

## Aromatic Sulphinates of Divalent Selenium

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This article describes the syntheses and some properties of the selenium benzene- and *p*-toluenesulphonyl derivatives:



These represent new types of selenium compounds \*. The sulphur analogues, *viz.*, the so-called bisphenyl- and bis-*p*-tolylsulphonyl sulphide, disulphide and trisulphide, are known <sup>3, 4</sup> since 1870—91.

In reactions with nucleophilic reagents, the new compounds eliminate the sulphonyl groups as sulphinate anions. The di- and triselenium derivatives in some cases do so without break-down of the selenium groupings. The compounds thus behave as selenium, diselenium and triselenium disulphinates.

The crystals of the *p*-toluene compounds and selenium di(benzenesulphinates) are, according to X-ray data, isomorphous with those of the corresponding sulphur compounds.

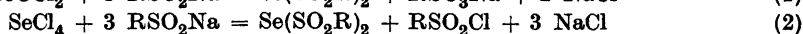
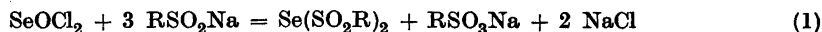
The 'sulphide' nomenclature for the sulphur analogues is misleading, inasmuch as the 'sulphide' terminology usually refers to sulphur bearing an excess of electronegative charge, whereas the divalent sulphur of the sulphonyl compounds is electropositively polarized. The 'trisulphides', in reactions with nucleophilic reagents, behave <sup>5, 6</sup> as thiosulphonates of divalent sulphur,  $\text{S}^{++}$ , and may conveniently be named as such, in analogy with the divalent selenium and tellurium thiosulphonates <sup>6, 7</sup>. The 'disulphides' possess, as a prominent characteristic, relatively strong oxidizing properties, thus giving measurable equilibria with iodide-iodine <sup>5, 8, 9</sup>. These 'thiosulphonatogens' <sup>8, 9</sup> are in this article termed disulphur disulphinates, and the 'sulphides' correspondingly, sulphur disulphinates. The last species behave as derivatives of divalent electropositive sulphur in reactions with sodium 2-naphtoxide <sup>10</sup>.

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\* For preliminary accounts, see Ref. 1 and 2.

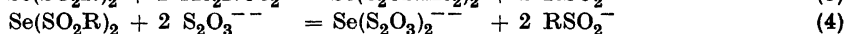
## SELENIUM DISULPHINATES

The compounds arise when sodium benzene- or *p*-toluenesulphinate, suspended in an inert solvent, reacts with selenium oxychloride or selenium tetrachloride:

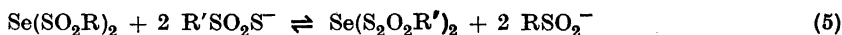


The crystals of the selenium disulphinates have a very pale greenish colour. When pure, the crystals are stable for months; in sunlight, or in an acid atmosphere, they liberate selenium fairly rapidly. The crystals decompose on heating; in preheated bath the benzenesulphinate melts at 132–133° C and the *p*-toluenesulphinate at 121–122° C to green liquids which ultimately become red. The compounds are insoluble in water, slightly soluble in warm ligroin, moderately soluble in warm ether, ethanol and acetic acid, and readily soluble in chloroform and in warm benzene and carbon tetrachloride.

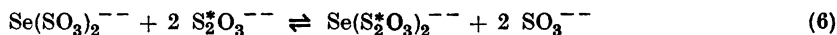
The following reactions serve to characterize the disulphinates as derivatives of divalent electropositive selenium,  $\text{Se}^{++}$ . The nucleophilic reagents, sodium dimethyldithiocarbamate and sodium thiosulphate, act rapidly and completely to give selenium *bis*(dimethyldithiocarbamate) and selenopentathionate, respectively:



Potassium *p*-toluenethiosulphonate reacts similarly, to displace the sulphinate groups:



The last change is comparable with the equilibrium of the inorganic analogue, *viz.*, selenotritrithionate, with sodium thiosulphate<sup>11</sup>:



Eq. (5) may, likewise, represent an equilibrium, which however, proceeds to the right because of the low solubility of the product, selenium di(*p*-toluenethiosulphonate).

## EXPERIMENTAL

Sodium benzene- and *p*-toluenesulphinate dihydrates, crystallized from water, were powdered, dried for two hours at 110° C, and finely powdered once more.

Ether and benzene, dried over sodium, were used as solvents for the preparations. The ligroin employed boiled at 60–90° C.

