

The Crystal Structure of Potassium Barium Hexathionate

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The salt, $K_2Ba(S_6O_6)_2$, crystallizes in the space group $C_{2h}^4 - P2/c$ with two formula units per unit cell, and $a = 11.58 \text{ \AA}$, $b = 10.81 \text{ \AA}$, $c = 9.14 \text{ \AA}$, $\beta = 112^\circ$. The structure has been determined by X-ray methods, and refined by difference syntheses for the $hk0$ and $h0l$ zones.

The *cis-cis* rotational isomer of the hexathionate ion occurs in this salt. The derived S—S bond lengths and S—S—S bond angles are, 2.10, 2.05, 2.04, 2.10 \AA , each $\pm 0.02 \text{ \AA}$, and 101° , 113° , 109° , 100° , each $\pm 1^\circ$, and the dihedral angles, 108° , 91° , 105° , each $\pm 2^\circ$, from one end of the sulphur chain to the other. The ion conforms approximately to C_2 symmetry.

The barium ions lie on crystallographic twofold axes, and are each surrounded by eight sulphonate oxygen atoms in a distorted square antiprism arrangement, at Ba—O distances from 2.73 to 2.86 \AA , and by two additional oxygen atoms at 3.02 \AA . The potassium ions lie on twofold axes and in symmetry centres, and are each surrounded by six nearest oxygen atoms. Columns of cation-oxygen polyhedra run through the crystal in the direction of the c axis, forming a square prism which encloses the sulphur atoms.

The dihedral angle of about 90° between the planes of the bonds of successive sulphur atoms, leads to three possible rotational-isomeric forms of a tetrasulphide, X—S—S—S—S—X, as was first pointed out by Woodrow, Carmack and Miller¹ in a discussion of the dipole moment of di-hexadecyl tetrasulphide. The same holds true for the hexathionate ion,^{2,3} in which X is a sulphonate group. In the six-membered chain of four divalent sulphur atoms and their terminal bond partners, the fifth atom may be located *cis* or *trans* relative to the first, and the sixth similarly relative to the second. That is, they may be located on the same or on opposite sides of the plane through the three intermediate atoms. The three forms which thus arise are, one *cis-cis* in which the fifth and sixth atom are in *cis* positions relative to the first and second, respectively; one *cis-trans*, and one *trans-trans*. A *cis-cis* form passes into a *trans-trans*, and *vice versa*, through a rotation of approximately 180° around the middle sulphur-sulphur bond. The *cis-cis* form corresponds to the S_8 and S_6 rings, and the *trans-trans* form to the helixes of fibrous sulphur. In solutions, equilibrium mixtures of rotational isomers probably occur, whereas in crystals, one of the forms will normally be present.^{3,4}

A preparative and X-ray survey of salts of hexathionic acid⁵ led to unit cell and space group data for potassium barium hexathionate and *trans*-dichlorobis(ethylenediamine)cobalt(III) hexathionate monohydrate, and later to structure determinations of these salts.^{2,3,6} The structure of the former is described here. The hexathionate ion occurs in the *cis-cis* form in this salt.

EXPERIMENTAL

The salt, $\text{K}_2\text{Ba}(\text{S}_6\text{O}_6)_2$, forms well developed prisms extended along the *c* axis, bounded by {100} (dominant) and {110} and terminated by $\{\bar{1}11\}$. The unit cell has the dimensions,⁵ $a = 11.58 \text{ \AA}$, $b = 10.81 \text{ \AA}$, $c = 9.14 \text{ \AA}$, $\beta = 112^\circ$, and contains two formula units. The space group, from systematic absences and structure analysis, is $C_{2h}^4 - P2/c$.

The intensities of the *h*0*l* and *hk*0 reflections were estimated visually from zero-level Weissenberg photographs around the *b* and *c* axes, taken with $\text{CuK}\alpha$ radiation using a double-film technique. 115 out of 122 attainable *h*0*l* reflections and 141 out of 158 attainable *hk*0 reflections were observed. The intensities were converted to relative structure amplitudes in the usual way, and later brought to an approximately absolute scale by comparison with the calculated values.

The calculated structure factors were based on the scattering curve of Viervoll and Ögrim⁷ for sulphur and those of Berghuis *et al.*⁸ for potassium ion and oxygen. For the barium ion, a curve was constructed based on the Thomas-Fermi values for xenon at low scattering angles and for electroneutral barium at intermediate and larger scattering angles. Summations were made by means of Beever-Lipson strips, at 6° intervals along all axes.

