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THERMALLY INDUCED ISOMERIZATION AND DECOMPOSITION OF *N*-METHYL-1,3-PROPANEDIAMINE COMPLEXES OF NICKEL(II) IN THE SOLID STATE

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ABSTRACT

$[NiL_2(H_2O)Cl]Cl \cdot nH_2O$ (L = *N*-methyl-1,3-propanediamine; $n = 0$ and 1), $[NiL_2X_2]$ [X = Br, CF_3CO_2 and CCl_3CO_2], and $[NiL_2(H_2O)Y] \cdot H_2O$ (Y = SO_4 and SeO_4) have been synthesized and their thermal investigations have been carried out in the solid state. $[NiL_2(H_2O)Cl]Cl \cdot nH_2O$ and $[NiL_2(H_2O)Y] \cdot H_2O$ exist in the *trans* form. On deaquation they transform to *cis*-$[NiL_2Cl_2]$ and *cis*-$[NiL_2Y]$. $[NiL_2(SO_4)]$ undergoes a reversible endothermic phase transition (117–169 °C $\Delta H = 6.5$ kJ mol^{-1}). The complex *trans*-$[NiL_2(CF_3CO_2)_2]$ has been found to transform into its isomer upon heating, showing an endotherm (135–150 °C, $\Delta H = 18.9$ kJ mol^{-1}); on keeping the product in a humid atmosphere (relative humidity 60–70%), it reverts to its original form. $[NiL_2Cl_2]$, $[NiLCl_2]$ and $[NiL(SO_4)]$ have been synthesized pyrolytically in the solid state from their parent diamine complexes. All the complexes possess octahedral geometry and diamine is chelated in all of them except in $[NiL(SO_4)]$ where it is bridged. The occurrence of phase transition phenomena is supposed to be due to conformational changes in the six-membered chelate rings.

INTRODUCTION

Thermal investigation of nickel(II) diamine complexes in the solid state have been carried out extensively by Chaudhuri and co-workers [1–11]. While performing these studies, we observed some novel thermally induced, reversible [1–3] as well as irreversible [1,4,6,11] phase transitions. On the basis of various physico-chemical studies, most of these phase transitions were assumed to be due to the conformational changes of the five- and six-membered diamine chelate rings. Recently, these types of conformational changes phenomena have been established in the light of single crystal X-ray analysis [10]. Besides these phase transitions, the decomposition of diamine

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complexes also appears to be very interesting since it occurs through several isolable intermediate complex species [2,5,9], some of which do not seem to have been prepared from solution. It has been noticed in those studies that both the phase transition phenomena as well as decomposition path of the diamine complexes largely depend on the substituent on the diamine and the anions associated with them. This is probably due to the fact that increasing temperature causes increasingly larger amounts of thermal motion in both the chelate ring and anion. For an anion that can undergo orientational reorientation (e.g. BF_4^-, ClO_4^-, NO_2^-, NO_3^-, SCN^-, etc.) [1,4,12–14], the onset of reorientation of the anion changes the strength of the hydrogen bonding, allowing the chelate ring to undergo conformational changes. It should be mentioned that these anions did not show this type of conformational change in all cases, and this is probably because the interconversion between the isomers is frequently prohibited by the presence of a high potential barrier which is not overcome before decomposition by the increasing temperature. In this context, studies of the thermal behaviour of *N*-methyl-1,3-propanediamine (L) complexes of NiX_2 [$X = Cl$, Br, CCl_3CO_2, CF_3CO_2, $0.5SO_4$ and $0.5SeO_4$] in the solid state are relevant.

EXPERIMENTAL

All the chemicals employed were AR grade. Nickel was estimated gravimetrically in our laboratory. Carbon, hydrogen and nitrogen were determined by a Perkin–Elmer 240C elemental analyser. The equipment employed for IR, electronic spectra (mull), magnetic susceptibility, and thermal measurements is the same as those reported earlier [1–4]. X-ray powder diffraction patterns were taken by Philips XRD diffractometer (PW 1730/1710) kept in a room (relative humidity 30%) using Cu K_α radiation. Table 1 lists the analytical, magnetic and electronic spectral data. Thermal, IR spectral and X-ray powder diffraction data are presented in Tables 2, 3 and 4, respectively.

