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# THERMAL BEHAVIOUR OF NICKEL COMPLEXES OF THE METHYL ESTERS OF DITHIOCARBAZIC AND *N*-SUBSTITUTED DITHIOCARBAZIC ACIDS

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## ABSTRACT

The thermal behaviour of the high-spin complexes $[NiL_3]X_2$ (X = Cl, Br, I), $[Ni(MeL)_3]Cl_2 \cdot 3\ H_2O \cdot 0.5$ EtOH, $[Ni(MeL)_3]Y_2$ (Y = Br, I), $[Ni(BuL)_3]X_2$ (X = Cl, Br, I) $[Ni(MeL)_2X_2]$ (X = Cl, Br, I), $[Ni(Me_2L)_2Cl_2]$ and the low-spin complexes $[Ni(L\text{-}H)_2]$, $[Ni(MeL\text{-}H)_2]$ and $[Ni(Me_2L\text{-}H)_2]$ (L = $NH_2NHC(S)SMe$; L-H = $NH_2N{=}C(S)SMe$; MeL = $NH_2NMeC(S)SMe$; MeL-H = $NHNMeC(S)SMe$; BuL = $NH_2NBu^nC(S)SMe$; $Me_2L$ = $NMe_2NHC(S)SMe$; MeL-H = $NMe_2NN{=}C(S)SMe$) have been investigated by DSC and TG and have been related to the structures of the compounds. New compounds which cannot be prepared by the usual synthetic routes have also been obtained.

## INTRODUCTION

We have previously reported [1] studies on nickel complexes of the methyl esters of dithiocarbazic and *N*-substituted dithiocarbazic acids. Work on some of these compounds has been extended using thermogravimetry (TG) and differential scanning calorimetry (DSC) and we now report the thermal behaviour of the high-spin complexes $[Ni(L)_3]X_2$ (X = Cl, Br, I), $[Ni(MeL)_3]Cl_2 \cdot 3\ H_2O \cdot 0.05$ EtOH, $[Ni(MeL)_2X_2]$ (X = Br, I), $[Ni(BuL)_3]X_2$ (X = Cl, Br, I), $[Ni(MeL)_2X_2]$ (X = Cl, Br, I), $[Ni(Me_2L)_2Cl_2]$ and the low-spin complexes $[Ni(L\text{-}H)_2]$, $[Ni(MeL\text{-}H)_2]$ and $[Ni(Me_2L\text{-}H)_2]$ (L = $NH_2NHC(S)SMe$; L-H = $NH_2N = C(S)SMe$; MeL = $NH_2NMe(S)SMe$; (MeL-H = $NHNMeC(S)SMe$; BuL = $NH_2NBu^nC(S)SMe$; $Me_2L$ = $NMe_2NHC(S)SMe$; $Me_2L$-H = $NMe_2NN = C(S)SMe$).

We note that except for our work on the thermal behaviour of $[Co(L\text{-}H)_2L]Cl \cdot H_2O$ [2] no other thermal investigations on complexes of dithiocarbazic acid and its *S*- and *N*-substituted derivatives have been reported in the literature. The ligands considered can coordinate in neutral form (L, MeL, BuL, $Me_2L$) or anionic deprotonated form (L-H, MeL-H, $Me_2L$-H). In both cases, coordination takes place through a thiono or thiolo S atom and a terminal N atom.

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## EXPERIMENTAL

### *Materials*

The chemicals were commercial analytical grade reagents and were used without further purification. The nitrogen gas was an ultrahigh-purity commercial product. All the compounds were dried in vacuo (1 mm Hg) over $P_2O_5$.

### *Preparation of the complexes*

All the complexes, except [Ni(MeL)$_2$I$_2$], were prepared as we reported in ref. 1.

[Ni(MeL)$_2$I$_2$] · [Ni(NH$_2$NMeCS$_2$)$_2$] (red form) [3] (0.5 g) was suspended in $CH_3I$ (20 ml) at room temperature (~ 15°C). After two months the green compound was filtered, washed with acetone and then with hexane. Analysis: calcd. for $C_6H_{16}N_4NiI_2$ (found): C, 12.34 (12.42); H, 2.76 (2.74); N, 9.59 (9.50); S, 21.91 (22.07); I, 43.44 (43.27).

### *Physical measurements*

The visible reflectance spectra and IR spectra were recorded as in ref. 1.

Thermoanalytical measurements. Thermogravimetric analyses (TG) were performed with a DuPont 950 Thermogravimetric Analyzer, and differential scanning calorimetry (DSC) measurements with a DuPont 900 Thermal Analyzer fitted with a DSC cell. Measurements were performed in a stream of $N_2$ (0.5 l min$^{-1}$); rate of heating: 3°C min$^{-1}$.

The residues of the thermal decomposition were identified by X-ray powder diagrams and by comparison with A.S.T.M. tables [4].

## RESULTS AND DISCUSSION

### *Thermal decomposition*

TG and DSC curves for the complexes in $N_2$ atmosphere are plotted in Figs. 1-5.

### *Ligands*

The DSC curves for the ligands show a sharp endothermic peak due to the melting and a subsequent broad endothermic peak produced by the evaporation of the compounds. The TG curves show in the same temperature range a single loss of about 100% of the compound.

