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THERMAL STUDIES ON CHROMIUM(II) SALTS

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ABSTRACT

The thermal behaviour of $CrCl_2 \cdot 4H_2O$, $CrBr_2 \cdot 6H_2O$ $CrSO_4 \cdot 4H_2O$, $[Cr(NH_3)_5]Cl_2$, $[Cr(NH)_3]Br_2$, $[Cr(NH_3)_4(OH_2)]SO_4$, $Cr(en)_3Cl_2 \cdot H_2O$, $[Cr(en)_2]Br_2$ and $[Cr(en)_2(OH_2)]SO_4$ was investigated using TG and DSC under nitrogen and helium atmospheres. The thermograms are interpreted and enthalpies of dissociation are calculated where possible.

INTRODUCTION

The thermal behaviour of chromium(III) salts has been extensively studied [1] and continues to be of interest [2]. However, to our knowledge, there have been no systematic studies of chromium(II) salts reported in the literature. Since we have been preparing chromium(II) salts as starting materials for the production of organochromium complexes [3,4], we have initiated investigation into the thermal properties of some of their aqua and amine complexes.

EXPERIMENTAL

Apparatus

Thermogravimetric (TG) and differential scanning calorimetric (DSC) measurements were made in nitrogen and helium atmospheres using a DuPont 910 DSC system and a DuPont 950 TGA system coupled to a DuPont 990 programmer/recorder. 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 10 to 25 mg.

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Samples

Aqueous solutions of chromium(II) salts were prepared by the reaction of electrolytically pure chromium metal (B.D.H.) with deoxygenated solutions of acid (≈ 2 M) [5]. The solutions were concentrated under vacuum until the salts began to precipitate. Precipitated salts were collected under nitrogen in a Schlenk filter, washed with deoxygenated acetone and ether and dried in vacuum at room temperature. The amine complexes were prepared according to the methods of Larkworthy [6,7] and Lux [8]. Their compositions were confirmed by the analysis of chromium as dichromate [9,10].

RESULTS AND DISCUSSION

The TG and DSC curves for the complexes are given in Figs. 1–9.

Aqua complexes

$CrCl_2 \cdot 4H_2O$

The TG curve (Fig. 1) shows that the complex begins to decompose at 45 ° C. Dehydration occurs in two distinct steps. In the first step (45–100 ° C) two H_2O ligands are lost (exp. 18.8%, calc. 18.5%), while in the second step (100–190 ° C) the other two H_2O ligands are lost (exp. 38.4%, calc. 37.0%). The anhydrous $CrCl_2$ subsequently decomposes above 250 ° C.

The first major peak in the DSC curve (Fig. 1) is a fairly sharp one with a shoulder extending from 45–100 ° C, and is associated with the loss of the first two H_2O ligands ($\Delta H_{1,2} = 27.32$ kJ mol^{-1} $CrCl_2 \cdot 4H_2O$). The second major peak (140–165 ° C) is associated with the loss of another two H_2O ligands ($\Delta H_{3,4} = 40.22$ kJ mol^{-1} $CrCl_2 \cdot 2H_2O$). A small endotherm is observed before each of these two large endotherms. Two overlapping endotherms (180–260 ° C) appear to be associated with phase changes ($\Delta H_{p1} = 56.24$ kJ mol^{-1} $CrCl_2$, $\Delta H_{p2} = 61.22$ kJ mol^{-1} $CrCl_2$) rather than decomposition, since further mass loss does not occur until 275 ° C is reached. The endotherm associated with the final decomposition is very broad and shallow.

$CrBr_2 \cdot 6H_2O$

This complex begins to decompose at about 35 ° C (Fig. 2). Two H_2O ligands are lost (exp. 11.4%, calc. 11.26%) in overlapping steps (35–90 ° C and ≈ 75–120 ° C). The remaining four H_2O ligands are lost in another two overlapping steps, (125– ≈ 160 ° C and ≈ 160–210 ° C). The composition of the residue at 160 ° C is approximately that of the bis(aqua) complex (exp. loss 20.6%, calc. 22.25%) and that at 210 ° C is approximately that of the