Preparation of $[NiL_2(H_2O)Cl]Cl$ (1), $[NiL_2Br_2]$ (4) and $[NiL_2(CCl_3CO_2)_2]$ (6)

These were prepared by the addition of diamine (L) (2–3 mmol) dropwise to the respective metal salts (1 mmol) dissolved in 10 ml ethanol–water mixture (9 : 1). The complexes, which separated within a few minutes on stirring, were purified by washing with ethanol and dried in a desiccator.

Preparation of $[NiL_2(CF_3CO_2)_2]$ (5)

This species separated in crystalline form on keeping the mixture prepared by the procedure adopted for complex (1) over-night at room temperature (ca. 25 °C).

TABLE 1

Analytical, magnetic and electronic spectral data of diamine (L) complexes of nickel(II)

Compound		Nickel (%) [a]	Carbon (%) [a]	Hydrogen (%) [a]	Nitrogen (%) [a]	μ_{eff} (B.M.)	λ_{max} (nm)
$[NiL_2(H_2O)Cl]Cl$	(1)	18.0 (18.1)	29.8 (29.6)	8.2 (8.0)	17.2 (17.3)	3.26	575, 360
$[NiL_2Cl_2]$	(1a)	19.0 (19.2)	31.7 (31.4)	7.9 (7.8)	18.2 (18.3)	3.32	600, 380
$[NiL_2(H_2O)Cl]Cl \cdot H_2O$	(1b)	17.3 (17.2)	28.0 (28.1)	8.0 (8.2)	16.4 (16.4)	3.25	575, 360
$NiLCl_2$	(1c)	26.8 (27.0)	21.8 (22.0)	5.6 (5.5)	12.7 (12.9)	3.42	650, 365
$[NiL_2(H_2O)(SO_4)] \cdot H_2O$	(2)	16.0 (16.0)	26.4 (26.2)	7.7 (7.6)	15.0 (15.3)	3.21	591, 366
$[NiL_2(SO_4)]$	(2a)	17.6 (17.7)	28.8 (29.0)	7.1 (7.2)	16.7 (16.9)	3.18	605, 372
$NiLSO_4$	(2c)	24.1 (24.2)	19.5 (19.8)	5.0 (4.9)	11.7 (11.5)	3.18	770(sh), 662, 395
$[NiL_2(H_2O)(SeO_4)] \cdot H_2O$	(3)	14.3 (14.2)	23.0 (23.2)	6.7 (6.8)	13.6 (13.5)	3.28	590, 368
$[NiL_2(SeO_4)]$	(3a)	15.4 (15.5)	25.2 (25.4)	5.6 (6.3)	14.6 (14.8)	3.20	604, 372
$[NiL_2Br_2]$	(4)	14.8 (14.9)	24.2 (24.3)	6.2 (6.1)	14.3 (14.2)	3.32	630, 390
$[NiL_2(CF_3CO_2)_2]$	(5)	12.8 (12.7)	31.2 (31.2)	5.2 (5.2)	12.2 (12.1)	3.22	580, 662
$[NiL_2(CF_3CO_2)_2]$	(5a)	12.7 (12.7)	31.0 (31.2)	5.3 (5.2)	12.1 (12.1)	3.36	580, 662
$[NiL_2(CCl_3CO_2)_2]$	(6)	10.4 (10.5)	25.8 (25.7)	4.4 (4.3)	10.2 (10.0)	3.27	582, 362

[a] Figures in parentheses are the calculated values.

TABLE 2

Thermal parameters of *N*-methyl-1,3-propanediamine (L) complexes of nickel(II)