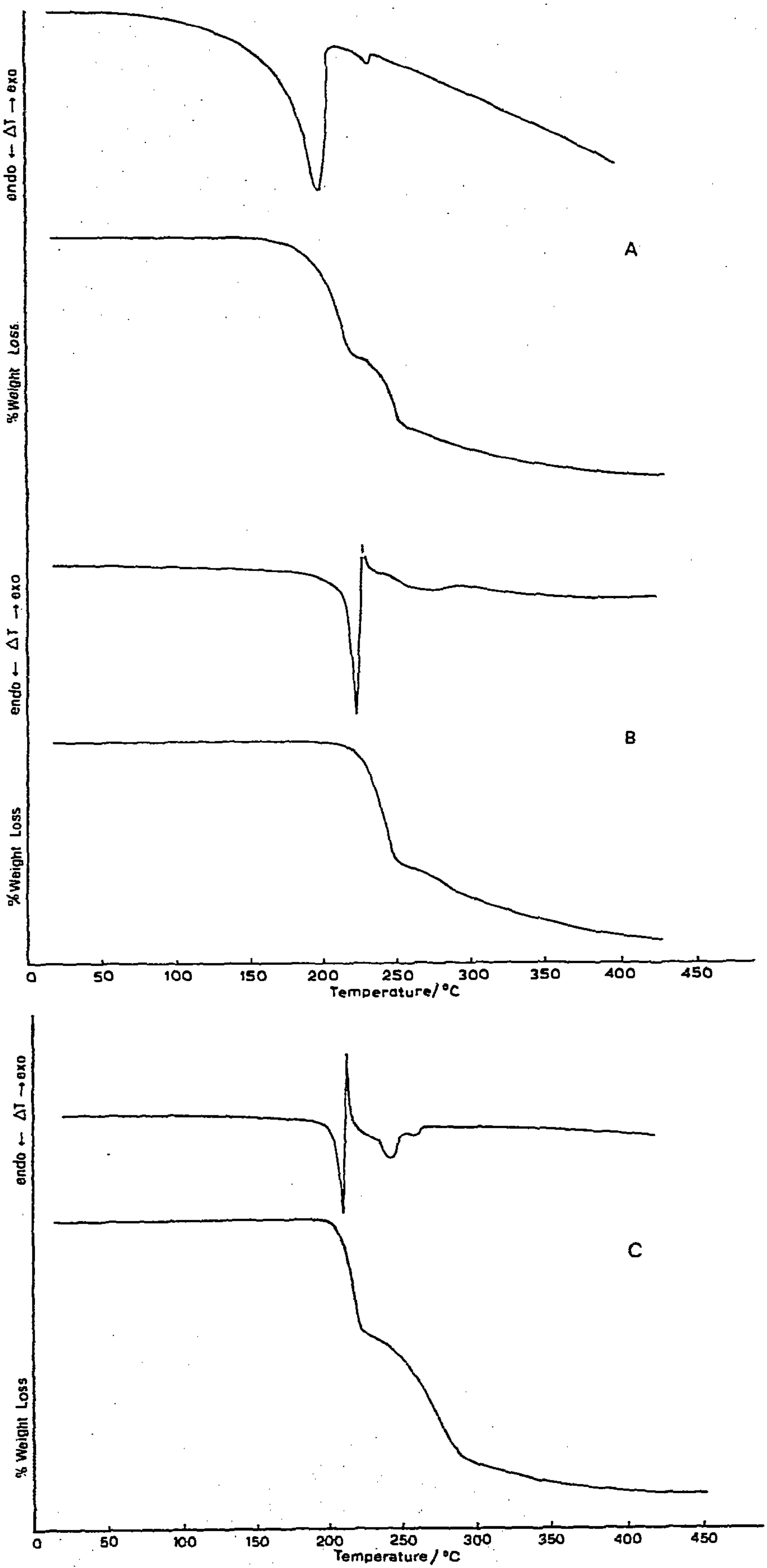
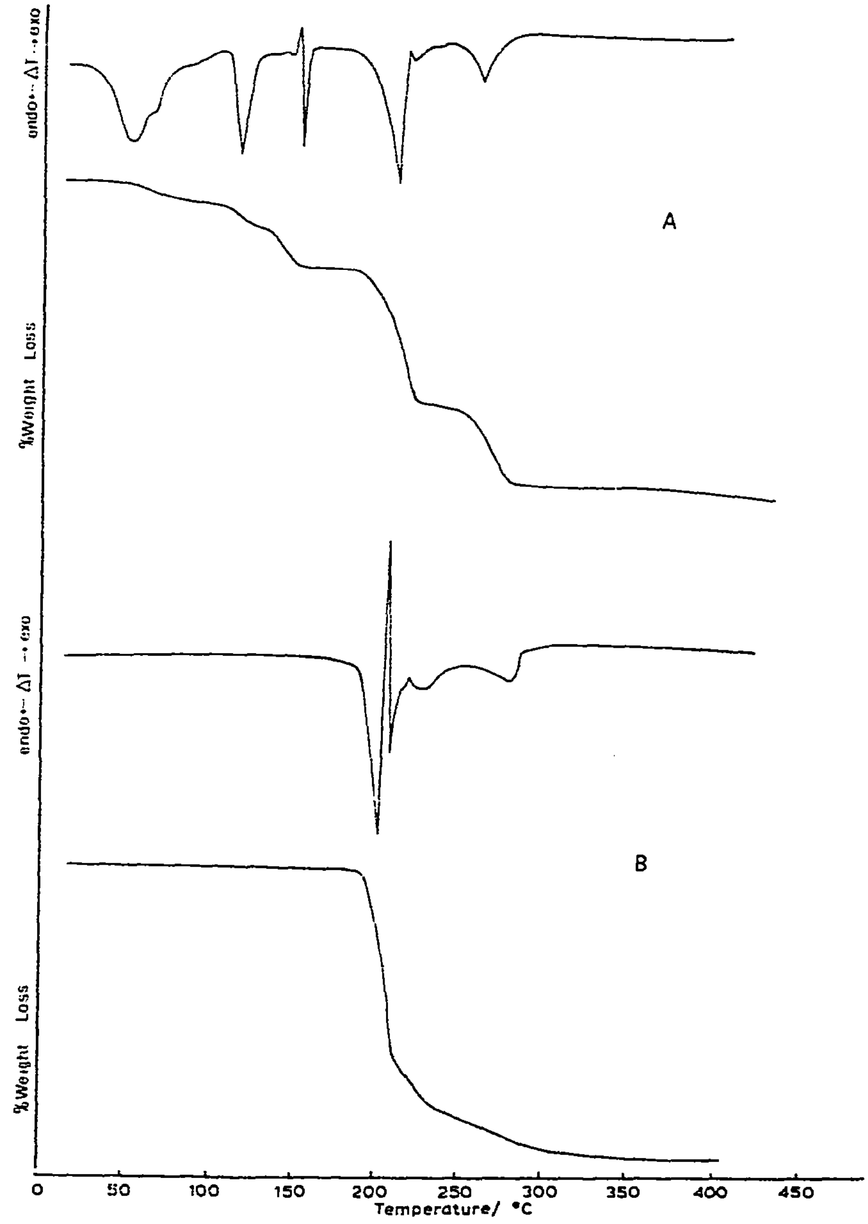