Selenium determinations were made gravimetrically by digesting with sulphuric acid-nitric acid, and precipitation of the selenium by means of hydrazine sulphate<sup>12</sup>. Removal

of the excess of nitric acid by means of urea and titration of the selenious acid according to Norris and Fay<sup>13</sup> does sometimes give unreliable results.

These details also apply to the experiments on di- and triselenium disulphinates described later in this article.

*Selenium oxychloride.* To 9 g (about 20 % excess) of sodium benzene- or *p*-toluenesulphinate, suspended in 50 ml of ether and cooled in ice, was added 1 ml of selenium oxychloride. The beaker was removed from the ice, and the contents were stirred with a glass rod for a few minutes. Then 50 ml of ether were added, and the mixture was heated, and filtered while warm. The pale greenish filtrate was evaporated to 10–20 ml on the water bath, and subsequently cooled in ice-sodium chloride. Yields of greenish crystals, about 3 g. Further, more impure crops were obtained by treatment of the sodium salt residue with hot chloroform, combining the filtrate with the ether mother liquor, and evaporation to dryness under reduced pressure.

For recrystallizations \*, 1 g of  $\text{SeBs}_2$  was dissolved in 15 ml of hot glacial acetic acid, and 1 g of  $\text{SeTs}_2$  in 25 ml of hot 80 % acetic acid, and the solutions were allowed to cool slowly. Yields, about 70 % based on the crude products.

0.5178 g substance: 0.1136 g Se.

$\text{Se}(\text{SO}_2\text{C}_6\text{H}_5)_2$  (361.3) Calc. Se 21.9 Found Se 21.9.

0.6841 g substance: 0.1379 g Se.

$\text{Se}(\text{SO}_2\text{C}_7\text{H}_7)_2$  (389.3) Calc. Se 20.3. Found Se 20.2.

From the sodium salts residue of a selenium di(*p*-toluenesulphinate) preparation was isolated \*\* 1.9 g of sodium *p*-toluenesulphonate; theoretically, according to Eq. (1), 2.8 g.

*Selenium tetrachloride.* Equivalent amounts (Eq. 2) of sodium sulphinates and selenium tetrachloride were employed, since an excess of the salts may react<sup>14</sup> with the sulphonyl chloride formed, to give disulphones.

4.4 g of selenium tetrachloride and 9.8 g of sodium benzenesulphinate (or 10.7 g of sodium *p*-toluenesulphinate) in 40 ml of benzene were triturated for a few minutes at room temperature. The mixture was then heated rapidly, and filtered while hot, giving a greenish filtrate. The solid residue was treated with 20 ml of hot benzene, and filtered once more. The filtrates were combined and heated, and 60 ml of ligroin were added. On cooling, crystals of selenium disulphinates separated out; yields, 4–6 g. The crude products were recrystallized as described above.

From the mother liquors, on treatment with aqueous ammonia, were isolated benzene- and *p*-toluenesulphonamide, respectively, formed from the sulphonyl chlorides.

*Sodium dimethyldithiocarbamate.* 0.3625 g of  $\text{SeBs}_2$  were dissolved in 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 greenish solid immediately separated out. The product was filtered off, washed with

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

\*\* Excess of sulphinate was precipitated by means of ferric chloride, and the excess of ferric iron, after filtering, was removed as hydroxide by means of ammonia. To the filtrate was added sodium hydroxide, the ammonia was expelled by boiling, and the solution was subsequently neutralized by means of hydrochloric acid and evaporated to dryness. The residue was extracted with boiling abs. ethanol, and the solvent evaporated off. The product was dried for one hour at 110° C, and identified as sulphonyl chloride and amide.

water and methanol, and dried *in vacuo* over sulphuric acid. Yield, 0.3145 g (98 %) of selenium *bis*(dimethyldithiocarbamate), identified by melting point and mixed melting point with an authentic sample <sup>15</sup>.

An analogous experiment with  $\text{SeTs}_2$  gave a yield of 96 % of the theoretical amount of the same product.

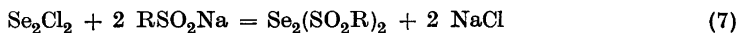
*Sodium thiosulphate.* 0.1590 g of  $\text{SeTs}_2$  were dissolved in 10 ml of chloroform in a 100 ml volumetric flask, and 10 ml of 0.1037 *N* sodium thiosulphate were added. On swirling, the pale greenish colour of the chloroform layer passed rapidly into the aqueous layer. After shaking for one minute, the volume was made up to 100 ml with water, and 25 ml of the aqueous layer (total volume, 90 ml) were pipetted out. 1 g of potassium iodide and 5 ml of 10 % acetic acid were added to the sample, and the excess of thiosulphate was titrated with 0.01130 *N* iodine: 7.3 ml, corresponding to a consumption of 0.740 millimoles of sodium thiosulphate; theoretically, 0.817 millimoles. However, in thiosulphate titrations sulphinate ions are partly oxidized by iodine, even in presence of potassium iodide <sup>5</sup>. The chloroform layer was devoid of selenium compounds, which indicates a quantitative change. The aqueous layer gave, with sodium dimethyldithiocarbamate and with alkalis, qualitative reactions on selenopentathionate.

