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SOME STUDIES ON THALLIUM OXALATES. XIII. SODIUM BIS-OXALATODIAQUOTHALLATE(III) MONOHYDRATE

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Sodium bis-oxalatodiaquothallate(III) monohydrate has been prepared and characterised by chemical, thermal, X-ray diffraction and infrared spectroscopic methods. Thermoanalytical studies indicated that the complex decomposes through the formation of a mixture of thallium(I) oxalate and sodium oxalate, the final product at 650° being a mixture of thallium(I) oxide, thallium(III) oxide and sodium carbonate.

The presence of a suitable concentration of NH_4^+, K^+, Rb^+, Cs^+, Tl^+, Sr^{++} or Ba^{++} in the potentiometric titration of thallium(III) with oxalic acid was found to alter the metal-ligand ratio from 1:1.5 to 1:2 [1–3]. The present article deals with the effect of variation of the Na^+ concentration on the formation of, and some studies on, the bis-oxalatothallate(III) complex.

Experimental

The materials used and the methods employed were similar to those already described [4, 5]. For DTA, a fabricated unit with an automatic recorder was used, with platinum cups as sample holders and recalcined Al_2O_3 as the reference material. The heating rate was 4–5 deg/min.

The effect of variation of the concentration of sodium sulphate was studied on the potentiometric titration of thallium(III) with oxalic acid in 0.075 *M* sulphuric acid medium. It was found that the bis-oxalatothallate(III) complex formed if the concentration of sodium sulphate was around 0.25 *M*. The results are shown in Fig. 1.

Under these conditions the complex was prepared. About 50 ml of 0.05 *M* thallium(III) sulphate in 1 *M* sulphuric acid was taken in a 600 ml beaker, and 50 ml of 1 *M* sodium sulphate and 350 ml of distilled water were added slowly while the contents were stirred to avoid the precipitation of thallium as thallic hydroxide.

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Then 50 ml of 0.10 *M* oxalic acid was added very slowly (dropwise from a burette) while the contents were stirred vigorously. The complex formed was filtered through a No. 4 sintered glass crucible, washed with acidulated (with sulphuric acid) water to free it from excess of oxalic acid, and dried in a vacuum desiccator over silica gel.

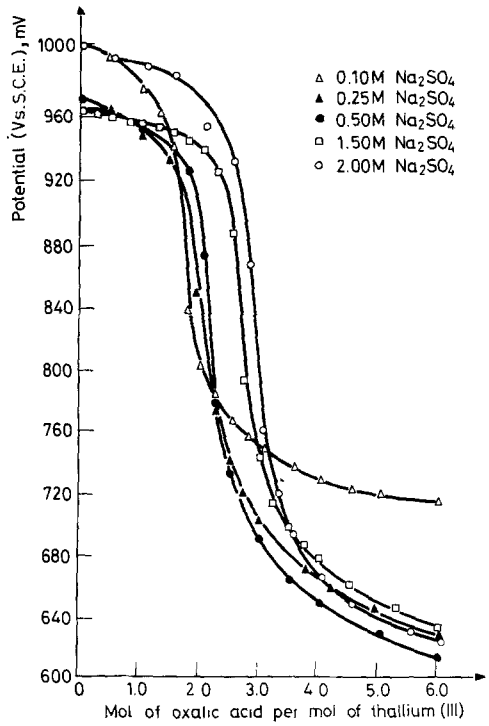

Fig. 1 Effect of variation of sodium sulphate concentration on potentiometric titration curve of thallium(III) sulphate with oxalic acid in 0.075 *M* sulphuric acid medium

The oxalate and thallium contents of the compound were determined using the methods developed by Sagi *et al.* [6, 7]. The weight of water was computed from the difference in weight.

$$\text{Found: } Na^+ = 4.7\%, \quad Tl(III) = 42.0\%$$
$$C_2O_4^{2-} = 37.0\% \text{ and } H_2O = 16.2\%$$

The data correspond to the Formula $NaTl(C_2O_4)_2 3H_2O$. As thallium(III) is known to exhibit octahedral coordination [8], the structural formula may be given as $Na[Tl(C_2O_4)_2(H_2O)_2].H_2O$.

