Thermal studies on chromium(II) salts: Part 2

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Abstract

The thermal behavior of $Cr(pn)_3Br_2 \cdot 2H_2O$, $Cr(pn)_3Cl_2 \cdot 2H_2O$, $Cr(pn)_3SO_4$, $Cr(dien)_2Br_2$, $Cr(dien)_2Cl_2$, $Cr(dien)Cl_2$ and $Cr(dien)Br_2$ was investigated using TG and DSC under nitrogen atmosphere. The thermograms are interpreted and the enthalpies of dissociation are calculated where possible. © 1998 Elsevier Science B.V.

1. Introduction

The thermal behavior of chromium(III) salts has been extensively studied [1] and continues to be of interest [2]. Chromium(II) salts have not received the same level of attention, perhaps because they are air-sensitive and many are also unstable towards water. Chromium(II) salts have been used as the starting materials for the production of organochromium complexes [3,4]. Since it is expected that the thermal properties of the organochromium complexes would be related to those of the chromium amines, we have initiated investigation into thermal properties of some simple complexes of chromium(II) [5] and herein report analyses on the mono- and bis-diethylenetriamine (dien) chloride and bromide and the tris-1,2-diaminopropane (pn) chloride, bromide and sulphate of chromium(II).

2. Experimental

2.1. Apparatus

Thermogravimetric (TG) and differential scanning calorimetric (DSC) measurements were made in a nitrogen atmosphere using a DuPont 950 TGA system coupled to a DuPont programmer/recorder. The TGA scans were recorded to $800°C$, however, the maximum temperature for the DSC cell was $600°C$. The heating rate used was $5°C\,min^{-1}$. Purge gas flow was controlled at $50\,cm^3\,min^{-1}$ throughout. Enthalpy calculations were calibrated against the latent heat of fusion of pure indium metal ($\Delta H = 24.8\,J\,g^{-1}$). Sample mass varied from 5–25 mg.

2.2. Samples

Aqueous solutions of chromium(II) were prepared by the reaction of electrolytically pure chromium metal (BDH) with deoxygenated solutions of the appropriate acid ($\sim 2\,M$) [6]. The solutions were concentrated under vacuum until the salts began to pre-

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cipitate. Precipitated salts were collected under dry nitrogen in a Schlenk filter, washed with deoxygenated acetone and ether and dried under vacuum at room temperature. The amines were prepared from the aquo complexes by direct reaction with an appropriate amount of the neat amine added to a solution of the complex in ethanol or *n*-butanol as reported by Larkworthy et al. [7,8]. The compositions of the salts were confirmed by elemental analysis. [9,10].

The tris(1,2-diaminopropane) complex was also prepared with the sulphate counter ion using the method of Larkworthy et al. [8] although this complex was not reported by them. Analysis of chromium for this new complex was in agreement with the calcu-

lated value. No attempt was made to prepare the mono- and bis(1,2-diaminopropane) complexes since it had been reported that only impure bis-complexes could be precipitated and no pure mono-complexes could be obtained. Similarly, no attempt was made to prepare the mono- or bis(diethylenetriamine) chromium(II) sulphate complexes since it was reported by Earnshaw et al. [7] that their efforts were unsuccessful.