THE STRUCTURE ANALYSIS

The space group, $C_{2h}^4 - P2/c$, indicated from the systematic absences and from the monoclinic prismatic morphology of the crystals, has beside fourfold general positions, six sets of special, twofold positions, two on twofold axes and four on symmetry centres. The latter are in the glide plane *c* at $y = 0$ and $\frac{1}{2}$, and atoms in these positions do not contribute to *hkl* reflections with *l* odd. With two barium ions per unit cell, these must lie in special positions. It was noted on oscillation photographs around the *c* axis that reflections on odd layer lines were, particularly for large scattering angles, weak relative to those on even layer lines, and it was therefore proceeded on the assumption that the barium ions lie in symmetry centres of the space group $C_{2h}^4 - P2/c$. This led to a direct solution of the structure.

The signs of the larger terms (74 *h*0*l* and 70 *hk*0 reflections) were put positive and Fourier syntheses made. The resulting maps gave the positions of the sulphur atoms, and also showed that the potassium ions lie in two sets of twofold positions, and that the barium ions lie, not in symmetry centres but on twofold axes with *y* equal to or very close to zero. Structure factor calculations including the barium, potassium and sulphur contributions and next also the oxygen contributions were carried out.

The projections were refined through repeated difference syntheses. Before the refinement, a new set of *hk*0 photographs were taken using a crystal with smaller and more uniform cross-section (126 *hk*0 reflections now observed) and the intensities were corrected for absorption: *h*0*l* reflections, spherical crystal⁹ with $\mu r = 3.0$; *hk*0 reflections, cylindrical crystal¹⁰ with $\mu r = 1.0$ ($\mu = 305 \text{ cm}^{-1}$ for $\text{CuK}\alpha$ radiation).

The difference maps indicated anisotropic vibrations of some of the atoms, particularly in the $hk0$ zone. In the temperature factor $\exp [-B(\sin^2\theta/\lambda^2)]$ applied to the calculated structure factors, the final values of B , in \AA^2 units, were: In the $h0l$ zone, $B = 4.0$ for potassium and oxygen, 4.5 for S_3 and S_4 and 3.5 for the other sulphur atoms, and $2.0 + 1.0 \cos^2\varphi$ for barium, where φ is the angle between the normal of the reflecting plane and the direction of maximum vibration of the atom; this direction made an angle of 45° with the c axis in the obtuse angle. In the $hk0$ zone, $B = 2.3$ for barium, 4.0 for K_2 and oxygen, 2.5 for S_1 and S_6 , and $2.5 + 10.0 \cos^2\varphi$ for K_1 with maximum vibration parallel to the b axis. For S_2 and S_5 in the $hk0$ zone, $B = 2.5 + 3.0 \cos^2\varphi$, and for S_3 and S_4 , $B = 3.0 + 3.0 \cos^2\varphi$, where for atoms in the positive quadrant the directions of maximum vibration, taken as positive when making an obtuse angle with the a axis, made the following angles with the b axis: S_2 , 30° ; S_3 , 45° ; S_4 and S_5 , 25° . In the $hk0$ zone, of symmetry ρmm , anisotropic vibration directions not parallel to an axis are mirror plane-related for two and two atoms of a fourfold set, and structure-factor calculations were made on the basis of two twofold sets instead of one fourfold set of each of the sulphur atoms S_2 to S_6 .

The two sets of x coordinates obtained, and used in the last structure-factor calculation for each zone, compare as follows: S_1 , $x = 0.140$ and 0.136 ; S_2 , 0.335 and 0.331 ; S_3 , 0.347 and 0.350 ; S_4 , 0.402 and 0.400 ; S_5 , 0.246 and 0.246 ; S_6 , 0.255 and 0.253 ; O_1 , 0.133 and 0.132 ; O_2 , 0.086 and 0.087 ; O_3 , 0.105 and 0.105 ; O_4 , 0.357 and 0.361 ; O_5 , 0.257 and 0.253 ; O_6 , 0.140 and 0.142 , from the $h0l$ and $hk0$ zone, respectively. The final values were chosen as weighted means.

The $hk0$ data do not give the sign of the barium y coordinate relative to the chosen hexathionate ion. However, reversal of the sign of the barium y coordinate would give too short barium-oxygen distances (2.62 and 2.51 \AA , instead of 2.75 and 2.79 \AA). Likewise, $y = 0.550$ instead of 0.450 for the potassium ion K_2 would give a potassium-oxygen distance of 2.17 \AA , instead of 2.67 \AA .