Table 1 X-ray diffraction data on the complex

2Θ	d, Å	$I/I_0 \times 100$	2Θ	d, Å	$I/I_0 \times 100$
11.5	7.69	9.0	38.2	2.36	13.0
13.6	6.51	100.0	40.8	2.21	7.0
18.5	4.80	32.0	42.2	2.14	1.0
21.3	4.17	21.0	43.0	2.10	16.0
23.2	3.83	26.0	45.2	2.01	7.0
29.8	3.00	3.0	46.7	1.95	7.0
31.8	2.81	15.0	47.5	1.91	5.0
32.0	2.80	67.0	48.6	1.87	7.0
34.2	2.62	3.0	50.6	1.80	4.0
35.6	2.52	7.0	52.6	1.74	5.0

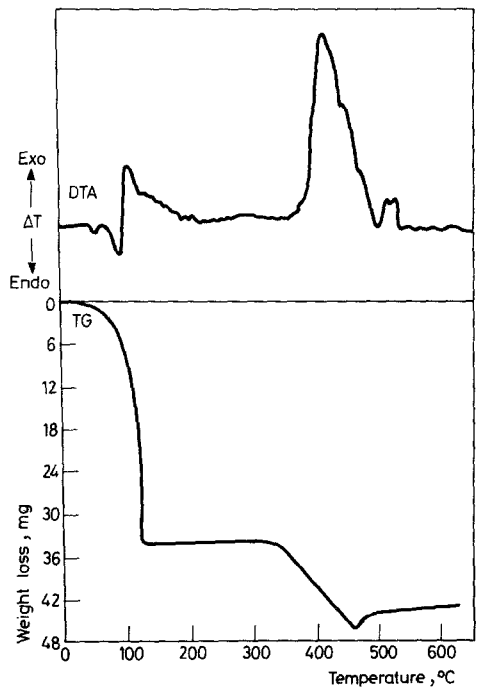

Fig. 2 TG and DTA of sodium bis-oxalatodiaquothallate(III) monohydrate

The X-ray data on the complex are given in Table 1. Their comparison with the data for sodium oxalate [9], thallium(III) oxalate [10] and thallium(I) oxalate [4] confirms that it is a new compound.

The TG and DTA curves of sodium bis-oxalatodiaquothallate(III) monohydrate are shown in Fig. 2. In the TG curve recorded with a sample weight of 109 mg, the

loss of weight from 50° to 130° corresponds to complete dehydration and decomposition of thallium(III) oxalate to thallium(I) oxalate. the salt having the empirical formula $NaTlC_2O_4$. The dehydration is stepwise, as indicated by endothermic peaks at 60° and 100° in the DTA curve. The exothermic peak at 120° corresponds to the redox decomposition of the complex. $NaTlC_2O_4$ further

Table 2 Infrared spectral data on the complex, cm^{-1}

Absorption frequency	Assignment	Reference
3600–3450 b, st	ν_a^{60s} and ν_s(H—O—H)	[11]
1600 b, vst	ν(C=O)+δ(H—O—H)	[12]
1460 sp, m	ν(C—O)+ν(C—C)	—
1230 sp, m	ν(C—O)+ν(C—C)	—
800 sp, m	δ(O—C=O)+ν(M—O) (coordinated water)	[13]

b = broad; st = strong; v = very; sp = sharp; m = medium

decomposes in the range 335–450° to give Na_2CO_3 and Tl_2O, as evidenced by the weight loss in this temperature range and the exothermic peak at 410°. The exothermic peak at 500° and the weight gain in the range 450–500° correspond to the partial oxidation of thallium(I) oxide to thallium(III) oxide.

