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X-ray Crystallographic Data on Selenotrithionates

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Selenotrithionic acid, $Se(SO_3H)_2$, was discovered by Rathke[1] in 1865, two and a half decades after the preparation of the first salts of trithionic acid, $S(SO_3H)_2$, by Langlois[2].

Whereas crystal data on potassium, rubidium and cesium trithionate were reported by Mackenzie and Marshall[3] in 1908, and Zachariasen[4] in 1934 worked out the crystal structure of potassium trithionate by X-ray methods, the only crystallographic data available on selenotrithionates are from a morphological study of potassium selenotrithionate by Rathke[5,6] in 1870.

The chemical evidence concerning the constitution of selenotrithionic acid and selenotrithionates, *e.g.*, the formation reaction from selenium acetylacetonate and hydrogen sulphite[7]:

$$(C_5H_6O_2Se)_2 + 4\ HSO_3^- = 2\ Se(SO_3)_2^{--} + 2\ C_5H_8O_2 \qquad (1)$$

and the nucleophilic displacement equilibrium[8] involving selenotrithionate/selenopentathionate and thiosulphate/sulphite ions:

$$Se(SO_3)_2^{--} + 2\ S_2O_3^{--} \rightleftharpoons Se(S_2O_3)_2^{--} + 2\ SO_3^{--} \qquad (2)$$

leave little doubt that the selenotrithionate ion is built up of a divalent selenium atom to which are attached two sulphonate groups. Thus, selenotrithionate is derived from trithionate by substitution of selenium for the middle sulphur atom. Two organic analogues, *viz.*, sulphur and selenium dibenzenesulphinate, arise from the acids by substitution of phenyl for the hydroxyl groups. The benzenesulphinates form isomorphous crystals[9], and the detailed structures have been determined recently by Mathieson and Robertson[10] and Furberg and Öyum[11].

In the present study, crystallographic measurements have been made on ammonium, potassium, rubidium, cesium and barium selenotrithionate, with the purpose of establishing whether isomorphism exists between these crystals and those of the corresponding trithionates. No such isomorphism has been found. In view of the undoubtedly similar constitution of the

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trithionate and selenotrithionate anions, and the manyfold cases of isomorphism reported earlier for crystals of analogous sulphur, selenium and tellurium compounds, this result appears rather surprising and may be largely fortuitous. Thus, in addition to the numerous examples among inorganic sulphides, selenides and tellurides, and the sulphur and selenium dibenzenesulphinates mentioned above, isomorphism exists, *e.g.*, between selenium, diselenium and triselenium di-*p*-toluenesulphinate and the corresponding sulphur compounds [9,12], and between salts of pentathionic, selenopentathionic and telluropentathionic acid [13]. Likewise, crystals of sulphur, selenium and tellurium dimethanethiosulphonate are isomorphous [14], and so are those of the corresponding *p*-toluenethiosulphonates [12].

SYNTHESIS OF SALTS

The selenotrithionates were prepared from selenium acetylacetonate and aqueous solutions of the respective hydrogen sulphites, as done earlier by Morgan and Smith [7]. The cesium salt, and particularly the ammonium salt, are very soluble in water and were crystallized by addition of relatively large amounts of anhydrous ethanol to the concentrated aqueous solutions. Due to a lack of selenium acetylacetonate at the appropriate moment, rubidium selenotrithionate was prepared from the potassium salt by metathesis with an equivalent amount of sodium perchlorate, cooling and filtering, and addition of a slight excess of rubidium chloride.

The products were analyzed iodometrically according to Eq. (2) above [8], *viz.*, by the reaction with an excess of 0.1 M sodium thiosulphate, in phosphate buffer in presence of formaldehyde, and back-titration of the excess of thiosulphate with 0.1 N iodine. The purities of the recrystallized salts, used for X-ray measurements, ranged from 99.6 % to 99.85 %.

The selenotrithionates gradually liberate selenium on exposure to light and to X-rays. The crystals of barium selenotrithionate were found to be the more sensitive and those of cesium selenotrithionate the less sensitive ones in this respect.

Selenium acetylacetonate, required for the above syntheses, was prepared from acetylacetone and selenium tetrachloride suspended in anhydrous ether [7]. In working up the reaction mixture, it was found to be essential, in order to avoid an extensive decomposition of the product, to remove the ether rapidly in a vacuum and then, immediately, to shake the remaining crystalline mass with a relatively large amount of water. After filtering, the product was recrystallized from boiling glacial acetic acid.

