

ment factor, calculated for the $h8l$ reflexions only, increased from 0.067 to 0.230. ($F_o - F_c$) syntheses confirmed this conclusion.

The Patterson and Fourier syntheses were calculated on punched-card machines. We wish to express our gratitude to Theodorus Niemeijer N. V. for generously putting their I.B.M. equipment at our disposal and to Mr M. R. van der Velde for his assistance. We are also indebted to Dra Aafje Vos for some valuable suggestions during this work and to Drs H. Lemmens and W. Heerspink for their cooperation during the first part of this investigation. The support of the Netherlands Organization for Pure Research (Z.W.O.) is gratefully acknowledged.

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The Crystal Structure of Barium Tetrasulfide Monohydrate*

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Barium tetrasulfide monohydrate forms strongly piezoelectric crystals belonging to the orthorhombic system, space group $D_2^3-P2_12_12$, with four molecules in a unit cell of dimensions $a = 9.67$, $b = 7.99$ and $c = 7.81$ Å. The crystal structure has been completely determined, and the values of the 17 atomic coordinates have been refined by double Fourier series and least-squares methods, based upon 296 terms derived from visual intensity measurements in the three principal zones. The barium atom is completely ionized, and is in ionic contact with the sulfur atoms and the oxygen atom of the water molecule. The tetrasulfide ion possesses C_2 symmetry. Like the anion of cesium hexasulfide, the tetrasulfide ion is non-branched and non-planar, and also exhibits a similar alternation in bond length. Two kinds of sulfur-sulfur bonds are present, of length 2.02 and 2.07 Å, allowing a new tentative bond-order v . bond-length curve for sulfur to be established.

Introduction

The crystal structure of cesium hexasulfide has been studied previously (Abrahams & Grison, 1953) in this laboratory, during the course of an investigation of the properties of the VI₆ group of the periodic table. This work unambiguously demonstrated the polysulfide chain to be non-branched and non-planar, and also indicated that two kinds of bond occurred in the hexasulfide ion, of length 2.02 and 2.11 Å, the standard deviation being 0.03 Å. The present study was undertaken to determine whether a similar alternation in bond length also occurred in the tetrasulfide ion.

Barium tetrasulfide is considerably more stable in contact with air than cesium tetrasulfide, although cesium forms the longer stable polysulfide (Schöne, 1862; Biltz & Wilke-Dörfurt, 1905). Barium tetrasulfide is reported to crystallize with varying amounts of water (Veley, 1886), but the conditions of crystallization used (Robinson & Scott, 1931) gave only the monohydrate.

The values of the dihedral angle in the hexasulfide ion were 78.8, 81.9 and 61.4°,† indicating that this angle was largely influenced by the crystallographic environment. Recently, Marsh, Kruse & McCullough

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† The angles quoted by Abrahams & Grison (1953) are, in fact, all complements of the correct values.

(1953) have reported the dihedral angle in *p,p'*-dichlorodiphenyl diselenide to be *c.* 74°. Marsh (1952) has found a value of 82° in diphenyl diselenide, and Toussaint's (1945) data indicate the corresponding angle in *p,p'*-dibromodiphenyl disulfide to be *c.* 78°. The values of these angles in the tetrasulfide ion were hence of further interest, particularly in view of Pauling's (1949) postulate that the most likely value for this angle is about 100°.

Crystal data

Barium tetrasulfide monohydrate, $\text{BaS}_4 \cdot \text{H}_2\text{O}^*$ forms strongly piezoelectric crystals; decomposes on melting; $D_{\text{meas.}} = 3 \cdot 107 \text{ g.cm.}^{-3}$ (determined by flotation in methylene iodide-carbon tetrachloride); $D_{\text{calc.}} = 3 \cdot 120 \text{ g.cm.}^{-3}$ for four molecules per unit cell; orthorhombic with

$$a = 9 \cdot 67 \pm 0 \cdot 02, \quad b = 7 \cdot 99 \pm 0 \cdot 02 \quad \text{and} \quad c = 7 \cdot 81 \pm 0 \cdot 02 \text{ \AA};$$