Fig. 1. Thermal decomposition (DSC and TG) of $[NiL_3Cl_2]$ (A), $[NiL_3Br_2]$ (B) and $[NiL_3]I_2$ (C).

## *Complexes*

$[NiL_3]X_2$ (X = Cl, Br, I). The thermal behaviour of the compounds depends on the nature of the halogen atoms. $[NiL_3]Cl_2$ shows one weight-loss step in the TG curve (Fig. 1) corresponding to the loss of one mole of L and two moles of HCl, leading to the formation of $[Ni(L\text{-}H)_2]$. In the same temperature range, a broad asymmetric peak is present in the DSC curve (Fig. 1). This is related to the opening of the chelate ring, the loss of one mole of L and two moles of HCl, and a phase change. A second endothermic peak at 235°C corresponds to the decomposition of $[Ni(L\text{-}H)_2]$ (see text).



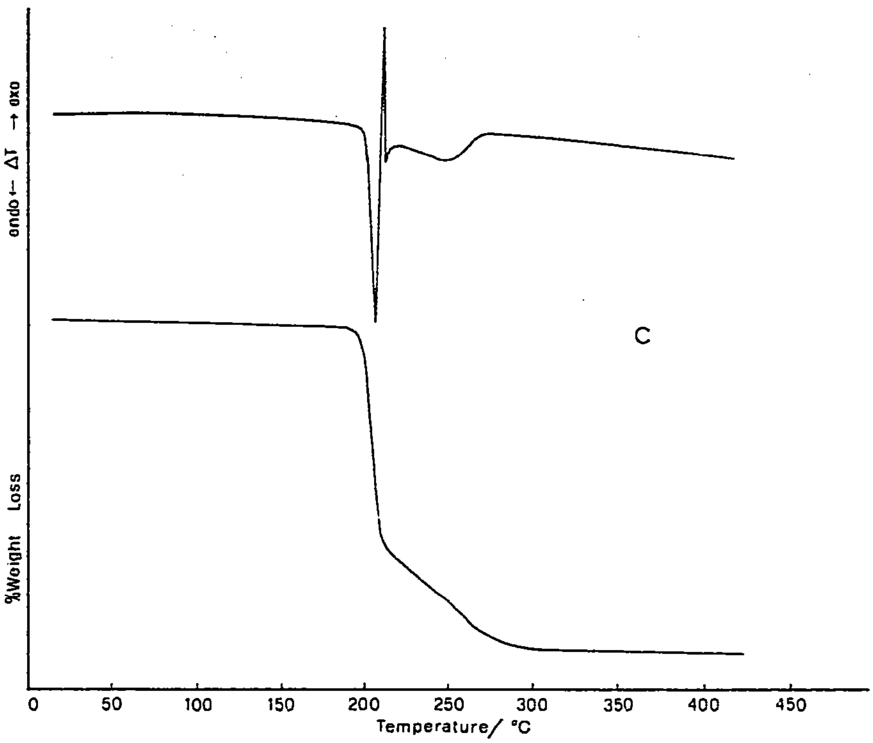


Fig. 2. Thermal decomposition (DSC and TG) of $[Ni(MeL)_3]Cl_2 \cdot 3\ H_2O \cdot 0.5\ EtOH$ (A), $[Ni(MeL)_3]Br_2$ (B) and $[Ni(MeL)_3]I_2$ (C).