*Potassium p-toluenethiosulphonate.* About 1 millimole of selenium disulphinate and 4 millimoles (about 100 % excess) of potassium *p*-toluenethiosulphonate hydrate were dissolved in 5 ml of chloroform and 5 ml of water, respectively. To a two-layer mixture of the two solutions, cooled in ice, were added 20 ml of methanol while stirring. A homogeneous solution resulted, from which crystals of selenium *p*-toluenethiosulphonate,  $\text{Se}(\text{STs})_2$ , rapidly began to separate out. After standing for 5 minutes in ice, the product was filtered off, washed with water, and dried *in vacuo* over sulphuric acid. The crystals sometimes had a faint reddish colour due to a slight catalytic decomposition of the selenium compounds.

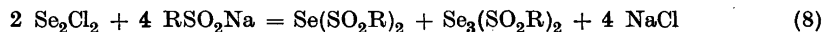
0.3760 g of  $\text{SeBs}_2$  gave 0.3770 g of  $\text{Se}(\text{STs})_2$  (80 %) and 0.4034 g of  $\text{SeTs}_2$  gave 0.4028 g of  $\text{Se}(\text{STs})_2$  (86 %). The crude products consisted of tiny tetragonal bipyramids and decomposed at about 180° C. Recrystallization from chloroform as described in a following article <sup>7</sup> gave in both cases about 75 % yields of pale greenish bipyramids, decomposing at about 200° C and containing 17.4 % and 17.2 % of Se, respectively; calc. for  $\text{Se}(\text{STs})_2$ , 17.4 %.

#### DISELENIUM AND TRISELENIUM DISULPHINATES

The compounds were prepared from diselenium dichloride, by reactions with an excess of sodium benzene- or *p*-toluenesulphinate suspended in benzene or ether. The course of the process is dependent upon the nature of the solvent. In benzene, diselenium disulphinates are the major products:



whereas in ether, selenium and triselenium disulphinates result almost exclusively:



Ethanol-free chloroform, according to one single experiment with sodium *p*-toluenesulphinate, gave equal amounts of di- and triselenium disulphinates,

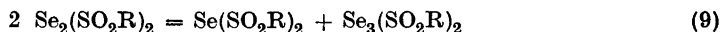
whereas carbon tetrachloride was like benzene, causing only a slight degree of rearrangement.

The disulphinates arise from diselenium dichloride through nucleophilic displacements of the chloride by sulphinate groups. No attempts have been made to establish the mechanism by which selenium and triselenium disulphinates result instead of diselenium disulphinates. It appears, however, that the different course is not due to a rearrangement of primarily formed diselenium disulphinate, since diselenium di(*p*-toluenesulphinate) is relatively stable when heated in ether or carbon tetrachloride. Catalysts may, though, play a role. Nor is it likely that diselenium dichloride, in ether and partly in chloroform, rearranges into selenium and triselenium dichloride, judging from the fact that diselenium dichloride<sup>16</sup> and dibromide<sup>17</sup> with organo-magnesium reagents in ether give rise to organic diselenides.

The analogous reactions of disulphur dichloride with sodium benzene- and *p*-toluenesulphinate in carbon tetrachloride lead to disulphur disulphinates beside small amounts of rearrangement products<sup>18</sup>. In presence of water, sodium benzenesulphinate gave the tri- and pentathionic compounds and no disulphur disulphinate. Rearrangements of this type take place in various reactions of disulphur dichloride. Thus, silver cyanide reacts<sup>19</sup> to give a mixture of sulphur dicyanide and sulphur di(thiocyanate). Likewise<sup>20</sup>, diselenium dibromide, with silver cyanide in ether, gives selenium dicyanide and selenium di(selenocyanate). Possible mechanisms have been discussed by Lecher and Goebel<sup>21</sup> and Kaufmann and Kögler<sup>20</sup>.

