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THERMAL PHASE TRANSITION AND DECOMPOSITION OF *N*-METHYL-1,2-ETHANEDIAMINE COMPLEXES OF NICKEL(II) IN THE SOLID STATE *

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ABSTRACT

$[NiL_3]X_2 \cdot H_2O$ (L = *N*-methyl-1,2-ethanediamine; $X^- = Cl^-$ and Br^-), $[NiL_3]X_2$ ($X^- = NO_3^-$ and BF_4^-) and $[NiL_2X_2]$ ($X^- = Cl^-$, Br^-, NCS^-, $CF_3CO_2^-$ and $CCl_3CO_2^-$) have been synthesized and their thermal studies have been investigated in the solid state. $[NiL_3]Br_2$, $[NiL_2Br_2]$ ($X^- = Cl^-$ and Br^-), $[NiLCl_2]$ and $NiL_{0.5}Cl_2$ have been synthesized pyrolytically in the solid state from their corresponding parent diamine complexes. $[NiL_2X_2]$ ($X^- = Cl^-$ and Br^-) undergo endothermic reversible phase transition whereas $[NiL_3]X_2$ ($X^- = NO_3^-$ and BF_4^-) and $[NiL_2(CF_3CO_2)_2]$ show endothermic time dependent reversible phase transition. All the complexes except $NiL_{0.5}Cl_2$ possess octahedral geometry. $NiL_{0.5}Cl_2$ possesses an unusually high magnetic moment (5.8 B.M. at 28 °C).

INTRODUCTION

Thermally induced solid-state isomerization and decomposition of nickel(II) diamine complexes have been reported by us [1–13]. It has been observed that the thermal behaviour of the complexes is found to be dependent on the substitution present in the diamine as well as the counter anion. These observations reflect the need for extensive research relating to these novel systems. The present paper reports thermally induced phase transition and decomposition of *N*-methyl-1,2 ethanediamine (L) complexes of NiX_2 ($X^- = Cl^-$, Br^-, NCS^-, NO_3^-, BF_4^-, $CF_3CO_2^-$ and $CCl_3CO_2^-$) in the solid state.

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EXPERIMENTAL

All the chemicals employed were AnalaR grade and the diamine, *N*-methyl-1,2-ethanediamine was purchased from Fluka and used as received. The instruments used for IR (both ambient and above ambient temperature up to 220 °C), elemental analyses, electronic spectra (mull), magnetic susceptibility, X-ray powder diffraction and thermal parameters (TG and DTA) were the same as reported earlier [1–13]. The enthalpy changes for the phase transition were evaluated using a Mettler 3000 thermal analyser. Indium metal was used as calibrant.

Preparation of the complexes

$[NiL_3]Cl_2 \cdot H_2O$ (**1**), $[NiL_3]Br_2 \cdot H_2O$ (**2**), $[NiL_2(NCS)_2]$ (**3**), $[NiL_3](NO_3)_2$ (**4**), $[NiL_3](BF_4)_2$ (**5**), $[NiL_2(CF_3CO_2)_2]$ (**6**) and $[NiL_2(CCl_3CO_2)_2]$ (**7**) were prepared by adding diamine (3–4 mmol) dropwise with constant stirring to the corresponding nickel(II) salts (1 mmol) in ethanolic medium. The resulting mixtures were kept in a desiccator for ca. 48 h. Fine crystalline compounds which separated from the solutions were filtered, washed several times with dry ethanol and finally dried in a desiccator.

$[NiL_2Cl_2]$ (**1b**) and $[NiL_2Br_2]$ (**2c**) were synthesized by adding the diamine (2 mmol) dropwise with stirring to the corresponding nickel(II) salts (1 mmol) dissolved in ethanol (5 ml). The desired complexes separated on keeping the resultant mixtures in a desiccator for ca. 72 h. Both the complexes could also be synthesized pyrolytically in the solid state from their corresponding tris analogue (Table 1).

$[NiLCl_2]$ (**1c**) and $NiL_{0.5}Cl_2$ (**1d**) were derived from the complex (**1**) by the temperature arrest technique.

$[NiL_3]Br_2$ (**2a**) was obtained upon dehydration of the complex (**2**) at 114 °C.

