226. *The Preparation and Constitution of the Thiostannates. Part II. Tetra- and Octa-sodium Dioxypentathiostannates.*

By Edwin E. Jelley.

As a result of an attempt to prepare sodium metathiostannate by the method of Kuhn (*Annalen*, 1852, **84**, 110) and Höring (*Pharm. Ztg.*, 1851, **3**, 120), who boiled sodium sulphide with an excess of materials capable of yielding stannic sulphide, two polynuclear thiostannates were isolated which are characterised by the unusual stability of their anions. These salts do not appear to have been previously investigated, although Höring seems to have obtained one of them, for he recorded that his preparations first deposited dirty white needles " of tin and sodium sulphides."

By prolonged boiling of an excess of tin and sulphur in concentrated sodium sulphide solution, a *tetrasodium dioxypentathiostannate* was formed of the empirical composition $Na_4Sn_5S_{10}O_2$,18 or $20H_2O$. By adding two equivalents of sodium sulphide to one of the tetrasodium salt, an *octasodium dioxypentathiostannate*, $Na_8Sn_5S_{12}O_2,32H_2O$, was obtained.

Experimental.

Preparation of Salts.—Tetrasodium dioxypentathiostannate was prepared by boiling 96 g. of crystalline sodium sulphide, 64 g. of sublimed sulphur, and 120 g. of tin foil (99% Sn) with not more than 300 ml. of water under reflux for about 50 hours until the evolution of hydrogen sulphide, at first copious, had ceased. Clean kieselguhr was added, and the solution filtered. On standing at 37°, the pale yellow, highly refractive filtrate afforded colourless prismatic crystals, which became opaque when cooled below 25°. If more water than that stated is used, reaction is very slow. Two preparations together yielded 158 g. of crystals. A considerable excess of stannic sulphide was dissolved by the concentrated solution, which set to a gelatinous mass on cooling. This difficulty was overcome by adding the calculated quantity of sodium sulphide to bring the ratio of sodium to tin to 4 : 5, followed by several hours' refluxing. The tetrasodium salt was also produced by boiling the calculated quantity of precipitated stannic sulphide in a concentrated solution of sodium sulphide or ortho- or meta-thiostannate, much hydrogen sulphide being liberated. A further method of producing the salt was by slowly adding 6 equivs. of *N*-hydrobromic acid to a solution of 5 equivs. of sodium metathiostannate with vigorous boiling. The liquid was evaporated to dryness in a vacuum, and sodium bromide was extracted by absolute alcohol. A concentrated solution of the tetrasodium salt deposits slender acicular crystals at room temperature.

Octasodium dioxypentathiostannate was prepared by crystallising a solution containing 8·02 g. of tetrasodium salt and 2·79 g. of sodium sulphide crystals. The yield of colourless acicular crystals was 9·6 g. It was established by optical measurements with the polarising microscope that a hot concentrated solution of the salt deposited crystals of sodium orthothiostannate and of the tetrasodium salt. After a few hours at room temperature, these substances redissolved and the octasodium salt crystallised in theoretical yield.

Analytical Methods.—Sodium, tin, and sulphur were determined by the methods described in Part I (J., 1933, 1580). As preliminary analyses of the tetrasodium salt showed that the ratio Na : Sn : S was 4 : 5 : 10, the following alternatives were investigated : (1) that two atoms of oxygen were present; (2) that one of the tin atoms was linked to the other four; and (3) that two bivalent tin atoms were present. The liberation of hydrogen sulphide during the formation of the tetrasodium salt was evidence in favour of the first hypothesis. Two analytical methods were applied to this problem. (1) The salt was boiled with 12*N*-hydrochloric acid in an atmosphere of carbon dioxide; the resulting solution was without reducing properties. (2) Sulphur in the salt was determined as barium sulphate, and the result compared with direct and alkaline iodometric titrations according to the methods previously described. Obviously the titration of the salt in acid solution would consume iodine equivalent to $2S + 2Sn^{\bullet\bullet} + 2$(Sn–Sn linkages), whereas the titration in boiling alkaline solution would equal $8S + 2Sn^{\bullet\bullet} + 2$(Sn–Sn linkages). The titres corresponded exactly to the percentage of sulphur determined gravimetrically, so neither stannous tin nor a tin atom linked to the other four is present.

Analyses. (1) Prismatic *tetrasodium dioxypentathiostannate* [Found : Na (mean of six determinations), 6·7; Sn (mean of eight), 43·5; S (mean of four), 23·7; Na : Sn : S = 4·00 : 5·00 : 10·09. $Na_4Sn_5S_{10}O_2,18H_2O$ requires Na, 6·8; Sn, 43·6; S, 23·5%].

