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Structure of a Solvate of Barium Pentathionate with Acetone

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The solvate, $BaS(S_2O_3)_2 \cdot (CH_3)_2CO \cdot H_2O$, is monoclinic with $a = 5.04$ Å, $b = 10.47$ Å, $c = 13.61$ Å, $\beta = 104°$, space group $C_{2h}^2 - P2_1/m$ and $Z = 2$. Fourier projections along the a and b axes show that the crystals are built up of layers which have the same internal structure as in the dimorphs of barium pentathionate dihydrate, but for the substitution of a water molecule by an acetone molecule.

The barium ion, the middle sulphur atom of the chain, and the water and acetone molecule lie in a crystallographic mirror plane. The values obtained for sulphur-sulphur bond lengths and angles agree within the experimental errors with those found in the dihydrates. The mean values in the three salts are: $S_1 - S_2 = S_4 - S_5 = 2.12 \pm 0.02$ Å, $S_2 - S_3 = S_3 - S_4 = 2.04 \pm 0.02$ Å, $\angle S_1 - S_2 - S_3 = \angle S_3 - S_4 - S_5 = 105 \pm 1.5°$, $\angle S_2 - S_3 - S_4 = 106 \pm 2°$, and the dihedral angles, $S_1S_2S_3/S_2S_3S_4 = S_2S_3S_4/S_3S_4S_5 = 108 \pm 1.5°$.

The data indicate that the outermost sulphur-sulphur bonds in the pentathionate ion are single bonds, while the middle bonds possess some double-bond character.

It was shown recently [1] that barium pentathionate, selenopentathionate and telluropentathionate when crystallized from aqueous acetone or tetrahydrofuran, occur as solvates containing one mole of water and one mole of the organic solvent per mole of salt. The crystals of the solvates are isomorphous. The solvate of barium pentathionate with acetone has now been studied by two-dimensional Fourier methods, and the pentathionate ion found to have the same configuration and dimensions as in the orthorhombic [2] and triclinic [3] dimorphs of the dihydrate.

CRYSTAL DATA

The crystals of $BaS(S_2O_3)_2 \cdot (CH_3)_2CO \cdot H_2O$ were obtained as thin, rhomb-shaped plates {001}, bounded by {110}. There is perfect cleavage along (001) and a rather pronounced tendency of twinning on the same plane. The crystals are monoclinic, with the unit cell dimensions [1]: $a = 5.04$ Å, $b = 10.47$ Å, $c = 13.61$ Å (± 0.5 %), $\beta = 104°$. There are two formula units per unit cell;

density, calc. 2.24, found 2.25 g/cm^3. The only systematic absences are in the $0k0$ reflections when k is odd. Of the two monoclinic space groups compatible with these absences, the centrosymmetric one, C_{2h}^2—$P2_1/m$, was assumed to be the correct one, and this choise seems justified through the outcome of the structure analysis.

The intensities of the $0kl$ and $h0l$ reflections were estimated visually from Weissenberg photographs taken with CuK radiation. The crystals used had cross-sections of 0.09×0.06 mm and 0.11×0.07 mm, respectively, in the case of the a and b axis photographs. They were transparent and apparently unchanged after the exposures. Some difficulties were experienced in finding untwinned crystals, and in cutting the crystals because of the ready cleavage, but relatively good intensity photographs were at last obtained. A double-film, multiple-exposure technique was used; the a axis photographs, except for the strongest-exposure ones, were taken on a Nonius integrating Weissenberg camera. 158 out of 186 $0kl$ reflections and 152 out of 171 $h0l$ reflections attainable with CuK_α radiation were observed. The intensities were corrected for the Lorentz and polarization factors, but not for absorption; with μ = 311 cm^{-1} for CuK_α radiation the absorption may introduce a serious error. The F_o^2 and F_o summations were made with Beevers-Lipson strips, at 6° intervals along the b and c axes and at 12° intervals along the a axis.

ANALYSIS OF THE STRUCTURE

The space group, $P2_1/m$, has fourfold general positions, and symmetry centres and mirror planes as special, twofold positions. With two formula units per unit cell, the middle sulphur atom of the pentathionate ion, the water molecule and the acetone molecule lie in mirror planes, as does also the barium ion.

