ACTA CHEMICA SCANDINAVICA 6 (1952) 521–530

Isomorphous Series of Pentathionic Compounds

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In a previous article[1], a new type of pentathionic compounds was described, *viz.*, triselenium disulphinates. The representatives investigated were those derived from benzene and *p*-toluene. The triselenium disulphinates arise from the corresponding thiosulphonates of divalent sulphur[2–4] by substitution of three selenium atoms for sulphur atoms. One purpose of the present article is to describe benzene- and *p*-toluenethiosulphonates of divalent selenium and tellurium, so as to complete a four-membered series of aromatic pentathionic compounds.

Within the series, the crystals of the *p*-toluene compounds are mutually isomorphous, and the compounds thus possess analogous structures.

The thiosulphates of divalent sulphur, selenium and tellurium, *viz.*, the pentathionate, selenopentathionate and telluropentathionate anions, give isomorphous salts[5], and the methanethiosulphonates of the same divalent elements are, likewise, mutually isomorphous[6]. We thus have the following three isomorphous series of pentathionic compounds.

Alkali salts with the anions:	*p*-Toluenethiosulphonates, and triselenium di(*p*-toluenesulphinate):	Methane-thiosulphonates:
$S(S_2O_3)_2^{--}$	$S(S_2O_2R)_2$	$S(S_2O_2CH_3)_2$
$Se(S_2O_3)_2^{--}$	$Se(S_2O_2R)_2$	$Se(S_2O_2CH_3)_2$
$Te(S_2O_3)_2^{--}$	$Te(S_2O_2R)_2$	$Te(S_2O_2CH_3)_2$
	$Se_3(SO_2R)_2$	

The chemical properties of members of the three series are closely analogous, and furthermore, the series are interconvertible in the order of increasing nucleophilic reactivities of the electronegative components. Thus, the methanethiosulphonates react with *p*-toluenethiosulphonate and thiosulphate anions to give the corresponding members of the *p*-toluenethiosulphonate and thiosulphate series. The chemical evidence therefore strongly indicates that the three series possess the same type of structure.

BENZENE- AND *p*-TOLUENETHIOSULPHONATES OF DIVALENT SELENIUM AND TELLURIUM *

The selenium compounds result when diselenium dichloride reacts with an excess of the potassium thiosulphonates suspended in ether. Half of the selenium is set free:

$$2\ Se_2Cl_2 + 2\ RSO_2SK = Se(S_2O_2R)_2 + Se + 2\ KCl \tag{1}$$

The same method was recently [6] employed for the preparation of selenium di(methanethiosulphonate).

The tellurium compounds were obtained from the potassium thiosulphonates, suspended in ethanol-free chloroform, by reactions with tellurium tetrachloride:

$$TeCl_4 + 4\ RSO_2SK = Te(S_2O_2R)_2 + S_2(SO_2R)_2 + 4\ KCl \tag{2}$$

Here, the corresponding disulphur disulphinate is formed in an equimolar amount. The procedure used for the methane analogue [6], *viz.*, tellurium dioxide dissolved in hydrochloric acid and aqueous sodium or potassium thiosulphonate, gives the same products. However, this method is less suitable for the aromatic thiosulphonates, because the disulphur disulphinates under aqueous conditions undergo rearrangement, and a mixture of sulphur and tellurium thiosulphonates results. This mixture is, especially in the case of the *p*-toluene compounds, difficult to separate into the components. By the tellurium tetrachloride-chloroform method, on filtering, the disulphur disulphinate occurs in the filtrate and most of the tellurium thiosulphonate in the residue.

The crystals of the selenium benzene- and *p*-toluenethiosulphonates are pale greenish. Those of the tellurium compounds are yellow, and so are dilute solutions, whereas more concentrated solutions have an orange tinge. The crystals are relatively stable, like those of the methanethiosulphonates [6].

