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# SPECTRAL AND THERMAL STUDIES OF MONOHALOGEN BENZOYLHYDRAZINE Ni(II) COMPLEXES

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## ABSTRACT

Thermal investigations by the TG/DTG technique in a nitrogen atmosphere were carried out on a series of Ni(II) complexes with *ortho-*, *meta-* or *para*-halogen monosubstituted benzoylhydrazines, to determine their stabilities and modes of decomposition.

Mass spectral data of the chloro-benzoylhydrazine ligands and their complexes with Ni(II) were also studied, for indications of a possible fragmentation pattern. It was established that there are two different decomposition mechanisms, dependent on the position of the halogen in the benzolic ring, while the decomposition process is weakly affected by the nature of the halogen.

## INTRODUCTION

A recent paper [1] reported on a study of the thermal behaviour of some dichloro-benzoylhydrazine complexes by the TG/DTG technique, in a nitrogen atmosphere. The results showed that the thermal stability of the ligand is an important determining factor in the thermal stability of the complexes, and that the position of the substituted chloride atoms does not affect the mode of decomposition. It was also established that the two substituted chloride atoms are eliminated as a part of the whole ring, i.e. there is no rupture of the C–Cl bonds.

As a continuation of our previous work, thermal investigations on a series of Ni(II) complexes with *ortho-*, *meta-* or *para*-halogen ring-monosubstituted benzoylhydrazines were undertaken. The complexes under study have the formulae $[Ni(XBh)_3]Cl_2$, where $X = F^-$, $Cl^-$, $Br^-$ or $I^-$ and $Bh = -C_6H_4CONHNH_2$. Their bonding and structure are described elsewhere [2].

In this paper we report results concerning mass spectral and thermogravimetric studies of these complexes. To date, such a study has not been

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performed for these complexes, and it is of interest to compare their thermal behaviour to that of the corresponding dichloro-benzoylhydrazines. Simultaneous TG/DTG studies in a dynamic atmosphere of nitrogen are reported. Mass spectral data are also reported, and possible fragmentation patterns discussed.

## EXPERIMENTAL

### *Preparation*

The monohalogen benzoylhydrazines and their complexes with Ni(II) were prepared by known methods [2,3].

### *Physical methods*

Thermogravimetric analyses (TG/DTG) were performed using a Du-Pont Instruments Series 99 thermal analyser with a combined apparatus Du-Pont Instruments Series 951 thermogravimetric analyser. The measurements were taken in a dynamic atmosphere of nitrogen with a flow rate of 60 ml $\text{min}^{-1}$ up to 800 ° C. The heating rate was 10 ° C $\text{min}^{-1}$ and the weight sample was about 10 mg.

Mass spectra were measured using a RMV-6L Hitachi Perkin–Elmer mass spectrometer with an ionization source of type T-2p operating at 70 eV.

## RESULTS AND DISCUSSION

### *Thermal analysis*

The thermoanalytical curves (TG and DTG) of some Ni(II) monohalogen benzoylhydrazine complexes in a dynamic nitrogen atmosphere are given in Figs. 1–10. The temperature ranges and mass losses of the decompositions, the temperatures of the greatest rate of decomposition ($\text{DTG}_{\text{max}}$), and the theoretical percentage mass losses are presented in Tables 1–4.

The data obtained for the complexes with the substituted halogen in the *ortho* and in the *meta* position indicate similar decomposition processes (Figs. 1, 2 and 4–6). First, a partial decomposition of the ligands occurs in the range 150–250 ° C leading to elimination of the ring-substituted halogenide, either alone or together with the $NHNH_2$ moiety. The second stage is a sudden loss of mass, owing to the elimination of two ligands followed by the gradually evolved CO moiety. An exception appears in the case of the $[Ni(o\text{-IBh})_3]Cl_2$ complex (Fig. 3), where decomposition occurs as one stage

TABLE 1

Thermoanalytical results (TG/DTG) for the fluoro-benzoylhydrazine Ni(II) complexes in nitrogen

| Complex | Stage | Temperature range (°C) | $DTG_{max}$ (°C) | % Mass loss | Evolved moiety formula | Calculated % mass loss |
|---|---|---|---|---|---|---|
| $[Ni(o\text{-}FBh)_3]Cl_2$ | 1 | 110–220 | 195 | 5.4 | $NHNH_2$ | 5.24 |
| | 2 | 220–340 | 275, 285 and 330 | 53.6 | $2\ FC_6H_4CONHNH_2$ | 52.05 |
| | 3 | 340–470 | 385 | 8.1 | $CO + F$ | 7.93 |
| | 4 | 470–650 | 560 | 18.9 | $C_6H_4 + Cl_2$ | 24.84 |
| | residue | > 650 | – | 13.9 | $Ni^0$ | 9.92 |
| $[Ni(m\text{-}FBh)_3]Cl_2$ | 1 | 150–120 | 195 | 2.9 | F | 3.20 |
| | 2 | 210–280 | 255 | 16.5 | $C_6H_4CO$ | 17.57 |
| | 3a | 280–400 | 315 and 340, 355 | 45.0 | $1\ FC_6H_4CONHNH_2 + C_6H_4CO$ | 43.59 |
| | 3b | 400–500 | 415 | 5.0 | $NHNH_2$ | 5.24 |
| | 4 | 500–700 | 565(br) | 9.5 | $F + NHNH_2$ | 8.45 |
| | residue | > 700 | – | 23.2 | $NiCl_2$ | 21.92 |
| $[Ni(p\text{-}FBh)_3]Cl_2$ | 1 | 150–275 | 235, 260 | 31.8 | $1\ FC_6H_4CONHNH_2 + NHNH_2$ | 31.26 |
| | 2 | 275–340 | 335 | 27.6 | $1\ FC_6H_4CONHNH_2$ | 26.02 |
| | 3 | 340–400 | 370 | 10.6 | $\frac{1}{2}\ FC_6H_4CO$ | 10.39 |
| | 4 | 400–700 | 440(br), 530(br) | 10.4 | $\frac{1}{2}\ FC_6H_4CO$ | 10.39 |
| | residue | > 700 | – | 15.4 | $NiCl_2$, $Ni^0$ | 22.12 |

