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The Crystal Structure of Barium Selenopentathionate Dihydrate

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The crystal structure of barium selenopentathionate dihydrate has been determined by X-ray methods. The crystals, which have a four-molecule unit cell based on the space group D_{2h}^{16} —*Pnma*, with $a = 4.98$ Å, $b = 10.36$ Å, $c = 22.20$ Å, are isomorphous with those of barium pentathionate dihydrate.

The selenopentathionate ion consists of a divalent selenium atom to which are attached two thiosulphate groups. The resulting S—S—Se—S—S chain is unbranched and non-planar, with dihedral angles of 109°, and S—S and S—Se bond lengths of 2.13 Å and 2.17 Å, respectively. The values, 103° and 101°, respectively, were found for the S—S—Se and S—Se—S bond angles.

Some comments are made on the occurrence of rotational isomers of the pentathionate, selenopentathionate and telluropentathionate anions.

It was pointed out some time ago [1], on the basis of the finding that pentathionic, selenopentathionic and telluropentathionic acids give isomorphous salts, that the anions of these acids have analogous structures. Meanwhile, the detailed structures of two other salts of the acids, not belonging to the isomorphous series but having more favourable unit cells, have been determined by X-ray methods. These are orthorhombic barium pentathionate dihydrate [2] and ammonium telluropentathionate [3]. In order to include a salt of selenopentathionic acid, and to secure dimensional data for the selenopentathionate ion, crystals of barium selenopentathionate dihydrate have now been prepared and found to be isomorphous with those of barium pentathionate dihydrate.

EXPERIMENTAL

The salt was obtained as follows. To 20 g of crude sodium selenopentathionate trihydrate [4,5], dissolved in 25 ml of 0.2 *N* hydrochloric acid and cooled in ice, was added a solution of 25 g of barium perchlorate trihydrate in 15 ml of water. Crystals of barium selenopentathionate rapidly began to separate out. After about five minutes, the product

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was filtered off, and washed with alcohol and ether. Yield, about 17 g. For recrystallization, 5 g of the crude product was dissolved, at about 40° C, in 15 ml of 0.5 *N* hydrochloric acid. The filtered solution was warmed gently again, a few milliliters of methanol were added, and the mixture was allowed to stand at room temperature.

The product was analyzed volumetrically by oxidation with potassium bromate, and determination of the selenious acid by the Norris and Fay method, as described earlier [4] in the case of the sodium and potassium salt. (0.2380 g substance: 19.87 ml of 0.09997 *N* sodium thiosulphate. $BaSe(S_2O_3)_2 \cdot 2H_2O$ (476.6): Calc. Se 16.57. Found Se 16.47).

The crystals of barium selenopentathionate dihydrate have a pale yellowish green colour. When kept in the dark, they remain unchanged for months, whereas they slowly decompose, with liberation of selenium, when exposed to light or to X-rays. The crystals appear as flat prisms, elongated along the *a* axis and bounded by {001} and {011}. There is perfect cleavage along (001), as in the case of barium pentathionate dihydrate [2].

The unit cell dimensions were determined from oscillation and Weissenberg photographs, with an accuracy of about 0.5 % (Cu$K\alpha$ radiation, $\lambda = 1.54$ Å). For comparison, data for barium pentathionate dihydrate [2] are listed below.

	a	*b*	*c*
$BaSe(S_2O_3)_2 \cdot 2H_2O$	4.98 Å	10.36 Å	22.20 Å
$BaS(S_2O_3)_2 \cdot 2H_2O$	5.00	10.30	21.78

There are four formula units per unit cell; density, calc. 2.75, found 2.76 g/cm^3. The systematic absences, *viz.*, 0*kl* when $k + l$ is odd, *hk*0 when *h* is odd, are the same as for barium pentathionate dihydrate. It is apparent that the two salts are isomorphous, and the space group was therefore taken as D_{2h}^{16}—*Pnma*. This choise appears to be justified by the outcome of the analysis. The space group has eightfold general positions, and implies that the selenopentathionate ion possesses either a mirror plane, or a centre, of symmetry, with the barium ion also in special positions. As borne out by the analysis of the pentathionate and the present structure, the barium ion and the selenium atom lie in mirror planes. A centre of symmetry is, furthermore, incompatible with any reasonable structure for these anions.