3. Results and discussion

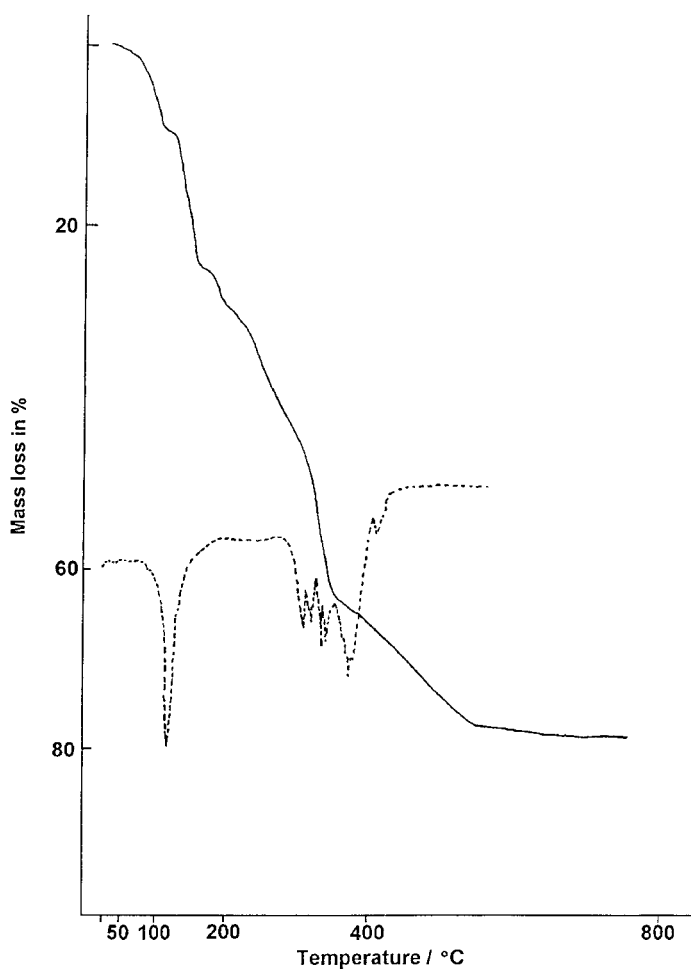The TG and DSC curves for the complexes are given in Figs. 1–7.
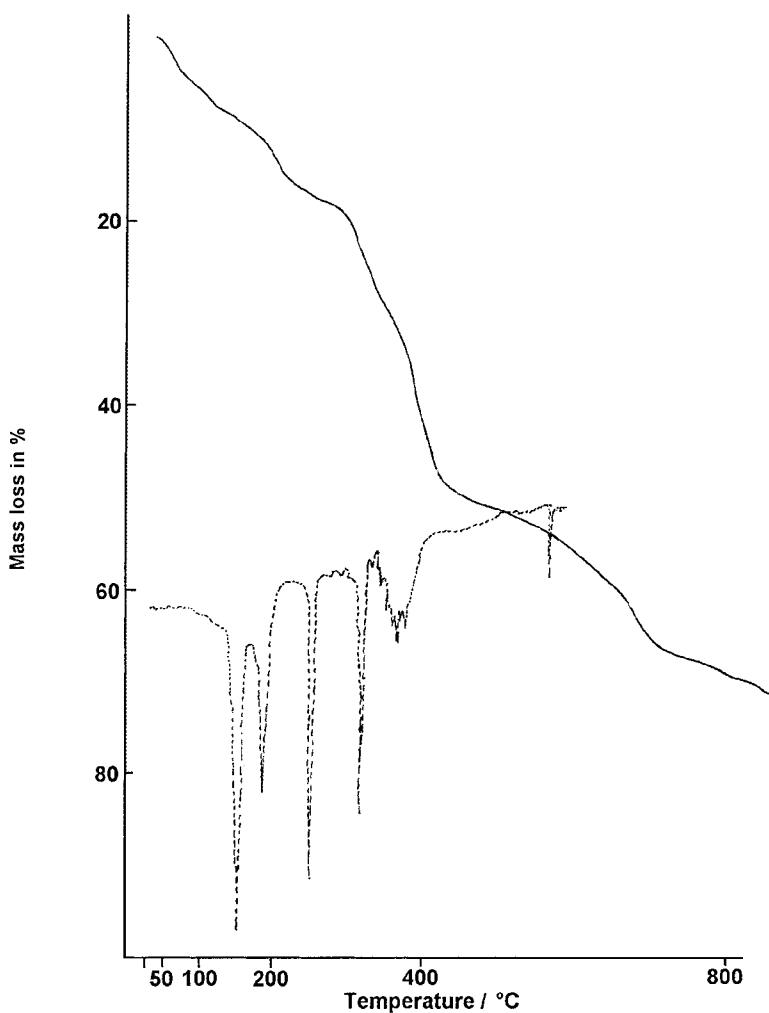

Fig. 1. TG/DSC of $Cr(pn)_3Cl_2 \cdot 2H_2O$.

Fig. 2. TG/DSC of Cr(pn)$_3$Br$_2$·2H$_2$O.