absent spectra, (*h*00) only with $h = 2n+1$ and (0*k*0) only with $k = 2n+1$. Space group is hence uniquely $D_2^3\text{-}P2_12_12_1$. No molecular or ionic symmetry is required. Absorption coefficient for Mo *K*α radiation ($\lambda = 0 \cdot 7107 \text{ \AA}$) is 82 cm.^{-1} , for Cu *K*α radiation ($\lambda = 1 \cdot 5418 \text{ \AA}$) is 670 cm.^{-1} . Volume of the unit cell is 603.6 \AA^3 . Total number of electrons per unit cell = $F(000) = 520$. Dielectric constant at room temperature (Westphal, 1953) is *c.* 8 ± 2 in each axial direction.

Analysis of the structure

An examination of the intensity distribution in the (*h*0*l*), (*h**k*0) and (0*k**l*) layers reveals the presence of an outstandingly strong superlattice (Table 5). In the (*h*0*l*) layer, reflections of the form $h = 4n$ when $l = 2n$, and $h = 2n+1$ when $l = 2n+1$ are very strong; in (*h**k*0), reflections of the form $h = 4n+2$ when $k = 2n+1$, and $h = 4n$ when $k = 2n$; and in (0*k**l*) reflections of the form $h = 2n$ when $l = 2n$ are outstanding. Assuming these strong reflections are pro-

duced by barium atoms contributing fully to these planes, it is easy to show from the structure factor expression (*International Tables*, 1952) that the barium atoms must lie close to the coordinates $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

The method of Wilson (1942) and Harker (1948) was used to place the intensities in the (*h**k*0) layer on an absolute scale. The scale factor thus derived was finally found to be 9.2% too high, by comparison with the scale derived from the coordinates given in Table 1 (in the case of Cs_2S_6 the scale factor derived by this method was finally found to be 10.4% too high). The temperature factor *B* in the expression $\exp\{-B[(\sin \theta)/\lambda]^2\}$, assumed to be isotropic and the same for each kind of atom present, obtained by this statistical treatment was 0.75 \AA^2 , and it was not found necessary to alter this value throughout the remainder of the investigation. Structure factors, calculated for barium at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, with the atomic scattering factor based on the Thomas field, and the above value of *B*, gave a value for R_1 (defined in the usual way) of 0.19 for the strong planes. The amplitudes of the remaining planes, of course, were identically zero. This good agreement encouraged the belief that the strong reflections were primarily due to a full contribution from the barium atoms. The phases associated with these atoms were then used to compute a Fourier series on XRAC, through the kindness of Prof. R. Pepinsky, using the limited set of superlattice planes only (Fig. 1). Since all other terms have been omitted, this series gives a rather inaccurate and artificially symmetrized view of the correct electron density projection, which could be obtained with complete (*h**k*0) data.

Attempts to desymmetrize Fig. 1 were made by introducing the next most intense reflections into the series in sets of three, with various phase combinations, using the non-negativity of the background as criterion. This method was not very successful, primarily owing to the diffraction effects of the heavy atom, which interfered with the criterion. Other efforts, based upon improving the general appearance of the projection, were also not very successful. The sulfur coordinates were then obtained by a consideration of the absolute intensities of those reflections to which the barium atom did not contribute. The various combinations of tetrasulfide group orientations present

* Analysis:

	I	II	Calc. for $\text{BaS}_4 \cdot \text{H}_2\text{O}$
H_2O	6.45 %	6.52 %	6.34 %
Ba	48.31	48.50	48.44
S	45.20	44.90	45.21

Table 1. Atomic coordinates in $\text{BaS}_4 \cdot \text{H}_2\text{O}$

(Origin at 112, plane of 2_12_1)

