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Thermochimica Acta 287 (1996) 155–163

thermochimica
acta

Thermal studies of *N*-propylethane-1,2-diamine and *N*-isopropylethane-1,2-diamine complexes of nickel(II) in the solid state

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Received 20 November 1995; accepted 17 March 1996

Abstract

$[\text{NiL}_3]\text{X}_2 \cdot 2\text{H}_2\text{O}$ (X is Cl^- , Br^- and ClO_4^- ; L is *N*-propylethane-1,2-diamine), $[\text{NiL}_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, $[\text{NiL}_2\text{X}_2]$ (X is Cl^- , Br^- , 0.5SO_4^{2-} and 0.5SeO_4^{2-}), $[\text{NiL}'_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (L' is *N*-isopropylethane-1,2-diamine), $[\text{NiL}'_2\text{X}_2]$ (X is Cl^- , Br^- , NCS^- and 0.5SeO_4^{2-}) and $[\text{NiL}'_2\text{SO}_4] \cdot 3\text{H}_2\text{O}$ have been synthesised from solution and their thermal studies have been carried out in the solid phase. $[\text{NiL}_2\text{X}_2]$ (X is Cl^- and Br^-), NiLCl_2 and $\text{NiL}'\text{SO}_4$ have been prepared pyrolytically from their respective parent species in the solid state. $[\text{NiL}_2](\text{ClO}_4)_2$ and $[\text{NiL}'_2](\text{ClO}_4)_2$ were prepared pyrolytically from their parents species, and also by storing $[\text{NiL}_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ and $[\text{NiL}'_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ in a CaCl_2 desiccator, respectively; these transformations are accompanied by a pink to yellow colour change due to octahedral to square-planar configurational changes. All other bis(diamine) species have octahedral geometry. Among them, $[\text{NiL}_2\text{X}_2]$ (X is Cl^- and Br^-) and $[\text{NiL}'_2\text{X}_2]$ (X is Cl^- , Br^- and NCS^-) possess trans-octahedral configuration, whereas $[\text{NiL}_2\text{X}]$ (X is SO_4^{2-} and SeO_4^{2-}), $[\text{NiL}'_2\text{SO}_4] \cdot 3\text{H}_2\text{O}$ and $[\text{NiL}'_2\text{SeO}_4]$ have cis-configuration. On heating, *trans*- $[\text{NiL}_2\text{Br}_2]$ and *trans*- $[\text{NiL}'_2(\text{NCS})_2]$ undergo reversible endothermic phase transitions (86–99°C, $\Delta H = 0.52 \text{ kJ mol}^{-1}$ for heating, and 92–81°C, $\Delta H = -0.53 \text{ kJ mol}^{-1}$ for cooling for the former, and 162–224°C, $\Delta H = 0.27 \text{ kJ mol}^{-1}$ for heating and 208–150°C, $\Delta H = -0.25 \text{ kJ mol}^{-1}$ for cooling for the latter), most likely due to conformational changes of the diamine chelate rings.

Keywords: DTA; Nickel compound; Phase transition; Stability; TG

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1. Introduction

Thermal studies of diamine complexes of nickel(II) have been of interest to inorganic chemists since the discovery of Lifschitz's salts [1–3], whose colours were found to change with temperature. It was established later that octahedral $\leftrightarrow$ square-planar geometrical isomerism was responsible for the colour change. The diamines form chelate rings with metal ions; on heating, these chelate rings may undergo dynamic disorder between the two stable conformations, causing a colour change of the complexes in most cases [4–7]. Both of these thermochromic phenomena were found to be dependent on the substitution in the diamine, as well as on the nature of the counter anions [8–15]. In addition, solid-state thermal decomposition of these complexes can provide a single method for isolation of the intermediate species [11,16,17] which could not otherwise be obtained from solution, or only with difficulty. We are investigating thoroughly the thermally induced phase transitions and decompositions of diamine complexes of nickel(II) and in continuation to these studies we report here the syntheses, characterisation and solid state thermal studies of the *N*-propylethane-1,2-diamine (L) and *N*-isopropylethane-1,2-diamine (L') complexes of Ni(II)X_2 (X is Cl^- , Br^- , NCS^- , ClO_4^- , 0.5SO_4^{2-} and 0.5SeO_4^{2-}).

