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The Crystal Structure of Barium Pentathionate Dihydrate

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This is the first in a series of papers on the crystal structure of pentathionic compounds. The structure of barium tetrathionate dihydrate has been published recently [1]. The work serves to confirm the old theories of Blomstrand [2] and Mendelejeff [3], that the polythionic acids and their salts are built up of unbranched sulphur chains.

Barium salts of pentathionic acid have been prepared by Lenoir [4], Fordos and Gélis [5], Lewes [6], and Deines and Christoph [7]. The crystal chemistry of barium and strontium pentathionate, selenopentathionate and telluropentathionate is rather complex, especially with regard to solvates with organic solvents. It is intended to make a fuller study of these phenomena later; meanwhile, it may suffice to say that the orthorhombic dihydrate, described here, was obtained from potassium pentathionate by metathesis with barium perchlorate, and recrystallization from water by addition of methanol. Ethanol, acetone, or dioxane can not be used, since in that case solvates, having different unit cells, result.

Preliminary data on the crystals have been reported earlier by one of us [8], and also some remarks on the stereochemistry of the pentathionate ion and other pentathionic compounds [9].

X-RAY DATA

The orthorhombic crystals of the salt, $BaS(S_2O_3)_2 \cdot 2H_2O$, appear as flat prisms, elongated along the *a* axis and with {001} predominant. {011} also occurs. There is perfect cleavage along (001). As is shown later, the cleavage probably takes place along the glide plane *a* normal to the *c* axis, there being no chemical bonds across this plane.

The unit cell dimensions [8] are: $a = 5.00$ Å, $b = 10.30$ Å, $c = 21.78$ Å. There are four molecules per unit cell; density, calc. 2.55, found 2.53 g/cm^3. Absent reflections, $0kl$ when $k + l$ is odd, $hk0$ when h is odd. The habit of the crystals, the Wilson [10] ratio for the $0kl$ reflections [9], and the Patterson projection along the *a* axis, are in accordance with the centrosymmetric space group D_{2h}^{16}—*Pnma*, and this may be regarded as confirmed by the relatively good agreement obtained between the observed structure factors and those calculated on the basis of this space group, particularly for the $0kl$ reflections.

For intensity measurements, a crystal elongated along *a* and with a cross-section of 0.05 × 0.08 mm was used to take a series of Weissenberg photographs recording the 0*kl* reflections. The crystal, later kept mounted on the glass fiber in a closed tube, was unchanged after ten months. For the *b* axis photographs, a crystal was cut to a cross-section of 0.08 × 0.15 mm. The cutting was difficult due to the pronounced cleavage along the *c* plane, and the *b* axis photographs were therefore not quite satisfactory.

142 of the 158 0*kl* reflections and 107 of the 144 *h*0*l* reflections theoretically observable with Cu*Ka* radiation were recorded on the films with measurable intensity. The intensities were estimated visually, and corrected for the Lorentz and polarization factors. No corrections for absorption were applied, although this might have been appropriate in the case of the *h*0*l* reflections. The resultant structure factors were eventually placed on an approximately absolute scale by comparison with the calculated values.

The calculated structure factors were based on the Hartree atomic scattering curves for sulphur and oxygen, and the Thomas-Fermi curve for xenon in the case of the barium ion. The same curve was used for all sulphur atoms, and no account was taken of the hydrogen atoms of the water molecules. A temperature factor $\exp - (B \sin^2\Theta/\lambda^2)$ with $B = 3.0$ Å^2 for the 0*kl* reflections and $B = 2.4$ Å^2 for the *h*0*l* reflections was applied to the calculated structure factors. The values of B were obtained by plotting $\log \Sigma|F_{\text{obs}}|/\Sigma|F_{\text{calc}}|$ against $\sin^2 \Theta$ in the ranges of $2 \sin \Theta = 0$—0.5, 0.5—0.6, 0.6—0.7, etc. to 2. The smaller value of B in the case of the *h*0*l* reflections may be due to absorption effects.

The Patterson and Fourier summations were made with Beevers-Lipson strips. It was considered accurate enough to sum a 6° intervals along the *c* axis, even though the length is 21.78 Å. Peaks were located by Booth's method [11], using graphical interpolation from three lines through each atom along each axis.

