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The Crystal Structure of Triclinic Barium Pentathionate Dihydrate

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The unit cell of triclinic barium pentathionate dihydrate has the dimensions, a = 5.00 Å, b = 10.36 Å, c = 11.53 Å, α = 109°, β = 97°, γ = 90°. The space group is $C_i^1-P\bar{1}$ with Z = 2. Fourier projections along the a and b axes show that the pentathionate ion has an unbranched, *cis* configuration, with S_1-S_2 = 2.13 Å, S_2-S_3 = 2.04 Å, S_3-S_4 = 2.04 Å, S_4-S_5 = 2.11 Å (all ± 0.04 Å), $\angle\ S_1S_2S_3$ = 106°, $\angle\ S_2S_3S_4$ = 107°, $\angle\ S_3S_4S_5$ = 105° (all ± 3°), and the dihedral angles, $S_1S_2S_3/S_2S_3S_4$ = 108° and $S_2S_3S_4/S_3S_4S_5$ = 107°. These values agree within the experimental errors with those found earlier for the orthorhombic dimorph.

The crystals of triclinic and orthorhombic barium pentathionate dihydrate are composed of layers which have the same internal structure in both dimorphs, but are differently arranged relative to each other.

A study of the crystal chemistry of barium salts of pentathionic, selenopentathionic and telluropentathionic acids has recently led to the structure determination of the isomorphous salts, barium pentathionate [1] and selenopentathionate [2] dihydrates. The orthorhombic crystals have four-molecule unit cells based on the space group, $D_{2h}^{16}-Pnma$, with a = 5.00 Å, b = 10.30 Å, c = 21.78 Å for the pentathionate. No orthorhombic dihydrate of barium telluropentathionate has been found, although two dihydrates, one monoclinic and one triclinic, have been characterized and will be described later.

As mentioned earlier [3], a triclinic dimorph of barium pentathionate dihydrate exists. The unit cell dimensions, from oscillation and Weissenberg photographs taken with copper radiation, $\lambda(\text{Cu}K\alpha)$ = 1.54 Å, are [3]

$$a = 5.00\ \text{Å}, \quad b = 10.36\ \text{Å}, \quad c = 11.53\ \text{Å}$$
$$\alpha = 109^\circ \quad \beta = 97^\circ \quad \gamma = 90^\circ$$

There are two molecules per unit cell, and the space group is the centrosymmetric one, $C_i^1-P\bar{1}$.

It is seen that within the experimental accuracy (± 0.5 %) the lengths of the a and b axes of the triclinic and orthorhombic dimorphs are the same, as are also the γ angles. The spacing of the triclinic c plane, d_{001} = 10.78 Å, is close to half the orthorhombic c axis, 10.89 Å. Both dimorphs exhibit perfect cleavage along the c plane, and appear as prisms, elongated along the a axis and with {001} predominant.

In the orthorhombic space group, $00l$ reflections are systematically absent for odd values of l and as many are thus present as in the triclinic crystals. The intensities of the $00l$ reflections of the two dimorphs, with the orthorhombic l indices halved, are very similar. The one-dimensional projections on to a line perpendicular to the c planes of the two unit cells should thus be the same, and the common features noted above indicate further structural similarities.

A preliminary report on the structure of the triclinic crystals has been published [4], giving atomic coordinates and principal bond lengths and angles *.

Barium salts of pentathionic acid were apparently the first salts of the acid to be isolated, over a century ago. Lenoir [5] prepared a barium pentathionate in 1847, one year after the discovery of the acid by Wackenroder [6]. Lenoir crystallized the salt from aqueous solutions containing ethanol, and although he noted that the salt contained ethanol, he described it as a dihydrate. Fordos and Gélis [7], in 1848, stated that the salt always retains some ethanol when precipitated from water by means of ethanol, and said that the best method for the isolation of an ethanol-free salt, a dihydrate, was to crystallize from water by addition of ether containing some ethanol. Lewes [8], in 1881, isolated barium pentathionate without the use of ethanol, but gave the composition as that of a trihydrate, the same water content as he erroneously gave for barium tetrathionate. Debus [9], of the same laboratory as Lewes, in 1888 referred to Lewes' barium pentathionate as but 'nearly pure'. In 1933, Deines and Christoph [10] in a footnote reported on the isolation of barium polythionates, presumably also the pentathionate, from aqueous solutions by addition of ethanol or acetone, but did not give the compositions.