Thermally induced reaction	Temperature range (° C)	DTA peak temperature (° C)
$[NiL_2(H_2O)Cl]Cl \cdot H_2O$ (1) → $[NiL_2Cl_2]$ (1a)	60– 80	75
$[NiL_2Cl_2]$ (1a) → $NiLCl_2$ (1c)	160–240	232
$NiLCl_2$ (2c) → $NiL_{0.75}Cl_2$	256–292	284
$NiL_{0.75}Cl_2$ → $NiL_{0.5}Cl_2$	292–305	295 [a]
$NiL_{0.5}Cl_2$ → $NiL_{0.25}Cl_2$	305–340	312 [a], 328 [a]
$NiL_{0.25}Cl_2$ → $NiCl_2$	340–392	384 [a]
$[NiL_2(H_2O)(SO_4)] \cdot H_2O$ (2) → $[NiL_2(SO_4)]$ (2a)	90–120	110
$[NiL_2(SO_4)]$ (2a) → $[NiL_2(SO_4)]$ (2b)	117–169	140, 155
$[NiL_2(SO_4)]$ (2b) → $[NiL_2(SO_4)]$ (2a)	157–109	137 [a]
$[NiL_2(SO_4)]$ (2b) → $NiLSO_4$ (2c)	205–235	220
$NiLSO_4$ (2c) → $NiL_{0.33}SO_4$	298–350	340
$NiL_{0.33}SO_4$ → $NiSO_4$	350–435	395, 410 [a]
$[NiL_2(H_2O)(SeO_4)] \cdot H_2O$ (3) → $[NiL_2(SeO_4)]$ (3a)	92–130	118
$[NiL_2(SeO_4)]$ (3a) → $NiLSeO_4$	188–258	235, 251
$NiLSeO_4$ → $NiSeO_4$	258–330	282
$[NiL_2Br_2]$ (4) → $NiL_{1.5}Br_2$	190–238	225, 232
$NiL_{1.5}Br_2$ → $NiLBr_2$	238–280	
$NiLBr_2$ → $NiBr_2$	280–362	308, 332
$[NiL_2(CF_3CO_2)_2]$ (5) → $[NiL_2(CF_3CO_2)_2]$ (5a)	135–150	143
$[NiL_2(CF_3CO_2)_2]$ (5a) → NiO	184–293	238, 252, 280 [a]
$[NiL_2(CCl_3CO_2)_2]$ (6) → $[NiL_2Cl_2]$ [b]	108–120	115

[a] Denotes exothermic peak; the rest are endothermic.

[b] On purification this compound shows identical behaviour to (1a).

Preparation of $[NiL_2(H_2O)(SO_4)] \cdot H_2O$ (2) and $[NiL_2(H_2O)(SeO_4)] \cdot H_2O$ (3)

These were prepared by the addition of diamine (L) (4–5 mmol) dropwise to the finely powdered metal salts (1 mmol) with vigorous stirring. After ca. 12 h, the mixture was treated with 15 ml ethanol–water (9 : 1) and the desired products separated out on stirring were thoroughly washed with ethanol and dried in a desiccator.

$[NiL_2Cl_2]$ (1a), $NiLCl_2$ (1c), $[NiL_2(CF_3CO_2)_2]$ (5a), $[NiL_2(SO_4)]$ (2a), $NiL(SO_4)$ (2c) and $[NiL_2(SeO_4)]$ (3a) were prepared in solid state by the temperature arrest technique [1–11] (see Table 2) from their respective parent diamine complexes under a nitrogen atmosphere. Species (1a) may also be synthesized pyrolytically from $[NiL_2(CCl_3CO_2)_2]$ (6).

RESULTS AND DISCUSSION

The notable phenomena that were observed in the thermal analysis of these diamine complexes are discussed in the following sections.

Deaquation–anation associated with geometrical isomerization in $NiL_2Cl_2 \cdot H_2O$ (1), $NiL_2SO_4 \cdot 2H_2O$ (2) and $NiL_2SeO_4 \cdot 2H_2O$ (3)

All these complexes possess octahedral geometry as is evident from their magnetic and electronic (mull) spectral data (Table 1). The complex $NiL_2Cl_2 \cdot H_2O$ behaves as 1 : 1 electrolyte ($\Lambda_m = 90$ mhos) whereas the complexes $NiL_2SO_4 \cdot 2H_2O$ and $NiL_2SeO_4 \cdot 2H_2O$ behave as non-electrolyte in methanol ($\Lambda_m = 10$ mhos and 12 mhos, respectively) suggesting the presence of SO_4^{2-}, SeO_4^{2-} and one of the Cl^- ions inside the coordination sphere. IR spectra of these complexes show the presence of $\rho_w(H_2O)$ * at 690 cm^{-1} [for (1)] and 730 cm^{-1} [for (2) and (3)] and from which it is suggested that the water molecule is probably co-ordinated with the Ni atom [14]. As a result these complexes may be represented as $[NiL_2(H_2O)Cl]Cl$, $[NiL_2(H_2O)(SO_4)] \cdot H_2O$ and $[NiL_2(H_2O)(SeO_4)] \cdot H_2O$.