Microscopic studies similar to those in earlier reports [4, 5], carried out on the intermediate obtained by heating the complex at 135°, confirmed that the product was a mixture of $Tl_2C_2O_4$ and $Na_2C_2O_4$.

The infrared spectral data on the complex are given in Table 2.

On the basis of the above observations, as well as on the chemical analysis data on the intermediates of the complex, the mechanism of thermal decomposition may be given as:

$$NaTl^{III}(C_2O_4)_2 . 3H_2O \longrightarrow NaTl^{III}(C_2O_4)_2 . 2H_2O + H_2O$$

$$NaTl^{III}(C_2O_4)_2 . 2H_2O \longrightarrow NaTl^{III}(C_2O_4)_2 + 2\,H_2O$$

$$2\,NaTl^{III}(C_2O_4)_2 \longrightarrow Na_2C_2O_4 + Tl_2C_2O_4 + 4\,CO_2$$

$$Na_2C_2O_4 + Tl_2C_2O_4 \longrightarrow Na_2CO_3 + Tl_2O + 2\,CO + CO_2$$

$$Na_2CO_3 + Tl_2O \xrightarrow{(0)} Na_2CO_3 + x\,Tl_2O + (1-x)\,Tl_2O_3$$

Hence, the structural formula of the complex may be given as $Na[Tl^{III}(C_2O_4)_2(H_2O)_2] . H_2O$.

References

1. S. R. Sagi and K. V. Ramana, Z. Anal. Chem., 245 (1969) 320.
2. S. R. Sagi and K. V. Ramana, Ind. J. Chem., 9 (1971) 587.
3. S. R. Sagi, M. S. Prasada Rao and Karri V. Ramana. J. Ther. Anal., 20 (1981) 93.
4. S. R. Sagi, Karri V. Ramana and M. S. Prasada Rao, Thermochim. Acta, 31 (1979) 285.
5. S. R. Sagi, Karri V. Ramana and M. S. Prasada Rao, Thermochim. Acta, 33 (1979) 187.
6. S. R. Sagi and K. V. Ramana, Talanta, 16 (1969) 1217.
7. S. R. Sagi and M. S. Prasada Rao, Talanta, 26 (1979) 52.
8. P. J. Durrant and B. Durrant, Introduction to Advanced Inorganic Chemistry, Longman, London, Second Edition, 1969, p. 599.
9. ASTM-Cards, X-ray diffraction data.
10. S. R. Sagi, Karri V. Ramana and M. S. Prasada Rao, Miller Ther. Anal. Vol. II, 506 (1982), Wiley and Sons, Chichester.
11. O. J. Lucchesi and W. A. Glasson, J. Am. Chem. Soc., 78 (1956) 1347.
12. J. Fujita, K. Nakamoto and M. Kobayashi, J. Am. Chem. Soc., 78 (1956) 3963.
13. J Fujita, A. E. Martell and K. Nakamoto, J. Chem. Phys., 36 (1962), 324, 331.

Zusammenfassung — Natrium-bis-oxalatodiaquothallat(III)-Monohydrat wurde hergestellt und chemisch, thermoanalytisch, röntgendiffraktometrisch und infrarotspektroskopisch charakterisiert. Thermoanalytische Untersuchungen haben ergeben, daß sich der Komplex unter Bildung eines Gemisches von Thallium(I)- und Natriumoxalat als Zwischenprodukt zersetzt. Endprodukt der Zersetzung bei 650° ist ein Gemisch von Thallium(I)-oxid, Thallium(III)-oxid und Natriumcarbonat.

Резюме — Получен и охарактеризован химическим, термическим рентгенофазовым анализом и методом ИК спектроскопии моногидрат бис-оксалато-диакво-таллат(III) натрия. Термоаналитические исследования показали, что соединение разлагается через стадию образования смеси оксалатов одновалентного таллия и натрия. Конечными продуктами реакции при температуре 650° является смесь окислов одно- и трехвалентного таллия и карбоната натрия.