

The Crystal Structure of Barium Tetrathionate Dihydrate

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This article reports the first crystal structure analysis of a salt of tetrathionic acid. A preliminary account has been published¹. The only other salt of the polythionic acids, the structure of which has been determined by X-ray methods, is potassium trithionate².

Barium tetrathionate dihydrate, $\text{BaS}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$, was first isolated by Fordos and Gélis in 1842³. For the present work, the salt was prepared by the original method, *viz.*, by interaction of iodine with an aqueous suspension of barium thiosulphate.

X-RAY DATA

The salt, crystallized from water by addition of ethanol, appears as prisms elongated in the direction of the a axis and bounded by $\{011\}$ and $\{001\}$. Twinning on (001) was occasionally observed.

From oscillation and Weissenberg photographs, taken with $\text{CuK}\alpha$ radiation, $\lambda = 1.54 \text{ \AA}$, the following unit cell dimensions were derived⁴: $a = 5.17 \text{ \AA}$, $b = 9.46 \text{ \AA}$, $c = 19.07 \text{ \AA}$, $\beta = 96^\circ$. With four molecules of $\text{BaS}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ per unit cell, the calculated density is 2.84 g/cm^3 , as compared with the measured value⁵ of 2.78 g/cm^3 .

The only systematic absences occur in the $h0l$ reflections when l is odd, and in the $0k0$ reflections when k is odd. The space group is therefore $C_{2h}^5 - P2_1/c$, from which follows that the asymmetric unit is one molecule.

The intensities of the $0kl$ and $h0l$ reflections were estimated visually from zero layer Weissenberg photographs about the a and b axes. 161 of the 237 $0kl$ reflections and 106 of the 130 $h0l$ reflections attainable with $\text{CuK}\alpha$ radiation were recorded on the films with measurable intensity. The crystal specimens used had cross-sections of about $0.05 \times 0.05 \text{ mm}$, and no correction was applied for absorption. The intensities were corrected for the Lorentz and polarization factors, using the method of Goldschmidt and Pitt⁶. The values were later placed on an approximately absolute scale by comparison of observed and calculated structure factors, a temperature factor $\exp(-B \sin^2\theta/\lambda^2)$ with $B = 1.4 \text{ \AA}^2$ for the $0kl$ reflections and $B = 1.6 \text{ \AA}^2$ for the $h0l$ reflections being applied to the calculated structure factors. The latter were based upon

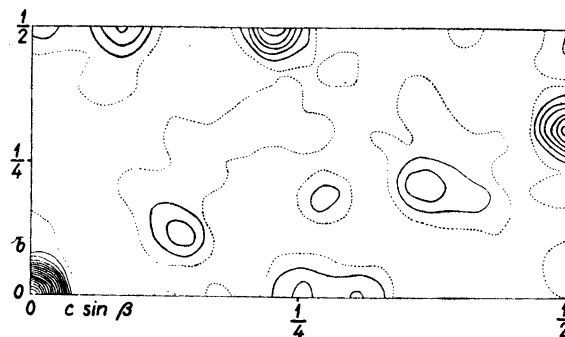


Fig. 1. Patterson projection along the a axis. Contours at arbitrary but equal intervals.

the Hartree atomic scattering curves for oxygen and sulphur, and on the Thomas-Fermi curve for xenon in the case of the barium ion. The same curve was used for all four sulphur atoms, and no account was taken of the hydrogen atoms of the water molecules.

The Patterson and Fourier summations were made at intervals of 6° along all three axes, using Beavers-Lipson strips. Peaks were located by Booth's method⁷.

ANALYSIS OF STRUCTURE

Use was made of the heavy atom technique, the position of the barium ion being found from Patterson projections along the a and b axes.