The present authors have isolated trihydrates of barium selenopentathionate and telluropentathionate, but of barium pentathionate, only dihydrates.

Of the earlier authors cited above, it appears that only Fordos and Gélis may have obtained a pure dihydrate. It will be shown later that several organic solvents, among them ethanol and acetone, give solvates when used for the crystallization of barium pentathionate. Lenoir, and Deines and Christoph, probably obtained solvates, and not pure hydrates.

EXPERIMENTAL

The barium pentathionate dihydrates were prepared as follows. A crude salt was obtained by mixing, at a temperature not above 40° C, saturated solutions of potassium pentathionate and a slight excess of barium perchlorate, filtering off the precipitated potassium perchlorate, and addition of ethanol and cooling. The crude preparation, which contained ethanol, was stable for months.

The triclinic dihydrate resulted when an aqueous solution of the crude product, saturated at 40—50° C, was allowed to cool to room or ice temperature. The orthorhombic dihydrate was obtained by addition of methanol to an aqueous solution saturated at 20—30° C. About 0.2 N hydrochloric acid, instead of pure water, was used to dissolve the pentathionates.

No study of the relative stabilities of the dimorphs at various conditions has been made. When pure, they both remain unchanged for months, and appear to be about equally stable.

The salts were analyzed iodometrically by means of the sulphite method [11]. In order to remove the barium as sulphate, so as to prevent the precipitation of barium sulphite which would interfere in the titration with iodine, some sodium sulphate was added to

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* In that report [3] and the earlier one [4], values for the α and β angles, respectively, were given which are larger than the present ones, believed to be more correct, by one degree. The change of β from 98° to 97° has led to bond lengths and angles which in a few cases differ slightly from those given in the preliminary report.

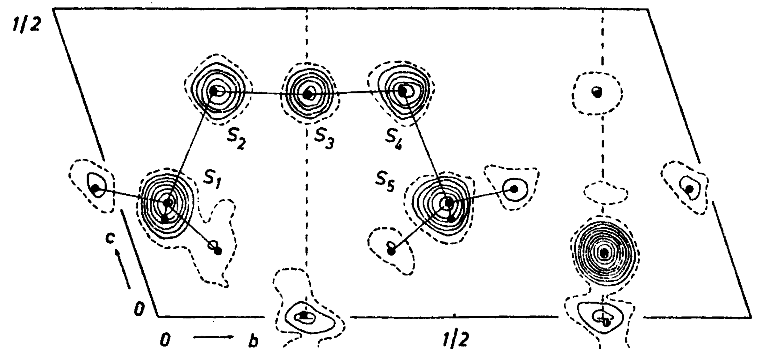

Fig. 1. Electron density projection of triclinic $BaS(S_2O_3)_2 \cdot 2H_2O$ *along the* a *axis. The atomic positions are marked with dots, and lines are drawn to show the outline of the pentathionate ion. The 5-electron line is dashed. Contour intervals: 10* $e \cdot Å^{-2}$ *for the barium ion, and 4* $e \cdot Å^{-2}$ *for sulphur and oxygen atoms and water molecules.*

the barium pentathionate solution before the addition of sodium sulphite reagent. One mole of pentathionate reacts with sulphite to produce two moles of thiosulphate, which is titrated with iodine after masking of excess of sulphite by means of formaldehyde.

Since analytical data have not been included in earlier communications on the salts [1,3], analyses of both modifications are reported here.

Orthorhombic dihydrate. 0.2839 × $\frac{1}{5}$ g substance: 26.20 ml of 0.01010 N iodine.

Triclinic dihydrate. 0.2719 × $\frac{1}{5}$ g substance: 24.88 ml of 0.01019 N iodine.

