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Some studies on thallium oxalates XIV. Indium(III) bis-oxalatodiaquathallate(III) hexahydrate

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Abstract

Thallium(III) was precipitated with oxalic acid in the presence of 0.01 M $In(NO_3)_3$ in 0.125 M HNO_3. Chemical analysis of the solid obtained corresponds to the formula $In[Tl(C_2O_4)_2]_3{\cdot}12H_2O$. Thermal studies (TG, DTG and DTA) indicated the dehydration and redox decomposition of the thallic salt to the thallous salt and finally to a mixture of indium(III) and thallium(III) oxides. The latter, however, volatilised leaving indium(III) oxide as residue. Infrared absorption spectra and X-ray diffraction data were used to characterise the original salt, as well as the intermediate formed during its thermal decomposition. On the basis of these results, the compound may be represented as $In^{3+}[Tl(C_2O_4)_2(H_2O)_2]_3{\cdot}6H_2O$.
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Keywords: Thermal analysis; Bis-oxalates; Thallium(III); Indium(III) salt; X-ray diffraction; IR data

1. Introduction

The formation of bis-oxalatothallate(III) ion is reported by earlier workers [1–4]. Sagi and coworkers [5–8] have reported that the presence of suitable concentrations of some monovalent or divalent metal ions in the potentiometric titration of thallium(III) with oxalic acid could in effect alter the metal–ligand ratio from 1:1.5 to 1:2 and also utilised UV spectral [9] and potentiometric [5] studies to know the complexation in solution and to find out the conditions for the isolation of thallium(III) bis-oxalatothallate(III) complex in solid state [10]. The thermal decomposition mechanisms of the complexes are reported and these studies are reviewed by Prasada Rao [11]. The present paper deals with the study of an analogous bis-oxalatothallate(III) salt of indium(III). The solid is isolated and characterised using thermal, IR and X-ray diffraction studies and chemical analysis. On the basis of the above data, a plausible mechanism for the thermal decomposition of the complex is proposed.

2. Experimental

2.1. Instrumentation

Thermal analysis unit. SEIKO-combined thermal analysis system (TG/DTA-32), temperature-programmable thermal balance made in Japan and platinum crucible as container are used for taking thermograms in air. The rate of heating is fixed to 10 °C/min, and sensitivity of the instrument is 0.1 mg.

Infrared spectra. The infrared spectra of the complexes homogenised in KBr pellets are recorded on

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SHIMADZU FTIR-8201 PC Infrared Spectrophotometer.

X-ray diffraction data. X-ray diffractometer of RICH SEIFERT (made in Germany) attached to a microprocessor is used for taking X-ray diffraction patterns at wavelength of Cu Kα1 = 1.540598 Å.

2.2. Preparation and analysis

About 40 cm^3 of 0.05 M indium(III) nitrate is taken in a 400 cm^3 beaker to which 20 cm^3 of 0.155 M thallium(III) nitrate in 1 M nitric acid and 100 cm^3 of triple-distilled water are added slowly while stirring the contents. Then about 40 cm^3 of 0.1 M oxalic acid is added drop-wise from a burette while stirring the contents vigorously. The precipitate so formed is allowed to settle and filtered through a G4 sintered glass crucible, and washed first with 0.1 M HNO_3 followed by distilled water to free it from excess oxalic acid and nitrate. The precipitate so obtained is then dried over silica gel in a vacuum desiccator and analysed for its contents.

The thallium and oxalate contents of the complex and the intermediate product of the decomposition are determined by the methods developed by Sagi et al. [9,12]. The indium(III) content is determined complexometrically using 1-(2-pyridyalazo)-2-naphthol (PAN) as indicator [13]. The water content of the sample is computed by the difference. Based on the results, the molecular formula of the complex may be given as $In^{3+}[Tl^{III}(C_2O_4)_2]_3{\cdot}12H_2O$ and the composition of the complex as indicated in Table 1.

3. Results and discussion

3.1. Thermal analysis

3.1.1. Thermogravimetric analysis (TGA)

The thermogram of indium(III) bis-oxalatodiaquathallate(III) hexahydrate and the data obtained from it are given in Fig. 1 and Table 2, respectively. The TG curve shows that the loss of crystal water may take place below 90 °C and this accounts for ca. 7.34% weight loss of the complex. The steepness in the curve between ∼90 and 138.5 °C indicates a significant weight loss which may be attributed to the simultaneous dehydration and redox decomposition of the complex. It is expected that up to about 100 °C the complex loses all its coordinated water. The observed loss of 13.79% at 99.5 °C against the calculated value of 14.68% supports the proposal.