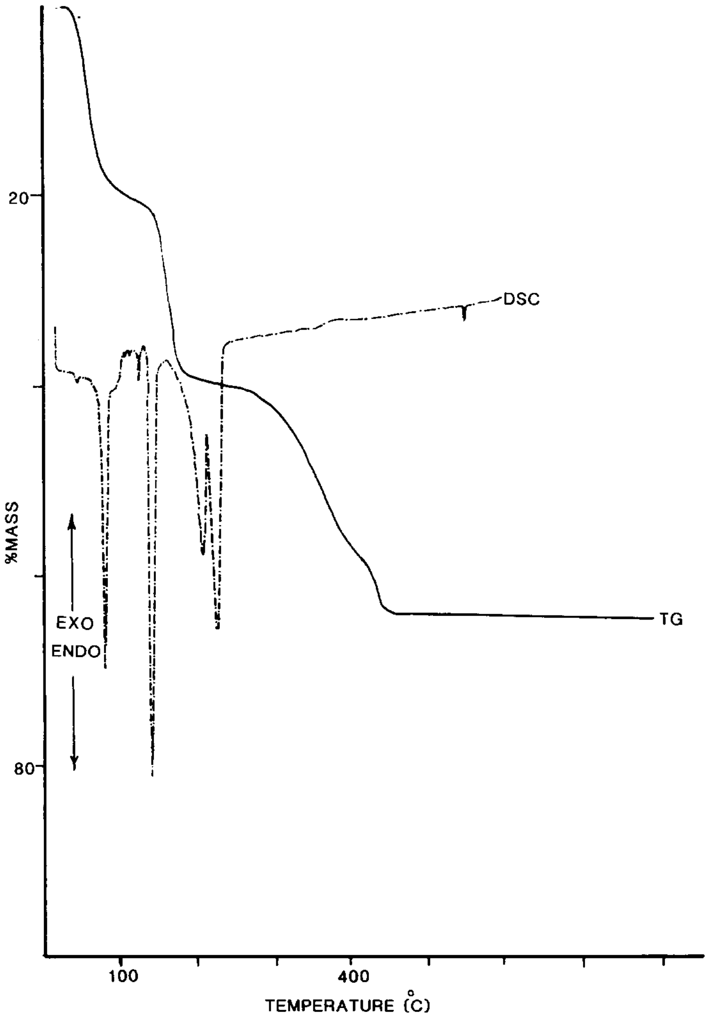

Fig. 1. TG/DSC of $CrCl_2 \cdot 4H_2O$.

anhydrous complex (exp. loss 34.2%, calc. 33.5%). At temperatures above 300 °C the anhydrous salt decomposes.

The DSC peaks (Fig. 2) reflect the overlapping losses described above. The steps involving loss of the first and second ligands are reasonably distinct ($\Delta H_1 = 14.56$ kJ mol^{-1} $CrBr_2 \cdot 6H_2O$, and $\Delta H_2 = 27.38$ kJ mol^{-1} $CrBr_2 \cdot 5H_2O$). The endotherms corresponding to the loss of the third and fourth H_2O ligands cannot be resolved (max. at 143 °C and 150 °C) ($\Delta H_{3,4} = 41.36$ kJ mol^{-1} $CrBr_2 \cdot 4H_2O$) and this is also the case for the final steps in the deaquation ($\Delta H_{5,6} = 10.26$ kJ mol^{-1} $CrBr_2 \cdot 2H_2O$). It is interesting to note that the endotherms associated with the loss of the first, third, fourth and fifth H_2O ligands are very sharp, while those for the second and sixth are comparatively broad. The DSC curve also shows an endotherm ($\approx$ 180–