The compounds ** liberate selenium or tellurium on heating, $Se(SBs)_2$ being more stable in this respect. In preheated bath, $Se(SBs)_2$ melts at 154 – 155° C to a greenish liquid which becomes red after a few minutes, while $Se(STs)_2$ melts and decomposes at about 200° C. The tellurium compounds,

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* For a preliminary account, see Ref. 7.

** The symbols Bs and Ts are sometimes used to designate the benzenesulphonyl and *p*-toluenesulphonyl group, respectively.

$Te(SBs)_2$ and $Te(STs)_2$, melt at about 170° C and about 215° C, respectively, to red liquids which liberate tellurium after a few seconds.

The benzene compounds are more soluble than the *p*-toluene compounds, $Se(SBs)_2$ being fairly readily and $Te(SBs)_2$ moderately soluble in warm ethylacetate, benzene and chloroform. The solubilities of the four isomorphous *p*-toluene derivatives, Se_3Ts_2, $S(STs)_2$, $Se(STs)_2$ and $Te(STs)_2$, decrease in the order of mentioning. 1 g of $Se(STs)_2$ and $Te(STs)_2$ dissolve in about 120 ml and about 160 ml, respectively, of boiling chloroform, the hot solutions being quite stable. The compounds are insoluble in water.

EXPERIMENTAL

Potassium benzene- and *p*-toluenethiosulphonate were crystallized from 96 % ethanol and from water, respectively. The salts were dried for two hours at 110° C, and subsequently powdered finely.

Selenium compounds. To 14 g of potassium benzenethiosulphonate, or 15 g of potassium *p*-toluenethiosulphonate, suspended in 50 ml of dry ether and cooled in ice, were added 2 ml of diselenium dichloride. On stirring, the dichloride colour vanished rapidly from the liquid phase, and selenium was liberated on the solid substance. The mixture was filtered, and the residue on the filter was dried *in vacuo* over sulphuric acid, while the filtrate was discarded. The residue was subsequently treated several times with water, drained, and dried once more.

The benzenethiosulphonate residue (about 10 g) was heated with 100 ml of ethylacetate, elemental selenium was filtered off, and the pale green filtrate was cooled in ice. Yield, 5—6 g of selenium di(benzenethiosulphonate).

The *p*-toluenethiosulphonate residue (about 12 g) was treated with boiling chloroform (100—120 ml per g) and the mixture was filtered. About three fourths of the chloroform were subsequently boiled off, until crystals began to separate out, and the solution was then allowed to cool slowly. Yield of selenium di(*p*-toluenethiosulphonate), about 50 % based on the crude product. Larger crystals were obtained by addition of an equal volume of carbon tetrachloride to the concentrated chloroform solution before cooling.

0.5392 g substance: 0.1008 g Se.

$Se(S_2O_2C_6H_5)_2$ (425.4) Calc. Se 18.6. Found Se 18.7.

0.6522 g substance: 0.1143 g Se.

$Se(S_2O_2C_7H_7)_2$ (453.5) Calc. Se 17.4. Found Se 17.5.

Tellurium compounds. The chloroform employed for the tellurium tetrachloride reactions was freed from ethanol by treatment, successively, with water, concentrated sulphuric acid, water, and anhydrous sodium sulphate, and was dried by distillation over phosphorus pentoxide and stabilized by addition of two parts per thousand of ligroin [8]. Ordinary, ethanol-stabilized chloroform was used for recrystallizations.

5.4 g of tellurium tetrachloride were suspended in 30 ml of chloroform and cooled in ice. To this mixture were added, in portions while stirring, 20 g of potassium benzenethiosulphonate, and the stirring and cooling were continued for 10 minutes. The yellow suspension was then filtered while cold, drained well, and the filtrate was discarded. The residue on the filter was treated with ice-cold chloroform (2 times 10 ml) and with 10 ml of ether, and was dried *in vacuo* over sulphuric acid. The substance was subsequently treated with water (3 times 30 ml), methanol (2 times 5 ml) and ether (2 times 5 ml), and was dried once more. Yield of yellow substance, about 8 g, containing, in various preparations, 22.5—24.5 % of Te. The crude product was treated with 80 ml of boiling chloroform, and the mixture was filtered. Half of the chloroform was subsequently boiled off, and the solution was cooled in ice and stirred. Yield, about 5 g of practically pure tellurium di(benzenethiosulphonate). Further recrystallizations were made by dissolving 2 g in 25 ml of boiling chloroform and slow cooling.