The asymmetric parts of these projections are reproduced in Figs. 1 and 2. The barium-barium vectors are easily recognized as the highest peaks in the maps beside the origin peaks. The following barium coordinates were derived from the Patterson projections: $x = 0.250$, $y = 0.600$, $z = 0.364$. Only the y coordinate differs, by 0.007, from the final value.

Fourier projections along the a and b axes were subsequently carried out, starting with signs of the reflections calculated from the barium contributions alone. The positions of the sulphur atoms, and partly the oxygen atoms, could be recognized in the first maps. The structure was refined by the Fourier method of successive approximations. The final electron density maps, $\rho(yz)$ and $\rho(xz)$, are shown in Figs. 3 and 4, and explanatory diagrams are reproduced in Figs. 5 and 6.

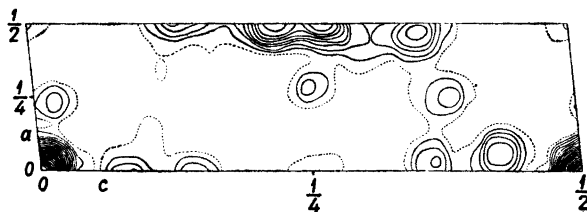


Fig. 2. Patterson projection along the b axis. Contours as in Fig. 1.

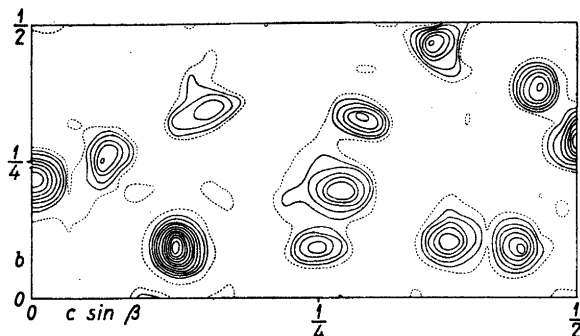


Fig. 3. Projection of $\text{BaS}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ along the a axis, $\rho(yz)$. A quarter of a unit cell (one asymmetric unit) is shown. The 4-electron line is dotted. Contour intervals: $10 \text{ e} \cdot \text{Å}^{-2}$ for the barium ion, $4 \text{ e} \cdot \text{Å}^{-2}$ for sulphur atoms, and $2 \text{ e} \cdot \text{Å}^{-2}$ for oxygen atoms and water molecules.

In $\rho(yz)$ all atoms are resolved except the oxygen atoms O_2 and O_5 , which each overlap with one of the terminal sulphur atoms. In $\rho(xz)$, O_1 overlaps with S_1 and O_2 lies near a screw axis and thus overlaps with another O_2 atom. The latter atoms were placed exactly on the screw axis although, from the shape of the peak in $\rho(xz)$, this does not appear to be quite correct. The coordinates, $x\text{O}_1$, $y\text{O}_2$ and $y\text{O}_5$, which could not be derived from any resolved peak in $\rho(yz)$ or $\rho(xz)$, were chosen so as to make the arrangement around the sulphur atoms conform with that of the other oxygen atoms. The overlapping with oxygen atoms introduces an uncertainty in the y coordinate of S_4 and the three S_1 coordinates, although attempts were made to estimate and correct for the displacing effect of the oxygen atoms.

The following z coordinates, from $\rho(yz)$ and $\rho(xz)$, respectively, differed in the two projections: S_1 , 0.285 and 0.292; S_3 , 0.446 and 0.444; O_2 , 0.244 and 0.250; O_3 , 0.253 and 0.261; O_5 , 0.507 and 0.515; $(\text{H}_2\text{O})_2$, 0.333 and 0.347. The discrepancies are due partly to overlapping from opposite directions.