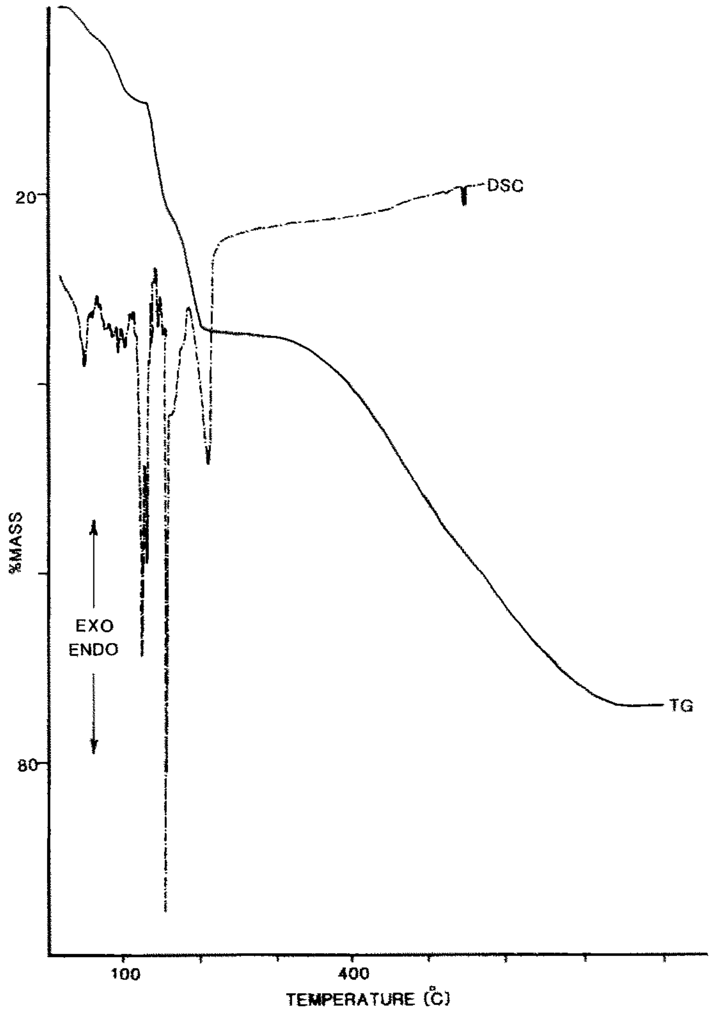

Fig. 2. TG/DSC of $CrBr_2 \cdot 6H_2O$.

250 °C) which does not correspond to any major mass loss and must therefore be associated with a phase change ($\Delta H_p = 17.58$ kJ mol^{-1} $CrBr_2$) in the anhydrous $CrBr_2$ prior to decomposition. Decomposition is accompanied by a broad endotherm ($\approx$ 300–500 °C).

$CrSO_4 \cdot 4H_2O$

Decomposition of this complex begins at 30 °C. Three aqua ligands (exp. loss 23.5%, calc. 24.5%) are lost between 30 °C and 275 °C (Fig. 3). The monoaqua complex decomposes most probably to Cr_2O_3 (exp. loss 66%, calc. 65.5%). The DSC trace (Fig. 3) shows a large endotherm (30–145 °C, $\Delta H_{1,2} = 112.3$ kJ mol^{-1} $CrSO_4 \cdot 4H_2O$) which corresponds to the loss of two aqua ligands (exp. loss at 145 °C 16.8%, calc. for loss of $2H_2O$ 16.37%). The

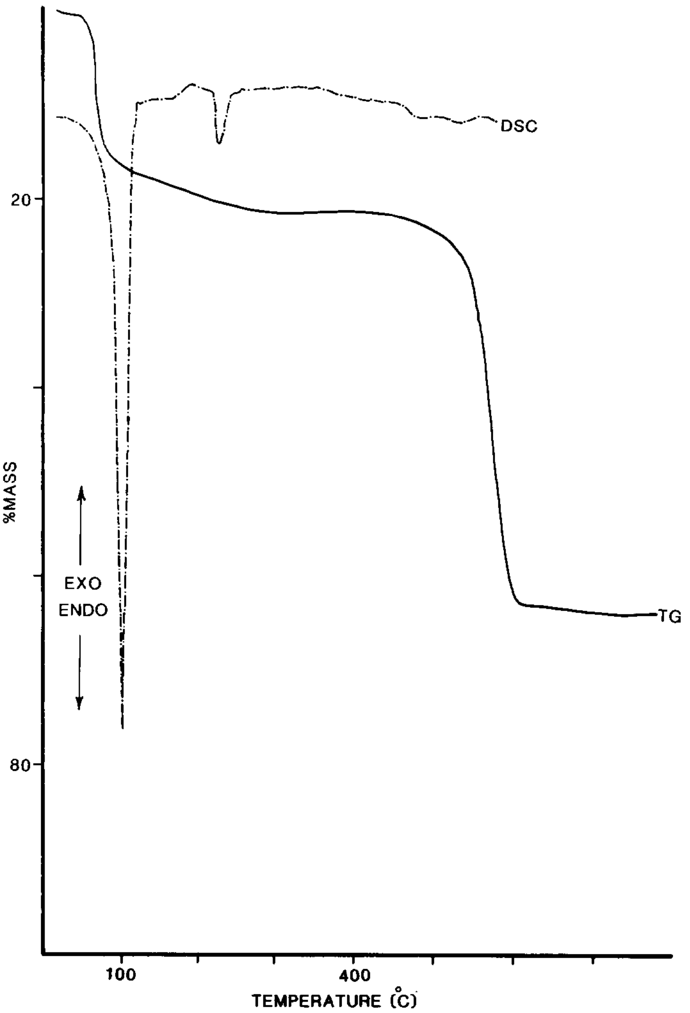

Fig. 3. TG/DSC of $CrSO_4 \cdot 4H_2O$.

loss of the third H_2O is evidenced by a rather broad endotherm (shoulder to ≈ 230 °C). The third endotherm observed up to $\Delta T_{\mathrm{max}} = 265\,^{\circ}\mathrm{C}$ is probably associated with a phase change prior to the decomposition of the monoaqua complex.

