 2919m, 2878m	1585s	630m, 615m, 670vw	1335s, 1035wsh, 1315m, 1020vs	911m, 890s, 868m
(3a)	3323mbr, 3260s, 3180s	2940mbr, 2865m	1580s	668m, 608m	1335s, 1038w, 1328w, 1025m, 1317w, 1005m	908m, 885s, 850m

Table 4. Prominent lines (d/Å) in the x-ray powder patterns of diethylenetriamine (L) complexes of nickel(II).

[NiL_2]$(CF_3CO_2)_2$ *(3)*	[NiL_2]$(CF_3CO_2)_2$ *(3a)*
8.49vs, 7.30vw, 6.90w, 6.45s, 6.41s, 5.82vw, 5.37s, 5.27vs, 5.00vs, 4.52m, 4.22w, 4.07vs, 3.67m, 3.43s, 3.19mbr, 2.99vw, 2.92w, 2.90w, 2.79w, 2.76vw, 2.65vw, 2.63vw, 2.59w, 2.49m, 2.45m, 2.35vw, 2.31w, 2.27vw, 2.22vwbr, 2.18w, 2.14w, 2.10w, 2.05vwbr, 1.97w, 1.94w, 1.92w, 1.84vw, 1.78vw, 1.77vw, 1.73vw, 1.69vw, 1.66vwbr, 1.58w, 1.50w	8.42s, 7.18m, 5.75vs, 5.53s, 5.43s, 4.82vs, 4.48w, 4.19m, 4.07m, 3.95m, 3.67m, 3.59s, 3.41m, 3.35m, 3.05m, 2.99m, 2.94w, 2.86w, 2.76vw, 2.70w, 2.65m, 2.57m, 2.49w, 2.40wsh, 2.35m, 2.33wsh, 2.25wbr, 2.17w, 2.10w, 2.06vw, 2.03vw, 2.00w, 1.87w, 1.84w, 1.80w, 1.74wbr, 1.69vw, 1.63vwbr, 1.58vw, 1.55vw, 1.53vw, 1.49vw, 1.42vw

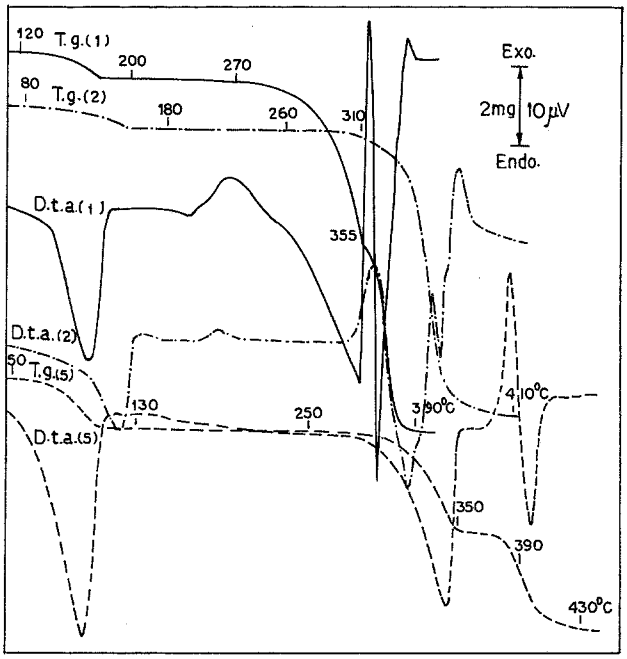

Figure 2. Thermal curves of $[NiL_2]Cl_2 \cdot H_2O$ *(1)* (wt. taken = 14.45 mg) (——), $[NiL_2]Br_2 \cdot H_2O$ *(2)* (wt. taken = 15.84 mg) (–·–·–) and $[NiL_2]SO_4 \cdot 3H_2O$ *(5)* (wt. taken = 9.77 mg) (–––).