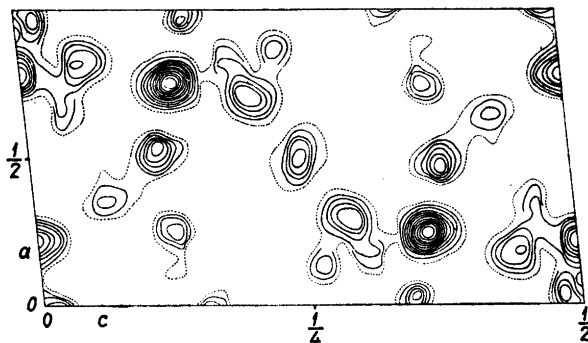


Fig. 4. Projection of $\text{BaS}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ along the b axis, $\rho(xz)$. Half a unit cell (two asymmetric units) is shown. The 6-electron line is dotted. Contour intervals as in Fig. 3.

The atomic coordinates finally chosen are collected in Table 1. The coordinates, x , y and z , are in fractions of cell edges, and refer to the monoclinic crystal axes, while x' , y' and z' , in Å, denote orthogonal coordinates referred to the a' , b and c axes, where a' is chosen normal to c in the ac plane.

Table 1. Atomic coordinates. Origin at a centre of symmetry.

	x	y	z	x' (Å)	y' (Å)	z' (Å)
Ba	0.250	0.593	0.364	1.29	5.61	6.81
S ₁	0.298	0.190	0.288	1.53	1.80	5.33
S ₂	0.473	0.101	0.382	2.43	0.96	7.03
S ₃	0.183	0.090	0.445	0.94	0.85	8.39
S ₄	0.217	0.283	0.502	1.11	2.68	9.46
O ₁	0.200	0.331	0.299	1.03	3.13	5.59
O ₂	0.500	0.220	0.250	2.57	2.08	4.50
O ₃	0.112	0.098	0.257	0.57	0.93	4.84
O ₄	0.350	0.381	0.465	1.80	3.60	8.68
O ₅	-0.036	0.328	0.515	-0.19	3.10	9.84
O ₆	0.362	0.251	0.569	1.87	2.37	10.66
(H ₂ O) ₁	0.750	0.463	0.370	3.86	4.38	6.65
(H ₂ O) ₂	0.027	0.850	0.340	0.14	8.04	6.47

In Table 6 the observed and calculated structure factors are compared for all $0kl$ and $h0l$ reflections within the range of $\text{CuK}\alpha$ radiation. The figures listed represent one fourth of the absolute values. The F_{calc} correspond to the coordinates of Table 1, except for the $0kl$ reflections, where the z coordinates from $\varrho(yz)$, listed above, were employed.

The reliability factor, $R = \frac{\sum |F_{\text{obs}}| - |F_{\text{calc}}|}{\sum |F_{\text{obs}}|}$, is 0.15 for the $0kl$ reflections and 0.16 for the $h0l$ reflections. The non-observed reflections are

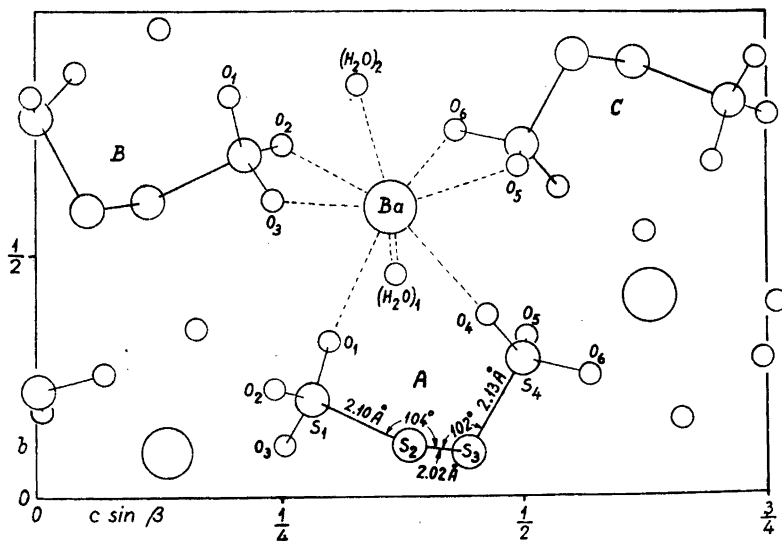


Fig. 5. Arrangement of ions as viewed along the a axis.