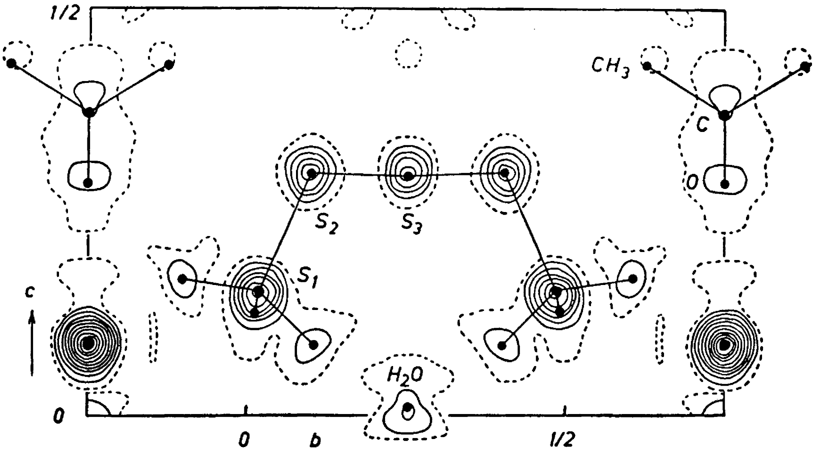

Fig. 1. Electron density projection of the acetone solvate along the a axis. The 3-electron line is dashed. Contour intervals: 10 e · Å^{-2} for the barium ion, 5 e · Å^{-2} for sulphur and oxygen atoms, and 2 e · Å^{-2} for carbon atoms.

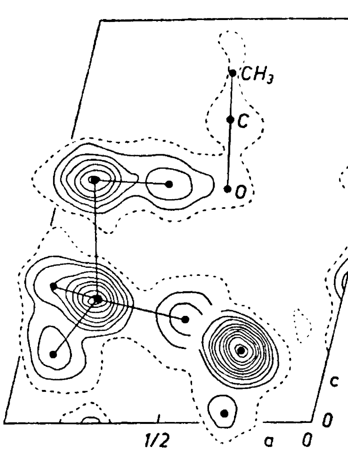

Fig. 2. Electron density projection along the *b* axis. The 5-electron line is dashed, and contours are at intervals of 8 e · Å^{-2} for the barium ion, otherwise as in Fig. 1.

The *y* and *z* coordinates of the barium ion and the three sulphur atoms of the asymmetric unit were first derived from a F_o^2 synthesis of the 0*kl* data. They differed on the average only 0.003 (maximum 0.006) from the final values. A F_o synthesis of about 60 of the largest 0*kl* terms, with signs based on the barium and sulphur contributions, gave approximate coordinates of the lighter atoms and permitted successive F_o refinements to be carried out. The *b*-axis projection was solved and refined by F_o^2 and F_o syntheses in the same way.

The 0*kl* and *h*0*l* electron density maps are reproduced in Figs. 1 and 2, and the atomic coordinates are listed in Table 1. In the Table, *x*, *y* and *z* are in fractions of monoclinic cell edges, and *x*′, *y*′ and *z*′ are orthogonal coordinates in Å referring to the same origin and to the *a*, *b* and *c*′ axes, where *c*′ is normal to *a* and *b*. The *z* coordinates from the two projections were the same for the barium ion and differed on the average 0.025 Å for the sulphur and for the oxygen atoms; the values of Table 1 are means of the two, weighted according to their apparent reliability.

The reliability index, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, with reflections not observed included when $|F_c|$ exceeds the observable limit, is 0.15 for the 0*kl* reflect-

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

	x	*y*	*z*	*x*′	*y*′	*z*′
Ba	0.711	0.250	−0.088	3.87	2.62	−1.16
S_1	0.798	0.015	0.153	3.52	0.16	2.02
S_2	0.903	0.097	0.299	3.57	1.02	3.95
S_3	0.655	0.250	0.294	2.33	2.62	3.88
O_1	0.495	0.010	0.127	2.08	0.10	1.68
O_2	0.953	−0.105	0.169	4.25	−1.10	2.23
O_3	0.897	0.102	0.085	4.24	1.07	1.12
H_2O	0.292	0.250	0.010	1.44	2.62	0.13
O_C	0.459	0.250	−0.285	3.67	2.62	−3.77
C_1	0.510	0.250	−0.372	3.69	2.62	−4.91
C_2	0.539	0.125	−0.430	3.74	1.31	−5.68

