SHORT COMMUNICATIONS

THIOSALICYLATES OF ALUMINIUM, TITANIUM, AND ZIRCONIUM*

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A considerable amount of work has been carried out on the preparation and properties of α-hydroxy acid derivatives (lactic, salicylic, and mandelic) of aluminium, titanium, and zirconium,[1–4] but no attempts have been made to prepare thio-acid derivatives of these elements.

Kumar and Nigam have synthesized the thiosalicylic acid derivatives of cadmium, copper, nickel, zinc, and lead,[5,6] and studied their physical properties. The corresponding derivatives of aluminium, titanium, and zirconium have therefore been studied.

TABLE 1

REACTIONS OF ISOPROPOXIDES OF Al, Ti, AND Zr WITH THIOSALICYLIC ACID: PRODUCTS AND ANALYTICAL DATA

Product	Sulphur (%)		Metal (%)		Alcohol (g)	
	Found	Calc.	Found	Calc.	Found	Calc.
$Al(OPr^i)(C_7H_4O_2S)$*	12·9	13·4	12·8	12·6	0·780	0·793
$Al(C_7H_4O_2S)(C_7H_5O_2S)$*	18·8	19·3	8·1	8·0	0·914	0·926
$Ti(OPr^i)_2(C_7H_4O_2S)$†	11·9	12·3	14·7	15·05	1·260	1·287
$Ti(C_7H_4O_2S)_2$†	17·8	18·1	12·3	13·5	1·380	1·414
$Zr(OPr^i)_2(C_7H_4O_2S)$‡	7·9	8·1	26·2	25·25	1·010	1·100
$Zr(C_7H_4O_2S)_2$§	15·7	16·1	12·35	11·9	1·100	1·180

* White powder.

† Exothermic reaction; soluble in benzene; dark brown.

‡ Pale yellow; soluble in benzene.

§ Light yellow; soluble in benzene.

The present work records the isolation of thiosalicylates and mixed alkoxide thiosalicylates formed by treating benzene solutions of the corresponding alkoxides with the requisite quantity of thiosalicylic acid. The technique of alcohol interchange was adopted. The isopropyl alcohol liberated was fractionated out azeotropically with benzene and estimated by the method described by Bradley and co-workers[7] and Mehrotra.[8] This method consists in adding a weighed sample to a

* Manuscript received December 18, 1967.

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measured amount (excess) of standard chromic acid (1N potassium dichromate in 12·5% sulphuric acid) in well-stoppered conical flasks; after allowing the reaction mixtures to stand for about 2 hr at room temperature, the unused chromic acid is titrated iodometrically. On the basis of analytical results and the amount of alcohol collected in the form of the binary azeotrope (summarized in Table 1), these reactions can be represented by the following general equations:

$$M(OPr^i)_4 + nLH_2 \rightarrow M(OPr^i)_2L_n + 2nPr^iOH$$

(where M is Ti or Zr, LH_2 is thiosalicylic acid, and n is 1 or 2).

$$Al(OPr^i)_3 + LH_2 \rightarrow Al(OPr^i)L + 2Pr^iOH$$

$$Al(OPr^i)_3 + 2LH_2 \rightarrow AlL(LH) + 3Pr^iOH$$

The effect of heat (280°/0·5 mm) on the derivatives suggest that they are non-volatile crystalline solids.

Acknowledgments

The authors thank Professor R. C. Kapoor, Head of Department of Chemistry, University of Jodhpur, for providing laboratory facilities. One of us (M.H.) is grateful to CSIR, New Delhi, for a research fellowship during the tenure of which this work was carried out. Thanks are also due to Evans Chemetics (New York) for the gift of thiosalicylic acid.