TABLE 2

Thermoanalytical results (TG/DTG) for the chloro-benzoylhydrazine Ni(II) complexes in nitrogen

| Complex | Stage | Temperature range (°C) | $DTG_{max}$ (°C) | % Mass loss | Evolved moiety formula | Calculated % mass loss |
|---|---|---|---|---|---|---|
| $[Ni(o\text{-}ClBh)_3]Cl_2$ | 1 | 140–250 | 140, 225 | 10.0 | $Cl+NHNH_2$ | 10.37 |
| | 2 | 250–330 | 265, 310 | 51.5 | $2\ ClC_6H_4CONHNH_2$ | 53.18 |
| | 3 | 330–410 | 385 | 12.1 | $C_6H_5$ | 12.01 |
| | 4 | 410–700 | 610 | 15.9 | $Cl_2+CO$ | 15.44 |
| | residue | > 700 | – | 10.5 | $Ni^0$ | 9.15 |
| $[Ni(m\text{-}ClBh)_3]Cl_2$ | 1 | 175–240 | 240 | 5.7 | Cl | 5.54 |
| | 2 | 240–365 | 300, 345 | 57.3 | $2\ ClC_6H_4CONHNH_2+NHNH_2$ | 58.01 |
| | 3 | 365–420 | 400 | 6.0 | CO | 4.36 |
| | 4 | 420–700 | 550(br), 620(br) | 13.2 | $C_6H_5$ | 12.01 |
| | residue | > 700 | – | 17.0 | $NiCl_2$, Ni | 20.23, 9.15 |
| $[Ni(p\text{-}ClBh)_3]Cl_2$ | 1 | 190–280 | 255 | 26.3 | $1\ ClC_6H_4CONHNH_2$ | 26.59 |
| | 2a | 280–350 | 345 | 33.5 | $1\ ClC_6H_4CONHNH_2+CONHNH_2$ | 35.79 |
| | 2b | 350–400 | 380 | 13.1 | $C_6H_5$ | 12.01 |
| | 3 | 400–700 | 520(br), 615(br) | 18.6 | $Cl_2+Cl$ | 16.62 |
| | residue | > 850 | – | 8.5 | $Ni^0$ | 9.15 |

TABLE 3

Thermoanalytical results (TG/DTG) for the bromo-benzoylhydrazine Ni(II) complexes in nitrogen

| Complex | Stage | Temperature range (°C) | $DTG_{max}$ (°C) | % Mass loss | Evolved moiety formula | Calculated % mass loss |
|---|---|---|---|---|---|---|
| [Ni(*o*-BrBh)$_3$]Cl$_2$ | 1 | 140–270 | – | 10.6 | Br | 10.32 |
| | 2 | 270–400 | 290, 330 | 62.0 | 2 $BrC_6H_4CONHNH_2 + CONHNH_2$ | 63.11 |
| | 3 | 400–750 | 660 | 19.7 | $C_6H_4 + Cl_2$ | 19.23 |
| | residue | > 750 | – | 8.0 | $Ni^0$ | 7.58 |
| [Ni(*m*-BrBh)$_3$]Cl$_2$ | 1 | 150–200 | – | 10.2 | Br | 10.32 |
| | 2 | 200–255 | 215, 245 | 22.0 | $C_6H_4CONHNH_2 + NHNH_2$ | 21.42 |
| | 3 | 255–360 | 315 | 37.1 | 1 $BrC_6H_4CONHNH_2 + Br$ | 38.07 |
| | 4 | 360–650 | 420, 570(br) | 18.8 | $C_6H_4CO$ + partial dec. of $NiCl_2$ | 13.42 + – |
| | residue | > 700 | – | 11.9 | $Ni^0$, $NiCl_2$ | 7.58, 16.74 |
| [Ni(*p*-BrBh)$_3$]Cl$_2$ | 1 | 155–275 | 255 | 17.7 | $C_6H_4CONHNH_2$ | 17.42 |
| | 2 | 275–360 | 355 | 50.9 | 1 $BrC_6H_4CONHNH_2 + NHNH_2 + 2Br$ | 52.40 |
| | 3 | 360–700 | 625 | 23.3 | $C_6H_4CO + Cl_2$ | 22.58 |
| | residue | > 700 | – | 8.2 | $Ni^0$ | 7.58 |

