

Thermal decomposition of potassium *bis*-oxalatoindate(III) monohydrate

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MS received 5 February 2001; revised 2 April 2001

Abstract. Indium(III) is precipitated with oxalic acid in the presence of potassium nitrate maintaining an overall concentration of 0.125 M in HNO₃. Chemical analysis of the complex salt obtained indicates the formula, K[In(C₂O₄)₂].3H₂O. Thermal decomposition studies show that the compound decomposes first to the anhydrous potassium indium oxalate and then to the final mixture of the oxides through formation of potassium carbonate and indium (III) oxide as intermediates. Isothermal study, X-ray diffraction pattern and IR spectral data support the proposed thermal decomposition mechanism.

Keywords. *bis*-oxalates; indium (III); potassium indium oxalate; thermal decomposition.

1. Introduction

Alkali metal oxalato complexes with In³⁺ to C₂O₄²⁻ ratio of 1:2 are known^{1,2}. Studies of stability constants of indium-oxalato system³⁻⁵ suggest that the reaction between In³⁺ and C₂O₄²⁻ ions takes place in stages, with the formation of [InC₂O₄]⁺, [In(C₂O₄)₂]⁻, and [In(C₂O₄)₃]³⁻ depending on the relative initial concentrations of indium and oxalate and the pH of the solution⁶⁻⁸. At very low concentrations, very stable positive [InC₂O₄]⁺ ions are formed. Increase in the oxalate concentration leads to the formation of [In(C₂O₄)₂]⁻ ion, which makes it impossible to precipitate indium quantitatively as hydroxide by the usual method. Recently, the In(III)-H₂C₂O₄-H₂O system has been studied⁵ by the alkalimetric titration method in perchloric acid medium maintaining an ionic strength of 0.2 M (NaCl) and the species distribution has been determined at various pH levels. The results of this study show that the *bis*-oxalato form is predominant in the pH range of 2–5. Thus, the precipitation of *bis*-oxalatoindate (III) complexes of the form Mⁿ⁺[In(C₂O₄)₂(H₂O)₂]_n.xH₂O is possible for n = 1, 2 and 3. In this article we present the results of our investigation on the preparation and physicochemical properties of the potassium complex on the basis of chemical and thermal analyses (TG/DTA), iso-thermal studies, IR spectra and X-ray diffraction data. A plausible mechanism for the thermal decomposition of the complex that has been arrived at from these results is discussed.

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2. Experimental

2.1 Instrumentation

2.1a *Thermal analysis unit:* A SEIKO combined thermal analysis system (TG/DTA-32), temperature programmable thermal balance, with platinum crucible as container, is used for taking thermograms in air. The rate of heating is fixed at 10°C/min, and sensitivity of the instrument is 0.1 mg.

2.1b *Infrared spectra:* The infrared spectra of the complexes homogenised in KBr pellets are recorded on Shimadzu FTIR-8201 PC infrared spectrophotometer.

2.1c *X-ray diffraction data:* X-ray diffractometer of Rich Seifert & Co. attached to a microprocessor is used for taking X-ray diffraction patterns at the wavelength of $\text{CuK}_{\alpha 1} = 1.540598 \text{ \AA}$.

2.2 Preparation and analysis

Potassium *bis*-oxalatodiaquaindate (III) complex salt is prepared by the following procedure.

About 80 cm³ of 0.05 M indium (III) nitrate in 0.625 M HNO₃ was taken in a 500 cm³ beaker to which about 60 cm³ 1 M potassium nitrate and 180 cm³ triple distilled water were added slowly while stirring the contents. Then about 80 cm³ of 0.1 M oxalic acid was added very slowly (drop-wise from a burette) while stirring the contents vigorously. The complex salt formed was allowed to settle and filtered through a G₄ sintered glass crucible. The precipitate was then washed several times (with a solution obtained by mixing 0.3 M KNO₃ and 0.25 M HNO₃ in 1:1 ratio) to free the excess oxalic acid. Finally the precipitate was washed free of KNO₃ with 0.1 M HNO₃. The precipitate was dried in a vacuum desiccator over silica gel. The compound thus obtained was tested to confirm the absence of nitrate.