3.1. 1,2-Diaminopropane complexes

Cr(pn)$_3$Cl$_2$·2H$_2$O: The TG curve (Fig. 1) of the compound showed that the water of crystallization evolved completely when the sample was heated to 105°C (exp. 10.0%, calc. 9.4%). An inflection at 175°C appears to mark the loss of one pn ligand (exp. 26.0%, calc. 28.8%) while another inflection at 390°C indicates the loss of the remaining two moles of pn ligand (exp. 64.8%, calc. 67.7%). The CrCl$_2$ subsequently decomposed above 400°C.

The first endotherm shown in the DSC trace stretches from 50–200°C with its maximum at

130°C and a slight shoulder at ∼140°C. These appear then to be an unresolvable combination of two events, that is the loss of two waters of crystallization and one pn ligand ΔH=66.7 kJ mol^{-1}). Possibly five overlapping thermal events are recorded between 275 and 450°C. These are associated with the loss of the final two pn ligands and the decomposition of the chromium(II) chloride. That there appear to be four endotherms associated with the loss of two pn ligands can be indicative of the loss occurring in half mole steps.

Cr(pn)$_3$Br$_2$·2H$_2$O: The bromide complex (Fig. 2), like the chloride, began to lose water of crystallization
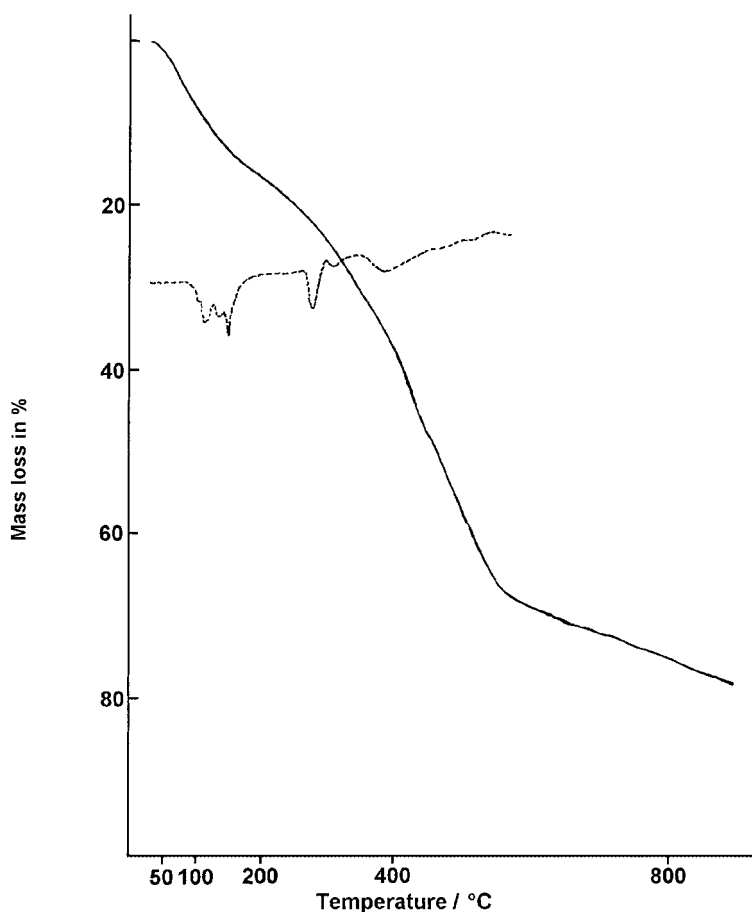
Fig. 3. TG/DSC of Cr(pn)$_3$SO$_4$.

just above room temperature. An inflection in the TG at ~50°C marks the end of the loss of the first mole of water (exp. ~4%, calc. 3.98%). A slight arrest is observed at ~100°C accounting for an additional mass loss of ~4% which is associated with the loss of the second mole of water of crystallization. The loss of the first pn ligand appears to occur in two steps of a half mole each (arrest at 210°C experimental loss of an additional 8.2%, calc. 8.18% and at ~310°C additional exp. loss of 8.4%, calc. 8.18%). By 425°C, a total mass loss of 48.8% has occurred, accounting for the loss of two waters and two and a half pn ligands. The remaining half pn is lost between 425 and 600°C by which point a total of 55.2% of the original mass was found to have been lost (calc. for loss of 2 H$_2$O and 3 pn ligands 54.88%). The remaining chro-

mium(II) bromide was found to undergo decomposition over a wide temperature range.

