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Thermal decomposition of ammonium bis-oxalatodiaquaindate(III)

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Abstract

Indium(III) was precipitated with oxalic acid in the presence of ammonium nitrate maintaining an over all concentration of 0.125 M in HNO_3. The chemical analysis of the complex salt obtained corresponded with the formula, $NH_4[In(C_2O_4)_2]\cdot 2H_2O$. Thermal decomposition studies of the complex indicated the formation of intermediates: ammonium indium oxalate and indium(III) oxalate and the final product to be indium(III) oxide. The isothermal decomposition, infrared absorption spectra, and X-ray diffraction patterns have been used to characterise the complex and the intermediate product of thermal decomposition.

Keywords: Thermal analysis; Bis-oxalates; Indium(III); Ammonium salt; X-ray diffraction; IR data

1. Introduction

A review on the thermal decomposition of some solid oxalates has been given by Krishna Murthy and Harris [1]. The oxalate ion was used in the automatic thermogravimetric analysis of various metals [2]. Differential thermal analysis of various metal oxalates under controlled atmospheres have been reported by Dollimore and Griffiths [3] and the decomposition of simple oxalates as well as the complex oxalates of various metals by Dollimore and co-workers [4–15]. Wendlandt [16] has reviewed the thermal analysis of some metal oxalates.

The thermal decomposition of metal oxalate complexes of the type $K[M(C_2O_4)_3]\cdot 3H_2O$ (where M = Co, Cr, Fe, Al and Ga) and *cis*-$K[Cr(C_2O_4)_2\cdot(H_2O)_2]\cdot 2H_2O$ complex have been studied [17] by TGA and DTA and Rao has reviewed the thermal decomposition of various thallium oxalates [18].

Systems consisting of an indium salt and the ammonium oxalates [19,20], as well as potassium and caesium [21] have been examined and the formation of two types of compounds, $InOHC_2O_4$ and $M[In(C_2O_4)_2]$, where $M = NH_4^+$, K^+ and Cs^+ established. The ammonium bis-oxalatodiaquaindate(III) complex was prepared by reaction of indium(III) with oxalic acid in the presence of ammonium ion. The thermal decomposition of the complex has been studied and a detailed account of the mechanism worked out on the basis of the thermal data, infrared spectroscopic and X-ray diffraction studies.

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2. Experimental

2.1. Instrumentation

2.1.1. Thermal analysis unit

A SEIKO combined (TG/DTA-32), temperature programmable thermal balance (made in Japan) and a platinum crucible container was used for taking thermograms in air. The rate of heating was fixed at 10°C min^{-1}, and sensitivity of the instrument is 0.1 mg.

2.1.2. Infrared spectra

The infrared spectra of the complexes were recorded on SHIMADZU FTIR-8201 PC Infrared Spectrophotometer using KBr pellets.

2.1.3. X-ray diffraction data

A RICH SEIFERT & Co. (made in Germany) X-ray diffractometer attached to a microprocessor was used to take X-ray diffraction patterns using a wave length of Cu $K\alpha_1$ of 1.540598 Å.

2.2. Preparation and analysis

The ammonium bis-oxalatodiaquaindate(III) complex salt was prepared by adopting the following procedure: about 80 cm^3 of 0.05 M indium(III) nitrate in 0.625 M HNO_3 was added to a 500 cm^3 beaker to which about 60 cm^3 1 M ammonium nitrate and 180 cm^3 triple distilled water were added slowly while stirring the contents. About 80 cm^3, 0.1 M oxalic acid was added slowly (drop wise from a burette) while stirring the contents vigorously. The complex salt formed was allowed to settle and filtered through a G_4 sintered glass crucible. The precipitate was washed several times (with a solution obtained by mixing 0.3 M NH_4NO_3 and 0.25 M HNO_3 in 1:1 ratio) to free the excess oxalic acid. Finally the precipitate was washed free from NH_4NO_3 with 0.1 M HNO_3. The precipitate was dried in a vacuum desiccator over silica gel. The compound was tested to confirm the absence of nitrate.

The bis-oxalato complex was isolated from the sulphate medium (containing 0.0625 M H_2SO_4 and 0.05 M $(NH_4)_2SO_4$) and purified following the procedure similar to that adopted in a nitrate medium.

The compound was analysed for indium, oxalate and water content. Indium(III) was estimated complexometrically using 1-(2-pyridyalazo)-2-naphthol (PAN) as an indicator [22] and oxalate by volumetric titration with standardised cerium(IV) sulphate solution [23]. Water content was determined by difference and from thermal data. The results of the analyses are shown in Table 1.

