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SOME STUDIES ON THALLIUM OXALATES. I. THERMAL DECOMPOSITION OF AMMONIUM BISOXALATOTHALLATE(III)

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ABSTRACT

Trivalent thallium is precipitated in the presence of 0.1 *M* HNO_3 (or 0.05 *M* H_2SO_4) and 0.1 *M* NH_4NO_3 (or 0.05 *M* $(NH_4)_2SO_4$) with oxalic acid. The chemical analysis of the salt obtained corresponds to the formula, $NH_4[Tl(C_2O_4)_2] \cdot 3H_2O$. The thermal decomposition studies of the complex indicate the formation of the intermediates ammonium thallous oxalate (stable from 150° to 160°C) and thallous oxalate (stable up to 290°C) and the final product to be a mixture of 25% of thallous oxide and 75% of thallic oxide (stable from 450° to 650°C). The infrared absorption spectra, X-ray diffraction patterns, microscopic observations and the electrical resistance measurements are used to characterise the complex and the intermediates of its thermal decomposition.

INTRODUCTION

A review on the thermal decomposition of some solid oxalates was given by Krishna Murty and Harris[1]. The oxalate ion was used in the automatic thermogravimetric analysis of various metals[2]. The differential thermal analysis of various metal oxalates under controlled atmospheres was reported by Dollimore and Griffiths[3] and the decomposition of simple oxalates as well as the oxalate complexes of various metals by Dollimore et al.[4–15]. Wendlandt[16] has given a review of the thermal methods of analysis of some metal oxalates.

The thermal decomposition of thallous carbonate was reported by Duval[17] and Karkhanavala and Dharoowalla[18]. The decomposition of thallium trioxide was reported by several workers[19–24]. The high temperature volatilization of thallic oxide[25], thermal behaviour of chlorate[26] and the salts of fatty acids[27] of thallium(I) are known.

So far, nobody appears to have reported on the thermal behaviour of thallium(III) oxalates though the ammonium salt of bisoxalatothallate(III) was known as early as the beginning of the present century[28–30]. So the present authors have studied the thermal, infrared, X-ray, microscopic and the electrical conductivity behaviour of the complex. The authors' observations on the potentiometric titration of thallium(III) with oxalic acid in the presence of a sufficient concentration of an ammonium ion[31], and the solubility determination of the complex using an isotopic tracer technique[32] suggest better conditions for the preparation of ammonium bisoxalatothallate(III). The complex was prepared under these conditions and analysed by the techniques mentioned above.

As thallous oxalate is found to be associated with the thermal decomposition of the complex, a knowledge of its thermal behaviour, infrared absorption, X-ray diffraction and optical properties is needed to characterise and suggest the probable mechanism of the decomposition of the complex. So the properties of thallous oxalate are also investigated in addition to those of the complex.

EXPERIMENTAL

Instruments

A Stanton thermobalance and a Derivatograph (MOM) were used for taking TG and simultaneous TG, DTG and DTA with silica and platinum crucibles as sample holders. The rate of heating was 4°C min^{-1} under atmospheric air in both the cases.

A Perkin Elmer 257 infrared spectrophotometer (4000–625 cm^{-1}) and a Beckman infrared-12 spectrophotometer (650–200 cm^{-1}) were used to obtain the infrared spectra using the nujol mull technique in both the regions.

The X-ray powder photographs were taken by an X-ray diffractometer, with a Phillips X-ray generator PW1010 with copper $K\alpha$ radiation.

A Carl Zeiss polaroid microscope with an adaptable camera was used for microscopic observations and to take the photomicrographs. A polarizing microscope with a universal stage was used to measure $2V$ values. The crystals were grown on the slide from saturated aqueous solutions of the salts and their intermediate products obtained during thermal decomposition.

A Phillips conductivity bridge with silver electrodes was used to measure the electrical resistance at different temperatures.

Preparation and analysis

Thallous oxalate was prepared[33] by mixing equivalent quantities of the aqueous solutions of thallous carbonate (0.05 M) and oxalic acid (0.05 M), and by crystallisation after concentrating the solution by boiling. The solid obtained was washed with water and finally with alcohol. It was dried under vacuum over silica gel. The oxalate and thallium contents of the compound so obtained were determined according to the method already reported[34] and the assay found to correspond to the formula, $Tl_2C_2O_4$.