RESULTS AND DISCUSSION

All the tris and bisdiamine complexes i.e., $[NiL_3]Cl_2 \cdot H_2O$ (**1**), $[NiL_3]Br_2$ H_2O (**2**), $[NiL_3]Br_2$ (**2a**), $[NiL_3](NO_3)_2$ (**4**), $[NiL_3](BF_4)_2$ (**5**), $[NiL_3](BF_4)_2$ (**5a**), $[NiL_2Cl_2]$ (**1b**), $[NiL_2Br_2]$ (**2c**), $[NiL_2(NCS)_2]$ (**3**), $[NiL_2(CF_3CO_2)_2]$ (**6**) and $[NiL_2(CCl_3CO_2)_2]$ (**7**) appear to possess octahedral geometry as is evident from their corresponding magnetic moment and electronic spectral (mull) data (Table 2). The IR spectra suggest that the diamine is chelated in all of the complexes.

Decomposition of $[NiL_3]Cl_2 \cdot H_2O$ (1) and $[NiL_3]Br_2 \cdot H_2O$ (2)

The complex, $[NiL_3]Cl_2 \cdot H_2O$ (**1**), on heating starts to lose the water molecule at 60 °C and transforms to $NiCl_2$ at 412 °C via the interesting

TABLE 1

Thermal parameters of *N*-methyl-1,2-ethanediamine (L) complexes of nickel(II)

Thermal reactions	Temperature range [d] (°C)	DTA peak temperature [d] (°C)	
		Endo	Exo
$[NiL_3]Cl_2 \cdot H_2O$ (**1**) → $[NiL_2Cl_2]$ (**1a**)	60–208	93, 177sh, 201	–
$[NiL_2Cl_2]$ (**1a**) → $[NiL_2Cl_2]$ (**1b**)	166.7–147.0	–	160.0
$[NiL_2Cl_2]$ (**1b**) → $[NiL_2Cl_2]$ (**1a**)	172.8–192.5	185.8	–
$[NiL_2Cl_2]$ (**1a**) → $[NiLCl_2]$ (**1c**)	232–307	301	–
$[NiLCl_2]$(**1c**) → $NiL_{0.5}Cl_2$ (**1d**)	317–348	–	345
$NiL_{0.5}Cl_2$ (**1d**) → $NiCl_2$	360–412	–	405
$[NiL_3]Br_2 \cdot H_2O$ (**2**) → $[NiL_3]Br_2$ (**2a**)	40–114	106	–
$[NiL_3]Br_2$ (**2a**) → $[NiL_2Br_2]$ (**2b**)	153–223	216	–
$[NiL_2Br_2]$ (**2b**) → $[NiL_2Br_2]$ (**2c**)	138.5–112.7	–	134.0
$[NiL_2Br_2]$ (**2c**) → $[NiL_2Br_2]$ (**2b**)	132.4–158.2	153.7	–
$[NiL_2Br_2]$ (**2b**) → $NiBr_2$	248–382	297, 311, 330	275, 348sh, 380
$[NiL_2(NCS)_2]$ (**3**) → [a]	222 [c]	211 [b]	–
$[NiL_3](NO_3)_2$ (**4**) → $[NiL_3](NO_3)_2$ (**4a**)	141.0–167.0	157.7	–
$[NiL_3](NO_3)_2$ (**4a**) → [a]	169 [c]	–	–
$[NiL_3](BF_4)_2$ (**5**) → $[NiL_3](BF_4)_2$ (**5a**)	103.8–123.9	114.7, 118.5sh	–
$[NiL_3](BF_4)_2$ (**5a**) → [a]	192 [c]	–	–
$[NiL_2(CF_3CO_2)_2]$ (**6**) → $[NiL_2(CF_3CO_2)_2]$ (**6a**)	200.0–213.2	205.5, 206.5	–
$[NiL_2(CF_3CO_2)_2]$ (**6a**) → [a]	215 [c]	–	–
$[NiL_2(CCl_3CO_2)_2]$ (**7**) → $[NiL_2Cl_2]$ (**1a**)	126–165	–	–

[a] Products are not identified.