3. Results and discussion

3.1. Thermal studies

3.1.1. Thermogravimetric analysis

The pyrolysis curve of ammonium bis-oxalatodiaquaindate(III) and the data obtained are shown in Fig. 1 and Table 2, respectively. The weight loss, on heating from 100 to 220°C, was 10.47% compared with the calculated value of 10.43% corresponds to the dehydration of the complex salt giving anhydrous ammonium indium oxalate. On further heating, the compound lost ammonium oxalate from 220 to

Table 1
Chemical analysis data of ammonium bis-oxalatodiaquaindate(III) (wt.%)

Methods of preparation	Composition percent			Total water	Ratio $C_2O_4^{2-}/In^{3+}$	Possible formula
	In^{3+}	$C_2O_4^{2-}$	NH_4^+			
Moeller [20]	33.25	50.77	5.07[a]	10.91[a]	1.99	$NH_4In(C_2O_4)_2{\cdot}2H_2O$
Deicman [19]	–	–	–	–	–	$NH_4In(C_2O_4)_2{\cdot}3H_2O$
Present work	33.19	51.55	5.20[a]	10.07[a]	2.03	$NH_4In(C_2O_4)_2{\cdot}2H_2O$
Calculated	33.28	51.04	5.23	10.43	2.00	$NH_4In(C_2O_4)_2{\cdot}2H_2O$

[a] Calculated from the formula.

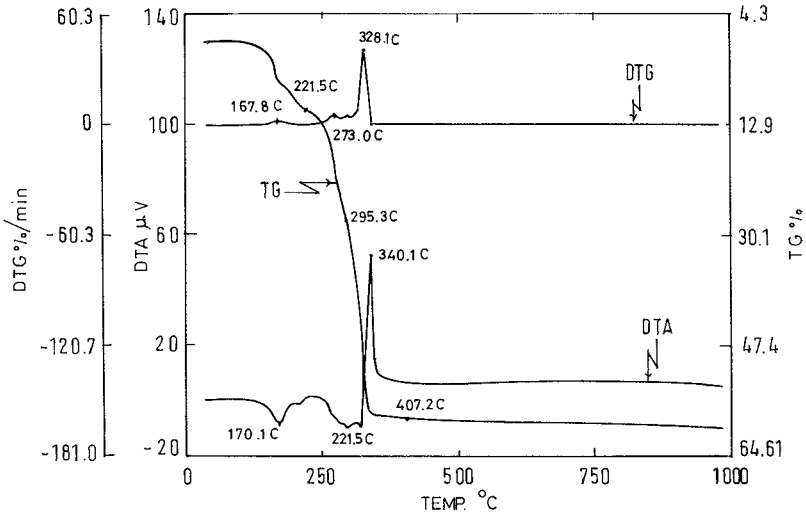

Fig. 1. TG/DTA curve of ammonium bis-oxalatodiaquaindate(III).

295.3°C leaving indium oxalate. The final stage in the decomposition of the complex was marked by a smooth and continuous weight loss in the TG curve over the range 295–407°C. This was 58.85% (ca. 59.71%). This corresponded with the decarboxylation of the indium(III) oxalate to give indium(III) oxide.

3.1.2. Differential thermogravimetric analysis

The DTG results obtained for ammonium bis-oxalatodiaquaindate(III) are given in Fig. 1. From the figure it is clear that there are three temperature ranges in which the complex lost weight. A very small peak in the DTG curve with a maximum at 167.8°C was attributed to the loss of co-ordinated water. A small peak with maximum observed at 273.0°C represented the loss of ammonium oxalate from the anhydrous salt. The strong and sharp DTG peak with maximum at 329.1°C shows the high rate of decomposition of the resulting indium(III) oxalate up to the final product, indium(III) oxide.

3.1.3. Differential thermal analysis

DTA of the complex are also shown in Fig. 1. From the figure it was clear that the dehydration of ammonium bis-oxalatodiaquaindate(III) complex produced an endotherm at 170.1°C. Whereas the decomposition of the anhydrous product, ammonium bis-oxalatoindate(III) gave indium oxalate as indicated by a broader peak with ΔT_{min} at around 295.3°C. A sharp exotherm with a ΔT_{max} at 340.1°C corresponded to the decomposition of indium(III) oxalate to the final product, In_2O_3.

The shift in the maxima and minima of the DTA endotherms to the higher temperatures compared to the DTG peaks was quite obvious as the DTA was based on the heat changes in the system which sub-

Table 2
Summary of the thermal decomposition of the ammonium salt

Weight of the compound	Step number	Temperature (°C)		Loss in weight (%)		Possible decomposition product (intermediate)
		Starting	Ending	Observed	Calculated	
9.80 mg	1	100	220	10.47	10.43	$NH_4In(C_2O_4)_2$
	2	220	295	27.98	28.41	$In_2(C_2O_4)_3$
	3	295	407	58.85	59.71	In_2O_3

sequently accompanies the weight losses. The shift in the values also depended on the heating rate.