ANALYSIS OF STRUCTURE

The space group, D_{2h}^{16}—*Pnma*, has eightfold general positions. The four molecules contained in the unit cell must lie in one of the fourfold positions, of which there are three sets, one having a mirror plane of symmetry and the others a centre.

The Patterson projection along the *a* axis is reproduced in Fig. 1. The barium-sulphur vectors are marked with points, and lines are drawn to indicate the outline of the pentathionate ion. It is apparent that the barium ion and the central sulphur atom of the pentathionate ion lie in the mirror plane.

Approximate values for the *y* and *z* coordinates of barium and of the sulphur atoms were derived from the Patterson map, and used to calculate signs of the 0*kl* reflections. 132 terms were included in the first Fourier synthesis, and none of the signs were later found to be incorrect. The first Fourier map revealed the positions of the oxygen atoms and the water molecules, and hence, by double Fourier series refinement in the usual way, the electron density map of Fig. 2 was produced. A line diagram is shown in Fig. 3.

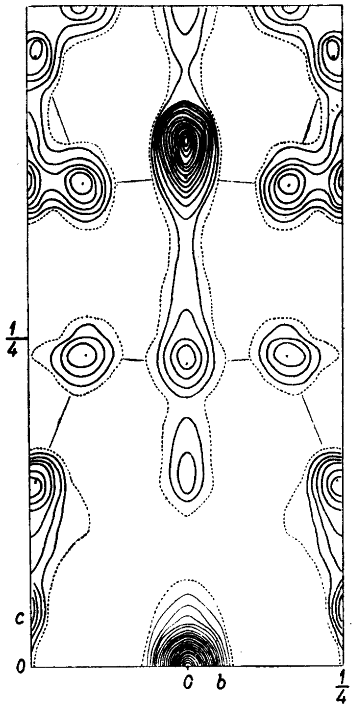

Fig. 1. Patterson projection along the a axis. A quarter of a unit cell (two asymmetric units) are shown. Contours at arbitrary but equal intervals except at the origin peak, where the intervals are doubled. The barium-barium vector overlaps partly with one of the barium-sulphur vectors.

The $h0l$ data were used to evaluate the x coordinates. The b axis Patterson projection could be interpreted to show that the barium ion and four of the sulphur atoms lie close to the glide plane at $x = \frac{1}{4}$, but gave no information as to the exact location relative to the glide plane. In this plane group, atoms at $x = \frac{1}{4}$ do not contribute to $h0l$ reflections with l odd, whereas for reflections with l even the contribution is large. Inspection of the $h0l$ data showed that for larger values of h, reflections with l odd were quite strong relative to those with l even, indicating that the barium ion does not lie exactly at $x = \frac{1}{4}$. Signs were then calculated for the $h0l$ reflections with l even on the basis of $x = \frac{1}{4}$ for barium and the four sulphur atoms, and a Fourier series was computed using these even l terms only. Such a projection contains peaks corresponding to the atomic positions, and also images of these atoms produced by the operation of a spurious centre of symmetry. The true peaks were identified by including in the series those reflections with l odd having h indices equal to or larger than three, with signs calculated from the barium contributions alone on the assumption that the ion was a little removed from the glide plane. Successive refinements could thereafter be carried out. The final electron density map, $\varrho(xz)$, is shown in Fig. 4, and an explanatory diagram is reproduced in Fig. 5.

The atomic coordinates, in fractions of cell edges, are listed in Table 1. In the case of resolved peaks, the atomic centres were taken as coincident with