$BaS(S_2O_3)_2 \cdot 2H_2O$ (429.7) Mol. weights found, 429.2 and 429.0, respectively.

Absence of tetrathionate was checked through control analyses by means of the cyanide method.

The intensities of the $0kl$ and $h0l$ reflections of triclinic barium pentathionate dihydrate were estimated visually from zero layer Weissenberg photographs taken with copper radiation. Small crystals were used in order to minimize absorption, for which no correction was made. The ready cleavage along the *c* plane made it difficult to cut the crystals for photographs about the *b* axis, and as in the case of the orthorhombic structure [1], the observed intensities of the $h0l$ reflections are therefore probably less reliable than those of the $0kl$ reflections. The intensities were corrected for the Lorentz and polarization factors, and converted into relative structure factors. They were later put to an approximately absolute scale through comparison with the calculated values.

Patterson and Fourier projections along the *a* and *b* axes were made. The summations were performed by means of Beevers-Lipson strips, the Patterson and first Fourier summations at 12° intervals along the axes, and the final Fourier refinements by summations at 6° intervals along the two longest axes. No great accuracy in bond lengths and angles was aimed at, the chief objective being to establish the relation of the structure to that of the orthorhombic dihydrate.

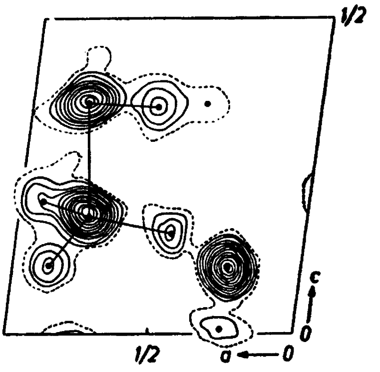

Fig. 2. Electron density projection of triclinic $BaS(S_2O_3)_2 \cdot 2H_2O$ along the b *axis. The 8-electron line is dashed. Contour intervals: 8 $e \cdot Å^{-2}$ for the barium ion, otherwise as in Fig. 1.*

DETERMINATION OF THE STRUCTURE

The $0kl$ Patterson map was prepared first, early in 1953, and on the basis of the barium y and z coordinates derived from the map, signs were calculated and used in a Fourier synthesis of 185 of the 265 observed $0kl$ reflections. The resulting map revealed the positions of the sulphur atoms, in accordance with the barium-sulphur vectors of the Patterson map, and also some of the oxygen atoms. At that phase of the work, attention was shifted from the triclinic to the orthorhombic dihydrate, the latter having a more favourable space group, and work on the former was resumed two years later, with Fourier refinement of the $0kl$ projection through successive approximations in the usual way.

The projection along the b axis was also solved by means of the heavy atom technique, using for the first sign calculation the already known z coordinate of barium and the x coordinate derived from the $h0l$ Patterson map. As was expected from the a axis projection and the orthorhombic structure, sets of two sulphur atoms and three oxygen atoms were found to overlap, having within the experimental accuracy the same x and z coordinates.

The electron density maps are shown in Figs. 1 and 2. The final atomic positions are marked with dots, and lines are drawn to show the sulphur-sulphur and sulphur-oxygen bonds. The coordinates of the positions, in fractions of cell edges and referring to the triclinic axes, are listed in Table 1.

Orthogonal coordinates, in Å, are given in Table 2 under the heading $P\bar{1}$. They refer to the same origin as in Table 1 and to the a, b and c' axes, where, since $\gamma = 90°$, c' is chosen normal to a and b. The coordinates listed in Table 2 under the heading *Pnma*, are those found in the orthorhombic dihydrate, cal-

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

	x	y	z		x	y	z
Ba	0.749	0.211	−0.104	O_1	0.462	0.070	0.158
S_1	0.755	0.077	0.186	O_2	0.920	−0.031	0.210
S_2	0.808	0.225	0.366	O_3	0.874	0.140	0.108
S_3	0.564	0.381	0.359	O_4	0.462	0.551	0.158
S_4	0.808	0.542	0.366	O_5	0.920	0.676	0.210
S_5	0.755	0.554	0.186	O_6	0.874	0.432	0.108
$(H_2O)_1$	0.253	0.250	0.007	$(H_2O)_2$	0.603	0.131	−0.363

culated from the fractional coordinates given earlier[1] and referred to a corresponding origin. In the orthorhombic structure, the Ba, S_3 and water oxygen atoms lie in a crystallographic mirror plane of symmetry, at $y = \frac{1}{4}$, and the S_5, S_4, O_4, O_5 and O_6 atoms are related to the S_1, S_2, O_1, O_2 and O_3 atoms, respectively, through this plane.