	<i>x</i>			<i>y</i>			<i>z</i>		
	<i>h</i> <i>k</i> 0	<i>h</i> 0 <i>l</i>	Weighted mean	<i>h</i> <i>k</i> 0	0 <i>k</i> <i>l</i>	Weighted mean	<i>h</i> 0 <i>l</i>	0 <i>k</i> <i>l</i>	Weighted mean
Ba	0.1195	0.1196	0.1195	0.2503	0.2498	0.2501	0.2480	0.2474	0.2477
S_1	0.1028	0.1052	0.1040	0.4694	0.4723	0.4708	0.6328	0.6346	0.6330
S_2	0.1828	0.1813	0.1820	0.3991	0.3970	0.3987	0.4320	0.4313	0.4318
S_3	0.3301	0.3304	0.3303	0.3626	0.3596	0.3620	0.9462	0.9439	0.9455
S_4	0.4679	0.4667	0.4670	0.3780	0.3774	0.3776	0.1413	0.1426	0.1415
O_1	0	0	0	0	0	0	0.4485	0.4473	0.4479
O_2	0	0	0	0.5000	0.5000	0.5000	0.9535	0.9553	0.9544

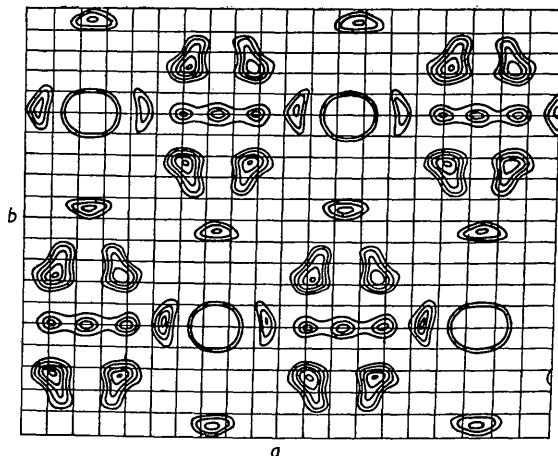


Fig. 1. Symmetrized c -axis projection, based only on the barium atom at $\frac{1}{2}, \frac{1}{2}$, computed on the X-Ray Analog Computer.

in Fig. 1 were used in this process. The first successful model gave a value of $R_1 = 0.312$ for all the planes observed in this zone. After six Fourier series refinements, the projection shown in Fig. 2 finally resulted.

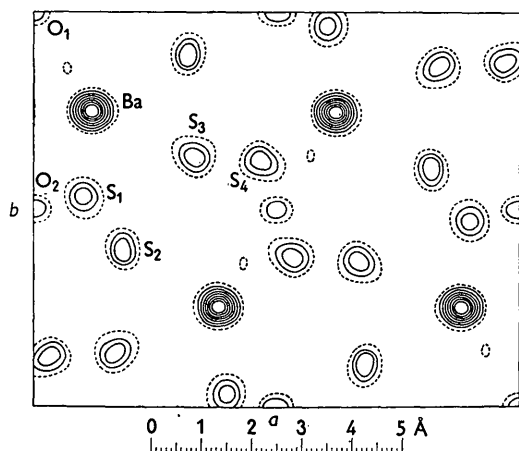


Fig. 2. Projection of the unit cell along the c axis. Each contour for the barium atom represents a density increment of $20 \text{ e.}\text{\AA}^{-2}$, for the sulfur atoms of $10 \text{ e.}\text{\AA}^{-2}$ and for the oxygen atom of $5 \text{ e.}\text{\AA}^{-2}$, the 10-electron line being broken.

The z coordinates were obtained from the $(h0l)$ data together with a consideration of the symmetrized $(0kl)$ map computed in the same way as Fig. 1. The coordinates thus found were not very good, for the initial value of $R_1(h0l)$ was 0.52. Seven subsequent Fourier series iterations then gave the electron density map in Fig. 3. The $(0kl)$ projection followed from the y and z coordinates already determined, and is given in Fig. 4. During the course of this refinement, it was noticed that the oxygen atoms had become clearly resolved, and inclusion of these atoms reduced R_1 in each zone by 1–2%.