The *bis*-oxalato complex can also be isolated from sulphate medium (containing 0.0625 M H₂SO₄ and 0.05 M K₂SO₄) and purified following a procedure similar to that in the nitrate medium.

The compound was analysed for its indium, oxalate and water content. Indium (III) was estimated complexometrically using 1-(2-pyridylazo)-2-naphthol (PAN) as indicator⁹ and oxalate by volumetric titration with standardised cerium (IV) sulphate¹⁰. Water content was determined by difference in weight and from thermal data. The results of the analysis of the complex are given below.

Found: In³⁺ = 30.11%; C₂O₄²⁻ = 45.73%*; K⁺ = 10.37%*; H₂O = 13.79%*; C₂O₄²⁻/
In³⁺ = 1.98

*Calculated from the possible formula

The data correspond to the formula KIn(C₂O₄)₂·3H₂O. As indium (III) is known to exhibit octahedral coordination^{1,2}, the structural formula may be given as KIn[(C₂O₄)₂(H₂O)₂]·H₂O.

3. Results and discussion

3.1 Thermal studies

3.1a *Thermogravimetric analysis (TG)*: The pyrolysis curve of potassium bis-oxalatodiaquaindate (III) monohydrate and the data obtained from it are given in figure 1 and table 1 respectively. From the TG curve it is evident that there are four regions where the complex has undergone weight loss. The first loss, between 50° and 150°C, is obviously due to loss of crystal water and amounts only to about 5% (ca. 4.68%) of the original weight of the complex. In the subsequent stage, from 150° to 203.7°C, the complex has lost the coordinated water as well. The total weight loss up to this stage is observed to be 14.26% against the calculated value of 14.06%. This confirms that complete dehydration of the potassium complex has taken place up to around 200°C.

The resulting anhydrous salt, KIn(C₂O₄)₂ undergoes continuous decomposition as shown by the TG curve from 203° to 346.9°C. This corresponds to the decarboxylation

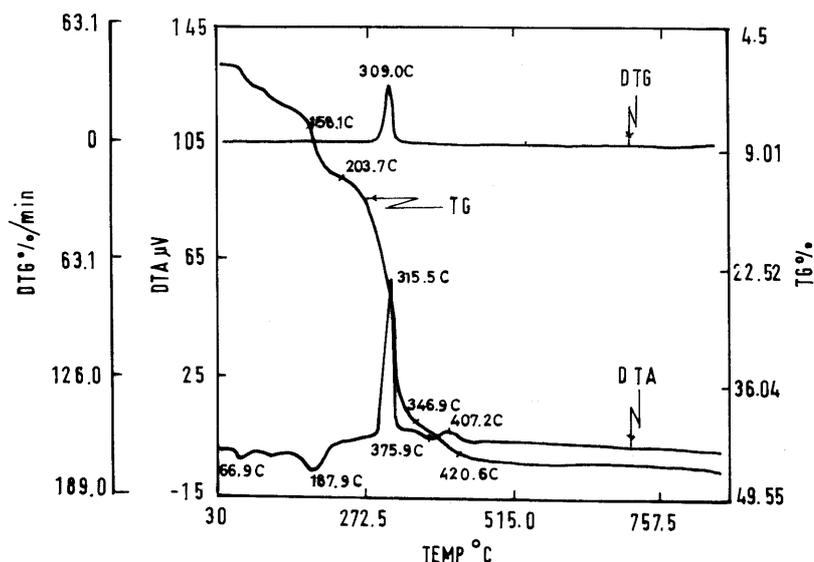


Figure 1. TG/DTA curve of potassium bis-oxalatodiaquaindate (III) monohydrate.

Table 1. Summary of the thermal decomposition of the potassium bis-oxalatodiaquaindate (III) salt.

