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# THERMAL INVESTIGATION OF DIAMINE COMPLEXES OF Ni(II) IN THE SOLID PHASE

S. MITRA, G DE and N. RAY CHAUDHURI *

*Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta-700032 (India)*

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## ABSTRACT

Thermochemical reactions of $[Nien_3]X_2 \cdot n\ H_2O$, where en = ethylenediamine, $X = \frac{1}{2}SO_4^{2-}$, $\frac{1}{2}SeO_4^{2-}$, $CH_3COO^-$, $CHCl_2COO^-$ and $CCl_3COO^-$, $n = 0$ or 2, $[Nitn_3]X_2\ 2\ H_2O$, where tn = 1,3-propanediamine, $X = \frac{1}{2}SeO_4^{2-}$ or $CH_3COO^-$, and $[Nitn_2X_2]\ n\ H_2O$, where $X = \frac{1}{2}SO_4^{2-}$, $CHCl_2COO^-$ and $CCl_3COO^-$ and $n = 0$ or 1, have been investigated using a Shimadzu DT-30 thermal analyzer All these complexes have been synthesized from solution The compounds $[Nitn_2X_2]$, where $X = \frac{1}{2}SeO_4^{2-}$ or $CH_3COO^-$, $[Nien_2(CCl_3COO)_2]$ and $[NitnX_2]$, where $X = \frac{1}{2}SO_4^{2-}$ or $CH_3COO^-$, have been synthesized in the solid state by a pyrolytic technique in a nitrogen atmosphere from the parent compounds synthesized from solution. $[Nien_3](CHCl_2COO)_2$, $[Nitn_2(CHCl_2COO)_2]$ and $[Nien_3](CCl_3COO)_2$ decompose through the formation of non-isolable $[Nien_3]CO_3$, $[Nitn_2CO_3]$ and $Nien_{1.5}CO_3$, respectively All the complexes were characterized by elemental analysis and magnetic and spectral data Tris and bisdiamine complexes appear to possess $O_h$ geometry. The monodiamine complexes possess $T_d$ geometry. $[NitnSO_4]$ and $[Nitn(CH_3COO)_2]$ undergo irreversible phase transition as soon as they are generated from their bis species Thermal parameters have been evaluated for each step of decomposition The probable mechanistic paths of decomposition have been proposed

## INTRODUCTION

Synthesis and characterization of complexes of diamine are well known in literature. A few studies relating to the thermal investigation of diamine complexes have been carried out [1–4]. Recently, we have reported the thermal studies of some diamine and substituted diamine complexes of nickel(II) [5–7], where we have explored the possibility of synthesizing several complex species in the solid state as intermediates by using a pyrolytic technique: it is not feasible to synthesize these species from solution. We have also reported conformational changes in the solid state in some of the diamine complexes [8]. These observations augment the need for

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* To whom correspondence should be addressed.

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further studies relating to the thermal investigation of diamine complexes of other nickel salts. The present paper reports the thermal investigation of $NiX_2$, where $X = \frac{1}{2}SO_4^{2-}$, $\frac{1}{2}SeO_4^{2-}$, $CH_3COO^-$, $CHCl_2COO^-$ or $CCl_3COO^-$, complexes of ethylenediamine(en) and 1,3-propanediamine(tn). We report the synthesis and characterization of diamine complexes in the solid state. Thermal parameters as well as probable mechanistic paths for each step of the decomposition are also reported.

## EXPERIMENTAL

All the chemicals used were of A.R. grade. The complexes were prepared by the methods reported earlier [9], except for $[Ni(tn)_2SO_4] \cdot H_2O$, which was prepared by the method described. 1 mmole $NiSO_4 \cdot 7\ H_2O$ was taken up in the minimum quantity of water, and 3 mmole tn were added dropwise with stirring to form a deep blue solution. Ethanol was added dropwise until slight turbidity appeared. Excess ethanol was added with stirring until shining blue crystals separated out. The crystals were filtered, washed with ethanol and air dried. The intermediate products were isolated in a nitrogen atmosphere by a temperature-arrest technique.