In the case of the b -axis projection, the experimental

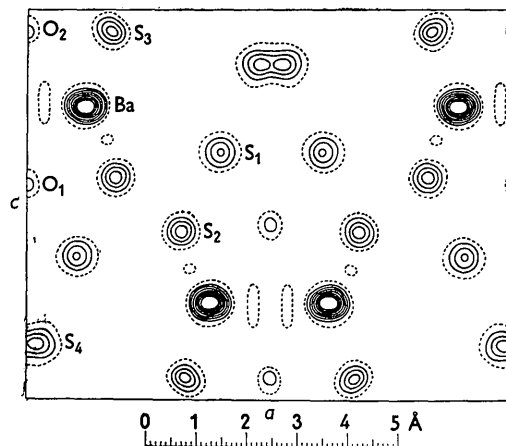


Fig. 3. Normal projection of the unit cell along the b axis. Contour scale as in Fig. 2.

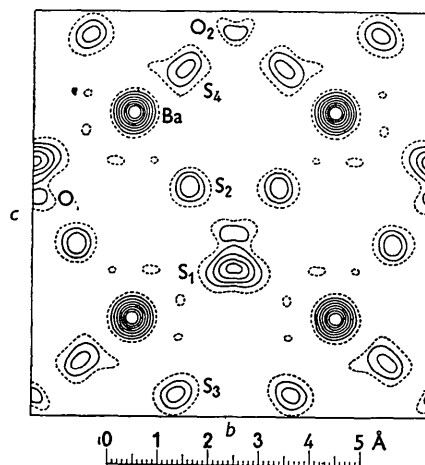


Fig. 4. Normal projection of the unit cell along the a axis. Contour scale as in Fig. 2.

arrangement permitted the entire reciprocal layer to be explored by means of $\text{Mo } K\alpha$ radiation. It is interesting to note that, with Cu radiation, the value of R_1 did not fall below 0.24, whereas substitution of Mo radiation not only added 38 new terms to the series, but also lowered the value of R_1 for the previously observed 92 terms to 0.108. This series was sufficiently complete to introduce only small errors in the resulting coordinates due to artificial termination. The maximum difference in the corresponding ξ_i 's derived from Fourier series based upon F_c and upon F_o as coefficients was 0.013 \AA in ξ_s and 0.06 \AA in ξ_o . In the other two zones, however, the series was abruptly terminated at $\sin \theta = 0.50$ for $\text{Mo } K\alpha$, the limit of the sphere of reflection observable with the precession camera. Hence further refinement was sought by the application of the method of least squares. In using this method, all weights were placed equal to unity since the method adopted for recording and measuring the intensities would not allow the standard error in each

intensity to be estimated. Only the diagonal terms of the matrix were solved because the largest off-diagonal terms in this case were found to be less than 0.03 of the corresponding diagonal element. A solution of the complete matrix produced a r.m.s. change in ξ_s of 0.004 Å. Hence expressions of the type

$$\Delta \xi_j = \sum \frac{\partial F_{hkl}}{\partial \xi_j} \cdot \Delta F_{hkl} \div \sum \left[\frac{\partial F_{hkl}}{\partial \xi_j} \right]^2$$

were used. The values of $\Delta \xi_j$ thus obtained were added to the original ξ_j 's and a further cycle of refinement was then completed. Three such cycles for the (0kl) data and two for the (hk0) data sufficed to reduce the largest value of $\Delta \xi_s$ to 0.0013 for (0kl) and 0.0009 for (hk0), which were well within the s.d. in ξ_s and hence inside the final convergence circle. This decreased the value of R_1 by 1.2 and 0.4%, respectively, in the two zones. At this stage, it was thought no further refinement was feasible. No signs changed during the least-squares process.

The final values of R_1 for the principal zones after these processes were completed were 0.110 for (hk0), 0.094 for (0kl), 0.134 for (h0l), and total $R_1 = 0.115$, based upon 296 observations and 17 parameters.