On heating, complexes (1), (2) and (3) become deaquated at 80, 120 and 130 ° C, respectively. Reports of elimination of co-ordinated water at such a low temperature are not rare in the literature [15], though, in general it takes place at comparatively higher temperatures (> 100 ° C). The magnetic moments (Table 1) of these deaquated species suggest that they also possess octahedral geometry. Their electronic spectra are analogous to those of the respective aquated complexes, except for a slight shift of the peaks to the longer wave length region (Table 1). This change in the peak positions, is consistent with the proposed formula (see above) as, on elimination of the water molecule from the coordination sphere, the counter anion takes the vacant position. In the case of complexes (2) and (3) the change in coordination behaviour of SO_4^{2-} and SeO_4^{2-} (from monodentate to chelating bidentate) is not interpretable from their characteristic IR bands as they are overlapped with the several diamine vibrations. IR spectra, due to the diamine vibration of the dehydrated species (1a), (2a) and (3a) are almost identical to those of *cis*-$[NiL_2(NCS)_2]$ ** which suggests that they also possess *cis*-configuration. On comparison of the IR spectra of the aquated and deaquated species, it is observed that $\delta(NH_2)$ [17], $\rho_r(CH_2)$ [18] and ν(M–N) [19] bands at ca. 1600, 900–800 and 610–500 cm^{-1}, respectively are much more split in the deaquated species than the corresponding aquated analogue and from this important observation it is proposed that the aquated complexes possess *trans* configuration [17–19]. From the foregoing discussion it is reasonable to assume that the hydrated complexes (1), (2) and (3), on heating undergo deaquation–anation associated with geometrical

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* This peak is identified by comparison of their IR spectra with those of $[NiL_2(NCS)_2]$ [16], $[NiL_2(CF_3CO_2)_2]$ (5) and their deaquated analogue.

** The structure of the complex $[NiL_2(NCS)_2]$ have been established by X-ray crystallography [16].

TABLE 3

IR spectral data (4000–400 cm^{-1}) of *N*-methyl-1,3-propanediamine complexes of nickel(II) in KBr [a]

Compound	Assignments								
	$\nu(NH_2)$	$\nu(CH_2)$ $+ \nu(CH_3)$	$\delta(NH_2)$	$\delta(CH_2)$	$\rho_w(CH_2)$	$\tau(NH_2)$ $+ \rho_w(NH_2)$ $+ \rho(CH_2)$	Stretching vibration of skeleton $\nu(C{-}N)$ $+ \nu(C{-}C)$	$\rho_r(CH_2)$	$\rho_r(CH_2)$ $+ \nu(M{-}N)$ $+ \nu(M{-}O)$ $+ \delta(NCC)$
$[NiL_2(H_2O)Cl]Cl$ (1) [b]	3250s, 3230s, 3145sh	2995w, 2957m, 2925m, 2890sh, 2862m, 2800w	1595m	1479sh, 1468s, 1457sh, 1429s, 1417s, 1400m	1370s, 1350m, 1327m	1280s, 1270sh, 1217m, 1185s, 1140m	1100w, 1092m, 1070s, 1030s, 1000w, 983s, 952m, 929w	900s, 867s	795m, (730m, 680s, 630s, 590sh) [c], 540m, 522m, 471m, 442m
$[NiL_2Cl_2]$ (1a)	3250sh, 3225s, 3180s, 3145s, 3115sh, 3100s	2990w, 2960sh, 2945sh, 2940m, 2925s, 2870s, 2800w	1590sh, 1580s	1470s, 1440m, 1430m, 1415sh, 1410m, 1400sh	1370w, 1365sh, 1350vw, 1330m	1305vw, 1278s, 1245vw, 1215m, 1195m, 1180s, 1152m, 1135w, 1115vw	1094w, 1090sh, 1067s, 1060sh, 1048s, 1010s, 981m, 946w, 926w	900s, 886m, 862m	800m, 674m, 640w, 530w, 522w, 510w, 468w, 450w, 446w