1300 cm^{-1}, and 650–600 cm^{-1} where the $\nu(NH_2)$, $\nu(CH_2)$, $\rho_w(CH_2)$ or $\rho_w(NH_2)$, and $\rho_r(NH_2)$ vibrations appear.

Conformational isomers of the diamine systems showed similar differences in their i.r. spectra(8–11). X-ray single crystal analysis of $[Cu(dieten)_2](ClO_4)_2$(18) and $[Ni(dmen)_2(NCS)_2]$(13) (dieten = N, N-diethylethylenediamine and dmen = N, N^1-dimethylethylenediamine) revealed that the conformational change phenomena are associated with structural changes of the unit cell (monoclinic for the low-temperature phase and triclinic for the high-temperature phase, in both the cases). As a result, the differences in x-ray powder diffraction patterns (Table 4) of two isomers of $[NiL_2]$ $(CF_3CO_2)_2$ are not inconsistent with the conformational changes. The thermochromic phenomena observed in $[M(dieten)_2]X_2$(18, 19) [M = copper(II) or nickel(II) and X = ClO_4 or BF_4] systems have been shown to be due to the weakening of the ligand field strength caused by the conformational changes in the ring system. If the anion is capable of undergoing rotational disorder then this type of discontinuous thermochromism is observed(18). Since, CF_3CO_2 is capable of undergoing rotational reorientation a similar mechanism(18) seems to be operative for the thermochromism phenomenon in the $[NiL_2]$ $(CF_3CO_2)_2$.

Phase transition in $[NiL_2]Cl_2 \cdot H_2O$ (1) and $[NiL_2]Br_2 \cdot H_2O$ (2)

The complexes, $[NiL_2]Cl_2 \cdot H_2O$ *(1)* and $[NiL_2]Br_2 \cdot H_2O$ *(2)* on heating become anhydrous at 170° C and 157° C, respectively (Figure 2). On further heating these complexes undergo irreversible exothermic phase transitions (Figure 2) without any colour change. Table 2 lists the temperature range and ΔH values of these transitions. The post-phase species on keeping in a humid atmosphere (relative humidity 70–80%) absorbs one mole of H_2O and these hydrated species lose the water on heating and then undergo similar types of phase transition as *(1)* and *(2)*, but the temperature range of phase transition is considerably reduced [peak temperatures are 218° C and 207° C for $[NiL_2]Cl_2$ and $[NiL_2]Br_2$, respectively]. The thermal profiles of the rehydrated species remain the same even on partial absorption of H_2O, the only differences are t.g. weight loss and d.t.a. peak area for the deaquation and phase transition. The d.t.a. peak area for the phase transition is proportional to the amount of water absorbed by the deaquated species. We observed this type of behaviour in $[Ni(tn)_3]SO_4 \cdot 2H_2O$ (tn = 1, 3-propanediamine)(9).

The electronic spectra, magnetic moment data and i.r. spectra of the deaquated species and post-phase species of the complexes completely eliminate the possibility of geometrical isomerisation (*e.g.*, *mer* → *fac*) as well as the configurational changes [*e.g.*, $\Delta \rightarrow \Lambda$(17)] in *(1a)* → *(1b)* or *(2a)* → *(2b)* transitions (Table 2). As both complexes $[NiL_2]Cl_2 \cdot H_2O$ *(1)* and $[NiL_2]Br_2 \cdot H_2O$ *(2)* are meridional(16, 21) (*vide supra*) there is possible racemisation on heating, but it is unlikely that a racemised product after absorbing water will invert to one pure optical isomeric form. Therefore, the isomerisation [*(1a)* → *(1b)* or *(2a)* → *(2b)*] is presumed to involve conformational changes in the individual chelate rings.