Atomic coordinates

The atomic positions were taken as coincidental with the center of electron mass in the (h0l) projection (Fig. 3) for the x and z coordinates. Together with the values derived from the least-squares refinement procedures for the groups of x and y, and y and z coordinates, these results are collected in Table 1. Every atom thus has two independent values for each of its three coordinates, and the weighted mean of these pairs was taken for the final coordinates, having due regard for the previous behavior of that coordinate (e.g., if the coordinate of an atom obtained by one process had not appreciably altered through several refinement cycles, whereas that obtained from a different set of data had oscillated, the former value would be favored). A common origin was used in computing the data in each zone, and is given in the heading of Table 1.

Dimensions in the tetrasulfide ions

In this crystal, there are two crystallographically independent tetrasulfide ions, since the twofold axes present pass through each ion. The bond lengths and

Table 2. Dimensions in the tetrasulfide ion

S_1-S_2	= 2.03 ₂ Å	S_3-S_4	= 2.02 ₁ Å
$S'_1-S'_1$	= 2.06 ₈ Å	$S'_4-S'_4$	= 2.06 ₈ Å
$S'_1-S'_1-S_2$	= 104° 4'	$S'_4-S'_4-S_3$	= 104° 54'

Dihedral angles

$S'_1S_1S_2/S'_1S_1S'_2$	= 74° 5'
$S'_3S'_4S'_4/S_3S_4S'_4$	= 77° 10'

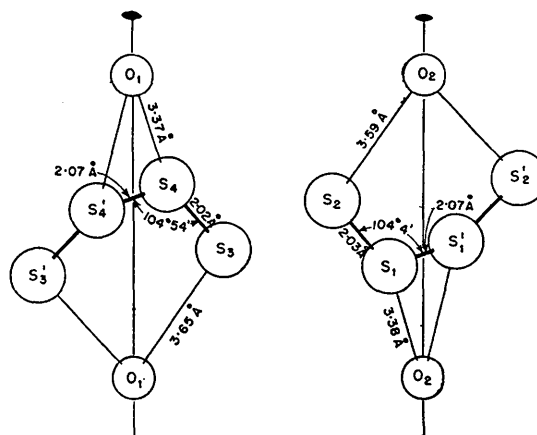


Fig. 5. Dimensions in the groups lying on the twofold axes.

angles of the two ions are given in Table 2, and are also represented in Fig. 5.

Errors in the coordinates

In the analysis of cesium hexasulfide, a variety of ways of estimating the errors in the coordinates were used (Booth, 1945, 1946, 1947; Cruickshank, 1949). Of these, the last method appeared the most satisfactory. In the present study, Cruickshank's method was applied to the (h0l) data. Using his notation, the average values of p obtained were 13.1, 10.4 and 5.4 for barium, sulfur and oxygen, respectively. These are higher than usual, probably because of the small

Table 3. Errors in the coordinates

	x		y		z		Standard deviation
	L.S.† σ_{hko}	F.S.† σ_{h0l}	L.S. σ_{hko}	L.S. σ_{0kl}	L.S. σ_{0kl}	F.S. σ_{h0l}	
Ba	0.0039 Å	0.0005 Å	0.0047 Å	0.0058 Å	0.0047 Å	0.0005 Å	0.010 Å
S ₁	0.016	0.005	0.016	0.016	0.015	0.005	0.027
S ₂	0.017	0.005	0.017	0.021	0.017	0.005	0.029
S ₃	0.017	0.005	0.016	0.018	0.018	0.005	0.026
S ₄	0.017	0.005	0.016	0.019	0.017	0.005	0.027
O ₁	0	0	0	0	0.067	0.028	0.07
O ₂	0	0	0	0	0.066	0.026	0.07

† L.S., least squares; F.S., Fourier series.