$[NiL_2(CF_3CO_2)_2]$ (5)	3325m, 3295s, 3280sh, 3270m, 3165w	3000w, 2970m, 2935m, 2885m, 2870m, 2810w	1600m	1466m, 1435m, 1427m, 1410sh, 1400w	1375w, 1355vw, 1320vw	1277m, (1205vs, 1185vs, 1167s, 1135vs) [d]	1090vw, 1075m, 1050vw, 1030m, 1015sh, 985m, 953vw	900s, 855m	800m, 630m, 605w, 525w, 510w, 470w, 420vw
$[NiL_2(CF_3CO_2)_2]$ (5a)	3325m, 3278s, 3265sh, 3165w	3000w, 2970m, 2935m, 2885m, 2870m, 2810w	1595m	1466m, 1460m, 1435m, 1430s, 1420w, 1400w	1375w, 1355vw, 1315vw	1277w, (1205vs, 1185vs, 1167s, 1135vs) [d]	1090vw, 1075m, 1050vw, 1035vw, 1025w, 985m, 953vw	900s, 855m	800m, 630m, 605w, 520w, 470w, 440vw, 420vw

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[a] IR spectra due to diamine vibration (2) and (3) are similar to (1) and those of (2a), (3a) and (4) are similar to (1a).

[b] Bands due to H_2O vibrations [$\nu(H_2O)$ and $\delta(H_2O)$] are omitted.

[c] Bands due to co-ordinated water are overlapped with ligand bands.

[d] Ligand bands are not distinguishable due to overlapping with trifluoroacetate bands: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

TABLE 4

The prominent lines in the X-ray powder patterns of complexes

$[NiL_2(CF_3CO_2)_2]$ (5) *d* (Å)	$[NiL_2(CF_3CO_2)_2]$ (5a) [a] *d* (Å)
9.61s	8.31vs
8.51s	7.93vs
7.97s	6.92w
6.92vs	6.39m
6.23m	6.09m
5.52vs	5.47vs
5.15ms	5.31vs
4.98ms	4.72s
4.82vs	4.40vs
4.62s	4.13m
4.57ms	3.99ms
4.33ms	3.85ms
4.19s	3.77s
4.15s	3.55m
4.09ms	3.47w
4.02ms	3.37m
3.90w	3.23w
3.78w	3.09vw
3.69w	3.05vw
3.53m	2.98vw
3.33mw	2.93vw
3.27m	2.88w
3.23m	2.78ms
3.14mw	
3.01w	
2.97m	

[a] Species (5a) was obtained after the phase transition of (5) was cooled in a desiccator and X-ray powder patterns were taken immediately. vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

isomerization with the retention of octahedral configuration and these can be represented as

$$trans\text{-}[NiL_2(H_2O)Cl]Cl \rightarrow cis\text{-}[NiL_2Cl_2] + H_2O \text{ and}$$
$$trans\text{-}[NiL_2(H_2O)X] \cdot H_2O \rightarrow cis\text{-}[NiL_2X] + 2H_2O$$
$$(X = SO_4 \text{ and } SeO_4)$$

In this context it may be noted that this type of geometrical isomerism was not observed in similar systems reported previously [2,7]. However, in complex $[NiL_2Br_2] \cdot 2H_2O$ (L = *N,N′*-dimethyl-1,2-ethanediamine) [2] some type of conformational changes of the diamine skeleton took place simultaneously with deaquation.

It is interesting to note that both species (1) and (1a) absorb water to form the dihydrate, $NiL_2Cl_2 \cdot 2H_2O$ (1b), when kept in a humid atmosphere.

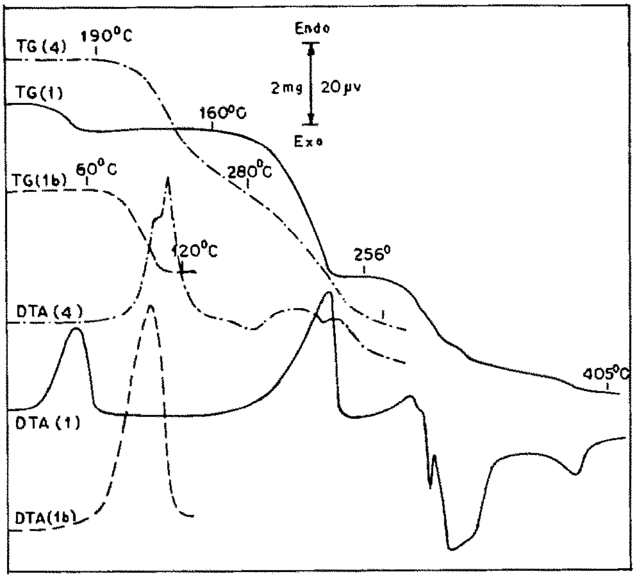

Fig. 1. Thermal curves of $[NiL_2Cl(H_2O)Cl]Cl$ (1) (———) sample mass, 12.37 mg; $[NiL_2(H_2O)Cl]Cl \cdot H_2O$ (1b) (------) sample mass, 18.76 mg and $[NiL_2Br_2]$ (4) (·—·—·) sample mass, 15.42 mg.