Comparision of the i.r. spectra of deaquated and post-phase species of $[NiL_2]Br_2 \cdot H_2O$ *(2)* shows some extra bands in the region $\nu(NH_2)$, $\delta(CH_2)$ (1000 cm^{-1} and 1460 cm^{-1}, respectively) which may be consistent with conformational changes in the chelate rings. The value of ΔH for the phase transition of the $[NiL_2]Cl_2$ *(1a)* is higher than that of $[NiL_2]Br_2$ *(2a)*, probably due to the fact that the chloro-complex has greater H-bonding ability than the corresponding bromo-analogue(18). The x-ray powder diffraction pattern of *(1b)* and *(2b)* could not be obtained due to their extreme hygroscopic nature. The i.r. spectrum of *(1b)* also could not be taken because its transition is at 282° C. The transitions are could not therefore be characterized.

Mono-(dien) complexes of nickel(II)

All the four mono-complexes $NiLCl_2 \cdot H_2O$ *(1c)*, $NiLBr_2 \cdot H_2O$ *(2c)*, $NiLSO_4 \cdot 3H_2O$ *(5b)* and $NiLSeO_4 \cdot 3H_2O$ *(6b)* possess octahedral geometry, as is evident from the magnetic moments and electronic spectra (Table 1). Structures of $NiLCl_2 \cdot H_2O$ *(1c)* and $NiLBr_2 \cdot H_2O$ *(2c)* and their respective deaquated species have been proposed(3).

The complex $NiLCl_2 \cdot H_2O$ *(1c)* starts to lose water at 70° C and at 127° C it becomes completely deaquated. This anhydrous species (green) $NiLCl_2$ *(1d)* absorbs one mole of H_2O to form blue $NiLCl_2 \cdot H_2O$ *(1c)* within *ca.* 3 h at a relative humidity 70–80%. The rehydrated species on heating loses the H_2O molecule at a higher temperature range (83–140° C) than the original. The i.r. spectra of the original $NiLCl_2 \cdot H_2O$ and $NiLCl_2$ show some remarkable differences. $NiLCl_2 \cdot H_2O$ possesses two single strong bands at 980 cm^{-1} and 680 cm^{-1} for $\rho_r(CH_2)$ and $\rho_r(NH_2)$ whereas for $NiLCl_2$ there are two pairs of strong bands at 978 cm^{-1}, 950 cm^{-1} and 687 cm^{-1}, 670 cm^{-1}, respectively. Besides this, some changes in the intensity ratios of the bands in the region $\nu(NH_2)$ and $\nu(CH_2)$ have also been observed in their i.r. spectra. It is interesting that the rehydrated species of $NiLCl_2$ *(1b)* possesses a similar i.r. spectrum to that of deaquated species $NiLCl_2$ *(1b)* except for the presence of the bands due to water molecule.

The two isomers, *fac* and *mer*, of the mono-(dien) complexes can easily be distinguished by the inspection of i.r. spectra in the region 1500–1400 cm^{-1}, *ca.* 1250 cm^{-1} and 850–700 cm^{-1} for CH_2 bending, NH wagging and NH_2 rocking, respectively(2). In the present case, all four mono-(dien) complexes of nickel(II) and their respective deaquated species possess three CH_2 bending at 1432 cm^{-1}, 1450 cm^{-1} and 1477 cm^{-1}; NH_2 rocking at 780 cm^{-1} but no NH wagging at *ca.* 1250 cm^{-1} which are compatible with the *fac* isomer. Therefore, the deaquation is not accompanied with geometrical isomerisation.