2. Experimental

High purity *N*-propylethane-1,2-diamine (L) (99%) and *N*-isopropylethane-1,2-diamine (L') (98%) were purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals were of AR grade. The thermal analyses (TG–DTA) were carried out using a Shimadzu DT-30 thermal analyser in a dynamic atmosphere of nitrogen (flow rate, $30\text{ cm}^3\text{ min}^{-1}$). The sample (particle size within 150–200 mesh) was heated in a platinum crucible at a rate of $10^\circ\text{C min}^{-1}$ with inert alumina as reference. The enthalpy changes of the phase transitions were calculated by a Perkin-Elmer DSC-2 differential scanning calorimeter using indium metal as calibrant (rate of heating/cooling, $10^\circ\text{C min}^{-1}$). Elemental analyses, IR spectra ($4000\text{--}250\text{ cm}^{-1}$), electronic spectra (mull) ($900\text{--}190\text{ nm}$ and $400\text{--}1400\text{ nm}$), magnetic susceptibility and conductance measurements were made using a Perkin-Elmer 240C elemental analyser, Perkin-Elmer IR 783, Shimadzu UV 2100, Hitachi UV-VIS-NIR model U 3410, and EG & G PAR 155 vibrating sample magnetometer and Systronics 304 conductivity bridge, respectively.

2.1. Preparation of the complexes

$[\text{NiL}_3]\text{X}_2 \cdot 2\text{H}_2\text{O}$ (X is Cl^- , Br^- and ClO_4^-) was prepared by addition of the ethanolic solution (5 cm^3) of the diamine (3 mmol) to the nickel(II) salts (1 mmol) dissolved in ethanol (10 cm^3). The resulting mixture was filtered and the filtrate was kept in a CaCl_2 desiccator. After a few days, the desired complex was filtered, washed with isopropanol and dried in a CaCl_2 desiccator.

$[\text{NiL}_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (**7**) and $[\text{NiL}'_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**14**) were obtained by following the above procedure, but changing the metal: diamine ratio to 1:2.

$[\text{NiL}_2](\text{ClO}_4)_2$ (**8**) and $[\text{NiL}'_2](\text{ClO}_4)_2$ (**15**) were obtained from the species (**7**) and (**14**) respectively, on keeping them in a CaCl_2 desiccator. The species (**8**) was also synthesised pyrolytically from $[\text{NiL}_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**6**) as well as from (**7**). Similarly, the species (**15**) was also obtained from (**14**).

$[\text{NiL}_2\text{X}]$ (X is SO_4^{2-} and SeO_4^{2-}), $[\text{NiL}'_2\text{SO}_4] \cdot 3\text{H}_2\text{O}$ (**16**) and $[\text{NiL}'_2\text{SeO}_4]$ (**18**) were synthesised by adding the diamines (2–3 mmol) to the finely powdered anhydrous nickel(II) salts (1 mmol) in a stoppered conical flask. After a few days, the resulting mixture was dissolved in ethanol (15 cm^3) and filtered. The filtrate was kept in a CaCl_2 desiccator from which the desired complex was separated out within a few days. It was then filtered, washed with isopropanol and dried in a CaCl_2 desiccator.

$[\text{NiL}_2\text{X}_2]$ (X is Cl^- and Br^-) and $[\text{NiL}'_2\text{X}_2]$ (X is Cl^- , Br^- and NCS^-) were synthesised according to the procedure reported earlier [18] and $[\text{NiL}_2\text{X}_2]$ (X is Cl^- and Br^-) was also obtained pyrolytically from the respective tris-species in the solid state.

NiLCl_2 (**3**) and $\text{NiL}'\text{SO}_4$ (**18**) were prepared pyrolytically from the species (**2**) and (**16**) respectively.