ions and 0.21 for the *h*0*l* reflections. A list of calculated and observed structure factors is available from the authors on request. The calculated values were based on the Thomas-Fermi atomic scattering curve for xenon in the case of the barium ion, and on the Hartree curves for sulphur, oxygen and carbon. The hydrogen contributions were ignored. In the temperature factor exp $[-B(\sin^2\Theta/\lambda^2)]$ finally chosen B was 2.0 Å^2 and 4.0 Å^2, respectively, for the 0*kl* and *h*0*l* reflections, except for the carbon atoms where the values, 4.0 Å^2 and 5.0 Å^2, respectively, were found to give better agreement.

DESCRIPTION OF THE STRUCTURE

The structure is built up of layers parallel to the *c* plane. The layers have the same internal structure as in the orthorhombic [2] and triclinic [3] dihydrates, but for the substitution of a water molecule by an acetone molecule. The orthogonal coordinates of Table 1, included to allow a comparison with the corresponding coordinates for the dihydrate structures [3], show close correspondence with the latter. Apart from the presence of the acetone molecule, the structures differ only in the way the layers are arranged relative to each other, as discussed earlier [1].

The pentathionate ion has mirror plane symmetry, required by the space group. The dimensions of the sulphur chain, from the coordinates of Table 1, are listed in Table 2. The standard deviations of the bond lengths and angles are probably not less than 0.04 Å and 3°, respectively. Primes are used to denote the equivalent of an atom across the mirror plane.

Table 2. Sulphur-sulphur bond lengths and angles.

$S_1-S_2 = 2.11$ Å	$\angle S_1-S_2-S_3 = 106°$
$S_2-S_3 = 2.02$	$\angle S_2-S_3-S_2' = 105°$

$S_1S_2S_3/S_2S_3S_2'$ (dihedral angle) = 108°

The non-bonded distances within the chain are $S_1—S_3 = 3.31$ Å, $S_2—S_2' = 3.20$ Å, $S_1—S_2' = 4.49$ Å, $S_1—S_1' = 4.92$ Å. The sulphur-oxygen bond lengths are $S_1—O_1 = 1.48$ Å, $S_1—O_2 = 1.47$ Å, $S_1—O_3 = 1.47$ Å, and the angles, $\angle O_1—S_1—O_2 = 119°$, $\angle O_1—S_1—O_3 = 111°$, $\angle O_2—S_1—O_3 = 112°$.

Within the experimental errors the above dimensions are the same as in the dihydrates. Also, the barium-oxygen coordination is the same, the barium ion being surrounded by nine oxygen atoms at an average distance of 2.78 Å. Six are sulphonate oxygen atoms and two are water oxygen atoms as in the dihydrates, and one is the oxygen atom of an acetone molecule. The water molecule is coordinated to two barium ions, at distances of 2.76 Å and 2.91 Å and an angle of 126°, and forms hydrogen bonds to the sulphonate oxygen atoms O_1 and O_1', at distances of 3.02 Å and an angle of 113°. This water molecule is firmly held in the lattice; it is the other water molecule of the dihydrates which in the solvate is replaced by acetone.

The carbon peaks in the electron density maps are low and diffuse, and the coordinates of these atoms are approximate only. Inclusion of the carbon contributions with half their weight in the calculated structure factors, with the same temperature factors as for the other atoms, gave about the same R index as when they were included with full weight and the larger temperature corrections. From the coordinates of Table 1 the closest approach between methyl carbon atoms of different acetone molecules, across symmetry centres at $z = \frac{1}{2}$ and $-\frac{1}{2}$, is 3.3 Å, which is rather short. As indicated earlier [1], there appears to be a possibility that the acetone content of the solvates is non-stoechiometric, in the sense that some of the acetone positions are, statistically, occupied by water. This might leave better space for the methyl groups. On the other hand, the large c spacing, *i.e.*, layer thickness, namely 13.21 Å as compared with 10.78 Å and 10.89 Å in the dihydrates [2, 3], is caused by the acetone molecules, and complete substitution of acetone by water would lead to collapse of the structure. The layers are held together through methyl-methyl contacts, the closest methyl-sulphur approach across a layer interface being 4.1 Å, which exceeds the sum of the van der Waals radii. Sulphur-sulphur contacts across the interface, which are 3.5—3.8 Å in the dihydrates [2, 3] and there hold the layers together, do not occur in the solvate, the shortest such distance being 5.3 Å.