The anhydrous intermediate product, indium(III) bis-oxalatothallate(III), $In^{3+}[Tl^{III}(C_2O_4)_2]_3$, is assumed to be thermally unstable, as it was already established for similar complex [10], and hence, undergoes redox decomposition in the above temperature range to give indium(III) thallous oxalate, $In^{3+}[Tl^{I}C_2O_4]_3$. The observed weight loss of 34.8% (at 138.5 °C) against the calculated 32.6% confirms this. The intermediate remains stable up to about 290 °C. During the next stage between 290 and 312 °C, the indium(III) thallousoxalate breaks down to thallous and indium(III) oxalates and almost immediately the latter decomposes to In_2O_3. The change in the slope of the TG curve between 312 and 360 °C indicates that the decomposition of $Tl_2C_2O_4$ to Tl_2O. Tl_2O then slowly gets oxidised to Tl_2O_3 up to about 600 °C which on further heating volatilises. The formation of the mixture of Tl_2O and In_2O_3 at the first instance may be confirmed from the weight loss of 46.98% at 360 °C against the calculated value of 47.31%.

The thermal decomposition pattern of this complex is basically the same as that of the thallic bis-oxalatothallate(III) which was reported by Sagi et al. [10]. Thus, the mechanism of the thermal decomposition can be described by the same analogy.

3.1.2. Differential thermogravimetric analysis (DTG)

The DTG data of indium(III) bis-oxalatodiaquathallate(III) is shown in Fig. 1. From the figure, it is

Table 1
Chemical analysis data of indium(III) bis-oxalatothallate(III)

Complex (mg)	Composition			Total H_2O (mg)	Ratio of Tl^{3+}:Ox^{2-}	Probable formula (number of water molecules)
	Tl^{3+} (mg)	Ox^{2-} (mg)	In^{3+} (mg)			
105	41.85	36.04	7.65	14.26	∼1:2	$In[Tl(C_2O_4)_2(H_2O)_2]_3{\cdot}6H_2O$

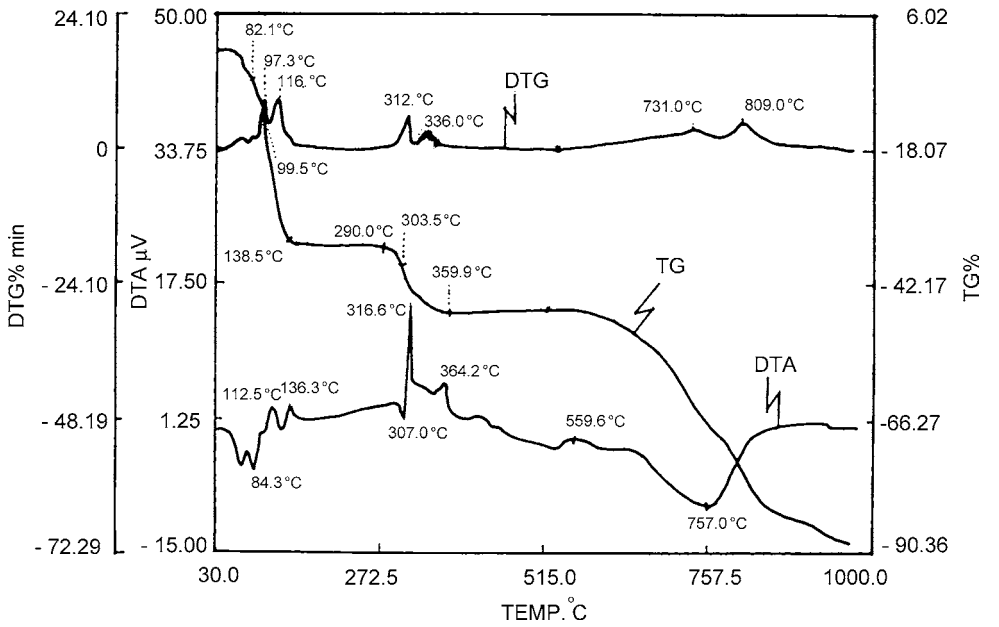

Fig. 1. TG/DTA of indium(III) bis-oxalatodiaquathallate(III).