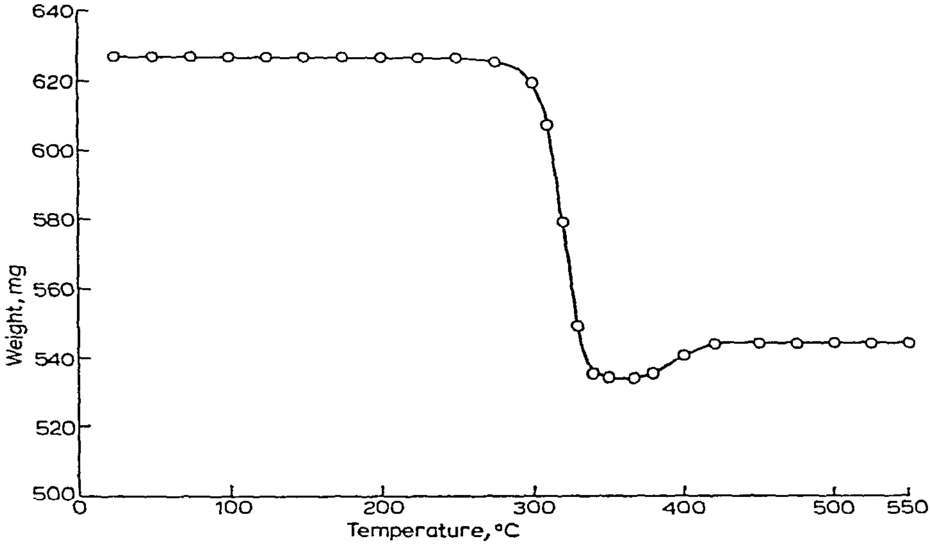
The ammonium salt of bisoxalatothallate(III) was prepared under the conditions reported earlier[32] and the white crystalline solid complex obtained was filtered through an IG4 sintered glass crucible, washed with minimum quantities of wash liquid and finally with water (acidified with nitric or sulphuric acid) and dried under vacuum over silica gel. The thallium and oxalate contents of the complex thus obtained were determined[34] and found to be in the ratio of 1:2. The thallium and oxalate contents of the decomposition products at the intermediate stages were also determined by chemical analysis. The absence of carbonate in the final product after TG was confirmed by the usual qualitative acid test. The water content of the complex was computed by the differential method and was confirmed from the TG data[35]. The analysis of the complex corresponded to the formula $NH_4[Tl(C_2O_4)_2] \cdot 3H_2O$.

Thermal studies

Thermogravimetric analysis of thallous oxalate. From the pyrolysis curve (Fig. 1) it is clear that thallous oxalate is thermally stable up to 250°C, and from there onwards it decomposes up to 350°C. This loss amounts to 14.6% which corresponds to the decomposition of thallous oxalate to thallous oxide (theoretical loss being 14.4%). The thallous oxide thus formed is stable up to 370°C and a part of it is then oxidised to thallic oxide up to 420°C. The gain amounts to about 2% which corresponds to the oxidation of 25% of thallium(I) to thallium(III). Normally, the metal oxalates decompose to oxides via the formation of carbonates but thallous oxalate is found to decompose directly to the oxide and there is no evidence for the formation of the carbonate in the thermogram. The overall decomposition of the thallous oxalate may be represented as