The apparatus employed in the investigations was the same as that reported earlier [6]. Thermal analysis was carried out with a thermal analyzer Model DT-30 (Shimadzu, Japan). Measurements were made under a constant flow of nitrogen. Platinum crucibles were used and $Al_2O_3$ was used as standard. Enthalpy changes were calculated from the DTA peak area using zinc metal as standard.

Results of the elemental analysis, magnetic moment and electronic spectral data are summarized in Table 1. Thermal parameters for the decomposition of complexes are shown in Table 2.

## RESULTS AND DISCUSSION

### *Tris(ethylenediamine)nickel(II) sulfate*

The synthesis and characterization of this complex were reported earlier [9]. George and Wendlandt [2] carried out TG and DTA studies on this compound. Electronic spectra and magnetic data (Table 1) corroborate the $O_h$ geometry reported earlier. But, we found a basic difference in the thermal profile (Fig. 1) compared with the observation made earlier [2]. Figure 1 shows the TG and DTA curves of this compound. The TG curve appears very complicated. As a result, it is very difficult to comment on the decomposition path. The DTA curve shows two endothermic and two exothermic peaks (Table 2, Fig. 1) for the elimination of three en molecules

TABLE 1

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

| Compound | Color | Ni | | N | | $\mu_{eff}$ (B.M.) | Absorbance maxima (nm) |
|---|---|---|---|---|---|---|---|
| | | Found (%) | Calcd. (%) | Found (%) | Calcd (%) | | |
| $[Nien_3]SO_4$ | Violet | 17.48 | 17.54 | 25.01 | 25.09 | 3.09 | 555, 360 |
| $[Nitn_2SO_4]\cdot H_2O$ | Very light blue | 18.01 | 18.30 | 17.81 | 17.46 | 3.19 | 680(sh), 560, 360 |
| $[Nien_3]SeO_4$ | Light pink | 15.21 | 15.37 | 21.80 | 22.08 | 3.13 | 550, 360 |
| $[Nitn_3]SeO_4\cdot 2H_2O$ | Bluish violet | 12.61 | 12.77 | 18.50 | 18.27 | 3.07 | 550, 350 |
| $[Nien_3](CH_3COO)_2$ | Light pink | 16.40 | 16.46 | 24.04 | 23.54 | 3.23 | 580, 350 |
| $[Nitn_3](CH_3COO)_2\cdot 2H_2O$ | Light blue | 13.41 | 13.50 | 19.01 | 19.32 | 3.28 | 570, 350 |
| $[Nien_3](CHCl_2COO)_2\cdot 2H_2O$ | Light violet | 11.38 | 11.06 | 15.15 | 15.82 | 3.19 | 680(sh), 570, 350 |
| $[Nitn_2(CHCl_2COO)_2]$ | Bluish violet | 12.65 | 12.68 | 12.02 | 12.10 | 3.00 | 730(sh), 560, 360 |
| $[Nien_3](CCl_3COO)_2$ | Light pink | 10.02 | 10.41 | 14.21 | 14.90 | 3.24 | 680(sh), 560, 350 |
| $[Nitn_2(CCl_3COO)_2]$ | Very light blue | 11.06 | 11.04 | 10.01 | 10.53 | 3.19 | 730(sh), 550, 350 |
| $[NitnSO_4]$ | Greenish yellow | 25.01 | 25.66 | 12.11 | 12.24 | 3.39 | 760(sh), 690, 416 |
| $[Nitn_2SeO_4]$ | Light blue | 16.70 | 16.78 | 15.90 | 16.01 | 3.08 | 680(sh), 580, 350 |
| $[Nitn_2Ac_2]$ | Greenish yellow | 17.89 | 18.08 | 17.01 | 17.24 | 3.13 | 730(sh), 570, 400 |
| $[NitnAc_2]$ | Greenish yellow | 23.12 | 23.41 | 10.96 | 11.16 | 3.82 | 750(sh), 680, 410 |
| $[Nien_2(CCl_3COO)_2]$ | Bluish pink | 11.58 | 11.65 | 11.02 | 11.11 | 3.15 | 670(sh), 550, 350 |
| $[Nitn_2CO_3]$ | Light greenish yellow | 22.15 | 22.00 | 20.51 | 20.99 | 3.01 | 550, 350 |