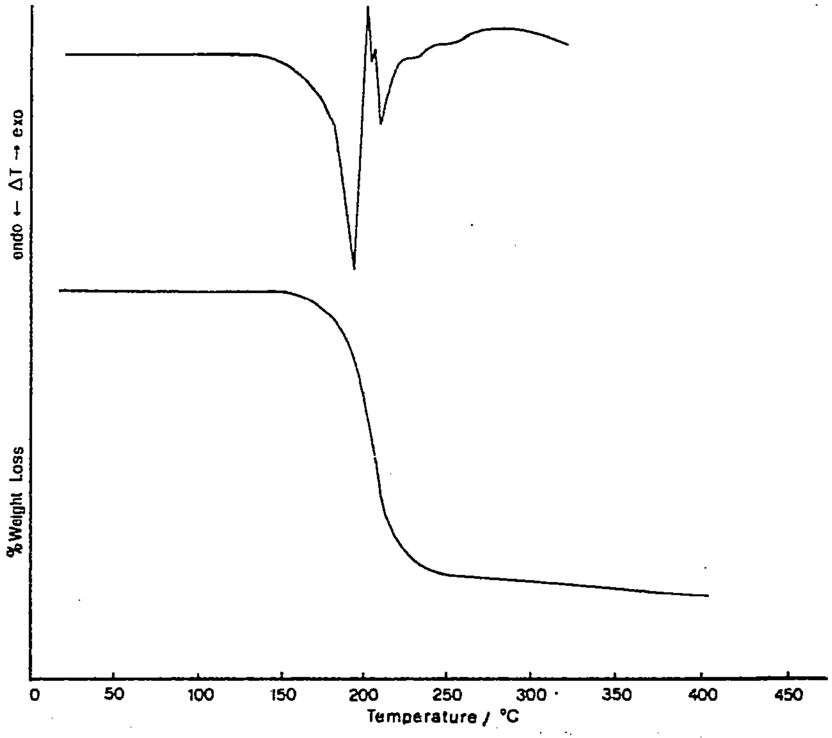
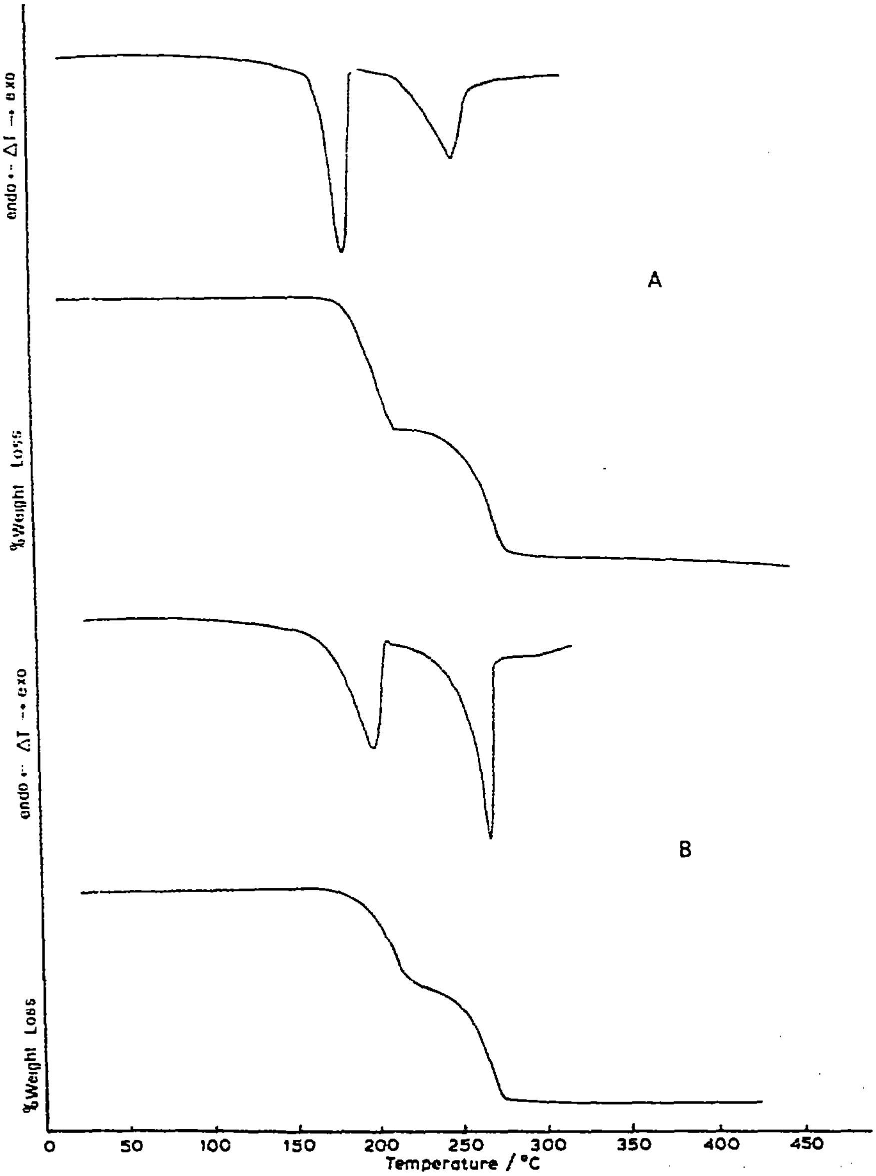


Fig. 3. Thermal decomposition (DSC and TG) of $[Ni(BuL)_3]X_2$ (X=Cl, I).