TABLE 4

Thermoanalytical results (TG/DTG) for the iodo-benzoylhydrazine Ni(II) complexes in nitrogen

| Complex | Stage | Temperature range (°C) | $DTG_{max}$ (°C) | % Mass loss | Evolved moiety formula | Calculated % mass loss |
|---|---|---|---|---|---|---|
| [Ni(*o*-IBh)$_3$]Cl$_3$ | 1a | 190–290 | 265 | 56.0 | $2\ IC_6H_4CONHNH_2$ | 57.22 |
| | 1b | 290–350 | 320 | 18.0 | $I + NHNH_2$ | 17.25 |
| | 2 | 350–600 | 450 | 18.0 | $C_6H_4CO + Cl_2$ | 19.11 |
| | residue | > 600 | – | 8.0 | $Ni^0$ | 6.41 |
| [Ni(*m*-IBh)$_3$]Cl$_2$ | 1 | 195–275 | 235 | 13.3 | I | 13.87 |
| | 2 | 275–370 | 325 | 50.0 | $1\ IC_6H_4CONHNH_2 + CONHNH_2 + C_6H_4CONHNH_2$ | 49.79 |
| | 3 | 370–700 | 500, 555 | 28.3 | $IC_6H_4 + Cl_2$ | 29.90 |
| | residue | > 700 | – | 8.3 | $Ni^0$ | 6.41 |
| [Ni(*p*-IBh)$_3$]Cl$_2$ | 1 | 200–275 | 260 | 13.8 | I | 13.87 |
| | 2 | 275–360 | 340 | 50.0 | $1\ IC_6H_4CONHNH_2 + CONHNH_2 + C_6H_4CONHNH_2$ | 49.79 |
| | 3 | 360–650 | 490 | 28.2 | $IC_6H_4 + Cl_2$ | 29.90 |
| | residue | > 650 | – | 8.0 | $Ni^0$ | 6.41 |

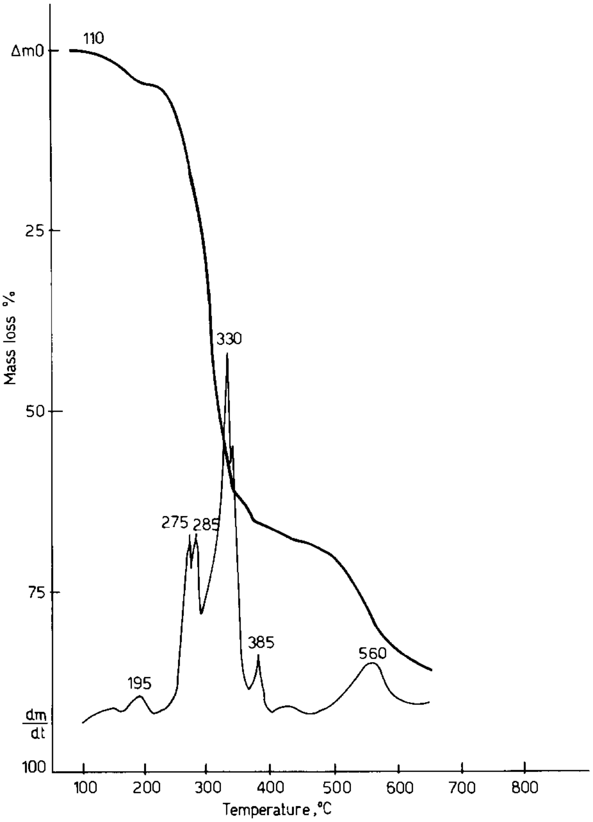


Fig. 1. Thermal curves for [Ni(*o*-FBh)$_3$]Cl$_2$ in nitrogen.

with two steps, corresponding to the elimination of two ligands and the NHNH$_2$ moiety. IR spectra of the intermediate at 450 °C showed bands corresponding to NiCl$_2$ and to an organic molecule. IR spectra of the residue at 800 °C indicated metal Ni or a mixture of Ni and NiCl$_2$ resulting from partial sublimation of the NiCl$_2$ [4] or evolution of the chlorine molecule (Figs. 7, 8).

The thermal decomposition curves for the *para*-benzoylhydrazine complexes reveal a quite different decomposition process. First, one undecomposed ligand is eliminated; then in a second stage, quite distinct from the first, there is a loss of mass attributable to elimination of the second ligand and partial decomposition of the third (Figs. 7, 8). An exception appears again in the case of the [Ni(*p*-IBh)$_3$]Cl$_2$ complex, where the first decomposition stage occurs with the elimination of one iodide atom (Fig. 9).

Thus, the determining factor in the thermal stability of the *para*-halogen benzoylhydrazine Ni(II) complexes is the strength of the coordination bonds, while the determining factor for the *ortho*- and *meta*-halogen benzoylhydrazine Ni(II) complexes is the thermal stability of the ligands.

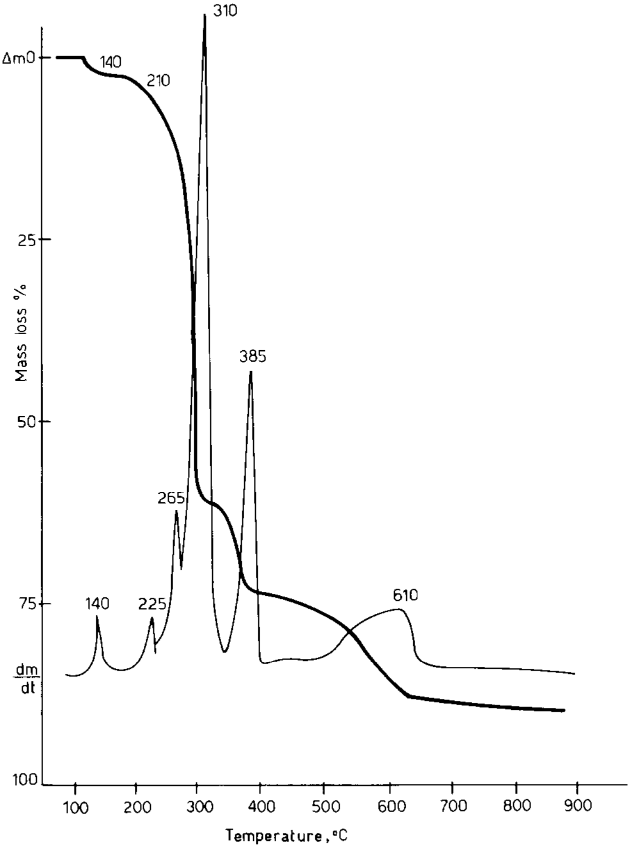


Fig. 2. Thermal curves for $[Ni(o\text{-}ClBh)_3]Cl_2$ in nitrogen.