3. Results and discussion

3.1. Characterisation of the complexes

Bassett et al. [18] have described $[\text{NiL}_2\text{X}_2]$ (X is Cl^- and Br^-). But there is no report on the corresponding tris-species. We have been able to synthesise the tris-species, along with the reported bis-species, as is evident from the elemental analyses (Table 1). However, the diamine (L') always yields the bis-species irrespective of the nature of the counteranions. IR spectral study of all the complexes shows that both (L) and (L') are chelated [2,10]. As a result, all the tris-species seem to possess the N_6 -chromophore around the nickel(II). And their magnetic and electronic spectral (mull) data (Table 1) suggest octahedral geometry. Among the bis-species of (L) and (L'), only yellow $[\text{NiL}_2](\text{ClO}_4)_2$ (**8**) and $[\text{NiL}'_2](\text{ClO}_4)_2$ (**15**) show a relatively strong absorption band at approx. 445 nm in their corresponding electronic spectra and the diamagnetic, indicating a square-planar geometry of nickel(II) [**8**], whereas all other bis-species show paramagnetism and their electronic spectra are characteristic of octahedral nickel(II) (Table 1). In the case of $[\text{NiL}'_2\text{SO}_4] \cdot 3\text{H}_2\text{O}$, SO_4^{2-} is coordinated as it exhibits very low conductivity ($16 \text{ cm}^2 \text{ mol}^{-1} \Omega^{-1}$) in dry methanol. The electronic spectra in the NIR region have been used for the identification of their cis- or trans-octahedral configuration. The occurrence of two bands in the NIR region for the complexes $[\text{NiL}_2\text{X}_2]$ (X is Cl^- and Br^-) (Fig. 1), $[\text{NiL}_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (**7**), $[\text{NiL}'_2\text{X}_2]$ (X is Cl^- , Br^- and SCN^-) and $[\text{NiL}'_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**14**) indicates that they possess trans-octahedral geometry [12], whereas $[\text{NiL}_2\text{X}]$ (X is SO_4^{2-} and SeO_4^{2-}), $[\text{NiL}'_2\text{SO}_4] \cdot 3\text{H}_2\text{O}$ (**16**) and $[\text{NiL}'_2\text{SeO}_4]$ (**19**) possess cis-configuration, as d–d bands do not show any splitting in the NIR region (Fig 1). The complexes NiLCl_2 and $\text{NiL}'\text{SO}_4$ are green and greenish-

Table 1
Elemental analyses, magnetic and electronic (mull) spectral data of *N*-propylethane-1,2-diamine (L) and *N*-isopropylethane-1,2-diamine (L') complexes of nickel(II)

Complex	No.	Colour	Elemental analyses % ^a			μ_{eff} BM	λ_{max} /nm
			C	H	N		
[NiL ₂]Cl ₂ ·2H ₂ O	1	Light blue	38.1(38.1)	9.7(9.7)	17.6(17.8)	3.1	565, 368
[NiL ₂ Cl ₂]	2	Blue	35.9(35.9)	8.3(8.4)	16.8(16.8)	3.2	571, 370
NiCl ₂	3	Green	25.8(25.9)	6.1(6.0)	12.0(12.1)	3.2	630, 380
[NiL ₃]Br ₂ ·2H ₂ O	4	Blue-violet	32.0(32.1)	8.1(8.2)	14.8(15.0)	3.1	558, 355
[NiL ₂ Br ₂]	5	Blue	28.4(28.4)	6.6(6.6)	13.2(13.2)	3.2	562, 358
[NiL ₃](ClO ₄) ₂ ·2H ₂ O	6	Pink	30.1(30.0)	7.7(7.7)	13.8(14.0)	3.2	552, 350
[NiL ₂ H ₂ O ₂](ClO ₄) ₂	7	Pink	24.1(24.1)	6.2(6.4)	11.1(11.2)	3.1	560, 356
[NiL ₂](ClO ₄) ₂	8	Yellow	26.0(26.0)	6.0(6.0)	12.1(12.1)	Diamagnetic	445
[NiL ₂ SO ₄]	9	Blue	33.2(33.4)	7.6(7.8)	15.6(15.6)	3.2	550, 348
[NiL ₂ SeO ₄]	10	Blue	29.5(29.5)	6.7(6.9)	13.6(13.8)	3.2	545, 345
[NiL ₂ Cl ₂]	11	Light blue	35.9(35.9)	8.2(8.4)	16.8(16.8)	3.2	560, 365
[NiL ₂ Br ₂]	12	Light blue	28.4(28.4)	6.6(6.6)	13.2(13.2)	3.2	555, 358
[NiL ₂ (NCS) ₂]	13	Pink	37.9(38.0)	7.3(7.4)	22.1(22.2)	3.2	548, 350
[NiL ₂ (H ₂ O) ₂](ClO ₄) ₂ ·2H ₂ O	14	Pink	22.3(22.5)	6.5(6.7)	10.4(10.5)	3.1	550, 348
[NiL ₂](ClO ₄) ₂	15	Yellow	26.0(26.0)	6.0(6.0)	12.1(12.1)	Diamagnetic	448
[NiL ₂ SO ₄ ·3H ₂ O]	16	Blue	29.0(29.0)	8.2(8.2)	13.4(13.5)	3.2	574, 370
[NiL ₂ SO ₄]	17	Blue	33.3(33.4)	7.6(7.8)	15.4(15.6)	3.2	570, 368
NiL ₂ SO ₄	18	Greenish yellow	23.3(23.4)	5.3(5.4)	10.8(10.9)	3.2	638, 378
[NiL ₂ SeO ₄]	19	Blue	29.3(29.5)	6.5(6.9)	13.7(13.8)	3.2	535, 342

^a Percentages in parentheses are theoretically calculated values.