[NiL$_3$]Br$_2$ and [NiL$_3$]I$_2$ show very similar thermal behaviour. The first step in the TG curve (Fig. 1) corresponds to the loss of two moles of L at 225°C and 212.5°C, respectively. Above 400°C, NiBr$_2$ and NiS, respectively, were isolated. For [Ni(MeL)$_3$]Cl$_2\cdot$3 H$_2$O$\cdot$0.5 EtOH (Fig. 2), the TG curve shows three steps corresponding to the loss of 0.5 moles of EtOH plus 1 mole of H$_2$O, 2 moles of H$_2$O and 0.5 moles of MeL, respectively. After the first loss [Ni(MeL)$_3$]Cl$_2\cdot$2 H$_2$O was isolated; in its IR spectrum sharp bands at 3500 cm$^{-1}$ are still present due to $\nu_{OH}$, the H atoms of which interact with Cl atoms as is suggested by the X-ray structure determination of compound [Ni(MeL)$_3$]Cl$_2\cdot$3 H$_2$O$\cdot$0.5 EtOH, (Cl$\cdots$H = 3.165(5) Å [5]).



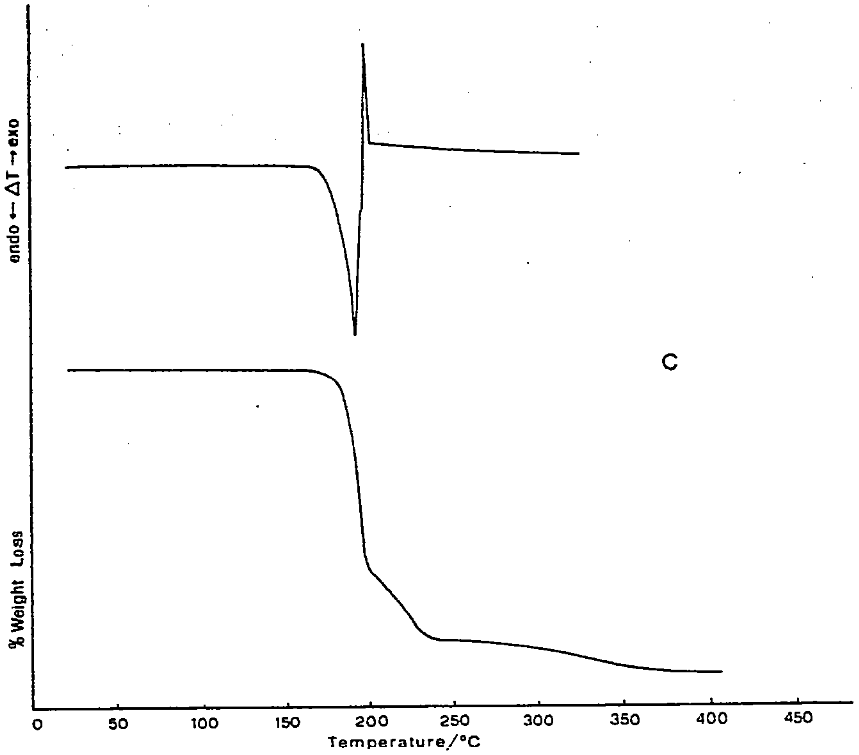
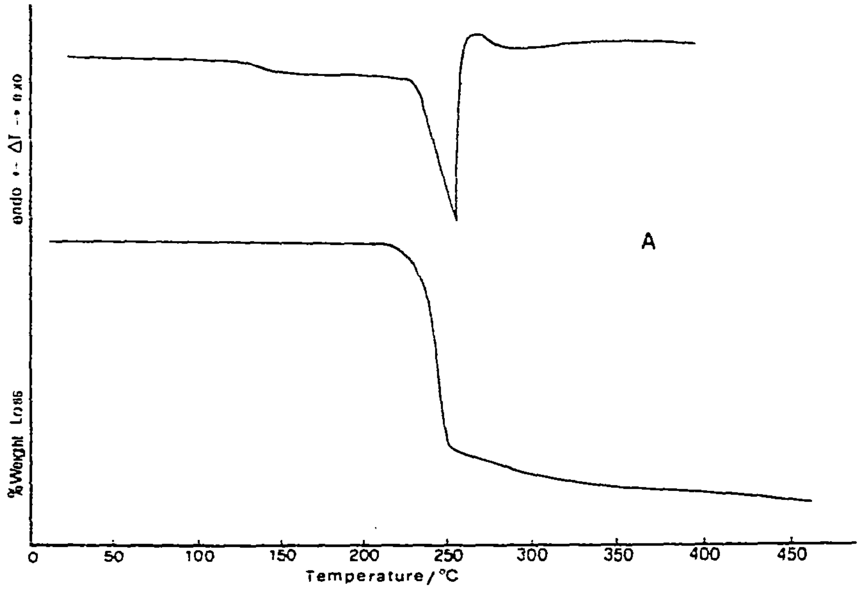