The $hk0$ Fourier map is reproduced in Fig. 1, and the final atomic coordinates are listed in Table 1. Observed and calculated structure factors are listed in Table 2. Some low order $h0l$ reflections have calculated values markedly higher than the observed ones, and were omitted from the difference syntheses and the calculation of scale factors. They were included in the final Fourier synthesis with their calculated instead of observed values. In the $hk0$ zone,

Table 1. Atomic coordinates for potassium barium hexathionate, in fractions of monoclinic cell edges. Origin at a centre of symmetry.

	x	y	z
Ba	0	0.0176	$\frac{1}{4}$
K_1	$\frac{1}{2}$	0	$\frac{1}{4}$
K_2	0	0.450	$\frac{1}{4}$
S_1	0.138	0.274	0.044
S_2	0.332	0.284	0.162
S_3	0.348	0.418	0.327
S_4	0.401	0.351	0.551
S_5	0.246	0.303	0.593
S_6	0.254	0.110	0.577
O_1	0.133	0.183	-0.074
O_2	0.086	0.227	0.158
O_3	0.105	0.397	-0.008
O_4	0.358	0.066	0.721
O_5	0.257	0.071	0.426
O_6	0.140	0.080	0.593

Table 2. Observed and calculated $h0l$ and $hk0$ structure factors for potassium barium hexathionate. The signs of the $h0l$ reflections correspond to origin on the twofold axis at $0,y,\frac{1}{4}$.

h	F_o	F_c	h	F_o	F_c	h	F_o	F_c
	$h0l$ zone		5	40	+ 40	2	40	+ 48
	$h00$		6	62	+ 60	3	< 11	- 3
1	56*	+ 98	7	70	+ 70	4	37	+ 33
2	11	- 2	8	17	+ 14	5	24	+ 32
3	106*	+ 124	9	< 10	- 2	6	26	+ 25
4	24	+ 28	10	35	+ 37		$h0\bar{8}$	
5	26	+ 30		$h0\bar{4}$		1	39	+ 36
6	64	+ 71	1	142	+ 133	2	78	+ 77
7	56	+ 57	2	168	+ 163	3	65	+ 64
8	160	+ 147	3	46	+ 43	4	68	+ 68
9	65	+ 65	4	21	+ 20	5	14	+ 7
10	< 13	- 1	5	100	+ 98	6	44	+ 44
11	17	+ 15	6	100	+ 109	7	51	+ 49
12	71	+ 62	7	22	+ 26	8	30	+ 38
13	15	+ 14	8	97	+ 109	9	14	+ 14
	$h02$		9	75	+ 74	10	74	+ 73
0	29	- 16	10	97	+ 90	11	47	+ 50
1	205	+ 203	11	25	+ 23	12	15	+ 14
2	102*	+ 118	12	< 12	+ 9	13	22	+ 24
3	172*	+ 198	13	30	+ 35		$h,0,10$	
4	55	+ 62	14	39	+ 35	0	26	+ 27
5	101	+ 108		$h06$		1	18	+ 15
6	106	+ 97	0	66	+ 71	2	19	+ 22
7	23	- 15	1	89	+ 90		$h,0,\bar{10}$	
8	< 14	+ 8	2	14	+ 5	1	32	+ 32
9	79	+ 76	3	43	+ 41	2	32	+ 32
10	38	+ 37	4	48	+ 57	3	27	+ 24
11	37	+ 28	5	37	+ 41	4	14	+ 5
12	10	+ 11	6	11	- 9	5	55	+ 54
	$h0\bar{2}$		7	41	+ 43	6	36	+ 38
1	57	- 42	8	49	+ 49	7	35	+ 33
2	111	+ 115		$h0\bar{6}$		8	18	+ 17
3	203*	+ 268	1	70	+ 77	9	31	+ 30
4	60*	+ 79	2	19	+ 20	10	29	+ 30
5	85	+ 94	3	< 13	+ 4	11	11	+ 14
6	144	+ 153	4	143	+ 141		$hk0$ zone	
7	61	+ 60	5	123	+ 127		$h00$	
8	16	- 6	6	15	- 4	1	75*	+ 100
9	71	+ 71	7	126	+ 130	2	12	- 1
10	31	+ 32	8	80	+ 74	3	106*	+ 121
11	104	+ 94	9	23	+ 22	4	25	+ 27
12	43	+ 44	10	14	+ 15	5	25	+ 33
13	11	+ 8	11	35	+ 31	6	61	+ 65
14	31	+ 30	12	48	+ 45	7	53	+ 60
	$h04$		13	49	+ 51	8	158	+ 162
0	67	+ 67	14	17	+ 18	9	67	+ 62
1	16	+ 15		$h08$		10	< 13	+ 3
2	128	+ 140	0	< 13	+ 3	11	15	+ 6
3	39	+ 48	1	39	+ 44			
4	67	+ 76						