This dihydrated species on heating loses both the water molecules in a single step as is evident from its TG–DTA curve (Fig. 1). The species (1) and (1b) cannot be distinguished by electrolytic conductance, magnetic

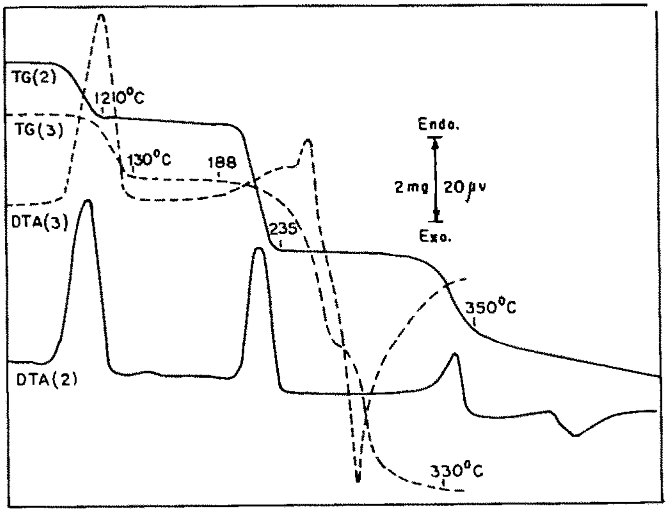

Fig. 2. Thermal curves of $[NiL_2(H_2O)(SO_4)] \cdot H_2O$ (2) (———) sample mass, 13.59 mg and $[NiL_2(H_2O)(SeO_4)] \cdot H_2O$ (3) (------) sample mass, 17.97 mg.

moment, electronic and IR spectral data. Consequently, (1b) is represented as *trans*-$[NiL_2(H_2O)Cl]Cl \cdot H_2O$. Species (2) and (3) are non-hygroscopic whereas their dehydrated species (2a) and (3a) are deliquescent. Here it may be noted that the complex NiL_2Br_2 (4) is not at all hygroscopic and it is synthesized in anhydrous form. It shows almost identical magnetic moment and IR spectral bands to $[NiL_2Cl_2]$ (1a). Electronic spectral bands of species (4) are shifted towards longer wavelengths in comparison to its chloro analogue. Such shifting is not unusual as the bromide ion possesses lower crystal field stabilization energy than the chloride ion. All these observations suggest that it also possesses the *cis* configuration like (1a), (2a) and (3a).

Irreversible phase transition in $NiL_2(CF_3CO_2)_2$ *(5)*

$[NiL_2(CF_3CO_2)_2]$ (5) possesses an octahedral geometry as is evident from its magnetic and electronic spectral data (Table 1). The non-electrolytic behaviour in methanol and the similarity (due to diamine vibration) in the IR spectra to *trans*-$[NiL_2(H_2O)Cl]Cl$ (1) and *trans*-$[NiL_2(H_2O)(SO_4)] \cdot H_2O$ (2) suggest that both the trifluoroacetate groups are monodentate and in the *trans* position. This complex, *trans*-$[NiL_2(CF_3CO_2)_2]$ (5) undergoes an endothermimc irreversible phase transition (135–150 °C, $\Delta H = 18.9$ kJ mol^{-1}) upon heating (see Fig. 3 and Table 2) yielding an isomer (5a). The similarity of the magnetic and electronic spectral data (Table 1) of these two isomers implies the presence of an identical $[NiN_4O_2]$ chromophore in both [1,4,11]. On the other hand the dissimilarity of $\nu(NH_2)$, $\delta(CH_2)$, $[\nu(C{-}N) +$

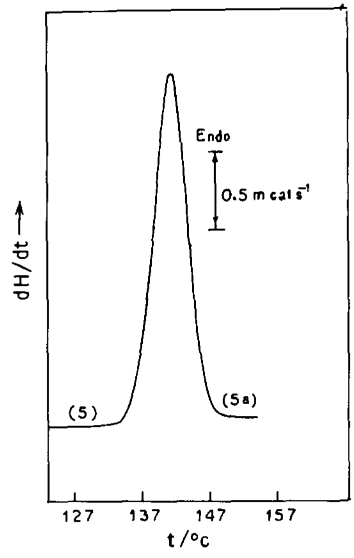

Fig. 3. DSC curve of $[NiL_2(CF_3CO_2)_2]$ (5) (———) sample mass, 8.54 mg.