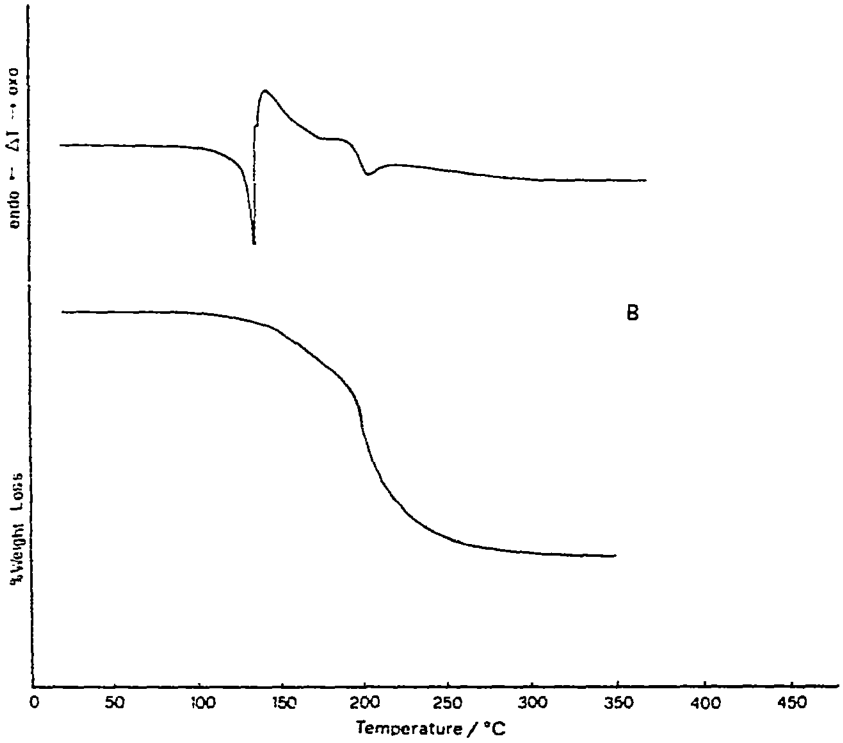
Fig. 4. Thermal decomposition (DSC and TG) of $[Ni(MeL)_2Cl_2]$ (A), $[Ni(MeL)_2Br_2]$ (B) and $[Ni(MeL)_2I_2]$ (C).

The second loss leads to the formation of $[Ni(MeL)_3]Cl_2$, which loses 0.5 moles of MeL in the temperature range 125–150°C, giving $Ni(MeL)_{2.5}Cl_2$.

In the same temperature range, DSC curve shows several overlapped processes related to the opening of the chelate ring, removal of the ligand and introduction of Cl atoms in the co-ordination sphere. The loss of $H_2O$ molecules, which, surrounding the Cl atoms [5] originate the complex ion $[(H_2O)_6Cl]^-$ indeed allows Cl coordination to the metal. $Ni(MeL)_{2.5}Cl_2$ shows an electronic spectrum corresponding to pseudo-octahedral patterns of nearly $O_h$ geometry (Table 1) according to its high-spin behaviour ($\mu_{eff} = 3.2$) with the first spin-allowed band $\nu_1$ ($= \Delta$) at 9.9 kK suggesting Cl coordination which is confirmed by the IR spectrum showing $\nu_{Ni-Cl}$ at 280 $cm^{-1}$. The compound can be formulated as $[Ni(MeL)_2Cl_2] \cdot 0.5$ MeL as in the case of $[Co(MeL)_2Cl_2] \cdot 0.5$ MeL [2]. In the IR spectra of both compounds the bands of MeL in the usual *cis–trans* conformation [6] are not present suggesting that the free disordered ligand is in a different conformation implying different IR spectra [7]. $[Ni(MeL)_2Cl_2] \cdot 0.5$ MeL loses 0.5 moles of ligand in the temperature range 180–200°C giving $Ni(MeL)Cl_2$; an exothermic peak in the DSC curve corresponds to this loss. The electronic spectrum of this compound (Table 1) clearly suggests pseudo-octahedral coordination around the Ni atom with Cl in the coordination sphere ($\nu_1 = \Delta = 9.1$ kK at lower value than $\nu_1 = \Delta = 11.6$ kK for the chromophore *trans*-$NiN_3S_3$). In the IR spectrum, bands attributable to $\nu_{CN}$ with partial double bond character due to electron delocalization in the chelate ligand are no longer present in the region of nearly 1500 cm$^{-1}$ where they are usually found, thus suggesting that bridged intermolecular coordination occurs.

The same compound is obtained by thermal decomposition of [Ni(MeL)$_2$Cl$_2$] which, in the same temperature range, loses one mole of ligand. In both cases the successive loss of the other mole of MeL at 243°C gives NiCl$_2$.





