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Methanethiosulphonates of Divalent Sulphur, Selenium and Tellurium

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These compounds, *viz.*:

$$S(S_2O_2CH_3)_2; \quad Se(S_2O_2CH_3)_2; \quad Te(S_2O_2CH_3)_2$$

are described in this article for the first time. They are polythionic compounds of the pentathionic type, and, supposedly, structural analoga of the pentathionate, selenopentathionate and telluropentathionate ions, *viz.*, the thiosulphates:

$$S(S_2O_3)_2^{--}; \quad Se(S_2O_3)_2^{--}; \quad Te(S_2O_3)_2^{--}$$

Thiosulphonates of divalent selenium and tellurium are new types of compounds. Sulphur thiosulphonates, *i. e.*, aromatic ones, are well known and have been the subject of much study *. Thus, the *p*-toluene derivative was isolated by Blomstrand [2] in 1870. The only aliphatic representative known hitherto, the ethane compound, dates from 1945 [1].

SYNTHESIS AND CHEMICAL PROPERTIES

Sulphur and selenium di(methanethiosulphonate) were obtained from sodium methanethiosulphonate, suspended in ether, and sulphur dichloride and diselenium dichloride, respectively:

$$2\ CH_3SO_2SNa + SCl_2 = S(S_2O_2CH_3)_2 + 2\ NaCl$$

$$2\ CH_3SO_2SNa + Se_2Cl_2 = Se(S_2O_2CH_3)_2 + Se + 2\ NaCl$$

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* For literature, see Ref. 1.

The first of these reactions is generally used [1] for the synthesis of thio derivatives of S^{++}. The only example of the second type seems to be that of Baroni [3], who prepared selenium di(phenylmercaptide) from diselenium dichloride and benzenethiol.

Tellurium di(methanethiosulphonate) resulted when aqueous sodium methanethiosulphonate was added to tellurium dioxide dissolved in hydrochloric acid:

$$TeOOH^+ + 4\ CH_3SO_2S^- + 3\ H^+ = Te(S_2O_2CH_3)_2 + (CH_3SO_2S)_2 + 2\ H_2O$$

Tellurium dioxide reacts in an analogous way with sodium thiosulphate [4] and with thiolactic acid [5].

Sulphur di(methanethiosulphonate) forms colourless crystals which melt at 70—70.5° C, and are readily soluble in ethylacetate, benzene and chloroform, sparingly soluble in ether and carbon disulphide.

Selenium di(methanethiosulphonate) appears as pale greenish crystals which are only moderately soluble in cold chloroform and ethylacetate, and almost insoluble in ether, carbon disulphide and benzene. The crystals of tellurium di(methanethiosulphonate) are yellow, and so are dilute solutions, whereas more concentrated solutions have an orange tinge. The solubility is very low, the best solvents being chloroform and, especially, bromoform. The melting points of selenium and tellurium di(methanethiosulphonate) depend on the rate of heating. The selenium compound starts to decompose (become red) at about 75° C and liquifies at 85—90° C; the tellurium compound becomes black at about 120° C and appears to melt at about 135° C.

The crystals, when pure, are relatively stable; thus, they have been kept unchanged for months. They are insoluble in water. With alkalies, they rapidly liberate sulphur, selenium or tellurium.

The following nucleophilic displacement reactions serve to characterize the compounds as derivatives of divalent electropositive sulphur, selenium and tellurium. The reactions are rapid and, seemingly, quantitative.

Sulphur di(methanethiosulphonate) reacts with piperidine to give sulphur dipiperidide, as do other derivatives [1] of S^{++}:

$$S(S_2O_2CH_3)_2 + 4\ C_5H_{10}NH = S(NC_5H_{10})_2 + 2\ C_5H_{10}NH_2^+ + 2\ CH_3SO_2S^-$$

Selenium and tellurium di(methanethiosulphonate) react with sodium dimethyldithiocarbamate to give selenium and tellurium *bis*(dimethyldithiocarbamate), as do the selenopentathionate and telluropentathionate ions [4, 6, 7]:

$$Se(S_2O_2CH_3)_2 + 2\ (CH_3)_2NCS_2^- = Se(S_2CN(CH_3)_2)_2 + 2\ CH_3SO_2S^-$$

$$Te(S_2O_2CH_3)_2 + 2\ (CH_3)_2NCS_2^- = Te(S_2CN(CH_3)_2)_2 + 2\ CH_3SO_2S^-$$

Sodium thiosulphate reacts to displace the methanethiosulphonate groups, thus forming pentathionate, selenopentathionate and telluropentathionate:

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

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

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

The reactions serve to emphasize the structural relationship of the thiosulphonates and the thiosulphates of divalent sulphur, selenium and tellurium. It appears, furthermore, that the nucleophilic reactivity of the methanethiosulphonate ion, in displacements on these divalent elements, is lower than that of the thiosulphate ion, as has been demonstrated earlier[1,8] in the case of displacements of ethane- and *p*-toluenethiosulphonate by thiosulphate, on divalent sulphur.