Some measurements were also made on ammonium and barium trithionate, no crystallographic data on these salts being available in literature. Ammonium trithionate was prepared according to Kurtenacker and Laszlo [15]. The recrystallized salt was, by iodometric titrations, found to contain 0.17 % of ammonium thiosulphate as an impurity. Barium trithionate [2,16] was obtained from the potassium salt by metathesis with barium perchlorate.

CRYSTAL DATA

X-ray measurements (oscillation and Weissenberg photographs on small single-crystal specimens) were carried out using Cu$K\alpha$ radiation, $\lambda = 1.54$ Å, and in some cases Fe$K\alpha$ radiation, $\lambda = 1.934$ Å. The values recorded below for axial lengths are believed to be accurate to within 0.5 %, except in the case of rubidium selenotrithionate and ammonium trithionate, where approximate data were obtained from layer-line separations in oscillation photographs only.

In the following, for comparison, data on selenotrithionates and corresponding trithionates are listed consequtively. Those on potassium, rubidium and cesium trithionate are taken from the literature.

Ammonium selenotrithionate, $(NH_4)_2Se(SO_3)_2$. Monoclinic, $a = 6.74$ Å, $b = 8.96$ Å, $c = 14.00$ Å, $\beta = 102°$. Four molecules per unit cell; density, calc. 2.19, found 2.24 g/cm³. Absent reflections, $h0l$ when l is odd. The $0k0$ reflections for odd values of k are very weak and present only in a limited number. The habit of the crystals is monoclinic prismatic. They occur as prisms, elongated along the c axis and flattened along the b axis, and showing the forms $\{100\}$, $\{010\}$ and $\{012\}$. The space group is probably C_{2h}^4—$P2/c$, with an atomic arrangement close to that required by C_{2h}^5—$P2_1/c$.

Ammonium trithionate, $(NH_4)_2S(SO_3)_2$, was obtained as poorly developed prisms which showed a pronounced tendency of twinning. The crystals are probably triclinic, with four molecules per unit cell, and a repeat distance of 7.63 Å along the prism axis.

Potassium selenotrithionate, $K_2Se(SO_3)_2$. Monoclinic prismatic, $a = 9.54$ Å, $b = 5.97$ Å, $c = 15.34$ Å, $\beta = 110.4°$. Four molecules per unit cell; density, calc. 2.56, found 2.57 g/cm³. Absent reflections, $h0l$ when l is odd, $0k0$ when k is odd. The space group is thus C_{2h}^5—$P2_1/c$. The crystals occur as prisms, elongated along the b axis and flattened along the c axis. The forms $\{100\}$, $\{001\}$ and $\{012\}$ were observed, the latter being less predominant. The crystals are described by Groth [6], on the basis of measurements by Rathke [5], as monoclinic prismatic, with $a' : b' : c' = 1.5050 : 1 : 0.6447$ and $\beta = 93° 26'$. With the transformations, $\mathbf{a} = \mathbf{a}' + \mathbf{c}'$ and $\mathbf{c} = -4\mathbf{c}'$, Groth's data give $a : b : c = 1.602 : 1 : 2.579$ and $\beta = 110.3°$, as compared with $a : b : c = 1.598 : 1 : 2.569$ from the X-ray data.

Potassium trithionate [4], $K_2S(SO_3)_2$, is orthorhombic bipyramidal, with $a = 9.77$ Å, $b = 13.63$ Å, $c = 5.76$ Å. There are four molecules per unit cell, and the space group is D_{2h}^{16}—$Pnam$.

Rubidium selenotrithionate, $Rb_2Se(SO_3)_2$. Orthorhombic, $a = 9.16$ Å, $b = 13.97$ Å, $c = 13.42$ Å. The morphology is like that of cesium selenotrithionate, described below, and this, together with the correspondence of axial lengths, makes it probable that the rubidium and cesium salts are isomorphous.

Rubidium trithionate [3] is isomorphous with potassium trithionate, referred to above.

Cesium selenotrithionate, $Cs_2Se(SO_3)_2$. Orthorhombic bipyramidal, $a = 9.21$ Å, $b = 14.45$ Å, $c = 14.11$ Å. Eight molecules per unit cell; density, calc. 3.55, found 3.53 g/cm³. The systematic absences, $0kl$ when k is odd, $h0l$ when l is odd, $hk0$ when h is odd, determine the space group as D_{2h}^{15}—$Pbca$. The crystals appear as flat prisms, elongated along the b axis and with $\{001\}$ predominant. The forms $\{102\}$ and $\{120\}$ also occur.