The di- and triselenium disulphinates form pale greenish crystals having only a slight yellow tinge. The green colour deepens slightly with increasing number of selenium atoms, from selenium to triselenium disulphinates. When pure, and kept in a dry, neutral atmosphere, shielded from light, the crystals remain unchanged for months. The compounds liberate selenium when heated, and so the melting points depend upon the rate of heating. In preheated bath, diselenium di(benzenesulphinate) and di(*p*-toluenesulphinate) melt at 79–80° C and 104–106° C, respectively, to green liquids which become red after about five minutes and half a minute. Likewise, triselenium di(benzenesulphinate) melts and decomposes rapidly at 101–102° C, and triselenium di(*p*-toluenesulphinate) decomposes at 136–140° C. The last compound is the least soluble (1 g dissolves in about 30 ml of chloroform at boiling temperature). The diselenium disulphinates and triselenium di(benzenesulphinate) are readily soluble in chloroform and relatively so in boiling benzene. They are appreciably soluble in ethanol and methanol, and insoluble in ligroin and water.

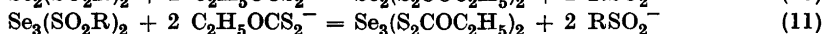
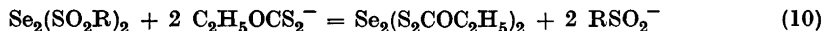
When heated in solutions, the diselenium disulphinates rearrange slowly into selenium and triselenium disulphinates, in analogy with the behaviour of the sulphur analogues:



The compounds are, though, relatively stable. Thus, 2 g of diselenium di(*p*-toluenesulphinate), dissolved in 50 ml of carbon tetrachloride and kept at boiling temperature of the solvent for one hour, rearranged to an extent of about 10 %. Disulphur di(*p*-toluenesulphinate), at the same molar concentration in carbon tetrachloride and treated in the same way, was recovered unchanged, and so was the diselenium compound from a saturated solution in warm ether (1.5 g per 100 ml) after 15 minutes' heating under reflux. In boiling acetic acid, according to Otto and Troeger<sup>4</sup>, disulphur di(*p*-toluenesulphinate) undergoes rearrangement, though less readily than does the benzene compound.

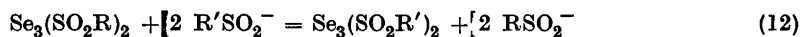
Similar rearrangements are those of thiocyanogen and selenocyanogen<sup>20</sup>, and of the tetrathionate ion to give trithionate and pentathionate.

Solutions of the di- and triselenium disulphinates in chloroform, on treatment with aqueous potassium ethylxanthate, acquire a deeper green colour, and two moles of ethylxanthate are consumed per mole of disulphinate. No selenium is set free during the process. The chloroform solutions of the new compounds are not stable, and so no attempts have been made to isolate the products. The reactions can hardly be anything else than nucleophilic displacements, as follows:



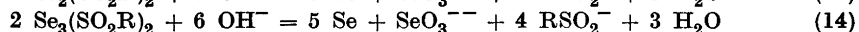
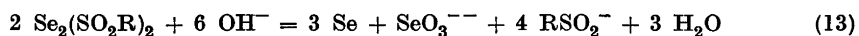
The sulphonyl groups are eliminated as sulphinate ions, the di- and triselenium groupings thereby remaining intact.

More strikingly, triselenium di(benzenesulphinate) reacts with sodium *p*-toluenesulphinate to give triselenium di(*p*-toluenesulphinate). The product is less soluble and separates as crystals, thus displacing a possible equilibrium completely to the right:

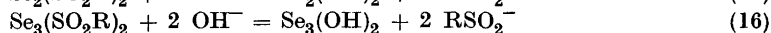
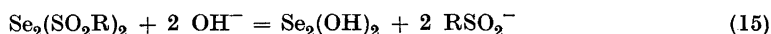


Corresponding experiments with the diselenium disulphinates were not made, since there is no appreciable solubility difference between the benzene and *p*-toluene compounds.

With aqueous sodium hydroxide, the di- and triselenium disulphinates in chloroform-ethanol solutions are rapidly and completely hydrolyzed. The net reactions are:



In view of the sodium *p*-toluenesulphinate and potassium ethylxanthate reactions (Eqs. 10–12) it appears reasonable to assume that the first steps are displacements of sulphinate by hydroxide, to give unstable di- and triselenium dihydroxides as intermediates:



The subsequent rearrangements would be:



The diselenium dihalides hydrolyze in an analogous way, whereas hydrolysis reactions of derivatives of  $\text{Se}_3^{++}$  have not been studied before, the triselenium disulphinates being the first representatives of this type.