At least three endotherms are distinguishable from the onset of decomposition until a temperature of 200°C, which are expected to be associated with the stepwise loss of the aquo and amine ligands as determined by TG. However, these endotherms are not sufficiently separated to enable calculation of individual enthalpies. Therefore the total energy associated with the loss of two aquo ligands and a half pn ligand between 30 and 210°C was determined (ΔH=95.47 kJ mol^{-1}). A well-defined endotherm centered at ~240°C is probably related to a phase change since there is no accompanying mass loss observed (ΔH=19.14 kJ mol^{-1}). The energy associated with the loss of the second half mole of pn
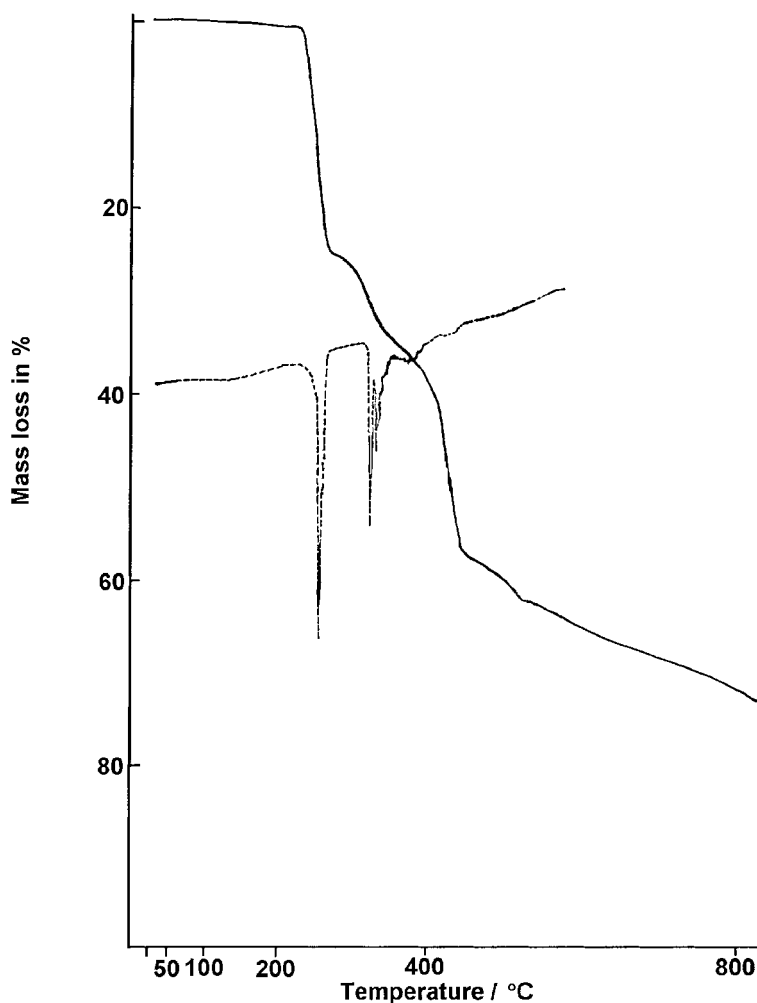
Fig. 4. TG/DSC of Cr(dien)$_2$Cl$_2$.

(ΔH=18.38 kJ mol^{-1}) is determined from the endotherm centered at 305°C. The broad endotherm stretching from 325 to ~420°C is related to the loss of the remaining pn (ΔH=36.99 kJ mol^{-1}).

Cr(pn)$_3$SO$_4$: The TG trace for the sulphate salt of the tris-1,2-diaminopropane complex (Fig. 3) is comparatively simple. The sample began to lose mass immediately upon heating. By 100°C an experimental loss of 10.8% had been recorded. This corresponds to the loss of a half mole of pn (calc. 9.99%). By 200°C the mass loss had reached 17.0% (calc. for one pn 19.99%). Gradual mass loss was observed up to 525°C at which point all the pn ligands had been evolved

(exp. 64%, calc. 59.93%). The sulphate proceeded to decompose at temperatures above 525°C.