Each geometric isomer of the mono-(dien) complexes may exist any of the three conformational forms(2, 17), $\delta\lambda$, $\lambda\delta$ and $\delta\delta$. The other possible $\lambda\lambda$ is enantiomeric and energetically equivalent to $\delta\delta$. Schmidtke *et al.*(2) suggested that most likely ring conformation for the anhydrous *fac* isomer is $\delta\delta$ or $\lambda\lambda$. It is evident that the H-bond formed by the water molecules with amine hydrogens are sometime capable of reversing or modifying the normal conformational preference(8). Therefore, it is assumed that $NiLCl_2$ possesses either of these conformational forms. However, the hydrated species $NiLCl_2 \cdot H_2O$ appears to possess a more symmetrical conformational form (i.e., $\delta\lambda$ or $\lambda\delta$) as on dehydration, the i.r. band for $\rho_r(CH_2)$ at 980 cm^{-1} splits into two bands at 985 cm^{-1} and 950 cm^{-1}, and $\rho_r(NH_2)$ at 680 cm^{-1} splits into two bands at 687 cm^{-1} and 670 cm^{-1}. The relative intensities of the other CH_2 and NH_2 vibration also change, which conforms that conformational changes have occurred(1–5, 8–15). Of the two symmetrical forms, $\delta\lambda$ and $\lambda\delta$, $\lambda\delta$ should be very unstable because of the steric hindrance due to hydrogen atoms which approach each other appreciably in this ring structure. As a consequence, it is assumed that the species $NiLCl_2 \cdot H_2O$ possesses the $\delta\lambda$ form.

The deaquation behaviour of $NiLBr_2 \cdot H_2O$ *(2b)* is similar to that of $NiLCl_2 \cdot H_2O$ *(1b)*. It starts to lose water at 118° C and becomes anhydrous at 195° C. Comparison of the i.r. spectra of the hydrated and dehydrated species shows similar differences to these observed in the corresponding chloro-complexes (*vide supra*). Therefore, in this case, similar conformational changes of the chelate ring are supposed to be associated with the deaquation. However, the species $NiLBr_2$ is more hygroscopic than $NiLCl_2$, and the rehydrated species on heating loses the H_2O at a higher temperature (125–210° C) in comparision to the original, like the corresponding chloro-complex.

The complex $NiLSO_4 \cdot 3H_2O$ *(5b)* starts to lose H_2O at 92° C, and at 132° C it becomes completely deaquated giving two overlapping endotherms (peak temperatures 101° C and 123° C) (Table 2). The deaquated species $NiLSO_4$ *(5c)* in a humid atmosphere (relative humidity 70–80%; *ca.* 24 h) becomes rehydrated, and takes up three molecules of water. This rehydrated species loses water on heating in two steps, giving two well separated endothermic peaks (peak temperatures 120° C and 160° C) even when it is stored in desiccator for a long time. However, when the deaquated species is exposed to a humid atmosphere (relative humidity 70–80%) for two days or more, the rehydrated species shows a similar deaquation behaviour to that of the original $NiLSO_4 \cdot 3H_2O$ *(5b)* (deaquation temperature range 92° C–132° C).

The complex $NiLSO_4 \cdot 3H_2O$ *(5b)* is a nonelectrolyte ($\Lambda_m \approx 5\,\Omega^{-1}\,\text{mol}\,\text{cm}^2$) in MeOH and EtOH but in water is 1:2 electrolyte ($\Lambda_m = 237.5\,\Omega^{-1}\,\text{mol}\,\text{cm}^2$). It can be assumed that in MeOH and EtOH the $SO_4{}^{2-}$ ion is coordinated. The deaquated species $NiLSO_4$ *(5c)* also possesses octahedral geometry as is evident from magnetic moment and electronic spectral data, and is insoluble in MeOH, EtOH, MeCN and $CHCl_3$. Therefore, the sulphate group is suggested to be bridged tridentate to satisfy the octahedral geometry and the species *(5c)* is likely to be polymeric. This coordination is not explicable by the i.r. spectrum due to the overlapping of amine bands. The i.r. spectra of the dehydrated and hydrated complexes show similar differences as $NiLCl_2 \cdot H_2O$ *(1b)* and $NiLBr_2 \cdot H_2O$ *(2b)*. In the case of $NiLSO_4 \cdot 3H_2O$ *(5b)* a single i.r. band at 995 cm^{-1} for $\rho_r(CH_2)$ splits into two bands at 1003 cm^{-1} and 958 cm^{-1} probably due to the change of conformation in individual chelate rings during dehydration.

