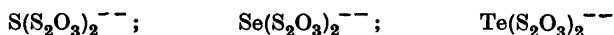


Isomorphous Thiosulphates of Divalent Sulphur, Selenium and Tellurium

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The purpose of this article is to report the preliminary results of a crystallographic study of some salts of pentathionic, selenopentathionic and telluropentathionic acids. The anions of these acids, *viz.* :



are, as indicated in the title, thiosulphates of divalent sulphur, selenium and tellurium¹⁻³. The salts investigated include potassium and rubidium pentathionate, and ammonium, potassium, rubidium and cesium selenopentathionate and telluropentathionate.

SYNTHESIS OF NEW SALTS

Potassium pentathionate hemitrihydrate, the first salt of pentathionic acid isolated in a pure state, has been known since 1888⁴. Rubidium pentathionate, described for the first time in this article, was prepared from the potassium salt by metathesis with sodium perchlorate and, subsequently, with rubidium chloride. The rubidium salt, like the potassium analogue, crystallizes with one and a half mole of water.

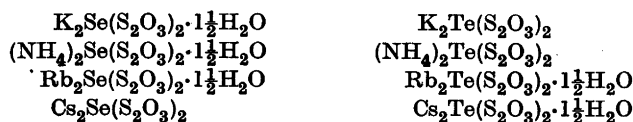
The only salts of selenopentathionic and telluropentathionic acids prepared hitherto are the sodium and potassium salts, which were isolated by one of us recently^{2,3}. Thus, the ammonium, rubidium and cesium salts, described below, are new.

Ammonium selenopentathionate and telluropentathionate were obtained from ammonium thiosulphate and selenious or tellurous acid in the same way as the sodium salts^{2,3}. The salts are less soluble than ammonium tetrathionate, which is formed in these reactions in equimolar proportions, and

crystallize from the mixtures contaminated with only a few per cent of the tetrathionate, as do the sodium salts ^{2,3}. In most cases a single recrystallization suffices to give the pure salts.

Rubidium and cesium selenopentathionate and telluropentathionate were prepared from the sodium salts by metathesis with rubidium and cesium chlorides.

Of the potassium, ammonium, rubidium and cesium selenopentathionates and telluropentathionates, only three salts are anhydrous, *viz.*, potassium and ammonium telluropentathionate, and cesium selenopentathionate. The remaining ones crystallize with one and a half mole of crystal water, like potassium and rubidium pentathionate, as appears from the following table:



The hydrates in most cases crystallize more readily and show better developed forms than the anhydrous salts. Also, the hydrates have a brighter colour; thus, among the telluropentathionates the rubidium and cesium salts are distinctly orange red while the potassium and ammonium salts are yellow. The crystal water of the hydrates is kept very firmly, and is not liberated *in vacuo* over sulphuric acid.

The salts, when pure, may be kept for weeks without any change; however, gradually selenium or tellurium appears within some of the crystals of a sample.

The solubilities in water of the selenopentathionates and telluropentathionates decrease in the order sodium, ammonium, potassium, rubidium and cesium salts. The telluropentathionates are a little less soluble than the corresponding selenopentathionates. The sodium and ammonium salts are appreciably soluble in methanol, and also to a slight extent in 96% ethanol, while the potassium, rubidium and cesium salts are insoluble in alcohols.

EXPERIMENTAL

Rubidium pentathionate. To 1.8 g (5 millimole) of potassium pentathionate dissolved, by gentle heating, in 3 ml of 0.5 N hydrochloric acid, was added 1.2 g (10 millimole) of sodium perchlorate dissolved in 2 ml of water. The mixture was cooled for a few minutes in ice water, the potassium perchlorate then filtered off, and 1.2 g (10 millimole) of rubidium chloride was added to the filtrate. On cooling in ice water, rubidium pentathionate crystallized as flat needles or oblong plates. Yield, 1.2 g (53 % of the theoretical amount). 1 g of the product was dissolved in 2 ml of 0.5 N hydrochloric acid at 40° C. On slow

cooling, rhombic bipyramidal crystals were obtained, of the shape described by Groth⁵ for potassium pentathionate.

