

## Refinement of the Crystal Structure of Barium Selenopentathionate Dihydrate

KJARTAN MARØY

*Chemical Institute, University of Bergen, Bergen, Norway*

The crystal structure of barium selenopentathionate dihydrate,  $\text{BaSe}(\text{Se}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ , has been refined by least squares for 1177 non-zero reflections, collected by means of a single-crystal diffractometer using (Nb-filtered)  $\text{MoK}\alpha$  radiation. The space group is  $Pnma$  (No. 62) with four formula units per unit cell, and  $a = 5.043(3)$  Å,  $b = 10.434(4)$  Å,  $c = 22.372(6)$  Å.

The selenopentathionate ion possesses mirror plane symmetry in the crystals, and thus occurs in the *cis* form, the sulphonate groups being located on the same side of the plane through the three middle atoms. The dimensions of the S-S-Se-S-S chain are: S(1)-S(2) = 2.096(3) Å, S(2)-Se = 2.180(3) Å,  $\angle \text{S}(1)-\text{S}(2)-\text{Se} = 103.96(11)^\circ$ ,  $\angle \text{S}(2)-\text{Se}-\text{S}(2') = 103.03(11)^\circ$ . The SSSe/SSeS dihedral angles are  $106.0^\circ$ .

Barium selenopentathionate dihydrate,  $\text{BaSe}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ , was prepared, and the crystal structure determined, by Foss and Tjomsland.<sup>1</sup> The structure was solved by Patterson and Fourier projections along the  $a$  and  $b$  axes, using intensity data estimated visually from Weissenberg photographs. A refinement has now been undertaken, to get more accurate dimensions of the selenopentathionate ion for comparison with the dimensions of the ion in barium selenopentathionate trihydrate<sup>2</sup> and in ammonium selenopentathionate hemitrihydrate.<sup>3</sup> In the two barium salts the selenopentathionate ion has the *cis* rotational-isomeric form,<sup>1,2</sup> whereas the ion has the *trans* form in the ammonium salt.<sup>3</sup>

### EXPERIMENTAL

Barium selenopentathionate dihydrate,  $\text{BaSe}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ , was prepared from sodium selenopentathionate trihydrate by metathesis with barium perchlorate, and recrystallized from aqueous methanol.<sup>1</sup> Most of the crystals obtained were thin plates elongated in the direction of the  $a$  axis and with (001) predominant. The shape of these crystals was not favourable for intensity measurements, and cutting was difficult due to a ready cleavage along (001). Some thicker flat prisms turned out to be twins. A few of the crystals were trigonal prisms elongated along the  $a$  axis and bounded by (001), (01 $\bar{1}$ ) and (01 $\bar{1}$ ). The crystal used for collecting intensity data was of the latter type; the length of the prism

was 0.245 mm and the distance from the intersection of the (01 $\bar{1}$ ) and (0 $\bar{1}1$ ) faces to the (001) face was 0.096 mm. The crystals, which have a pale yellowish-green colour, slowly decompose, with liberation of selenium, when exposed to X-rays or light. The crystal used became red during the data collection, but no decrease in the scattering power was observed.

The data were collected by means of a Siemens automatic single-crystal diffractometer using (Nb-filtered) MoK $\alpha$  radiation and a scintillation counter. The crystal was mounted with the *a* axis parallel to the  $\phi$  axis of the diffractometer. The orientation of the crystal and the unit cell dimensions were determined by least squares from the  $\theta$ ,  $\chi$ , and  $\phi$  angles of 19 reflections. The setting angles for all reflections were then calculated on the basis of the orientation of the crystal and the unit cell dimensions.

The intensity data were collected using the five-value measuring procedure and  $\theta-2\theta$  scan technique,<sup>4</sup> with scan width of 1.0° for all reflections. The background was measured for one half of the total scan time at each side of the reflection. The maximum measuring time for one reflection was preset to about 1½ min. For strong reflections the diffractometer automatically selects higher scan speed and, if needed to avoid counting losses, inserts a proper attenuation filter into the primary beam. In order to bring the net intensities to a common scale and to check the orientation of the crystal, three reference reflections were measured at intervals of 50 reflections. The setting angles of the reference reflections were checked by horizontal and vertical half shutters.

