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# Salts of Monotelluropentathionic Acid

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In an earlier paper[1] the preparation and some properties of sodium and potassium selenopentathionate were described. They were prepared by use of the Norris and Fay reaction[2] between selenious acid and thiosulphate:

$$H_2SeO_3 + 4\ S_2O_3^{--} + 4\ H^+ = S_4O_6^{--} + Se(S_2O_3)_2^{--} + 3\ H_2O$$

Norris and Fay (*l. c.*) said that 'An acid solution of tellurium dioxide is reduced by sodium thiosulphate, giving a bright yellow solution, from which sodium hydroxide precipitates tellurium. Tellurium, therefore, probably forms a compound analogous to selenopentathionate'. Later, Norris[3] made use of these reactions in order to purify tellurium for atomic weight determinations. He made no attempts, however, to isolate the telluropentathionate.

By use of the above-mentioned process, *viz.*:

$$TeOOH^+ + 4\ S_2O_3^{--} + 3\ H^+ = S_4O_6^{--} + Te(S_2O_3)_2^{--} + 2\ H_2O$$

sodium and potassium telluropentathionate have been isolated in a pure state, as the first salts of telluropentathionic acid.

We thus have the following series of analogous thiosulphate compounds:

| | |
|---|---|
| Pentathionate | $S(S_2O_3)_2^{--}$ |
| Selenopentathionate | $Se(S_2O_3)_2^{--}$ |
| Telluropentathionate | $Te(S_2O_3)_2^{--}$ |

In reactions with nucleophilic reagents, pentathionate and selenopentathionate behave as a monosulphur di(thiosulphate) and a selenium di(thiosulphate), respectively[1, 4]. Correspondingly, telluropentathionate is a tellurium (dithiosulphate), its thiosulphate groups being displaceable by ethylxanthate, diethyldithiocarbamate, and hydroxide.

## SODIUM AND POTASSIUM TELLUROPENTATHIONATE

The salts were prepared by an experimental procedure analogous to that used in the case of the selenopentathionates[1]. Since tellurium dioxide and tellurous acid are but sparingly soluble in water and in acetic acid, a mixture of hydrochloric acid and acetic acid was used as a solvent. An excess of tellurous acid was maintained at every stage of the process.

Sodium telluropentathionate forms small plates or flat needles. The salt is readily soluble in water, though less soluble than is sodium selenopentathionate. It is insoluble in ethanol and insoluble or very sparingly soluble in methanol. It crystallizes with two moles of water.

Potassium telluropentathionate forms tiny plates or flat prisms. It crystallizes rather slowly from its solutions, is less soluble in water than the sodium salt, and insoluble in methanol. The crystals contain no water.

The salts, when pure, are quite stable. The bulk of crystals is yellow with an orange tinge, single crystals yellow with a greenish tinge. Dilute, aqueous solutions are yellow, concentrated solutions are orange red. The solutions seem, from the preliminary observations made, to be at least as stable as those of pentathionate or selenopentathionate.

Telluropentathionate is readily oxidized by iodine, to give tellurous acid, and tetrathionate:

$$Te(S_2O_3)_2^{--} + 2\ J_2 + 2\ H_2O = TeOOH^+ + S_4O_6^{--} + 4\ J^- + 3\ H^+$$

The process may be utilized for the iodometric analysis of telluropentathionate. The tetrathionate formed may be estimated by means of the well-known sulphite method of Kurtenacker[5].

0.5 millimole of telluropentathionate is dissolved in 100—150 ml of water, and the solution is titrated with 0.1 *N* iodine (*a* ml). Towards the end of the titration 2 ml of 1 *M* potassium acetate may be added in order to precipitate the tellurous acid, the end point thus being reached more rapidly. To the titrated solution are added 30 ml of 0.2 *M* sodium sulphite and 10 ml of 1 *N* sodium hydroxide. After standing for 5 minutes, 5 ml of 40 % formaldehyde and 20 ml of 10 % acetic acid are added, and the solution is titrated with 0.1 *N* iodine (*b* ml).