The relative thermal stability of complexes with the same substituted halogen, as indicated by their procedural decomposition temperatures (Table 5), depends on the position of the halogen in the benzolic ring and follows the series *ortho* < *meta* ⩽ *para*.

TABLE 5

Procedural decomposition temperatures of monohalogen benzoylhydrazine Ni(II) complexes

| Complex | T (°C) | Complex | T (°C) |
|---|---|---|---|
| $[Ni(o\text{-}FBh)_3]Cl_2$ | 110 | $[Ni(o\text{-}BrBh)_3]Cl_2$ | 140 |
| $[Ni(m\text{-}FBh)_3]Cl_2$ | 150 | $[Ni(m\text{-}BrBh)_3]Cl_2$ | 150 |
| $[Ni(p\text{-}FBh)_3]Cl_2$ | 150 | $[Ni(p\text{-}BrBh)_3]Cl_2$ | 155 |
| $[Ni(o\text{-}ClBh)_3]Cl_2$ | 140 | $[Ni(o\text{-}IBh)_3]Cl_2$ | 190 |
| $[Ni(m\text{-}ClBh)_3]Cl_2$ | 175 | $[Ni(m\text{-}IBh)_3]Cl_2$ | 195 |
| $[Ni(p\text{-}ClBh)_3]Cl_2$ | 190 | $[Ni(p\text{-}IBh)_3]Cl_2$ | 200 |

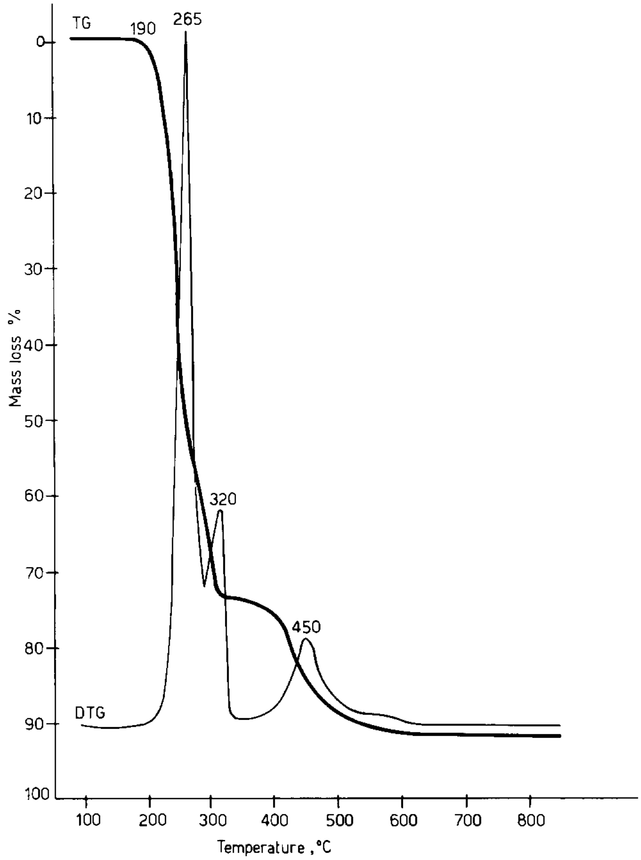


Fig. 3. Thermal curves for $[Ni(o\text{-}IBh)_3]Cl_2$ in nitrogen.

### *Mass spectra*

Mass spectral data for both the monochloro-benzoylhydrazine ligands and their complexes with Ni(II) were also studied for indications of a possible fragmentation pattern. The mass spectra of the ligands (*o*-, *m*- and *p*-ClBh) showed peaks corresponding to the molecular ion $M^+$ ($m/e = 170$) and to the daughter ion $ClC_6H_4CO^+$ ($m/e = 139$). This last was the base peak in all cases, and can be regarded as the direct fragment ion upon elimination of the $NHNH_2$ group from the molecular ion. The existence of a metastable peak at $m^\star = 88.5$ confirms the following fragmentation path

$$\begin{array}{lcl} ClC_6H_4CO^+ & \rightarrow & ClC_6H_4^+ \\ m/e = 139 & & m/e = 111 \end{array}$$

Ions corresponding to those detected at $m/e = 170$, 139 and 111 were observed at $m/e = 172$, 141 and 113, but in lower relative intensities, owing to the isotopic ratio of the chloride atoms $^{35}Cl$ and $^{37}Cl$.