$$Tl_2C_2O_4 \xrightarrow[(O_2)]{250\text{–}250°C} Tl_2O + CO_2$$

$$Tl_2O \xrightarrow[(O_2)]{370\text{–}420°C} Tl_2O_3 + Tl_2O$$



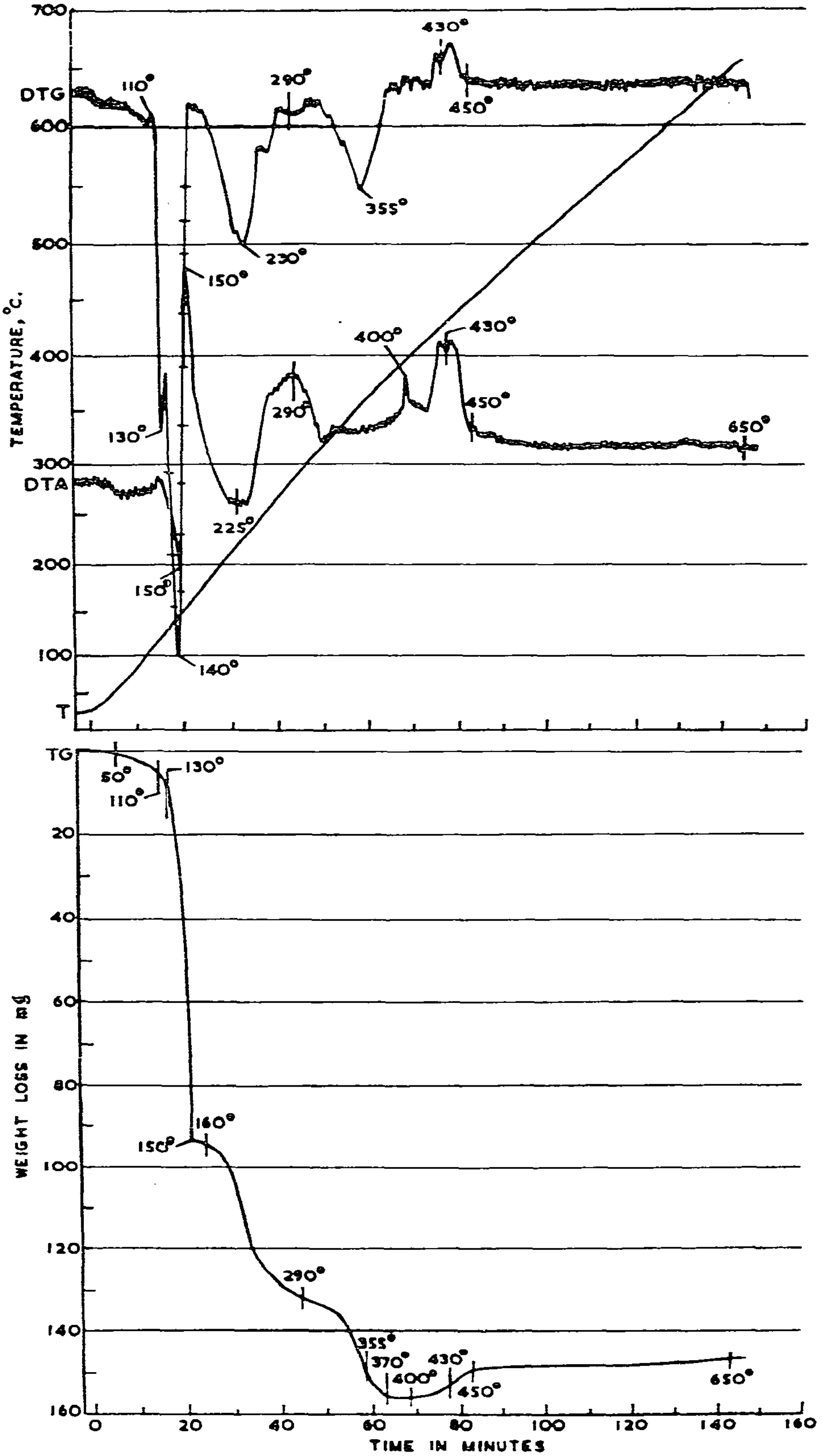


Fig. 2. TGA, DTG and DTA curves for the thermal decomposition of ammonium bisoxalatothallate(III) trihydrate.

Thermogravimetric analysis of the complex (*TGA*). The thermogram of the ammonium bisoxalatothallate(III) complex is shown in Fig. 2. The first loss in weight, on heating from 50 to 150°C corresponds to the simultaneous dehydration and reduction of the complex to ammonium thallous oxalate, which on further heating loses ammonium oxalate from 160 to 290°C, giving thallous oxalate, followed by its decomposition to thallous oxide up to 370°C. The thallous oxide thus formed is stable up to 400° and 75% of it is oxidised to thallic oxide from 400 to 450°C. It can be seen from the pyrolysis curve (Fig. 2) that the decomposition of ammonium thallous oxalate is almost continuous, except for a change in the slope of the curve around 290°C.

In order to substantiate the decomposition mechanism suggested from this dynamic method, an isothermal decomposition study is carried out at 220°C for the intermediate, ammonium thallous oxalate. Such a study clearly indicated the completion of the decomposition of ammonium oxalate leaving thallous oxalate unaffected at that temperature (220°C). However, when the temperature is raised, further thallous oxalate decomposes as usual, giving rise to a mixture of oxides of thallium(I) and thallium(III).