The fact that the latter compounds behave as triselenium disulphinates,  $\text{Se}_3(\text{SO}_2\text{R})_2$ , and not as selenium selenosulphonates,  $\text{Se}(\text{SeSO}_2\text{R})_2$ , whereas the corresponding sulphur compounds react as sulphur thiosulphonates,  $\text{S}(\text{S}_2\text{O}_2\text{R})_2$ , is in accordance with the existence of thiosulphonate and non-existence of selenosulphonate ions. Selenocyanate ions are relatively stable, and so the cyanide analogue,  $\text{Se}(\text{SeCN})_2$ , behaves as a selenium di(selenocyanate)<sup>22</sup>.

## EXPERIMENTAL

*Diselenium disulphinates.* The following proportions of reagents and solvent were employed: 10 g of sodium benzenesulphinate in 20 ml of benzene, or 12 g of sodium *p*-toluenesulphinate in 40 ml of benzene, 2 ml of diselenium dichloride. The suspensions were cooled in ice, and the dichloride was added from a pipette while stirring. The beaker was subsequently removed from the ice, and the contents were triturated for a few minutes, until the diselenium dichloride colour disappeared. The mixture was then heated rapidly, and the sodium chloride and the excess of sodium sulphinate were filtered off, giving a greenish yellow filtrate. The sodium salt residue was treated with 10 ml of hot benzene, filtered once more, and the filtrates were combined \*. 40–50 ml of ligroin were added to the mixture, and the beaker was placed in ice. The resulting, pale greenish crystals of diselenium disulphinate were filtered off, washed with ligroin and small amounts of ether, and dried *in vacuo* over sulphuric acid. Yields, 5–7 g.

The recrystallizations were made as follows.

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\* The *p*-toluenesulphinate solutions, on standing, deposited 0.5–1.0 g of the less soluble triselenium disulphinate. These crystals may be filtered off at this stage, or later at the recrystallization.

2 g of  $\text{Se}_2\text{Bs}_2$  were dissolved in 3 ml of chloroform at room temperature. 10 ml of benzene and 10 ml of ligroin were added, and the mixture was cooled, ultimately in ice-sodium chloride. Yield, 1.3–1.5 g of pale green prisms.

2 g of  $\text{Se}_2\text{Ts}_2$  were dissolved in 5 ml of chloroform at room temperature, and 5 ml of ether were added. The triselenium disulphinate, if present, is slightly soluble in this mixture, and may be filtered off, whereas the diselenium disulphinate is soluble. 10 ml of ether were added to the filtrate, and the beaker was ultimately placed in ice-sodium chloride; yield, as above.

0.3413 g substance: 0.1229 g Se.

$\text{Se}_2(\text{SO}_2\text{C}_6\text{H}_5)_2$  (440.3) Calc. Se 35.9. Found Se 36.0.

0.3206 g substance: 0.1086 g Se.

$\text{Se}_2(\text{SO}_2\text{C}_7\text{H}_7)_2$  (468.3) Calc. Se 33.7. Found Se 33.9.

*Triselenium disulphinates.* To 10 g of sodium benzenesulphinate (or 12 g of sodium *p*-toluenesulphinate) suspended in 50 ml of ether and cooled in ice, were added 2 ml of diselenium dichloride while stirring. The beaker was removed from the ice, and the solid particles were treated with a glass rod for a few minutes, until the diselenium dichloride colour vanished from the liquid phase. The insoluble substance, which had a faint reddish colour, was filtered off, treated with 20 ml of ether, drained well, and dried *in vacuo* over sulphuric acid. The solid was subsequently treated repeatedly with water to remove the sodium salts, drained, and dried as above.

(1) Benzenesulphinate. The yield was about 3 g. A further crop of about 3 g was obtained from the ether filtrate on evaporation on the water bath to 30–40 ml, and cooling in ice-sodium chloride. Usually, a reddish oil first separated out, which on stirring changed to greenish yellow crystals.

The crude product was recrystallized by dissolving 3 g in 15–20 ml of hot benzene, filtering, if necessary, and addition of 10–15 ml of ligroin to the filtrate while still hot. On cooling, triselenium di(benzenesulphinate) separated as yellowish green plates. Yield, 2.0–2.3 g. Better developed crystals were obtained by slow crystallization from chloroform-ether.

(2) *p*-Toluenesulphinate. The residue from the water treatment was extracted with two times 10 ml of chloroform, drained, and dried once more. Yield, about 8 g. The substance was dissolved in boiling chloroform (30 ml per g) and the solution filtered. About two thirds of the chloroform were subsequently boiled off, and the solution was then allowed to cool to room temperature. Yield, about 4 g of triselenium di(*p*-toluenesulphinate).

0.2867 g substance: 0.1303 g Se.