For analysis, about 0.25 millimole was dissolved to 50 ml in a volumetric flask, and 20 ml samples were pipetted out and analyzed by means of the sulphite⁶ and the cyanide^{1,6} method, using 0.01 *N* iodine.

0.1283 g substance: 20.56 ml (sulphite) and 10.32 ml (cyanide) of 0.01094 *N* iodine (for pentathionates, the sulphite value is, theoretically, twice the cyanide value).

$\text{Rb}_2\text{S}(\text{S}_2\text{O}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ (454.3)	Calc.	S	35.29
	Found	»	35.18

Ammonium selenopentathionate and telluropentathionate. The reactions were carried out as described earlier for the sodium salts^{2,3}. Suitable proportions of reagents are: 20 g of selenious acid (H_2SeO_3) dissolved in 20 ml of water and 100 ml of glacial acetic acid; 80 g of ammonium thiosulphate in 40 ml of water. 18.8 g of tellurium dioxide (from 15 g of tellurium) dissolved in 45 ml of concentrated hydrochloric acid and 75 ml of glacial acetic acid; 66 g of ammonium thiosulphate in 40 ml of water. The thiosulphate solutions were added drop-wise, under mechanical stirring, to the solutions of selenious and tellurous acid which were kept at a temperature of about 0° C by means of an ice-salt freezing mixture. The stirring and cooling were afterwards continued for about 10 minutes. The products, which contained 30–35 g of the desired salts, with 3–8 mole % of ammonium tetrathionate, were subsequently filtered off, drained well, washed with a little ethanol and with ether, and dried *in vacuo* over sulphuric acid. The selenium salt was recrystallized by dissolving in about an equal amount of 0.5 *N* hydrochloric acid at about 40° C, filtering with suction through a sintered glass filter, and cooling in ice-water. The tellurium salt was dissolved in three halves of its weight (or a little less) of the same solvent at about 35° C, and after filtering, an equal amount of ethanol was added. Yields, about 20 g of pure products.

0.2071 g substance: 21.56 ml of 0.1074 *N* sodium thiosulphate (Norris & Fay, after oxidation by means of bromate as described earlier²).

$(\text{NH}_4)_2\text{Se}(\text{S}_2\text{O}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ (366.3)	Calc.	Se	21.55
	Found	»	21.46

0.2050 g substance: 20.92 ml of 0.1007 *N* iodine (titrated directly, as described earlier³).

$(\text{NH}_4)_2\text{Te}(\text{S}_2\text{O}_3)_2$ (388.0)	Calc.	Te	32.89
	Found	»	32.76

Rubidium and cesium selenopentathionate and telluropentathionate. To 0.5 millimole of the sodium salts (2.1 g and 2.2 g, respectively) dissolved in 5 ml of 0.5 *N* hydrochloric acid (traces of selenium or tellurium were filtered off, when necessary) were added, at room temperature, 10 millimole of rubidium or cesium chloride (1.2 g and 1.7 g, respectively) dissolved in 5 ml of water. The salts rapidly crystallized in a pure state.

Samples, which on standing had liberated selenium or tellurium, were purified by dissolving in 0.2 *N* hydrochloric acid at 40–50° C, filtering with suction through a sintered glass filter, and cooling in ice water. The same procedure was used for recrystallizations.

The analyses were performed volumetrically in the same way as for the ammonium salts.

0.3881 g substance: 29.89 ml of 0.1027 *N* sodium thiosulphate.

$\text{Rb}_2\text{Se}(\text{S}_2\text{O}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ (501.2) Calc. Se 15.75
 Found » 15.62

0.07594 g substance: 5.19 ml of 0.1027 *N* sodium thiosulphate.

$\text{Cs}_2\text{Se}(\text{S}_2\text{O}_3)_2$ (569.0) Calc. Se 13.88
 Found » 13.86

0.3090 g substance: 23.11 ml of 0.09754 *N* iodine.

$\text{Rb}_2\text{Te}(\text{S}_2\text{O}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ (549.9) Calc. Te 23.20
 Found » 23.27

0.2487 g substance: 15.80 ml of 0.09754 *N* iodine.