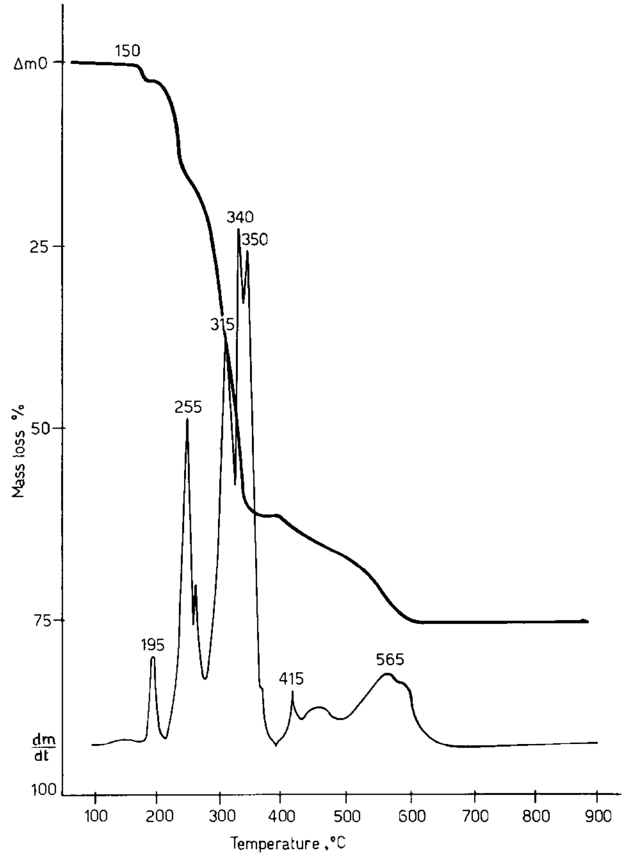


Fig. 4. Thermal curves for $[Ni(m\text{-}FBh)_3]Cl_2$ in nitrogen.

The ion at $m/e = 75$ is due to cleavage of the C–Cl bond and loss of the HCl moiety from the benzolic ring. The genesis of the ions mentioned above is demonstrated by the general fragmentation pattern in Scheme 1.

Molecular ions are not detected in the mass spectra of the complexes studied. This absence can be attributed to pyrolytic decomposition in the direct inlet under the high temperature used (200–250 °C), or to electron impact. The fragmentation pattern is not the same for all the complexes. Only in the case of $[Ni(p\text{-}ClBh)_3]Cl_2$ does the fragmentation pattern agree with that observed for the ligand, with a base peak at $m/e = 139$ corresponding to the fragment $ClC_6H_4CO^+$, and a peak at $m/e = 170$ corresponding to the daughter ion of the ligand. The genesis of these ions is demonstrated by the general pattern shown in Scheme 2. Support for the fragmentation pathways comes from the presence of metastable peaks.

The fragmentation pattern of the *o*- and *m*-ClBh complexes appears to be different. Here the daughter ion of the ligand is absent, and the highest mass number ion, observed at $m/e = 136$, can be attributed to the daughter

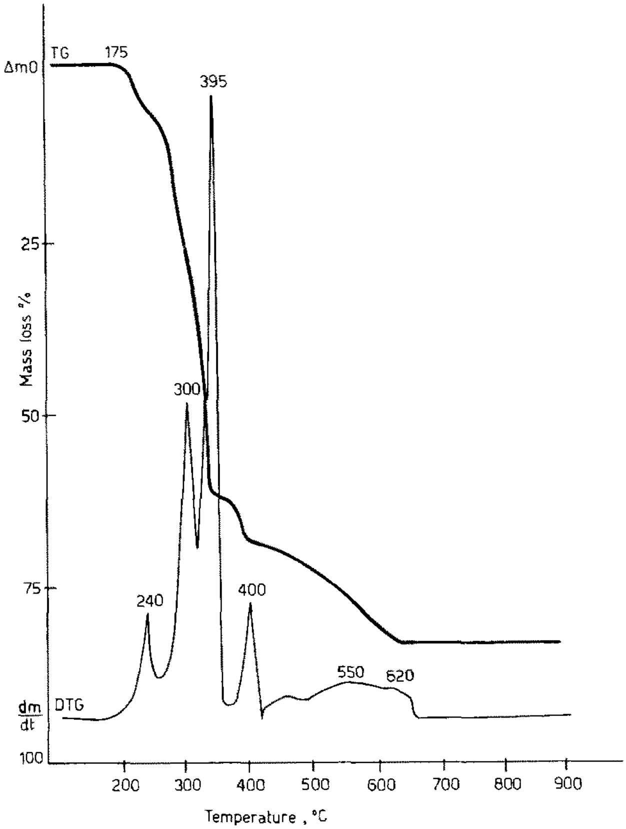
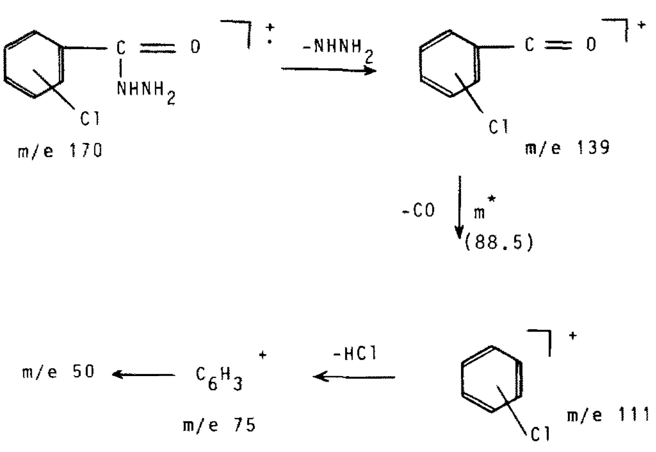


Fig. 5. Thermal curves for $[Ni(m\text{-}ClBh)_3]Cl_2$ in nitrogen.



Scheme 1. Possible fragmentation pattern for the ligands *ortho*-, *meta*- and *para*-chlorobenzoylhydrazine.