ν(C–C)] and [ν(M–N) + ν(M–O)] in the regions 3350–3150, 1470–1420, 1120–1020, and 530–420 cm^{-1}, respectively, in the IR spectra (Table 3) and the X-ray powder diffraction patterns (Table 4) of the two isomers (5) and (5a) indicate that they probably differ only in their chelate ring conformations [1,4,11]. For the six-membered diamine ring systems in *trans*-[Ni(tn)$_2$a$_2$] (tn = 1,3-propanediamine) different conformational isomers have been isolated and their relative stabilities have been discussed [1,20,21]. Among these isomers, the most energetically favoured one is that in which the rings are in chair conformations with the two sets of carbon atoms on opposite sides of the *NNMNN* plane [20]. Crystallographic studies of the complexes *trans*-[Cu(tn)$_2$(NO$_3$)$_2$] [22], *trans*-[Co(tn)$_2$Cl$_2$]Cl · HCl · 2H$_2$O [23] and *trans*-[Ni(tn)$_2$(NO$_2$)$_2$] [24] reveal that all of them have the two chairs on the opposite sides of the plane of the metal–amine coordinate bond. Consequently, it is assumed here that complex (5) exists in this most stable *trans*-chair-chair conformational form. Complex (5a), which exists in a higher energy state (18.9 kJ mol^{-1}) than (5), may therefore possess any of the following conformational forms of the two *trans* six-membered chelate ring: (i) *cis*-chair-chair (ii) chair-skew boat (iii) skew boat-skew boat. From the energy difference it is very difficult to suggest the structure of (5a), as the conformational energies of all the forms are very much dependent on the apical ligands, a (a = CF$_3$CO$_2$ in the present case) due to their non-bonded interactions with the chelate rings [20] and no calculated value is available for a = CF$_3$CO$_2$ in the literature. It is interesting to note that the complex (5a) reverts to (5) in a humid atmosphere but retains its identity in a desiccator. This observation suggests that moisture present in the atmosphere acts as a heterogeneous catalyst as observed earlier [1,10].

This reversal [(5a) → (5)] also takes place if (5a) is crystallized from any solvent, e.g. CHCl$_3$, CH$_3$OH, C$_2$H$_5$OH, etc. The reason for this reversion may be explained as follows: the species (5a) exists in a high energy state. When it is dissolved in the solvents mentioned above, the potential barrier that prevents the reversion of (5a) to (5) in solid state is lost and the chelate rings preferentially arrange themselves in the most stable conformational form. Naturally, on crystallization, the stable form (5) is obtained. It is interesting to note that a humid atmosphere also catalyses the conversion, (5a) → (5). It is expected that water molecules first become attached to complex (5a) due to van der Waals attraction thus lowering the potential barrier.

Reversible phase transition in NiL$_2$SO$_4$ (2a)

The species [NiL$_2$SO$_4$] (2a) undergoes a reversible phase transition (ΔH = 6.5 kJ mol^{-1}) upon heating to form species (2b) without any visual colour change, showing two overlapping endotherms in its DSC curve. But on cooling (2b) reverts to (2a), showing only one exothermic peak (see Fig. 4

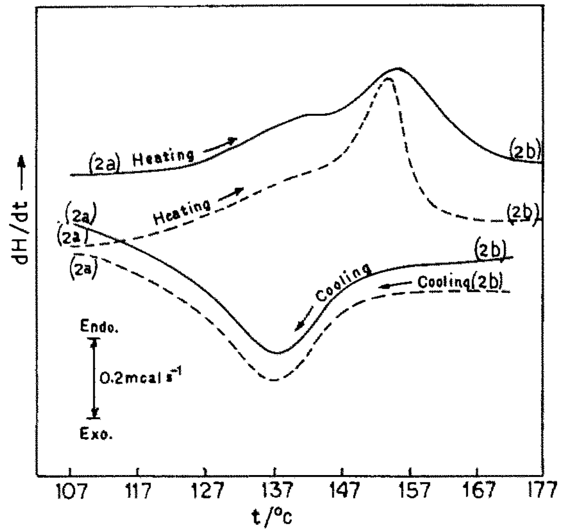

Fig. 4. DSC curves of $[NiL_2(SO_4)]$ (2a) (———) sample mass, 9.21 mg, first heating and cooling; (- - - - - -), second heating and cooling.