$\text{Cs}_2\text{Te}(\text{S}_2\text{O}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ (644.7) Calc. Te 19.79
 Found » 19.76

X-RAY DATA

The unit cells and space groups were determined from rotation, oscillation and Weissenberg photographs on small single-crystal specimens, using FeK_α radiation, $\lambda = 1.934 \text{ \AA}$. The values recorded below for axial lengths are accurate to within 0.5 %. Density determinations were made by flotation in suitable solvents.

Six of the salts have the same orthorhombic bipyramidal space group and unit cells of nearly the same size, and are thus isomorphous. These salts include potassium pentathionate, ammonium selenopentathionate, cesium telluropentathionate, and the three rubidium salts.

Table 1. *Isomorphous hemitrihydrates. Axial lengths in \AA.*

Salt	<i>a</i>	<i>b</i>	<i>c</i>	Density	
				calc.	found
$\text{K}_2\text{S}(\text{S}_2\text{O}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	20.09	9.17	12.30	2.12	2.11 ⁵
$\text{Rb}_2\text{S}(\text{S}_2\text{O}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	20.81	9.26	12.50	2.51	2.50
$(\text{NH}_4)_2\text{Se}(\text{S}_2\text{O}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	20.58	9.24	12.57	2.03	2.01
$\text{Rb}_2\text{Se}(\text{S}_2\text{O}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	20.84	9.23	12.48	2.76	2.71
$\text{Rb}_2\text{Te}(\text{S}_2\text{O}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	21.14	9.35	12.46	2.96	2.91
$\text{Cs}_2\text{Te}(\text{S}_2\text{O}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	21.76	9.55	12.91	3.19	3.16

There are eight molecules per unit cell. Absent spectra, for all six salts: $(hk0)$ when $h+k$ is odd, $(h0l)$ when l is odd, and $(0kl)$ when k is odd. The space group is therefore $D_{2h}^{14}-Pbcn$.

Of the above salts, potassium pentathionate, the only one which is not new, is described by Groth ⁵, as orthorhombic bipyramidal with axial ratios $a:b:c = 0.4564:1:0.3051$. The X-ray data give the ratios $0.4565:1:0.6124$ which show that the c axis of Groth must be doubled. In the X-ray unit, the a and b axes of Groth have been interchanged in order to comply with the International Space Group Nomenclature; the c axis of Groth (needle axis) has been retained.

The crystals of the five other salts of Table 1 show the same morphology as potassium pentathionate as described by Groth. Occasionally, in some preparations, other shapes were observed; *e. g.*, rubidium pentathionate was first obtained as flat needles elongated along the c axis and flattened along the b axis of the X-ray unit, the most prominent form thus being $\{100\}$.

Potassium selenopentathionate, $K_2Se(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$, has the same axial lengths as the hemitrihydrates of Table 1: $a = 20.18 \text{ \AA}$, $b = 9.21 \text{ \AA}$, $c = 12.24 \text{ \AA}$. There are, likewise, eight molecules per unit cell; density, calc. 2.38, found 2.36. However, the only reflexions which are entirely absent are $(0kl)$ when k is odd, which is characteristic for the space group D_{2h}^5-Pbmm and the space groups of lower symmetry, C_{2v}^2 or C_{2v}^4 . The morphology of the crystals is the same as that of the other hemitrihydrates, *viz.*, orthorhombic bipyramidal, indicating that D_{2h}^5-Pbmm may be the correct space group. The reflections distinguishing from $D_{2h}^{14}-Pbcn$, *viz.*, $(hk0)$ when $h+k$ is odd and $(h0l)$ when l is odd, are present only in a limited number. The elongation of the crystals along the c axis is frequently quite pronounced, thus giving the crystals the appearance of prismatic needles.