The *p*-toluene compound was prepared in the same way, from 5.4 g of tellurium tetrachloride, 50 ml of chloroform, and 22 g of potassium *p*-toluenethiosulphonate. Tellurium di(*p*-toluenethiosulphonate) is less soluble than the benzene compound, and so the residue may be treated with larger amounts of chloroform for removal of the disulphur disulphinate. Yield of water-treated, dry product, about 12 g, containing about 20 % of Te. The yellow substance was treated with boiling chloroform (100—120 ml per g) as described above for selenium di(*p*-toluenethiosulphonate). Yield, 40—50 %. A further recrystallization was necessary to remove small amounts of the isomorphous sulphur analogue (1 g dissolved in 160 ml of boiling chloroform, about three fourths subsequently boiled off). The compound is more soluble in dibromoethane and tetrachloroethane at boiling temperature, but the hot solutions are less stable.

0.4572 g substance: 0.1222 g Te.
$Te(S_2O_2C_6H_5)_2$ (474.1) Calc. Te 26.9. Found Te 26.7.
0.5193 g substance: 0.1313 g Te.
$Te(S_2O_2C_7H_7)_2$ (502.1) Calc. Te 25.4. Found Te 25.3.

PRELIMINARY X-RAY DATA ON AROMATIC SELENO- AND TELLUROPENTATHIONIC COMPOUNDS

The crystals of the three *p*-toluene compounds, $Se(STs)_2$, $Te(STs)_2$ and Se_3Ts_2, are tetragonal trapezohedral, and are isomorphous with those of the sulphur analogue, $S(STs)_2$, the unit cell and space group of which has been reported by Dawson, Mathieson and Robertson[4]. The crystals appear as beautifully developed bipyramides $\{101\}$.

The dimensions of the unit cells were obtained from oscillation and Weissenberg photographs, using FeK_α radiation, $\lambda = 1.934$ Å, and in some cases CuK_α radiation, $\lambda = 1.54$ Å. Density determinations were made by flotation in suitable solvents.

In the table below, data for the sulphur analogue, from the paper by Robertson and co-workers[4], have been included for comparison.

Table 1. Unit cells of isomorphous p-*toluenesulphonyl compounds.*

	$a \pm 0.02$ Å	$c \pm 0.06$ Å	Density calc.	Density found
$S(STs)_2$	7.70	29.50	1.53	1.55
$Se(STs)_2$	7.70	29.60	1.72	1.72
$Te(STs)_2$	7.73	29.88	1.87	1.85
Se_3Ts_2	7.79	29.75	2.01	2.00

There are four molecules per unit cell. Absent reflections, ($h00$) when h is odd, ($0k0$) when k is odd, ($00l$) except when $l = 4n$. Space group, D_4^4—$P4_12_1$ (or the enantiomorph, D_4^8—$P4_32_1$). Since the general position of the space group is eightfold, each molecule must possess twofold symmetry; this can only be the twofold axis which lies in the only fourfold positions:

$$x, x, 0; \quad \bar{x}, \bar{x}, \tfrac{1}{2}; \quad \tfrac{1}{2}-x,\ \tfrac{1}{2}+x,\ \tfrac{1}{4}; \quad \tfrac{1}{2}+x,\ \tfrac{1}{2}-x,\ \tfrac{3}{4}.$$

The middle atoms of the molecules, *e.g.*, the tellurium atoms of the $Te(STs)_2$ molecules, thus lie in these positions.