The species $NiLSeO_4 \cdot 3H_2O$ *(6b)* starts to lose water at 165° C and at 200° C it is completely deaquated. Unlike $NiLSO_4 \cdot 3H_2O$ *(5b)*, $NiLSeO_4 \cdot 3H_2O$ *(6b)* shows one endothermic peak during dehydration. The i.r. spectra of the hydrated and dehydrated species show differences similar to those of the sulphate analogues. In this case we also observed a single band appearing at 935 cm^{-1} for $\rho_r(CH_2)$ of $NiLSeO_4 \cdot 3H_2O$ *(6b)* which on deaquation splits into two bands at 920 cm^{-1} and 950 cm^{-1}. Therefore, we conclude that some type of conformational change is associated with the dehydration.

Decomposition of mono- and bis-(dien) complexes

The complex $[NiL_2]Cl_2$ *(1b)* starts to decompose at 284° C and transforms to $NiCl_2$ at 390° C *via* $NiLCl_2$ *(1d)* as is evident from the break in the t.g. curve (Figure 2). The $NiLCl_2$ *(1d)* is not isolable in pure form as the decomposition temperatures (T_i) (Table 2) of *(1b)* and *(1d)* are very close.

The complex $[NiL_2]Br_2$ *(2b)* starts to decompose at 302° C and transforms straight to $NiBr_2$ without any break in the t.g. curve for the formation of $NiLBr_2$.

$[NiL_2]SO_4$ *(5a)* starts to decompose at 290° C and transforms to $NiLSO_4$ *(5c)*, which is greenish-blue at 350° C (Figure 2). *(5c)* also possesses octahedral geometry, as is evident from its magnetic moment and electronic spectrum (Table 1). The i.r. spectrum of the species *(5c)* derived from $NiLSO_4 \cdot 3H_2O$ *(5b)* appears to be similar to that of $NiLSO_4$ *(5c)*, synthesised pyrolytically from $[NiL_2]SO_4$ *(5a)* by temperature arrest technique. The species $NiLSO_4$ *(5c)* transforms to $NiSO_4$ at 430° C. The complex $[NiL_2]SeO_4$ starts to decompose at 262° C and transforms straight to $NiSeO_4$ at 315° C. The species $NiLSeO_4$ *(6c)*, obtained from $NiLSeO_4 \cdot 3H_2O$ *(6b)* starts to decompose at 290° C and transforms to $NiSeO_4$ at 320° C.

The post-phase species of *(3)*, $[NiL_2](CF_3CO_2)_2$ *(3a)*, decomposes at 218° C and transforms to NiO at 260° C.

The complex $[NiL_2](CCl_3CO_2)_2$ *(4)* starts to decompose at 129° C and transforms to $[NiL_2]Cl_2$ admixed with some impurities at 138° C. This on washing with EtOH-H_2O mixture (9:1) yields the species *(1a)* (*vide supra*).

The decomposition temperatures (T_i) (Table 2) of the complexes $[NiL_2]X_2$ ($X = Cl$, Br, $0.5SO_4$ or $0.5SeO_4$) follows the sequence $SeO_4 < Cl \sim SO_4 < Br$, whereas the decomposition temperatures (T_i) (Table 2) of the complexes $NiLX_2$ ($X = Cl$, Br, $0.5SO_4$ or $0.5SeO_4$) follow the sequence $SeO_4 \sim Cl < Br < SO_4$. During the decomposition of the bis-(dien) complexes we obtained only the species NiLSO$_4$ *(5c)* as an isolable intermediate, the most stable species among the deaquated mono-complexes. This is not unexpected form to the proposed structure(3) of the deaquated mono-complexes, as the sulphate group has a greater ability to act as a bridged ligand then the other anions.

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