374. *The Preparation and Constitution of the Thiostannates. Part I. Sodium Ortho- and Meta-thiostannate.*

By Edwin E. Jelley.

Two classes of thiostannate have been described, the meta-, M'_2SnS_3,xH_2O, and the ortho-, M'_4SnS_4,yH_2O. The apparent difference between the covalency of tin in the two classes is the main subject of the present investigation.

Sodium orthothiostannate was prepared by Kuhn (*Annalen*, 1852, **84**, 110) by melting a mixture of sodium sulphide, stannous sulphide, and sulphur. When extracted with hot water, the black mass gave a very dark solution, which deposited colourless monoclinic crystals on cooling; these had the composition $Na_4SnS_4,15H_2O$ when first prepared, but lost 3 mols. of water when dried over sulphuric acid. Weinland and Gutmann (*Z. anorg. Chem.*, 1898, **17**, 418) obtained a yellow salt by boiling a solution of sodium thiosulphate and sodium stannite. It has now been prepared as an *octadecahydrate* by heating sodium stannate with sodium sulphide.

Sodium metathiostannate has been prepared by fusing together a mixture of tin, sodium carbonate, sodium sulphide, carbon, and sulphur (Berzelius, *Ann. Chim. Phys.*, 1817, **5**, 41; 1822, **20**, 138; 1826, **32**, 60; Höring, *Pharm. Ztg.*, 1851, **3**, 120; Ditte, *Ann. Chim. Phys.*, 1907, **12**, 236). Kuhn (*loc. cit.*) obtained it by the action of molten sodium pentasulphide on tin, and ascribed to it the formula $Na_2SnS_3,2H_2O$. The salt was said to form colourless octahedral crystals. By boiling the ortho-salt with stannic sulphide, the meta-salt has now been obtained as a *tri*- and an *octa-hydrate*.

Experimental.

1. *Preparation of Salts.*—Sodium orthothiostannate was prepared by adding 100 g. of technical sodium stannate [79% $Na_2Sn(OH)_6$] and 250 g. of sodium sulphide ($Na_2S,9H_2O$) to 700 c.c. of boiling water. The mixture, which was greenish-black from impurities derived from the stannate, was kept at 90—100° for 3 hours. About 40 g. of "light" magnesium oxide were added, and the heating was continued for 2—3 hours, ferrous sulphide and other impurities being then adsorbed on the oxide. After filtration, the clear pale yellow liquid was concentrated to about 300 c.c. on the water-bath, and then set aside. The crystals which separated were rinsed with a little ice-cold water and twice recrystallised. The yield was 80 g., but in subsequent preparations this was raised successively to 120, 135, and 145 g. by utilising the mother-liquor from previous recrystallisations. In a later preparation, in which 400 g. of sodium stannate [71% $Na_2Sn(OH)_6$] and 800 g. of sodium sulphide crystals in 600 c.c. of boiling water were treated as before, 420 g. of very large colourless crystals were obtained. These monoclinic crystals readily lost water on exposure to the air, and as the loss of the first 2 mols. was not accompanied by any change in their appearance, it was necessary to recrystallise the salt immediately before analysis.

For the preparation of the metathiostannate, 50 g. of pure orthothiostannate in 1500 c.c. of aqueous solution were boiled and treated with *N*-hydrochloric acid from a burette until a spot test with bromocresol-green showed slight excess. The liquid was gently boiled for 4 hours and then set aside. The precipitated stannic sulphide was washed ten times by decantation (each settling operation took 2 days) and then filtered off by suction (this took 5 days owing to the colloidal nature of the precipitate); it was dried at 120°, and the resulting brownish substance was powdered and boiled with 50 g. of sodium orthothiostannate in 100 c.c. of aqueous solution until it had dissolved. The addition of a fragment of granulated tin prevented atmospheric oxidation of the solution. After concentration by boiling, the solution was set aside over calcium chloride. The octahydrate separated as colourless prismatic crystals. The yield after recrystallisation was 37 g. A second preparation yielded 42 g. The trihydrate prepared from the octahydrate was only stable in hot solutions, and difficulty was experienced in freeing the crystals from their mother-liquor on account of the ease with which they changed to octahydrate. This difficulty was overcome by drying the hot drained crystals over some of the partly dehydrated substance. The salts were contained in a desiccator maintained at 110°, a temperature within the stability range of the trihydrate. A series of analyses showed that the crystals rapidly reached a constant composition. In the first preparation 40 g. of octahydrate yielded 11 g. of trihydrate; in the second, 20 g. yielded 9 g. The trihydrate forms strongly birefringent tetragonal bipyramids which are uniaxial with a positive sign. The octahydrate is biaxial with a positive sign, and shows oblique and dispersed extinction. It is, therefore, either monoclinic or triclinic.