TABLE 2

Thermal parameters for the decomposition of Ni(II) diamine complexes

| Decomposition reactions | Temp range (°C) | DTA peak temp (°C) | | $\Delta H$ (kJ mole$^{-1}$) |
|---|---|---|---|---|
| | | Endo | Exo | |
| $[Nien_3]SO_4 \rightarrow NiO$ | 265–500 | 335, 360 | 355, 395, 485 | |
| $[Nitn_2SO_4]\ H_2O \rightarrow [Nitn_2SO_4]$ | 80–130 | 115 | | 67 |
| $[Nitn_2SO_4] \rightarrow [NitnSO_4]$ | 270–325 | 320 | 325 | |
| $[NitnSO_4] \rightarrow NiSO_4$ | 325–500 | | 425, 438 | 89 |
| $[Nien_3]SeO_4 \rightarrow NiSeO_4$ | 305–360 | | 320, 340 | |
| $[Nitn_3]SeO_4 \cdot 2\ H_2O \rightarrow [Nitn_3]SeO_4$ | 35–110 | 110 | | 37 |
| $[Nitn_3]SeO_4 \rightarrow [Nitn_2SeO_4]$ | 180–240 | 235 | | 83 |
| $[Nitn_2SeO_4] \rightarrow NiSeO_4$ | 250–315 | | 300 | |
| $[Nien_3](CH_3COO)_2 \rightarrow [Nien_{0.5}(CH_3COO)_2]$ | 280–385 | 350, 370, 385 | | 230 [a] |
| $[Nien_{0.5}(CH_3COO)_2] \rightarrow NiCO_3$ | 385–610 | | 412, 432, 465, 500, 600 | |
| $[Nitn_3](CH_3COO)_2\ 2\ H_2O \rightarrow [Nitn_3](CH_3COO)_2$ | 65–102 | 95 | | 122 |
| $[Nitn_3](CH_3COO)_2 \rightarrow [Nitn_2(CH_3COO)_2]$ | 140–190 | 180 | | 96 |

| | | | | |
|---|---|---|---|---|
| $[Nitn_2(CH_3COO)_2] \rightarrow [Nitn(CH_3COO)_2]$ | 260–325 | 290, 315 | 325 | |
| $[Nitn(CH_3COO)_2] \rightarrow NiCO_3$ | 325–605 | | 435, 450, 535, 570, 600 | |
| $[Nien_3](CHCl_2COO)_2 \cdot 2\,H_2O \rightarrow [Nien_3](CHCl_2COO)_2$ | 80–130 | 90 | | 50 |
| $[Nien_3](CHCl_2COO)_2 \rightarrow [Nien_3]CO_3$ | 130–315 | | 160, 190, 270, 310 | |
| $[Nien_3]CO_3 \rightarrow NiCO_3$ | 315–600 | | 500, 550 | |
| $[Nitn_2(CHCl_2COO)_2] \rightarrow [Nitn_2CO_3]$ | 200–405 | | 200, 222, 300, 345, 385 | |
| $[Nitn_2CO_3] \rightarrow NiCO_3$ | 405–605 | | 540, 590 | |
| $[Nien_3](CCl_3COO)_2 \rightarrow [Nien_2(CCl_3COO)_2]$ | 44–110 | 70 | | 73 |
| $[Nien_2(CCl_3COO)_2] \rightarrow [Nien_{1.5}CO_3]$ | 175–245 | | 220, 255 | 298 |
| $[Nien_{1.5}CO_3] \rightarrow NiCO_3$ | 245–390 | | 310, 340, 380 | 317 |
| $[Nitn_2(CCl_3COO)_2] \rightarrow [Nitn_2CO_3]$ | 130–150 | | 150 | 111 |
| $[Nitn_2CO_3] \rightarrow [Nitn_{1.5}CO_3]$ | 188–272 | | | 101 [a] |
| $[Nitn_{1.5}CO_3] \rightarrow [Nitn_{1.25}CO_3]$ | 272–300 | | 280 | |
| $[Nitn_{1.25}CO_3] \rightarrow [NitnCO_3]$ | 300–370 | | 335 | 18 |
| $[NitnCO_3] \rightarrow [Nitn_{0.5}CO_3]$ | 370–480 | | 400 | 45 |
| $[Nitn_{0.5}CO_3] \rightarrow NiCO_3$ | 480–540 | | 500 | |

[a] Overall enthalpy change.