0.5 millimole of telluropentathionate corresponds to $a = 20$ ml and $b = 5$ ml of 0.1 *N* iodine. For a mixture of telluropentathionate and tetrathionate, *b* is larger than one fourth of *a*: The amount of tetrathionate originally present together with the telluropentathionate, is equal to $0.1\ (b - \frac{a}{4})$ millimole.

The fact that telluropentathionate is not indifferent to iodine explains why tellurous acid cannot be analyzed iodometrically by a method analogous to the Norris and Fay method for selenious acid.

Telluropentathionate reacts quantitatively with ethylxanthate and diethyldithiocarbamate to give tellurium di(ethylxanthate) and tellurium *bis*-(diethyldithiocarbamate), respectively, and thiosulphate (R = ethyl):

$$\begin{aligned} \mathrm{Te(S_2O_3)_2^{--} + 2\ ROCS_2^{-} = Te(S_2COR)_2 + 2\ S_3O_3^{--}} \\ \mathrm{Te(S_2O_3)_2^{--} + 2\ R_2NCS_2^{-} = Te(S_2CNR_2)_2 + 2\ S_2O_3^{--}} \end{aligned}$$

This is analogous to the behaviour of pentathionate[4] and selenopentathionate[1]. The thiocarbonyl anions act, with little doubt, as nucleophilic reagents, and the reactions are therefore ionic displacements on $\mathrm{Te^{++}}$. Telluropentathionate is thereby characterized as being a tellurium di(thiosulphate). It has the same type of structure as pentathionate and selenopentathionate, *i. e.*, two thiosulphate groups are bonded to a tellurium atom, through the thio sulphur atoms of the thiosulphate groups.

The amount of ionic character of the covalent tellurium-sulphur bonds, in the sense:

$$\mathrm{O_3S_2^{--}\quad Te^{++}\quad S_2O_3^{--}}$$

should be definitely larger than in the case of the corresponding bonds in pentathionate and selenopentathionate, the electronegativity values[6] of sulphur, selenium and tellurium being 2.5, 2.4 and 2.1, respectively.

## Experimental

*Sodium telluropentathionate,* $Na_2Te(S_2O_3)_2 \cdot 2H_2O$. Tellurous acid was prepared from potassium tellurite as follows: 30 g potassium tellurite were dissolved in 30 ml of hot water, and 90 ml of 10 % acetic acid were added slowly with stirring. The tellurous acid was filtered off, washed with water containing a little acetic acid, and drained well.

The tellurous acid thus obtained (corresponding to 15 g of tellurium) is dissolved in 45 ml of concentrated hydrochloric acid and 75 ml of glacial acetic acid. To this solution are added dropwise, in the course of about 15 minutes, under mechanical stirring and cooling with ice-sodium chloride freezing mixture, 110 g of sodium thiosulphate pentahydrate in 60 ml of water (dissolved by heating, and cooled to room temperature). The temperature of the reaction mixture should be kept at about 0° C. To the clear, viscous, yellowish red solution of sodium tetrathionate and sodium telluropentathionate, containing a slight excess of tellurous acid, are added 150 ml of ethanol. The cooling and stirring are continued for about 15 minutes, the product is then filtered off, drained well, washed with ethanol and with ether, and dried *in vacuo* over sulphuric acid.

The product, which is quite stable *, contains about 35 g of $\mathrm{Na_2Te(S_2O_3)_2 \cdot 2H_2O}$ with about 4 mole % of tetrathionate.

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* The amount of tellurous acid used should not be larger than described, since in that case the product becomes contaminated with this substance, which is difficult to remove, and also seems to decrease the stability of the product.