(2) Acicular *tetrasodium dioxypentathiostannate* (Found : Na, 6·5, 6·6; Sn, 42·6, 42·5; S, 23·0, 23·0. $Na_4Sn_5S_{10}O_2,20H_2O$ requires Na, 6·6; Sn, 42·45; S, 22·9%). The above two salts when dried to constant weight at 180° gave the *dihydrate* (Found : S, 29·85. $Na_4Sn_5S_{10}O_2,2H_2O$ requires S, 29·85%).

(3) Acicular *octasodium dioxypentathiostannate* [Found : Na, 10·4, 10·3; Sn (mean of four), 33·3; S (mean of three), 21·7; loss on heating, 24·5. $Na_8Sn_5S_{12}O_2,32H_2O$ requires Na, 10·4; Sn, 33·5; S, 21·7; $24H_2O$, 24·4%]. This salt loses $8H_2O$ when exposed to the air.

Chemical Properties.—The reactions of the dioxypentathiostannates with various reagents are contrasted with those of the ortho- and meta-thiostannates in the following table.

	Thiostannate.			
Reagent.	Na_4SnS_4.	Na_2SnS_3.	$Na_4Sn_5S_{10}O_2$.	$Na_8Sn_5S_{12}O_2$.
$N/10$-HCl	Yellow ppt.	Orange-yellow ppt.	No change	No change
$6N$-HOAc	White ppt.	Deep yellow ppt.	No change	No change
H_2O_2	Yellow solution →yellow ppt. →white ppt.	Yellow ppt. →white ppt.	White ppt. forms slowly	White ppt. forms slowly
$N/10$-I_2 in KI	Yellow ppt., sol. in excess ortho solution	Heavy yellow ppt.	White ppt.	White ppt. (faint yellowish tinge)
$K_3Fe(CN)_6$	White ppt.	Yellow ppt.	Clear, followed by slow gelation	Clear, followed by slow precipitation
$K_3Fe(CN)_6$ + 10% HOAc	White ppt.	Yellow ppt.	Clear for 1—2 mins. Deep chrome-green ppt. on boiling	Clear for 1—2 mins. Pale chrome-green ppt. on boiling
$K_2Cr_2O_7$	Ppt. of S; solution darkens to green	Ppt. of S; solution darkens to brown	Slowly darkens →opalescent	Slowly darkens →opalescent
$Pb(OAc)_2$	Chocolate ppt.	Reddish-brown ppt.	Yellow ppt., changes to dark brown	Yellow ppt., changes to dark brown
$Pb(OAc)_2$ + HOAc	Chocolate ppt.	Reddish-orange ppt., changes to reddish-brown	Pale yellow ppt., very slowly darkens	Pale yellow ppt., very slowly darkens
$TlNO_3$	Chocolate ppt.	Reddish-orange ppt.→scarlet	Yellow ppt., darkens to orange	Yellow ppt., darkens to orange
$TlNO_3$ in 25% HOAc	Red ppt.	Orange-red ppt.	Yellow ppt.	Yellow ppt.
$AgNO_3$	Brownish-black ppt.	Brownish-black ppt.	Brownish-black ppt.	Brownish-black ppt.
$ZnSO_4$	White ppt.	White ppt.	White ppt.	White ppt.
$CoSO_4$	Greenish-brown ppt.	Brown ppt.	Greenish-brown coloration	Greenish-brown coloration

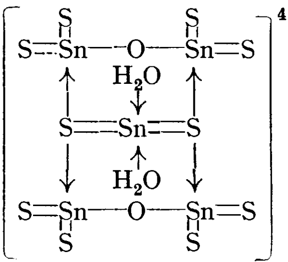
If a dilute solution of tetrasodium dioxypentathiostannate is titrated with $N/10$-hydrochloric acid against methyl-orange in either hot or cold solution, the colour change occurs for a titre equivalent to exactly half the sodium. The reactions with lead acetate, hydrogen peroxide, and acid ferricyanide also indicate that the dioxypentathiostannate anions possess greater stability than those of the ortho- and meta-salts. The tetrasodium salt dries to constant weight in 2 hours at 150—180°, giving an orange residue which readily dissolves in water to yield the original substance. It does not further lose weight on heating to 300°, but the anion is apparently disrupted, as only part of the residue then passes into solution, even on boiling, and much stannic sulphide remains undissolved.