[b] Peak, due to melting.

[c] Temp. at which decomposition starts.

[d] Temperatures shown up to one decimal are taken from DSC curves.

TABLE 2

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

Compound	Found (calc.) (%)				μ_{eff} (B.M.)	λ_{max} (nm)
	Nickel	Carbon	Hydrogen	Nitrogen		
$[NiL_3]Cl_2 \cdot H_2O$ (**1**)	15.5 (15.8)	29.0 (29.1)	8.7 (8.6)	22.5 (22.7)	3.3	562, 370
$[NiL_2Cl_2]$ (**1b**)	21.0 (21.1)	25.5 (25.8)	7.2 (7.1)	20.0 (20.1)	3.2	570, 384, 310
$[NiLCl_2]$ (**1c**)	28.5 (28.7)	17.3 (17.6)	4.8 (4.9)	13.5 (13.7)	3.4	661, 405
$NiL_{0.5}Cl_2$ (**1d**)	35.0 (35.2)	10.6 (10.7)	3.1 (3.0)	8.3 (8.4)	5.8	–
$[NiL_3]Br_2 \cdot H_2O$ (**2**)	12.5 (12.7)	23.4 (23.5)	6.9 (6.9)	18.2 (18.3)	3.4	542, 361
$[NiL_3]Br_2$ (**2a**)	13.1 (13.3)	24.3 (24.4)	6.5 (6.8)	19.0 (19.0)	3.3	551, 365
$[NiL_2Br_2]$ (**2c**)	15.9 (16.0)	19.5 (19.6)	5.3 (5.4)	15.1 (15.2)	3.2	550, 356
$[NiL_2(NCS)_2]$ (**3**)	17.9 (18.1)	29.6 (29.7)	6.0 (6.2)	25.8 (26.0)	3.1	545, 350
$[NiL_3](NO_3)_2$ (**4**)	14.3 (14.4)	26.5 (26.6)	7.1 (7.4)	27.3 (27.6)	3.2	536, 345
$[NiL_3](BF_4)_2$ (**5**)	12.8 (12.9)	23.4 (23.7)	6.5 (6.6)	18.2 (18.4)	3.2	542, 350
$[NiL_3](BF_4)_2$ (**5a**)	12.8 (12.9)	23.4 (23.7)	6.5 (6.6)	18.2 (18.4)	3.0	541, 350
$[NiL_2(CF_3CO_2)_2]$ (**6**)	13.4 (13.5)	27.5 (27.7)	4.5 (4.6)	12.7 (12.9)	3.3	543, 351
$[NiL_2(CCl_3CO_2)_2]$ (**7**)	10.9 (11.0)	22.4 (22.5)	3.5 (3.7)	10.4 (10.5)	3.2	552, 367

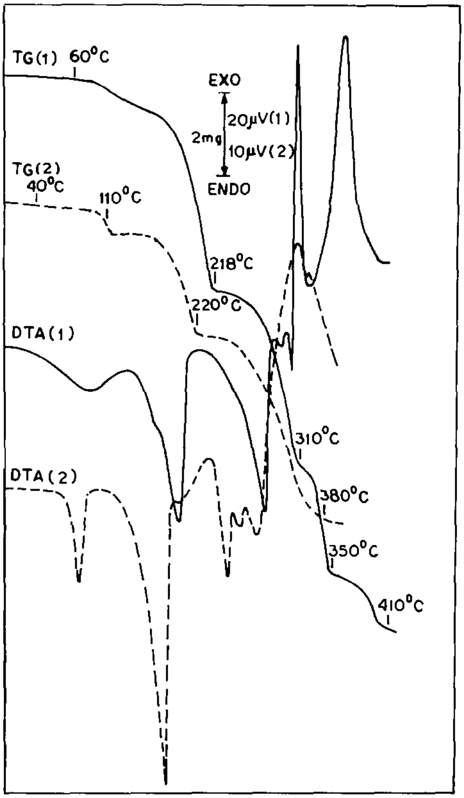


Fig. 1. TG, DTA curves of $[NiL_3]Cl_2 \cdot H_2O$ (**1**) (mass taken = 20.73 mg) (———) and $[NiL_3]Br_2 \cdot H_2O$ (**2**) (mass taken = 15.09 mg) (— — —).