Differential thermogravimetric analysis of the complex (*DTG*). In Fig. 2, the DTG curve shows four weight loses at different temperatures (130, 140, 230 and 355°C) corresponding to the dehydration of the complex, redox decomposition of the thallic salt to thallous salt, decomposition of ammonium oxalate and finally to the decomposition of thallous oxalate to thallous oxide, respectively. The gain in weight indicated by the peak around 430°C corresponds to the oxidation of a part of the thallous oxide to thallic oxide.

Differential thermal analysis of the complex (*DTA*). The DTA curve in Fig. 2 shows an endothermic peak due to dehydration and an exothermic peak due to redox decomposition at almost the same temperature ($\Delta T_{\mathrm{min}} = \Delta T_{\mathrm{max}} = 150$°C). But the sequence of these peaks clearly shows that the dehydration precedes the redox decomposition. From the DTG curve and the results of the isothermal studies given above it is evident that the thermal decomposition of ammonium thallous oxalate takes place in two steps. The first step is the decomposition of ammonium oxalate and the second step is the decomposition of thallous oxalate.

The decomposition of ammonium oxalate is indicated by a single step in TG as well as in DTG, whereas in DTA there are two peaks (broad endothermic peak with ΔT_{min} at 225°C and a very broad exothermic peak with ΔT_{max} at 290°C) indicating the decomposition of ammonium oxalate taking place probably through the formation of oxamide and cyanogen respectively, as suggested by Duval[36] and Martens[37] for pure ammonium oxalate.

A sharp and small endothermic peak (with a little lag) with ΔT_{max} at 400°C indicates the decomposition of thallous oxalate to give the oxide and a broad exothermic peak with two shoulders with ΔT_{max} at 430°C is due to the atmospheric oxidation of a part of thallium(I) to thallium(III).

The results are summarised in Tables 1 and 2.

TABLE 1

THERMAL DECOMPOSITION DATA OF AMMONIUM BISOXALATOTHALLATE(III)

Weight of the complex taken (mg)	Step number	Temperature (°C)		Change in weight of the complex (mg)		Reaction involved
		Starting	Ending	Observed	Calculated	
300	I (loss)	50	150	93	95.00	$8\ NH_4\,[Tl\,(C_2O_4)_2]\cdot 3H_2O \rightarrow 4\,(NH_4)_2C_2O_4 + 4\,Tl_2C_2O_4 + 24\ H_2O + 16\ CO_2$
	II (loss)	160	370	53	54.70	$4\,(NH_4)_2C_2O_4 + 4\,Tl_2C_2O_4 \rightarrow 8\ NH_3 + 4\,Tl_2O + 4\ H_2O + 8\ CO_2 + 8\ CO$
	III (gain)	400	450	8	8.30	$4\,Tl_2O \rightarrow Tl_2O + 3\,Tl_2O_3$
	Overall (loss)	50	450	148	150.40	$8\ NH_4\,[Tl\,(C_2O_4)_2]\cdot 3\ H_2O \rightarrow Tl_2O + 3\,Tl_2O_3 + 8\ NH_3 + 28\ H_2O + 24\ CO_2 + 8\ CO$

TABLE 2

DTG AND DTA DATA OF AMMONIUM BISOXALATOTHALLATE(III)

	Reaction	Peak		
		Temp. (°C)	Nature	Type
DTG	Dehydration of the complex	130	Loss	Sharp
	Redox decomposition of the complex	140	Loss	Sharp
	Decomposition of ammonium oxalate	230	Loss	Broad
	Decomposition of thallous oxalate	355	Loss	Broad
	Partial oxidation of thallous oxide	430	Gain	Medium
DTA	Dehydration of the complex	150	Endothermic	Very sharp
	Redox decomposition of the complex	150	Exothermic	Very sharp
	Decomposition of ammonium oxalate	225	Endothermic	Broad
	Polymerisation of cyanogen[37]	290	Exothermic	Broad
	Decomposition of thallous oxalate	400	Exothermic	Medium
	Partial oxidation of thallous oxide	430	Exothermic	Broad