Table 2. Orthogonal coordinates for the two dimorphs of barium pentathionate dihydrate.

	x'(Å)		y'(Å)		z'(Å)	
	$P\bar{1}$	$Pnma$	$P\bar{1}$	$Pnma$	$P\bar{1}$	$Pnma$
Ba	3.89	3.90	2.58	2.58	−1.12	−1.09
S_1	3.51	3.50	0.10	0.13	2.01	2.05
S_2	3.53	3.58	0.96	0.95	3.96	4.03
S_3	2.32	2.35	2.60	2.58	3.88	3.90
S_4	3.53	3.58	4.24	4.20	3.96	4.03
S_5	3.51	3.50	5.04	5.02	2.01	2.05
O_1	2.09	2.11	0.13	0.08	1.71	1.70
O_2	4.31	4.10	−1.11	−1.12	2.27	2.37
O_3	4.22	4.15	1.05	0.97	1.17	1.09
O_4	2.09	2.11	5.12	5.07	1.71	1.70
O_5	4.31	4.10	6.22	6.27	2.27	2.37
O_6	4.22	4.15	4.07	4.18	1.17	1.09
$(H_2O)_1$	1.26	1.50	2.56	2.58	0.08	0.04
$(H_2O)_2$	3.53	3.25	2.72	2.58	−3.92	−3.70

In Table 4, observed and calculated values of structure factors are compared for all $0kl$ and $h0l$ reflections within the range of Cu$K\alpha$ radiation. The calculated values are based on the coordinates of Table 1, and the atomic scattering curves of the *International Tables*, with the xenon curve for the barium ion, and a temperature factor of $B = 2.2$ Å^2 for both zones. The reliability factor, $R = \Sigma \| F_{\text{obs}} | - | F_{\text{calc}} \| / \Sigma | F_{\text{obs}} |$, with non-observed reflections included only when $| F_{\text{calc}} |$ is greater than the smallest observable value of $| F_{\text{obs}} |$, is 0.18 for the $0kl$ and 0.19 for the $h0l$ reflections.

DISCUSSION

The average differences between the atomic coordinates of the triclinic and orthorhombic structures, as listed in Table 2, are 0.01 Å for the barium ion, 0.03 Å for the five sulphur atoms, 0.07 Å for the six sulphonate oxygen atoms, and 0.16 Å for the two water oxygen atoms. These differences are considered to be within the probable errors of the two structure determinations.

It follows that the configuration of the pentathionate ion in the triclinic crystals is the same as in the orthorhombic ones, and within the probable errors this applies also to the dimensions. The sulphur chain is unbranched and occurs in a *cis* form. The sulphur-sulphur bond lengths given in Table 3, and angles involving these atoms, are considered to be correct to within 0.04 Å and 3°, respectively.

Table 3. Sulphur-sulphur bond lengths and angles.

$S_1{-}S_2 = 2.13$ Å $\angle S_1S_2S_3 = 106°$ $S_4{-}S_5 = 2.11$ Å
$S_2{-}S_3 = 2.04$ $\angle S_2S_3S_4 = 107°$ $S_3{-}S_4 = 2.04$
$\angle S_3S_4S_5 = 105°$