Ammine complexes

$[Cr(NH_3)_5]Cl_2$

Deammination and decomposition of this complex were very gradual, beginning at room temperature and continuing in a series of unresolvable steps to 800 °C (Fig. 4). An inflection is observed at ≈ 90 °C corresponding to the loss of one NH_3 (exp. ≈ 8.5%, calc. 8.18%) and another at ≈ 200 °C

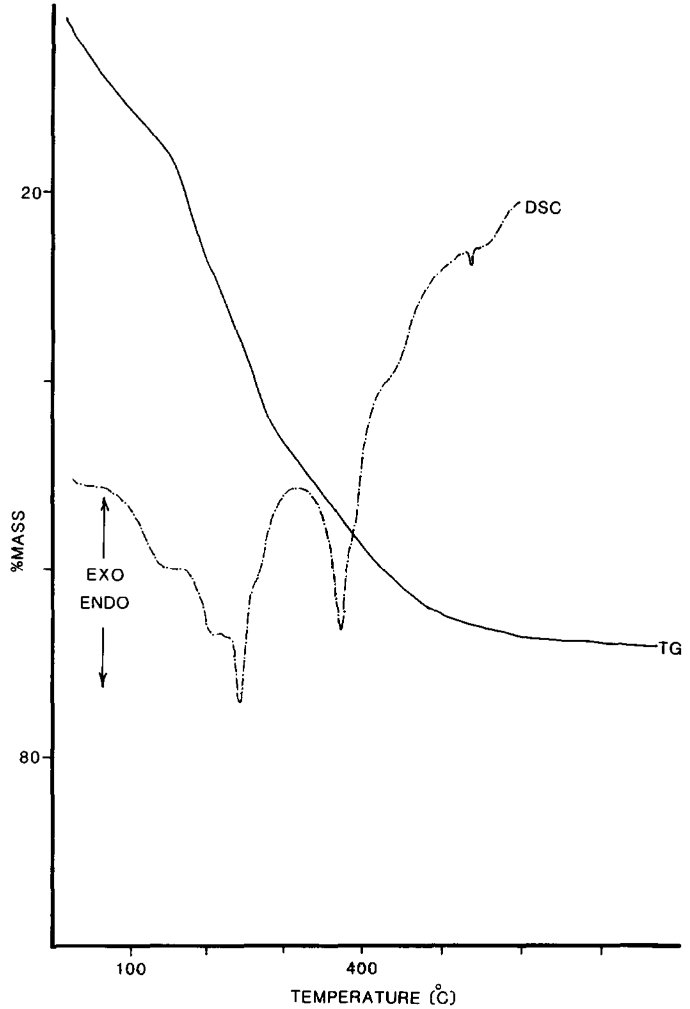

Fig. 4. TG/DSC of $[Cr(NH_3)_5]Cl_2$.

corresponding to the loss of the second and third NH_3 ligands (exp. ≈ 25%, calc. 24.56%) and a third inflection occurs at ≈ 280 °C corresponding to the loss of the fourth and fifth ammine ligands (exp. ≈ 42%, calc. 40.93%).

Spectral and magnetic evidence [8] was reported to lead to the conclusion that the halide ions in the chromium pentaammine halide complexes were not coordinated and that five-coordinate $[Cr(NH_3)_5]^{2+}$ ions were present. These were proposed as having a square pyramidal structure. The diammines were reported as most likely being halide-bridged structures with tetragonal six-coordinate Cr(II) ions present. The thermal decomposition pattern observed in the case of the chloride can be understood in terms of these assignments.

The DSC peaks (Fig. 4) are broad and overlapping, precluding the calculation of enthalpies of decomposition. Maxima appear at ≈ 170, 225, 245 and 262 °C which may be associated with the loss of the second to fifth ligands. There appears to be very little heat involved in the loss of the first ligand. Another thermal event occurs (ΔT_{max} 380 °C) which appears to be associated with the decomposition of the deamminated salt.

$[Cr(NH_3)_5]Br_2$

The bromide complex appears to be slightly more stable initially than the chloride complex; however, the decomposition pattern is not unlike that of the chloride discussed above. This would be expected considering that the two are most probably isomorphs [7]. Deammination begins at ≈ 37 °C (Fig. 5). Loss of the first two ammine ligands occurs in overlapping steps. An inflection is observed at ≈ 80 °C ($-NH_3$ calc. 8.31%, exp. ≈ 7.2%), a short arrest occurs between ≈ 175 and 195 °C ($-2NH_3$ calc. 16.61%, exp. ≈ 14.2%) and the remaining ligands are lost as the bromide decomposes (≈ 200–400 °C) with a short horizontal mass level observed (≈ 335–370 °C) similar to those observed in the decomposition of the corresponding Cr(III) ammine halides [10].