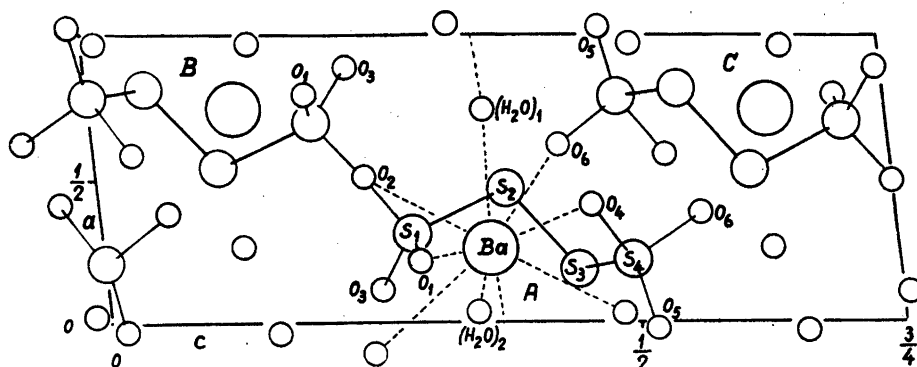


Fig. 6. Arrangement of ions as viewed along the *b* axis.

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 TETRATHIONATE ION

Interatomic distances and angles, calculated on the basis of the coordinates of Table 1, are given below. The numbering of atoms is shown in Figs. 5 and 6.

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

$S_1-S_2 = 2.10 \text{ \AA}$	$\angle S_1S_2S_3 = 104^\circ$
$S_2-S_3 = 2.02$	$\angle S_2S_3S_4 = 102^\circ$
$S_3-S_4 = 2.13$	$*S_1S_2S_3/S_2S_3S_4 = 90^\circ$

*Dihedral angle

The sulphur-sulphur distances, $S_1-S_3 = 3.25 \text{ \AA}$, $S_1-S_4 = 4.15 \text{ \AA}$, and $S_2-S_4 = 3.25 \text{ \AA}$. It is apparent that no chemical bonds exist between the atoms S_1 and S_3 , S_1 and S_4 , or S_2 and S_4 . The sulphur atoms of the tetrathionate ion thus form an unbranched and non-planar chain.

The terminal sulphur atoms, S_1 and S_4 , are each surrounded by three oxygen atoms, in approximately tetrahedral positions. The pertinent data are collected in Table 3. The average S—O distance, 1.41 \AA , is in fair agreement with values found in other sulphur-oxy compounds⁸.

Table 3. Sulphur-oxygen bond lengths and bond angles.

$S_1-O_1 = 1.45 \text{ \AA}$	$\angle S_2S_1O_1 = 112^\circ$	$\angle O_1S_1O_2 = 101^\circ$
$S_1-O_2 = 1.36$	$\angle S_2S_1O_2 = 105^\circ$	$\angle O_1S_1O_3 = 113^\circ$
$S_1-O_3 = 1.39$	$\angle S_2S_1O_3 = 109^\circ$	$\angle O_2S_1O_3 = 114^\circ$
$S_4-O_4 = 1.38$	$\angle S_3S_4O_4 = 109^\circ$	$\angle O_4S_4O_5 = 114^\circ$
$S_4-O_5 = 1.42$	$\angle S_3S_4O_5 = 108^\circ$	$\angle O_4S_4O_6 = 111^\circ$
$S_4-O_6 = 1.45$	$\angle S_3S_4O_6 = 105^\circ$	$\angle O_5S_4O_6 = 109^\circ$
Average: 1.41 \AA	Average: 108°	Average: 111°
* $\delta = 0.04 \text{ \AA}$	$\delta = 2 \frac{1}{2}^\circ$	$\delta = 4^\circ$

*Standard deviation

The average distance from the oxygen atoms to the nearest non-bonded sulphur atom is 2.87 Å, and the average oxygen-oxygen distance within sulphonate groups is 2.32 Å, with standard deviations of 0.06 Å and 0.05 Å, respectively. The shortest oxygen-oxygen distance between sulphonate groups is $O_1-O_4 = 3.21$ Å.

