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SOME STUDIES ON THALLIUM OXALATES – IV

THERMAL DECOMPOSITION OF RUBIDIUM *bis*-OXALATO DIAQUO THALLATE(III) DIHYDRATE

S. R. SAGI, KARRI V. RAMANA and M. S. PRASADA RAO

Inorganic Chemistry Laboratories, Andhra University, Waltair, India

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Thallium(III) was precipitated with oxalic acid in the presence of 0.025 *M* $RbNO_3$ (or 0.0125 *M* Rb_2SO_4) in 0.1 *M* HNO_3 (or 0.05 *M* H_2SO_4). Chemical analysis of the solid obtained corresponds to the formula $Rb[Tl^{III}(C_2O_4)_2] \cdot 4\,H_2O$. 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 rubidium carbonate and oxides of thallium(I) and thallium(III). Infrared absorption spectra, microscopic observations and X-ray diffraction data were used to characterize the original salt, as well as the intermediates formed during the thermal decomposition of the salt. On the basis of these results, the salt may be represented as:

$$Rb[Tl^{III}(C_2O_4)_2(H_2O)_2] \cdot 2\,H_2O\ .$$

Ideal conditions for the formation of rubidium *bis*-oxalato diaquo thallate(III) dihydrate [1], and its solubility [2], were reported earlier. The present article deals with the preparation and the thermal behaviour of the complex salt, and the characterization of the complex and its intermediate products of thermal decomposition, using infrared absorption spectra, microscopic observations and X-ray diffraction data.

Experimental

Instruments: The details of the thermobalance, infrared spectrophotometers, X-ray diffractometer and microscope used have already been described [3].

Preparation and chemical analyis: The complex was prepared using the conditions already reported [1, 2]. The complex obtained was filtered through an IG 4 sintered-glass crucible, washed with minimum quantities of wash liquid (0.125 *M* with respect to HNO_3 and 0.025 *M* with respect to $RbNO_3$, or 0.06 *M* with respect to H_2SO_4 and 0.0125 *M* with respect to Rb_2SO_4, and finally washed with acidified water with HNO_3 or H_2SO_4). The white crystalline solid obtained was then dried under reduced pressure over anhydrous silica gel.

The thallium and oxalate contents of the original complex and of the intermediate were found [4, 5] to be in the ratio 1 : 2 and 1 : 1, respectively. The ratio of rubidium and thallium in the intermediate and hence in the original complex was found by difference to be 1 : 1. The presence of the carbonate in the final product after heating was confirmed by the usual acid test. The water content of the original complex was computed, by difference, to be four moles per atom of thallium. This observation is in agreement with the thermal decomposition data recorded now and calculated by the methods suggested earlier [6]. From these date the compound may be represented as $Rb[Tl(C_2O_4)_2(H_2O)_2] \cdot 2\,H_2O$, as thallium(III) is known to exhibit octahedral coordination [7] which was supported by the results of the following studies.

Results and discussion

Thermal studies

Thermogravimetric analysis (TG): The TG curve of rubidium *bis*-oxalato diaquo thallate(III) dihydrate is shown in Fig. 1. The first loss in weight on heating from 50 to 130° corresponds to the simultaneous dehydration and the redox decomposition of the thallium(III) to thallium(I) (loss of four moles of water and one oxalate ion). The intermediate thus obtained at this temperature ($RbTlC_2O_4$ or an equimolar mixture of $Rb_2C_2O_4$ and $Tl_2C_2O_4$) is stable up to 230°. This intermediate starts decomposing from 230° to 460°. The final residue corresponds to a mixture of rubidium carbonate and oxides of thallium(I) and thallium(III), which is stable up to 600°.

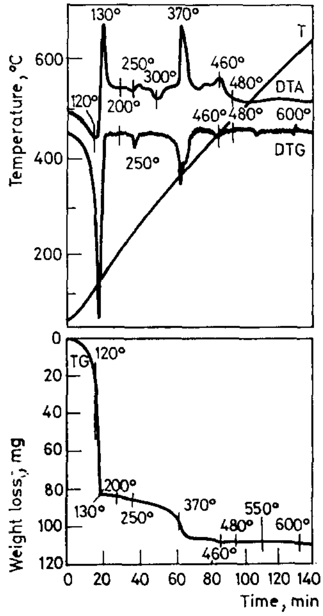

Fig. 1. TG, DTG and DTA curves of the thermal decomposition of rubidium *bis*-oxalato thallate(III) tetrahydrate