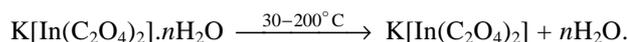
Temp. (°C)		Loss in weight (%)		DTA peaks (°C)	Reaction	Possible decomposition product (intermediate)
Start	End	Obsv.	Calc.			
50.0	158.1	5.62	4.80	66.9	Dehydration	K[Ln(C ₂ O ₄) ₂ (H ₂ O) ₂]
158.1	203.7	14.26	14.06	187.9	Dehydration	KIn(C ₂ O ₄) ₂
203.7	346.9	40.69	40.80	315.5	Decomposition	K ₂ C ₂ O ₄ + In ₂ O ₃
346.9	420.0	44.53	44.87	407.2	Decomposition	K ₂ CO ₃ + In ₂ O ₃

of the indium (III) oxalate as evidenced by the observed loss in weight of 40.69% at 346.9°C against that of the calculated 40.80% for the residue containing $K_2C_2O_4$ and In_2O_3 . On further heating, the potassium oxalate decomposes to the carbonate in the range of 346.9° to 420°C. The residue, which is a mixture of In_2O_3 and K_2CO_3 , remains stable up to about 850°C.

3.1b *Differential thermogravimetric analysis (DTG)*: The DTG curve given in figure 1 shows no significant peaks attributed to the dehydration of the complex even if gradual weight loss is observed in the TG curve. The strong peak with ΔT_{max} at 309.0°C, having a rate of decomposition of 29.8%/min. indicates that the thermal decomposition of the anhydrous complex is a continuous process in which the decomposition of indium oxalate is followed by the decomposition of potassium oxalate.

3.1c *Differential thermal analysis (DTA)*: From figure 1 it is clear that the dehydration of potassium *bis*-oxalatodiaquaindate (III) monohydrate takes place in two steps. The first is indicated by the small peak with ΔT_{min} at 66.9°C and the second by a broad endothermic peak with ΔT_{min} at 187.9°C. These are obviously due to the loss of crystal and coordinated water respectively. A sharp exothermic peak with ΔT_{max} at 315.5°C is due to the decomposition of the anhydrous potassium indium oxalate to a mixture of potassium oxalate and indium (III) oxide. The DTA curve also indicates a small exothermic peak with ΔT_{max} at 407.2°C, which corresponds to the decomposition of potassium oxalate to the carbonate.

3.1d *Isothermal decomposition of potassium bis-oxalatodiaquaindate (III) monohydrate*: Pyrolysis curve of the potassium salt (figure 1) indicates that dehydration is complete around 200°C to give rise to potassium indium oxalate. Thus, if the original complex salt is heated to an appropriate temperature in the range of 175° to 200°C the intermediate product can be obtained. The decomposition may be given by,



In this study a known weight (ca. 300 mg) of potassium *bis*-oxalatoindate (III) monohydrate was taken in a dry and weighed porcelain crucible and heated up to about 175°C and maintained at this temperature for half an hour. The product so obtained was analysed for indium and oxalate contents^{9,10}. The ratio of $C_2O_4^{2-}$ to In(III) was found to be 2:1.

The water content of the complex salt was determined by back-calculating from the weight of the intermediate, $KIn(C_2O_4)_2$. The number of water molecules was found to be three per molecule of $KIn(C_2O_4)_2$. Thus the probable formula of the potassium complex is $K[In(C_2O_4)_2].3H_2O$ or $K[In(C_2O_4)_2(H_2O)_2].H_2O$.

3.2 *Infrared spectra of potassium bis-oxalatodiaquaindate (III) monohydrate*

The infrared spectra of potassium *bis*-oxalatodiaquaindate (III) monohydrate is shown in figure 2. A broad and strong absorption peak at 3573 cm^{-1} and a shoulder at 3497 cm^{-1} in

the figure are indicative of the asymmetric and symmetric stretching modes of vibration of H–O–H¹¹. A very broad and strong absorption peak at 1617 cm⁻¹ is indicative of bending modes of vibration of H–O–H¹² suggesting the presence of water. The same band also corresponds to the asymmetric stretching modes of vibration of C=O¹³. A very sharp and strong absorption at 808 cm⁻¹ indicates the wagging modes of vibration of coordinated water as well as the bending modes of vibration of O–C=O¹³ and the M–O bond in the complex. The shoulder at 550 cm⁻¹ may be indicative of crystal water.