isolable intermediates $[NiL_2Cl_2]$ (**1a**), $[NiLCl_2]$ (**1c**) and $NiL_{0.5}Cl_2$ (**1d**) at 208, 307 and 348 °C respectively as is evident from TG breaks and DTA peaks (Fig. 1; Table 1). The corresponding bromo analogue, $[NiL_3]Br_2 \cdot H_2O$ (**2**) becomes anhydrous at 114 °C and then starts to decompose at 153 °C and generates $[NiL_2Br_2]$ (**2b**). This on further heating transforms to $NiBr_2$ without any isolable intermediate unlike the corresponding chlorocomplex, (**1a**). Earlier [4,5,9,11,12] also, we did not observe the formation of Ni(diamine)$_x$Br$_2$ (where $x < 2$) during pyrolysis of either Ni(diamine)$_3$Br$_2$ or Ni(diamine)$_2$Br$_2$ complexes whereas the corresponding chloro complexes were observed to generate Ni(diamine)$_x$Cl$_2$ ($x < 2$) species. This difference in behaviour is probably because of the reduced ability of the bromide ion to act as bridging ligand compared to the chloride ion.

The electronic spectra (mull) of $[NiLCl_2]$ (**1c**) shows two low intensity bands in the visible region, typical of the octahedral nickel(II). The magnetic moment also supports the octahedral geometry. The IR spectrum suggests that the chelating character of the diamine is retained. Therefore to satisfy the octahedral geometry both the chloride ions should act as bridging ligands as reported by us [5,12].

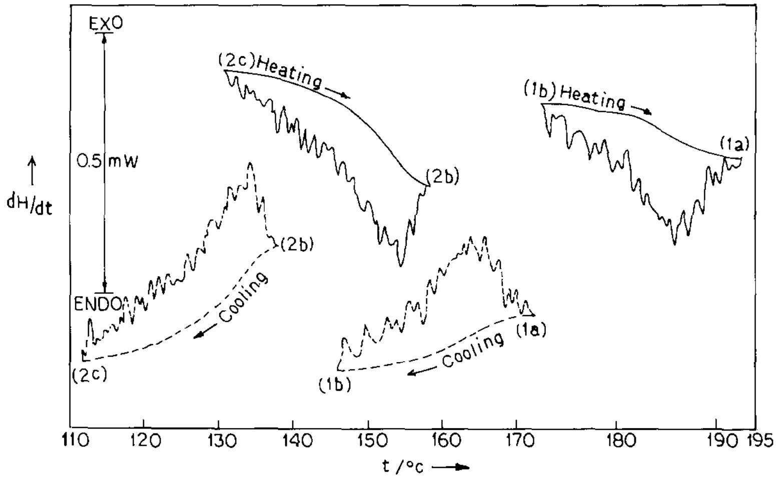
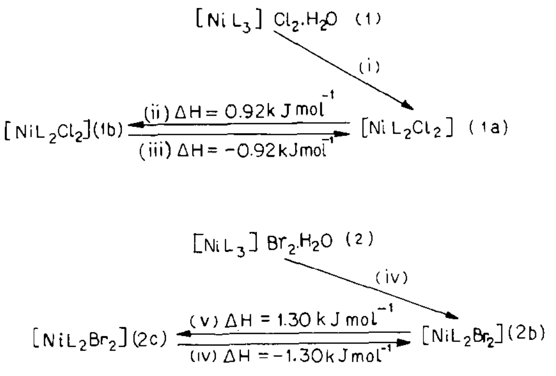


Fig. 2. DSC curves of [NiL_2Cl_2] (**1b**) (heating) (mass taken = 3.08 mg) (———), [NiL_2Cl_2] (**1a**) (cooling) (mass taken = 3.08 mg) (— — —), [NiL_2Br_2] (**2c**) (heating) (mass taken = 4.02 mg) (———), and [NiL_2Br_2] (**2b**) (cooling) (mass taken = 4.02 mg) (— — —). (Noises are due to higher sensitivity. Peak temperatures are obtained from the built-in computer.)