<i>h</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>F</i> _o	<i>F</i> _c
12	68	+ 65	6	95*	+ 104	5	20	+ 18
13	15	+ 17	7	45	+ 48	6	< 13	+ 8
	<i>h</i> 10		8	25	+ 26	7	16	+ 21
0	89*	+ 98	9	45	+ 48	8	19	+ 23
1	78*	+ 74	10	36	+ 32	9	< 11	+ 1
2	45	+ 47	11	12	+ 10	10	19	+ 17
3	14	- 12	12	25	+ 22	11	9	+ 14
4	112*	+ 137		<i>h</i> 50			<i>h</i> 90	
5	17*	+ 23	0	12	+ 2	0	28	+ 16
6	39*	+ 48	1	61	+ 62	1	22	+ 19
7	46	+ 49	2	166	+ 161	2	33	+ 31
8	75	+ 70	3	49	+ 51	3	39	+ 34
9	16	+ 10	4	< 13	+ 3	4	64	+ 68
10	21	+ 21	5	39	+ 40	5	37	+ 39
11	28	+ 25	6	72	+ 73	6	< 13	- 7
12	35	+ 31	7	< 13	+ 7	7	15	+ 12
13	14	+ 14	8	15	+ 13	8	12	+ 14
	<i>h</i> 20		9	20	+ 21	9	12	+ 7
0	42	+ 45	10	66	+ 64	10	15	+ 21
1	47	+ 46	11	40	+ 39		<i>h</i> ,10,0	
2	132*	+ 155	12	< 7	+ 10	0	41	+ 39
3	98*	+ 108		<i>h</i> 60		1	18	+ 15
4	120*	+ 149	0	27	- 31	2	13	- 17
5	72*	+ 96	1	18	+ 22	3	< 13	+ 11
6	80*	+ 95	2	84	+ 86	4	30	+ 28
7	29	+ 28	3	22	+ 20	5	< 12	- 6
8	60	+ 58	4	76	+ 79	6	< 11	+ 2
9	23	+ 23	5	66	+ 63	7	< 10	+ 1
10	56	+ 56	6	21	+ 17	8	17	+ 20
11	55	+ 54	7	36	+ 37	9	12	+ 13
12	27	+ 28	8	< 13	+ 8		<i>h</i> ,11,0	
13	17	+ 12	9	< 13	+ 8	0	30	+ 35
	<i>h</i> 30		10	54	+ 53	1	28	+ 22
0	190	+ 183	11	< 9	+ 4	2	< 12	+ 11
1	14	- 11	12	16	+ 20	3	< 12	+ 3
2	65	+ 65		<i>h</i> 70		4	< 11	0
3	63	+ 70	0	81	+ 78	5	< 11	+ 8
4	44*	+ 54	1	45	+ 45	6	22	+ 21
5	59	+ 62	2	22	+ 21	7	29	+ 28
6	56	+ 51	3	53	+ 53		<i>h</i> ,12,0	
7	30	+ 31	4	48	+ 48	0	< 11	+ 2
8	61	+ 60	5	16	+ 5	1	< 11	- 1
9	28	+ 27	6	70	+ 72	2	< 10	+ 12
10	41	+ 39	7	24	+ 27	3	< 10	+ 3
11	< 12	- 1	8	33	+ 34	4	< 9	+ 9
12	32	+ 32	9	44	+ 46	5	< 8	+ 9
13	17	+ 19	10	< 10	- 1	6	< 7	+ 9
	<i>h</i> 40		11	< 8	+ 8		<i>h</i> ,13,0	
0	67	+ 62		<i>h</i> 80		0	< 8	- 13
1	100	+ 102	0	< 13	+ 11	1	9	+ 8
2	106	+ 112	1	28	+ 27	2	10	+ 11
3	37	+ 41	2	44	+ 41	3	< 7	+ 5
4	57*	+ 66	3	< 13	+ 8			
5	12	+ 11	4	23	+ 23			

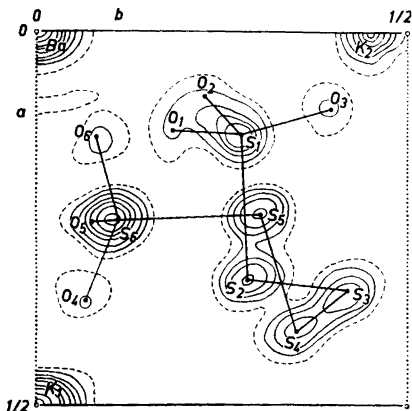


Fig. 1. Electron density projection of potassium barium hexathionate along the c axis. The 7-electron line is dashed. Contour intervals: $20 \text{ e.}\text{\AA}^{-2}$ for barium, $4 \text{ e.}\text{\AA}^{-2}$ for the other atoms.

reflections within a limited region of reciprocal space may have been subject to excessive absorption, and were treated in the same way. These $h0l$ and $hk0$ reflections are marked with an asterisk in Table 2.

The reliability index, R , with non-observed reflections included when $|F_c|$ exceeds the observable limit, is 0.10 for both zones, and reduces to 0.08 when the strong reflections, referred to above, are omitted.