The infrared spectral data of potassium bis-oxalatodiaquaindate (III) monohydrate and its decomposition product (heated to 175°C and cooled to room temperature) are compared in table 2. From the thermal data of the complex it is inferred that an intermediate corresponding to the empirical formula, KIn(C₂O₄)₂, is obtained between 150° and 203°C. Infrared spectrum of the intermediate (figure 3) confirms the

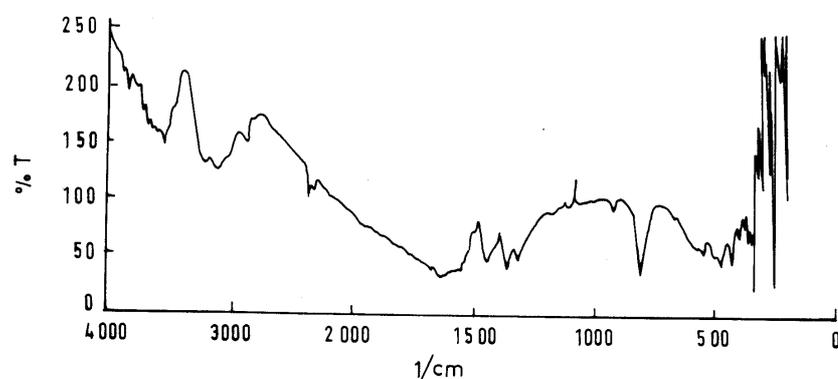


Figure 2. Infrared spectrum of potassium bis-oxalatodiaquaindate (III) monohydrate.

Table 2. Infrared absorption data of potassium bis-oxalatodiaquaindate (III) monohydrate and the heated product at 175°C.

Complex		
Original	Heated at 175°C	Band assignment
3573 <i>b, vs</i>	3520 <i>b, vs</i>	$n_{as, s}$ (H–O–H)
3497 <i>sh</i>		
3100 <i>b, s</i>		
1617 <i>b, s</i>	1620 <i>b</i>	n_a (C=O) + d (H–O–H)
1450 <i>m</i>		n_s (C=O) + d (O–C=O)
1350 <i>m</i>	1350 <i>m</i>	
1300 <i>sh</i>	1300 <i>sh</i>	
910 <i>sp, w</i>		Coordinated water and d (O–C=O) + n (M–O)
808 <i>sp, vs</i>	808 <i>sp, m</i>	
550 <i>sh</i>		Crystal water
490 <i>sp, m</i>	480 <i>w</i>	n (M–O) + d (O–C=O)
420 <i>sp, m</i>	400 <i>sh</i>	d (O–C=O) + n (C–C)
350 <i>sh</i>	350 <i>w</i>	