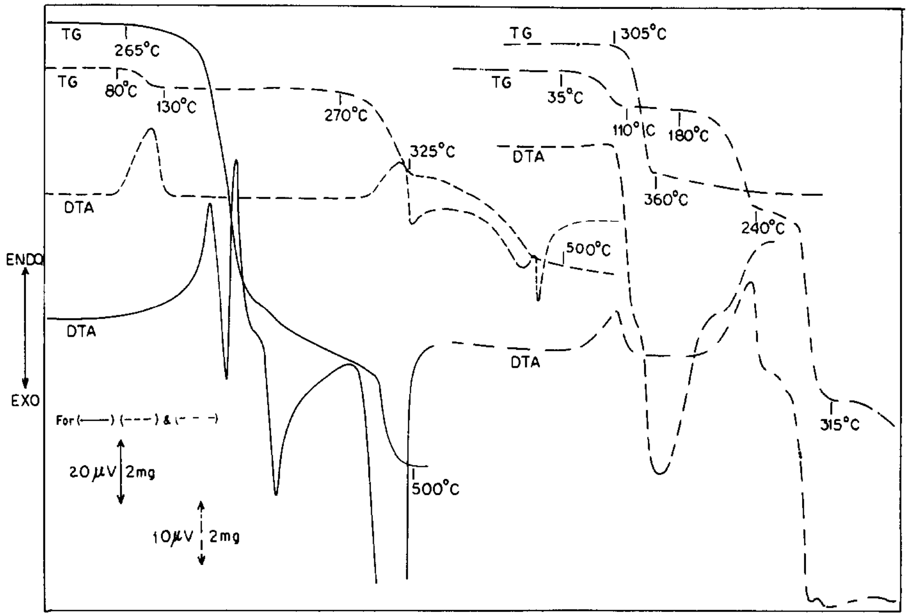

Fig 1. Thermal curves of ——, $[Nien_3]SO_4$, sample mass 19.39 mg, — — —, $[Nitn_2SO_4]$ $H_2O$, sample mass 12 73 mg, – –·, $[Nien_3]SeO_4$, sample mass 8 39 mg; — —, $[Nitn_3]SeO_4$ 2 $H_2O$, sample mass, 19 47 mg

and the last exothermic peak appears to be due to the decomposition of $NiSO_4$ to NiO.

*Sulfatobis(1,3-propanediamine)nickel(II) monohydrate*

The literature does not contain any report on the synthesis of this compound. Its electronic spectral and magnetic data (Table 1) suggest that it exists as $O_h$ geometry. The water molecule exists outside the coordination sphere and the sulfate group and diamine act as bidentate chelated ligands, as inferred from the IR spectrum [10]. This bisdiamine complex should exist as the *cis* form as shown by the IR spectrum as well as the tendency of the sulfato complex to attain *cis*-geometry. This compound becomes anhydrous at 130°C (Fig. 1 and Table 2). The anhydrous species starts to decompose at 270°C and transforms to the monodiamine complex at 325°C. The corresponding DTA curve first shows an endotherm for the elimination of water and then another endotherm followed by an exotherm (Table 2) for the elimination of the first mole of diamine. This exotherm suggests that some type of phase transition is taking place in the just-born monodiamine species as it is very difficult to characterize the species before and after the phase transition. However, it is noticed that this phase transition is not reversible. The derived monodiamine species immediately starts to decompose to the metal sulfate. The DTA profile for the monodiamine decomposition shows two overlapping exotherms, indicating that the decomposition probably takes place through the formation of the hemidiamine species. The monodiamine species, [NitnSO$_4$], is isolated by a temperature-arrest technique. 1,3-Propanediamine can exist here either as chelated or bridging bidentate, since the IR spectral bands for tn overlap the bands due to the sulfate group. The composition, electronic spectrum and magnetic data suggest that it exists as $T_d$ geometry, though its magnetic value (Table 1) is slightly low for $T_d$ complexes.