Characterisation

From the above results, the stepwise thermal decomposition of the complex can be given as:

$$\underset{(1)}{NH_4[Tl(C_2O_4)_2]\cdot 3H_2O} \xrightarrow{50\text{–}150^\circ C} \underset{(2)}{NH_4[Tl(C_2O_4)_2]} \xrightarrow{150^\circ C}$$

$$\underset{(3)}{(NH_4)_2C_2O_4 + Tl_2C_2O_4} \xrightarrow{160\text{–}290^\circ C} \underset{(4)}{Tl_2C_2O_4} \xrightarrow{290\text{–}370^\circ C} \underset{(5)}{Tl_2O}$$

$$\xrightarrow{400\text{–}450^\circ C} \underset{(6)}{(Tl_2O + Tl_2O_3)}$$

The decomposition of hydrated ammonium bisoxalatothallate(III) (1) to ammonium thallous oxalate (3) via anhydrous ammonium bisoxalatothallate(III) (2) is clear from the TG and DTA results. The decomposition of intermediate 3 to thallous oxalate (4) is evident from the isothermal studies. The decomposition of thallous oxalate (4) to thallous oxide (5) and the oxidation of a part of Tl_2O (5) giving a mixture of Tl_2O and Tl_2O_3 (6) is evident from the TG, DTG and DTA results. Steps 4–6 are similar to those in the thermal decomposition of thallous oxalate.

A separate thermogram of an equimolar mixture of ammonium oxalate monohydrate and thallous oxalate gave results which are almost the same as that of intermediate 3 in the above experiment except for the extra dehydration of ammonium oxalate monohydrate between 60 and 130°C. This indicates that the intermediate (3) obtained at 150°C may be a mixture of $(NH_4)_2C_2O_4$ and $Tl_2C_2O_4$ rather than a single compound, $NH_4TlC_2O_4$.

Infrared spectral studies

The infrared spectrum of ammonium bisoxalatothallate(III) is shown in Fig. 3(a). The absorption at 3160 cm^{-1} and 3040 cm^{-1} indicates the presence of ammonium[38] and a very strong absorption at 3470 cm^{-1}, a shoulder at 3410 cm^{-1} [39], and a very broad and very strong absorption at 1600 cm^{-1} [40], indicate the presence of water. A very sharp and strong absorption at 795 cm^{-1} and weak shoulder at 640 cm^{-1} indicate the presence of coordinated water[41] and crystal water[41], respectively, in the complex. The infrared spectrum of the complex is compared with the spectra of thallous oxalate [Fig. 3(b)] and a mixture of ammonium oxalate monohydrate and thallous oxalate in 1 : 1 molar ratio [Fig. 3(c)].

The lattice water in the mixture [Fig. 3(c)] has a strong absorption at 640 cm^{-1} while in the complex [Fig. 3(a)] it has only a weak shoulder at 640 cm^{-1}. This might be probably due to the hydrogen bonding between the lattice and coordinated water[40] of the complex. The continuous loss of water from the complex at about 120°C (Fig. 2) without any discontinuity in TG also supports this view.

The absorption due to the metal–oxygen bonding in thallous oxalate [Fig. 3(b)]