The net intensities were brought to a common scale by means of the reference reflections. Out of 1517 reflections attainable within  $\theta=28^\circ$ , 1197 were found to have net intensity stronger than twice its standard deviation. The remaining reflections were labelled as unobserved, and given the value of twice its standard deviation as the observable limit.

Lorentz and polarization corrections were applied, and a weight factor,  $W_o = (I_t - I_b)^2 / [I_t + I_b + k^2 (I_t - I_b)^2]$ , used in the least squares weighting scheme, was calculated for each of the reflections. Here  $I_t$  is the total intensity,  $I_b$  the background intensity, and  $k$  the relative standard deviation in the scaling curve based on the reference reflections. The value of  $k$  was put equal to 0.014.

The intensities were eventually corrected for absorption ( $\mu = 74.9 \text{ cm}^{-1}$ ) by the method described by Coppens *et al.*<sup>5</sup> The number of grid points used along the *a*, *b*, and *c* axes were 12, 6, and 6, respectively.

The structure factor calculations were based on the Thomas-Umeda scattering curve for barium ion,<sup>6</sup> and the curves given in *International Tables for X-Ray Crystallography*,<sup>7</sup> Table 3.3. 1A, for selenium, sulphur, and oxygen atoms. The scattering curves for barium and selenium were corrected for anomalous dispersion, using the  $\Delta f'$  and  $\Delta f''$  values given by Cromer,<sup>8</sup> and taking the amplitude of  $f$  as the corrected value.

The calculations were carried out on an IBM 360/50H computer. The programs used for preparation of input tape data for the diffractometer, and conversion of diffractometer output tape data to the IBM computer, were written by Mr. K. Maartmann-Moe, and the programs used for data processing and Fourier summations by Mr. K. Åse, both of this Institute. The programs used for least squares refinement and absorption corrections were made available by the Chemical Department of X-Ray Crystallography, Weizmann Institute of Science, Rehovoth, Israel. The latter program was modified by Mr. K. Åse.

The space group is *Pnma* (No. 62) with four formula units per unit cell.<sup>1</sup> The unit cell dimensions, calculated by means of a least squares program using the  $\theta$  angles ( $\theta=20-25^\circ$ ) of 19 reflections measured on the diffractometer, are  $a=5.043(3) \text{ \AA}$ ,  $b=10.434(4) \text{ \AA}$ , and  $c=22.327(6) \text{ \AA}$ . The calculated density is  $2.69 \text{ g/cm}^3$ , and the density observed by flotation was  $2.72 \text{ g/cm}^3$ .

## REFINEMENT

The first structure factor calculations were based on the atomic coordinates derived from the two-dimensional Fourier maps,<sup>1</sup> and isotropic temperature factors,  $\exp[-8\pi^2 U(\sin^2\theta/\lambda^2)]$  with  $U=0.025$ , were used for all atoms. The resulting reliability index,  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ , was 0.19.

Least squares refinement was carried out with a full-matrix program minimizing the function

$$r = \sum W(|F_o| - |F_c|)^2$$

Here  $W = 4W_o F_o^2$ , where  $W_o$  is the weight factor mentioned earlier. Unobserved reflections were included with  $|F_o|$  equal to the observable limit when  $|F_c|$  exceeded this limit. With individual isotropic temperature parameters, the  $R$  index was reduced to 0.106. Absorption corrections were then carried out, and anisotropic temperature parameters were introduced for barium, selenium, and sulphur.

The temperature parameters,  $U$ , for the three sulphonate oxygen atoms and for  $H_2O(1)$  were in the range 0.038 – 0.055 Å<sup>2</sup>, whereas the one for  $H_2O(2)$  was 0.114 Å<sup>2</sup>. On refinement, the occupancy factor for  $H_2O(2)$  was reduced from 0.500 to 0.375, and using this value, the temperature parameter was reduced to 0.093 Å<sup>2</sup>. In a final electron density map the electron density in the position of  $H_2O(2)$  was about half of that in the positions of the other oxygen atoms. The  $R$  value was at this stage 0.058.

For most of the 20 reflections with  $\theta$  values below 6°, the observed structure factors were considerably higher than the calculated ones. These reflections were now excluded from the least squares refinement. The resulting  $R$  value was 0.054, and the greatest shift of a parameter was about one time its standard deviation.