### *Tris(ethylenediamine)nickel(II) selenate*

Physicochemical studies of this complex suggest that it exists as $O_h$ geometry as does the nickel(II) sulfate complex. This compound starts to decompose at 305°C and transforms to nickel(II) selenate in a single step as is shown in its TG curve (Fig. 1). The corresponding DTA curve shows two overlapping exotherms. This complex shows a very unusual thermal stability in comparison to the other complexes of Ni(II) salts. As a result of the temperature at which the decomposition of [Nien$_3$]SeO$_4$ starts, the possibility of the formation of an isolable as well as a non-isolable intermediate is very poor. The only exotherm which appears here is probably due to the elimination and simultaneous decomposition of the evolved diamine at this elevated temperature. This phenomenon was also noticed in our earlier studies [6]. The stability of this complex in comparison to that of the sulfate is very interesting, as the geometry of the sulfate and selenate do not differ much.

### *Tris(1,3-propanediamine)nickel(II) selenate dihydrate*

Electronic and IR spectra and magnetic data (Table 1) suggest that the complex possesses $O_h$ geometry. This dihydrate complex species becomes anhydrous at 110°C (Fig. 1 and Table 2). The anhydrous species derived starts to decompose at 180°C and transforms to [Nitn$_2$SeO$_4$] at 240°C This diamine species is isolated by a temperature-arrest technique. It retains its original geometry as is evident from its electronic and IR spectral and magnetic data. The unique feature of the diamine species is that it decomposes directly to nickel(II) selenate in a single step without going through the mono or hemidiamine intermediates as happened in the diamine complexes of other nickel(II) salts reported earlier.

### *Tris(ethylenediamine)nickel(II) acetate*

Physicochemical studies of this complex suggest that it exists as $O_h$ geometry. It starts to decompose at 280°C (Fig. 2 and Table 2) and

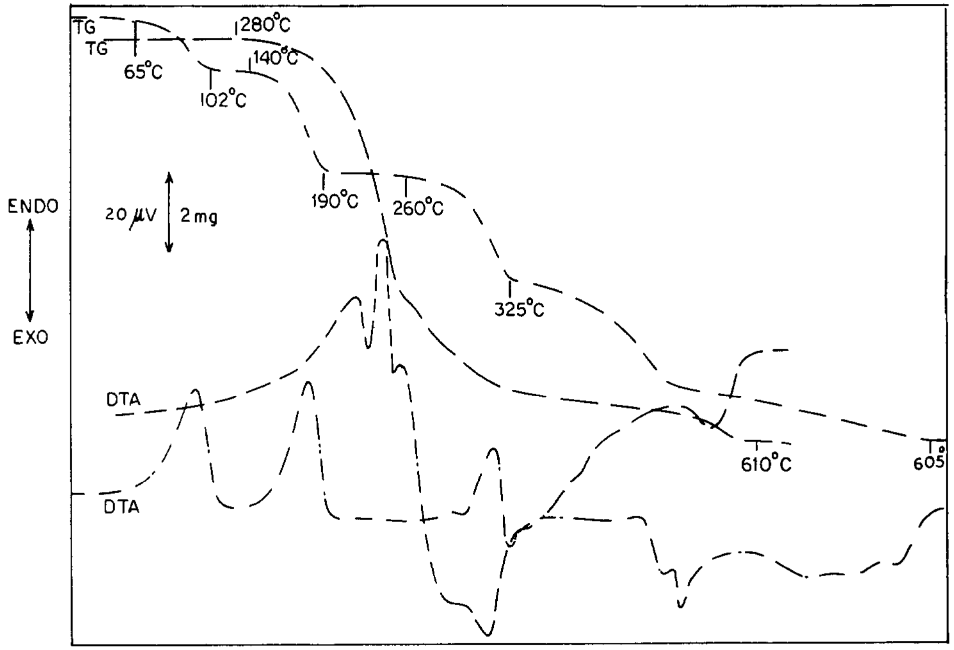

Fig 2 Thermal curves of – – , $[Nien_3](CH_3COO)_2$, sample mass 16 87 mg, — —, $[Nitn_3](CH_3COO)_2$ 2 $H_2O$, sample mass 16 80 mg.