$\text{Se}_3(\text{SO}_2\text{C}_6\text{H}_5)_2$  (519.2) Calc. Se 45.6. Found Se 45.4.

0.2806 g substance: 0.1215 g Se.

$\text{Se}_3(\text{SO}_2\text{C}_7\text{H}_7)_2$  (547.3) Calc. Se 43.3. Found Se 43.3.

The ether filtrate from a triselenium di(*p*-toluenesulphinate) preparation, on partial evaporation and addition of ligroin, gave 1.5 g of almost colourless crystals which contained 24.2 % of Se. The substance was treated with boiling ligroin, and the extract, on cooling, gave long, thin needles of selenium disulphinate,  $\text{SeTs}_2$ , identified by analysis (found, 20.5 % of Se) and by an X-ray oscillation photograph around the needle axis.

*Potassium ethylxanthate.* About 0.8 millimoles of di- or triselenium disulphinate were dissolved in 20 ml of chloroform, and the solution was cooled in ice. 50 ml of 0.04 *M* potassium ethylxanthate (5 ml of which consumed 19.64 ml of 0.01130 *N* iodine) were



added, and the two-layer mixture was stirred for two minutes under continued cooling, the chloroform layer thereby acquiring a deeper green colour. 5 ml of the aqueous layer were subsequently pipetted out, and the excess of potassium ethylxanthate was titrated with 0.01130 *N* iodine after addition of 1 g of potassium iodide and 50 ml of water.

0.3884 g (0.8294 millimoles) of  $\text{Se}_2\text{Ts}_2$ : 5.27 ml of 0.01130 *N* iodine. Amount of potassium ethylxanthate thus consumed by the disulphinate: 1.624 millimoles, *i. e.*, 97.9 % of theory (Eq. 10).

0.4410 g (0.8492 millimoles) of  $\text{Se}_3\text{Bs}_2$ : 4.76 ml of 0.01130 *N* iodine. Amount of potassium ethylxanthate thus consumed by the disulphinate: 1.682 millimoles, *i. e.*, 99.0 % of theory (Eq. 11).

After 15 minutes, the chloroform layer from the  $\text{Se}_2\text{Ts}_2$  experiment had become faintly yellow, while that from the  $\text{Se}_3\text{Bs}_2$  experiment was reddish and had deposited small amounts (8 mg) of selenium. These chloroform solutions of, supposedly, di- and triselenium di(ethylxanthate) gave, with sodium dimethyldithiocarbamate in methanol, precipitates of selenium and selenium *bis*(dimethyldithiocarbamate). The aqueous layers, after destruction of the excess of potassium ethylxanthate by means of hydrochloric acid, gave a red colour with ferric chloride and thus contained sulphinate ions.

*Sodium p-toluenesulphinate.* A two-layer mixture of 0.5583 g of  $\text{Se}_3\text{Bs}_2$  in 5 ml of chloroform, and 0.85 g (about 100 % excess) of sodium *p*-toluenesulphinate dihydrate in 5 ml of water, was cooled in ice, and 20 ml of methanol were added while stirring. A homogeneous solution resulted, from which pale greenish crystals rapidly began to separate out; however, a reddish colour soon appeared, indicating a slight degree of decomposition. After standing for five minutes in the ice the product was filtered off, washed with water and dried *in vacuo* over sulphuric acid. Yield, 0.5400 g, *i. e.*, 91.9 % of theory (Eq. 12). The substance consisted, when viewed in a microscope, of tetragonal bipyramides, having a greenish colour with a faint reddish tinge. The crude product was dissolved in 15 ml of boiling chloroform, and the solution was filtered, leaving 6 mg of selenium on the filter. The greenish filtrate, on evaporation and cooling, gave 0.40 g of  $\text{Se}_3\text{Ts}_2$  crystals, decomposing at 135–140° C and containing, by analysis, 43.2 % of Se.

*Hydrolysis reactions.* About 1 millimole of di- or triselenium disulphinate was dissolved in 5 ml of chloroform and 25 ml of ethanol, and 5 ml of 1 *M* sodium hydroxide were added. Selenium immediately separated out, and was after five minutes filtered off, washed with water, methanol and ether, dried *in vacuo* over sulphuric acid, and weighed. The filtrate was evaporated to dryness on the water bath. The residue was, in order to destroy the sodium sulphinate, treated with nitric acid, and the selenium was finally precipitated by means of hydrazine sulphate, dried and weighed.

0.4430 g (1.006 millimole) of  $\text{Se}_2\text{Bs}_2$  gave 0.1185 g of Se and, from the filtrate, 0.0388 g of Se, corresponding to 1.49 and 0.49 g atoms of Se, respectively, per mole of diselenium disulphinate.