The sulphur chain of the tetrathionate ion possesses, within experimental accuracy, a twofold axis of symmetry, passing midway between S_2 and S_3 and between S_1 and S_4 . The sulphonate groups are rotated out of the relative positions required by a twofold axis.

THE IONIC ENVIRONMENT

The shortest barium-oxygen distances are listed in Table 4. All other such distances exceed 3.7 Å. The letters *A*, *B* and *C* refer to different tetrathionate ions, as shown in Figs. 5 and 6. A prime denotes nearest corresponding atom in adjacent unit cell along the *a* axis.

Table 4. Barium-oxygen distances.

Ba- O_{1A} = 2.77 Å	Ba- O_{6C} = 2.75 Å	Ba- $(H_2O)_1$ = 2.86 Å
Ba- O_{4A} = 2.79	Ba- $O_{3B'}$ = 2.81	Ba- $(H_2O)_{1'}$ = 2.86
Ba- O_{2B} = 2.90	Ba- $O_{5C'}$ = 2.77	Ba- $(H_2O)_2$ = 2.73

It appears that the barium ion is surrounded by nine oxygen atoms at an average distance of 2.80 Å. Six of these are sulphonate oxygen atoms and three are water oxygen atoms. Within a tetrathionate ion, two oxygen atoms, one from each sulphonate group, are coordinated to the same barium ion, whereas the three oxygen atoms of a sulphonate group are all coordinated to different barium ions. The six sulphonate oxygen atoms surrounding a barium ion thus belong to as many different sulphonate groups, and to five different tetrathionate ions.

The water molecule, $(H_2O)_1$, lies equidistant from two barium ions, Ba and Ba'. The oxygen of this water molecule thus probably coordinates to both of the barium ions. The angle between the directions to the barium ions is 125°.

The shortest distances from water molecules to sulphonate oxygen atoms are summarized in Table 5. The error in these distances may be as large as 0.1 Å, as discussed later, and those only are included which, within this limit, have been found shorter than 3.0 Å.

Table 5. Water oxygen-sulphonate oxygen distances.

$(H_2O)_1-O_{4A}$ = 2.99 Å	$(H_2O)_1-O_{6C}$ = 3.03 Å	$(H_2O)_{2'}-O_{1B}$ = 2.79 Å
$(H_2O)_1-O_{3B}$ = 2.88	$(H_2O)_1-O_{1A'}$ = 3.08	$(H_2O)_2'-O_{6C}$ = 2.94

The lengths of O—H...O bonds in crystalline hydrates usually^{9,10} lie in the range 2.75 Å—2.90 Å. In the present structure, hydrogen bonding probably occurs from $(H_2O)_2'$ to O_{1B} and O_{6C} . The angle, $O_{1B}-(H_2O)_2'-O_{6C}$, is 112°. Furthermore, there are possibilities for hydrogen bonds from $(H_2O)_1$ to one or two of the atoms, O_{4A} , O_{3B} , O_{6C} and $O_{1A'}$.

Table 6. Observed and calculated values of structure factors for barium tetrathionate dihydrate. The figures represent one fourth of the absolute values.