The solubilities of these salts in water are (g./100 g. of solution) : $Na_4SnS_4,18H_2O$, 57·1 at 18°; $Na_2SnS_3,8H_2O$, 38·1 at 16°.

2. *Analytical Methods.—Determination of sulphur.* The most trustworthy method of those tried was based on Szeberényi's procedure (*Z. anal. Chem.*, 1932, **88**, 187), which depends on the oxidation of sulphur to sulphate by a warm, strongly alkaline solution of a hypoiodite. An amount of the salt equivalent to about 0·04 g. of sulphur was dissolved in a few c.c. of water, 50 c.c. of approximately *N*/5-sodium hydroxide were added, the mixture boiled, and *N*/10-iodine was run in gradually; after each addition, the solution soon became colourless, and a drop was tested with an external indicator of starch and 6*N*-hydrochloric acid. When excess of iodine was indicated, the liquid was cooled, acidified with a slight excess of 6*N*-hydrochloric acid, and the excess of iodine titrated with *N*/10-thiosulphate : 1 c.c. of *N*/10-iodine = 0·4008 mg. of sulphur.

Determination of tin. Most of the difficulties encountered in the determination of tin as stannic oxide were traced to two sources of error : (i) the precipitated metastannic acid strongly adsorbed sodium ions unless a few hundred times as much ammonium salt was present; (ii) the acid was appreciably soluble in water, particularly if ammonium sulphate was used instead of the acetate to avoid the preceding source of error. The following procedure was found satisfactory. A weighed amount of thiostannate, equivalent to 0·05—0·2 g. of tin, was dissolved in about 50 c.c. of water, and a considerable excess of 6*N*-ammonia was added, followed by a slight excess of hydrogen peroxide (10- or 20-vol.; A.R.). The liquid was boiled gently (vigorous boiling caused some metastannic acid to deposit as a film on the beaker, and subsequent removal was very difficult), acidified with 6*N*-acetic acid, and 5 c.c. of 20% ammonium acetate added. The beaker with its contents was kept on the water-bath for an hour, and the liquid then filtered through a Whatman No. 40 filter. The collected precipitate was washed many times with a 1% solution of ammonium acetate, the filter was dried and incinerated in the usual way, and the weight of stannic oxide determined.

Determination of sodium. Acidimetric titration with *N*/10-hydrochloric acid, with bromocresol-green as an external indicator, gave accurate and reproducible results with sodium orthothiostannate, but was not sufficiently accurate for use with the metathiostannates. For these, (i) direct determination as sodium sulphate and (ii) an indirect method were used.

(i) The filtrate from the tin determination was made alkaline with ammonia, evaporated to dryness in a palladium-gold dish, and the residue heated to expel ammonium salts. The dish was cooled, a few drops of concentrated ammonia were added to decompose any bisulphate (this precaution was probably unnecessary), and the dish was finally raised to a dull red heat. The sodium was weighed as sulphate. The evaporation and heating could be performed without loss by spattering if a layer of glass wool was placed in the evaporating basin : asbestos was unsatisfactory for this purpose.

(ii) The indirect method, which gave consistently good results, was as follows. A weighed amount of thiostannate was dissolved in water, and an excess of *N*/10-sodium carbonate, together with a slight excess of hydrogen peroxide, added. The liquid was boiled for some minutes, cooled, and then back-titrated with *N*/10-hydrochloric acid and bromocresol-green. The alkali consumption was equivalent to the sulphur content over that required to form sodium sulphate from the sodium of the thiostannate. The total sulphur was determined as described above, and the difference gave the amount of sodium present. This method is generally applicable to all complex sulphides.