Relative intensity measurements in the 0*kl* and *h*0*l* zones were made visually on Weissenberg photographs, using a double film technique, and after applying corrections for the Lorentz and polarization factors, the intensities were converted into relative structure amplitudes. They were ultimately put to an approximately absolute scale by comparison with calculated structure factors. 134 of the 161 0*kl* reflections and 132 of the 147 *h*0*l* reflections theoretically accessible with Cu$K\alpha$ radiation were recorded. The crystals used for the *a* and *b* axis photographs had cross-sections of 0.08 mm × 0.04 mm and 0.11 mm × 0.08 mm, respectively, and although absorption was certainly not negligible, no corrections were made. As before [2], difficulties were experienced in the cutting of the crystal for the *b* axis photographs, due to the ready cleavage. There was a slight but persistent tendency for twinning to occur, possibly with triclinic crystals [6], and this may have affected the reliability of the observed intensities.

The Patterson and Fourier summations, and the location of peaks, were made as described earlier [2], the summations being performed at 6° intervals along the *b* and *c* axes and at 12° intervals (0.166 Å) along the *a* axis.

DETERMINATION OF THE STRUCTURE

The Patterson projection along the *a* axis was worked out first. The resulting vector map was very similar to the corresponding one for barium pentathionate dihydrate [2], and is not reproduced here. As before, the map gave a very good resolution of vector peaks, and allowed approximate values for the *y* and *z* coordinates of the barium ion and the selenium and sulphur atoms to be determined and used for the calculation of signs of the 0*kl* reflections. The first Fourier map proved successful in indicating the positions of the oxygen atoms and water molecules, and the structure was refined in the usual way by successive electron density projections, leading to the final map, $\varrho(yz)$, shown in Fig. 1 and explained in Fig. 3. The *y* and *z* coordinates derived from this projection were corrected for termination-of-series errors as described by Booth[7], to give the final values of Table 1. The reliability factor, *R*, for the 0*kl* reflections changed from 0.187 to 0.181 as a result of this process.

The *x* coordinates were found chiefly from Patterson and Fourier projections along the *b* axis. The *h*0*l* Patterson map indicated that the barium ion and the four sulphur atoms lie close to the glide plane *n* normal to the *a* axis, and emphasized further the similarity of this structure with that of barium pentathionate dihydrate. Provisional *x* coordinates were estimated partly from the vector map and partly by reference to the pentathionate structure, and were employed for the calculation of signs of the *h*0*l* reflections. The first Fourier synthesis was based on 57 terms having *h*0*l* indices with *l* even and 50 terms with *l* odd. The analysis then proceeded by successive syntheses until the signs of all observed *h*0*l* reflections were thought to be established. The final electron density map, $\varrho(xz)$, is shown in Fig. 2, and a line diagram is reproduced in Fig. 4.

The oxygen atom, O_1, is better resolved in $\varrho(xz)$ than in $\varrho(yz)$, where overlapping with S_1 occurs. Trial and error calculations, however, showed that the *z* coordinate of O_1, 0.076, estimated from $\varrho(yz)$ gave a lower value for the reliability factor than the value, 0.080, derived from $\varrho(xz)$, or an intermediate value. In $\varrho(xz)$, the oxygen atom, O_2, overlaps with S_1, and the water molecule, $(H_2O)_2$, is not visible, probably due to the proximity to the selenium atom in this projection. The *x* coordinate of $(H_2O)_2$ was therefore obtained by trial and error calculations, and those of S_1, S_2, O_2 and O_3 were checked in the same way.