temperature factor and the extent of the series, which effectively sharpens the series very considerably. Also in the $(h0l)$ zone, $\sigma(A_h) = 5.37$ and $\sigma(A_l) = 4.93$ e.Å⁻³. The error in the coordinates may also be calculated from the least-squares data by a standard procedure (Whittaker & Robinson, 1944). Here,

$$\sigma(\xi_j) = \left\{ \frac{\Sigma(\Delta F_{hkl})^2}{(m-s) \Sigma \left[\frac{\partial F_{hkl}}{\partial \xi_j} \right]^2} \right\}^{\frac{1}{2}},$$

where m is the number of observational equations and s is the number of parameters. The standard deviation is then $[\sigma(x)^2 + \sigma(y)^2 + \sigma(z)^2]^{\frac{1}{2}}$. The errors in the coordinates thus computed are collected in Table 3. The corresponding s.d. in the S-S bond is $\sqrt{2} \cdot \sigma(x, y, z)$ and hence is about 0.04 Å. This may be compared with the differences between those bonds and angles in the two tetrasulfide ions which chemically should be identical, but crystallographically are not required to be the same. The maximum difference in length observed is 0.01 Å and in angle is 1°, so it appears likely in this analysis that the calculated standard deviation for the S-S bond length, if in error at all, is on the high side. It thus seems probable that the differences in the lengths of the two kinds of bond apparently present in the tetrasulfide ion are real, although these are comparable with the s.d. in the bond lengths.

Interatomic distances

The closest approach distances, less than 4 Å, among the barium and the tetrasulfide ions and the water

Table 4. *Interatomic distances less than 4.0 Å*

Ba-O ₂ = 2.79 ₆ Å	Ba-O ₁ = 2.78 ₇ Å
S ₁ -O ₂ = 3.37 ₇	S ₄ -O ₁ = 3.36 ₉
S ₂ -O ₂ = 3.58 ₆	S ₃ -O ₁ = 3.65 ₁
S ₁ -S ₃ = 3.38 ₉	Ba-S ₂ = 3.21 ₁
Ba-S ₃ = 3.18 ₀	Ba-S ₂ * = 3.37 ₁
Ba-S ₃ * = 3.30 ₄	Ba-S ₂ = 3.46 ₂
Ba-S ₃ * = 3.48 ₇	Ba-S ₁ = 3.49 ₂
Ba-S ₄ * = 3.52 ₉	

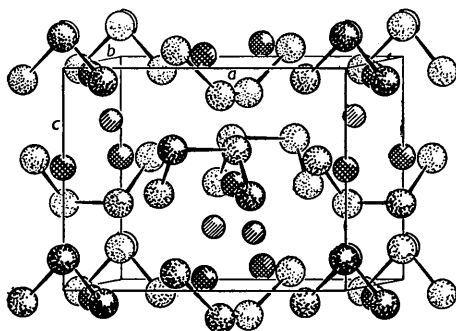


Fig. 6. A clinometric view of the structure, showing the outlines of one unit cell. The hatched circles represent barium atoms, the shaded circles sulfur atoms, and the cross-hatched circles oxygen atoms.

molecule are listed in Table 4. The primed atoms are related to the unprimed by the two-fold axes, and the starred atoms are related to the unprimed by the relation $(x, y, z)^* = (\frac{1}{2}-x, \frac{1}{2}+y, \bar{z})$. A clinometric view of the structure is shown in Fig. 6.

Discussion

As in the case of cesium hexasulfide, this study confirms the view that the polysulfide group is non-branched and non-planar, although in BaS₄·H₂O the tetrasulfide ion possesses C₂ symmetry. In this crystal the barium atom is surrounded by nine other atoms at distances less than 4 Å apart. Two of these distances are between oxygen and barium, and are equal at 2.80 Å. This compares very closely with the ionic separation between barium and oxygen in BaO of 2.76 Å. The shortest barium-sulfur contact is 3.18 Å, which may be compared with the corresponding distance in BaS of 3.17 Å. It is thus entirely likely that the barium atom is completely ionized, and that the tetrasulfide group, in consequence, possesses a two-electron charge. The apparent alternation of bond lengths in the tetrasulfide ion may now be explained if it is assumed that the longer central bond in the anion is single, i.e. with order zero. Then each of the remaining two bonds will contain one extra electron, and will hence possess a bond order of 0.5. The bond lengths corresponding to these bond orders, together with the similar data found in the cesium hexasulfide study, are combined in Fig. 7, in which each length is given, together with its estimated standard error. Further, continuing the argument of Evans & de Heer (1949), a bond-order v . length curve for carbon-sulfur may be established, in which a straight-line relation