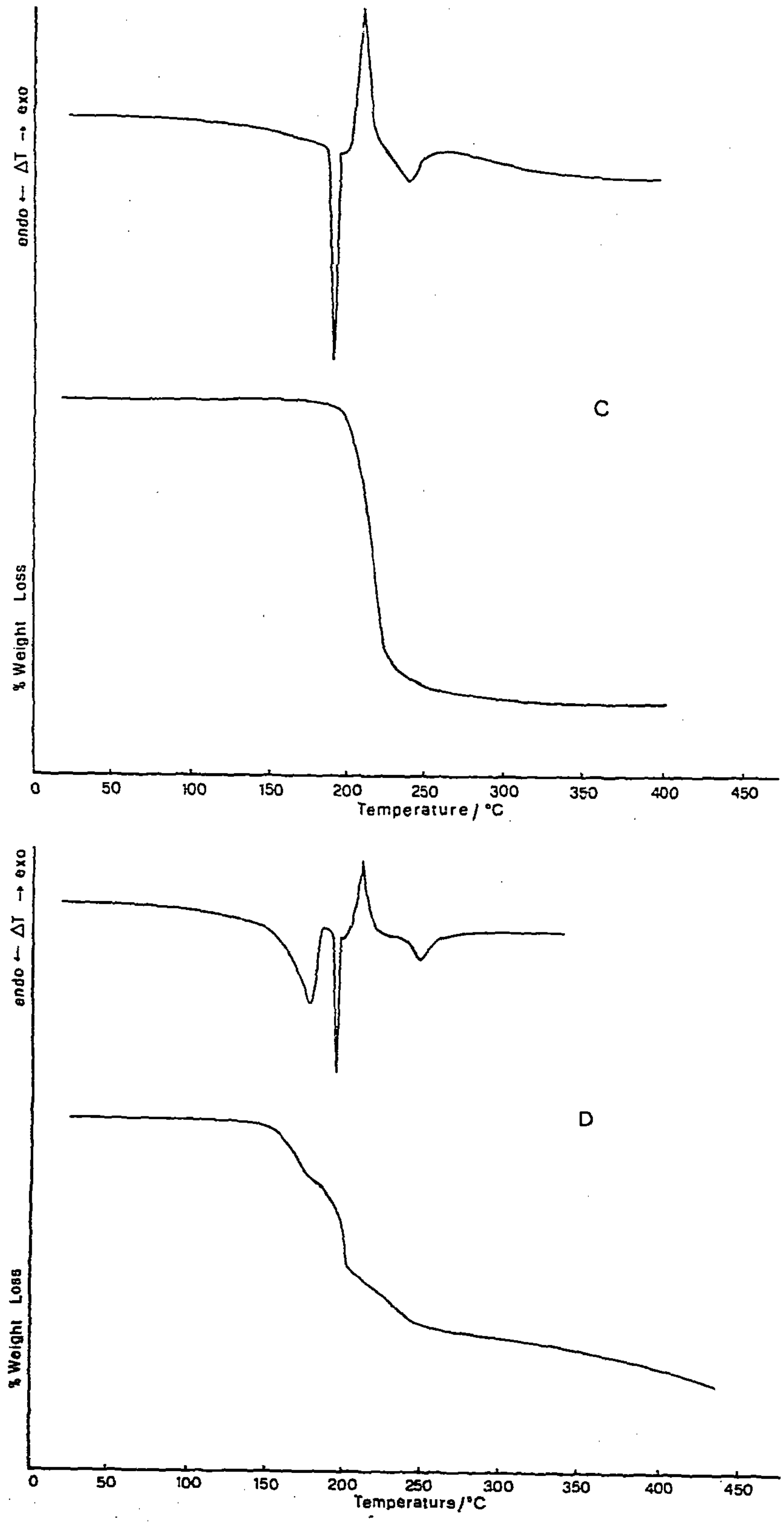


Fig. 5. Thermal decomposition (DSC and TG) of [Ni(L-H)$_2$] (A), [Ni(MeL-H)$_2$] (B), [Ni(Me$_2$L-H)$_2$] (C) and [Ni(Me$_2$L)$_2$Cl$_2$] (D).

TABLE 1

Electronic visible (reflectance) spectra (kK) of nickel complexes [a]

| Compound | Chromophore | $\nu_1$ [b] | $\nu_2$ [b] | $\nu_3$ [b] |
|---|---|---|---|---|
| $[Ni(MeL)_3]Cl_2 \cdot 3\ H_2O \cdot 0.5\ EtOH$ | trans-$NiN_3S_3$ | [10.5] 11.6 | 17.9 | [26.7] |
| $[Ni(MeL)_3]Cl_2$ | | [10.3] 11.5 | 17.8 | |
| $[Ni(MeL)_2Cl_2] \cdot 0.33\ EtOH$ | | 9.7[11.1] | 16.0 | [26.6] |
| $[Ni(MeL)_2Br_2] \cdot 0.33\ EtOH$ | | 10.0[10.8] | 15.9 | [26.2] |
| $[Ni(MeL)_2I_2]$ | | 10.2 | 15.9 | |
| $Ni(MeL)_{2.5}Cl_2$ | | 9.9[11.1] | 16.0 | [26.3] |
| $Ni(MeL)Cl_2$ | | 9.1 | 14.0 | 23.5 |
| $Ni(MeL)Br_2$ | | 9.8 | 13.5 | 25.0 |

[a] Shoulder in brackets.

[b] $\nu_1$, $\nu_2$, $\nu_3$ correspond to the three spin-allowed *d–d* transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$.

The DSC curves of $[Ni(MeL)_3]Br_2$ and $[Ni(MeL)_3]I_2$ (Fig. 2) show an endothermic peak at 200 and 195°C, respectively, overlapped by an exothermic peak.

Definite steps are not present in the TG curves (Fig. 2) and formation of intermediates is not indicated. Only $Ni_3S_4$ is obtained at 400°C.

$[Ni(BuL)_3]X_2$ ($X = Cl$, I): the compounds show very similar thermal behaviour consisting of the loss of ligand (Fig. 3) and isolation of $NiCl_2$ and NiS, respectively.

$[Ni(MeL)_2Cl_2]$ and $[Ni(MeL)_2Br_2]$ lose 1 mole of MeL in the temperature range 175–220°C and 170–220°C, respectively (Fig. 4) leading to the formation of the intermediates described above, $Ni(MeL)Cl_2$ and $Ni(MeL)Br_2$, which have been isolated.