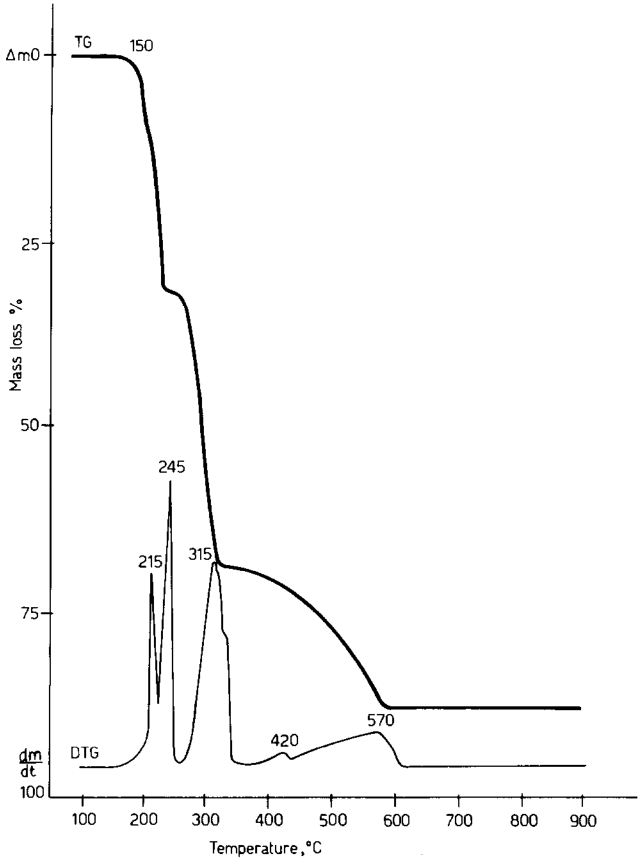
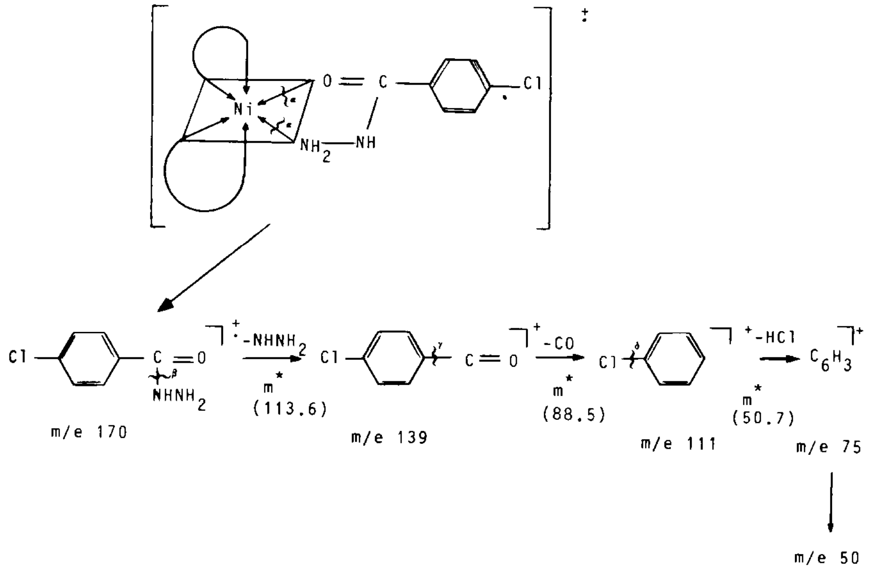


Fig. 6. Thermal curves for [Ni(*m*-BrBh)$_3$]Cl$_2$ in nitrogen.



Scheme 2. Possible fragmentation pattern for the [Ni(*p*-ClBh)$_3$]Cl$_2$ complex.

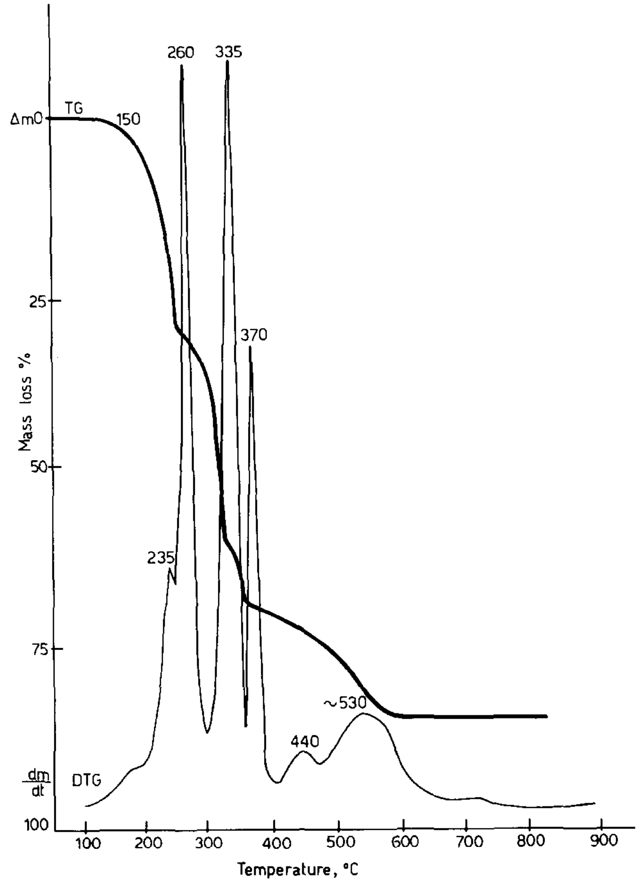
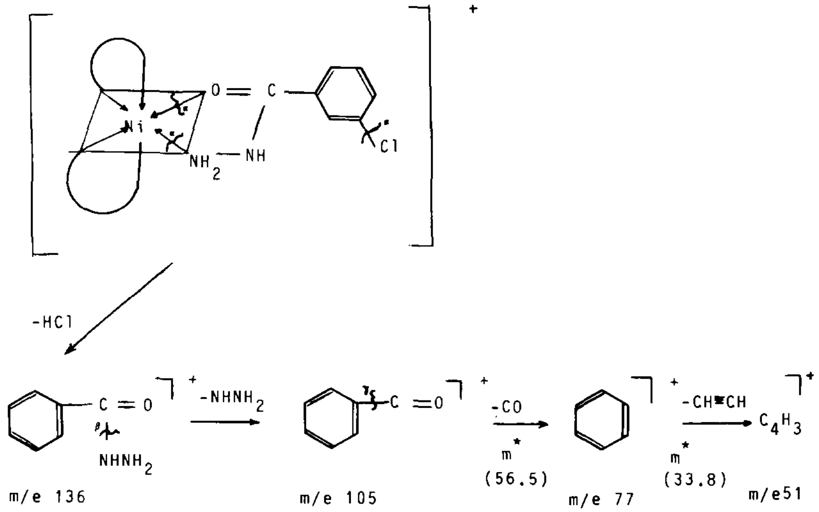