The final atomic coordinates, as fractions of corresponding cell edges and referring to a centre of symmetry as origin, are listed in Table 1.

Table 1. Atomic coordinates for barium selenopentathionate dihydrate.

Fourfold positions				*Eightfold positions*			
	x	*y*	*z*		*x*	*y*	*z*
Ba	0.227	0.250	−0.049	S_2	0.285	0.088	0.181
Se	0.561	0.250	0.177	S_1	0.305	0.012	0.092
$(H_2O)_1$	0.743	0.250	0.010	O_1	0.590	0.005	0.076
$(H_2O)_2$	0.320	0.250	−0.160	O_2	0.180	−0.106	0.098
				O_3	0.177	0.095	0.054

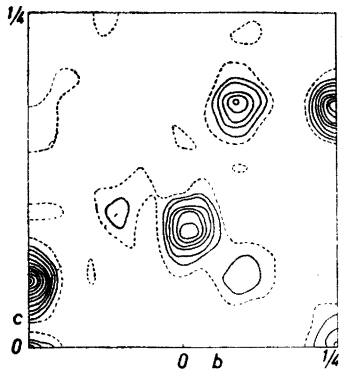

Fig. 1. Electron density projection of BaSe $(S_2O_3)_2 \cdot 2H_2O$ along the a *axis,* ϱ(yz). *One asymmetric unit is shown. Contour intervals: 10 e·Å^{-2} for the barium ion, 6 e·Å^{-2} for the selenium atom, and 4 e·Å^{-2} for the sulphur and oxygen atoms and water molecules. The 4-electron line is dashed.*

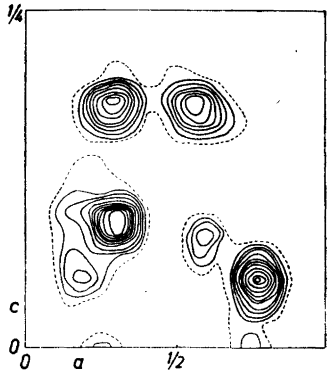

Fig. 2. Electron density projection of BaSe $(S_2O_3)_2 \cdot 2H_2O$ along the b *axis,* ϱ(xz). *One asymmetric unit is shown. The 8-electron line is dashed, and contour intervals are as in Fig. 1.*

The atomic scattering curves of the *International Tables* were employed for the calculation of structure factors, with the xenon curve in the case of the barium ion, and a temperature factor of $B = 2.0$ Å^2 for both zones. The reliability factor, $R = \Sigma||F_{obs}| - |F_{calc}||/\Sigma|F_{obs}|$, with non-observed reflections included when $|F_{calc}|$ is larger than the smallest observable value of $|F_{obs}|$, is 0.18 for the $0kl$ reflections and 0.23 for the $h0l$ reflections. A list of observed and calculated structure factors can be supplied by the authors on request.

THE SELENOPENTATHIONATE ION

The ion is built up of an unbranched and non-planar S—S—Se—S—S chain, and possesses, by space group requirements, a mirror plane of symmetry. Distances and angles, calculated on the basis of the coordinates of Table 1, are given below. The numbering of atoms, and the outline of the ion in the two projections, are shown in Figs. 3 and 4. A prime denotes the image of an atom across the mirror plane. It is believed that the error in the Se—S and S—S bond lengths is less than 0.04 Å, and in the S—S—Se and S—Se—S bond angles less than about 3°. The errors in S—O and O—O distances and angles may be considerably greater due to the overlapping of atoms and the obscuring effect of the heavy atoms.

Table 2. Sulphur-sulphur and selenium-sulphur bond lengths and bond angles.

$S_1—S_2 = 2.13$ Å	$\angle S_1S_2Se = 103°$	S_1S_2Se/S_2SeS_2'
$S_2—Se = 2.17$	$\angle S_2SeS_2' = 101°$	(dihedral angle) = 109°

Non-bonded distances.