THE NATURE OF BONDING IN THE SULPHUR CHAIN OF THE PENTATHIONATE ION

The objective of the structure determinations of the dimorphs of barium pentathionate dihydrate and of the solvate with acetone, has been more to establish the structure of the pentathionate ion than to obtain accurate dimensional data. However, each distance and angle has in the three structures been determined independently four times, once in each half of the ion in the triclinic dihydrate and once in each of the two other structures where mirror plane symmetry is crystallographically required. Taking the standard deviation of the individual measurements as 0.04 Å for S—S bond lengths and 3° for S—S—S bond angles, the standard deviation of the arithmetical mean of the four values should be 0.02 Å for bond lengths and 1.5° for angles *. The individual and mean values are listed in Table 3, and a drawing of the pentathionate ion, with the mean bond lengths and angles indicated, is shown in Fig. 3.

Table 3. Dimensions of the sulphur chain of the pentathionate ion in barium salts.

Bond or angle	Orthorhombic dihydrate	Triclinic dihydrate	Acetone solvate	Mean value
S_1-S_2	2.14 Å	2.13, 2.11 Å	2.11 Å	2.12 Å
S_2-S_3	2.04 Å	2.04, 2.04 Å	2.02 Å	2.04 Å
$\angle S_1-S_2-S_3$	103°	106, 105°	106°	105°
$\angle S_2-S_3-S_4$	106°	107°	105°	106°
$S_1S_2S_3/S_2S_3S_4$ (dihedral angle)	110°	108, 107°	108°	108°

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* The S_2—S_3—S_4 angle occurs only once also in the triclinic dihydrate, and the mean value of this angle should thus have a standard deviation of 2°.

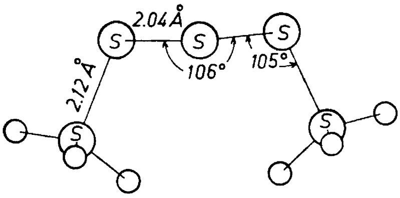

Fig. 3. The pentathionate ion as it occurs in the barium salts.

The difference, Δ, between the outermost S—S bonds, 2.12 Å, of the pentathionate ion, and the middle bonds, 2.04 Å, both with e.s.d. $\sigma = 0.02$ Å, gives $\Delta/\sqrt{2}\sigma = 2.8$ and should thus be significant. Variations in bond lengths along sulphur chains have been reported also for cesium hexasulphide[4], barium tetrasulphide monohydrate[5], barium tetrathionate dihydrate[6], and dimethanesulphonyl disulphide[7].

The middle S—S bonds in the pentathionate ion are between divalent sulphur atoms, and correspond formally to the S—S bonds of trisulphides, X—S—S—S—X. Data are available for dimethyl trisulphide[8] (S—S = 2.05 ± 0.02 Å), *bis*(trifluoromethyl) trisulphide[9] (2.065 ± 0.016 Å) and 2,2′-diiododiethyl trisulphide[10, 11] (2.05 ± 0.04 Å). In disulphides, X—S—S—X, the S—S bond length is 2.05 ± 0.02 Å in hydrogen disulphide[12], 2.04 ± 0.03 Å in dimethyl disulphide[12], 2.053 ± 0.019 Å in *bis*(trifluoromethyl) disulphide[9], 2.04 ± 0.005 Å in N,N′-diglycyl-L-cystine dihydrate[13], and 2.04 ± 0.02 Å and 2.04 ± 0.01 Å, respectively, in the monohydrates of formamidinium disulphide diiodide[14] and dibromide[15]. The weighted mean of these nine values, if they are assumed to be equal, is 2.045 Å, as compared with 2.04 Å for the short bonds in pentathionate. In orthorhombic sulphur[16], the S—S bonds are 2.037 ±0.005 Å.

The outermost S—S bonds in pentathionate are between a divalent sulphur atom and a sulphonate sulphur atom. Bonds of this type are 2.13 ± 0.04 Å in barium selenopentathionate dihydrate[17], 2.12 ± 0.03 Å in ammonium telluropentathionate[18], 2.10 ± 0.02 Å in monoclinic barium telluropentathionate dihydrate[19], and 2.12 ± 0.03 Å in barium tetrathionate dihydrate[6]. The weighted mean is 2.115 Å, again not significantly different from the length of the corresponding bond in pentathionate.