The standard deviations of the atomic coordinates were estimated from the root-mean-square gradients in the difference maps and the curvatures of peaks in the electron density maps. Where overlapping occurred, the s.d. were increased relative to those which would otherwise have applied. The s.d. thus arrived at, were 0.01 \AA for the barium and K_2 y coordinates, $0.01 - 0.02 \text{ \AA}$ for the sulphur coordinates, and $0.02 - 0.04 \text{ \AA}$ for the oxygen coordinates. The corresponding s.d. of bond lengths and angles are $0.015 - 0.02 \text{ \AA}$ for S—S bond lengths, $0.03 - 0.04 \text{ \AA}$ for S—O bond lengths, 0.8° for S—S—S bond angles, and about 1.5° and 2° , respectively, for S—S—O and O—S—O bond angles.

THE HEXATHIONATE ION

The dimensions of the sulphur chain of the hexathionate ion, as calculated from the atomic coordinates of Table 1, are listed in Table 3. The chain con-

Table 3. Dimensions of the sulphur chain of the hexathionate ion.

Bond lengths and angles.		
$S_1-S_2 = 2.10 \text{ \AA}$	$S_3-S_4 = 2.04 \text{ \AA}$	$S_5-S_6 = 2.10 \text{ \AA}$
$S_2-S_3 = 2.05$		$S_4-S_5 = 2.04$
$\angle S_1-S_2-S_3 = 101^\circ$		$\angle S_4-S_5-S_6 = 100^\circ$
$\angle S_4-S_3-S_2 = 113$		$\angle S_3-S_4-S_5 = 109$
Dihedral angles.		
$S_1S_2S_3/S_2S_3S_4 = 108^\circ$	$S_3S_4S_5/S_4S_5S_6 = 89^\circ$	$S_3S_4S_5/S_4S_5S_6 = 105^\circ$

forms approximately to C_2 symmetry, and corresponding distances and angles in the two halves are arranged on the same row in the first and third column of the table.

The three middle sulphur-sulphur bonds, between divalent sulphur atoms, are of equal length, 2.04 Å, within the experimental error. This value is the same as found for the two middle bonds in the pentathionate ion.¹¹⁻¹³ The terminal bonds, between a divalent and a sulphonate sulphur atom, are 2.10 Å and thus longer, in accordance with the average, 2.12 Å, for this type of bond in the tetrathionate,¹⁴ pentathionate,¹¹⁻¹³ selenopentathionate,¹⁵ and telluropentathionate^{16,17} ions.

The S—O bonds of the sulphonate groups are found to be 1.42–1.49 Å, with an average of 1.45 Å. Two of the S—S—O angles (S₂—S₁—O₁ and S₅—S₆—O₆) are found to be 99°, the other four 104°–112°, with an average for the four of 108°. This is as in the tetrathionate ion,¹⁴ where also one of the S—S—O angles of a sulphonate group was found smaller than the other two: 98.6°, 107.6°, and 108.1°, each ± 1°. The O—S—O angles range from 108° to 117°, with an average of 114°.

The *cis-cis* and *trans-trans* forms of a six-membered sulphur chain possess a twofold axis of symmetry when bond lengths and angles are like in the two halves. In the crystals of potassium barium hexathionate, no such molecular symmetry is crystallographically required, and it appears from Table 3 that bond angles and dihedral angles in the two halves are slightly different. The difference is outside the experimental error; for example, the non-bonded distance S₁—S₄ is 4.57 Å while in the other half S₃—S₆ is 4.40 Å. An orthogonal coordinate system, with origin midway between S₃ and S₄, with the *Z* axis passing through the coordinate midpoint of the six sulphur atoms, and the *X* plane passing through S₃ and S₄, is defined by the planes

$$9.4291x - 6.0659y - 4.0488z + 0.5786 = 0 \quad (\text{I})$$

$$1.2289x + 4.2794y - 8.0934z + 1.4474 = 0 \quad (\text{II})$$

$$-6.6093x - 7.8580y - 1.2821z + 6.0594 = 0 \quad (\text{III})$$

where *x*, *y*, and *z* are the fractional monoclinic coordinates. The *X* and *Y* coordinates of the sulphur atoms in this coordinate system, listed in Table 4, show that the sulphur chain as projected along the *Z* axis on to plane III, has