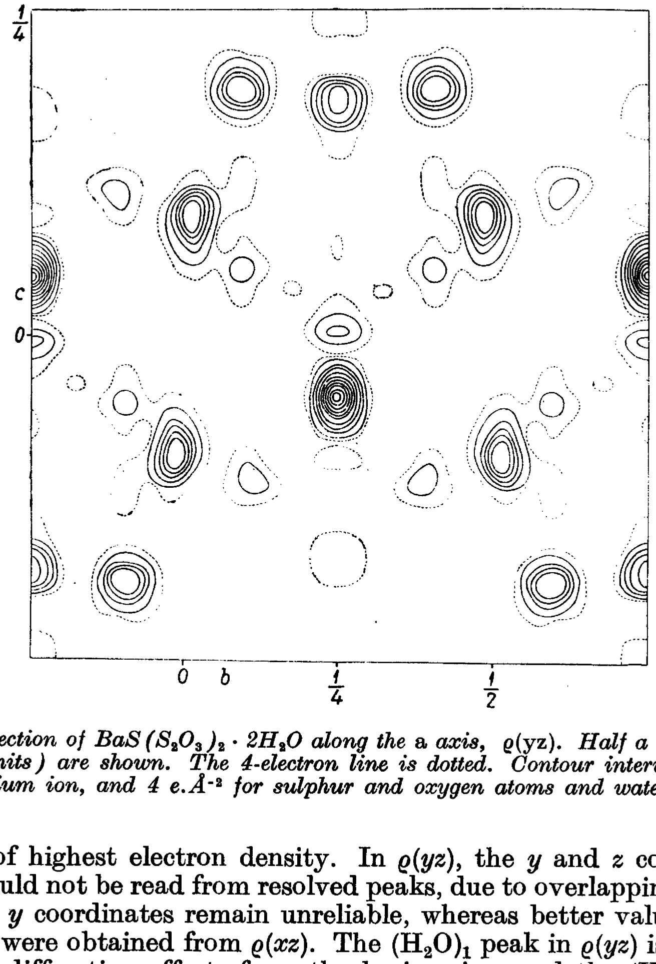

Fig. 2. Projection of $BaS(S_2O_3)_2 \cdot 2H_2O$ along the a *axis,* ϱ(yz). *Half a unit cell (four asymmetric units) are shown. The 4-electron line is dotted. Contour intervals: 10 e.Å^{-2} for the barium ion, and 4 e.Å^{-2} for sulphur and oxygen atoms and water molecules.*

the points of highest electron density. In $\varrho(yz)$, the y and z coordinates of S_1 and O_1 could not be read from resolved peaks, due to overlapping of the two atoms. The y coordinates remain unreliable, whereas better values for the z coordinates were obtained from $\varrho(xz)$. The $(H_2O)_1$ peak in $\varrho(yz)$ is excessively high due to diffraction effects from the barium ion, and the $(H_2O)_2$ peak is rather diffuse. In $\varrho(xz)$, overlapping of S_1 and O_2 occurs, and the x coordinates of these atoms may be correspondingly inaccurate. The $(H_2O)_1$ peak is distorted, and $(H_2O)_2$ is obscured by S_3. The x coordinate of $(H_2O)_2$ was therefore arrived at through trial and error calculations.

Table 1. Atomic coordinates, referring to the positions (c) *and* (d) *of the* Int. Tables [12]. *Origin at centre of symmetry.*

	Fourfold positions				*Eightfold positions*		
	x	y	z		x	y	z
Ba	0.220	0.250	− 0.050	S_2	0.285	0.092	0.185
S_3	0.530	0.250	0.179	S_1	0.300	0.013	0.094
$(H_2O)_1$	0.700	0.250	0.002	O_1	0.579	0.008	0.078
$(H_2O)_2$	0.350	0.250	− 0.170	O_2	0.180	− 0.109	0.109
				O_3	0.170	0.094	0.050