$S_1—S_1' = 4.93$ Å	$S_1—Se = 3.36$ Å
$S_1—S_2' = 4.59$	$S_2—S_2' = 3.36$

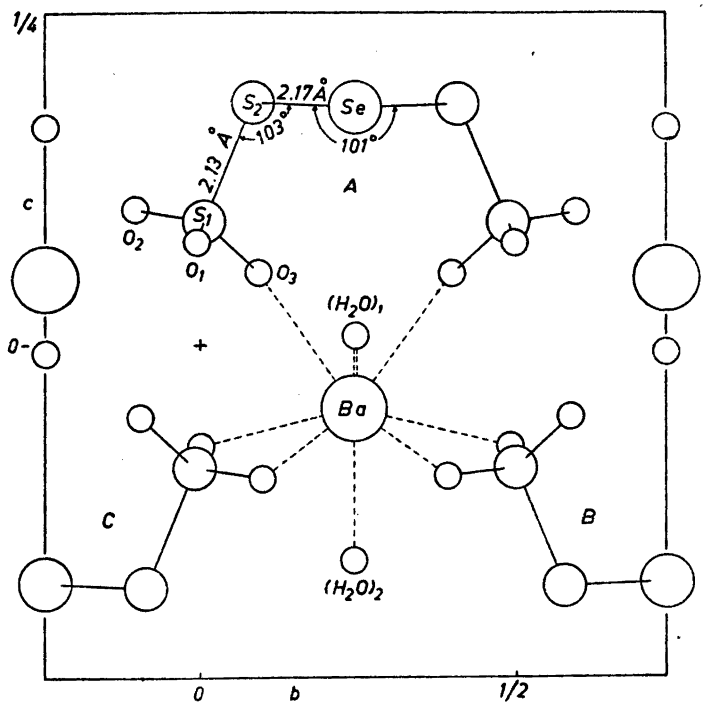

Fig. 3. Arrangement of the ions as seen along the a axis. Half a unit cell (four asymmetric units) is shown. Origin at the midpoint of the left half of the figure.

The Se—S bond is a little shorter than corresponding to the sum of the single bond radii [8], *i.e.*, 2.21 Å. The difference is within the experimental error, but similar shortenings, relative to the single bond lengths, were observed for the middle S—S bonds in the isomorphous crystals of barium pentathionate dihydrate [2], and for the Te—S bonds in ammonium telluropentathionate [3].

The S_2SeS_2' bond angle, 101°, differs slightly from the corresponding angle, $\angle S_2S_3S_2' = 106°$, in the pentathionate. It is likely that the smaller value found for the selenium bond angle is significant.

The crystal structures of two compounds containing Se—S bonds, *viz.*, selenium dibenzenesulphinate [9] and selenium dithiocyanate [10], have been described in literature earlier. The Se—S bond lengths observed are 2.20 Å and 2.21 Å, respectively, and the S—Se—S angles, 105° and 101°. As for the benzenesulphinate, the bonds from selenium are to sulphonyl sulphur and not to divalent sulphur, and the data are therefore not strictly comparable.

The oxygen atoms and the terminal sulphur atoms, together with the divalent sulphur atoms situated next to the selenium atom, constitute two thiosulphate groups. The shape of these is a distorted tetrahedral one. From the data of Table 3 it appears that the average S—O bond length is 1.40 Å. The difference between the individual values may, partly at least, be due to