Fig. 7. Thermal curves for $[Ni(p\text{-}FBh)_3]Cl_2$ in nitrogen.



Scheme 3. Possible fragmentation pattern for the $[Ni(m\text{-}ClBh)_3]Cl_2$ complex.

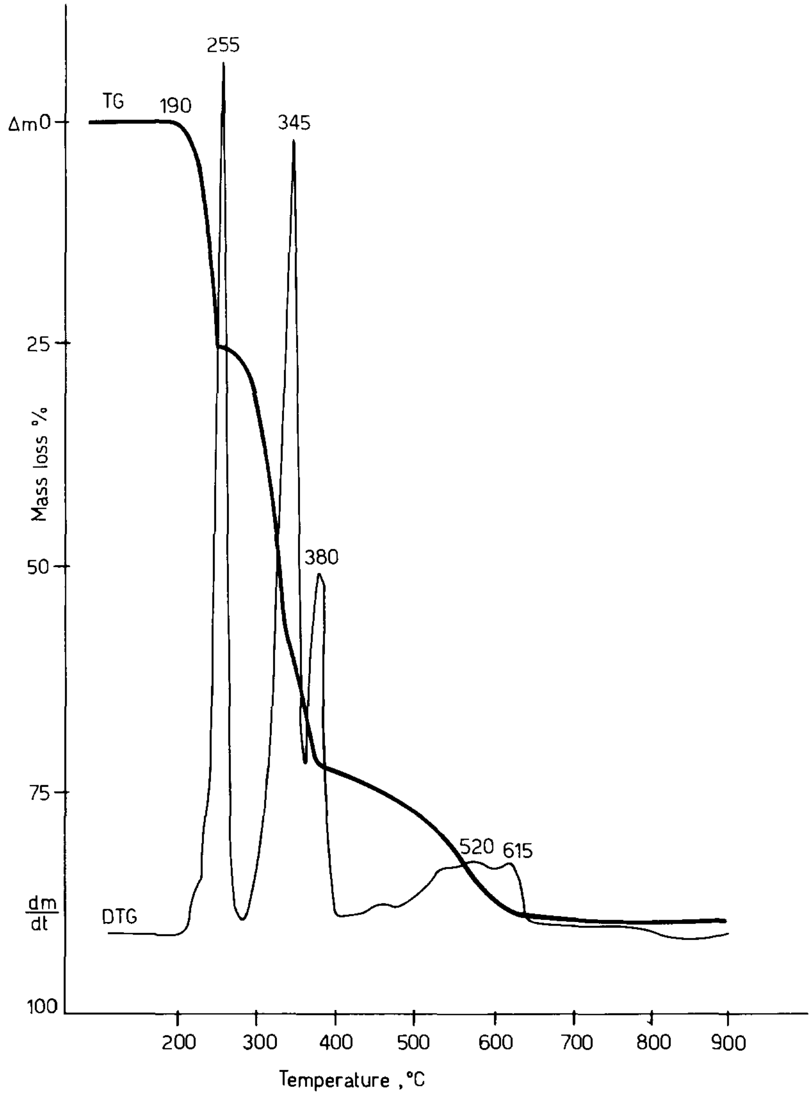


Fig. 8. Thermal curves for [Ni($p$-ClBh)$_3$]Cl$_2$ in nitrogen.

fragment $C_6H_4CONHNH_2^+$. The base peak ($m/e = 105$) corresponds to the fragment $C_6H_4CO^+$, while a metastable peak at $m^\star = 56.5$ indicates elimination of the CO moiety from the former ion (Scheme 3).