From a chemical point of view, the reactions with piperidine and with dimethyldithiocarbamate and thiosulphate ions demonstrate the structure of the compounds as methanethiosulphonates of divalent sulphur, selenium and tellurium. The reactions strongly indicate that in each compound a divalent sulphur, selenium or tellurium atom forms a bridge between two methanethiosulphonate groups, through the thio sulphur atom of these groups, *cf.* the analogous argument for the presence of unbranched chains in the pentathionate, selenopentathionate and telluropentathionate ions[1,4,6,9].

Experimental

Sulphur and selenium di(methanethiosulphonate). About 20 % excess, with respect to sulphur dichloride and diselenium dichloride, of finely powdered, dry sodium methanethiosulphonate was employed, and 4 ml of dry ether per g of thiosulphonate. The suspensions were cooled in ice-salt, and the chloride slowly added from a pipet. On treatment of the solid particles with a glass rod the sulphur dichloride colour vanished rapidly; in the case of diselenium dichloride, selenium was liberated. The mixtures, while cold, were filtered, drained well, and the solid residues on the filters were dried *in vacuo* over sulphuric acid, while the filtrates were discarded. The residues were subsequently treated several times with water, drained, and dried again. The sulphur di(methanethiosulphonate) was recrystallized by dissolving 2 g of the crude product in 8 ml of warm chloroform, and adding an equal volume of carbon disulphide. The crude selenium compound, containing an equimolar amount of selenium, was treated with ethylacetate at about 60° C (10 ml per g of sodium methanethiosulphonate employed). The mixture was filtered, and the pale green filtrate cooled in ice-salt. The selenium di(methanethiosulphonate) thus obtained was recrystallized from ethylacetate (1 g dissolved in 15—20 ml at 60° C, and cooled in ice-salt) or from chloroform (1 g dissolved in 25 ml at boiling temperature, and 25 ml of carbon disulphide added).

0.1007 g substance: 0.4616 g $BaSO_4$.
$S(S_2O_2CH_3)_2$ (254.4) Calc. S 63.01 Found S 62.96
0.1138 g substance: 15.05 ml of 0.1002 *N* iodine (Norris & Fay).
$Se(S_2O_2CH_3)_2$ (301.3) Calc. Se 26.20 Found Se 26.15

Tellurium di(methanethiosulphonate). To 4 g of tellurium dioxide dissolved in 15 ml of concentrated hydrochloric acid and 5 ml of water were added dropwise, over a period of 10—15 minutes, under stirring and cooling in ice-salt, 15 g (about 10 % excess) of sodium methanethiosulphonate dissolved in 15 ml of water. A semi-solid oil separated out, which, on continued stirring and treatment with a glass rod, changed to a yellow solid. It was filtered off, washed with 10 ml of 6 *N* hydrochloric acid, and treated on the filter with portions of methanol (3 times 10 ml), ether (3 times 10 ml), and warm chloroform (5 times 20 ml), and finally washed with ether and dried *in vacuo* over sulphuric acid. The crude products (5—6 g) thus obtained, in various preparations, contained about 32 % of tellurium, or 85—90 % of tellurium di(methanethiosulphonate). It was dissolved in boiling chloroform (100—150 ml per g) and the solution filtered. About half of the chloroform was subsequently boiled off, until crystals began to separate out, and the solution was then allowed to cool to room temperature. The crystals were filtered off, washed with ether and dried *in vacuo* over sulphuric acid.

0.3063 g substance: 0.1114 g Te.
$Te(S_2O_2CH_3)_2$ (349.9) Calc. Te 36.47 Found Te 36.37

The reactions with piperidine and with sodium dimethyldithiocarbamate. (1) To 2.067 millimole (0.5260 g) of sulphur di(methanethiosulphonate) dissolved in 20 ml of chloroform were added 10 millimole (1 ml) of piperidine. After a few minutes the chloroform was evaporated off *in vacuo* and the excess of piperidine removed *in vacuo* over sulphuric acid. The colourless crystalline residue was then treated with water, and the sulphur dipiperidide filtered off, dried *in vacuo* over sulphuric acid, and weighed: 0.4092 g, *i. e.*, 2.042 millimole of $S(NC_5H_{10})_2$. It was recrystallized from methanol [1] and thus melted at 75° C, not depressed in mixture with a sample obtained from other sources. The aqueous filtrate, containing piperidinium methanethiosulphonate, was made up to 500 ml in a volumetric flask, and 25 ml were pipetted out and analyzed iodometrically as described earlier [1] in the case of analogous experiments with sulphur ethanethiosulphonates and dimethylthiophosphates: 16.16 ml of 0.1002 *N* iodine, corresponding to 4.048 millimole of piperidinium methanethiosulphonate.

(2) 1.004 millimole (0.3025 g) of selenium di(methanethiosulphonate) dissolved in 30 ml of ethylacetate were added rapidly, with stirring, to 100 % excess (4 millimole) of sodium dimethyldithiocarbamate in 15 ml of methanol. A yellowish green solid immediately separated out. It was filtered off, washed with methanol and ether, and dried: 0.3032 g, *i. e.*, 0.9491 millimole of selenium *bis*(dimethyldithiocarbamate). It melted at 180—182° C and was found to contain 24.78 % Se; calc. [7] for $Se(S_2CN(CH_3)_2)_2$: 24.72 %.