Derivative thermogravimetric analysis (DTG): In the DTG curve (Fig. 1) there are three peaks indicating a loss in weight. The first sharp peak around 130° corresponds to the complete dehydration and redox decomposition of the complex. The second peak, with $\Delta T_{\min}$ at 250°, indicates the decomposition of rubidium oxalate to rubidium carbonate, while the third medium peak, with $\Delta T_{\min}$ at 370°, corresponds to the decomposition of thallous oxalate to a mixture of thallium(I) and thallium(III) oxides.

Differential thermal analysis (DTA): The DTA curve (Fig. 1) shows a broad endothermic peak due to dehydration and an exothermic peak due to redox decomposition at almost the same temperature ($\Delta T_{\min} \simeq \Delta T_{\max} \simeq 130°$). The sequence of these peaks shows that the dehydration precedes the redox decomposition. The small endothermic peak with $\Delta T_{\min}$ at 250° corresponds to the decomposition of rubidium oxalate to the carbonate. The exothermic peak with $\Delta T_{\max}$ at 370° is due to the decomposition of thallous oxalate to thallous oxide, while the other exothermic peak around 460° is due to the partial oxidation of thallium(I) to thallium(III). In this connection, it may be noted that the thallium(I) oxalate decomposes first to the metal [8], which is immediately oxidized to thallium(I) oxide. In the present case the endothermic peak at 300° may be due to the melting of the thallium metal [9] first formed, which is oxidized to thallium(I) oxide.

From these results, which are summarized in Tables 1 and 2, the stepwise thermal decomposition of the complex may be given as:

$$2\,\mathrm{Rb[Tl(C_2O_4)_2]\cdot 4\,H_2O} \rightarrow 2\,\mathrm{Rb[Tl(C_2O_4)_2]} \rightarrow 2\,\mathrm{RbTlC_2O_4} \dashrightarrow$$

$$(\text{or } \mathrm{Rb_2C_2O_4+Tl_2C_2O_4})$$

$$\dashrightarrow \mathrm{Rb_2CO_3} + \mathrm{Tl_2C_2O_4} \rightarrow \mathrm{Rb_2CO_3} + x\,\mathrm{Tl_2O} + y\,\mathrm{Tl_2O_3}.$$

Table 1

Thermogravimetric data of rubidium *bis*-oxalato diaquo thallate(III) dihydrate

Weight of the complex, mg	Step No.	Temperature, °C		Loss in weight of the complex, mg		Thermal decomposition reaction proposed
		Starting	Ending	Observed	Calculated	
290	I	50	130	88	86.13	$2\,\mathrm{Rb[Tl(C_2O_4)_2]\cdot 4\,H_2O}$ $\rightarrow \mathrm{Rb_2C_2O_4} + \mathrm{Tl_2C_2O_4}$
	II	230	460	21	22.67	$\mathrm{Rb_2C_2O_4} + \mathrm{Tl_2C_2O_4}$ $\rightarrow \mathrm{Rb_2CO_3} + x\mathrm{Tl_2O} + y\mathrm{Tl_2O_3}$
	Overall	50	460	109	108.80	$2\,\mathrm{Rb[Tl(C_2O_4)_2]\cdot 4\,H_2O}$ $\rightarrow \mathrm{Rb_2CO_3} + x\mathrm{Tl_2O} + y\mathrm{Tl_2O_3}$

Table 2

DTG and DTA data of rubidium *bis*-oxalato diaquo thallate(III) dihydrate

	Reaction	Peak		
		Temp. °C	Nature	Type
DTG	dehydration	130	loss	very sharp
	redox decomposition	130	loss	sharp
	decomposition of $Rb_2C_2O_4$	250	loss	small
	decomposition of $Tl_2C_2O_4$	370	loss	medium
DTA	dehydration	130	endothermic	broad
	redox decomposition	130	exothermic	sharp
	decomposition of $Rb_2C_2O_4$	250	endothermic	small
	(melting of metal Tl)	300	endothermic	small
	decomposition of $Tl_2C_2O_4$	370	exothermic	sharp
	partial oxidation of Tl_2O	460	exothermic	sharp

From these results it is not possible to know whether the intermediate formed at around 130° is $RbTlC_2O_4$ or an equimolar mixture of $Rb_2C_2O_4$ and $Tl_2C_2O_4$. To differentiate these, the following studies have been carried out, which confirmed the intermediate to be a mixture of $Rb_2C_2O_4$ and $Tl_2C_2O_4$.