The only selenopentathionate, of the four ones examined, which crystallizes without crystal water, is the cesium salt, $Cs_2Se(S_2O_3)_2$. It appears as prisms having a great tendency to branch off at the ends and which in most cases are twins. From oscillation and Weissenberg photographs around the a axis (needle axis) the crystals definitely appear to be orthorhombic, with the axial lengths, $a = 6.40 \text{ \AA}$, $b = 18.16 \text{ \AA}$, $c = 9.74 \text{ \AA}$. Density, calc. on the basis of four molecules per unit cell, 3.32, found, 3.30. Absent reflections, $(hk0)$ when k is odd, and $(00l)$ when l is odd. These extinctions do not, however, fit with any orthorhombic space group, and further work is required.

Potassium and ammonium telluropentathionate, both anhydrous, are monoclinic prismatic, but not isomorphous. They appear as prisms, the former elongated along the b axis, the latter along the a axis. In both cases, as for cesium selenopentathionate, the needle axis is the shortest axis. The salts frequently crystallize in rosette-shaped aggregates of crystals too tiny for single-crystal X-ray work. The cell dimensions are as follows.

Potassium telluropentathionate, $K_2Te(S_2O_3)_2$. $a = 11.20 \text{ \AA}$, $b = 5.54 \text{ \AA}$, $c = 16.64 \text{ \AA}$, $\beta = 91.2^\circ$. Four molecules per unit cell; density, calc. 2.75,

found 2.74. Absent spectra, ($h0l$) when $h + l$ is odd, and ($0k0$) when k is odd. Space group, $C_{2h}^5-P2_1/n$.

Ammonium telluropentathionate, $(NH_4)_2Te(S_2O_3)_2 \cdot a = 5.03 \text{ \AA}$, $b = 18.90 \text{ \AA}$, $c = 11.48 \text{ \AA}$, $\beta = 91.0^\circ$. Four molecules per unit cell; density, calc. 2.35, found 2.34. Absent spectra, ($h0l$) when l is odd, and ($0k0$) when k is odd. Space group, $C_{2h}^5-P2_1/c$.

STRUCTURAL RELATIONSHIP OF THE ANIONS

The fact that pentathionic, selenopentathionic and telluropentathionic acids give salts which are isomorphous, strongly indicates that the anions have analogous structures. This finding is in accordance with the chemical reactivity of the anions¹⁻³.

The possibilities for the salts to crystallize as hemitrihydrates appear to depend upon the relative sizes of the cations and of the divalent atoms, sulphur, selenium and tellurium. The ionic radii of the cations and the covalent radii of the atoms (in \AA) are⁷:

K ⁺	NH ₄ ⁺	Rb ⁺	Cs ⁺	S	Se	Te
1.33	1.48	1.48	1.69	1.04	1.17	1.37

The cation should apparently be larger than the divalent atom but not too much larger, as evidenced by the fact that potassium telluropentathionate, on one side, and cesium selenopentathionate, on the other side, do not fit into the isomorphous series. In other words, the cation and the divalent atom should not have too different atomic numbers. Rubidium, which is of medium size, is the only cation which gives isomorphous salts with all three acids. Although the cesium sulphur salt, cesium pentathionate, has not been investigated, it may be predicted, on this basis, that it is not a hemitrihydrate.

SUMMARY

Some new salts of pentathionic, selenopentathionic and telluropentathionic acids are described, *viz.*, rubidium pentathionate, and ammonium, rubidium and cesium selenopentathionate and telluropentathionate.

Unit cells and space groups are reported for these and for the potassium salts. Six of the salts, two of each acid, are isomorphous, which shows that the anions have analogous structures.

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REFERENCES

1. Foss, O. *Kgl. Norske Vid. Selsk. Skrifter* (1945) no. 2.
2. Foss, O. *Acta Chem. Scand.* **3** (1949) 435.
3. Foss, O. *Acta Chem. Scand.* **3** (1949) 708.
4. Debus, H. *J. Chem. Soc.* **53** (1888) 280.
5. Groth, P. *Chemische Krystallographie. II* Leipzig (1908) p. 717.
6. Kurtenacker, A. *Analytische Chemie der Sauerstoffsäuren des Schwefels*. Stuttgart (1948) p. 154.
7. Pauling, L. *The nature of the chemical bond*. Ithaca (1945).

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