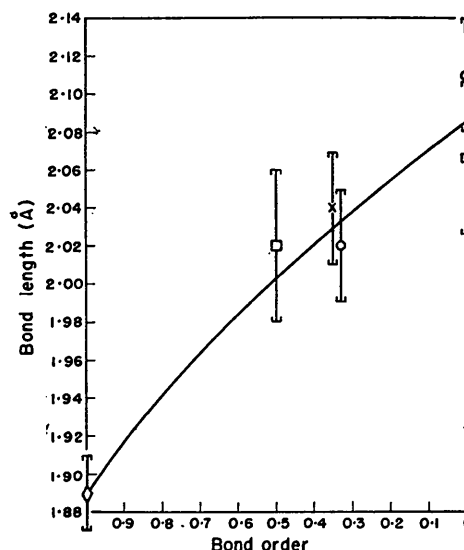


Fig. 7. Relation between interatomic distance and bond order in the sulfur-sulfur bond. The squares represent BaS₄·H₂O data, the circles are for Cs₂S₆, the cross is for thiophene, and the diamond is for S₂.

feature is the relation of the water group to the tetrasulfide ions. Both groups lie on twofold symmetry axes, and each tetrasulfide ion has two water molecules as neighbors, unsymmetrically arrayed on either side (Fig. 5). The closest oxygen-sulfur approach is 3.37 Å, which is rather more than the sum of the ionic radii. A possibility of interest is that this piezoelectric crystal might become ferroelectric at a different temperature by inducing a cooperative movement of the water or tetrasulfide groups, relative to the barium ions. Efforts are now being made to grow a crystal large enough to examine this possibility experimentally.

The results of the present study, together with those cited earlier, now appear to establish the value of the dihedral angle in a sulfur chain as close to 76°.

Experimental

The orange needle crystals of barium tetrasulfide monohydrate were prepared by the method of Robinson & Scott (1931). They are quite stable in contact with the atmosphere, in contrast with cesium hexasulfide. The largest of the three crystals examined had dimensions 0.25 × 0.42 × 0.70 mm. and the smallest 0.16 × 0.16 × 0.45 mm.

Weissenberg and precession cameras were employed in this study, using only Mo $K\alpha$ ($\lambda = 0.7107$ Å) radiation for the final determination of the atomic coordinates. A new Weissenberg camera was used, built in this laboratory, with a 3½ in. diameter film holder, to spread the reflections obtained with Mo radiation and hence make it easier to measure the intensities. The beam stop was designed so that the 1st order reflection of a 10 Å axis could be observed with this radiation. The film holder had a section subtending c. 90° removed from the back-reflection region on the lower side, to let it slip over the cylindrically split and hinged layer-line screen, a modification similar to that previously described by Abrahams & Lipscomb (1952), which enables the camera to be used conveniently at low or high temperatures. The intensities were measured visually, using a multiple-exposure technique for correlating the weak and strong reflections. Absorption corrections were not made since the crystals were small and very regular in shape and the principal reflections were measured using the smallest crystal. The ratio of the strongest intensity to the weakest in each of the three zones studied was about 600:1.

The excellent agreement obtained between observed and calculated structure factors did not appear to warrant the use of a correction for the anomalous dispersion of the K and L electrons, especially as the latter is not well known for barium. A study in this laboratory is under way to measure this dispersion

experimentally for several atoms with atomic number about 50.

The values for the measured structure factors were derived from the intensities in the usual way, applying Waser's (1951) Lorentz and polarization correction to the intensities in the zero layers measured with the precession camera. The calculated structure factors were based on the atomic coordinates in Table 1, and both sets of structure factors are assembled in Table 5.

The structure factor and the least-squares calculations were computed on punched card machines with four-figure accuracy. The Fourier series were all summed using Beevers-Lipson strips, sampling the electron densities at intervals of 12° along each axis. The positions of the contour lines were obtained from the summation totals by careful graphical interpolation on a scale of 5 cm. to 1 Å, in directions parallel with each axis.

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