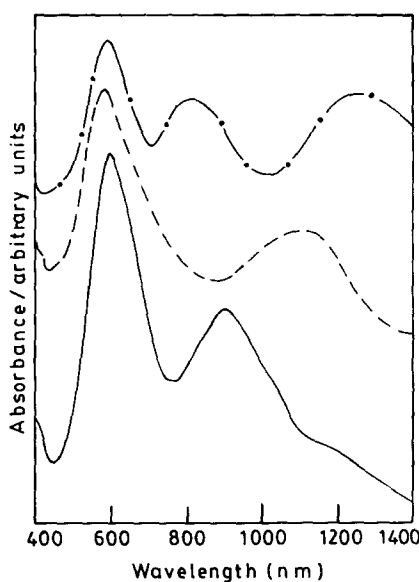


Fig. 1. Electronic spectra of *trans*-[NiL₂Cl₂] (**2**) (---), *cis*-[NiL₂SO₄] $\cdot$ 3H₂O (**16**) (-·-·-), and *cis*-[NiL₂SeO₄] (**17**) (—).

yellow in colour respectively and their IR spectral study shows that the diamines are chelated. Similar mono-diamine complexes of NiCl₂ were also reported to be synthesised pyrolytically with the diamines, ethane-1,2-diamine, and its methyl and ethyl analogue [11]. NiLCl₂ and NiL'SO₄ exhibit paramagnetism (Table 1) and also show two absorption bands of low intensity in the visible region in their electronic spectra, suggesting they contain octahedrally coordinated nickel(II). And as in previous cases, here it is also assumed that to satisfy octahedral geometry both the chloride ions and sulphate ion act as bridging ligands [11,16,17].

3.2. Phase transition of the complexes

The complexes [NiL₂Br₂] (**5**) and [NiL₂(NCS)₂] (**13**) undergo a reversible endothermic phase transition on heating (86–99°C = 0.52 kJ mol⁻¹ for heating, and 92–81°C, $\Delta H = -0.53$ kJ mol⁻¹ for cooling for (**5**), and 162–224°C, $\Delta H = 0.27$ kJ mol⁻¹ for heating, and 208–150°C, $\Delta H = -0.25$ kJ mol⁻¹ for cooling for (**13**), respectively, see Fig. 2), without any visual colour change. But due to lack of equipment, IR and electronic spectra, XRD, and magnetic susceptibility measurements could not be made for the high-temperature phase species and thus the reason behind the phase transitions remains unexplored. However, since no visual colour change is associated with these transitions we can exclude the possibility of configurational (Oh $\leftrightarrow$ Sq-pl or *cis* $\leftrightarrow$ *trans*) change in these transformations.

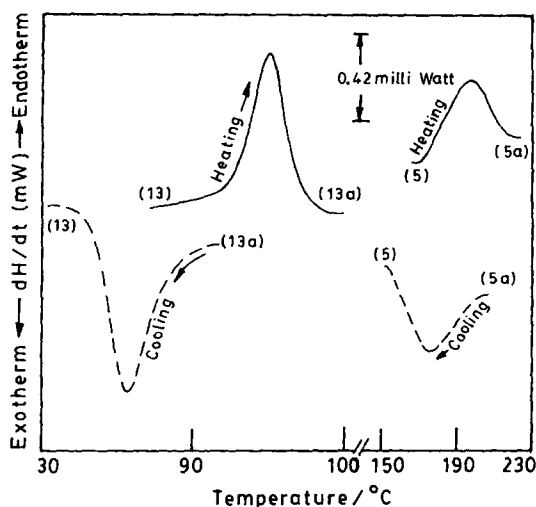


Fig. 2. DSC curves of *trans*-[NiL₂Br₂] (5) (sample mass, 8.3 mg) and *trans*-[NiL₂(NCS)₂] (13) (sample mass, 7.8 mg): —, heating; and ---, for cooling cycle.