The DSC trace is more complicated than would be predicted on the basis of the TG. These overlapping endotherms follow a pattern similar to that observed for the bromide and the chloride and may be interpreted in a similar manner. The first group of endotherms from 30 to ~200°C indicate stepwise loss of one pn ligand in half mole steps (ΔH=67.65 kJ mol^{-1}). The endotherm centered at 270°C is most likely associated with a phase change as observed for the bromide salt (ΔH=29.68 kJ mol^{-1}). The energy associated with
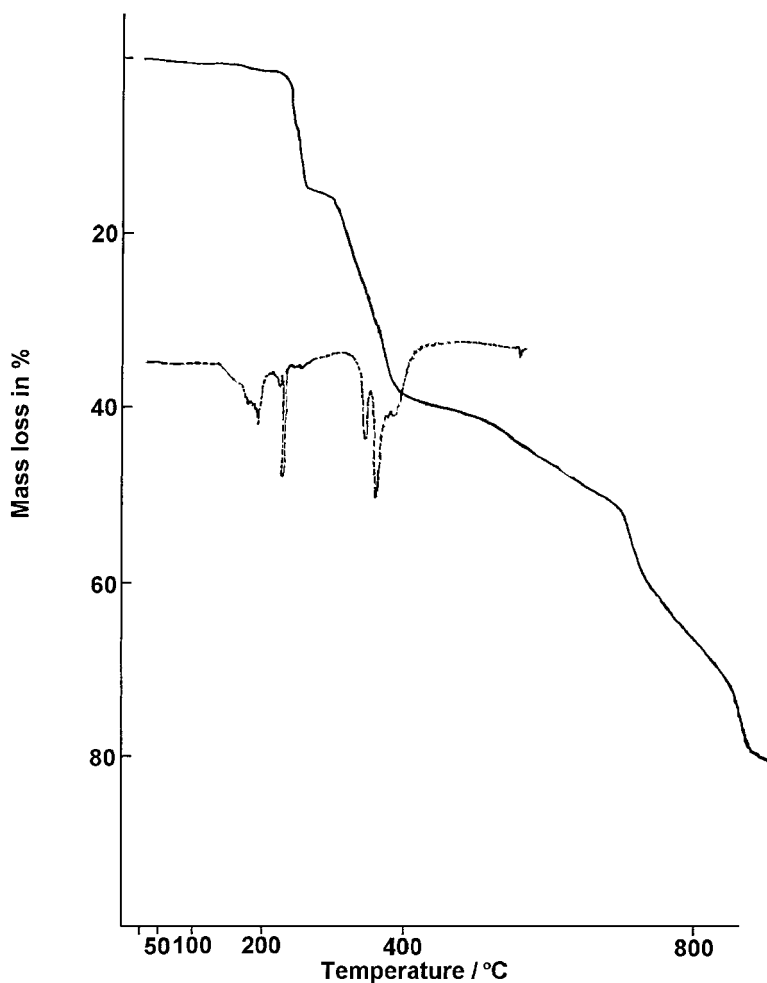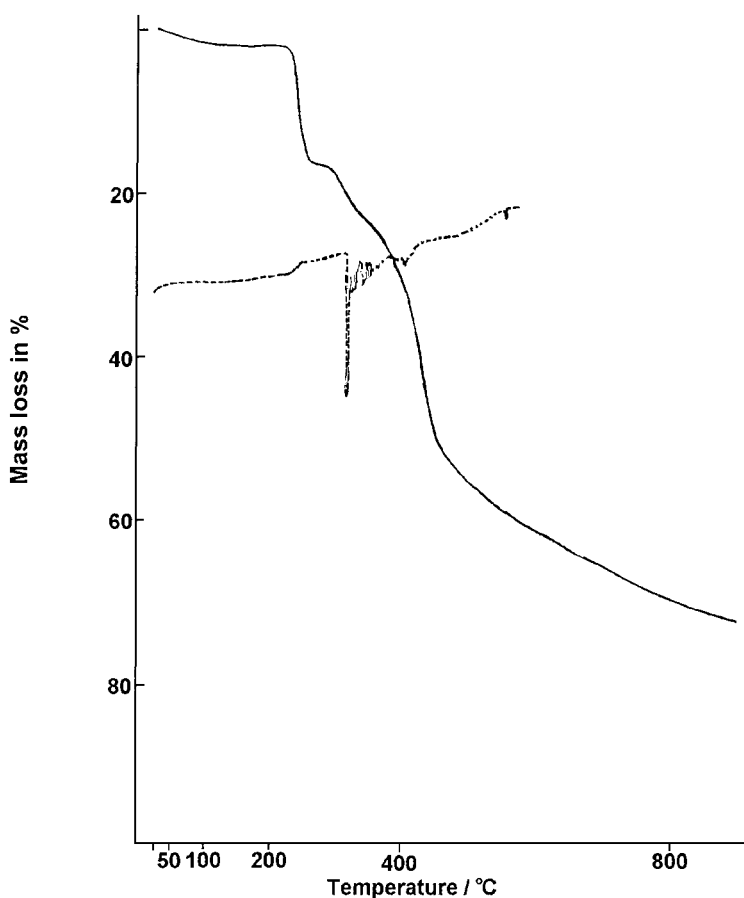
Fig. 5. TG/DSC of Cr(dien)$_2$Br$_2$.