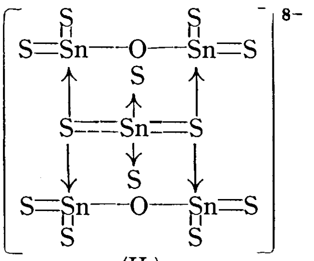
Optical Properties for $\lambda = 589$ mμ.—Mixtures of thiostannates are best identified by optical means, for which purpose the following measurements are supplied. The birefringence of 1, 4, 5, and 6 (see below) was determined with a Berek compensator, and the optic axial angles of 1 and 4 were measured on a Leitz universal stage. The refractive indices of 1 and 3 were determined by the immersion method with a probable error of ± 0·002, but those of 2, 4, 5, and 6 were too high to be measured either by this method or on a crystal refractometer. The values were higher than 1·78, which was that of the most refractive liquid available. The refractive indices of 2 and 4 fell, and those of 1, 5, and 6 rose, when the substance was left exposed to the air, variations which were traced to the gain or loss of moisture respectively.

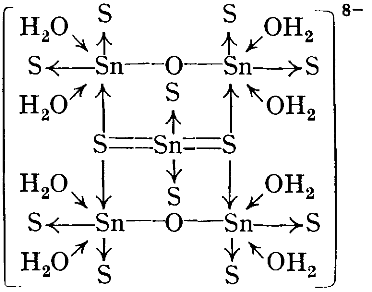
1. $Na_4SnS_4,18H_2O$. Monoclinic prisms; positive biaxial. $2V = 68{\cdot}2^\circ$; $N_\alpha = 1{\cdot}643$; $N_\gamma = 1{\cdot}663$; $N_\gamma - N_\beta = 0{\cdot}0145$. Elongation positive.
2. $Na_2SnS_3,3H_2O$. Tetragonal bipyramids, positive uniaxial; $N_\omega > 1{\cdot}8$; $N_\epsilon - N_\omega$ extreme.
3. $Na_2SnS_3,8H_2O$. Monoclinic (?) prisms; positive biaxial, $2V =$ *ca.* 66°; $N_\alpha = 1{\cdot}605$; $N_\gamma = 1{\cdot}746$.
4. $Na_4Sn_5O_2S_{10},18H_2O$. Triclinic (?) prisms; negative biaxial; N mean = *ca.* 1·80; $2V = 60^\circ$; $N_\gamma - N_\beta = 0{\cdot}0016$; strong dispersion of optic axes.
5. $Na_4Sn_5O_2S_{10},20H_2O$. Orthorhombic needles; negative biaxial, $2V$ small; N mean = *ca.* 1·79; $N_\beta - N_\alpha = 0{\cdot}019$; elongation negative.
6. $Na_8Sn_5O_2S_{12},32H_2O$. Orthorhombic needles; negative biaxial, $2V$ small; N mean = *ca.* 1·79; $N_\beta - N_\alpha = 0{\cdot}024$; elongation negative.

DISCUSSION.

The stability of the $Sn_5O_2S_{10}{}^{IV}$ anion indicates a nuclear, rather than a chain, structure. Attempts to replace the two oxygen atoms by sulphur by heating the salt under pressure with hydrogen sulphide failed. If we assume that all the tin atoms are six-covalent as in the ortho- and meta-salts, there does not appear to be any reasonable alternative to the structural formula (I), which accounts for the presence of two oxygen atoms, and two molecules of firmly-attached water.


(I.)


(II.)


(III.)

On the basis of this formula the sodium ions in both the (prismatic) salt ($18H_2O$) and the acicular one ($20H_2O$) must be exerting their maximum covalency of four, and it is probable that the two oxygen atoms are acting as donors to hydrogen of the two extra water molecules in the 20-hydrate.

It might be supposed that the octasodium salt is merely a molecular compound of $2Na_2S$ with $Na_4(Sn_5S_{10}O_2,2H_2O)$, but the very close chemical and optical similarity of the octasodium and tetrasodium salts rather indicates that the two extra sulphur atoms have entered the complex anion. Free sulphide ions in the aqueous solution would at once react with lead acetate and potassium ferricyanide, whereas no such reactivity is exhibited. It is therefore considered probable that the anion of the octasodium salt has the configuration (II). This formula does not account for the 8 molecules of firmly attached water, but the alternative (III) appears improbable, as the co-ordinated water is not necessary to satisfy the condition of six-covalency of the tin atoms, and it would leave eight sodium ions to share 24 molecules of water. Perhaps the heavy anionic charge is responsible for the retention of this water at elevated temperatures.

In conclusion, I wish to express my sincere gratitude to Professor J. R. Partington for his valuable advice and continued interest in this work.

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