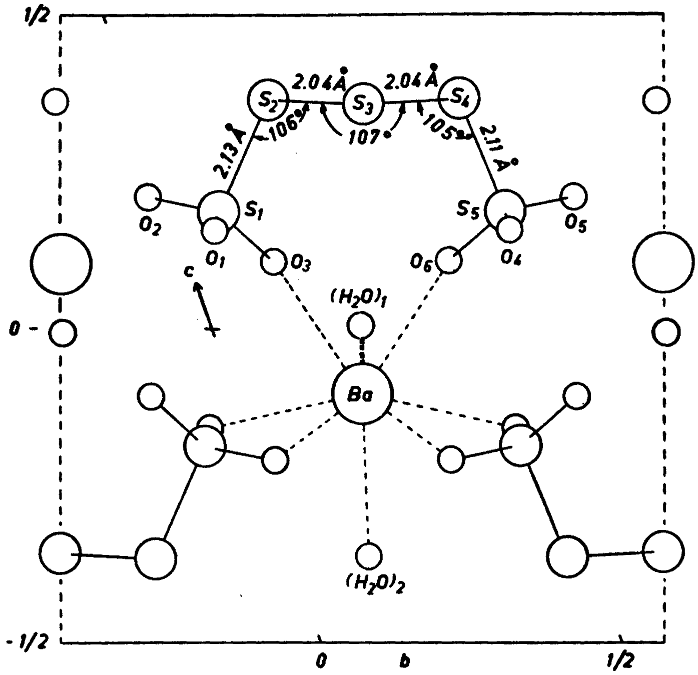

Fig. 3. Arrangement of the ions as seen along the a *axis. Origin at the midpoint of the left half of the figure.*

The dihedral angles, $S_1S_2S_3/S_2S_3S_4$ and $S_2S_3S_4/S_3S_4S_5$, are 108° and 107°, respectively. The corresponding data for the orthorhombic structure are[1], $S_1{-}S_2 = S_4{-}S_5 = 2.14$ Å, $S_2{-}S_3 = S_3 - S_4 = 2.04$ Å, $\angle S_1S_2S_3 = \angle S_3S_4S_5 =$ 103°, $\angle S_2S_3S_4 =$ 106°, and the dihedral angles, 110°.

The six sulphur-oxygen bonds of the sulphonate groups have an average length of 1.46 ± 0.01 Å. The electron density peaks of the oxygen atoms are rather low and diffuse, and the oxygen atoms were moved within the peaks to give reasonable and uniform S—O distances.

Each barium ion is surrounded by nine oxygen atoms, of which six are sulphonate oxygen atoms and three are water oxygen atoms. The average distance to barium for these nine atoms is 2.78 Å in both dimorphs. The water molecule, $(H_2O)_1$, is coordinated to two barium ions, at distances of 2.89 Å and 2.66 Å, and forms hydrogen bonds to the oxygen atoms O_1 and O_4, at distances of 3.04 Å and 3.15 Å and an angle of 108°.

In the orthorhombic space group, the barium ion and the middle sulphur atom of the pentathionate chain, as well as the two water oxygen atoms, lie in a mirror plane of symmetry. Although the triclinic space group possesses no crystallographic mirror plane of symmetry, an apparent mirror plane is present. From the Fourier maps, and the orthogonal coordinates of Table 2, is seen that the asymmetric unit possesses mirror plane symmetry within the