The crystals of selenium di(benzenethiosulphonate), $Se(SBs)_2$, are, likewise, tetragonal trapezohedral, and possess, from absent reflections, the same space group as the *p*-toluene compounds of Table 1. They show the form $\{101\}$ and frequently also $\{001\}$; in the latter case they are sometimes elongated along the a axis. The axial lengths are, $a = 7.80 \pm 0.02$ Å, $c = 26.54 \pm 0.06$ Å. Density, calculated on the basis of four molecules per unit cell, 1.75, found 1.77. According to Dawson, Mathieson and Robertson[4], the sulphur analogue, $S(SBs)_2$, has a four-molecule unit cell with the dimensions, $a = 7.80$ Å, $c = 26.29$ Å, and the same tetragonal trapezohedral space group as the compounds above.

The two remaining benzene compounds, $Te(SBs)_2$ and Se_3Bs_2, do not belong to the isomorphous series.

The crystals of tellurium di(benzenethiosulphonate), $Te(SBs)_2$, are orthorhombic bipyramidal, and show the forms $\{111\}$ and $\{100\}$. The latter is frequently the more predominant, thus giving the crystals the appearance of plates. The axial lengths are, $a = 14.46 \pm 0.04$ Å, $b = 11.18 \pm 0.02$ Å, $c = 10.48 \pm 0.02$ Å. There are four molecules per unit cell; density, calc. 1.86, found 1.88. Absent reflections, ($hk0$) when $h + k$ is odd, ($h0l$) when l is odd, ($0kl$) when k is odd. The space group is therefore D_{2h}^{14}—$Pbcn$. The general position of this space group is eightfold, and there are three sets of fourfold positions, two of which have a centre and one has a twofold axis of symmetry. Since the molecule cannot reasonably have a centre of symmetry, it must possess a twofold axis, which thus passes through the tellurium atoms in the positions:

$$0, y, \tfrac{1}{4}; \quad 0, \bar{y}, \tfrac{3}{4}; \quad \tfrac{1}{2}, \tfrac{1}{2}+y, \tfrac{1}{4}; \quad \tfrac{1}{2}, \tfrac{1}{2}-y, \tfrac{3}{4}.$$

The crystals of triselenium di(benzenesulphinate), Se_3Bs_2, are triclinic. They appear as plates or prisms with (001) as the most predominant face. The unit cell dimensions are, $a = 8.24 \pm 0.03$ Å, $b = 8.54 \pm 0.03$ Å, $c = 12.80 \pm 0.06$ Å, $\alpha = 105°$, $\beta = 95°$, $\gamma = 101°$. No absent spectra.

Space group, C_1^1-P1 or $C_i^1-P\bar{1}$. Two molecules per unit cell; density, calc. 2.04, found 2.01. No molecular symmetry is required by any of the two possible space groups.

Thus, among the eight compounds discussed above, seven compounds possess, by space group requirements, a twofold axis of symmetry. As pointed out by Dawson, Mathieson and Robertson[4] in their study of the sulphur thiosulphonates, this property limits the number of possible molecular configurations, and is consistent with the presence of unbranched chains.

ANALOGOUS REACTIONS AND INTERCONVERTIBILITY OF THE ISOMORPHOUS SERIES

In the following, attempts are made to demonstrate, on chemical basis, that the three isomorphous series of pentathionic compounds possess analogous structures. Part of the reactions have been reported previously; the remaining ones are described in this article.

The sulphur thiosulphate[9], methanethiosulphonate[6] and aromatic thiosulphonates[3] arise from sulphur dichloride by analogous reactions:

$$SCl_2 + 2\ S_2O_3^{--} = S(S_2O_3)_2^{--} + 2\ Cl^- \tag{3}$$
$$SCl_2 + 2\ CH_3SO_2S^- = S(S_2O_2CH_3)_2 + 2\ Cl^- \tag{4}$$
$$SCl_2 + 2\ ArSO_2S^- = S(S_2O_2Ar)_2 + 2\ Cl^- \tag{5}$$