The hemidiamine complex, $NiL_{0.5}Cl_2$ (**1d**) possesses unusually high magnetic moment (μ_{eff} = 5.8 B.M. at 28° C) considering the formula $NiL_{0.5}Cl_2$. This may be due to the ferromagnetic behaviour which is possibly developed from the Cl^- bridging [14–16] and metal–metal interaction [17]. These phenomena and the stoichiometry of the compound would require either pentacoordinated or tetracoordinated tetrahedral species [9]. In this type of geometry, two nickel(II) ions probably come closer to each other to satisfy the proposed interaction. Since the compound is very much hygroscopic in nature, its IR spectrum is not well resolved. However, comparing the IR spectrum of [$NiLCl_2$] (**1c**) with that of $NiL_{0.5}Cl_2$, it is expected that the diamine is possibly bridged. Electronic spectrum in mull of this compound is also not well resolved. Therefore, it is very difficult to comment on the structure of the complex.

*Reversible phase transitions in [NiL_2Cl_2] (**1b**) and [NiL_2Br_2] (**2c**)*

Both the complexes (**1b**) and (**2c**) undergo endothermic reversible phase transitions, on heating (172.8–192.5° C; $\Delta H = 0.92$ kJ mol^{-1} and 132.4–158.2° C; $\Delta H = 1.30$ kJ mol^{-1}, respectively) (Fig. 2). Both the species ((**1b**) and (**2c**)) synthesized by the thermal decomposition of corresponding trisdiamine complexes, also show identical thermally induced reversible phase transitions. These two transformations are shown in Scheme 1 in a schematic way. The complexes (**1b**) and (**2c**) possess *cis*-octahedral geometry like the corresponding 1,2-ethanediamine complexes [9] as is evident from the corresponding IR spectra. The IR spectra of the complexes (**1b**) and (**2c**)



Scheme 1 (i) 60–208°C ; (ii) 166.7–147.0°C; (iii) 172.8–192.5°C
(iv) 40–223°C ; (v) 138.5–112.7°C ; (vi) 132.4–158.2°C

were recorded at elevated temperatures (ca. 200 and ca. 170 °C respectively) but no noticeable spectral changes were observed. Other physicochemical studies of the high-temperature phases ((**1a**) and (**2b**)) could not be performed due to limitations of instrumental facility. However, on the basis of the enthalpy changes and the temperature ranges of transition, it may be assumed that some type of conformational change with a dynamic disorder of the diamine chelate ring is responsible for the phase transition as reported for the similar type of transition in $[Ni(tn)_2Br_2]$ [8], $[Ni(tn)_2SO_4]$ [8], $[Ni(tn)_2SeO_4]$ [8] and $[Ni(metn)_2SO_4]$ [12] (where tn = 1,3-propanediamine and metn = *N*-methyl-1,3-propanediamine).

Phase transitions of $[NiL_3](NO_3)_2$ (4) and $[NiL_3](BF_4)_2$ (5)

Complex (**4**) undergoes endothermic phase transition (141.0–167.0 °C; $\Delta H = 27.3$ kJ mol^{-1}) (Fig. 3, Table 1) and transforms to (**4a**). The post-phase species is not stable. It reverts slowly. The time needed for this transformation is ~ 6 h. Complex (**5**) also undergoes endothermic phase transition (103.8–123.9 °C; $\Delta H = 12.1$ kJ mol^{-1}) (Fig. 3, Table 1) and transforms to (**5a**). The derived post-phase, (**5a**) remains stable for ~ 5 h and then reverts slowly to (**5**). It takes ~ 50 h for complete reversion, but instantaneous reversion of (**5a**) → (**5**) takes place just on shaking the post-phase species either with methanol, ethanol, acetonitrile or chloroform. It is observed that the reversion process is found to be independent of humid atmosphere and that none of the transitions are associated with any visual colour change. The rate of reversion does not alter even by keeping the species (**5a**) at ~ 90 °C whereas this becomes accelerated in the case of (**4a**) → (**4**) when (**4a**) is kept at ~ 120 °C. The electronic spectra (mull) and the magnetic moments of the isomers (**5**) and (**5a**) * are found to be almost identical,

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* Measurements are carried out before the reversion process starts.