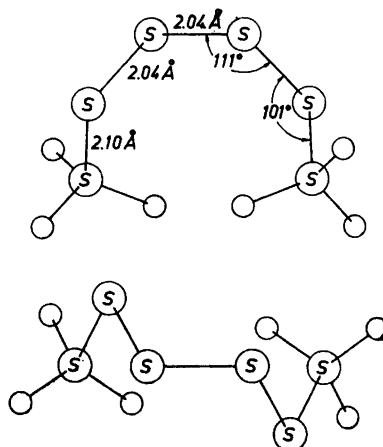


Fig. 2. Two views of the *cis-cis* form of the hexathionate ion, drawn on the basis of averaged dimensions of the two slightly different halves. Below, as seen down the idealized twofold axis. Above, as seen normal to this axis and to a line through S₂ and S₄ (or through S₃ and S₅).

twofold symmetry within 0.01 Å. The asymmetry of the sulphur chain arises from differences in Z coordinates of the two halves. In the same projection, along the Z axis, the oxygen atoms of the two sulphonate groups are not quite symmetrically located, their positions correspond to a difference in rotation around the S_1-S_2 and S_5-S_6 bonds of about 7° . The idealized C_2 symmetry of the hexathionate ion, with dimensions in the two halves averaged, is shown in Fig. 2.

The reason for the *cis-cis* form of the hexathionate ion in the potassium barium salt probably is that the ion in this form can act as a chelating agent towards a barium ion, like the pentathionate ion in its *cis* form in the barium salts.¹¹⁻¹³

THE PACKING IN THE CRYSTAL

The barium ion, on the twofold axis $0, y, \frac{1}{4}$, lies 0.19 Å from the glide plane c at $y = 0$, and is repeated every $c/2 = 4.57$ Å in an only slightly zigzagging line. The potassium ion K_2 , on the same twofold axis, lies 0.54 Å from the glide plane c at $y = \frac{1}{2}$, and is similarly repeated by this plane. The potassium ion K_1 , at $\frac{1}{2}, 0, \frac{1}{2}$, lies in symmetry centre and glide plane. Fig. 3 shows the arrangement in the unit cell as seen along the c axis.

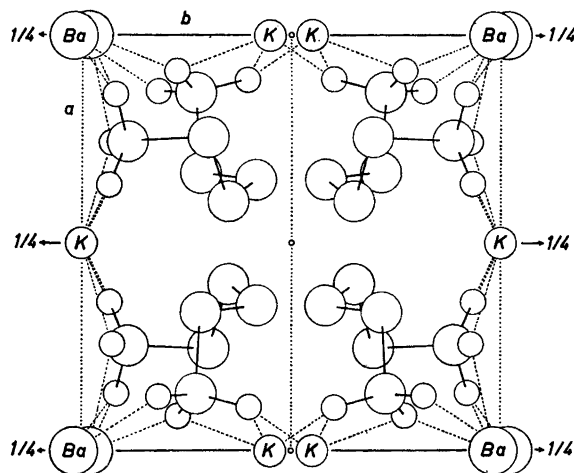


Fig. 3. The arrangement of cations and anions in the unit cell of potassium barium hexathionate, as seen along the c axis.

The six oxygen atoms of the hexathionate ion coordinate to three barium ions and four potassium ions, namely to $Ba(0, y, \frac{1}{4})$, $Ba''(0, -y, \frac{3}{4})$, $K_1(\frac{1}{2}, 0, \frac{1}{2})$, $K_1'(\frac{1}{2}, 0, 1)$, $K_2(0, y, \frac{1}{4})$, and $K_2'(0, 1 - y, -\frac{1}{4})$. The coordinates of these cations in the orthogonal coordinate system defined by the quasi-twofold axis of the hexathionate ion are included in Table 4. They show that the quasi-twofold axis, the Z axis of Table 4, passes relatively close to the barium ion at

Table 4. Atomic coordinates in orthogonal coordinate system defined by planes I, II, and III. X, Y, and Z, respectively, are the distances from these planes.

	X	Y	Z
Ba	-0.540 Å	-0.501 Å	5.601 Å
K ₁	3.269	-1.985	2.114
K ₂	-3.163	1.350	2.203
S ₁	0.040	2.433	2.938
S ₂	1.330	1.760	1.426
S ₃	0	1.017	0.056
S ₄	0	-1.017	-0.056
S ₅	-1.341	-1.753	1.292
S ₆	-0.030	-2.440	2.776
O ₁	1.022	2.993	3.837
O ₂	-0.627	1.246	3.505
O ₃	-0.807	3.340	2.256
O ₄	0.635	-3.666	2.250
O ₅	0.846	-1.381	3.257
O ₆	-0.988	-2.838	3.745
Ba'	1.698	3.395	6.518
Ba''	-2.351	-4.698	5.236
K ₁ '	1.244	-6.032	1.473
K ₂ '	-1.745	5.824	2.058

0, $y, \frac{1}{4}$, and that Ba', K₁, and K₁' are related to Ba'', K₂, and K₂', respectively, through the quasi-twofold axis. Likewise, O₁, O₂, and O₃ of one sulphonate group are related to O₆, O₅, and O₄, respectively, of the other group. The relevant cation-oxygen distances are listed in Table 5, in two columns, one for

Table 5. Barium-oxygen and potassium-oxygen distances.