It is dissolved in 60—70 ml of 0.2 *N* hydrochloric acid at 45° C, and the solution is filtered with suction through a fine sintered glass filter. 80 ml of methanol are added, and the mixture is cooled in ice water. The product, consisting of about 15 g of pure sodium telluropentathionate dihydrate, is washed with ethanol and with ether, and dried *in vacuo* over sulphuric acid.

It was analyzed by means of the procedure described p. 709. The method gives accurate and consistent results. In control experiments (with 25 ml of 0.02 *M* potassium tellurite and 20 ml 0.1 *N* sodium thiosulphate, slightly acidified with acetic acid) tellurous acid was found to have no influence on the titration of thiosulphate with iodine, nor on the subsequent determination, by means of the sulphite method, of the tetrathionate thereby formed.

0.2327 g substance: (*a*) 21.31 ml (*b*) 5.33 ml 0.1006 *N* iodine.

$Na_2Te(S_2O_3)_2 \cdot 2H_2O$ (433.9) Calc. Te 29.41 Found Te 29.39

The tellurium content was also estimated directly. The substance was oxidized with concentrated nitric acid, the excess of nitric acid was destroyed by heating with several portions of concentrated hydrochloric acid, and the tellurium was filtered off and weighed after reduction with hypophosphorous acid according to Clauder[7].

0.4010 g substance: 0.1176 g Te. Found Te 29.33.

*Potassium telluropentathionate,* $K_2Te(S_2O_3)_2$. To a filtered solution of the crude sodium telluropentathionate in 80 ml of 0.2 *N* hydrochloric acid is added in portions, under mechanical stirring and cooling with ice-sodium chloride freezing mixture, a suspension of potassium acetate prepared as follows: 20 g of potassium acetate are dissolved by heating in 40 ml of ethanol, 20 ml of glacial acetic acid are added, and the mixture is cooled to room temperature. The crystals of potassium telluropentathionate are filtered off, and washed with ethanol and with ether. Yield, about 30 g of a product which contains only traces of tetrathionate. It is dissolved in a double amount of 0.2 *N* hydrochloric acid at about 30° C, and the solution is filtered with suction through a fine sintered glass filter. To the filtrate is added, with stirring, one third of its volume of warm methanol, and the mixture is cooled, finally in ice-water. Yield, 15—20 g of pure product.

0.2285 g substance: (*a*) 21.11 ml (*b*) 5.25 ml 0.1006 *N* iodine.

$K_2Te(S_2O_3)_2$ (430.1) Calc. Te 29.66 Found Te 29.64

*The reactions with thiocarbonyl salts.* To 2.176 g $Na_2Te(S_2O_3)_2 \cdot 2\,H_2O$ dissolved in 100 ml of water were added, with stirring, 50 ml of 0.3 *M* sodium diethyldithiocarbamate. A flesh-coloured product immediately separated out. The stirring was continued for 5 minutes, the product was then filtered off, washed with water, and dried *in vacuo* over sulphuric acid. Yield, 2.11 g; theoretically, 2.13 g $Te(S_2CN(C_2H_5)_2)_2$. In the filtrate the excess of diethyldithiocarbamate was removed by means of cadmium carbonate as described earlier[1]. Found, 19.87 ml 0.1006 *N* iodine (theoretically, 19.94 ml).

The tellurium *bis*(diethyldithiocarbamate) was recrystallized from carbon disulphide-ether. Red crystals, m. p. 164° C.

0.3208 g substance: 0.0959 g Te.

$Te(S_2CN(C_2H_5)_2)_2$ (424.2) Calc. Te 30.07 Found Te 29.89

In the same way was obtained, from 2.200 g $Na_2Te(S_2O_3)_2 \cdot 2H_2O$ and 50 ml of 0.3 *M* potassium ethylxanthate, 1.86 g of a flesh-coloured product; theoretically, 1.88 g tellurium di(ethylxanthate). It was recrystallized from benzene-ethanol. Red needles, m. p. 94° C.

0.3314 g substance: 0.1138 g Te.