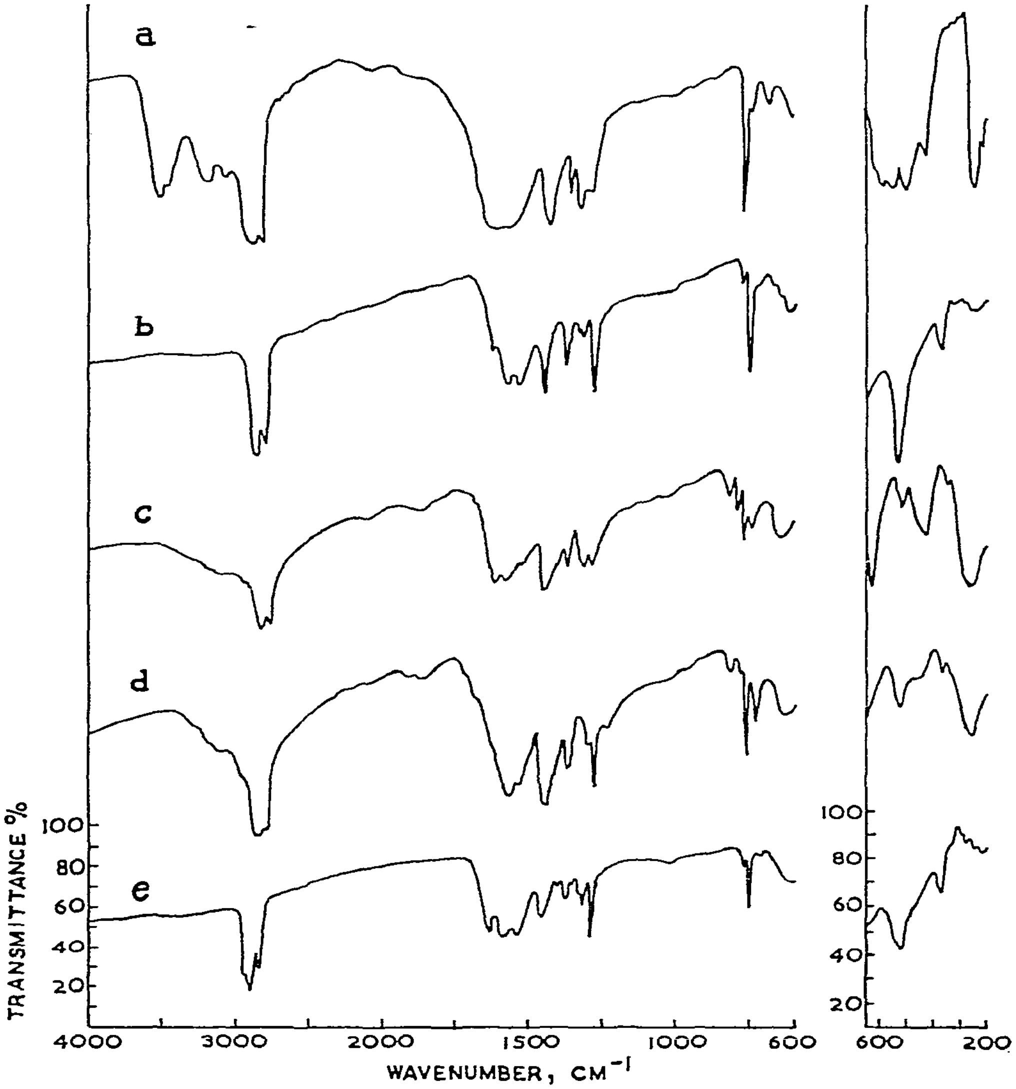


Fig. 3. Infrared absorption spectra of (a) the complex, (b) thallous oxalate, (c) an equimolar mixture of ammonium oxalate monohydrate and thallous oxalate, (d) and (e) intermediates 3 and 4.

is at 530 cm^{-1} while in the complex the absorption is at 500 cm^{-1}. This shift in the wavelength indicates the difference in the covalent character of the M–O bonds of the complex and thallous oxalate.

Two separate samples of the complex are heated at 150 and 250 °C, cooled, and their spectra are taken [Figs. 3(d) and (e)]. A comparison of the spectra, Figs. 3(c) and 3(d) shows that they are identical, indicating the intermediate to be a mixture of ammonium oxalate and thallous oxalate. The absorption at 3325, 1570 and 640 cm^{-1} in Fig. 3(d) indicate that the intermediate obtained by heating the complex to 150 °C and cooling to room temperature contains water. This is because even though ammonium oxalate monohydrate gets dehydrated below 130 °C, the dehydrated form absorbs moisture from the atmosphere. Figure 3(e) is identical to Fig. 3(b), indicating the intermediate obtained at 250 °C to be thallous oxalate.

TABLE 3

X-RAY DIFFRACTION DATA

Complex	*Complex heated to*		$Tl_2C_2O_4$
	150°C Intermediate 3	*250°C Intermediate 4*	
7.803_2			
		6.657_3	
	6.511_2		6.511_2
6.371_x			
4.720_6			
	4.332_3	4.353_4	4.311_2
4.250_3			
3.934_2			
	3.802_4	3.803_2	3.802_3
3.590_4			
	3.447_x	3.435_x	3.440_x
	3.267_3	3.267_4	3.278_6
	3.115_5	3.121_5	3.111_4
	2.921_2	2.903_7	2.912_2
2.885_3			
2.880_6			
	2.767_5	2.771_7	2.763_7
	2.656_3	2.659_4	2.659_3
	2.522_2	2.522_2	2.522_2
2.398_2			
	2.186_3	2.186_5	2.186_6
	2.137_3		
2.090_2			
	2.040_2	2.045_4	2.036_2
1.965_2			
	1.868_2	1.873_3	1.877_4
1.752_2			
	1.701_1		
	1.598_2	1.595_2	1.598_2

X-ray diffraction data d (Å)

The prominent peaks of the X-ray diffraction data of the complex, its heated products (intermediates 3 and 4) and the thallous oxalate are given in Table 3. It is evident from the table that the intermediate (4) is thallous oxalate. The table also indicates the presence of free thallous oxalate in the intermediate (3). None of these *d* values are in coincidence with those of the complex. The prominent *d* values of the complex (6.371_x, 4.720_6 and 2.880_6) may be utilised to differentiate the ammonium salt from the other salts of the bisoxalatothallate(III) ion[42].