Infrared absorption spectra

The infrared specta of rubidium *bis*-oxalato thallate(III) and the product obtained by heating the complex to 170° and cooling to room temperature are shown in Figs 2 and 3. In Fig. 2 very broad and very strong absorption peaks, one around 3480 cm^{-1} [10] (indicative of asymmetric and symmetric stretches of H–O–H) and the other around 1600 cm^{-1} [11] (indicative of bending modes of H–O–H) confirm the presence of water in the complex. A weak absorption in the complex at 595 cm^{-1} may be due to the presence of crystal water [12]. A very sharp and very strong absorption in the complex at 790 cm^{-1} indicates the water in the coordinated [12] form.

The infrared spectral data of the complex, its heated product and thallous oxalate [3] were compared. The similarity of Fig. 3 with that of thallous oxalate [3] clearly shows that the heated product is a mixture (of thallous oxalate and rubidium oxalate) and not a single compound (rubidium thallous oxalate), as all the prominent characteristic peaks of thallous oxalate are present in the heated product.

It is also clear that the absorption due to bending modes of O–C=O (770 and 750 cm^{-1}) in thallous oxalate, as well as in the heated product, are shifted to 790 and 765 cm^{-1} in the case of the complex. This shift suggests an increase in covalency between the metal, thallium(III), and the oxygen of the ligand, oxalate. Similar shifts from 530 and 225 cm^{-1} in thallous oxalate to 475 and 245 cm^{-1} in the complex also suggest the difference in bond character.

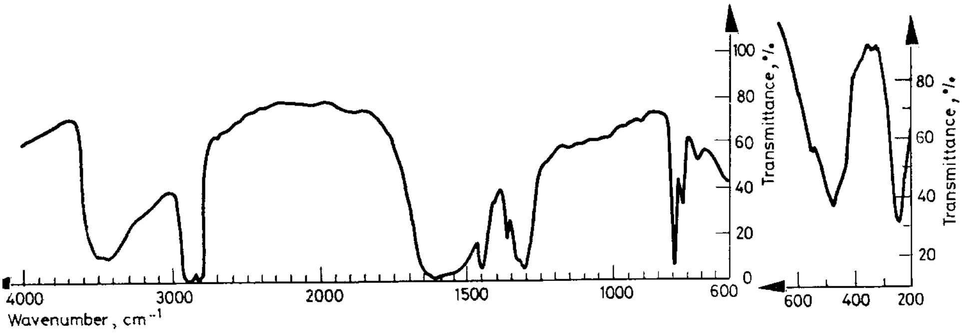

Fig. 2. Infrared spectrum of rubidium *bis*-oxalato thallate(III)

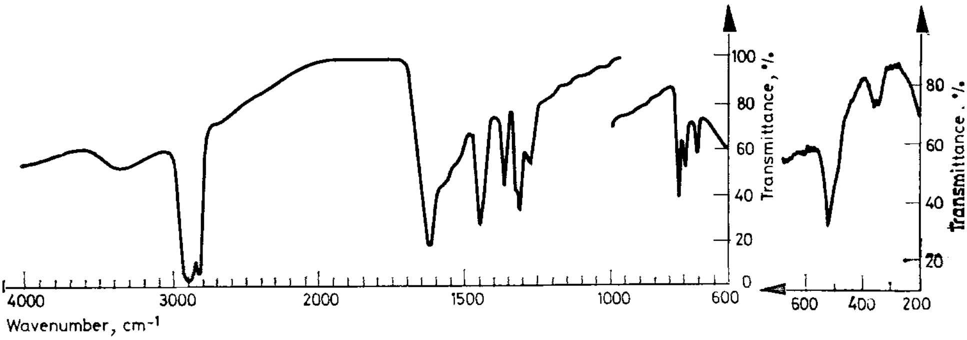

Fig. 3. Infrared spectrum of rubidium *bis*-oxalato thallate(III) after heating[to 170°

Microscopic observations

Rubidium *bis*-oxalato diaquo thallate(III) dihydrate occurs as irregular aggregates having low birefringence. The lower refractive index is 1.600 ± 0.002 and the higher one 1.604 ± 0,002.