Ba-O ₂ = 2.73 Å	Ba-O ₅ = 2.86 Å
Ba-O ₁ = 4.22	Ba-O ₆ = 3.02
Ba'-O ₁ = 2.79	Ba''-O ₆ = 2.75
K ₂ -O ₂ = 2.85	K ₁ -O ₅ = 2.75
K ₂ '-O ₃ = 2.67	K ₁ '-O ₄ = 2.57
K ₂ -O ₃ = 3.08	K ₁ -O ₄ = 3.13

each sulphonate group, and with distances related by the quasi-twofold axis on the same row.

In barium tetrathionate dihydrate,¹⁸ orthorhombic¹¹ and triclinic¹² barium pentathionate dihydrate, barium pentathionate hydrate acetate,¹³ barium selenopentathionate dihydrate¹⁵ and barium telluropentathionate dihydrate,¹⁶ each barium ion is surrounded by nine oxygen atoms at an average Ba-O distance of 2.80 Å. In barium thiosulphate monohydrate¹⁹ the average of eight Ba-O distances not exceeding 3.00 Å is 2.86 Å. In potassium pyrosulphate,²⁰ methylenedisulphonate,²¹ and iminodisulphonate,²² each potassium ion is surrounded by nine oxygen atoms at distances between 2.70 and 3.23 Å; in the first and third salt the average K-O distance is 2.89 Å while in the

second it is 2.96 Å. Two thirds of the K—O distances in the three salts do not exceed 3.00 Å, and are on the average 2.80 Å. It appears that of the distances listed in Table 5, Ba—O₁ is definitely outside the normal range, Ba—O₆, K₂—O₃, and K₁—O₄ are large while K₁'—O₄ is rather short. With a standard deviation of 0.03—0.04 Å, the low value for K₁'—O₄ may be the result of a maximum error. The data show that the six oxygen atoms of a hexathionate ion coordinate to barium and potassium as follows.

The oxygen atoms O₂ and O₅, one from each sulphonate group, coordinate to one barium ion, at 2.73 and 2.86 Å, respectively, and at an O₂—Ba—O₅ angle of 66°. Each of these oxygens also coordinates to a potassium ion, O₂ to K₂ at 2.85 Å and O₅ to K₁ at 2.75 Å. The oxygen atoms O₁ and O₆ coordinate to Ba' and Ba'', respectively, at 2.79 and 2.75 Å. They lie 4.22 and 3.02 Å, respectively, from the barium ion to which O₂ and O₅ coordinate. The two remaining oxygen atoms, O₃ and O₄, one from each sulphonate group, do not coordinate to barium but to potassium: O₃ to K₂' at 2.67 Å and to K₂ at 3.08 Å, and O₄ to K₁' at 2.57 Å and to K₁ at 3.13 Å. These atoms, O₃ and O₄, are on the far sides of the hexathionate ion, 7.15 Å apart; the closest potassium ions, K₂' and K₁', lie outside the oxygen atoms, 12.24 Å apart, while K₂ and K₁ are 7.25 Å apart.

The hexathionate ion thus coordinates to three barium ions, one close to the quasi-twofold axis and one on either side of the ion, and to four potassium ions, two on either side.

The barium ion has eight closest oxygen neighbours, at Ba—O distances from 2.75 to 2.86 Å, in a distorted square antiprism arrangement. The eight oxygen atoms are, O₂, O₅, O₁', and O₆', where O₁' and O₆' are related to O₁ and O₆ through the glide plane at $y=0$, and located at $x, -y, \frac{1}{2} + z$ and $x, -y, z - \frac{1}{2}$, respectively, relative to these. The distances Ba—O₁' and Ba—O₆' are equivalent to Ba'—O₁ and Ba''—O₆, respectively, of Table 5. The four equivalent atoms, O₂', O₅', O₁'', and O₆'', on the other side of the twofold axis through the barium ion, complete the antiprism. These eight oxygen atoms belong to as many different sulphonate groups, of six different hexathionate ions. The square faces of the distorted antiprism are made up of O₅, O₁', O₆'', and O₂' and are located one on either side of the twofold axis through the barium ion. The O—O edges of the square faces range from 3.10 to 4.11 Å. Of the eight O—O edges between the squares, O₁'—O₁' = 3.45 Å and O₂—O₂' = 3.05 Å, and lie across the twofold axis, while the other six, three on either side of the axis, are 3.03, 3.27, and 3.27 Å. The shortest of these, 3.03 Å, occurs between atoms, O₂ and O₅, of one hexathionate ion. The O—Ba—O angles are from 66° to 95° for O—O edges of the square faces and from 66° to 76° for O—O edges between the square faces.