For comparison, TG/DTG curves for the unsubstituted benzoylhydrazine Ni(II) complex were also obtained (Fig. 10). This complex is stable up to 170 °C and appears to undergo a decomposition process similar to that observed for the *ortho*- and *meta*-monohalogen Ni(II) complexes. Thus, the

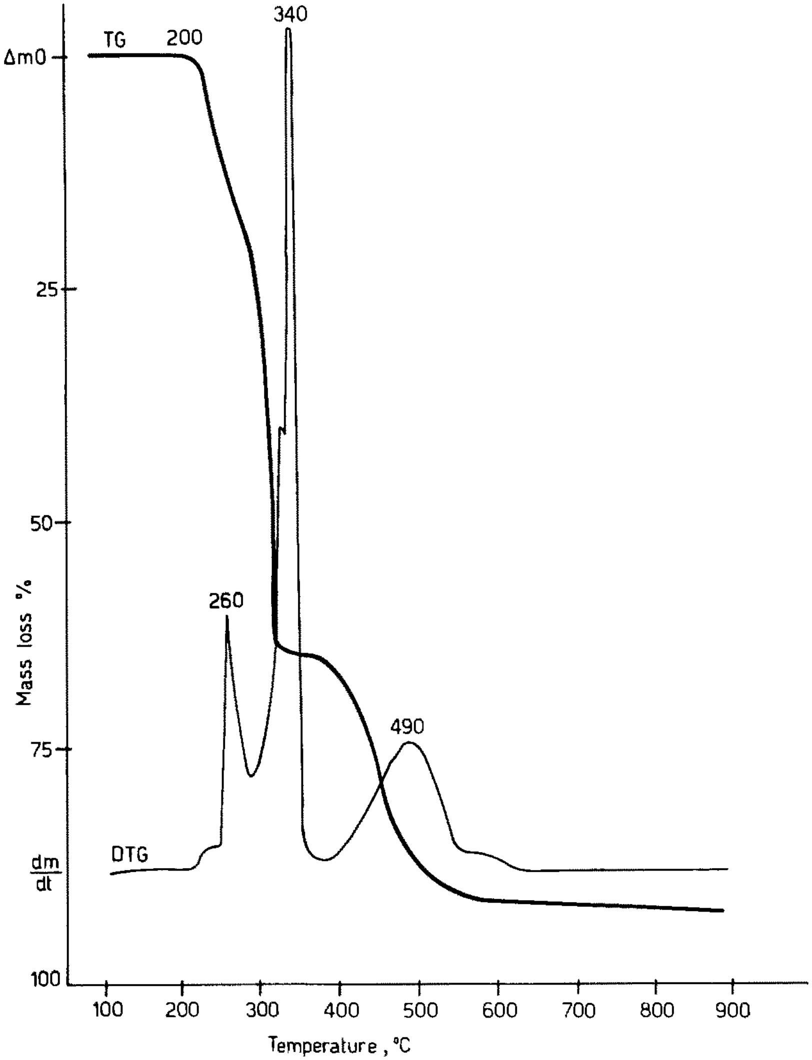


Fig. 9. Thermal curves for $[Ni(p\text{-}IBh)_3]Cl_2$ in nitrogen.

first stage occurs at $DTG_{max} = 235\,°C$ with the elimination of the $NHNH_2$ moiety. The same decomposition process is observed in the mass spectrum of this complex, where the base peak ($m/e = 105$) corresponds to the ion $M\text{-}NHNH_2^+$. Here again, the fragmentation pattern is confirmed by the existence of two metastable peaks at $m^\star = 56.5$ and $m^\star = 33.5$.

In conclusion, we can say that the mass spectral and thermogravimetric analysis data for the Ni(II) complexes investigated are in agreement. There are two different decomposition mechanisms, dependent on the position of

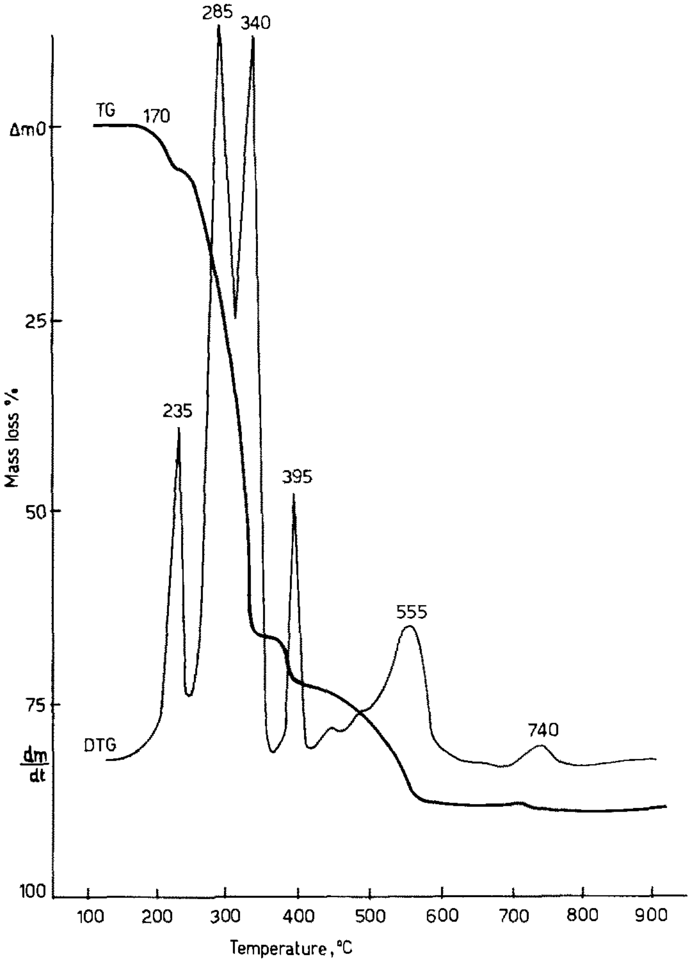


Fig. 10. Thermal curves for $[NiBh_3]Cl_2$ in nitrogen.

the halogen in the benzolic ring, while the decomposition process is weakly affected by the nature of the halogen.

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