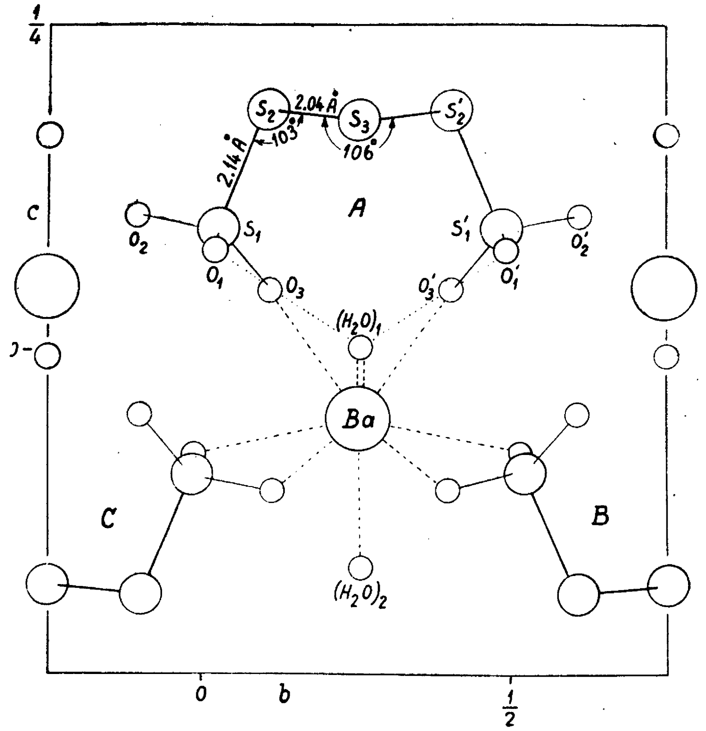

Fig. 3. Arrangement of the ions as viewed along the a *axis.*

In Table 5, the observed and calculated structure factors are compared for all 0*kl* and *h*0*l* reflections within the range of Cu*K*α radiation. The signs of the 0*kl* data correspond to the origin of the plane group *cmm* of the *Int. Tables*[12] p. 64, situated at $y = \frac{1}{4}$, $z = -\frac{1}{4}$ with respect to the origin of Table 1. The 0*kl* and *h*0*l* data were calculated on the basis of $z = 0.049$ and $z = 0.053$, respectively, for O_3; otherwise, the *z* coordinates are the same for both zones.

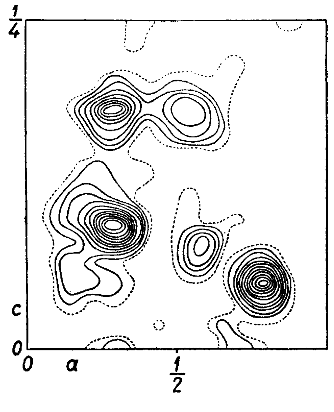

Fig. 4. Projection of $BaS(S_2O_3)_2 \cdot 2H_2O$ *along the* b *axis,* ϱ(xz). *A quarter of a unit cell (one asymmetric unit) is shown. The 6-electron line is dotted. Contour intervals as in Fig. 2, except for the water molecule,* $(H_2O)_1$*, where the intervals are 2 e.Å*$^{-2}$.

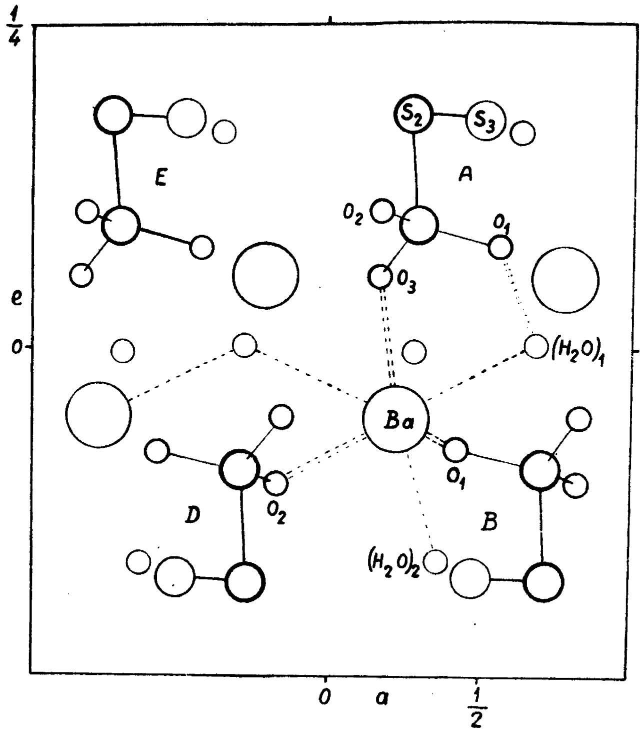

Fig. 5. Arrangement of the ions as viewed along the b *axis. Origin at the midpoint of the diagram.*

The reliability factor, $R = \Sigma||F_{\text{obs}}| - |F_{\text{calc}}||/\Sigma|F_{\text{obs}}|$, is 0.15 for the $0kl$ reflections and 0.19 for the $h0l$ reflections. For both zones together, $R = 0.17$. The unobserved reflections are included in R, as the difference between $|F_{\text{calc}}|$ and the lowest observable value of $|F_{\text{obs}}|$, only when $|F_{\text{calc}}|$ is greater than the smallest value of $|F_{\text{obs}}|$. They are not included in $\Sigma|F_{\text{obs}}|$.