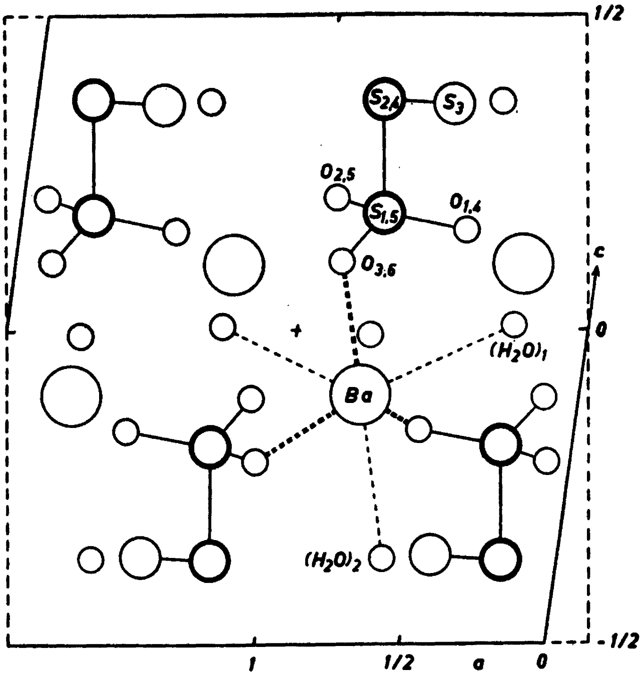

Fig. 4. Arrangement of the ions as seen along the b *axis.*

experimental error. The mirror plane, depicted through broken lines in Fig. 1, is normal to the b axis at $z = 0$, $y = \frac{1}{4}$ and $\frac{3}{4}$, as in the orthorhombic space group, and passes through the same atoms.

The similarity of atomic arrangement in the triclinic and orthorhombic dimorphs extends to within the boundaries of layers parallel to the c planes. The centres of symmetry which have been chosen as the origins of the coordinate systems are located in the middle of a layer, the thickness of which is equal to the triclinic c spacing, $d_{001} = 10.78$ Å, and half the orthorhombic c axis, $c/2 = 10.89$ Å. The line diagrams of Figs. 3 and 4, with boundaries at $z = \frac{1}{2}$ and $-\frac{1}{2}$, cover the thickness of one layer. The similarity of structure within a layer is apparent from a comparison of these diagrams with the corresponding ones for the orthorhombic structure[1].

The triclinic and orthorhombic dimorphs differ in the way in which the layers are arranged relative to each other. In the space group, D_{2h}^{16}-*Pnma*, layers are related to each other through glide planes a in their interface, at $z = \frac{1}{4}$ and $-\frac{1}{4}$, whereas in the space group C_i^1—$P\bar{1}$, the layers are related through symmetry centres in the interface. Since the layer thickness equals the triclinic c spacing, and the α and β angles are different from 90°, the symmetry centres operate to produce a simple repetition of layers, with successive relative displacements in the directions of the a and b axes. A transition from the orthorhombic to the triclinic structure, or *vice versa*, requires a rotation of

Table 4. Observed and calculated values of structure factors for triclinic barium pentathionate dihydrate.

hkl	F_{obs}	F_{calc}	*hkl*	F_{obs}	F_{calc}	*hkl*	F_{obs}	F_{calc}
001	61	+102	$0\bar{2}1$	51	−33	$0\bar{4}3$	47	+44
2	35	−42	2	43	−46	4	22	−23
3	48	−48	3	88	−92	5	58	−58
4	130	−153	4	21	−32	6	38	−42
5	20	−2	5	63	+75	7	19	−7
6	11	+11	6	79	+88	8	<7	+5
7	65	−58	7	44	+51	9	7	−3
8	37	+39	8	7	−11	10	11	+7
9	36	+34	9	52	−60	11	31	+26
10	34	+35	10	39	−45	12	31	+32
11	53	+61	11	18	−18	13	17	+24
12	17	−12	12	<7	−9	14	10	−5
13	23	−24	13	<6	+3	050	78	−67
010	3	+8	14	10	+7	1	57	+58
1	61	+75	030	92	+85	2	43	+39
2	95	+105	1	82	−70	3	20	+22
3	11	+12	2	112	−115	4	49	−47
4	27	+31	3	25	−39	5	61	−55
5	16	−6	4	47	+43	6	36	−30
6	70	−63	5	32	+41	7	21	−23
7	37	−32	6	63	+66	8	18	+13
8	37	−40	7	36	+36	9	25	+23
9	17	−17	8	9	+3	10	11	+13
10	31	+31	9	10	+5	11	10	+18
11	15	+16	10	34	−29	$0\bar{5}1$	9	+8
12	20	+18	11	30	−31	2	6	+3
13	16	+17	12	11	−14	3	18	−18
$0\bar{1}1$	21	+3	$0\bar{3}1$	18	−13	4	82	−75
2	75	−100	2	100	+79	5	61	−52
3	65	−79	3	69	+66	6	27	−35
4	12	−8	4	109	+117	7	<6	−3
5	22	−35	5	46	+58	8	59	+59
6	32	+28	6	31	−39	9	38	+47
7	63	+59	7	31	−37	10	24	+28
8	33	+29	8	20	−64	11	11	+16
9	37	+43	9	17	−45	12	14	−19
10	12	+1	10	7	−6	13	19	−18
11	31	−31	11	<7	−10	14	14	−14
12	16	−12	12	27	+23	060	44	−44
13	23	−22	13	31	+35	1	24	−27
14	9	−11	14	11	+15	2	79	+84
020	39	−34	040	60	+42	3	39	+38
1	68	−63	1	35	−29	4	39	+43
2	79	−79	2	59	−56	5	18	+21
3	20	+21	3	53	−49	6	50	−69
4	86	+94	4	21	−7	7	32	−35
5	68	+72	5	10	+13	8	23	−18
6	23	+25	6	<7	0	9	21	−19
7	33	−40	7	15	+8	10	15	+20
8	54	−63	8	35	+24	$0\bar{6}1$	12	−3
9	32	−30	9	29	+29	2	108	−94
10	9	−12	10	21	+26	3	49	−31
11	<6	−3	11	<5	−3	4	19	−19
12	9	+8	$0\bar{4}1$	116	+109	5	58	−62
13	10	+7	2	117	+103	6	64	+60