evident that there are two significant weight losses. The splitting in the first peak, having ΔT_{max} at 97.3 and 116.8 °C, indicates the formation of a very unstable intermediate product. The presence of these doublet peaks may be attributed to the simultaneous dehydration and redox decomposition of the complex to give the intermediate, $In[TlC_2O_4]_3$. The second significant loss at 312.3 °C is attributed to the decomposition of the latter to the corresponding oxalates which is immediately followed by the decomposition of $In_2(C_2O_4)_3$ to In_2O_3. The adjacent small peak at 336 °C signifies the decomposition of $Tl_2C_2O_4$ to Tl_2O. The Tl_2O so formed is oxidised in due course to give Tl_2O_3, which is then volatilised at around 600 °C.

3.1.3. Differential thermal analysis (DTA)

DTA results of the compound are also shown in Fig. 1. From the DTA curve, it is evident that the endothermic doublet peaks with ΔT_{min} at 66.9 and 84.3 °C indicate the dehydration of the complex. The exothermic peaks (also doublet) with ΔT_{min} at 112.5 and 136.3 °C suggest the redox decomposition of the anhydrous compound and a readjustment of the bonds to give $In[Tl(C_2O_4)]_3$. A small endothermic peak with ΔT_{min} at 307.8 °C suggests the possible decomposition of the intermediate into the corresponding indium(III) and thallium(I) oxalates. A sharp exothermic peak with ΔT_{min} at 316.6 °C marks the complete decomposition of indium(III) oxalate to indium(III) oxide. A very small exothermic peak with ΔT_{max} at

Table 2
Summary of the thermal decomposition of the indium(III) bis-oxalatodiaquathallate(III) salt

Weight of complex	Step No.	Temperature (°C)		Loss in weight (%)		Possible decomposition product (intermediate)
		Start	End	Observed	Calculated	
10.00	1	30	82.1	6.07	7.34	$In^{3+}[Tl^{III}(C_2O_4)_2(H_2O)_2]_3$
	2	82.1	99.5	13.79	14.68	$In^{3+}[Tl^{III}(C_2O_4)_2]_3$
	3	99.5	138.5	34.80	32.63	$In^{3+}[Tl^{I}C_2O_4]_3$
	4	312.3	359.9	46.98	47.31	$Tl_2O + In_2O_3$

364.2 °C indicates the decomposition of thallous oxalate to thallous oxide. There is, however, a very strong and very broad endothermic peak at 757.0 °C, which may be attributed to the loss of material (possibly Tl_2O_3) due to volatilisation.

3.1.4. Isothermal decomposition of indium(III) bis-oxalatothallate(III)

Water content of the complex is determined using thermogravimetric results. Pyrolysis curve of the title complex indicates that complete dehydration and redox decomposition may take place simultaneously in the range of 30–140 °C to give indium(III) thallous oxalate, an intermediate which is probably a mixture of thallous oxalate and indium(III) oxalate in a 3:1 ratio. This may be described by the reaction

$$2In^{3+}[Tl^{III}(C_2O_4)_2]_3 \cdot nH_2O \xrightarrow{30-140^{\circ}C} 2In^{3+}[Tl^{I}C_2O_4]_3 + 12CO_2 + nH_2O$$

The thermogram (Fig. 1) also indicates that the intermediate formed is expected to be thermally stable between 140 and 290 °C. Thus, if the complex salt is to be heated to a particular temperature in the given range the above-mentioned intermediate can be obtained. To this effect, the complex sample (ca. 300 mg) was heated to 176 °C and the temperature maintained for about half-an-hour. Then a portion of the residue (ca. 100 mg) was taken and analysed for its contents as per the established methods [10,12,13] and a 1:1 ratio of $C_2O_4^{2-}$ to Tl(I) is obtained suggesting that the intermediate is thallium(I) complex viz., $In[TlC_2O_4]_3$.

The water content of the complex is calculated back from the experimental data and the value is found to be 12 molecules for each $In[TlC_2O_4]_3$ molecule. This gives rise to the most-probable formula of the complex as $In^{3+}[Tl^{III}(C_2O_4)_2(H_2O)_2]_3 \cdot 6H_2O$.