The largest discrepancy occurs for the 002 structure factor, the observed value of which is about 70 units smaller than the calculated value. This relatively strong reflection is probably subject to extinction.

THE PENTATHIONATE ION

The ion possesses an exact mirror plane of symmetry, passing through the middle atom of the sulphur chain and not through any other atom of the ion. Distances and angles, calculated on the basis of the coordinates of Table 1, are as follows. The numbering of atoms is shown in Figs. 3 and 5. A prime denotes the image of an atom across the mirror plane.

Table 2. Sulphur-sulphur bond lengths and angles.

$S_1-S_2 = 2.14$ Å
$S_2-S_3 = 2.04$
$\angle S_1S_2S_3 = 103°$
$\angle S_2S_3S_2' = 106°$
$S_1S_2S_3/S_2S_3S_2'$ (dihedral angle) = 110°

Non-bonded sulphur-sulphur distances.

$S_1-S_1' = 4.88$ Å
$S_1-S_2' = 4.53$
$S_1-S_3 = 3.27$ Å
$S_2-S_2' = 3.25$

The length of a single sulphur-sulphur bond [13] being about 2.11 Å and the van der Waals radius of sulphur [14] about 1.60 Å, the data of Table 2 show that the pentathionate ion is built up of an unbranched sulphur chain *.

The terminal sulphur atoms are rotated an angle of 110° out of the plane of the three middle atoms, to the same side of the plane. The pentathionate ion thus occurs in a *cis* form [9] in this salt.

Three oxygen atoms, in approximately tetrahedral positions, surround each of the terminal sulphur atoms. The data are collected in Table 3. The average sulphur-oxygen bond length, 1.43 Å, compares with the corresponding average, 1.41 Å, in barium tetrathionate dihydrate [1].

Table 3. Sulphur-oxygen bond lengths and angles.

$S_1-O_1 = 1.44$ Å
$S_1-O_2 = 1.43$
$S_1-O_3 = 1.43$
$\angle O_1S_1O_2 = 115°$
$\angle O_1S_1O_3 = 106°$
$\angle O_2S_1O_3 = 118°$
$\angle S_2S_1O_1 = 106°$
$\angle S_2S_1O_2 = 96°$
$\angle S_2S_1O_3 = 113°$

The non-bonded sulphur-oxygen distances, S_2—O_1=2.89 Å, S_2—O_2=2.70 Å, S_2—O_3 = 3.00 Å, and the non-bonded oxygen-oxygen distances, O_1—O_2 = 2.42 Å, O_1—O_3 = 2.31 Å, O_2—O_3 = 2.47 Å. The sulphur atom, S_3, lies 3.33 Å, 4.32 Å, and 3.70 Å, respectively, from the oxygen atoms O_1, O_2 and O_3.

The shortest oxygen-oxygen approach between sulphonate groups of the same pentathionate ion is 3.21 Å and occurs in the case of O_3 and its equivalent across the mirror plane.

Regarding the sulphur chain of the pentathionate ion, it is of interest to note that the configuration is similar to that of the S_8 ring of orthorhombic sulphur [15] with three adjacent sulphur atoms removed. The latter three atoms represent the sulphur chain of the trithionate ion [16]. Likewise, the sulphur chain of the tetrathionate ion [1] resembles that of the S_8 ring, divided in two halves of four sulphur atoms each.