<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc.}	<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc.}	<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc.}
	0 <i>kl</i> zone		12	19	- 21	14	< 7	- 2
	00 <i>l</i>		13	30	+ 32	15	< 7	+ 9
2	2	+ 1	14	< 6	- 5	16	< 7	- 5
4	28	- 19	15	< 7	+ 2	17	11	- 12
6	21	+ 16	16	< 7	+ 3	18	10	+ 9
8	49	+ 50	17	17	- 18	19	9	+ 8
10	24	- 21	18	10	- 11	20	< 5	+ 3
12	27	- 25	19	< 7	+ 1	21	5	+ 4
14	38	+ 30	20	< 6	- 5	22	4	- 5
16	23	+ 26	21	< 5	+ 8	23	4	- 7
18	9	- 5	22	< 5	+ 4			
20	< 6	+ 2	23	6	- 11			
22	8	+ 14	24	3	- 3			
24	< 4	+ 7						
				03 <i>l</i>				
	01 <i>l</i>		1	8	- 10	1	5	- 3
1	20	+ 23	2	16	- 17	2	8	- 6
2	13	- 15	3	19	- 19	3	34	+ 36
3	27	- 24	4	42	+ 36	4	< 6	+ 2
4	< 4	+ 1	5	12	- 8	5	10	+ 9
5	8	- 6	6	38	+ 35	6	< 6	- 3
6	35	+ 34	7	16	- 15	7	21	- 16
7	48	+ 48	8	17	- 14	8	< 6	+ 3
8	31	- 22	9	< 6	- 4	9	< 7	- 1
9	7	+ 10	10	18	- 18	10	< 7	- 5
10	7	+ 2	11	8	- 8	11	32	+ 27
11	21	- 19	12	19	+ 17	12	< 7	+ 4
12	15	+ 12	13	< 7	- 3	13	< 8	- 3
13	< 6	+ 7	14	< 8	+ 2	14	< 8	+ 3
14	7	- 5	15	< 8	- 8	15	14	- 11
15	20	+ 22	16	25	- 26	16	8	- 8
16	16	- 15	17	< 8	- 1	17	24	+ 23
17	13	- 14	18	< 8	+ 1	18	< 7	- 1
18	8	- 12	19	< 7	+ 3	19	14	+ 17
19	16	- 20	20	17	+ 19	20	< 5	+ 3
20	10	+ 13	21	8	- 10	21	< 4	- 2
21	10	+ 12	22	< 4	+ 4	22	< 4	+ 2
22	< 4	- 6	23	< 4	- 2			
23	5	+ 11						
24	4	- 5						
				04 <i>l</i>				
	02 <i>l</i>		0	39	- 39			
0	9	- 8	1	20	- 21	0	36	- 37
1	44	- 50	2	8	+ 6	1	8	+ 6
2	4	- 1	3	26	- 28	2	10	- 9
3	26	- 25	4	32	+ 31	3	16	+ 14
4	47	- 46	5	28	+ 26	4	28	+ 31
5	18	+ 18	6	6	- 8	5	17	- 17
6	4	0	7	5	+ 3	6	< 6	+ 1
7	27	+ 28	8	15	- 15	7	11	- 11
8	10	+ 9	9	20	- 19	8	25	- 22
9	38	- 39	10	24	+ 20	9	10	+ 11
10	24	- 21	11	11	+ 5	10	24	+ 24
11	< 5	- 3	12	24	+ 23	11	< 8	- 2
			13	19	+ 18	12	14	+ 15
						13	11	- 9
						14	14	- 10
						15	8	- 7
						16	14	- 18
						17	7	+ 10