the loss of the remaining pn ligands is determined from the endotherm which stretched to 525°C (ΔH=44.84 kJ mol^{-1}).

The loss of amine ligands in half mole steps as reported for these pn complexes is not unprecedented; it has been reported previously in the case of the decomposition of en-Cr(III) complexes [11] and also the en-Cr(II) complexes [12]. In consideration of the fact that the coordination in the tris(en) and tris(pn) complexes have been found to be similar on the basis of their reflectance spectra [8], a similar decomposition mode is not unexpected, especially since the ethylenediamine and 1,2-diaminopropane ligands themselves are so closely related in structure.

3.2. Diethylenetriamine complexes

Cr(dien)$_2$Cl$_2$: The TG trace for bis-diethylenetriamine chromium(II) chloride (Fig. 4) shows that the complex is thermally well behaved. The complex is stable with relatively no mass loss before 200°C. The complex lost 30.0% of its mass in what appears to be a clean thermal event between 200 and 300°C. This corresponds to the loss of one dien ligand (calc. 31.51%). Between 300 and 600°C the second dien ligand is lost (exp. 63.02%, calc. 63.6%) in two steps. The DSC is reflective of the TG. The first endotherm is clean and sharp (ΔH=76.85 kJ mol^{-1}) while the following events present as two unresolvable endotherms

Fig. 6. TG/DSC of Cr(dien)Cl$_2$.

which are associated with the stepwise loss of the remaining dien ligand (ΔH=109.9 kJ mol^{-1}).

Cr(dien)$_2$Br$_2$: As in the case of the chloride, the bis-diethylenetriamine chromium(II) bromide complex (Fig. 5) was found to be thermally well behaved with relatively well defined steps in its decomposition. The bromide is also comparatively stable with negligible mass loss occurring before 225°C. The sequence of ligand loss, however, appears different in the case of the bromide which occurs in three steps, beginning with the loss of a half dien, followed by one dien and then subsequently the remaining half dien. The first step is observed between 225 and 275°C (exp. 12.8%, calc. 12.4%), the second step between 275 and 400°C (exp. 24.4%, calc. 24.8%) and the last step between 475 and 600°C (exp. 11.2%, calc. 12.4%). Following

the loss of dien the chromium bromide underwent decomposition.

The DSC reflects the observations outlined for the TG. It is interesting to note, however, that the complex does seem to undergo an endothermic phase change below 200°C prior to the loss of the first half dien. The enthalpy change for this step is unfortunately merged with that associated with the first loss of dien ligand (ΔH=148.7 kJ mol^{-1}). The discernible (but again unresolved) endotherms between 300 and 420°C may indicate that the dien is lost in three half-mole steps (ΔH=211.9 kJ mol^{-1}).