Microscopic observations

Thallous oxalate crystals are colourless, transparent and highly birefringent with symmetrical extinction. The refractive index, $\bar{n} > 1.516$. The crystals are biaxial and negative with a $2V$ value of 70°.

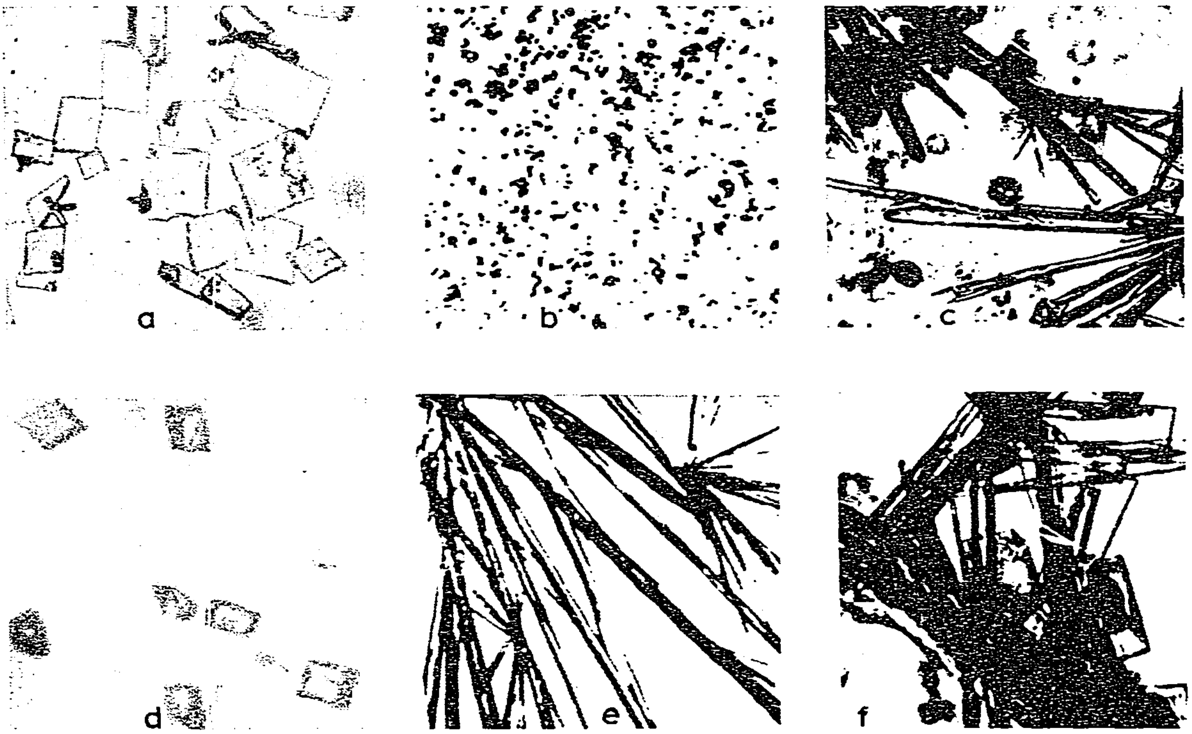


Fig. 4. Photomicrographs of (a) thallous oxalate, (b) the complex, (c) and (d) intermediates 3 and 4, (e) ammonium oxalate monohydrate, (f) an equimolar mixture of ammonium oxalate monohydrate and thallous oxalate.

From the photomicrograph [Fig. 4(a)] it can be seen that the crystals of thallous oxalate are prismatic and base flattened. Some are flakes with almost square surfaces.