3.1.4. Isothermal decomposition of the complex

In studying the thermal decomposition pattern of the ammonium bis-oxalatoindate(III) complex, a known weight (ca. 200 mg) of the salt was taken in a dry and weighed porcelain crucible and heated to about 205°C (based on the TG/DTA curves in Fig. 1) and the sample was maintained at this temperature for 30 min. The decomposition may be given by the equation

$$(NH_4)[In(C_2O_4)_2] \cdot nH_2O \overset{30-205^{\circ}C}{\rightarrow} NH_4In(C_2O_4)_2 + nH_2O$$

The product so obtained in this manner was analysed following the established procedures [22,23]. The $C_2O_4^{2-}$ to In^{3+} ratio was found to be 2:1. Thus, the possible formula of the intermediate is $NH_4In(C_2O_4)_2$ and this is in conformity with the TG/DTA analyses as described earlier.

The water content of the complex was computed from the weight loss data. Accordingly, the possible formula of the original complex is $(NH_4)[In(C_2O_4)_2]\cdot 2H_2O$ $(NH_4)[In(C_2O_4)_2(H_2O)_2]$.

3.2. Infrared spectra of ammonium bis-oxalatoindate(III)

Infrared spectra of ammonium bis-oxalatoindate(III) is shown in Fig. 2. A very strong absorption at 3506 cm^{-1} and a shoulder at 3460 cm^{-1} correspond to asymmetric and symmetric stretching modes of vibration of water [24]. A very broad and strong absorption at 3208 cm^{-1} and a broad absorption at 3050 cm^{-1} correspond to the stretching modes of vibration of N–H of ammonium ion [25]. A very broad and very strong absorption at 1614 cm^{-1} may be due to bending vibrations of H–O–H [26] and asymmetric stretching vibrations of C=O [27]. A very sharp and very strong absorption at 807 cm^{-1} may be due to bending vibrations of O–C=O [27] and M–O stretching vibration of co-ordinated water [27].

The IR absorption band of the complex at 500 cm^{-1} which is assigned in the simple salts of oxalic acid to bending vibrations of O–C=O [27] was indicative of the bonding between the metal ion, indium(III) and the oxygen of the oxalate ligand.

Studies on the thermal decomposition of the complex indicated the formation of two intermediates, one at about 220°C and the other at about 300°C. These two products correspond to the empirical formulae $NH_4In(C_2O_4)_2$ and $In_2(C_2O_4)_3$, respectively. The infrared spectrum of the complex was taken after heating at 205°C and on cooling to room temperature. This spectrum is shown in Fig. 3. The results are compared with the original complex and are listed in Table 3. It appears from Fig. 3 that the product after heating at 205°C and cooling contains water as indicated by the absorptions at about 3550, 3470 and 1650 cm^{-1}. But such water is not expected normally for the product obtained by heating at such an elevated temperature (205°C). The authors are of the opinion that the anhydrous ammonium indium oxalate partially absorbs moisture when exposed to the atmosphere. It may be noted that the presence of the absorption bands at around 3100 cm^{-1} in the infrared

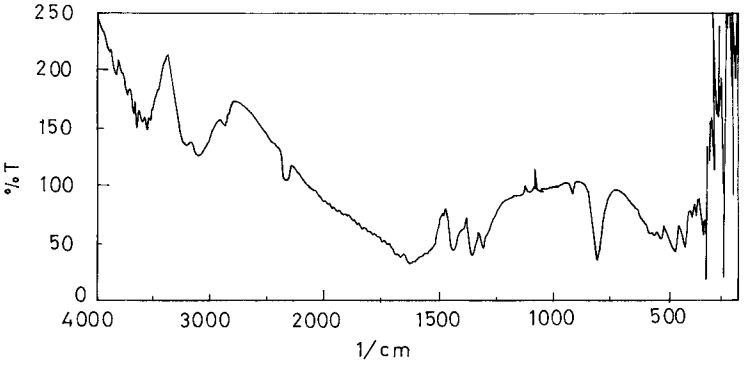

Fig. 2. Infrared spectrum of ammonium bis-oxalatodiaquaindate(III).

