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THERMAL DECOMPOSITION OF THALLIUM(I) BIS-OXALATODIAQUAINDATE(III) MONOHYDRATE

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Abstract

Thallium(I) bis-oxalatodiaquaindate(III) monohydrate was obtained by precipitation of indium(III) with oxalic acid from slightly acidic solution in the presence of thallium(I). The complex was subjected to chemical analysis. The thermal decomposition behavior of the complex was studied using TG, DTA and DTG techniques. The solid complex salt and the intermediate product of its thermal decomposition were characterized using IR absorption and X-ray diffraction spectra. Based on data from these physicochemical investigations the structural formula of the complex was proposed as $Tl[In\,(C_2O_4)_2\,(H_2O)_2]\cdot H_2O$.

Keywords: bis-oxalates, indium(III), IR data, thallium(I) salt, thermal analysis, X-ray diffraction

Introduction

The thermal decompositions of the oxalates of some transition metal ions and lanthanides were investigated by several workers [1–6]. Ramana [7] has prepared bis-oxalatothallate(III) salts of different ions and studied their thermal, infrared absorption, microscopic and X-ray diffraction properties. Thermal decomposition of thallium(I) oxalate [8] has been reported. Rao [9] has also studied different types of thallium oxalates, which include simple and hydro oxalates of thallium(I); thallium(I) salt of bis-oxalatothallate(III) (mixed valence compound). The physicochemical properties of these oxalates are also studied.

In studying the reaction of indium salts with metal oxalates, limited reports are found in the literature. So far, first Moeller [10] and later Deichman [11, 12] prepared compounds of the type $M[In(C_2O_4)(H_2O)_2]\cdot xH_2O$ with M to be only NH_4^+ or alkali metal ion. Incidentally all the indium oxalates isolated by them are complexes with coordination number six. The solubility studies showed that bis-oxalatodiaquaindate is the most stable oxalato complex of indium(III) in aqueous solutions [11, 12]. Compared to the sulphato-compounds, the oxalato-compounds of indium [13] have a

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lower tendency to add on hydroxo-groups in the presence of an excess of alkali metal oxalate and lower total water content. It is also shown that the compounds $M[In(C_2O_4)_2(H_2O)_2]\cdot xH_2O$ have an increased solubility in concentrated metal oxalate solutions, indicating further complex formation.

However, no report has been found in literature on the preparation and physico-chemical investigation of the analogous bis-oxalatoindate complex salt of thallium(I). Therefore, the present investigation aimed at establishing suitable conditions for the preparation of thallium(I) bis-oxalatodiaquaindate(III) complex. In this preparation oxalic acid was added directly, with continuous stirring, to a mixture containing an indium salt and an excess of thallium(I) ion under slightly acidic pH (2–4) condition. The thermal behaviour of the complex salt was described in detail with the support of IR and X-ray diffraction evidences.

Experimental

Instrumentation

Thermal analysis unit

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

Infrared spectra

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

X-ray diffraction data

X-ray diffractometer of RICH SEIFERT & Co. (made in Germany) attached to a microprocessor was used for taking X-ray diffraction patterns at wavelength of CuK_{α_1}=1.540598 Å.

Preparation and analysis

The thallium(I) 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 taken in a 500 cm^3 beaker to which about 60 cm^3 1 M thallous nitrate and 180 cm^3 triple distilled water were added slowly while stirring the contents. Then about 80 cm^3 of 0.1 M oxalic acid was added very slowly (drop-wise) while stirring the contents vigorously. The complex salt formed was allowed to settle and filtered through a G_4 sintered glass crucible. Then the precipitate was washed several times (with a solution obtained by mixing 0.3 M $TlNO_3$ and 0.25 M HNO_3 in 1:1 ratio) to remove the excess oxalic acid.

Finally, the precipitate was washed with 0.1 M HNO_3 to remove $TlNO_3$. The precipitate was then dried in a vacuum desiccator over silica gel. The compound thus obtained was tested to confirm the absence of nitrate.