<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}
18	9	+ 11	9	< 7	+ 1	10 <i>l</i>		
19	< 5	- 2	10	< 9	+ 11	0	< 4	- 4
20	< 3	+ 1	11	< 6	- 5	2	58	+ 56
21	3	- 3	12	6	- 5	4	8	- 6
			13	6	+ 8	6	14	+ 8
	07 <i>l</i>		14	< 5	- 3	8	14	+ 6
1	13	- 9	15	5	+ 5	10	26	+ 29
2	17	+ 18	16	5	+ 12	12	17	- 14
3	9	+ 8				14	14	- 15
4	18	- 16	0,10, <i>l</i>			16	19	+ 13
5	< 7	+ 2	27		+ 27	18	< 8	- 1
6	17	- 13	1	9	+ 7	20	10	- 6
7	30	- 25	2	7	- 1	22	7	+ 5
8	< 8	+ 1	3	7	+ 8			
9	7	- 6	4	10	- 11		20 <i>l</i>	
10	12	+ 12	5	< 6	- 4	0	65	- 54
11	< 8	+ 2	6	< 6	+ 3	2	< 5	+ 4
12	12	- 16	7	< 6	+ 1	4	32	+ 28
13	9	- 10	8	10	+ 17	6	18	- 13
14	7	- 6	9	7	+ 8	8	15	- 13
15	12	- 11	10	6	- 7	10	7	+ 1
16	18	+ 21	11	< 5	+ 2	12	13	+ 15
17	< 5	+ 1	12	7	- 14	14	30	- 36
18	< 4	+ 1	13	5	- 10	16	11	- 11
19	5	+ 8	14	3	+ 9	18	17	+ 16
20	4	- 11				20	< 6	- 3
						22	8	- 14
	08 <i>l</i>		0,11, <i>l</i>					
0	7	- 3	1	< 6	+ 1			
1	28	+ 31	2	< 6	+ 3		30 <i>l</i>	
2	8	+ 5	3	13	- 13	0	13	- 9
3	17	+ 17	4	< 5	+ 1	2	35	- 30
4	< 8	- 5	5	6	- 7	4	15	+ 10
5	18	- 18	6	< 5	+ 1	6	24	+ 20
6	< 8	- 4	7	13	+ 15	8	21	- 16
7	8	- 9	8	< 4	- 1	10	12	- 10
8	< 8	+ 1	9	< 4	- 2	12	18	+ 19
9	22	+ 24	10	< 3	+ 2	14	15	+ 18
10	< 8	- 6				16	25	- 30
11	< 7	+ 1	0,12, <i>l</i>			18	< 6	+ 2
12	< 7	+ 4	10		+ 11	20	7	+ 5
13	18	- 21	1	7	- 13			
14	< 6	- 8	2	< 4	- 1		40 <i>l</i>	
15	< 6	- 5	3	6	- 6	0	40	+ 37
16	< 5	+ 3				2	10	- 9
17	9	+ 14	<i>h0l</i> zone			4	29	- 33
18	< 4	- 3	00 <i>l</i>			6	21	+ 19
19	< 4	- 4	4		+ 1	8	24	+ 28
			24		- 21	10	< 8	- 1
	09 <i>l</i>		6	18	+ 15	12	10	- 10
1	8	+ 6	8	47	+ 48	14	16	+ 25
2	11	+ 9	10	22	- 22	16	9	+ 15
3	< 8	- 3	12	26	- 28	18	6	- 11
4	< 8	- 6	14	34	+ 30			
5	< 8	+ 4	16	24	+ 24		50 <i>l</i>	
6	21	- 22	18	11	- 8	0	< 8	+ 1
7	15	+ 12	20	< 8	+ 3	2	28	+ 33
8	13	+ 12	22	10	+ 11	4	< 7	- 5
			24	< 4	+ 6	6	12	- 13