3.2. Infrared spectra of indium(III) bis-oxalatodiaquathallate(III)

The infrared spectra of the indium(III) thallic oxalate complex salt and the thermal decomposition product obtained by heating the complex to 176 °C and cooling to room temperature are given in Figs. 2 and 3, respectively. From the spectral data of the original complex, it is observed that there are strong absorption peaks at around 3600, 3495 and 1627 cm^{-1} which may be attributed to the existence of water. The presence of similar bands in the spectrum of the decomposition product suggests that the product might have absorbed moisture from the atmospheric air. There is, however, additional peak in the spectrum of the original complex at about 650 cm^{-1} which may be attributed to the presence of crystal water.

A very sharp and very strong absorption at 800 cm^{-1} and additional bands at 885 and 720 cm^{-1} in the complex, compared to the heated product, also confirm the presence of water in the coordinated form in the complex.

The spectral data of indium(III) bis-oxalatodiaquathallate(III) and the product obtained by heating the complex to 176 °C are given in Table 3 for comparison. From this table it is clear that some of the peaks in the spectrum of the complex are not observed in that of the heated product suggesting that the two are obviously different.

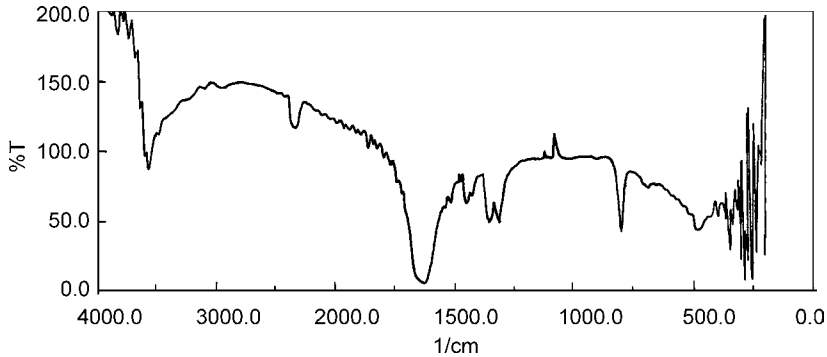

Fig. 2. Infrared spectrum of indium(III) bis-oxalatodiaquathallate(III).

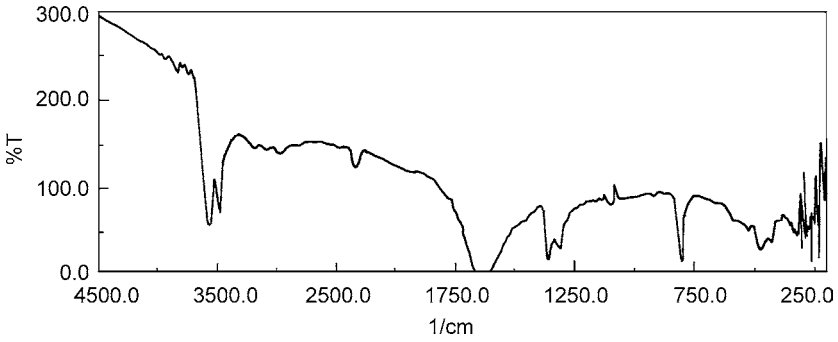

Fig. 3. Infrared spectrum of indium(III) bis-oxalatodiaquathallate(III) after heating to 176 °C.

3.3. X-ray diffraction data

The X-ray diffraction data of indium(III) bis-oxalatodiaquathallate(III) and that of the product obtained after heating the original complex to 176 °C and cooling are given in Table 4 along with those of indium(III) oxalate and thallous oxalate for comparison.