The compound was analysed for its indium, oxalate and water content. Indium(III) was estimated complexometrically using 1-(2-pyridylazo)-2-naphthol (PAN) as indicator [14] and oxalate by volumetric titration with standardised cerium(IV) sulpahate [15]. Water content was obtained by difference and from thermal data. The results of the analyses are shown in Table 1.

Table 1 Chemical analysis data of thallium(I) bis-oxalatodiaquaindate(III)

Mass of the complex taken	Composition/%				Ratio	Possible Formula
	In^{3+}	$C_2O_4^{2-}$	Tl^+	Total water	$C_2O_4^{2-}/In^{3+}$	
110 mg	21.07	31.04	37.46	10.44	~2.0	$Tl^I[In^{III}(C_2O_4)_2(H_2O)_2]\cdot H_2O$

Results and discussion

Thermal analysis

Thermogravimetric analysis (TG)

The pyrolysis curve of thallium(I) bis-oxalatodiaquaindate(III) hydrate and the data obtained from it are given in Fig. 1 and Table 2 respectively. From the curve it is clear that the complex loses crystalline water between 303 to 400 K. The observed mass loss is 3.22% as compared to the calculated value of 3.28%. This is followed by loss of coordinated water in the range of 400–453 K, which amounts to 9.57% of the total as observed on the TG curve (ca 9.84%).

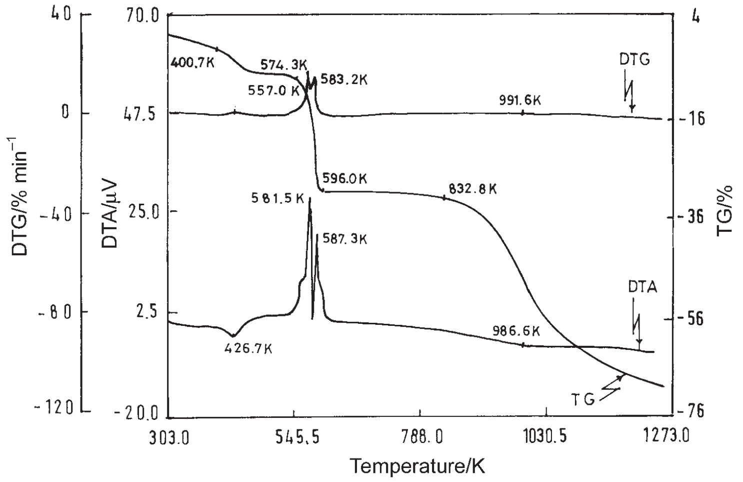

Fig. 1 TG/DTA curve of thallium(I) bis-oxalatodiaquaindate(III)

Table 2 Summary of the thermal decomposition of the thallium(I) salt

Mass of comp/mg	Step no.	Temperature/K		Mass loss/%		Possible decomposition product (intermediate)
		start	end	obs.	calc.	
10.00	1.	303.0	400.7	3.22	3.28	$Tl^{+}[In(C_2O_4)_2(H_2O)_2]$
	2.	400.7	557.0	9.57	9.84	$TlIn(C_2O_4)_2$
	3.	557.0	596.0	31.30	32.06	Tl_2CO_3+In_2O_3
	4.	832.6	915.0	36.12	36.04	Tl_2O_3+In_2O_3

The complete dehydration product, which may be thallium(I) indium oxalate intermediate is supposed to be stable upto about 557 K. The continuous and major loss, 31.30% on the TG (ca 32.06%) from 557 upto 596 K may be attributed to the decomposition of this intermediate to give rise to Tl_2CO_3 and In_2O_3. The formation of thallous carbonate may be evidenced from the similarity of the thallium(I) salt to those of the alkali metal salts. Furthermore, a number of literature reports [16, 17] support the possibility of formation of thallous carbonate as an intermediate. In due course the thallous oxide is converted into a mixture of Tl_2O and Tl_2O_3 (Tl_2O is first formed and then oxidised to Tl_2O_3) with a continuous increase in the Tl_2O_3 percentage with increase in temperature. The latter remains stable up to ~873 K where it starts volatilising up to 1223 K above which there will be no more residue other than the indium oxide. These observations are in agreement with those reported by Karkhanavala and Daroowalla [17].