transforms to nickel carbonate through the formation of a non-isolable intermediate, $Nien_{0 5}(CH_3COO)_2$, as observed from its TG curve. The corresponding DTA curve shows three overlapping endotherms for the elimination of two and a half moles of diamine and five overlapping exotherms for the elimination of residual diamine and then decomposition of nickel acetate to nickel carbonate. The decomposition of this tris complex at 280°C indicates its higher stability compared with the other complexes of Ni(II) salts, except nickel(II) selenate. It is interesting to note that nickel acetate is found to decompose at a comparatively higher temperature. This probably occurs due to the complexation which might have changed the orientation of nickel acetate in a complex molecule in comparison to free nickel acetate [6].

*Tris(1,3-propanediamine)nickel(II) acetate dihydrate*

This compound also shows $O_h$ geometry. This dihydrate species becomes anhydrous at 102°C (Fig. 2) showing an endothermic peak at 95°C. The anhydrous species starts to decompose at 140°C and becomes $[Nitn_2(CH_3COO)_2]$ at 190°C in a single step. This was isolated by a pyrolytic technique. Spectral as well as magnetic studies indicate that this bisdiamine species also exists in $O_h$ geometry with a *cis* orientation of the acetate group.

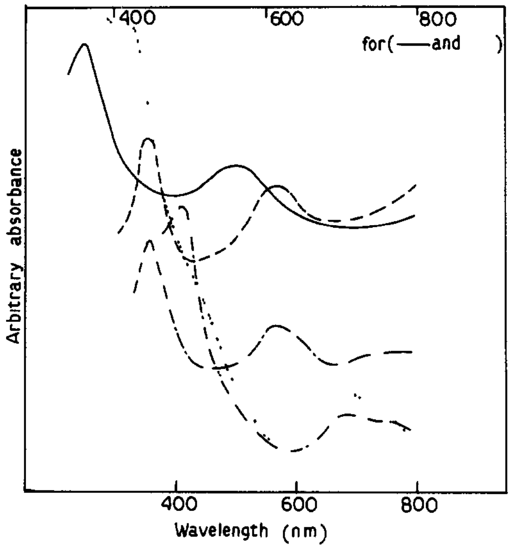

Fig 3. Electronic spectra of — — —, $[Nitn_3](CH_3COO)_2\ 2\ H_2O$, — · — , $[Nitn_2(CH_3COO)_2]$; — · · —, $[Nitn(CH_3COO)_2]$, ———, $[Nitn_2SO_4]\cdot H_2O$, · ·· , $[NitnSO_4]$

The bis species derived starts to decompose at 260°C and transforms to an isolable monodiamine species, $[Nitn(CH_3COO)_2]$, at 325°C as shown in its TG curve (Fig. 2). The corresponding DTA curve shows two overlapping endotherms (Table 2) for the elimination of diamine, followed by an exotherm. The appearance of this exotherm is not due to the elimination of diamine but rather to some kind of rearrangement occurring just after formation of the monodiamine species. This transition is not reversible. The monodiamine species derived after transition exists in $T_d$ geometry as is evident from its electronic spectrum (Fig. 3) and its high magnetic moment value (3.82 B.M.). On further heating, the monodiamine complex decomposes to nickel carbonate at 605°C. The corresponding DTA curve shows five overlapping exotherms for the elimination of diamine and decomposition of acetate to carbonate. It is difficult to suggest the nature of the coordination of diamine, i.e. chelating or bridging bidentate character, due to the overlapping of the IR spectral bands of acetate and diamine.