*Table 1.* Atomic coordinates for barium selenopentathionate dihydrate. Origin at a centre of symmetry. Standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
Ba	0.22222(12)	1/4	-0.04861(3)
S(1)	0.30568(36)	0.01506(17)	0.09255(9)
S(2)	0.29945(60)	0.08640(22)	0.18010(10)
Se	0.56814(30)	1/4	0.17724(6)
O(1)	0.5783(10)	-0.0001(5)	0.0760(3)
O(2)	0.1720(12)	-0.1051(5)	0.1025(3)
O(3)	0.1650(10)	0.1034(5)	0.0543(3)
H <sub>2</sub> O(1)	0.7137(14)	1/4	0.0146(4)
H <sub>2</sub> O(2)	0.3390(34)	1/4	-0.1723(8)

*Table 2.* Anisotropic thermal parameters expressed in the form  $\exp[-2\pi^2(h^2a^{-2}U_{11} + \dots + 2hka^{-1}b^{-1}U_{12} + \dots)]$ . All values have been multiplied by 10<sup>4</sup>, and standard deviations are given in parentheses.

	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>
Ba	243(3)	262(3)	436(4)	0	0	-44(3)
S(1)	263(9)	250(9)	421(11)	-7(8)	-21(8)	-31(8)
S(2)	935(20)	405(12)	419(12)	-142(14)	-16(10)	105(14)
Se	662(10)	375(7)	560(8)	0	0	180(7)
O(1)	246(28)	443(35)	759(44)	83(26)	-125(32)	-12(28)
O(2)	583(39)	306(30)	778(46)	-199(29)	51(25)	-146(33)
O(3)	331(28)	485(34)	561(45)	51(25)	106(30)	0(27)
H <sub>2</sub> O(1)	196(36)	487(45)	470(45)	0	0	-29(35)
H <sub>2</sub> O(2) <sup>a</sup>	935(121)	1160(135)	1002(124)	0	0	352(99)

<sup>a</sup> Occupancy factor for H<sub>2</sub>O(2) oxygen atom, 0.375 instead of 0.500.







refinement cycle, the greatest shift of a parameter was about one tenth of its standard deviation. The final  $R$  value was 0.048, with unobserved reflections included when  $|F_c|$  exceeds the observable limit.

The highest peak in a final difference electron density map was about 1.3 e/Å<sup>3</sup>. The water hydrogen atoms were not located.

The final atomic parameters, with standard deviations, are listed in Tables 1 and 2. The observed structure factors, and those calculated from the final parameters, are listed in Table 3.

## RESULTS

The dimensions of the selenopentathionate ion, calculated from the atomic coordinates of Table 1, are listed in Table 4. A prime denotes the image of an atom across the mirror plane passing through the barium ion, selenium atom, and water oxygen atoms.

Table 4. Dimensions of the selenopentathionate ion. Standard deviations are given in parentheses.

Bond lengths and angles	
S(1) - S(2) = 2.096(3) Å	∠S(1) - S(2) - Se = 103.96(11)°
S(2) - Se = 2.180(3)	∠S(2) - Se - S(2') = 103.06(11)°
S(1) - O(1) = 1.432(5)	∠S(2) - S(1) - O(1) = 107.1(3)°
S(1) - O(2) = 1.441(6)	∠S(2) - S(1) - O(2) = 99.1(3)°
S(1) - O(3) = 1.444(6)	∠S(2) - S(1) - O(3) = 108.6(3)°
	∠O(1) - S(1) - O(2) = 113.1(3)°
	∠O(1) - S(1) - O(3) = 112.9(3)°
	∠O(2) - S(1) - O(3) = 114.7(3)°
Dihedral angles	
S(1)S(2)Se/S(2)SeS(2') = 106.0°	
SeS(2)S(1)/S(2)S(1)O(1) = 50.6°	S(2)S(1)O(1)/S(2)S(1)O(2) = 117.7°
SeS(2)S(1)/S(2)S(1)O(2) = 168.3°	S(2)S(1)O(1)/S(2)S(1)O(3) = 122.3°
SeS(2)S(1)/S(2)S(1)O(3) = 71.7°	S(2)S(1)O(2)/S(2)S(1)O(3) = 120.0°
Non-bonded distances	
S(1) - S(1') = 4.903(3) Å	S(1) - Se = 3.369(2) Å
S(1) - S(2') = 4.597(3)	S(2) - S(2') = 3.414(3)

Since the selenium atom is situated in a mirror plane, the S - S - Se - S - S chain has the *cis* form, and the two halves of the ion are exactly similar. This configuration of the selenopentathionate ion was also found in the crystals of barium selenopentathionate trihydrate.<sup>2</sup> The found dimensions of the ion in the two barium salts agree closely.