The first thermal event shown in the DSC curve (Fig. 5) is a broad endotherm stretching from ≈ 65–285 °C, which contains two peaks, $\Delta T_{max}(1)$ at 150 °C and $\Delta T_{max}(2)$ at 165 °C. These are most likely associated with the loss of the first two ammine ligands. A third endotherm is observed between 285 and 380 °C with $\Delta T_{max}(3)$ at 310 °C. This is expected to be associated with the loss of the remaining ligands and the decomposition of the salt. The last peak (≈ 380– ≈ 475 °C) is a merger of at least three endotherms: $\Delta T_{max}(4)$ at ≈ 400 °C (shoulder), $\Delta T_{max}(5)$ at 420 °C and $\Delta T_{max}(6)$ at 440 °C.

$[Cr(NH_3)_4(OH_2)]SO_4$

The sulphate, like the chloride, begins to lose ammonia ligands at room temperature. The TG trace is given in Fig. 6. An inflection occurs at a composition of ≈ 20% mass loss (180 °C) which corresponds approximately to the loss of three ammine ligands (calc. 21.81%) or two ammine ligands and one water molecule (calc. 22.24%). A second inflection is observed at ≈ 275 °C which may be associated with the loss of another ammine ligand (exp. ≈ 27%, calc. ≈ 29%). A third inflection (≈ 390 °C) may indicate the loss of part of the remaining water or ammine (exp. 34.4%, calc. for loss of all ammines and water 36.77%) before the salt decomposes. On the basis of magnetic and spectroscopic data, the aqua(tetraamine)Cr(II) sulphate has been proposed as having an essentially square pyramidal structure most probably involving coordinated water [8]. The bis(ammine)Cr(II) sulphate, which was prepared by continuous pumping of $Cr(NH_3)_4(SO_4) \cdot H_2O$ for 1–2 h at 80–90 °C, was said to comprise sulphato-bridged chains of metal

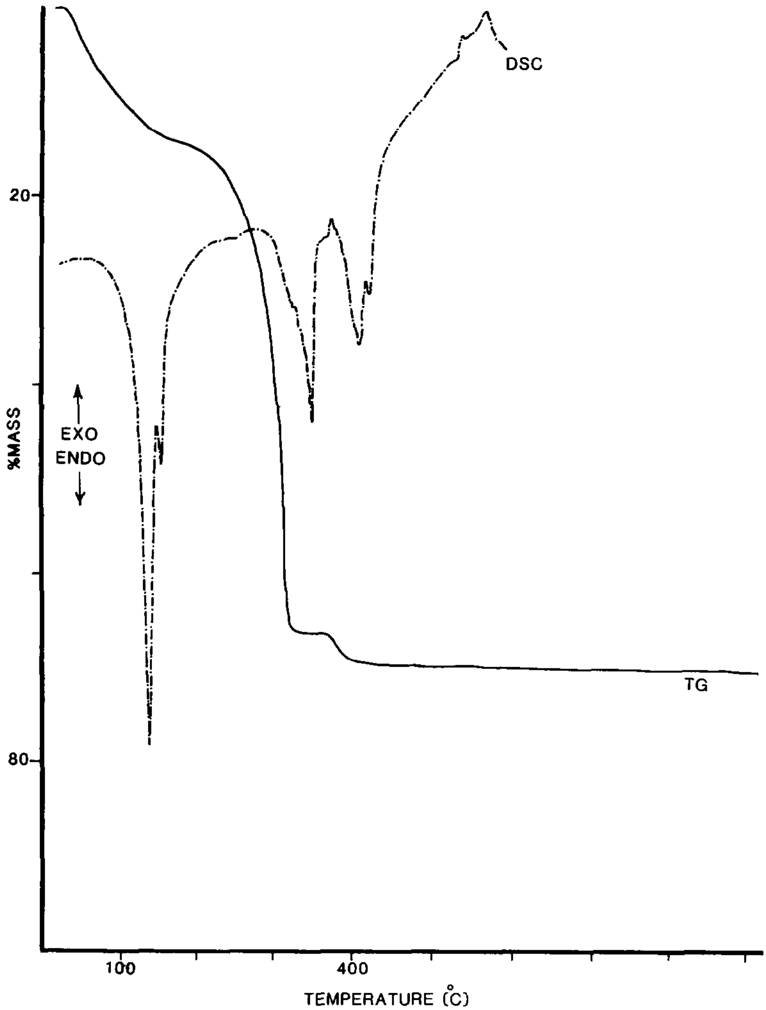

Fig. 5. TG/DSC of $[Cr(NH_3)_5]Br_2$.

ions with axially coordinated ammonia molecules. The thermal behaviour observed in this work is consistent with coordination of aqua and ammine ligands as suggested for the initial complex and sulphate bridging in the partially deamminated complex.