The products react with piperidine to give sulphur dipiperidide[6,9]:

$$S(S_2O_3)_2^{--} + 4\ C_5H_{10}NH = S(NC_5H_{10})_2 + 2\ C_5H_{10}NH_2^+ + 2\ S_2O_3^{--} \tag{6}$$
$$S(S_2O_2CH_3)_2 + 4\ C_5H_{10}NH = S(NC_5H_{10})_2 + 2\ C_5H_{10}NH_2^+ + 2\ CH_3SO_2S^- \tag{7}$$
$$S(S_2O_2Ar)_2 + 4\ C_5H_{10}NH = S(NC_5H_{10})_2 + 2\ C_5H_{10}NH_2^+ + 2\ ArSO_2S^- \tag{8}$$

The selenium and tellurium thiosulphates[10], methanethiosulphonates[6] and aromatic thiosulphonates react with sodium dimethyldithiocarbamate to give selenium and tellurium *bis*(dimethyldithiocarbamate):

$$Se(S_2O_3)_2^{--} + 2\ Me_2NCS_2^- = Se(S_2CNMe_2)_2 + 2\ S_2O_3^{--} \tag{9}$$
$$Se(S_2O_2CH_3)_2 + 2\ Me_2NCS_2^- = Se(S_2CNMe_2)_2 + 2\ CH_3SO_2S^- \tag{10}$$
$$Se(S_2O_2Ar)_2 + 2\ Me_2NCS_2^- = Se(S_2CNMe_2)_2 + 2\ ArSO_2S^- \tag{11}$$

with analogous equations for the tellurium compounds.

The sulphur, selenium and tellurium thiosulphates[10] and thiosulphonates, under the catalytic influence of thiosulphate and thiosulphonate ions, respectively, decompose to give the free elements and the tetrathionic compounds. These phenomena appear so characteristic for thio derivatives of these divalent elements as, alone, to constitute evidence for analogous structures.

The nucleophilic reactivities of the electronegative components, in displacements on divalent sulphur, selenium and tellurium, increase in the order methanethiosulphonate, aromatic thiosulphonate, and thiosulphate anions. Thus the following interconversions take place.

The sulphur, selenium and tellurium methane- and benzenethiosulphonates react with potassium *p*-toluenethiosulphonate to give the sulphur, selenium and tellurium *p*-toluenethiosulphonates:

$$S(S_2O_2CH_3)_2 + 2\ ArSO_2S^- = S(S_2O_2Ar)_2 + 2\ CH_3SO_2S^- \tag{12}$$

$$Se(S_2O_2CH_3)_2 + 2\ ArSO_2S^- = Se(S_2O_2Ar)_2 + 2\ CH_3SO_2S^- \tag{13}$$

$$Te(S_2O_2CH_3)_2 + 2\ ArSO_2S^- = Te(S_2O_2Ar)_2 + 2\ CH_3SO_2S^- \tag{14}$$

with analogous equations for the benzenethiosulphonates. The same compounds react with sodium thiosulphate to give the sulphur, selenium and tellurium thiosulphates, as do also the *p*-toluenethiosulphonates:

$$S(S_2O_2CH_3)_2 + 2\ S_2O_3^{--} = S(S_2O_3)_2^{--} + 2\ CH_3SO_2S^- \tag{15}$$

$$Se(S_2O_2CH_3)_2 + 2\ S_3O_3^{--} = Se(S_2O_3)_2^{--} + 2\ CH_3SO_2S^- \tag{16}$$

$$Te(S_2O_2CH_3)_2 + 2\ S_2O_3^{--} = Te(S_2O_3)_2^{--} + 2\ CH_3SO_2S^- \tag{17}$$

with analogous formulations for the benzene and *p*-toluene compounds.

It appears that members of the three isomorphous series possess analogous chemical properties, and that members of one series, through nucleophilic displacement reactions, may be converted into the corresponding member of another series. On this basis, it is highly unlikely that the three series should have different structures.