Cesium trithionate, according to Mackenzie and Marshall [3], may be obtained as a monohydrate and in the anhydrous state, the crystals in both cases being triclinic.

Barium selenotrithionate dihydrate, $BaSe(SO_3)_2 \cdot 2H_2O$. Orthorhombic, $a = 9.00$ Å, $b = 17.84$ Å, $c = 10.74$ Å. Eight molecules per unit cell; density, calc. 3.05, found 2.96 g/cm³. Absent reflections, hkl when $h + k$ is odd, $h0l$

when l is odd. These absences are characteristic for the centrosymmetric space group, D_{2h}^{17}—$Cmcm$, and for the space groups of lower symmetries, C_{2v}^{12}—$Cmc2_1$ and C_{2v}^{16}—$C2cm$. The crystals have an orthorhombic bipyramidal appearance. They occur as well developed prisms, bounded by $\{110\}$ and usually also $\{100\}$, and terminated by $\{011\}$.

The Wilson ratio [17], calculated for $0kl$ and $hk0$ reflections corresponding to interplanar spacings smaller than [18] 2.0 Å, are in accordance with centrosymmetric distributions of intensities.

Patterson projections along the a, b and c axes have been made, and the results indicate the correctness of the centrosymmetric space group. The barium ion appears to lie in eightfold positions (f) of D_{2h}^{17}—$Cmcm$, as described in the *Int. Tables* [19], with $x = 0$, $y = 0.16$ and $z = 0.04$. On the basis of preliminary Fourier projections along the a and c axes, using signs of the reflections calculated from the barium contributions alone, the selenium and sulphur atoms have been tentatively assigned to two sets of fourfold positions (c) and two sets of eightfold positions (g), respectively. These positions are in the intersection-line of the two mirror planes and in the mirror plane normal to the c axis. The selenotrithionate ion would thus have the symmetry C_{2v}—mm in this salt.

Barium trithionate dihydrate, $BaS(SO_3)_2 \cdot 2H_2O$, gave poorly developed crystals which were invariably twinned. As far as could be ascertained, they are not isomorphous with those of barium selenotrithionate dihydrate.

INSTABILITY OF ANALOGOUS TELLURIUM COMPOUNDS

Tellurotrithionates, $Te(SO_3)_2^{--}$, are apparently not capable of existence. In reactions where such salts might be expected to be formed, from analogy with the selenium derivatives, elemental tellurium results. This is the case, *e. g.*, in the reaction of tellurous acid with sulphurous acid, and by the interaction of telluropentathionate with an excess of sulphite ions.

Likewise, attempts to prepare tellurium disulphinates, $Te(SO_2R)_2$, have met with no success. Thus, tellurium tetrachloride in benzene or chloroform does apparently not react with sodium benzenesulphinate or p-toluenesulphinate, but gradually, tellurium is set free. Furthermore, tellurium dimethanethiosulphonate and the aromatic analogues, in ethylacetate or chloroform solutions, immediately liberate tellurium on addition of methanol solutions of sodium benzenesulphinate or p-toluenesulphinate. This catalytic effect of sulphinate ions on tellurium thiosulphonates is, presumably, due to a displacement of thiosulphonate by sulphinate groups, to produce equilibrium amounts of rapidly decomposing tellurium disulphinates.

It thus appears that the grouping, divalent tellurium—sulphonate or sulphonyl sulphur, is unstable. The fact [8] that the selenotrithionate/selenopentathionate equilibrium (2) is displaced farther to the right than is the corresponding trithionate/pentathionate equilibrium:

$$S(SO_3)_2^{--} + 2\ S_2O_3^{--} \rightleftharpoons S(S_2O_3)_2^{--} + 2\ SO_3^{--}$$

together with the apparent non-existence of tellurotrithionates and tellurium disulphinates, suggests that the thermodynamic stabilities of the compounds, $X(SO_3)_2^{--}$ and $X(SO_2R)_2$, decrease progressively in the order X = S, Se and Te. The thio derivatives, $X(S_2O_3)_2^{--}$ and $X(S_2O_2R)_2$, show no corresponding variance of stability.

SUMMARY

Unit cell and space group data are reported for ammonium, potassium, rubidium and cesium selenotrithionate, and barium selenotrithionate dihydrate. No isomorphism appears to exist between the crystals of these salts and those of the corresponding trithionates.

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