hkl	F_{obs}	F_{calc}	*hkl*	F_{obs}	F_{calc}	*hkl*	F_{obs}	F_{calc}
$0\bar{6}7$	70	+ 59	093	30	− 29	$0, \overline{12}, 6$	<5	− 1
8	30	+ 33	4	37	− 44	7	<5	+ 6
9	34	+ 49	5	46	− 17	8	18	− 25
10	37	− 47	6	<5	+ 5	9	20	− 20
11	44	− 53	7	8	+ 9	10	5	+ 3
12	9	− 14	$0\bar{9}1$	31	+ 21	$0, \overline{13}, 2$	12	+ 14
13	20	− 28	2	15	+ 18	3	17	+ 21
14	<4	+ 7	3	39	+ 10	4	8	− 8
070	63	+ 54	4	9	− 12	5	9	− 8
1	27	+ 19	5	21	− 11	6	<4	+ 1
2	9	− 8	6	38	− 43	7	17	− 25
3	25	+ 17	7	41	− 44	100	13	+ 1
4	32	+ 27	8	19	− 2	1	57	+ 61
5	<7	+ 4	9	23	+ 16	2	81	− 85
6	39	+ 33	10	32	+ 40	3	77	− 77
7	16	+ 9	11	29	+ 34	4	48	− 47
8	24	− 22	12	<5	+ 3	5	33	− 33
9	19	− 10	13	<4	0	6	56	+ 61
$0\bar{7}1$	99	− 79	0, 10, 0	11	+ 4	7	41	+ 46
2	<6	− 6	1	33	+ 35	8	26	+ 15
3	<6	+ 1	2	30	+ 34	9	24	+ 24
4	68	+ 57	3	<5	+ 2	10	31	− 15
5	61	+ 63	4	10	− 14	11	<23	− 15
6	17	− 14	5	19	− 25	12	<20	− 10
7	9	+ 12	$0, \overline{10}, 1$	11	− 11	13	18	− 25
8	<7	0	2	22	− 21	$\bar{1}01$	49	− 33
9	36	− 32	3	20	− 12	2	82	+ 81
10	12	− 9	4	15	− 8	3	57	+ 54
11	32	− 33	5	33	− 30	4	91	+ 91
12	21	− 19	6	20	− 24	5	24	+ 33
13	21	+ 21	7	9	0	6	95	−117
14	13	+ 10	8	28	+ 26	7	70	− 72
080	31	− 29	9	33	+ 39	8	25	− 21
1	49	− 49	10	47	+ 14	9	24	+ 2
2	32	− 21	11	10	− 9	10	46	+ 53
3	9	+ 2	12	13	− 16	11	23	+ 11
4	9	− 11	0, 11, 0	<6	+ 5	12	<22	− 5
5	15	+ 7	1	9	+ 8	13	30	+ 23
6	26	+ 22	2	18	+ 21	14	<10	+ 4
7	24	+ 22	3	16	+ 15	200	114	−113
8	18	+ 26	$0, \overline{11}, 1$	26	− 23	1	26	− 13
$0\bar{8}1$	<7	− 5	2	36	− 44	2	21	− 3
2	52	+ 57	3	29	− 27	3	46	− 38
3	89	+ 96	4	<7	0	4	49	+ 46
4	40	+ 40	5	27	+ 27	5	<21	+ 9
5	7	− 4	6	35	+ 42	6	31	+ 31
6	31	− 31	7	23	+ 26	7	<24	+ 7
7	38	− 44	8	<6	+ 3	8	25	− 22
8	18	− 12	9	<6	− 4	9	23	− 18
9	12	− 9	10	14	− 18	10	37	− 44
10	15	− 14	11	14	− 17	11	27	− 26
11	8	+ 12	0, 12, 0	23	− 31	12	16	+ 7
12	23	+ 21	1	7	+ 4	$\bar{2}01$	126	−120
13	22	+ 26	$0, \overline{12}, 1$	21	− 18	2	39	− 35
14	10	+ 23	2	<5	+ 1	3	18	+ 3
090	50	− 48	3	<5	0	4	67	+ 69
1	28	+ 22	4	30	+ 47	5	40	+ 51
2	13	− 13	5	27	+ 33	6	24	+ 9