Aqua(ammine)Cr(III) complexes (chloride, bromide, iodide and nitrate) have been studied [12]. The TG studies showed that the H_2O ligand was lost first and the minimum deaquation temperature was taken as a measure of the relative stabilities of these complexes.

The DSC trace reflects the thermal events described above. An endotherm stretching from ≈ 40–165 °C is associated with the loss of three ligands [$\Delta H_{1,2,3} = 97.34$ kJ mol^{-1} $Cr(NH_3)_4SO_4 \cdot H_2O$] while the second endotherm (165 to 275 °C) is probably associated with the loss of the remaining

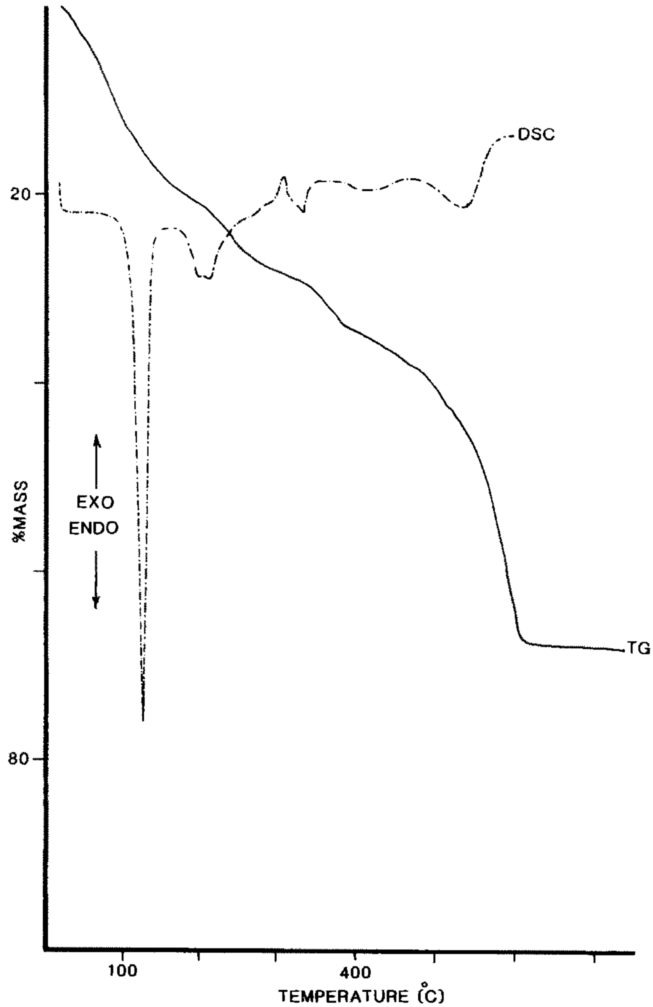

Fig. 6. TG/DSC of [Cr(NH)$_3$)$_4$(OH$_2$)]SO$_4$.

ammine ligand ($\Delta H_4 = 22.33$ kJ mol^{-1} Cr(NH$_3$)SO$_4 \cdot$ H$_2$O]. The loss of part of the water and decomposition of the deaminated complex are evidenced by a broad unsymmetrical endotherm (375–470 °C).

Cr(en)$_3$Cl$_2 \cdot$ H$_2$O

This complex began losing mass at room temperature. The first inflection in the TG curve (Fig. 7) occurs at 40 °C and represents a mass loss of ≈ 2.6%, which may correspond to the loss of a half mole of water (calc. 2.8%), while the second inflection is observed at ≈ 95 °C and could have indicated the loss of a half mole of ethylenediamine (en) per mole of chromium (exp. 10.4%, calc. 12.1%). A short arrest (125–≈ 140 °C) marked the completion of the loss of one mole of en and one mole of H$_2$O (exp.