3.3. Thermal decomposition of the complexes

On heating, the complex [NiL₃]Cl₂·2H₂O (1) initially loses two molecules of water and one molecule of diamine in a single step, as is evident from its TG–DTA curves (Fig. 3) and transforms to the bis-species, [NiL₂Cl₂]. Here a dehydration and deamination reaction takes place, followed by an anation reaction to maintain the octahedral geometry of the bis-species. And the colour change, light blue to blue, is due to the N₆ → N₄Cl₂ chromophoric change around nickel(II). This bis-species shows exactly the same magnetic, electronic and solid state thermal properties as the bis-species [NiL₂Cl₂] (2) prepared from solution. On further heating, [NiL₂Cl₂] decomposes to NiCl₂ through the formation of NiLCl₂ and NiL_{0.5}Cl₂ as is evident from the plateaus in its TG curve (Fig. 3). Attempts to synthesise NiL_{0.5}Cl₂ pyrolytically in a pure form in the solid state failed. But NiLCl₂ can be prepared in a pure form in the solid state and characterised (see above). The elimination of diamine from [NiL₂Cl₂] is associated with a colour change, blue to green, which is assumed to be due to the chromophoric change (N₄Cl₂ → N₂Cl₄) around nickel(II). However, on heating [NiL₃]Br₂·2H₂O (4) shows water and diamine elimination in two separate steps, evident from its TG–DTA curves (Fig. 3), and transforms to [NiL₂Br₂]. This bis-species, upon further heating, decomposes straight to NiBr₂, unlike its chloro-analogue. Here also, deamination-anation reaction takes place in the [NiL₃]Br₂ → [NiL₂Br₂] transformation to maintain the octahedral geometry of the bis-species, and the colour change, blue-violet to pale blue, is due to change in the chromophore (N₆ → N₄Br₂) like its chloro-analogue. This bis-species shows identical electronic, magnetic and solid-state thermal properties to the bis-species, [NiL₂Br₂] (5), prepared from solution. On heating the complex, [NiL₃](ClO₄)₂·2H₂O (6) transforms to [NiL₂](ClO₄)₂ in one step. This transformation

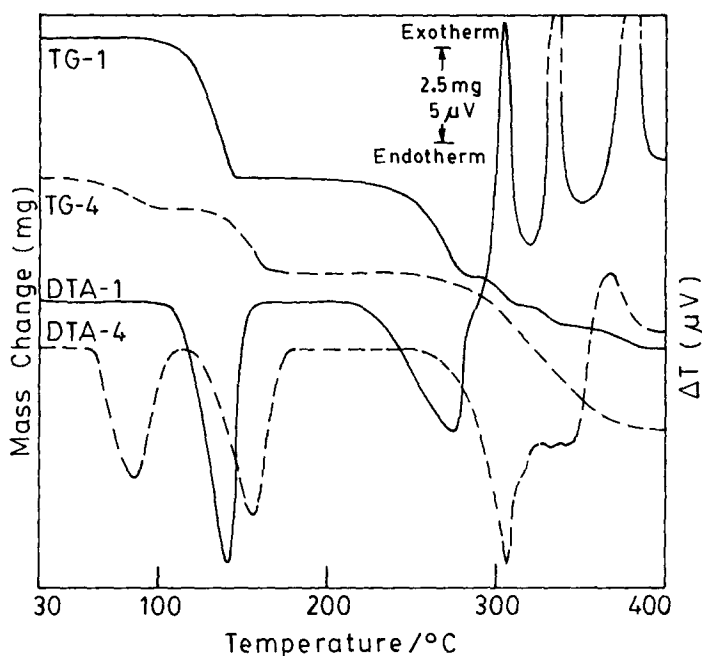


Fig. 3. TG-DTA curves of $[\text{NiL}_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (1) (sample mass, 11.35 mg) (—) and $[\text{NiL}_3]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (4) (sample mass, 11.00 mg) (---).