Differential thermogravimetric analysis (DTG)

Differential mass losses obtained at regular intervals are noted *vs.* temperature for thallium(I) bis-oxalatodiaquaindate(III) hydrate as shown in Fig 1. The small peak on the DTG curve at ΔT_{max} at 426 K may be assigned to the dehydration of the complex. The prominent doublet peaks with maxima at 574.3 and 583.2 K may represent the decomposition of the anhydrous product at various stages. It is likely that the two peaks represent the decomposition of the anhydrous salt to In_2O_3 and $Tl_2C_2O_4$ and further to In_2O_3 and Tl_2CO_3.

Differential thermal analysis (DTA)

The DTA results of the complex are shown in Fig 1. The broad endothermic peak on the DTA curve with ΔT_{min} at 426.7 K may be assigned to the dehydration of the complex. The doublet exothermic peaks with ΔT_{max} at 581.5 and 587.3 K as well as the shoulder on the left side at 559.1 K may be attributed to the step-wise decomposition of $TlIn(C_2O_4)_2$ to In_2O_3 and Tl_2CO_3. More specifically the peak at 587.3 K can be assigned to the decomposition of $Tl_2C_2O_4$ [16]. The decomposition of the intermediate to form In_2O_3 and $Tl_2C_2O_4$ is accompanied by the loss of $3CO_2$ and 3CO molecules where as the next steps involved the loss of one CO. So, the magnitude of the two exothermic peaks suggests that the first peak corresponds to the formation of In_2O_3 and the second to Tl_2CO_3. As the DTA was recorded in ordinary atmospheric air (in the presence of O_2) the release of more CO molecules favoured higher exothermic changes due to their thermodynamically favourable conversion into CO_2 molecules.

The combined results of TG, DTG, and DTA as discussed above, are strongly supporting the mechanism which is suggested at the end of this article for the decomposition of thallium(I) bis-oxalatodiaquaindate(III) hydrate. The fact that there is no horizontal in the range of 557–596 K indicates that the decomposition of the anhydrous product, at this stage, is continuous and hence lacks thermally stable intermediates.

Isothermal decomposition of thallium(I) bis-oxalatodiaquaindate(III) monohydrate

The pyrolysis curve of the thallium(I) bis-oxalatodiaquaindate(III) hydrate (Fig. 1) can be used to select the possible dehydration temperature of the complex as 445 K. In this study ca 350 mg of the complex salt was first heated up to this temperature and the heating continued isothermally for about half an hour. The equation for the decomposition(dehydration) process may be given as,

$$Tl^{I}[In(C_2O_4)_2]\cdot nH_2O \xrightarrow{303-445\ K} Tl^{I}[In(C_2O_4)_2]+nH_2O$$

The analysis of the residue gave the ratio of $C_2O_4^{2-}$ to In(III) as 2:1 suggesting the possible formula of the intermediate as $Tl^{I}[In(C_2O_4)_2]$.

Similarly, the water content of the complex was calculated from the experimental data and found to be three molecules for each $Tl^{I}[In(C_2O_4)_2]$ molecule. This may imply that the original complex has the possible formula of $Tl^{I}[In(C_2O_4)_2]\cdot 3H_2O$ or $Tl^{I}[In(C_2O_4)_2(H_2O)_2]\cdot H_2O$.