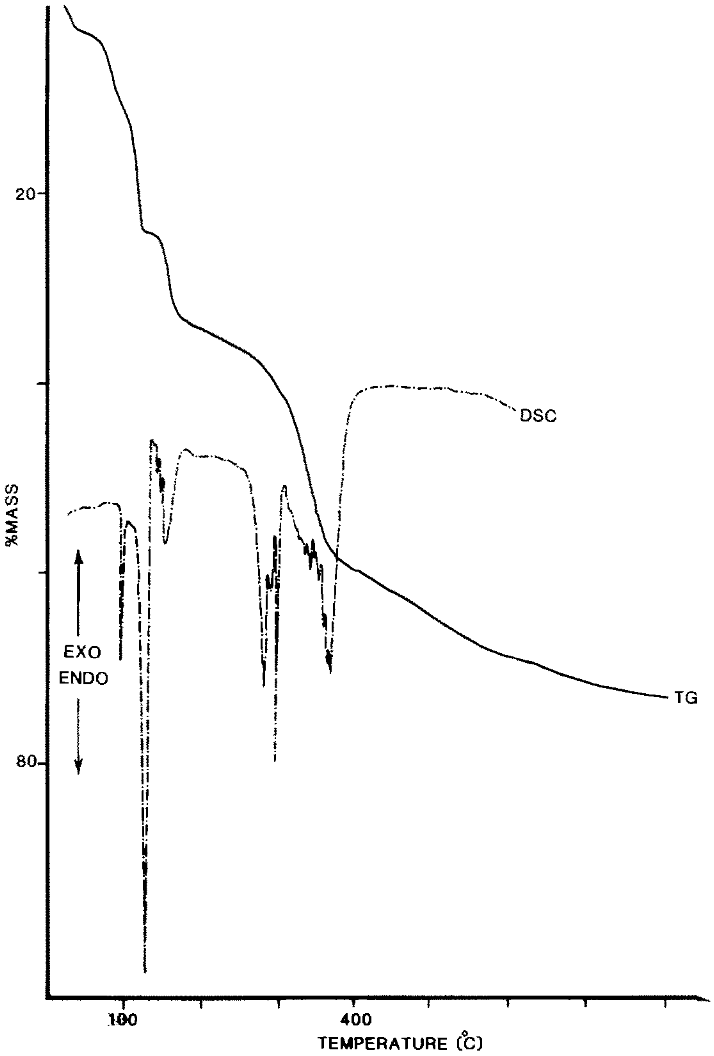

Fig. 7. TG/DSC of Cr(en)$_3$Cl$_2$·H$_2$O.

24.1%, calc. 24.3%). At ≈ 170 °C an inflection was observed which was associated with the loss of another half mole of en per mole of metal (exp. 32.8%, calc. 33.6%). The subsequent mass loss was smooth up to an inflection point at ≈ 385 °C (exp. 59.6%, calc. for loss of 3 moles of en, 1 mole of H_2O 61.73%) after which the decomposition continued gradually. Loss of a half mole of en per mole of metal is not unprecedented; it has been reported previously in the case of the Cr(III) decomposition [12].

The DSC trace (Fig. 7) is comparatively complex. Two broad, shallow endotherms (≈ 25–45 °C and 45–95 °C) appear to be associated with the initial deaquation and deamination steps. Two sharp endotherms (100– ≈ 110 °C and ≈ 110–140 °C) are probably related to the loss of the second half moles of en and H_2O. The endotherm which is observed between 140 °C and ≈ 175 °C corresponds to the loss of half a mole of en. Three overlapping thermal events were then recorded (250–315 °C) which could mark the stepwise loss of the remaining 1.5 moles of en. The last endotherm is evidence of the final decomposition (315–400 °C).

[Cr(en)$_2$]Br$_2$

This complex also began to lose mass just above room temperature (Fig. 8). An inflection at ≈ 365 °C appears to mark the end of the deamination (exp. ≈ 36%, calc. 36.2%) while another inflection at ≈ 600 °C indicates that a residue of CrBr (exp. ≈ 62%, calc. 60.3%) may have been formed.