$Te(S_2COC_2H_5)_2$ (370.0) Calc. Te 34.48 Found Te 34.35

The behaviour of tellurium di(ethylxanthate) towards alkalies is described p. 714-5.

These ethyl compounds are apparently the first xanthate and dithiocarbamate of divalent tellurium isolated in a pure state. The only analogous compound seems to be the tellurium di(thiolactic acid) prepared from tellurium dioxide and thiolactic acid by Bersin and Logemann[8].

The light absorption of telluropentathionate solutions was measured by means of a Beckman quartz spectrophotometer, model DU (1 cm cells). Distilled water was used as a solvent and as a blank. The solutions were not quite stable; though, when the measurements were made rapidly the change of transmittance was small. The solutions obeyed Beer's law in the range measured, *viz.*, from 0.01 *M* to 0.04 *M*. For the log $\varepsilon$ curve, see **Fig. 1.**

## THE ALKALINE HYDROLYSIS OF SELENOPENTATHIONATE AND TELLUROPENTATHIONATE

Telluropentathionate in aqueous solutions is rapidly destroyed by alkalies, tellurium being liberated. The sensitivity of this test for telluropentathionate is the same as that of the corresponding test for selenopentathionate[1]. A brownish-black colour is rapidly produced when 1 drop of 2 *N* sodium hydroxide is added to 10 ml of $10^{-4}$ *M* telluropentathionate.

With excess alkalies, selenopentathionate and telluropentathionate were found to undergo hydrolysis quantitatively as follows:

$$2\ Se(S_2O_3)_2^{--} + 6\ OH^- = 4\ S_2O_3^{--} + Se + SeO_3^{--} + 3\ H_2O$$
$$2\ Te(S_2O_3)_2^{--} + 6\ OH^- = 4\ S_2O_3^{--} + Te + TeO_3^{--} + 3\ H_2O$$

In view of the properties of selenopentathionate and telluropentathionate as a selenium di(thiosulphate) and a tellurium di(thiosulphate), respectively, it seems probable that the first step of hydrolysis involves ionic displacements of thiosulphate by hydroxide, to give selenium dihydroxide and tellurium dihydroxide, respectively:

$$Se(S_2O_3)_2^{--} + 2\ OH^- = Se(OH)_2 + 2\ S_2O_3^{--}$$
$$Te(S_2O_3)_2^{--} + 2\ OH^- = Te(OH)_2 + 2\ S_2O_3^{--}$$

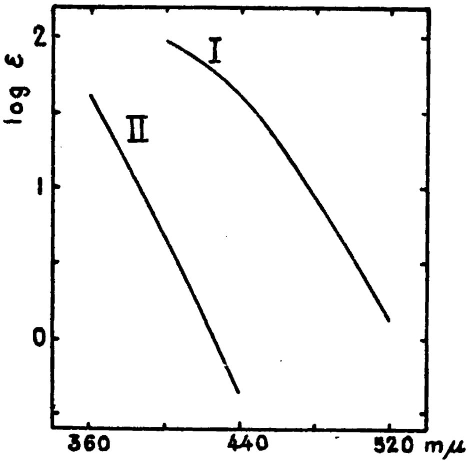

*Fig. 1. Optical transmittance of*

*(I) telluropentathionate (in water)*
*(II) selenopentathionate*[1] *(in 0.01 N HCl)*

The next step would be an immediate rearrangement of the hydroxides into selenium and selenite, and tellurium and tellurite:

$$2\ Se(OH)_2 + 2\ OH^- = Se + SeO_3^{--} + 3\ H_2O$$
$$2\ Te(OH)_2 + 2\ OH^- = Te + TeO_3^{--} + 3\ H_2O$$