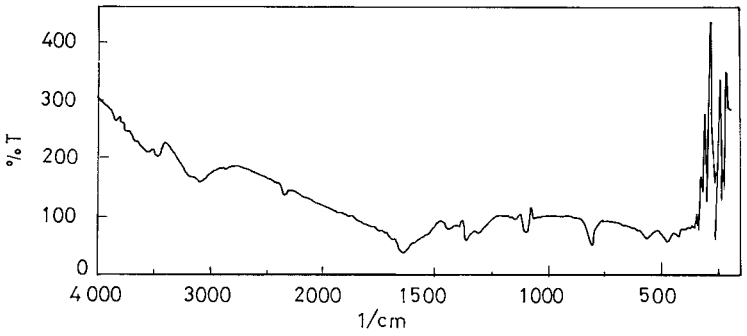

Fig. 3. Infrared spectrum of ammonium bis-oxalatodiaquaindate(III) after heating at 205°C.

spectra of the heated product (Fig. 3) suggests the existence of NH_4^+ in the intermediate. The intermediate at 300°C could not be isolated as the loss of $(NH_4)_2C_2O_4$ is immediately followed by the decomposition of $In_2(C_2O_4)_3$.

3.3. X-ray diffraction data

The X-ray diffraction data of ammonium bis-oxalatoindate(III) and that of the product obtained after heating the original complex to 205°C and cooling are

Table 3
Infrared absorption data of ammonium bis-oxalatoindate(III) and the heated product at 205°C[a]

Complex		Band assignment
Original	Heated at 205°C	
3506 b, s	3550 m	
3460 sh	3470 sh	$\nu_{as,s}$ (H–O–H)
3208 vb, vs	3100 vb	ν(N–H)
1614 vb	1650 b	ν_a(C=O) + δ(H–O–H)
1450 m	1400 m	
1350 m	1350 m	ν_s(C=O) + δ(O–C=O)
1300 sh	1300 sh	
	1100 m	
910 sp, w		
807 sp, vs	807 m	Coordinated water & δ(O–C=O) + ν(M–O)
550 sh	550 sh	
480 m	460 w	ν(M–O) + δ(O–C=O)
400 m	420 sh	
350 w		δ(O–C=O) + ν(C–C)

[a] b: Broad, m: medium, s: strong, sp: sharp, sh: shoulder, w: weak.

Table 4
X-ray diffraction data of ammonium bis-oxalatoindate(III) and the product after heating it to 205°C, compared with indium(III) oxalate and ammonium oxalate monohydrate

NH_4^+ complex	Complex heated to 205°C	$In_2(C_2O_4)_3$	$(NH_4)_2C_2O_4 \cdot H_2O$
7.701_1	8.504_8		
6.364_x	6.406_x	5.671_3	6.320_9
4.550_2		5.515_x	4.380_7
4.161_1	4.064_8	5.357_1	
3.888_1		5.092_2	
		5.035_2	
3.511_2	3.560_7	4.794_1	3.256_6
		4.648_1	
2.848_2		4.026_2	
2.705_3		3.921_2	2.666_x
		3.807_3	
		3.677_2	
2.361_1		3.555_2	
2.251_1	2.135_6	3.306_1	2.142_3
		3.231_2	
2.040_1	2.052_5	3.143_1	2.041_1
2.021_1		3.050_4	2.008_2
1.951_1		3.001_2	
1.934_1		2.773_1	
1.795_1		2.740_2	
1.770_1		2.529_2	1.870_6
1.685_1		2.431_2	
		2.334_2	1.750_2
		2.218_1	
		2.168_1	
		2.134_1	1.696_2
		2.005_2	1.668_2
		1.952_1	
	1.460_4	1.937_2	
		1.840_1	
		1.779_2	
		1.693_1	
		1.529_1	

given in Table 4 along with those of indium(III) oxalate and ammonium oxalate for comparison.

The data in the table clearly show that the heated product obtained at 205°C is not a mixture of ammonium and indium oxalates.

The complex was also heated to 500°C and maintained at this temperature for 30 min and the product tested for the presence of carbonate by the usual acid test. This indicated the absence of carbonate in the product.

Based on these results, the following thermal decomposition mechanism is proposed as

$$2NH_4[In(C_2O_4)_2(H_2O)_2] \overset{100-220^\circ C}{\rightarrow}$$

$$2NH_4In(C_2O_4)_2 \overset{220-295^\circ C}{\rightarrow} In_2(C_2O_4)_3 \overset{295-407^\circ C}{\rightarrow} In_2O_3$$

Overall

$$2NH_4[In(C_2O_4)_2(H_2O)_2] \rightarrow In_2O_3 + (NH_4)_2C_2O_4 + 3CO + 3CO_2 + 4H_2O$$

The proposed mechanism suggests the most probable structural formula of the complex with octahedral coordination of indium(III) as $(NH_4)[In(C_2O_4)_2(H_2O)_2]$.

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