Determination of water. The total water content was determined by difference, and water of crystallisation by drying the substances at 140—200° in an atmosphere of pure nitrogen or in a vacuum over phosphoric anhydride.

Analyses.—1. *Sodium orthothiostannate* [Found : S, 19·29, 19·39, 19·40, 19·14, 19·41 (mean 19·33); Sn, 17·82, 17·77, 17·94 (mean 17·84); Na, 13·93, 13·92, 13·65, 13·87, 13·85 (mean 13·84);

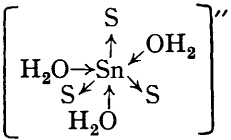
loss at 200—270°, 44·0, 43·04, 43·5; loss over P_2O_5, 43·2 (mean 43·43); $Na_4SnS_4,18H_2O$ requires Na, 13·88; Sn, 17·91; S, 19·31; $16H_2O$, 43·44%]. The two molecules of water which were not removed by drying could not be driven off unless the substance was so strongly heated that it decomposed, stannous sulphide and sodium polysulphides being produced.

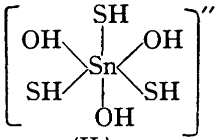
2. *Sodium metathiostannate octahydrate* (Found: S, 23·66, 23·73; Sn, 29·34, 29·67; Na, 11·36, 11·33; loss on heating, 33·05, 33·17; loss in 3 months over P_2O_5, 35·08; $Na_2SnS_3,8H_2O$ requires S, 23·75; Sn, 29·31; Na, 11·36; $8H_2O$, 35·58%).

3. *Sodium metathiostannate trihydrate* (Found: S, 30·10, 30·30; Sn, 38·13, 37·84; Na, 14·34; loss on heating, 15·5; loss over P_2O_5, 16·11; $Na_2SnS_3,3H_2O$ requires S, 30·54; Sn, 37·69; Na, 14·61; $3H_2O$, 17·16%).

DISCUSSION.

Tin shows a great tendency to form complex ions, in many of which it undoubtedly has a valency shell of twelve electrons; *e.g.*, in $(SnCl_6)''2M^{\cdot}$, $[Sn(H_2O)_6]^{\cdot\cdot\cdot\cdot}4Cl'$, and $[Sn(OH)_6]''2Na^{\cdot}$. Dickinson (*J. Amer. Chem. Soc.*, 1922, **44**, 276), on examination of the alkali chlorostannates by the *X*-ray crystallographic method, found that each tin atom is surrounded by six chlorine atoms arranged at the corners of an octahedron, which is strong confirmatory evidence of the 6-covalency of tin. The constitutions of the thiostannates described above are easily explained on this basis. The existence of an octa- and a tri-hydrate of sodium metathiostannate requires explanation; the former is readily formed at room temperature and decomposes on warming, but the latter is formed at higher temperatures and is stable at 115°. It is doubtful if sodium ions can be hydrated at this temperature, and, moreover, there are three molecules of water to two atoms of sodium. It seems reasonable to suppose that the anion in the trihydrate is either (I) or (II), whereas


(I.)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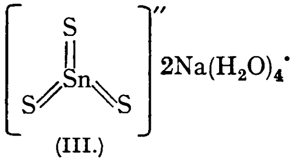
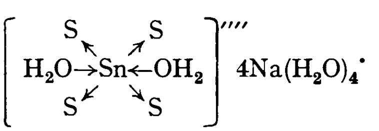
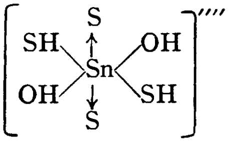

(III.)

in the octahydrate the sodium ions are hydrated (III), owing to the lower temperature. The trihydrate takes up an extra molecule of water if left exposed to the laboratory air for a few weeks, without, however, changing in appearance; and the transition from trihydrate to octahydrate is extremely sluggish if the mother-liquor contains a slight excess of stannic sulphide.

The tenacity with which two molecules of water are held by sodium orthothiostannate strongly suggests that this water is part of a complex ion, and the structure (IV) seems

(IV.)





(V.)

probable. The fact that 18 molecules of water are present supports this view, for sodium ions have a maximum covalency of four. An alternative structure for the anion (V) is possible. In either of these formulæ the tin is 6-covalent.

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