A similar primary step probably takes place[4] in the alkaline hydrolysis of pentathionate, in analogy with the hydrolysis of other derivatives of divalent electropositive sulphur:

$$S(S_2O_3)_2^{--} + 2\ OH^- = S(OH)_2 + 2\ S_2O_3^{--}$$

It is generally assumed * that monosulphur dihydroxide in alkaline media undergoes spontaneous rearrangement to thiosulphate:

$$2\ S(OH)_2 + 2\ OH^- = S_2O_3^{--} + 3\ H_2O$$

This change is fully analogous to the rearrangements of selenium dihydroxide and tellurium dihydroxide, formulated above. Divalent sulphur dismutates into the electroneutral and the tetravalent state, followed by the union of sulphur and sulphite to give thiosulphate. No ions corresponding to thiosulphate exist in the case of selenium and tellurium.

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* For literature references, see Ref. 4. In a recent article, Goehring, Helbing and Appel[9] arrive at the same conclusions concerning monosulphur dihydroxide as an intermediate in the alkaline hydrolysis of pentathionate (and tetrathionate). They also report the reactions [4, 10, 11] of pentathionate and tetrathionate with piperidine, to give monosulphur dipiperidide, in support of this view.

Tellurium di(ethylxanthate) was found to react with alkalies in the same way as telluropentathionate:

$$2\ Te(S_2COC_2H_5)_2 + 6\ OH^- = 4\ C_2H_5OCS_2^- + Te + TeO_3^{--} + 3\ H_2O$$

The primary step in this case would be:

$$Te(S_2COC_2H_5)_2 + 2\ OH^- = Te(OH)_2 + 2\ C_2H_5OCS_2^-$$

Indications may be found in literature concerning the behaviour of oxygen compounds of divalent selenium and tellurium. No hydroxides are known to exist, neither is selenium monoxide[12]. If formed, it changes very rapidly into selenium and selenium dioxide[13]. The black solid ordinarily regarded as a tellurium monoxide[14] appears to be an equimolecular mixture of tellurium and tellurium dioxide[15].

Tellurium dichloride and dibromide are unstable in the solid state and changes gradually into tellurium and the tellurium tetrahalides[16]. In their hydrolysis reactions, they produce tellurium and tellurous acid or tellurite, *e. g.*:

$$2\ TeBr_2 + 6\ OH^- = 4\ Br^- + Te + TeO_3^{--} + 3\ H_2O$$

Damiens[16] mentioned the possibility of a transitory occurrence of an unstable tellurium monoxide in this hydrolysis.

Bersin and Logemann[8] formulated the alkaline hydrolysis of selenium di(2-oxy-3-bromo-5-methylphenylmercaptide) as involving a primary formation of selenium monoxide, which would rapidly rearrange into selenium and selenium dioxide. The intermediate occurrence of selenium monoxide in the reactions of selenium dioxide with sulphite, thiosulphate and selenosulphate, and in the equilibrium of selenosulphate with hydrogen ions, was assumed by Foerster, Lange, Drossbach and Seidel[17] and Foerster and Haufe[18].

The terms, selenium and tellurium monoxide, in these last reactions, would be synonymous with selenium and tellurium dihydroxide.

## Experimental

*Selenopentathionate.* To approx. 2.5 millimole of the sodium salt dissolved in 25 ml of water were added 50 ml of 0.2 N sodium hydroxide. The mixture was stirred for about 5 minutes, the red selenium filtered off, washed with water, dried, and weighed. The filtrate and the washings were diluted to 250 ml, and two 100 ml samples were pipetted out for analysis.

To the first sample were added 10 ml of 6 N hydrochloric acid and 10 ml of a saturated solution of potassium bromide. A saturated solution of potassium bromate was added until a slight excess of bromine was present, and the excess was subsequently destroyed by means of acetanilide. This procedure serves to oxydize the thiosulphate to sulphate, without affecting the selenious acid. The sample was diluted to 200 ml, and the selenious acid was determined by means of the Norris and Fay method: 25 ml of 0.1 $N$ thiosulphate (consuming 24.92 ml of 0.1006 $N$ iodine) was added, and the excess back-titrated with 0.1006 $N$ iodine.