In the *trans* rotational-isomeric form of the selenopentathionate ion in ammonium selenopentathionate hemitrihydrate,<sup>3</sup> the bond lengths and angles are only slightly different from the corresponding bond lengths and angles in the present structure. The SSSe/SSeS dihedral angles in the present salt are 22° larger than the average of the corresponding dihedral angles in the ammonium salt.<sup>3</sup>

Table 5. Distances (Å), and angles (°) between directions, from barium ion to oxygen atoms. Standard deviations of the bond lengths and angles are 0.005–0.017 Å, and 0.2–0.4°, respectively.

			I	II	III	IV	V	VI	VII	VIII
I	H <sub>2</sub> O(1)	(x,y,z)	2.853							
II	H <sub>2</sub> O(1)	(x-1,y,z)	2.928	121.4						
III	H <sub>2</sub> O(2)	(x,y,z)	2.828	107.7	130.9					
IV	O(3)	(x,y,z)	2.780	71.3	60.6	146.3				
V	O(3)	(x,½-y,z)	2.780	71.3	60.6	146.3	66.7			
VI	O(1)	(1-x,y,z)	2.862	78.5	114.3	73.6	73.3	135.7		
VII	O(1)	(1-x,½+y,z)	2.862	78.5	114.3	73.6	135.7	73.3	131.4	
VIII	O(2)	(x,y,z)	2.773	146.9	65.3	74.0	89.2	125.9	70.2	130.9
IX	O(2)	(x,½+y,z)	2.773	146.9	65.3	74.0	125.9	89.2	130.9	70.2 66.1

The barium-oxygen distances and related angles are listed in Table 5. Each barium ion is surrounded by nine oxygen atoms, six of which are sulphonate oxygen atoms and three water oxygen atoms. The six sulphonate oxygen atoms coordinated to one barium ion are from five different selenopentathionate ions. O(3) and O(3'), both of the same ion and related to each other through the mirror plane passing through the selenium atom, are coordinated to the same barium ion. O(1) and O(1'), and O(2) and O(2'), also related to each other through this mirror plane, are all coordinated to different barium ions. The six oxygen atoms of one selenopentathionate ion are thus coordinated to five different barium ions.

The water molecules are both situated in the mirror plane. The H<sub>2</sub>O(1) oxygen atom is in close contact with O(1), at distance H<sub>2</sub>O(1)–O(1)=3.027(7) Å and angle O(1)–H<sub>2</sub>O(1)–O(1')=119.1(2)°, and with O(3), at distance H<sub>2</sub>O(1)–O(3)=2.882(8) Å and angle O(3)–H<sub>2</sub>O(1)–O(3')=64.1(2)°. Although the hydrogen atoms were not located in the difference electron density map, this water molecule probably forms hydrogen bonds to O(1) and its image across the mirror plane, O(1'), and not to O(3) and its image O(3'), due to the small O(3)–H<sub>2</sub>O(1)–O(3') angle. The water molecule is coordinated to two barium ions, at a Ba–H<sub>2</sub>O(1)–Ba' angle of 121.4(2)°. The Ba–H<sub>2</sub>O(1)–O(1) and Ba–H<sub>2</sub>O(1)–O(1') angles are 91.7(2)°, and the Ba'–H<sub>2</sub>O(1)–O(1) and Ba'–H<sub>2</sub>O(1)–O(1') angles are 114.6(2)°. Here, Ba' is at 1+x,y,z relative to Ba.

The H<sub>2</sub>O(2) oxygen atom is coordinated to one barium ion, at distance 2.828(17) Å. The only possibility of hydrogen bonds from this water molecule is to O(1) (1-x,½+y,z) and its image across the mirror plane. The distances are 3.407(13) Å and the angle is 99.9(3)°. These distances are longer than found for hydrogen bonds of this type.<sup>9</sup>

The closest interionic Se–Se, Se–S, and S–S approaches are Se–Se'=4.118(2) Å, Se–S(2')=3.803(3) Å, and S(2)–S(2')=4.017(4) Å, where the primes denote atoms at ½+x,y,½-z relative to those of Table 1.

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