From the data given in Table 4, it is clear that the product obtained by heating the original complex to 176 °C is not a mixture of thallous and indium oxa-

Table 3
Infrared absorption data of indium(III) bis-oxalatodiaquathallate(III) and the heated product at 176 °C[a]

Complex		Band assignment
Original	Heated at 176 °C	
3600 sp, s	3600 sp, s	
3495 sh	3495 sp, s	$\nu_{as,\ s}$(H–O–H)
2900 w	2900 w	
1627 vs	1630 b, s	ν_a(C=O) + δ(H–O–H)
1520 sh		
1450 w		ν_s(C–O) + ν(C–C)
1360 sp, m	1360 sp, m	ν_s(C=O) + δ(O–C=O)
1300 sp, m	1320 b, m	
885 w	900 w	
800 sp, s	800 sp, s	Coordinated water and δ(O–C=O) + ν(M–O)
720 w		
650 w		Crystal water
	525 w	
495 b, m	495 b, m	
430 sh	430 sh	ν(M–O) + δ(O–C=O)
390 sp, w	390 w	δ(O–C=O) + ν(C–C)
370 sp, m		
350 sp, s	350	

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

Table 4
X-ray diffraction data of indium(III) bis-oxalatodiaquathallate(III) and the product after heating it to 176 °C, compared with indium(III) oxalate and thallous oxalate

$In^{3+}[Tl^{III}]$ complex	Complex after heating to 176 °C	$In_2(C_2O_4)_3$	$Tl_2C_2O_4$
6.628_1			
5.653_3		5.671_3	
5.529_x		5.515_x	
5.092_2	4.953_4	5.357_1	
4.239_1		5.092_2	4.311_2
4.030_2	4.066_9	5.035_2	
3.956_1		4.794_1	
3.905_1		4.648_1	
3.817_2	3.857_6	4.026_2	3.802_3
3.702_2		3.921_2	3.440_x
3.581_3	3.444_6	3.807_3	3.278_6
3.051_6	3.361_5	3.677_2	
3.002_1	3.241_6	3.555_2	2.849_1
2.781_2	2.813_4	3.306_1	2.763_7
2.544_2	2.716_x	3.231_2	
2.438_2		3.143_1	
2.418_1		3.050_4	
2.343_2		3.001_2	
2.289_1	2.224_3	2.773_1	
2.165_1		2.740_2	2.186_6
2.028_1		2.530_2	2.137_3
2.011_2	2.015_3	2.431_2	2.036_2
1.982_1	1.934_5	2.334_2	
1.899_1		2.218_1	
1.812_1		2.168_1	
1.789_2	1.694_1	2.134_1	1.752_3
1.526_1	1.552_2	2.005_2	1.634_2
		1.952_1	1.623_2
		1.937_2	1.544_2
		1.840_1	1.455_1
		1.780_2	1.427_1
		1.693_1	
		1.530_1	

lates instead it is an individual compound with the composition $In^{3+}[Tl^{I}C_2O_4]_3$.

The original complex was also heated to 500 °C and maintained at this temperature for half-an-hour. The product obtained in this manner was tested for carbonate following the usual acid test and the absence of the same was confirmed. This suggests that the thermal decomposition of the complex may not proceed through a carbonate intermediate owing that indium carbonate cannot be formed in this condition.

On the basis of the results of the above investigations, the following thermal decomposition mechanism is proposed:

$$2In^{3+}[Tl^{III}(C_2O_4)_2(H_2O)_2]_3 \cdot 6H_2O$$
$$\overset{30-90^{\circ}C}{\rightarrow} 2In^{3+}[Tl^{III}(C_2O_4)_2(H_2O)_2]_3$$
$$\overset{90-100^{\circ}C}{\rightarrow} 2In^{3+}[Tl^{III}(C_2O_4)_2]_3$$
$$\overset{100-140^{\circ}C}{\rightarrow} 2In^{3+}[Tl^{I}C_2O_4]_3 \overset{*140-360^{\circ}C}{\rightarrow} 3Tl_2O + In_2O_3$$
$$\underset{[O]}{\overset{360-500^{\circ}C}{\rightarrow}} 3Tl_2O_3 + In_2O_3 \overset{>600^{\circ}C}{\rightarrow} In_2O_3 + 3Tl_2O_3{}^{**}$$

Overall

$$2In^{3+}[Tl^{III}(C_2O_4)_2(H_2O)_2]_3 \cdot 6H_2O$$
$$\rightarrow 3Tl_2O_3{}^{*} + In_2O_3 + 24H_2O + 12CO_2 + 12CO$$

where $*$ indicates stability in the range of 140–290 °C according to the TG curve and $**$ indicates volatility.

According to the above thermal decomposition mechanism, the compound may be represented by the formula

$$In^{3+}[Tl^{III}(C_2O_4)_2(H_2O)_2]_3 \cdot 6H_2O$$

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