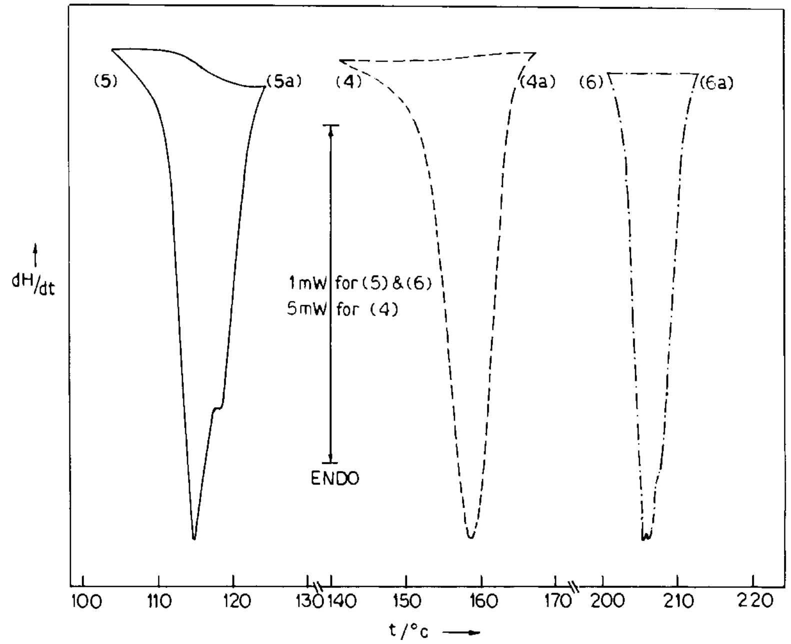

Fig. 3. DSC curves of $[NiL_3](BF_4)_2$ (**5**) (heating) (mass taken = 2.89 mg) (———), $[NiL_3](NO_3)_2$ (**4**) (heating) (mass taken = 5.01 mg) (— — —), $[NiL_2(CF_3CO_2)_2]$ (**6**) (heating) (mass taken = 3.33 mg) (·—·—·).

suggesting $[NiN_6]$ chromophore in both. The non-coordination of BF_4 ion in both of the isomers is also evident from their similar IR active bands [18]. However, the IR bands due to the diamine vibrations of these two isomers differ considerably in the regions 3000–2800, 1570–1450, 1350–1250 and 850–750 cm^{-1} which correspond to ν_{CH_2}, δ_{CH_2}, $(\tau_{NH_2} + \rho_{\omega_{CH_2}} + \tau_{CH_2})$ skeletal and $\rho_{r_{CH_2}}$ vibrations respectively. As a consequence, the change in the spatial arrangements of the individual chelate rings may be considered to account for the formation of the two isomers [1–7]. The X-ray diffraction powder patterns do not show any significant difference (Fig. 4). Almost all the lines of (**5**) are reproduced in (**5a**) with considerable broadening and the intensity ratio of the different lines remains almost the same. Thus a major change in unit cell does not appear to take place. The above data, although inconclusive, are not inconsistent to consider the conformational changes of the chelate rings as the most probable explanation for the phase transition.

In the case of $[NiL_3](NO_3)_2$ (**4**), we could not isolate (**4a**) in pure form at ambient temperature (~ 35 °C). As a result we could not record the X-ray powder diffraction patterns, electronic spectra (mull) and magnetic moment of (**4a**). However, the high-temperature (ca. 170 °C) IR spectra of (**4a**) exhibit a single, sharp narrow band at ~ 1750 cm^{-1} like the IR spectra of (**4**) indicating the non-coordination of NO_3 ion in both [18]. The IR active diamine vibrations show considerable differences in the regions ν_{CH_2}, $(\tau_{NH_2}$