<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}
8	9	+ 2	6	27	- 24	6	11	+ 12
10	9	+ 11	8	20	- 18	8	38	+ 34
12	5	- 4	10	22	+ 22	10	15	- 11
14	< 3	- 3	12	29	+ 34	12	19	- 18
	60 <i>l</i>		14	35	- 35	14	12	+ 8
0	9	- 8	16	11	- 10	16	< 8	+ 7
2	< 6	+ 1	18	11	+ 10	18	9	- 7
4	10	+ 16	20	< 7	- 3	20	< 5	- 2
6	7	- 7	22	23	- 29			
8	5	- 7	24	4	+ 2		50 <i>l</i>	
	10 <i>l</i>			30 <i>l</i>		2	12	- 8
2	43	- 54	2	29	+ 26	4	11	+ 10
4	28	+ 31	4	9	- 11	6	28	+ 30
6	28	+ 26	6	14	- 8	8	12	+ 14
8	20	- 20	8	< 7	- 1	10	18	- 15
10	32	- 37	10	16	+ 16	12	17	+ 15
12	37	+ 36	12	26	- 23	14	12	+ 12
14	27	+ 26	14	12	- 9	16	8	- 10
16	22	- 20	16	< 8	+ 4	18	< 4	- 3
18	< 8	+ 3	18	< 8	- 5		60 <i>l</i>	
20	18	+ 18	20	18	- 20	2	< 6	+ 5
22	< 6	+ 4	22	< 5	- 3	4	10	+ 12
24	12	- 17		40 <i>l</i>		6	9	- 12
	20 <i>l</i>		2	< 7	+ 2	8	19	- 22
2	12	- 8	4	23	- 16	10	8	+ 10
4	17	+ 15				12	6	+ 6

ESTIMATE OF ERRORS

Errors in the coordinates due to finite termination of Fourier series were estimated from a Fourier synthesis based on the calculated *0kl* structure factors¹¹. The average shift in the *y* and *z* coordinates of the sulphur and the oxygen atoms was 0.013 Å and 0.028 Å, respectively, with maximum shifts of 0.02 Å and 0.057 Å.

The accuracy of the results is further influenced by the overlapping of the terminal sulphur atoms with oxygen atoms, and by the obscuring effect of the heavy barium ion, particularly on the oxygen atoms.

It is believed that the S₂—S₃ bond length, 2.02 Å, and the average S₁—S₂ and S₃—S₄ bond length, 2.12 Å, are in error by not more than ± 0.03 Å, with a corresponding error of ± 2° in angles involving sulphur atoms alone. The average S—O bond length, 1.41 Å, is probably correct to ± 0.04 Å, whereas the oxygen-oxygen distances may be in error by as much as ± 0.1 Å.

SULPHUR-SULPHUR BOND LENGTHS

The average length, 2.12 Å, of the two terminal sulphur-sulphur bonds in the tetrathionate ion, is in close agreement with the recent value, 2.11 Å, for a single sulphur-sulphur bond¹². The middle sulphur-sulphur bond is 2.02 Å and thus shorter by an amount which is outside the experimental error. Two

kinds of sulphur-sulphur bonds, of lengths 2.02 Å and 2.11 Å, also exist in cesium hexasulphide¹².

The crystal structure of a close analogon of tetrathionate, *viz.*, dimethane-sulphonyl disulphide, has recently been determined by Sörum¹³. The compound, $S_2(SO_2CH_3)_2$, arises from tetrathionate by substitution of one oxygen atom in each sulphonate group by methyl. The bond lengths reported are, 2.06 Å for the middle sulphur-sulphur bond and 2.10 Å for the two terminal bonds. The difference between the lengths of the middle bond in the two compounds is within the experimental error; however, the larger value in the methyl derivative may be significant in view of the fact that the methanethiosulphonate group is more electronegative than the thiosulphate group¹⁴.

SUMMARY

The crystal structure of barium tetrathionate dihydrate has been determined by two-dimensional Patterson and Fourier methods, by use of the heavy atom technique.

The sulphur chain of the tetrathionate ion is unbranched and non-planar. Three oxygen atoms are arranged in approximately tetrahedral positions around each of the terminal sulphur atoms, at an average distance of 1.41 Å.

The length of the middle sulphur-sulphur bond is 2.02 Å and that of the two terminal sulphur-sulphur bonds is 2.12 Å. The bond angle of the two divalent sulphur atoms is 103° and the dihedral angle is 90°.

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