0.5536 g (1.066 millimole) of  $\text{Se}_3\text{Bs}_2$  gave 0.2126 g of Se and, from the filtrate, 0.0399 g of Se, corresponding to 2.53 and 0.47 g atoms of Se, respectively, per mole of triselenium disulphinate.

*Non-existence of selenosulphonate ions.* 10 g of sodium *p*-toluenesulphinate dihydrate were dissolved in 10 ml of water. 4 g of freshly precipitated, red selenium, moistened with ethanol, were added, and the mixture was heated under reflux for one hour. 10 ml of water were subsequently added, and the mixture was filtered. 1 ml of the colourless filtrate, diluted to 10 ml with water and 1 ml of concentrated hydrochloric acid added, remained colourless and slowly deposited crystals of *p*-toluenesulphinic acid.

*Disulphur di(p-toluenesulphinate)*,  $S_2Ts_2$ , has previously been prepared from aqueous potassium *p*-toluenethiosulphonate and iodine <sup>4</sup>, and from sodium *p*-toluenesulphinate, suspended in carbon tetrachloride, and disulphur dichloride <sup>18</sup>. For the rearrangement experiment and X-ray measurements of the present work, the compound was obtained from potassium *p*-toluenethiosulphonate and bromine, as follows.

A suspension of 10 g (about 20 % excess) of dry, powdered potassium *p*-toluenethiosulphonate in 25 ml of carbon tetrachloride was cooled in ice, and 1 ml of bromine was added drop-wise with stirring. The bromine colour disappeared rapidly, and the mixture was heated and filtered. The residue was treated with 25 ml of boiling chloroform, filtered once more, and the filtrates were combined. On cooling in ice, 0.8 g of sulphur di(*p*-toluenethiosulphonate),  $S(STs)_2$ , separated out and was filtered off. The filtrate was evaporated under reduced pressure to a volume of about 20 ml, then 40 ml of ligroin were added, and the mixture was cooled in ice. Yield, 5.0 g. 4 g of the crude product were dissolved in 6 ml of chloroform, small amounts of  $S(STs)_2$  were filtered off, and 15 ml of ligroin were added to the filtrate. Yield, 2.5 g of  $S_2Ts_2$ . The substance melted at 114° C as reported by Christiansen <sup>23</sup>.

#### THE STRUCTURE OF THE SELENIUM AND DISELENIUM DISULPHINATES

A search was made for a possible isomorphism relationship between the crystals of the selenium, diselenium and triselenium disulphinates and the parent sulphur compounds. These are, as mentioned before, the sulphur and disulphur disulphinates,  $S(SO_2R)_2$  and  $S_2(SO_2R)_2$ , and the sulphur thiosulphonates,  $S(S_2O_2R)_2$ . For reasons of analogy with the corresponding thiosulphonates of divalent selenium and tellurium,  $Se(S_2O_2R)_2$  and  $Te(S_2O_2R)_2$ , crystallographic data on the triselenium disulphinates will be reported in a subsequent article <sup>7</sup>, the present discussion being concerned with the selenium and diselenium compounds only.

X-ray measurements (oscillation and Weissenberg photographs) were carried out using  $FeK_\alpha$  radiation,  $\lambda = 1.934 \text{ \AA}$ , and in some cases  $CuK_\alpha$  radiation,  $\lambda = 1.54 \text{ \AA}$ . Density determinations were made by flotation in suitable solvents.

The unit cells and space group of the sulphur disulphinates,  $SBs_2$  and  $STs_2$ , and a detailed structure analysis of the former substance, have been reported recently by Robertson and co-workers <sup>24,25</sup>. The crystals are monoclinic prismatic, with the unit cell dimensions:  $SBs_2$ ,  $a = 15.88 \text{ \AA}$ ,  $b = 5.52 \text{ \AA}$ ,  $c = 15.88 \text{ \AA}$ ,  $\beta = 112.9^\circ$ .  $STs_2$ ,  $a = 16.50 \text{ \AA}$ ,  $b = 5.85 \text{ \AA}$ ,  $c = 18.88 \text{ \AA}$ ,  $\beta = 119.9^\circ$ . There are four molecules per unit cell. Absent reflections,  $(hkl)$  when  $k + l$  is odd,  $(h0l)$  when  $h$  is odd or when  $l$  is odd. These absences are characteristic for the space groups  $C_s^4 - Aa$  and  $C_{2h}^6 - A2/a$ , of which the latter, from studies of the intensities, was found to be the correct one. The molecules possess a twofold axis of symmetry parallel to the  $b$  crystal axis.