THE IONIC ENVIRONMENT

The barium ion is surrounded by nine oxygen atoms, at an average distance of 2.81 Å. Six of these are sulphonate oxygen atoms and three are water oxygen atoms. In Table 4, the letters *A* to *E* refer to different pentathionate

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* The significance of variations in sulphur-sulphur bond lengths will be discussed in a later article in connection with data on some analogous pentathionic compounds.

ions, as shown in Figs. 3 and 5. 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} = 2.72 Å	$\text{Ba-(H}_2\text{O)}_{1A}$ = 2.65 Å
Ba-O_{1B} = 2.91	$\text{Ba-(H}_2\text{O)}_{1E}$ = 2.84
Ba-O_{2D} = 2.79	$\text{Ba-(H}_2\text{O)}_{2A}$ = 2.69

The three oxygen atoms of a sulphonate group are all coordinated to different barium ions. Within a pentathionate ion, two oxygen atoms, one from each sulphonate group, are coordinated to the same barium ion. The coordinating powers of barium towards oxygen are thus, perhaps, responsible for the *cis* form of the pentathionate ion occurring in this salt. The six sulphonate oxygen atoms surrounding a barium ion belong to six different sulphonate groups, and to five different pentathionate ions. The arrangement is like that found in barium tetrathionate dihydrate [1].

The water molecules lie in the mirror plane. One of the molecules, $(H_2O)_1$, is approximately equidistant from two barium ions, situated in adjacent unit cells along the *a* axis, and the water molecule probably coordinates to both of the barium ions. The angle, $\text{Ba-(H}_2\text{O)}_1\text{-Ba}$, is 131°. The hydrogen atoms of this water molecule probably form hydrogen bonds to the oxygen atoms, O_1 and its mirror image, belonging to different sulphonate groups of the same pentathionate ion. The $(H_2O)_1\text{-}O_1$ distance is 3.05 Å and the angle, $O_1\text{-}(H_2O)_1\text{-}O_1'$, is 110°. The $\text{Ba-(H}_2\text{O)}_1\text{-Ba}$ and the $O_1\text{-}(H_2O)_1\text{-}O_1'$ bonds lie in perpendicular planes. This hydrate structure is similar to that occurring in lithium perchlorate trihydrate [17].

The water molecule, $(H_2O)_2$, is coordinated to one barium ion, at 2.69 Å, and is located 3.07 Å from two oxygen atoms, O_2 and its image, belonging to different pentathionate ions. The angles, however, appear to be unfavourable for hydrogen bonds to exist from this water molecule.

No chemical bonds occur across the glide plane *a* normal to the *c* axis at $z = \frac{1}{4}$ and $-\frac{1}{4}$. The only contacts are the van der Waals ones between the sulphur atoms S_2, S_3 and S_2' and their equivalents, produced by the operation of the glide plane. The approaches are, $S_2—S_2 = S_2'—S_2' = 3.78$ Å, $S_3—S_3 = 3.98$ Å, and $S_2—S_3 = S_2'—S_3 = 3.61$ Å. The closest contacts between S_8 molecules in orthorhombic sulphur [15] are 3.28 Å and 3.32 Å, and between hexasulphide chains in the cesium salt [13], 3.39 Å. The lack of strong attractive forces across the glide plane accounts for the ready cleavage of the crystals along the *c* plane.

ESTIMATE OF ERRORS

A Fourier synthesis based on the calculated 0*kl* structure factors was made in order to correct for errors due to finite termination of Fourier series [18]. Average shifts of 0.015 Å for sulphur and 0.04 Å for oxygen atoms, respectively, occurred in the *y* and *z* coordinates. When the 0*kl* structure factors were recalculated on the basis of the corrected coordinates, the reliability factor

Table 5. Observed and calculated values of structure factors for barium pentathionate dihydrate.