The O₆ atom, 3.02 Å from the barium ion, and the equivalent one on the other side of the twofold axis, lie approximately outside the middle of the square faces of the antiprism. The distances from O₆ to the oxygen atoms at the corners of the square faces, are 2.39 Å (to O₅ of the same sulphonate group), 3.21, 3.50, and 3.18 Å. Within 3.02 Å, the barium ion thus is surrounded by ten oxygen atoms.

The barium-oxygen polyhedra are repeated every $c/2$ by the glide plane at $y=0$, and by the symmetry centres in the glide plane midway between the twofold axes on which the barium ions lie. Adjacent polyhedra have one common edge, O₆—O₆'', and are otherwise joined through four O—S—O bridges connecting the corners of square faces, two (O₁—S₁—O₂ and O₆—S₆—O₅) on either side of a symmetry centre. The four O—S—O bridges come from four different hexathionate ions.

The potassium ion K₁, in symmetry centre at $\frac{1}{2}, 0, \frac{1}{2}$, lies 2.75 Å from O₅, 3.13 Å from O₄, and 2.57 Å from O₄', where O₄' is the equivalent, at $x, -y, z - \frac{1}{2}$, of O₄ across the glide plane at $y=0$. These three oxygen atoms, together with the equivalent ones across the symmetry centre, form a distorted octahedron around the potassium ion, with O—O

edges from 2.50 Å (between O_4 and O_5 of one sulphonate group) to 5.33 Å. The potassium ion K_2 , on twofold axis $0, y, \frac{1}{2}$, lies 2.85 Å from O_2 , 3.08 Å from O_3 , and 2.67 Å from O_3' , where O_3' is the equivalent, at $x, 1-y, \frac{1}{2}+z$, of O_3 across the glide plane at $y = \frac{1}{2}$. Again a distorted octahedron results, of these three oxygen atoms and the equivalent ones across the twofold axis. The O—O edges of the octahedron range from 2.44 Å (between O_2 and O_3 of one sulphonate group) to 5.08 Å.

The K_1 ions are repeated in a straight line every $c/2$. Adjacent K_1 -oxygen octahedra along this line are joined through a common edge, of length 3.13 Å, between O_4 and its equivalent across the twofold axis $\frac{1}{2}, y, \frac{1}{2}$, and through two $O_4-S_6-O_6$ bridges, one on either side of the twofold axis. Adjacent K_2 -oxygen octahedra, repeated every $c/2$ by the glide plane at $y = \frac{1}{2}$, are joined through a common edge, of length 3.34 Å, between O_3 and its equivalent across the symmetry centre at $0, \frac{1}{2}, 0$, and through two $O_2-S_1-O_3$ bridges, one on either side of the symmetry centre.

Three different columns of cation-oxygen polyhedra thus run through the crystal parallel to the c axis. At the corners of the unit cell, as seen along the c axis, columns of barium-oxygen polyhedra, $a \sin \beta = 10.74$ Å and $b = 10.81$ Å apart; at $x = \frac{1}{2}, y = 0$ and 1, columns of K_1 -oxygen octahedra; and at $x = 0$ and 1, $y = \frac{1}{2}$, columns of K_2 -oxygen octahedra. The barium-oxygen and K_1 -oxygen columns are interconnected through shared O_5 atoms and through $O_4-S_6-O_6$ bridges, and the barium-oxygen and K_2 -oxygen columns through shared O_2 atoms and through $O_1-S_1-O_3$ bridges. The space inside this square-prism framework of cations and coordinated sulphonate groups is occupied by the divalent sulphur atoms.

These, S_2 through S_5 , lie 2.95, 1.86, 1.93, and 3.46 Å, respectively, from the centre line of the square prism; no other atom lies closer than 4.39 Å (O_3) to this line. The quasi-twofold axis of the hexathionate ion passes only 0.28 Å from the symmetry centre at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, and the midpoint between S_3 and S_4 (origin of the orthogonal coordinate system of Table 4) lies only 1.84 Å from this centre. The closest non-bonded approaches, around the centre line, are 3.50 Å from S_4 to its equivalent across the twofold axis $\frac{1}{2}, y, \frac{3}{4}$, 3.61 Å from S_2 to its equivalent across the twofold axis $\frac{1}{2}, y, \frac{1}{4}$, 3.67 Å from S_3 to the equivalent of S_4 across the symmetry centre at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, and 3.76 Å from S_3 to the equivalent of S_4 across the glide plane at $y = \frac{1}{2}$. Other such distances are larger than 4 Å.

The work has been aided by a grant from *Norges Almenvitenskapelige Forskningsråd*.

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Received August 2, 1965.