To the second sample were added 100 ml of water, 5 ml of 6 $N$ hydrochloric acid, and 5 ml of 0.1 $N$ thiosulphate (consuming 4.99 ml of 0.1006 $N$ iodine). The excess of thiosulphate was back-titrated with 0.1006 $N$ iodine . This method gives the amount of thiosulphate present in the sample relative to the amount of selenious acid.

(1) 1.018 g $Na_2Se(S_2O_3)_2 \cdot 3H_2O$ gave 0.0995 g Se (theoretically, 0.0996 g). Selenious acid: 24.92 ml − 4.90 ml = 20.02 ml 0.1006 $N$ iodine (theoretically, 20.06 ml). Thiosulphate: 20.02 ml − 4.99 ml + 5.02 ml = 20.05 ml 0.1006 $N$ iodine (theoretically, 20.06 ml).

(2) 1.062 g $Na_2Se(S_2O_3)_2 \cdot 3H_2O$ gave 0.1044 g Se (theoretically, 0.1040 g). Selenious acid: 24.92 ml − 3.96 ml = 20.96 ml 0.1006 $N$ iodine (theoretically, 20.93 ml). Thiosulphate: 20.96 ml − 4.99 ml + 5.03 ml = 21.00 ml 0.1006 $N$ iodine (theoretically, 20.93 ml).

*Telluropentathionate.* The procedure employed was the same as in the case of selenopentathionate. The tellurium was washed with water and with alcohol before drying. The filtrate and the aqueous washings were diluted to 250 ml, and one 100 ml sample was pipetted out for analysis: 5 ml of 10 % acetic was added (whereby tellurous acid settled out) and the mixture was titrated with 0.1006 $N$ iodine ($a$ ml). This titration gives directly the amount of thiosulphate present (tellurous acid does not interfere, *cf.* p. 711). As a check on this value, the amount of tetrathionate formed was determined by means of the sulphite method as described p. 709 ($b$ ml).

(1) 1.093 g $Na_2Te(S_2O_3)_2 \cdot 2H_2O$ gave 0.1602 g Te (theoretically, 0.1607 g). Thiosulphate: ($a$) 20.00 ml ($b$) 10.00 ml 0.1006 $N$ iodine (theoretically, 20.03 ml and half of this value, respectively).

(2) 1.084 g $Na_2Te(S_2O_3)_2 \cdot 2H_2O$ gave 0.1605 g Te (theoretically, 0.1593 g). Thiosulphate: ($a$) 19.84 ml ($b$) 9.92 ml 0.1006 $N$ iodine (theoretically, 19.86 ml and 9.93 ml, respectively).

*Tellurium di(ethylxanthate).* 0.9933 g $Te(S_2COC_2H_5)_2$ was dissolved in 50 ml of warm ethanol, and 10 ml of 1 $M$ sodium hydroxide were added with stirring. The mixture was cooled and diluted to about 100 ml, and the tellurium was filtered off, washed with water and with ethanol, and dried: 0.1682 g (theoretically, 0.1712 g). The filtrate and the aqueous washings were diluted to 250 ml, and one 100 ml sample was pipetted out. 10 ml of a phosphate buffer (being 0.5 $M$ with respect to dihydrogen phosphate and 0.1 $M$ with respect to monohydrogen phosphate) were added (whereby tellurous acid settled out). The mixture was titrated with 0.1006 $N$ iodine: 21.39 ml (theoretically, for oxidation of the xanthate to dixanthyl disulphide, 21.34 ml).

## SUMMARY

Sodium and potassium telluropentathionate have been isolated in a pure state, as the first salts of telluropentathionic acid. Telluropentathionate is a tellurium di(thiosulphate).

The alkaline hydrolysis reactions of selenopentathionate and telluropentathionate have been investigated, and the intermediate occurrence of selenium dihydroxide and tellurium dihydroxide, respectively, has been made probable.

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