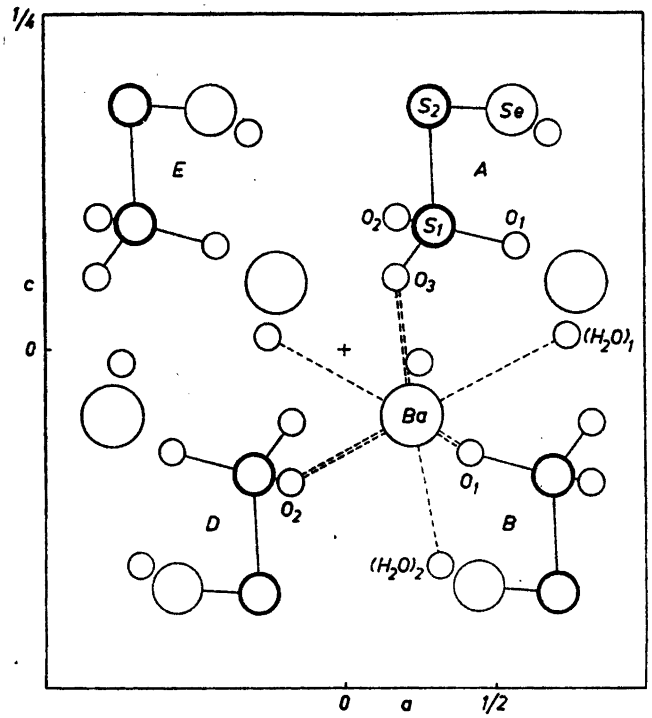

Fig. 4. Arrangement of the ions as seen along the b *axis. Four asymmetric units are shown. In this projection, two sets of sulphur atoms and sulphonate oxygen atoms overlap exactly due to the mirror plane normal to the* b *axis. The barium-sulphonate oxygen approaches, which occur once on each side of the mirror plane, are indicated by double lines (broken). Origin at the midpoint of the figure.*

experimental errors. A larger x coordinate of S_1 would have brought the S—O bond lengths closer to the average, but such a change, when tried, was found to cause a higher value of the reliability factor.

Table 3. Sulphur-oxygen bond lengths and angles.

$S_1-O_1 = 1.47$ Å	$\angle O_1S_1O_2 = 115°$	$\angle S_2S_1O_1 = 105°$
$S_1-O_2 = 1.38$	$\angle O_1S_1O_3 = 111°$	$\angle S_2S_1O_2 = 103°$
$S_1-O_3 = 1.36$	$\angle O_2S_1O_3 = 114°$	$\angle S_2S_1O_3 = 109°$

Non-bonded distances within the thiosulphate groups.

$S_2-O_1 = 2.91$ Å	$O_1-O_2 = 2.40$ Å
$S_2-O_2 = 2.78$	$O_1-O_3 = 2.32$
$S_2-O_3 = 2.87$	$O_2-O_3 = 2.30$

The non-bonded distances from the selenium atom to the oxygen atoms O_1, O_2 and O_3 are 3.39 Å, 4.50 Å and 3.70 Å, respectively. These distances are dependent on rotations about the S_1—S_2 bond. The shortest approach between the two sulphonate groups of a selenopentathionate ion is O_3—O_3' = 3.21 Å, which is the same value as found in barium pentathionate dihydrate.

THE BARIUM-OXYGEN COORDINATION

The relative arrangement of the selenopentathionate ions, the barium ions and the water molecules, as seen along the *a* and *b* axes, is shown in Figs. 3 and 4. The environment of a barium ion is, when allowance is made for minor variations in distances and angles, exactly the same as described earlier [2] for the isomorphous structure of the pentathionate. Thus, each barium ion is surrounded by nine oxygen atoms, six of which are sulphonate oxygen atoms and three are water oxygen atoms.

In Table 4, the letters *A* to *E* refer to different selenopentathionate ions, as shown in the figures. Distances listed in the left column of the table occur two times, once on each side of the mirror plane.

Table 4. Barium-oxygen distances.