Cr(dien)Cl$_2$: The mono-diethylenetriamine chromium(II) chloride (Fig. 6) was also found to be quite stable up to ∼225°C. Between 225 and 260°C the complex appears to have lost about one quarter mole
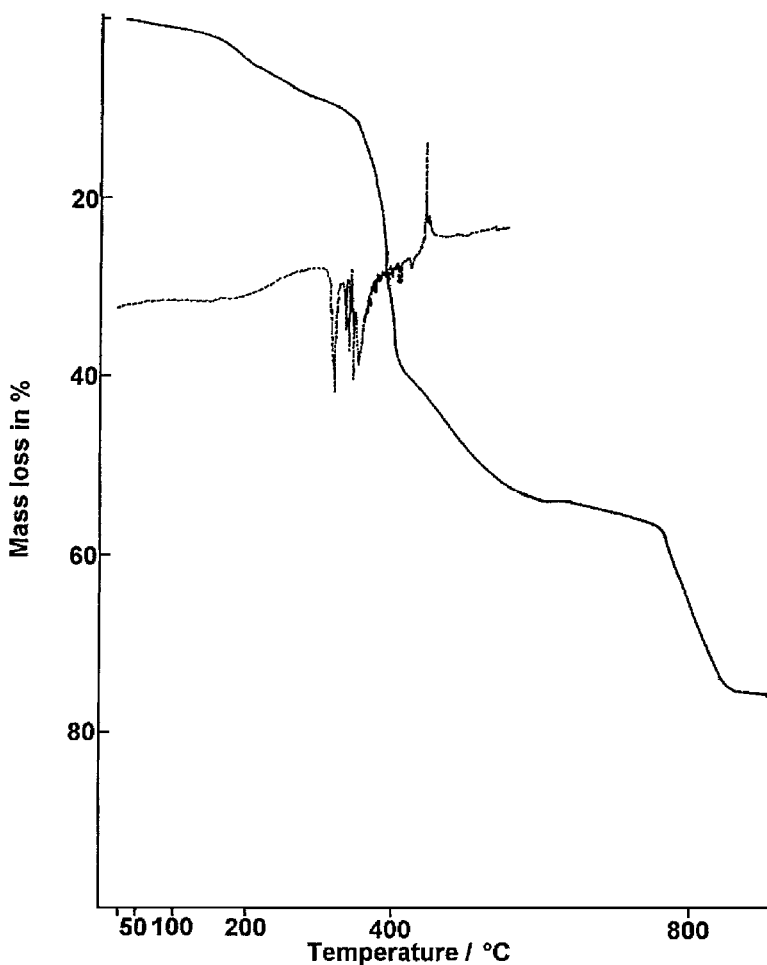
Fig. 7. TG/DSC of Cr(dien)Br$_2$.

dien (exp. 14%, calc. 11.4%). The final half mole was lost between ∼350 and 400°C (exp. total loss 50%, calc. 46%). At higher temperatures CrCl$_2$ decomposes slowly.

It was not possible to calculate the enthalpy change for the first stage of the decomposition. The endothermic absorption between 260 and 450°C gives an overall ΔH for the loss of the remaining dien ligands of 68.99 kJ mol^{-1}.

Cr(dien)Br$_2$: The mono-dien bromide complex (Fig. 7) is also comparatively stable, although less stable than the other dien complexes studied. There is very little mass loss before 175°C. The decomposition follows the pattern observed for the mono-dien chlor-

ide complex in which the ligand was lost in quarter, half and quarter mole amounts in succession (exp. 9.6%, calc. 8.3%; exp. ∼23%, calc. 16.6%; and exp. ∼10%, calc. 8.3%) prior to slow decomposition of the CrBr$_2$. A very sharp exotherm at ∼460°C is likely associated with a phase change just before decomposition.

As in the case of the chloride complex, the enthalpy change for the first stage of the decomposition could not be accurately calculated. In parallel with the bis(dien) bromide complex, there is an endotherm which is not associated with a mass loss which is probably indicative of a phase change (ΔH=40.48 kJ mol^{-1}) prior to the stepwise loss of

the remaining dien (ΔH=141.2 kJ mol^{-1}). The ΔH associated with the sharp exotherm is not reported since its assignment is uncertain.

The bis(dien) complexes of chromium(II) have been shown to have distorted octahedral structures almost identical with those of the tris(en)Cr(II) complexes [7]. The observed loss of ligand in half mole amounts is therefore not unexpected.

On the basis of the reflectance spectra and magnetic behavior, it has been proposed that the mono(dien) complexes have a halide-bridged, binuclear distorted octahedral structure [7]. Such a structure would explain the decomposition of the mono(dien) in quarter mole step losses of ligand and the relatively high stability of these complexes compared to others reported so far.

Acknowledgements

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