l	F_{obs}	F_{calc}
	0*kl* zone	
	00*l*	
2	135	− 206
4	55	− 72
6	82	+ 70
8	235	− 270
10	36	+ 14
12	30	− 10
14	112	+ 128
16	42	+ 43
18	53	− 56
20	51	+ 69
22	81	− 104
24	< 10	− 1
26	27	+ 19
28	10	− 15
	01	
1	10	− 13
3	138	− 185
5	158	+ 176
7	20	− 25
9	62	+ 94
11	32	+ 32
13	101	− 106
15	56	+ 53
17	86	− 91
19	32	+ 16
21	39	+ 44
23	< 20	− 11
25	30	+ 39
27	20	− 27
	02*l*	
0	96	+ 69
2	73	− 76
4	155	+ 149
6	113	− 129
8	82	− 86
10	148	+ 184
12	110	− 105
14	25	+ 26
16	63	+ 66
18	77	− 96
20	35	+ 36
22	23	− 26
24	17	+ 18
26	< 10	+ 8
	03*l*	
1	125	+ 120
3	149	− 143
5	177	+ 186
7	178	− 207
9	17	− 1
11	62	+ 55
13	81	− 80
15	102	+ 105
17	55	− 46
19	32	+ 43
21	< 17	+ 2
23	49	− 55
25	30	+ 37
27	14	− 32
	04*l*	
0	254	+ 230
2	170	− 162
4	25	+ 11
6	93	+ 82
8	101	− 104
10	67	+ 66
12	25	+ 17
14	< 17	+ 4
16	27	− 20
18	39	− 38
20	54	+ 50
22	45	− 55
24	17	+ 30
26	17	+ 27
	05*l*	
1	23	− 16
3	80	− 73
5	143	+ 125
7	79	− 84
9	74	+ 79
11	44	+ 40
13	98	− 100
15	62	+ 53
17	56	− 56
19	17	+ 11
21	29	+ 27
23	14	− 11
25	20	+ 30
	06*l*	
0	187	+ 195
2	49	− 34
4	72	+ 70
6	85	− 90
8	121	− 138
10	92	+ 94
12	72	− 67
14	66	+ 70
16	72	+ 88
18	62	− 63
20	23	+ 27
22	36	− 45
24	< 10	− 3
	07*l*	
1	< 14	+ 9
3	140	− 130
5	110	+ 98
7	36	+ 25
9	30	+ 31
11	< 18	+ 14
13	56	− 44
15	25	+ 14
17	65	− 68
19	36	+ 21
21	27	+ 28
23	14	− 10
	08*l*	
0	186	+ 166
2	94	− 80
4	< 17	− 12
6	50	+ 42
8	78	− 66
10	45	+ 27
12	25	− 8
14	35	+ 32
16	< 17	+ 4
18	34	− 35
20	35	+ 35
22	25	− 37
	09*l*	
1	23	+ 26
3	32	− 26
5	66	+ 58
7	86	− 91
9	39	+ 26
11	30	+ 16
13	59	− 55
15	63	+ 67
17	25	− 21
19	< 10	+ 6
	0,10,*l*	
0	28	+ 13
2	50	− 35
4	44	+ 39
6	< 17	− 16
8	34	− 24
10	65	+ 66
12	45	− 33
14	< 14	0
16	17	+ 14
18	25	− 35
	0,11,*l*	
1	25	+ 15
3	59	− 55

l	F_{obs}	F_{calc}
5	56	+ 56
7	25	− 20
9	< 14	+ 3
11	17	+ 16
13	25	− 22
15	17	+ 14
	0,12,l	
0	69	+ 84
2	27	− 25
4	< 14	+ 4
6	< 10	− 8
8	42	− 53
10	23	+ 16
12	10	− 7
	0,13,l	
1	17	− 15
3	17	− 14
5	20	+ 28
	$h0l$ zone	
	00l	
2	134	+ 206
4	60	− 80
6	83	− 75
8	232	− 281
10	43	− 15
12	38	− 5
14	146	− 130
16	49	+ 62
18	72	+ 66
20	69	+ 76
22	110	+ 116
24	< 29	− 6
26	38	− 25
28	< 13	− 19
	10l	
1	55	− 48
2	84	− 90
3	105	+ 108
4	125	+ 143
5	38	− 31
6	157	+ 147
7	22	+ 11
8	137	+ 160
9	< 22	+ 10
10	59	+ 35
11	107	+ 116
12	136	− 172
13	31	− 32
14	104	− 80
15	< 30	+ 16
16	54	+ 46
17	< 32	0
18	42	− 27
19	58	+ 51
20	47	+ 45
21	< 33	+ 7