Infrared spectra of thallium(I) bis-oxalatodiaquaindate(III) monohydrate

The infrared spectrum of thallium(I) bis-oxalatodiaquaindate(III) monohydrate is shown in Fig. 2. A doublet absorption peaks at 3600, and 3495 cm^{-1} and a very broad and strong absorption at 1600 cm^{-1} confirm the presence of water in the complex. A very sharp and strong absorption at 800 cm^{-1} confirms the presence of coordinated water as well as the bending vibrations of O–C=O and the M–O stretching vibration of coordinated water.

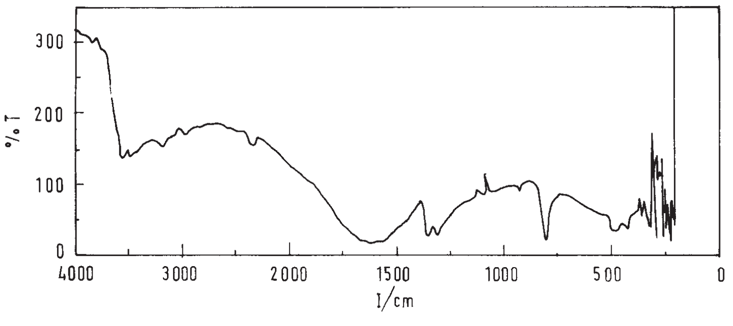

Fig. 2 Infrared spectrum of thallium(I) bis-oxalatodiaquaindate(III) monohydrate

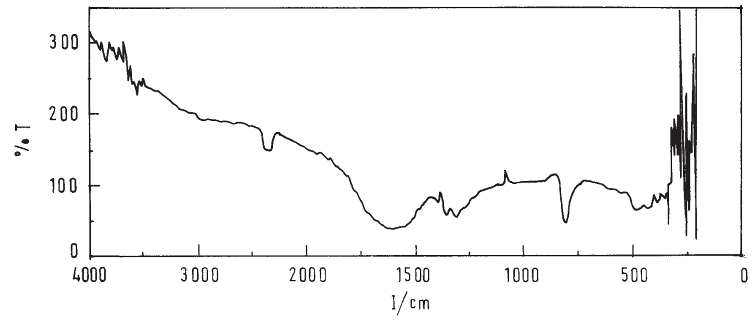

Fig. 3 Infrared spectrum of thallium(I) bis-oxalatodiaquaindate(III) monohydrate after heating at 445 K

The group of absorption peaks between 500 and 300 cm^{-1}, which may be assigned in the normal salts of oxalic acid to bending vibrations of O–C=O, indicates the bonding between indium(III) and the oxygen of the ligand, oxalate.

Table 3 Infrared absorption data of thallium(I) bis-oxalatodiaquaindate(III) monohydrate and the heated product at 445 K

Complex		Band assignment
Original	Heated at 445 K	
3600 b,m		
3495 sh		$\nu_{as,s}$(H–O–H)
3200 w		
2900 w		
1600 vb,vs	1600 vb,vs	ν_a(C=O)+δ(H–O–H)
	1400 vw	
1350 m	1350 m	ν_s(C–O)+ν(C–C)
1300 m	1300 m	ν_s(C=O)+δ(O–C=O)
900 vw		
800 sp,vs	800 sp,vs	Coordinated water and δ(O–C=O)+ν(M–O)
495 m	495 m	ν(M–O)+δ(O–C=O)
410 m	410 m	
350 vw	350 w	δ(O–C=O)+(C–C)

b=broad, m=medium, s=strong, sp=sharp, sh=shoulder, w=weak

Table 4 X-ray diffraction data of thallium(I) bis-oxalatodiaquaindate(III) and the product obtained after heating it to 445 K, compared with indium(III) oxalate and thallous oxalate