is associated with a drastic colour change from pink to yellow and the change in colour is assumed to be due to a change in configuration from octahedral to square-planar (see above). The complex $[\text{NiL}_2\text{SO}_4]$ (9) starts to decompose at 265°C and transforms to NiSO_4 via the formation of NiLSO_4 , as is evident from the plateau in its TG curve (Fig. 4), but attempts to synthesise NiLSO_4 in a pure form failed. In contrast, $[\text{NiL}_2\text{SeO}_4]$ (10) decomposes straight to NiSeO_4 without showing any plateau in its TG curve. For the complexes of L' , TG-DTA analyses show that $[\text{NiL}'_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (14) loses lattice water and coordinated water in a single step accompanied by pink to yellow thermochromism. And here also, the colour change is assumed to be due to an octahedral to square-planar configurational change (see above). $[\text{NiL}'_2](\text{ClO}_4)_2$ (15) is also obtained on keeping $[\text{NiL}'_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (14) in the open atmosphere for a few hours. It is interesting to note that this transformation ($14 \rightarrow 15$) slows down on keeping the complex (14) in a desiccator. On heating, $[\text{NiL}'_2\text{SO}_4] \cdot 3\text{H}_2\text{O}$ (16) transforms to $[\text{NiL}'_2\text{SO}_4]$ (17) (Fig. 4), without showing any visual colour change and it reverts to (16) in the open atmosphere within an hour. The complex (17), on further heating, yields $\text{NiL}'\text{SO}_4$ (18) in pure form. $[\text{NiL}'_2\text{SeO}_4]$ (19), on heating, decomposes straight to NiSeO_4 without showing any plateau in its TG curve.

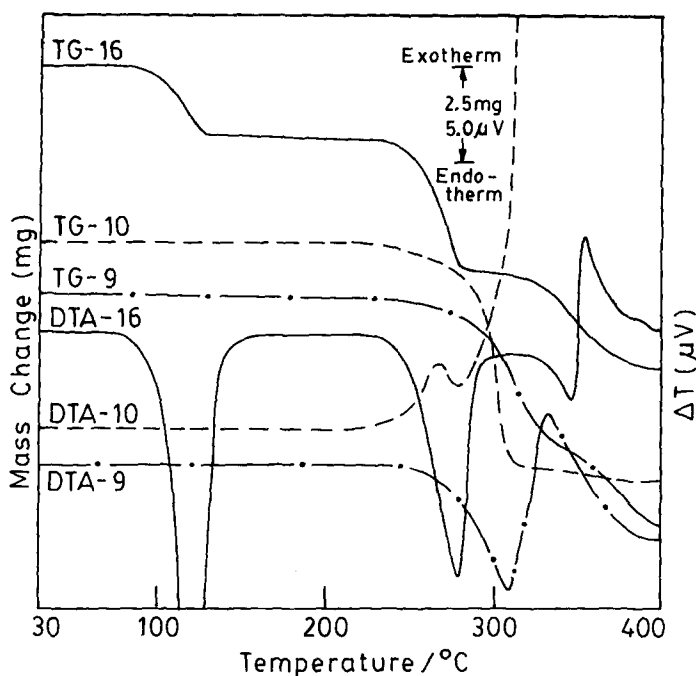


Fig. 4. TG-DTA curves of *cis*-[NiL₂SO₄] (**9**) (sample mass, 10.55 mg) (---); *cis*-[NiL₂SeO₄] (**10**) (sample mass, 12.45 mg) (---); and *cis*-[NiL₂SO₄]·3H₂O (**16**) (sample mass, 14.00 mg) (—).

Table 2
Initial decomposition temperature, *T*_i (°C), of [NiL₂X₂] and [NiL'₂X₂]

Diamine	X				
	Cl [−]	Br [−]	I [−]	0.5SO ₄ ^{2−}	0.5SeO ₄ ^{2−}
L	200	270	280	255	250
L'	192	205	210	230	235

4. Conclusions

The diamines (L) and (L') are isomeric. (L) produces both tris- and bis-species with nickel(II), whereas (L') yields only bis-species, irrespective of the nature of the counter-anions, because of the greater steric hindrance of the bulkier isopropyl group; this is also responsible for the lower thermal stability of complexes of (L') (Table 2). However, among the anions, only ClO₄[−] yields square-planar bis-species with both (L) and (L'), in conformation of its very low coordinating ability. [NiL₂Br₂] and [NiL'₂(NCS)₂] exhibit an endothermic reversible phase transition upon heating, most probably due to conformational changes in the diamine chelate rings. Perhaps due to the greater

bridging capability of Cl^- and SO_4^{2-} (to some extent), the unusual intermediates NiLCl_2 and $\text{NiL}'\text{SO}_4$ have been synthesised pyrolytically.

Acknowledgements

We are grateful to Professor A.K. Pal, Department of Material Science, IACS, for NIR spectra and the Council of Scientific and Industrial Research, New Delhi, India, for financial support to NRC.

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