l	F_{obs}	F_{calc}
22	< 33	+ 2
23	< 30	− 17
24	< 28	+ 9
25	< 25	+ 7
26	40	+ 55
27	< 17	− 10
	20l	
0	282	− 288
1	< 20	0
2	160	+ 144
3	< 20	− 3
4	< 21	− 7
5	25	+ 27
6	65	+ 62
7	27	+ 24
8	100	+ 101
9	< 25	− 2
10	68	+ 33
11	< 27	+ 17
12	60	+ 77
13	< 29	+ 2
14	69	+ 69
15	32	− 21
16	< 33	− 21
17	33	− 19
18	58	− 50
19	54	− 40
20	79	− 96
21	< 31	− 1
22	66	− 65
23	35	+ 34
24	< 25	+ 7
25	22	+ 14
26	< 17	+ 15
	30l	
1	60	− 49
2	38	+ 52
3	69	− 54
4	92	+ 107
5	< 27	+ 5
6	88	+ 65
7	28	+ 28
8	84	− 76
9	82	+ 72
10	56	− 71
11	91	+ 104
12	72	+ 97
13	46	+ 40
14	81	+ 70
15	< 33	− 10
16	38	+ 40
17	42	− 48
18	37	+ 47
19	40	− 39
20	29	− 29
21	< 26	+ 2
22	28	− 19

	F_{obs}	F_{calc}
23	< 22	+ 2
24	18	− 11
25	< 3	− 7
	40l	
0	92	+ 98
1	72	− 78
2	45	+ 23
3	83	+ 63
4	< 32	+ 13
5	59	− 36
6	< 33	+ 17
7	42	− 54
8	60	− 66
9	43	+ 54
10	43	+ 18
11	33	+ 18
12	33	− 24
13	< 33	+ 23
14	32	− 40
15	35	+ 36
16	30	+ 26
17	32	+ 12
18	26	+ 18
19	28	+ 29
20	25	+ 27
21	21	+ 20
22	17	+ 42
	50l	
1	38	+ 24
2	46	+ 34
3	56	+ 60
4	55	+ 54
5	< 32	− 17
6	44	+ 30
7	< 31	+ 18
8	< 30	+ 15
9	54	− 46
10	< 29	− 2
11	62	− 88
12	26	− 23
13	25	− 8
14	27	− 27
15	22	+ 12
16	23	+ 28
17	18	+ 18
	60l	
0	< 23	− 9
1	26	+ 32
2	< 26	− 8
3	41	+ 39
4	< 22	− 10
5	32	+ 34
6	< 20	0
7	19	− 28
8	17	+ 17
9	< 16	− 12
10	14	+ 18

remained the same as was obtained from the coordinates of Table 1. The back-shift corrections would have caused minor changes only in bond lengths, *viz.*, —0.01 Å for S_1—S_2, +0.01 Å for S_2—S_3, and +0.02 Å for S_1—O_2 and S_1—O_3.

As in the case of barium tetrathionate dihydrate [1], the object of the structure determination has been, more to establish the constitution of the polythionate anion, than to arrive at accurate values for bond lengths and angles. The accuracy of the present structure is probably about the same as for the tetrathionate structure [1], *i. e.*, ±0.03 Å for sulphur-sulphur bond lengths, ±0.04 Å for the average sulphur-oxygen bond length, and ±0.1 Å for oxygen-oxygen distances. Errors in angles involving sulphur atoms only are not likely to exceed ±2°.

SUMMARY

The crystal structure of barium pentathionate dihydrate, and the constitution of the pentathionate ion, has been determined by two-dimensional Patterson and Fourier methods.

The crystals are orthorhombic bipyramidal, with the axial lengths, $a = 5.00$ Å, $b = 10.30$ Å, $c = 21.78$ Å. The space group is D_{2h}^{16}—*Pnma*, and there are four molecules per unit cell.

The sulphur chain of the pentathionate ion is unbranched and non-planar. The ion possesses, by space group requirements, a mirror plane of symmetry, and occurs in a *cis* form. Three oxygen atoms, in approximately tetrahedral positions, surround each of the terminal sulphur atoms.

The length of the middle sulphur-sulphur bonds is 2.04 Å and that of the terminal sulphur-sulphur bonds is 2.14 Å. The bond angle of the middle sulphur atom of the chain is 106° and that of the two other divalent sulphur atoms is 103°. The dihedral angles are 110°, and the average sulphur-oxygen bond length is 1.43 Å.

Weak van der Waals contacts only occur between layers normal to the c axis, resulting in a ready cleavage of the crystals along the c plane.

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