Tl^+ complex	Complex heated to 445 K	$In_2(C_2O_4)_3$	$Tl_2C_2O_4$
7.684_4	7.609_5		
7.468_4		5.671_3	
6.595_2		5.515_x	
6.465_x	6.479_2	5.357_1	
6.128_7	6.201_4	5.092_2	
5.731_4	5.741_2	5.035_2	
5.039_3	4.813_8	4.794_1	
4.767_9		4.648_1	
4.466_3	4.473_x	4.026_2	
4.220_2	4.241_7	3.921_2	4.311_2
4.064_8	4.048_6	3.807_3	
3.983_4		3.677_2	
3.889_6		3.555_2	
3.855_5	3.843_6	3.306_1	3.802_3
3.735_5	3.606_8	3.231_2	
3.573_4		3.143_1	
3.476_3	3.494_6	3.050_4	
3.437_5		3.001_2	3.440_x
3.231_4	3.277_4	2.773_1	3.278_6
3.087_3	3.102_4	2.740_2	
2.815_8	2.877_5	2.529_2	2.849_1
2.711_8	2.723_8	2.431_2	2.763_7
2.620_2		2.334_2	
2.590_2	2.546_3	2.218_1	
2.518_2	2.430_3	2.168_1	
2.391_4	2.344_5	2.134_1	
2.097_3	2.249_4	2.005_2	2.186_6
2.065_4	2.206_2	1.952_1	2.137_3
2.020_3	2.084_3	1.937_2	2.036_2
1.934_8	2.019_6	1.840_1	
1.707_2	1.940_5	1.779_2	1.752_3
	1.871_2	1.693_1	1.634_2
	1.821_2	1.529_1	1.623_2
	1.784_3		1.544_2
	1.751_3		1.455_1
	1.706_3		1.427_1

The infrared spectra of the product obtained by heating thallium(I) bis-oxalatodiaquaindate(III) to 445 K is shown in Fig. 3. For comparison the spectral data of the original complex and its decomposition product are presented in Table 3. From the spectral data of the latter, it appears that the peaks observed in the original complex at around 3500 cm^{-1} are missing. This indicates the absence of water in the heated product and hence it is anhydrous. Moreover, from the thermal data of the original complex it is also inferred that an intermediate corresponding to the empirical formula, $Tl^+In(C_2O_4)_2$ is obtained between 400 and 557 K.

X-ray diffraction data

X-ray diffraction data of thallium(I) bis-oxalatodiaquaindate(III) monohydrate and that of the product obtained after heating the original complex to 445 K and cooling are given in Table 4 along with those of indium(III) oxalate and thallous oxalate for comparison.

Data in the above table shows that the characteristic ‘d’ spacings of $Tl_2C_2O_4$ do not match with those of the product obtained by heating the thallium(I) complex to 445 K. Hence the intermediate product is an individual compound rather than a mixture of indium(III) and thalium(I) oxalates.

The product obtained by heating the original complex at 773 K for about 30 min was tested for the presence of carbonate. It is found that the residue does not contain carbonate but turned into dark brown in colour.

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

$$2Tl^+[In^{III}(C_2O_4)_2(H_2O)_2]\cdot H_2O \xrightarrow{303-\sim 400\ K} 2Tl^+[In^{III}(C_2O_4)_2(H_2O)_2] \xrightarrow{\sim 400-453\ K}$$

$$2Tl^+In^{III}(C_2O_4)_2 \xrightarrow{557-596\ K} Tl_2CO_3 + In_2O_3 \xrightarrow{596-873\ K} In_2O_3 + Tl_2O_3^{**}$$

$$\xrightarrow{>923\ K} In_2O_3 + Tl_2O_3^{***}$$

$$\text{Overall:}\ 2Tl^+[In^{III}(C_2O_4)_2(H_2O)_2]\cdot H_2O \rightarrow Tl_2O_3^{***} + In_sO_3 + 6H_2O + 6CO + 2CO_2$$

The proposed mechanism suggests the most probable structural formula of the complex with indium(III) at the centre of the octahedron as: $Tl^+[In^{III}(C_2O_4)_2(H_2O)_2]\cdot H_2O$.

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[**] First Tl_2O is formed which gradually gets oxidised to Tl_2O_3

[***] Volatalises

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