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

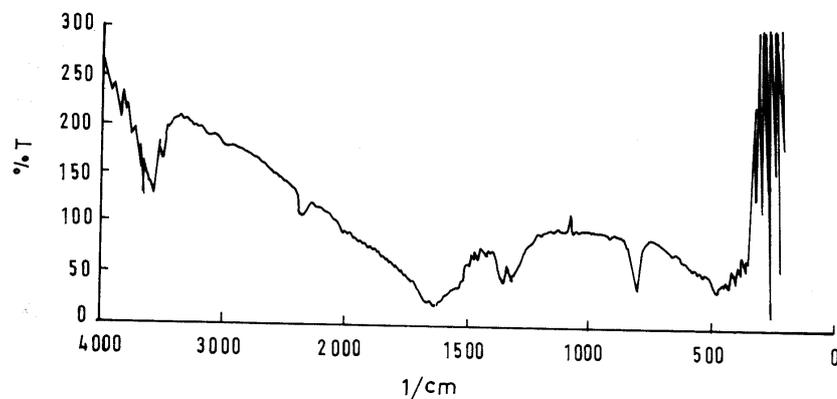
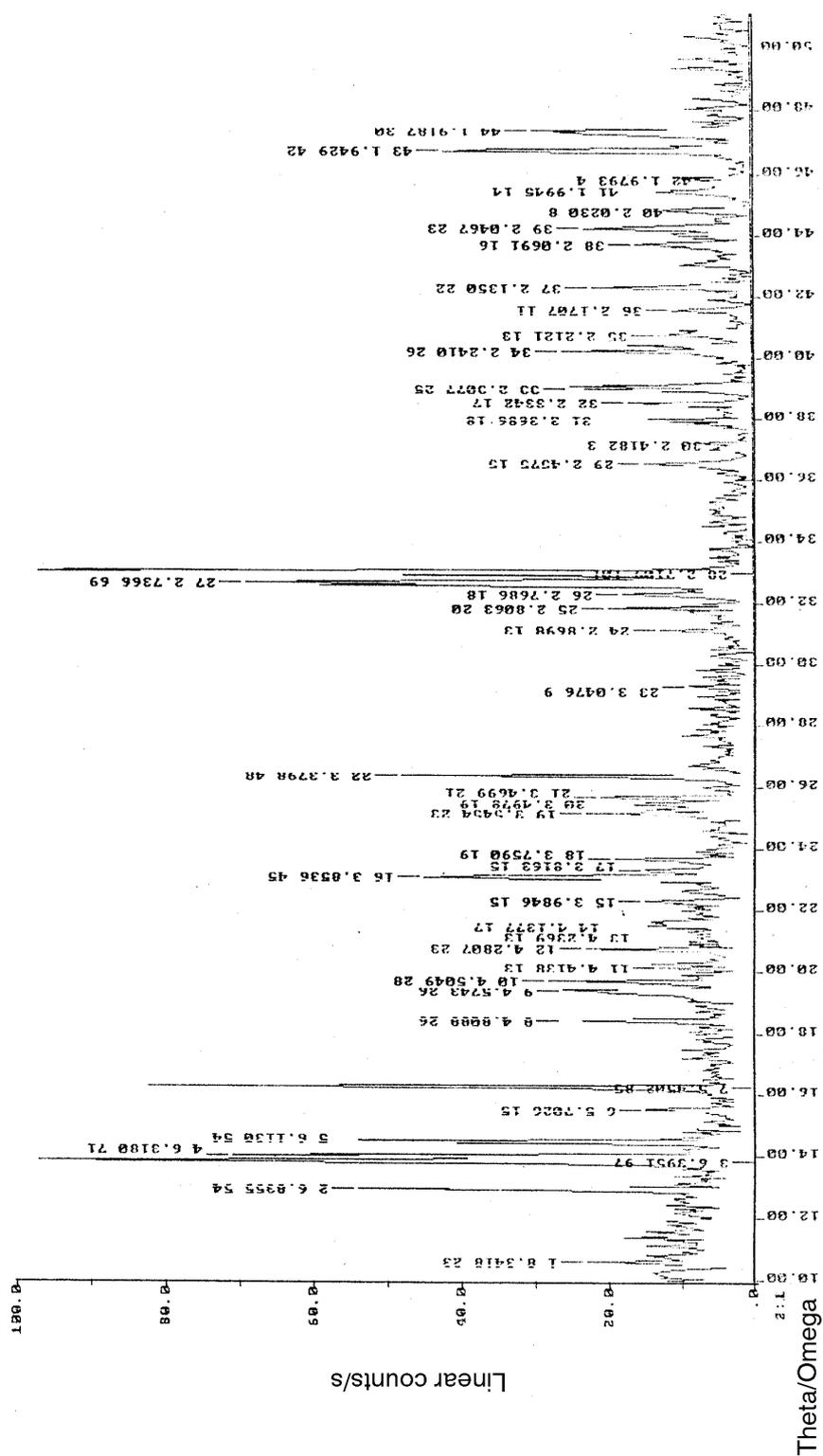
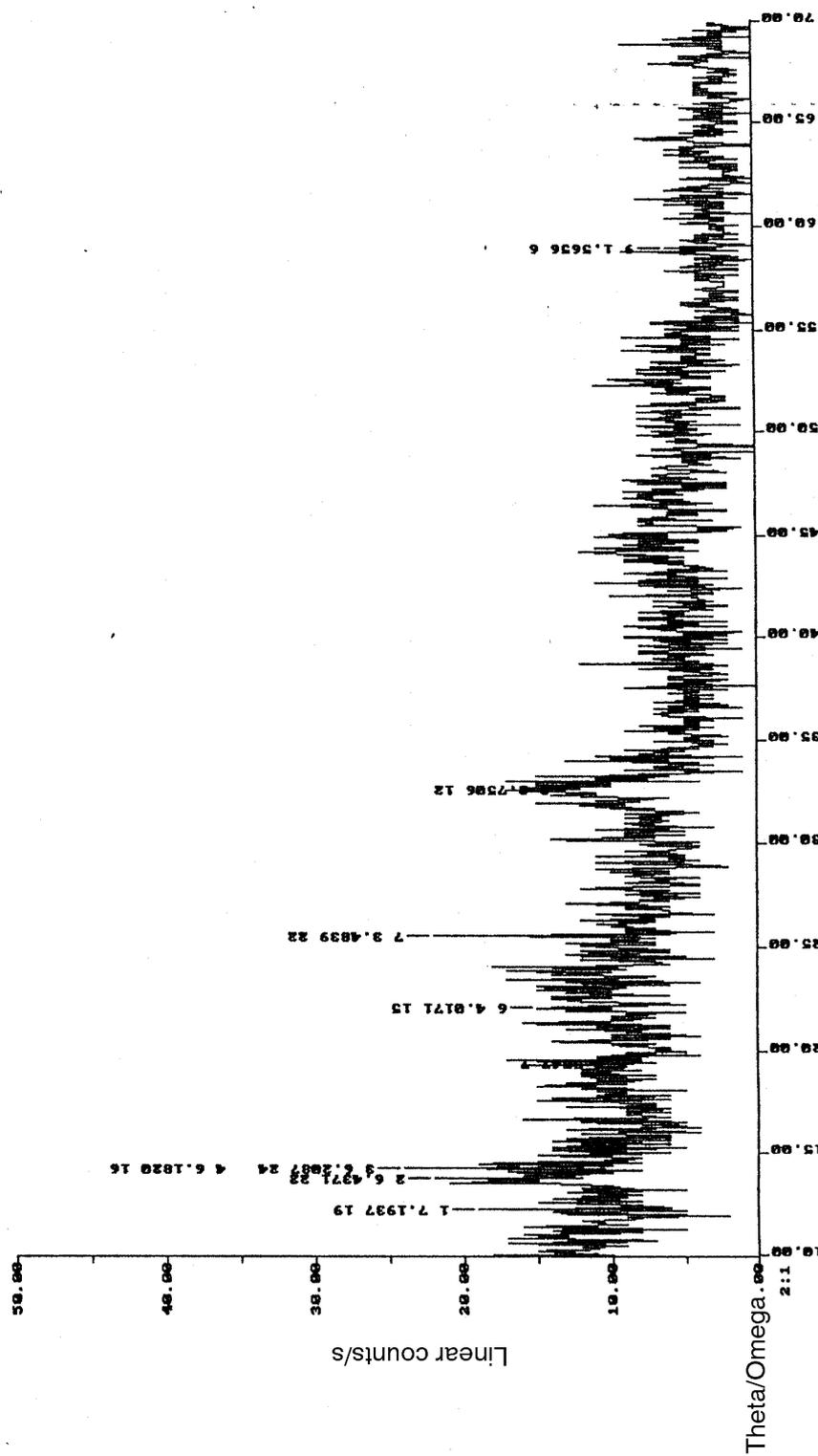