The structural problem of particular interest is that of branched or unbranched chains[11]. The methanethiosulphonate series having been found by X-ray methods to possess an unbranched structure[12], we conclude that the sulphur, selenium and tellurium thiosulphates and aromatic thiosulphonates, and the triselenium disulphinates, are also built up of unbranched chains.

EXPERIMENTAL

Reactions with sodium dimethyldithiocarbamate and sodium thiosulphate. About 1 millimole of selenium or tellurium di(benzenethiosulphonate) was dissolved in 5—10 ml of chloroform and 15 ml of ethylacetate, and the solution was cooled in ice. 0.75 g (about 100 % excess) of sodium dimethyldithiocarbamate, dissolved in 15 ml of methanol, were added while stirring. A solid immediately separated out, which was filtered off, washed with methanol and water, and dried *in vacuo* over sulphuric acid.

(1) 0.4528 g of $Se(SBs)_2$ gave 0.3372 g of a greenish yellow substance; theoretically, 0.3400 g of selenium *bis*(dimethyldithiocarbamate). The product was identified by melting point (180—181° C) and mixed melting point with an authentic sample[10].

(2) 0.5006 g of $Te(SBs)_2$ gave 0.3899 g of a pale red substance; theoretically, 0.3886 g of tellurium *bis*(dimethyldithiocarbamate). M. p., above 250° C [10].

Selenium and tellurium di(*p*-toluenethiosulphonate) react analogously with sodium dimethyldithiocarbamate. The corresponding reactions of the methanethiosulphonates have been described previously [6], and so have the reactions of sulphur, selenium and tellurium di(methanethiosulphonate) with sodium thiosulphate [6]. The aromatic thiosulphonates react similarly with the last reagent. Experiments with sodium thiosulphate and sulphur and selenium di(benzenethiosulphonate) were performed exactly as described for the methane compounds [6]:

(3) 0.1578 g of $S(SBs)_2$[3] in 5 ml of ethylacetate and 20 ml of ethanol, 10 ml of 0.1033 *N* sodium thiosulphate. Volume made up to 100 ml with water, and 25 ml pipetted out and titrated with 0.01130 *N* iodine, after addition of 1 g of potassium iodide and 5 ml of 10 % acetic acid: 5.00 ml; theoretically, 4.41 ml.

(4) 0.1771 g of $Se(SBs)_2$ in 10 ml of chloroform, 10 ml of 0.1037 *N* sodium thiosulphate. On shaking, the greenish colour of the chloroform layer passed into the aqueous layer. Volume made up to 100 ml with water, and 25 ml of the aqueous layer (total volume, 90 ml) titrated as above: 5.63 ml of 0.01130 *N* iodine; theoretically, 5.02 ml. The aqueous layer contained selenopentathionate, as shown by reactions with sodium dimethyldithiocarbamate and sodium hydroxide, and the chloroform layer was devoid of selenium compounds. The too high iodine values found above are, partly at least, due to a slight oxidation of thiosulphonate ions by iodine [9].

In the case of the tellurium compounds the excess of sodium thiosulphate cannot be back-titrated with iodine, since the product, telluropentathionate, is not indifferent to iodine [13]. Instead, the amount of telluropentathionate formed was estimated by means of sodium dimethyldithiocarbamate:

(5) 0.4806 g of $Te(SBs)_2$ were dissolved in 20 ml of chloroform in a 100 ml volumetric flask, and 25 ml of 0.1 *N* sodium thiosulphate were added. On shaking, the yellow, faintly orange colour of the chloroform layer rapidly vanished, reappearing in the aqueous layer. The volume was made up to 100 ml with water, and 50 ml of the aqueous layer (total volume, 90 ml) were pipetted out. An excess of aqueous sodium dimethyldithiocarbamate was added, and the resulting reddish solid was filtered off, washed with water and methanol, and dried *in vacuo* over sulphuric acid. Yield, 0.2346 g; theoretically, 0.2331 g of tellurium *bis*(dimethyldithiocarbamate). M. p., above 250° C [10].