hkl	F_{obs}	F_{calc}	*hkl*	F_{obs}	F_{calc}	*hkl*	F_{obs}	F_{calc}
$\bar{2}07$	29	+ 30	$\bar{3}09$	<25	+ 11	500	23	+ 12
8	<24	− 3	10	24	− 21	1	30	− 24
9	33	− 32	11	27	− 39	2	29	− 29
10	47	− 43	12	19	− 10	3	28	− 17
11	41	− 51	13	14	− 11	4	26	− 39
12	<21	− 3	400	60	+ 60	5	<19	+ 8
13	23	+ 26	1	36	+ 28	6	21	+ 35
300	40	− 47	2	24	+ 34	7	14	+ 18
1	26	+ 23	3	38	− 47	$\bar{5}01$	<25	− 13
2	58	+ 53	4	36	− 39	2	35	+ 29
3	51	+ 43	5	<25	+ 6	3	43	+ 61
4	66	+ 81	6	24	− 20	4	30	+ 13
5	<24	+ 6	7	<22	+ 5	5	<23	+ 9
6	43	− 49	8	<19	+ 9	6	34	− 27
7	38	− 39	9	<14	− 3	7	39	− 54
8	35	− 52	$\bar{4}01$	53	+ 57	8	<19	− 5
9	<22	0	2	26	− 36	9	<16	− 6
10	24	+ 29	3	30	− 11	10	<12	+ 2
11	<13	+ 8	4	32	− 12	600	24	− 36
$\bar{3}01$	23	− 12	5	33	− 35	1	16	− 18
2	34	− 42	6	<25	+ 17	2	<14	+ 1
3	66	− 65	7	<25	− 12	$\bar{6}01$	21	− 31
4	33	− 16	8	<24	− 12	2	<16	+ 5
5	22	− 25	9	27	+ 32	3	17	+ 19
6	39	+ 33	10	26	+ 14	4	20	+ 20
7	73	+ 79	11	24	+ 25	5	16	+ 15
8	33	+ 31	12	12	+ 19	6	<13	+ 1

180° of every second layer about an axis normal to the *c* plane, as well as displacements of layers along the *a* and *b* axes.

In both structures, weak van der Waals contacts only, between sulphur atoms, occur across the layer interfaces, and account for the ready cleavage of the crystals along the *c* plane. The different arrangements of layers lead to different sulphur-sulphur approaches, but the distances of the closest ones are practically the same, *viz.*, 3.61 Å and 3.78 Å in the orthorhombic and 3.51 Å, 3.57 Å, 3.73 Å and 3.74 Å in the triclinic structure.

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