Figure 3. Infrared spectrum of potassium *bis*-oxalatoindate(III) monohydrate after heating to 175°C.

Table 3. X-ray diffraction data of potassium *bis*-oxalatoindate(III) monohydrate and the product after heating it to 175°C, compared with indium(III) oxalate and potassium oxalate.

K ⁺ complex	Complex heated to 175°C	In ₂ (C ₂ O ₄) ₃	K ₂ C ₂ O ₄
8.342 ₂	7.194 ₈		
6.836 ₅		5.671 ₃	
6.395 ₉	6.437 ₉	5.515 _x	
6.318 ₇	6.209 _x	5.357 ₁	
6.113 ₅	6.182 ₇	5.092 ₂	
5.450 ₈		5.035 ₂	
4.809 ₃		4.794 ₁	
4.574 ₃	4.555 ₃	4.648 ₁	
4.505 ₃		4.026 ₂	
4.281 ₂		3.921 ₂	4.310 ₁
4.138 ₂	4.017 ₆	3.807 ₃	
3.854 ₄		3.677 ₂	
3.759 ₂		3.555 ₂	
3.545 ₂		3.306 ₁	
3.498 ₂	3.484 ₉	3.231 ₂	
3.470 ₂		3.143 ₁	
3.380 ₅		3.050 ₄	3.100 ₁
2.806 ₂		3.001 ₂	2.920 _x
2.769 ₂	2.751 ₅	2.773 ₁	
2.737 ₇		2.740 ₂	
2.711 _x		2.529 ₂	
2.369 ₂		2.431 ₂	2.460 ₆
2.334 ₂		2.334 ₂	2.320 ₆
2.308 ₂		2.218 ₁	
2.241 ₃		2.168 ₁	
2.135 ₂		2.134 ₁	2.140 ₁
2.069 ₂		2.005 ₂	
2.047 ₂		1.952 ₁	
1.943 ₄		1.937 ₂	
1.919 ₃		1.840 ₁	
1.740 ₄		1.779 ₂	
	1.566 ₃	1.693 ₁	
		1.529 ₁	





XRD spectrum of the product obtained after heating potassium bis-oxalatoaquaindate (III) monohydrate to 175 °C.

presence of water in the product obtained by heating at 175°C and cooling to room temperature. This is due to the absorption of moisture by the product. Comparison of the infrared spectra of the original complex and the decomposition product indicates that the two compounds are basically different. The absence of strong absorption bands at 1450 cm⁻¹ and 910 cm⁻¹ supports this assertion.

3.3 X-ray diffraction spectra

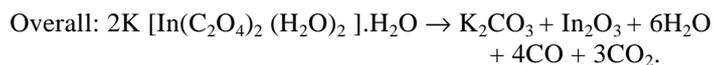
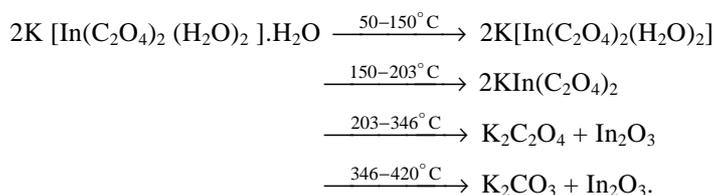
Powder XRD spectra of potassium bis-oxalatodiaquaindate (III) monohydrate and that of the product obtained after heating the original complex to 175°C and cooling are given in figures 4 and 5 respectively. Table 3 is also given to show the major *d*-spacings of the same along with those of indium (III) oxalate and potassium oxalate for comparison.

The data in the table clearly show that the decomposition product obtained at 175°C is the potassium indium oxalate complex rather than a mixture of indium and potassium oxalates. The next decomposition product could not be isolated as the decomposition of potassium oxalate immediately followed the decomposition of indium oxalate to indium oxide. However, when the sample was heated to 400°C a pale yellow product was obtained suggesting that In₂O₃ is actually formed. In the literature we find the decomposition of In₂(C₂O₃)₃ occurs in the range² of 210°–520°C and that of K₂C₂O₄ in the range¹⁴ of 425°–550°C.

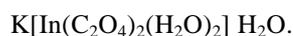
The potassium complex was also heated to 500°C and maintained at this temperature for half an hour. The product obtained in this manner was tested for carbonate by the usual acid test. The result of this test indicates that one of the products at this stage of the thermal decomposition is a carbonate salt. The present authors also noted that the XRD data in the literature for K₂CO₃ match some of the *d*-spacings in the heated product obtained at 500°C. Thus the thermal decomposition behaviour of the potassium complex and the literature reports suggest the presence of potassium carbonate at this stage.

4. Conclusions

Basing on the results of all these investigations the following thermal decomposition mechanism is proposed.



The proposed mechanism suggests that the most probable structural formula of the complex with octahedral coordination of indium (III) is:



Acknowledgements

One of the authors (Tesfahun Kebede) thanks the Ethiopian Embassy, New Delhi for financial assistance.

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