### *Tris(ethylenediamine)nickel(II) dichloroacetate dihydrate*

This complex possesses $O_h$ geometry as is evident from its composition, spectral and magnetic data (Table 1). It begins to lose water at 80°C and becomes anhydrous at 130°C in a single step (Fig. 4), showing an endothermic peak at 90°C. The anhydrous species immediately undergoes decomposition and transforms to $[Nien_3]CO_3$ at 315°C. The corresponding DTA curve

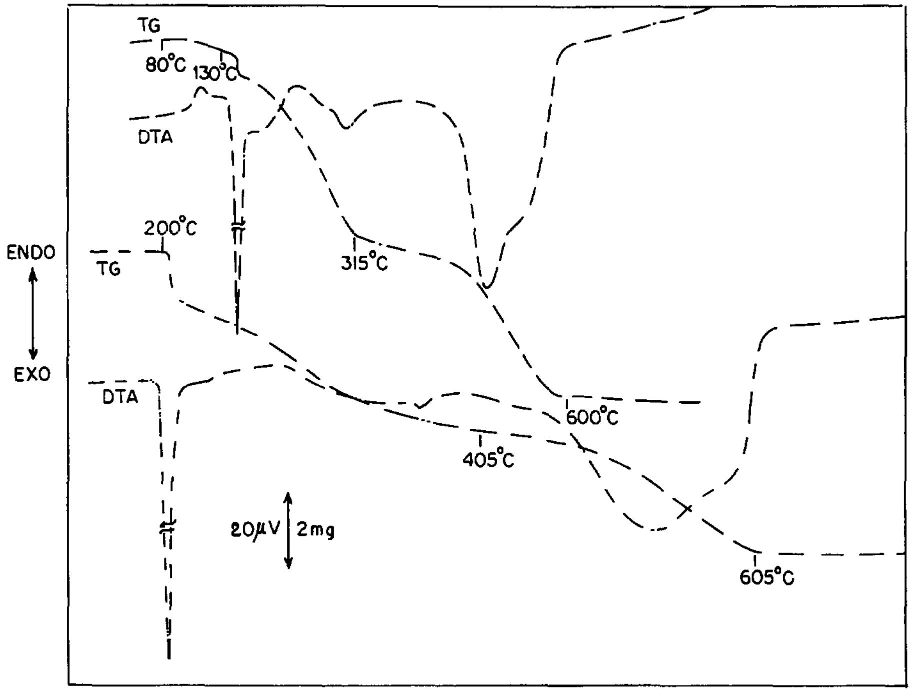

Fig. 4. Thermal curves of ·– –·, [Nien$_3$](CHCl$_2$COO)$_2$·2 H$_2$O, sample mass 11.13 mg; —·· —, [Nitn$_2$(CHCl$_2$COO)$_2$], sample mass 10.66 mg.

shows four overlapping exotherms. This observation suggests that the degree of complicacy may arise from the decomposition of the haloacetate group. The derived nickel carbonate complex immediately starts to decompose and transforms to nickel carbonate showing two overlapping exotherms.

### *Dichloroacetatobis(1,3-propanediamine)nickel(II)*

This bisdiamine complex also possesses $O_h$ geometry. It starts to decompose at 200°C and transforms to the bisdiamine carbonato complex at 405°C without altering its geometry, showing five overlapping exotherms (Fig. 4). On heating, the derived carbonato complex transforms to NiCO$_3$ showing two overlapping exotherms.

### *Tris(ethylenediamine)nickel(II) trichloroacetate*

Spectral and magnetic data (Table 1) suggest that this complex exists in $O_h$ geometry. This complex begins to decompose at 44°C and becomes [Nien$_2$(CCl$_3$COO)$_2$] at 110°C (Fig. 5) in a single step. The derived bis species also exists in $O_h$ geometry as is observed from its spectral and magnetic data. The haloacetate groups are in the *cis* position [11]. This bis