The crystals of the selenium disulphinates,  $\text{SeBs}_2$  and  $\text{SeTs}_2$ , appear as flat prisms or long needles, elongated along the  $b$  axis. They are isomorphous with those of the sulphur disulphinates.

Table 1. Unit cells of selenium di(benzenesulphinate) and di(*p*-toluenesulphinate).

	$a \pm 0.06 \text{ \AA}$	$b \pm 0.02 \text{ \AA}$	$c \pm 0.06 \text{ \AA}$	$\beta$	Density	
					calc.	found
$\text{SeBs}_2$	16.14	5.60	15.84	$112^\circ$	1.81	1.79
$\text{SeTs}_2$	16.81	5.76	19.07	$119^\circ$	1.61	1.60

There are four molecules per unit cell. The absent reflections, for both compounds, are the same as for the sulphur disulphinates, referred to above. Analogy with the latter compounds indicates the space group  $C_{2h}^6 - A2/a$ , and this has been made probable by a comparison of the intensities of the ( $h0l$ ) zones of sulphur and selenium di(benzenesulphinate).

The crystals of disulphur and diselenium di(benzenesulphinate) are not mutually isomorphous, nor is any of the crystals isomorphous with those of disulphur and diselenium di(*p*-toluenesulphinate). The latter compounds, however, are mutually isomorphous, which shows that they have analogous structures. Since there are no chemical indications of a structural difference between the benzene and *p*-toluene compounds, it may be inferred that disulphur and diselenium di(benzenesulphinate) possess the same structure.

The isomorphous *p*-toluene compounds,  $\text{S}_2\text{Ts}_2$  and  $\text{Se}_2\text{Ts}_2$ , crystallize as flat prisms, elongated along the  $c$  axis and flattened along the  $b$  axis.

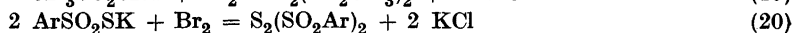
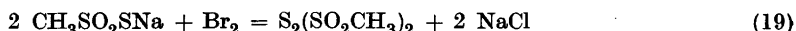
Table 2. Unit cells of disulphur and diselenium di(*p*-toluenesulphinate).

	$a \pm 0.04 \text{ \AA}$	$b \pm 0.03 \text{ \AA}$	$c \pm 0.03 \text{ \AA}$	$\beta$	Density	
					calc.	found
$\text{S}_2\text{Ts}_2$	9.96	15.07	11.24	$95^\circ$	1.48	1.46
$\text{Se}_2\text{Ts}_2$	10.15	15.48	11.26	$94^\circ$	1.76	1.76

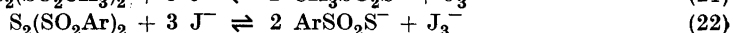
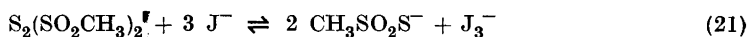
There are four molecules per unit cell. Absent reflections, ( $h0l$ ) when  $l$  is odd, ( $0k0$ ) when  $k$  is odd. Space group, for both compounds,  $C_{2h}^5 - P2_1/c$ .

No structure analysis, by X-ray or other physical methods, is available for the aromatic disulphur disulphinates. However, the methane analogue<sup>9</sup>,  $\text{S}_2(\text{SO}_2\text{CH}_3)_2$ , possesses an unbranched sulphur chain structure<sup>26</sup>. The chemical evidence indicates structural analogy between the aliphatic and the aromatic

disulphur disulphinates. Thus, the compounds arise from the sodium or potassium thiosulphonates by reactions with bromine:



and give reversible equilibria with iodide-iodine <sup>5, 8, 9</sup>:



The evidence, therefore, points towards the presence of unbranched S—Se—Se—S chains in the diselenium disulphinates.

Isomorphism of disulphur and diselenium compounds has been reported in earlier cases, *e. g.*, for *bis*(diacetylmethyl) disulphide and diselenide <sup>27</sup>, and diphenyl and dibenzyl disulphide and diselenide <sup>28</sup>.

#### SUMMARY

Selenium, diselenium and triselenium di(benzenesulphinate) and di(*p*-toluenesulphinate) have been prepared for the first time. Reactions are demonstrated, in which the compounds behave as derivatives of  $\text{Se}^{++}$ ,  $\text{Se}_2^{++}$  and  $\text{Se}_3^{++}$ , respectively.

The structure of the selenium and diselenium disulphinates have been discussed on the basis of isomorphism of the crystals with those of the corresponding sulphur compounds.

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