From the photomicrographs of thallous oxalate (Fig. 4(a), the complex [Fig. 4(b)], the intermediates 3 and 4 [Figs. 4(c) and (d)], ammonium oxalate monohydrate [Fig. 4(e)] and an equimolar mixture of ammonium oxalate monohydrate and thallous oxalate [Fig. 4(f)], it is evident that the microphotograph of the intermediate 3 [Fig. 4(c)] and the equimolar mixture of ammonium oxalate monohydrate and thallous oxalate [Fig. 4 (f)] are one and the same, consisting of separate characteristic base flattened, prismatic highly birefringent, monoclinic crystals of thallous oxalate and needle shaped, highly refracting crystals of ammonium oxalate monohydrate. It clearly suggests that the intermediate 3 is a mixture of ammonium oxalate and thallous oxalate.

Similarly, the intermediate 4 [Fig. 4(d)] is similar to thallous oxalate [Fig. 4(a)] and its $2V$ value is found to be 70° suggesting the intermediate to be thallous oxalate.

Electrical conductivity measurements

The complex was made into a pellet and this was used for measuring its resistance. A plot of the resistance of the complex versus temperature (rate of heating,

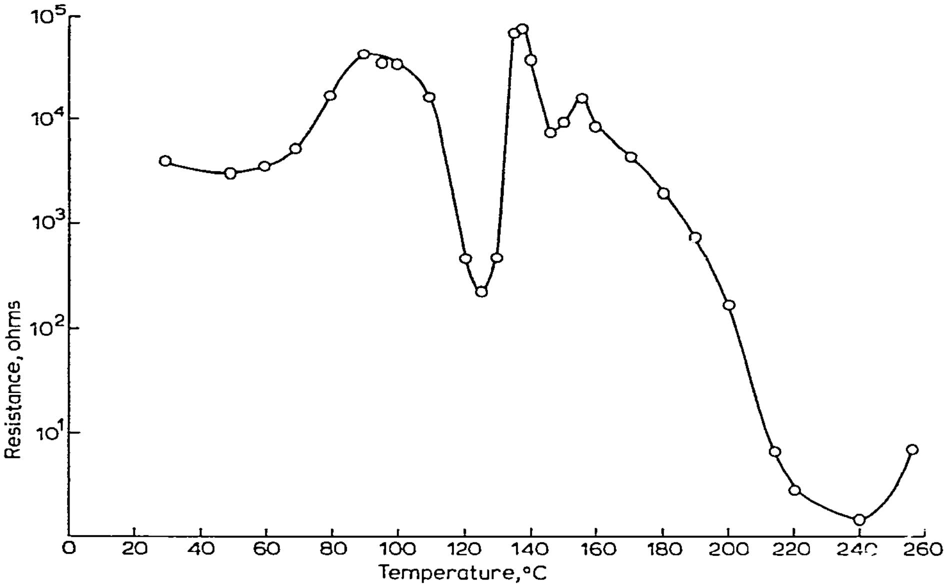


Fig. 5. Variation of resistance with increase in temperature of ammonium bisoxalatothallate(III).

5 °C min^{-1}) is shown in Fig. 5. From the figure, it is clear that there is an initial rise in the resistance due to the evaporation of the adsorbed moisture. The peaks in the conductivity at 125 and 145 °C are obviously due to the dehydration and the redox decomposition of the complex. The product obtained at this stage shows similar behaviour to that of an equimolar mixture of anhydrous ammonium oxalate and thallous oxalate. In spite of the limitations of the method due to decomposition, it can be broadly seen that these observations are also in agreement with the suggested scheme of thermal decomposition of the complex.

Bisoxalatothallate(III) is reported[28-30] to be octahedral in $H[Tl(C_2O_4)_2] \cdot 3H_2O$ and $K[Tl(C_2O_4)_2] \cdot 3H_2O$ and to be tetrahedral in $NH_4[Tl(C_2O_4)_2] \cdot H_2O$. Our present findings show that the ammonium salt of bisoxalatothallate(III) contains 3 molecules of water (when prepared according to the procedure[32] described by us). The acid and potassium bisoxalatothallate(III), containing 3 molecules of water, are assumed to be octahedral on the grounds that octahedral bonds are stronger than tetrahedral bonds[43]. The same argument can be extended to ammonium bisoxalatothallate(III) trihydrate also. Moreover, the infrared spectral studies confirm the presence of both coordinated and crystal water in the complex suggesting that it is more likely to be octahedral. Hence the complex may be formulated as $NH_4[Tl(C_2O_4)_2(H_2O)_2] \cdot H_2O$.

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