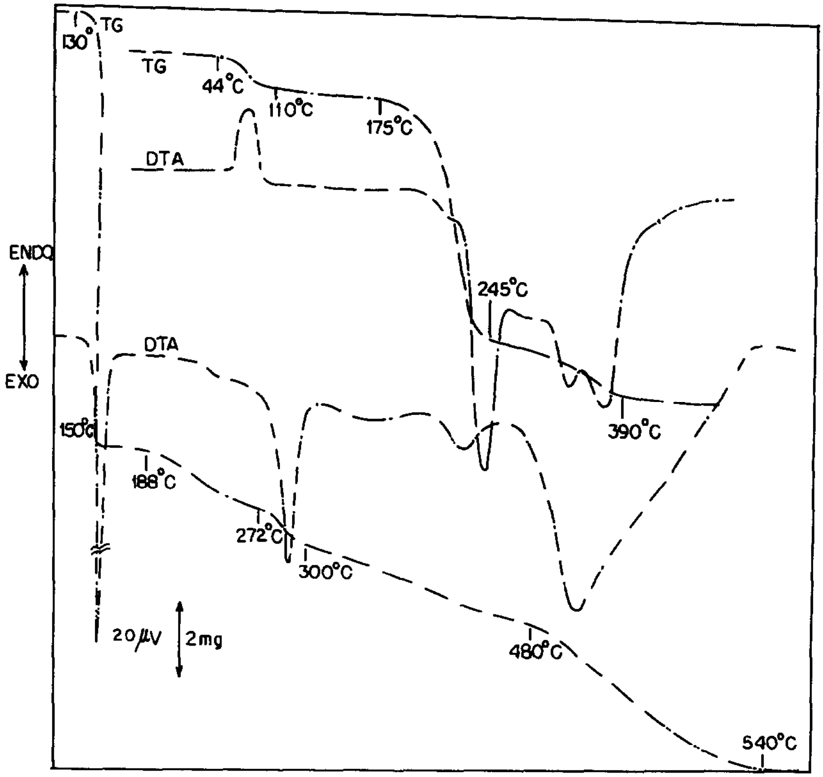

Fig 5 Thermal curves of ·—·— , [Nien$_3$](CCl$_3$COO)$_2$, sample mass 12.12 mg; —· –, [Nitn$_2$(CCl$_3$COO)$_2$], sample mass 23.32 mg.

species starts to decompose at 175 °C and decomposes to nickel(II) carbonate through the formation of a non-isolable intermediate, Nien$_{1.5}$CO$_3$, as observed from its TG curve. The corresponding DTA curve first shows two overlapping exotherms for the elimination of 0.5 mole of diamine as well as the decomposition of nickel halo carboxylate to nickel carbonate, and then three overlapping exotherms for the elimination of residual diamine. The thermal profile does not show any endotherm for the elimination of half a mole of diamine at the second step of decomposition of [Nien$_3$](CCl$_3$COO)$_2$. This is due to the elimination of ethylenediamine and the decomposition of halocarboxylate taking place simultaneously and merging the endotherm responsible for diamine elimination at temperatures where the diamine does not get decomposed.

### *Ditrichloroacetatobis(1,3-propanediamine)nickel(II)*

An interesting feature is that this complex first transforms to the carbonato complex without losing the diamine till 150°C (Fig. 5) in a single step. The bisdiamine carbonato complex is isolable in the solid state by a pyrolytic technique. Spectral and magnetic studies of the parent as well as its pyrolytic product, the biscarbonato complex, indicate $O_h$ geometry. The haloacetate groups are expected to be in the *cis* position as is evident from its IR spectrum [11] as well as its decomposition to the carbonato species. The derived bisdiamine carbonato nickel(II) species starts to decompose at 188°C and transforms to nickel carbonate through the formation of several non-isolable intermediates (Table 2).

From the foregoing discussion, it is noticed that ethylenediamine appears to always generate the trisdiamine complex, whereas, 1,3-propanediamine produces tris as well as bisdiamine complexes. This is probably due to the effect of the chain length of the diamine. The tris complexes of ethylenediamine are thermally more stable than that of 1,3-propanediamine. The thermal stability of $[\mathrm{Nitn_2X_2}]$, where $X = \frac{1}{2}SO_4^{2-}$, $\frac{1}{2}SeO_4^{2-}$, $CH_3COO^-$, $CHCl_2COO^-$ and $CCl_3COO^-$, is: $SO_4^{2-} \geqslant CH_3COO^- \geqslant SeO_4^{2-} > CHCl_2COO^- > CCl_3COO^-$.

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