(3) To 0.9936 millimole (0.3476 g) of tellurium di(methanethiosulphonate) dissolved in 10 ml of bromoform were added 2.5 millimole of sodium dimethyldithiocarbamate in 5 ml of methanol. A reddish solid immediately separated out, which was filtered off and treated as under (2): 0.3430 g, *i. e.*, 0.9322 millimole of tellurium *bis*(dimethyldithiocarbamate). It was found to contain 34.56 % Te; calc.[7] for $Te(S_2CN(CH_3)_2)_2$: 34.67 %.

The reactions with sodium thiosulphate. About 0.4 millimole of sulphur, selenium or tellurium di(methanethiosulphonate) was employed in each experiment, and about 1 millimole (25 % excess) of sodium thiosulphate.

(4) 0.1080 g of $S(S_2O_2CH_3)_2$ was dissolved in 5 ml of ethylacetate and 20 ml of ethanol in a 100 ml volumetric flask. 10 ml of 0.09977 *N* sodium thiosulphate were added, and the solution was made up to 100 ml by means of water. 25 ml were pipetted out, and, after addition of 5 ml of 10 % acetic acid and 1 g of potassium iodide, the excess of thiosulphate was back-titrated with 0.01096 *N* iodine: 3.71 ml (theoretically, 3.40 ml). The original reaction mixture became faintly opaque after about 10 minutes. On addition of sodium hydroxide, a distinct turbidity developed immediately (sulphur being liberated from the formed pentathionate).

The addition of potassium iodide serves to depress the oxidation of methanethiosulphonate ions by iodine. Although thiosulphonate ions are indifferent to iodine in presence of iodide, in neutral and acid solutions, their oxidation by iodine is to a slight degree induced by the simultaneous oxidation of thiosulphate by iodine [1].

(5) 0.1234 g of $Se(S_2O_2CH_3)_2$ were dissolved in 10 ml of chloroform in a 100 ml volumetric flask, and 25 ml of 0.09977 *N* sodium thiosulphate were added. On shaking, the chloroform layer became rapidly colourless, its greenish colour reappearing in the aqueous layer. The mixture was made up to 100 ml, and 25 ml of the aqueous layer (total volume, 90 ml) were pipetted out and titrated with 0.01096 *N* iodine as described under (4): 2.43 ml (theoretically, 2.00 ml).

The pale greenish aqueous layer showed the typical reactions of selenopentathionate; thus, selenium was liberated when alkalies were added, and, on addition of sodium dimethyldithiocarbamate, greenish selenium *bis*(dimethyldithiocarbamate) separated out.

(6) 0.1392 g of $Te(S_2O_2CH_3)_2$ was dissolved in 10 ml of bromoform, and 10 ml of 0.09977 *N* sodium thiosulphate were added. On shaking, the yellow colour of the bromoform layer became rapidly transferred to the aqueous layer. In this case, the excess of thiosulphate cannot be back-titrated with iodine, since the product, telluropentathionate, is not indifferent to iodine [4]. However, since tellurium di(methanethiosulphonate) is insoluble in water, the shifting of the yellow colour from the bromoform layer to the aqueous layer provides definite evidence that telluropentathionate has been formed. Furthermore, the aqueous layer liberated tellurium with alkalies and gave tellurium *bis*(dimethyldithiocarbamate) with sodium dimethyldithiocarbamate.

PRELIMINARY X-RAY DATA

The crystals of sulphur, selenium and tellurium di(methanethiosulphonate) are monoclinic prismatic. They appear as needles or prisms elongated along the *b* axis, and in most cases flattened along the *a* axis. The most frequent forms are $\{001\}$ and $\{102\}$ and, less developed, $\{10\bar{1}\}$.

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

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* The data reported at *Det 7de Nordiska Kemistmøtet,* Helsingfors, Aug. 21—25, 1950, correspond to a different choise of *c* axis (space group symbol, $P2_1/c$).

Table 1. Unit cells of sulphur, selenium and tellurium di(methanethiosulphonate).

	a ± 0.02 Å	b ± 0.02 Å	c ± 0.04 Å	β	Density calc.	 found
$S(S_2O_2CH_3)_2$	11.33	5.21	16.14	91°	1.78	1.77
$Se(S_2O_2CH_3)_2$	11.38	5.23	16.23	91°	2.07	2.05
$Te(S_2O_2CH_3)_2$	11.43	5.29	16.32	91°	2.36	2.35

There are four molecules per unit cell. Absent spectra, $(h0l)$ when $h + l$ is odd, and $(0k0)$ when k is odd. Space group, for all three compounds, C_{2h}^5 — $P2_1/n$.

SUMMARY

Methanethiosulphonates of divalent sulphur, selenium and tellurium are described for the first time. X-ray data show that the crystals are is isomorphous, and, thus, that the compounds have analogous structures.

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