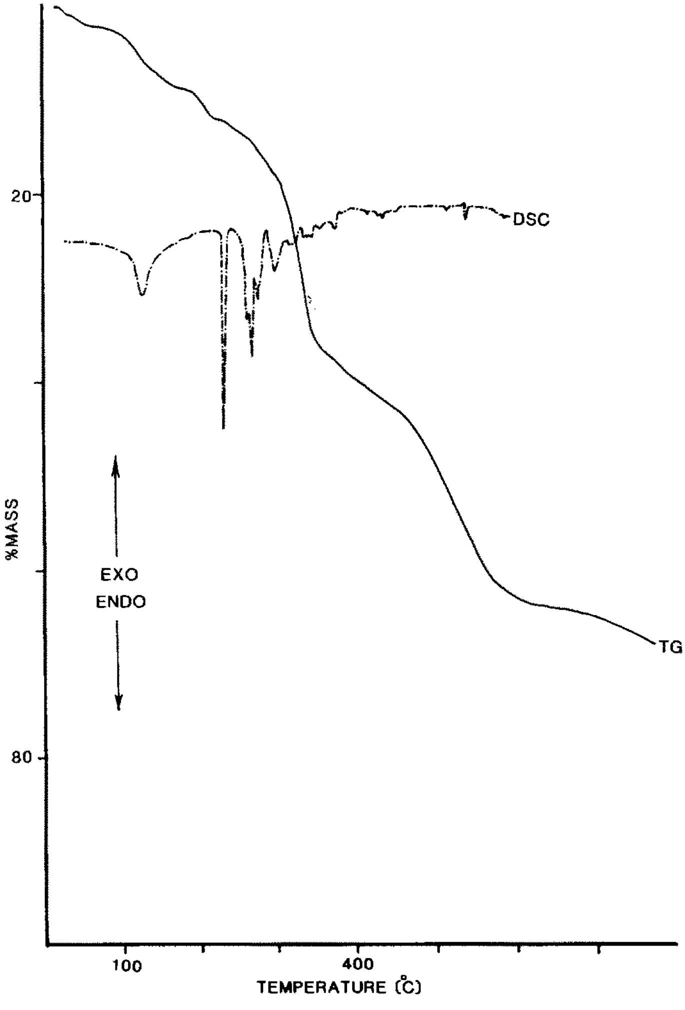

Fig. 8. TG/DSC of [Cr(en)$_2$]Br$_2$.

The DSC curve (Fig. 8) shows a broad endotherm (≈ 50– ≈ 200 °C) which may be associated with the loss of 0.5 mole of en, since the TG curve does show a slight inflection at ≈ 200 °C (exp. ≈ 8.8%, calc. 9.05%). A single sharp peak occurs between 245 °C and 255 °C but there is no indication of an arrest in the TGA trace, nor can the mass loss (exp. ≈ 12%) in this temperature range be associated with any integral or half integral loss of en. Therefore, this thermal event is perhaps indicative of a phase change. The suggestion of a phase change at this point is also supported by the fact that the endotherm is sharp. The next thermal event comprises a series of endotherms (≈ 255–300 °C and 300–500 °C) which are similar to those observed for the chloride complex (250–315 °C and 315–400 °C). These could therefore be interpreted in a like manner.

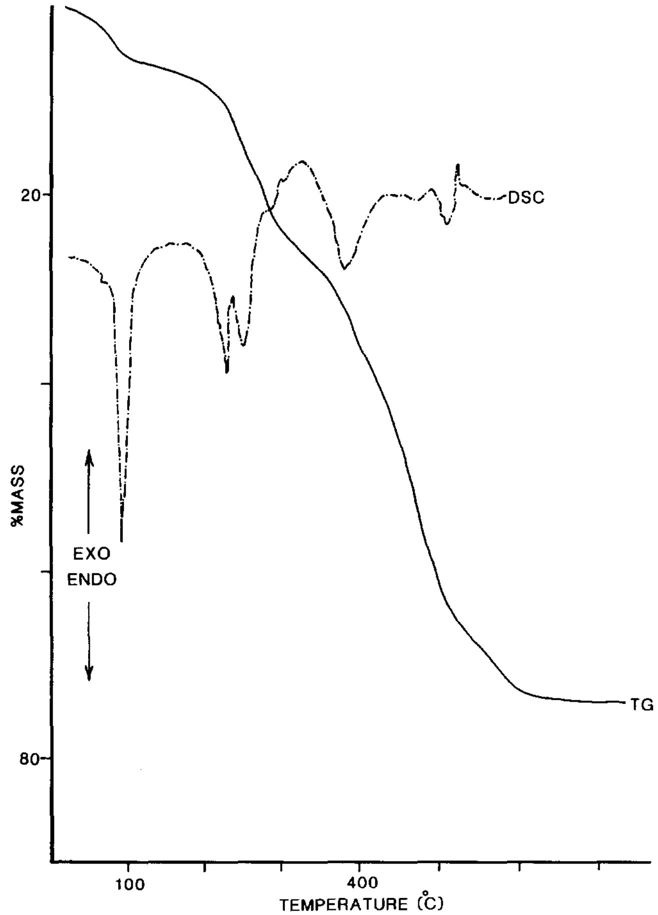

Fig. 9. TG/DSC of $[Cr(en)_2(OH_2)]SO_4$.

$[Cr(en)_2(OH_2)]SO_4$

Dehydration of this complex occurs between 35 °C and 150 °C (Fig. 9) in a single step. (exp. 6.4%, calc. 6.31%). Deamination follows the dehydration in a series of overlapping steps merging with the decomposition steps. These steps may be distinguished with the aid of the DSC curve (Fig. 9), which shows two overlapping endotherms ($\approx 170-\approx 350$ °C) each of which is probably associated with the loss of 0.5 mole of en. The TG trace shows a mass loss of 26.8% at 350 °C which correlates with the total loss of one mole each of water and en, calculated to be 27.38%. The thermal event which follows ($\approx 350-\approx 450$ °C) corresponds roughly to the loss of the second en ligand (exp. 44%, calc. 48.45%). The sulphate decomposes above 450 °C.

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