$Ba-O_{3A} = 2.81$ Å	$Ba-(H_2O)_{1A} = 2.89$ Å
$Ba-O_{1B} = 2.86$	$Ba-(H_2O)_{1E} = 2.74$
$Ba-O_{2D} = 2.74$	$Ba-(H_2O)_{2A} = 2.51$

The water molecule, $(H_2O)_1$, is coordinated to two barium ions, in adjacent unit cells along the *a* axis, at distances of 2.89 Å and 2.74 Å and an angle of 124°. This water molecule probably forms hydrogen bonds to the oxygen atoms, O_1 and its image across the mirror plane in which the water molecule and the barium ions are located. The distance, $(H_2O)_1—O_1$, is 3.05 Å and the $O_1—(H_2O)_1—O_1'$ angle is 113°. It may be noted that $(H_2O)_1—O_3 = 3.39$ Å and $\angle O_3—(H_2O)_1—O_3' = 57°$, so that hydrogen bonding to O_3 and O_3' instead of to O_1 and O_1' is unlikely.

The second water molecule does apparently not form any hydrogen bonds. The distance from this water molecule to the barium ion, 2.51 Å, is very short and may be subject to maximum errors, since the *z* coordinate and particularly the *x* coordinate of $(H_2O)_2$ are probably the most uncertain ones in the structure.

As in the pentathionate structure, weak van der Waals contacts only occur across the glide plane *a*, normal to the *c* axis at $z = \frac{1}{4}$ and $-\frac{1}{4}$. The shortest approaches are Se—Se″ = 4.09 Å, S_2—Se″ = 3.74 Å and $S_2—S_2'' = 3.95$ Å, where a double-prime denotes the equivalent of an atom produced by the operation of the glide plane. The result is a layer structure which accounts for the ready cleavage of the crystals along the *c* plane. The thickness of the layers is half the *c* axis, 10.10 Å.

ROTATIONAL ISOMERISM

With the present work, the crystal structure of a salt of each of the pentathionic acids has been determined, *i.e.*, the parent acid and those derived from it by substitution of selenium and tellurium for the middle sulphur atom. In the salts, the anions are built up of unbranched and non-planar chains.

As noted earlier [11], such chains may exist in rotational-isomeric forms. The terminal sulphur atoms are rotated out of the plane of the three middle atoms, either to the same side of the plane — *cis* — or to opposite sides — *trans*.

The pentathionate and selenopentathionate ions in the isomorphous barium salts occur in the *cis* form, the ions being located in a crystallographic mirror plane. The occurrence of *cis* forms in these salts is perhaps due to the oxygen-coordinating powers of the barium ion, the anions in the *cis* form being able to act, in a sense, as bidentate chelating agents.

In the ammonium salt [3], $(NH_4)_2Te(S_2O_3)_2$, the telluropentathionate ion has a *trans* configuration, as contrasted with the pentathionate and selenopentathionate ions in the barium salts.

Unit cell and space group data are available for some other salts of these acids [1]. The following hemitrihydrates are isomorphous:

$K_2S(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$	$(NH_4)_2Se(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$	$Cs_2Te(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$
$Rb_2S(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$	$Rb_2Se(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$	$Rb_2Te(S_2O_3)_2 \cdot 1\frac{1}{2}H_2O$

The space group is D_{2h}^{14}—*Pbcn*, and there are eight molecules per unit cell. The crystal structure has not yet been worked out, and no molecular symmetry is crystallographically required, so it is not known whether the configuration is *cis* or *trans*. It is evident, however, that the three anions have the same configuration in the isomorphous salts. Therefore, either the pentathionate and selenopentathionate anions, or the telluropentathionate anion, must be able to occur in different forms in different salts.

It is perhaps to be expected, for all three anions, that *trans* forms occur in alkali salts, and *cis* forms in salts of the alkali earth metals. Preliminary experiments indicate that crystals of strontium and barium telluropentathionate may be obtained which are isomorphous with those of barium pentathionate and selenopentathionate dihydrate.

In solutions of salts of these acids, equilibrium mixtures of *cis* and *trans* forms probably occur. Inferring, however, from the structure of the anions in the crystalline salts, the nature of the cation must be expected to influence the position of the equilibria in solutions. Thus, in solutions of strontium and barium salts the relative amounts of the *cis* form should be larger than in solutions of the alkali salts.

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