$[Ni(MeL)_2I_2]$ shows a different decomposition pattern: no intermediates can be isolated and NiS is obtained (Fig. 4). In the temperature range 120–180°C $[Ni(Me_2L)_2Cl_2]$ loses 2 moles of HCl giving the low-spin complex $[Ni(Me_2L\text{-}H)_2]$ (Fig. 5). At higher temperature the decomposition pattern is the same as that of the low-spin complex.

### *Low-spin complexes*

The low-spin complexes $[Ni(L\text{-}H)_2]$, $[Ni(MeL\text{-}H)_2]$ and $[Ni(Me_2L\text{-}H)_2]$ show very similar thermal behaviour: all the compounds decompose losing the ligand (Fig. 5) and NiS is obtained in all cases.

## CONCLUSION

The decomposition routes of the complexes examined are very different and not easy to correlate as they depend on the ligand and/or the anion.

The anhydrous high-spin complexes $[NiL_3]X_2$ ($X = Cl$, Br, I) decompose giving $[Ni(L\text{-}H)_2]$ as intermediate when $X = Cl$, and the polymeric $NiLX_2$ when $X = Br$ or

I. The order of thermal stability of $[NiL_3]X_2$ compounds, as signified by the lowest temperature at which weight loss begins, is I = Br > Cl.

The formation of $[Ni(L\text{-}H)_2]$ as intermediate in the decomposition route of $[NiL_3]Cl_2$ is related to the probable presence of NH · · · Cl hydrogen bonds (already observed in other similar complexes), which allows the deprotonation of ligands by Cl anions and justifies the lower decomposition temperature of the complex.

The high-spin complexes of the ligand MeL decompose by different routes in analogy with the different methods which had been used to prepare them.

When the anion is $Cl^-$, only the compound $[Ni(MeL)_3]Cl_2 \cdot 3\ H_2O \cdot 0.5\ EtOH$ is formed. Its constitution is conditioned by the essential role of the molecules of $H_2O$ [1]. The compound is only obtained by reacting $NiCl_2$ with MeL in 95% ethanol, whereas if anhydrous ethanol is employed $[Ni(MeL)_2Cl_2] \cdot 0.33\ EtOH$ is obtained. It is therefore very interesting that it is possible to isolate $[Ni(MeL)_3]Cl_2$ by thermal decomposition.

$[Ni(MeL)_3]Br_2$ and $[Ni(MeL)_3]I_2$ were obtained starting from $NiBr_2$ and $NiI_2$, respectively in 95% ethanol.

The high-spin inner complexes $[Ni(MeL)_2X_2] \cdot 0.33\ EtOH$ (X = Cl, Br) decompose giving the isolable intermediates $Ni(MeL)Cl_2$ and $Ni(MeL)Br_2$.

The former is also obtained *via* decomposition of $[Ni(MeL)_3]Cl_2$ whereas the decomposition of the bromide does not give rise to the latter. Presumably a steric effect of the Br is in operation in this case; indeed, when X = I, no intermediates at all are obtained.

The thermal stability of these inner complexes is similar for X = Cl or Br: the low thermal stability of $[Ni(MeL)_2I_2]$ is due to the fact that it is difficult to coordinate an iodide ion as indicated by the unusual synthesis: all efforts to prepare the compound by reacting $NiI_2$ with MeL were unsuccessful.

The high-spin $[Ni(Me_2L)_2Cl_2]$ gives the low-spin $[Ni(Me_2L\text{-}H)_2]$ as intermediate. The presence of the easily deprotonable N(2) atom in the ligand and the presence of a chloride ion in the coordination sphere allows the formation of the compound.

The low-spin complexes $[Ni(L\text{-}H)_2]$, $[Ni(MeL\text{-}H)_2]$ and $[Ni(Me_2L\text{-}H)_2]$ decompose without formation of intermediates. The thermal stability follows the order: $[Ni(L\text{-}H)_2]$ (210°C) > $[Ni(MeL\text{-}H)_2]$ (181°C) > $[Ni(Me_2L\text{-}H)_2]$ (135°C) which seems to be related to the donor power of the terminally coordinated N atoms ($NH_2$, $NH^-$ and $NMe_2$) as indicated by their electronic spectra $\nu_{1[Ni(L\text{-}H)_2]} = 17.4$ kK > $\nu_{1[Ni(MeL\text{-}H)_2]} = 16$ kK > $\nu_{1[Ni(Me_2L\text{-}H)_2]} = 15.8$ kK [1].

Summarizing, the different thermal behaviour observed for the high-spin ionic complexes seems to be related to the extent (if any) of deprotonation of the N(2) of the ligands. We noted, previously, that by thermal decomposition at 190°C the complex $[Ni(NH_2NHC(O)OEt)_3]Cl_2$ gives the pseudo-octahedral polymeric compound $Ni(NH_2NHC(O)OEt)Cl_2$ [8], which is similar to $Ni(MeL)Cl_2$.

This behaviour indicates that a decreased electron-withdrawal by the –C(O)OEt group compared with that of the –C(S)SMe group lowers the tendency of N(2) to deprotonate, notwithstanding the presence of hydrogen bonds between chloride ions and $-NH-NH_2$ groups in the structure of $Ni[(NH_2NHC(O)OEt)_3]Cl_2$ [9].

All the complexes with N(2) deprotonable ligands give low-spin complexes.

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