A -S—SO$_3$ bond should be expected to be close to a single bond, or possibly a little shorter if some of the *pd* π-bond character of the S—S bond in the thiosulphate ion[20] is retained when two such ions combine with divalent sulphur to give pentathionate. There does not appear to be any reason for the bond to be longer than a single bond. The S—S single-bond length is somewhat uncertain; the Pauling value[21] is 2.08 Å, and Abrahams first[4] proposed 2.11 Å and later[5, 22] 2.08 Å. A S—S double-bond length of[4, 21, 22] 1.89 Å, as in the S$_2$ molecule in the ground state, leads, with 0.21 Å as the difference between single- and double-bond length[21, 23], to 2.10 Å, and the same value is obtained from 1.82 Å as the length of a S—C single bond[22], and the C—C single-bond radius of 0.77 Å. The data indicate that Abrahams' first proposal[4], 2.11 Å, is closer to the S—S single-bond length than is 2.08 Å. A discussion of so small differences in bond lengths may be meaningless unless the hybridization ratio of the bond orbitals is defined, more *s* character in a σ bond leading to shorter bond lengths; however, for sulphur little information is available on this point. It appears that the 2.12 ± 0.02 Å S—S bonds of pentathionate are, at least, fairly close to single bonds.

The middle S—S bonds, of lengths 2.04 ± 0.02 Å, like the S—S bonds of the same length in di- and trisulphides and in orthorhombic sulphur, probably possess some double-bond character, arising from overlap of the $p\pi$ electron pair of one divalent sulphur atom with available 3*d* orbitals of a bond partner. Pauling's relation [23], $R = R_1 - 0.706 \log n$, leads to 22 % π-bond character, if R_1 is taken as 2.10 Å. Abrahams' curves [4, 5] give about 25 %. In view of the uncertain nature of the bond order and bond length data, the figures serve only to indicate orders of magnitude.

The sulphur-sulphur bonds of the pentathionate ion readily undergo heterolysis in reactions with nucleophilic reagents [24], [25]. The principal reaction type involves a nucleophilic attack on the middle sulphur atom of the chain, and leads to the elimination of one or both of the thiosulphate groups as anions. The pentathionate thus behaves as a thiosulphate of divalent sulphur. This has been interpreted [24] as due to a certain amount of ionic character, or polarity of the σ bond, in the direction of heterolysis, on the ground that ionic character, or polarity already present, ordinarily serves to facilitate the further polarizability of the bond in the direction of polarity. The degree of ionic character can hardly be more than a few per cent; it would, however, leave a fractional positive charge on the middle sulphur atom, if the bonds from this atom were pure σ bonds.

It has been argued [26], on the basis of the K_α X-ray emission spectra from sulphur in solid potassium pentathionate, that the divalent sulphur atoms, including the middle one, have not a positive, but a negative charge. The interpretation of X-ray emission spectra in terms of charge distributions may not be quite clear-cut, and a net negative charge on the divalent sulphur atoms appears unlikely in view of the, presumably *, positive charge on the sulphur atom of the terminal sulphonate groups. However, if the middle S—S bonds of pentathionate, of lengths 2.04 Å, possess π-bond character, electroneutrality of the middle sulphur atom may not be in disagreement with ionic character, as indicated, of the σ bonds. The π-bonding, if involving for each bond to a higher degree the 3*d* orbitals of the middle sulphur atom than of the adjacent sulphur atoms, will tend to neutralize the positive charge on the middle sulphur atom due to ionic character of the σ bonds. This would not contradict the formulation, on a reactivity basis, of pentathionate as a thiosulphate of divalent sulphur, it being the direction of polarity of the σ bond, notwithstanding neutralizing charges due to π-bonding, which is indicative of the preferred direction of heterolysis of a bond, and *vice versa.*

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* A positive charge (though less than one) on the sulphur atom of an ionized sulphonate group, $—SO_3^-$, may be inferred from its Hammett σ values [27-30], its acidifying effect on aliphatic acids [31], and the dipole moment of sulphur-oxygen bonds [32].

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