The crystals developed from the aqueous solution of the intermediate were observed under the microscope. These observations show the presence of base-flattened, prismatic, highly birefringent, monoclinic crystals with symmetrical extinction and having a '2V' value of 70°, which are exactly similar to the properties of thallous oxalate [3], confirming that the intermediate is a mixture of $Rb_2C_2O_4$ and $Tl_2C_2O_4$.

X-ray diffraction data

The prominent peaks of the X-ray diffraction data of the complex, the intermediate and the thallous oxalate are given in Table 3. The data in the Table clearly show that the intermediate contains free thallous oxalate [3], thus confirming the

Table 3

X-ray diffraction data d Å

Rubidium *bis*-oxalato diaquo thallate(III) dihydrate	Intermediate	Thallium(I) oxalate
8.979_1	3.439_x	3.440_x
6.511_x		3.278_6
5.810_3	3.251_2	
5.471_2	3.105_3	3.110_4
4.708_5	2.911_2	2.912_2
4.230_3	2.756_5	2.763_7
4.220_3	2.661_2	2.660_3
3.934_1	2.530_1	2.522_2
3.892_4	2.193_6	2.186_6
3.583_3	2.150_3	2.137_3
2.867_2	2.051_2	
2.755_7		2.010_2
2.481_1	1.984_2	
2.386_1	1.884_1	1.969_1 1.863_4
2.129_1	1.757_4	1.752_3
2.099_2	1.698_1	1.675_2
2.036_1	1.587_1	1.593_3
1.961_2	1.407_2	
1.955_2		1.386_2
1.768_1		

intermediate as a mixture of thallous oxalate and rubidium oxalate. The prominent '*d*' values of the complex (6.511, 2.755_7 and 4.708_5) may be utilized to differentiate the rubidium salt from the other salts of *bis*-oxalato thallate(III) ion [3, 13, 14, 15].

Conclusion

All the above results support the proposed structural formula for the rubidium salt as $Rb[Tl(C_2O_4)_2(H_2O)_2]2\,H_2O$, as well as the proposed thermal decomposition mechanism.

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Zusammenfassung — Thallium (III) wurde mit Oxalsäure in Gegenwart von 0.025 M $RbNO_3$ (oder 0.0125 M Rb_2SO_4) in 0.1 M HNO_3 (oder 0.05 M H_2SO_4) gefällt. Die chemische Analyse der erhaltenen Festsubstanz entspricht der Formel $Rb[Tl^{III}(C_2O_4)_2] \cdot 4H_2O$. Thermische Untersuchungen (TG, DTG und DTA) zeigen die Dehydratisierung und Redoxzersetzung vom Thallitsalz zum Thallitsalz und schließlich zu einem Gemisch von Rubidiumcarbonat und Oxiden der Thallium(I) und Thallium(III). Infrarot-Absorptionsspektren, mikroskopische Beobachtungen und Röntgendiffraktionsdaten werden zur Charakterisierung des ursprünglichen Salzes sowie der während der thermischen Zersetzung des Salzes entstandenen Zwischenprodukte angewandt. Durch diese Ergebnisse kann das Salz wie folgt beschrieben werden:

$$Rb[Tl^{III}(C_2O_4)_2(H_2O)_2] \cdot 2H_2O.$$

Резюме — Таллий(III) образует с щавелевой кислотой в присутствии 0.025 M $RbNO_3$ (или 0.0125 M Rb_2SO_4) и в среде 0.1 M HNO_3 (или 0.05 M H_2SO_4) твердый осадок, химический анализ которого соответствует формуле $Rb[Tl^{III}(C_2O_4)_2]. 4H_2O$. Термические изучения (ТГ, ДТГ и ДТА) указали на дегидратацию и на окислительно-восстановительное разложение соли трехвалентного таллия до соли одновалентного таллия и в конце до смеси карбоната рубидия и окисей таллия(I) и таллия(III). ИК спектры, микроскопические наблюдения и рентгенографические данные были использованы для характеристики как начальной соли, так и промежуточных продуктов, образующихся во время термического разложения соли. Основываясь на этих результатах, соль может быть представлена в виде

$$Rb[Tl^{III}(C_2O_4)_2(H_2O)_2 \cdot 2H_2O.$$