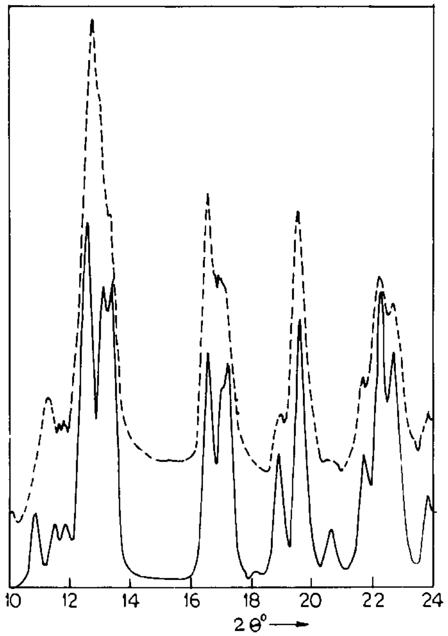

Fig. 4. X-ray powder diffraction patterns of $[NiL_3](BF_4)_2$ (**5**) (———) and $[NiL_3](BF_4)_2$ (**5a**) (— — —).

$+ \rho_{w_{CH_2}} + \tau_{CH_2}$) skeletal, ($\nu_{C-N} + \nu_{C-C}$) skeleton and $\rho_{r_{CH_2}}$ vibrations, respectively. Therefore, it is suggested that here also conformation changes of the diamine are responsible for the phase transition.

The mechanism for the transition may be considered as follows. In both the complexes (**4**) and (**5**) the anions are H-bonded with the amine hydrogen. As the temperature is raised, the thermal vibrations of both the anions and diamine chelate ring increase and a point is reached at which thermal motion energy sufficiently weakens the H-bonding network, allowing the chelate rings to undergo conformational changes [19,20]. The stronger H-bonding ability of the NO_3 ion as compared to that of BF_4 ion is comparable with the higher ΔH value and temperature range of transition (Table 1).

Phase transition in $[NiL_2(CF_3CO_2)_2]$ *(6)*

The complex (**6**), upon heating transforms to its isomer (**6a**) showing two endotherms overlapping with each other followed by a shoulder in the corresponding DSC curve (200.0–213.2 °C; $\Delta H = 7.6$ kJ mol^{-1}) (Fig. 3; Table 1). Here also the phase transition is not associated with any visual colour change which tentatively nullifies the possibility of configurational changes in the system. The post-phase species (**6a**) is also not isolable like (**4**) and reverts slowly to (**6**). At ambient temperature this reversion (**6a**) → (**6**) requires ~ 6 h, whereas at ~ 150 °C it takes place within ~ 1 h. The enthalpy values as well as temperature range for this transition are comparable with those of analogous bis(diamine) complexes [1–7,12,13] where the phase transitions were assumed to be due to the conformational changes of the chelate rings and/or weakening of the H-bonding network caused by the reorientation of the anions. It was observed in most of these systems that the IR spectra of the conformational isomers differ in some specific regions. However, the IR spectra of the species (**6a**) recorded at ~ 215 °C are found to be almost identical with those of (**6**). Therefore, it is very difficult to comment on the exact nature of this phase transition.

Decompositions of $[NiL_2(NCS)_2]$ (3) and $[NiL_2(CCl_3CO_2)_2]$ (7)

The IR spectrum of $[NiL_2(NCS)_2]$ (*3*) shows a single, sharp, very strong $\nu_{(C-N)}$ vibration at 2096 cm^{-1} and a weak peak at 832 cm^{-1} for the $\nu_{(CS)}$ vibration, from which it may be concluded that the thiocyanato groups are N-bonded and in *trans*-position. The species (**3**) melts at 211 °C (melting peak temperature) and starts to decompose at 222 °C.

The IR spectrum of $[NiL_2(CCl_3CO_2)_2]$ (**7**) shows a $\nu_{as}(COO)$ band at 1687 cm^{-1} and $\nu_s(COO)$ at 1368 and 1337 cm^{-1} suggesting monodentacy of the carboxylate groups. This also supports the non-electrolytic behaviour in methanol ($\Lambda_m = 20\ \Omega^{-1}\ mol\ cm^2$) and acetonitrile ($\Lambda_m = 26\ \Omega^{-1}\ mol\ cm^2$). This complex, upon heating decomposes at 126 °C and transforms to $[NiL_2Cl_2]$ (**1a**) at 165 °C (Table 1).

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