and Table 2). On reheating (2a) again shows two overlapping endotherms in almost the same temperature region as is observed in the first heating curve, but the first peak appears (140 °C) as a shoulder. On recycling, the heating as well as the cooling curves are found to be identical to the second heating and first cooling curves, respectively. Recently, the analogous endothermic reversible phase transition observed in $Cu(dmtn)_2(NO_3)_2$ [25] has been reported to be due to the occurrence of a dynamic equilibrium between the different conformational forms of the six-membered diamine chelate. Here the observed energy change for the transition (4) → (4a) is found to be ca. 6.5 kJ mol^{-1} and is comparable with the enthalpy change for the analogous endothermic phase transition due to conformational changes of the chelate rings of some other nickel(II) bisdiamine complexes [1,4,10,11]. As a consequence, it may be assumed that some types of conformational changes and/or a dynamic disorder of the diamine chelate is responsible for this phase transition. However, the IR spectra of (2b) at ca. 165 °C are found to be almost identical with those of (2a) which is in contrast to the behaviour of the high-temperature phase of the analogous bisdiamine complexes [1,4,10,11,24]. As a result, the exact nature of the phase transition remains unexplored due to the lack of facilities for obtaining other spectral and structural data at higher temperature.

Decomposition of the complexes

The complex $[NiL_2Cl_2]$ (1a) on heating transforms to $NiCl_2$ via $NiLCl_2$ (1c), $NiL_{0.75}Cl_2$, $NiL_{0.5}Cl_2$ and $NiL_{0.25}Cl_2$ as is evident from the breaks of the TG curve as well as DTA peaks (Fig. 1). Amongst these intermediates, only the monodiamine species (1c) is isolable in pure form by the temperature arrest technique. Species (1c), greenish yellow in colour, also possesses octahedral geometry as is evident from its magnetic moment and electronic spectral data (Table 1). The IR spectra suggest that the chelating behaviour of the diamine is retained. Then its structure should be polymeric pseudo-octahedral with the bridging chloride as reported by Dokum et. al [26] in Co(II) and Mn(II) complexes of 2-2-bipyridyl and by us in analogous Ni(diamine) systems [2,8,9].

The complex [NiL_2SO_4] (2b) upon heating starts to decompose at 205 °C and transforms to $NiLSO_4$ (2c), which is light green in colour, at 235 °C. Species (2c) also possesses octahedral geometry as is evident from magnetic and electronic spectral data (Table 1). The diamine is acting here as a bridging bidentate ligand which is evident from its much simpler IR spectra compared with that of the bis species (2a). The sulphate group is supposed to be bridged quadridentate to satisfy its octahedral geometry. This quadridentency is not interpretable from its IR spectra due to the overlapping of diamine bands. Species (2c) starts to decompose at 298 °C and transforms to $NiSO_4$ via a non-isolable intermediate $NiL_{0.33}SO_4$ as is evident from the break in the TG curve (Fig. 2).

The complex [NiL_2SeO_4] (3a) starts to decompose at 185 °C and transforms to $NiSeO_4$ via a non-isolable intermediate $NiLSeO_4$ (Table 2; Fig. 2). The instability of the monodiamine species is probably due to the lesser ability of the selenate group to act as a quadridentate bridged ligand in comparison with that of the sulphate group. This type of behaviour of the selenate group has also been reported earlier [2].

The complex [NiL_2Br_2] (4) transforms to $NiBr_2$ upon heating via non-isolable intermediates $NiL_{1.5}Br_2$ and $NiLBr_2$ as is evident from the TG breaks and the corresponding DTA peaks (see Fig. 1 and Table 2).

On further heating the complex [$NiL_2(CF_3CO_2)_2$] (5a) starts to decompose at 180 °C and transforms straight to NiO at 293 °C.

The complex [$NiL_2(CCl_3CO_2)_2$] (6) starts to decompose at 108 °C and transforms to [NiL_2Cl_2] admixed with some impurities at 120 °C. This on thorough washing with ethanol–water mixture (9 : 1) yields complex (1) (see above). Similar thermal decomposition of diamine complexes of nickel(II) trichloroacetate has also been observed previously [2].

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