Catalytic decompositions. The decompositions of sulphur, selenium and tellurium di(thiosulphate) ions, into tetrathionate and the free elements, are strongly catalyzed by thiosulphate ions [10]. The corresponding decompositions of the thiosulphonates of these divalent elements are, analogously, susceptible to catalysis by thiosulphonate ions. As with the thiosulphates, the thiosulphonates of divalent tellurium are more stable in this respect than are the sulphur and selenium derivatives. Some experiments, at room temperature, with selenium thiosulphonates are described below.

0.01 *M* solutions of (a) selenium di(methanethiosulphonate) and (b) selenium di(benzenethiosulphonate) in chloroform are stable for several days. To 5 ml of these pale greenish solutions were added various amounts of 0.01 *M* solutions, in methanol, of (c) sodium methanethiosulphonate and (d) potassium benzenethiosulphonate. Time from mixing till appearance of red selenium colour:

(a); 5 ml of (c): 10 seconds. 2 ml of (c): 20 seconds.
(b); 5 ml of (d): 30 seconds. 2 ml of (d): 2 ½ minute.

The benzenethiosulphonate thus appears to be more stable than the methanethiosulphonate.

Sulphur, selenium and tellurium di(p-*toluenethiosulphonate*) *from the methane and benzene analogues.* The experiments were made with the following solutions: (1) 0.3917 g of $S(SBs)_2$, (2) 0.2592 g of $S(S_2O_2CH_3)_2$, (3) 0.4265 g of $Se(SBs)_2$, (4) 0.3159 g of $Se(S_2O_2CH_3)_2$, (5) 0.4721 g of $Te(SBs)_2$, in 5 ml, 5 ml, 10 ml, 15 ml and 20 ml of chloroform, respectively, and (6) 0.3592 g of $Te(S_2O_2CH_3)_2$ in 15 ml of bromoform. The solutions were cooled in ice, and 1 g (about 100 % excess) of potassium *p*-toluenethiosulphonate hydrate, dissolved in 5 ml of water, were added. On stirring, crystals rapidly began to separate out, except in the case of (1) where crystallization was effected by addition of 20 ml of methanol to produce a homogeneous mixture. After five minutes' stirring and cooling the products were filtered off, washed with water and dried *in vacuo* over sulphuric acid. The yields were as follows. Of $S(STs)_2$: (1) 0.3937 g or 94 %, (2) 0.3631 g or 89 %. Of $Se(STs)_2$: (3) 0.3981 g or 88 %, (4) 0.3913 g or 82 %. Of Te(STs): (5) 0.4840 g or 97 %, (6) 0.4702 g or 91 %. No selenium or tellurium and apparently no sulphur were set free in the experiments.

The crude products, when viewed in a microscope, consisted of tiny tetragonal bipyramides as characteristic for the sulphur, selenium and tellurium *p*-toluenethiosulphonates. The products were recrystallized from chloroform, and identified by crystal habit and by melting or decomposition points, and by selenium or tellurium determinations in the case of the $Se(STs)_2$ and $Te(STs)_2$ samples.

The percentage yields stated above refer to complete conversions of the methane- and benzenethiosulphonates to *p*-toluenethiosulphonates. The use of heterogeneous reaction mixtures (chloroform and water phases) serves to depress catalytic decompositions of the sulphur, selenium and tellurium thiosulphonates.

SUMMARY

Selenium and tellurium di(benzenethiosulphonate) and di(*p*-toluenethiosulphonate) have been described for the first time. Unit cells and space groups are reported for the crystals of these compounds and of the corresponding triselenium disulphinates. The *p*-toluene compounds, together with the previously known sulphur *p*-toluenethiosulphonate, constitute a four-membered isomorphous series of pentathionic compounds.

Evidence, based on interconvertibility and similarity of chemical behaviour, indicates that members of this series, and of the pentathionate, selenopentathionate and telluropentathionate series, possess the same type of structure as the sulphur, selenium and tellurium di(methanethiosulphonate) series.

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Received March 4, 1952.