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## A Neutron Diffraction Determination of the Structure of Beryllium Sulphate Tetrahydrate, $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$

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The crystal structure of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  (space group  $I\bar{4}c2$ ;  $a = 7.990 \text{ \AA}$ ,  $c = 10.688 \text{ \AA}$ ;  $Z = 4$ ) has been directly determined from the intensities of 251 independent three-dimensional single-crystal neutron reflexions with  $\sin \theta/\lambda \leq 0.7 \text{ \AA}^{-1}$ . The coordinates of the heavy atoms were obtained by the use of symmetry minimum and minimum functions and the hydrogen atoms were located from a 'weighted heavy atom' three-dimensional neutron scattering density Fourier synthesis. The parameters were further refined by the full-matrix least-squares method to an  $R$  value of 0.071. The positional parameters of the heavy atoms are in excellent agreement with a recent independent X-ray study of the same compound. The S-O distance in the sulphate group is  $1.464 \pm 0.004 \text{ \AA}$ . Four sulphate oxygens form a tetrahedron around beryllium with a Be-O distance of  $1.618 \pm 0.004 \text{ \AA}$ . The structure contains two hydrogen bonds from the water molecule to the sulphate oxygens of length  $2.684 \pm 0.005 \text{ \AA}$  and  $2.617 \pm 0.005 \text{ \AA}$ , the O-H distances being  $0.971 \pm 0.006 \text{ \AA}$  and  $0.967 \pm 0.006 \text{ \AA}$  (both uncorrected for thermal motion); the H-O-H angle is  $112.7 \pm 0.8^\circ$ .

### Introduction

The crystal structure of beryllium sulphate tetrahydrate was first studied using X-rays by Schonefeld (1931), who described the structure (in the space group  $I4/mcm$ ) as consisting of planar  $\text{SO}_4$  and tetrahedral  $\text{Be}(\text{H}_2\text{O})_4$  groups. Beevers & Lipson (1932) reinvestigated the structure and showed that the true space group is  $I\bar{4}c2$ ; the postulated structure had tetrahedral  $\text{SO}_4$  and  $\text{Be}(\text{H}_2\text{O})_4$  groups linked together by strong hydrogen bonds of length  $2.56 \text{ \AA}$  between the water and sulphate oxygens. That the hydrogen bonds were strong was also suggested from the study by Glemser & Hartert (1955) of the correlation between the O-H stretching frequency and the O---O distance in hydrates. Our aim in taking up the neutron diffraction study of this crystal was to investigate the effect of strong hydrogen bonds (if these were present in the crystal) on the shape of the water molecule.

Recently, Dance & Freeman (1969) have refined this structure using X-rays and this has also provided an opportunity to compare the structural parameters determined by the two methods.

### Experimental

The neutron diffraction intensity data were collected at the CIRUS reactor in Trombay using the double-crystal diffractometer 'DCD' (Chidambaram, Sequeira & Sikka, 1964) on which a General Electric single crystal orienter had been mounted in the 'symmetrical' position. The crystal used for data collection was parallelepiped in shape, of weight 25 mg, and was mounted with the longest dimension (8.4 mm) corresponding to the [110] direction along the  $\varphi$  axis. Before mounting the crystal on the goniometer, it was coated with an adhesive (brand name 'Stickfast') and then repeatedly dipped in liquid nitrogen to reduce extinction affects. The intensities of all the 275 independent reflexions up to  $\sin \theta/\lambda = 0.70 \text{ \AA}^{-1}$  were then measured at a wavelength of  $1.031 \text{ \AA}$  using the  $\theta-2\theta$  scan technique. The orientation angles,  $2\theta$ ,  $\chi$ ,  $\varphi$ , for each reflexion were set by hand. 24 reflexions had intensities less than their standard deviations computed from the counting statistics, and were treated as unobservables.

The integrated intensities were corrected for absorption ( $\mu = 1.78 \text{ cm}^{-1}$ , as measured experimentally). The

absorption factors, which were computed by the program *ORABS*\* (Wehe, Busing & Levy, 1962), varied from 0.773 to 0.810. The intensities were brought to a near-absolute scale by comparison with the 440 reflexion from a NaCl single crystal and  $|F_o|^2$  were then derived in the usual manner. The space group extinctions,  $hkl$  when  $h+k+l=2n+1$  and  $h0l$  when  $h$  or  $l=2n+1$ , were consistent with the tetragonal space groups  $I\bar{4}c2$  and  $I4/mcm$ . The cell constants used in our bond-length and angle calculations are:  $a=7.990 \pm 0.001 \text{ \AA}$  and  $c=10.688 \pm 0.006 \text{ \AA}$  (Dance & Freeman, 1969); there are four formula units in the unit cell.

### Solution of the structure

Because of the indirect manner in which Beevers & Lipson (1932) had derived their structure and also since we had three-dimensional data, we considered it worth while to determine the structure directly from neutron intensities. The statistical  $N(z)$  test of Howells, Phillips & Rogers (1950) seemed to favour the non-centred space group  $I\bar{4}c2$ , so it was chosen to be the correct space group. The structure was solved by the procedure described by Simpson, Dobrott & Lipscomb (1965), in which the Patterson function  $P(uvw)$  is interpreted through the use of symmetry minimum and minimum functions.† The computation of the sym-

\* This and all other calculations were carried out in the CDC 3600 computer at the Tata Institute of Fundamental Research, Bombay.

† The structures of potassium hydrogen chloromaleate (Ellison & Levy, 1965) and orthorhombic acetamide (Hamilton, 1965) have been solved by the same procedure.

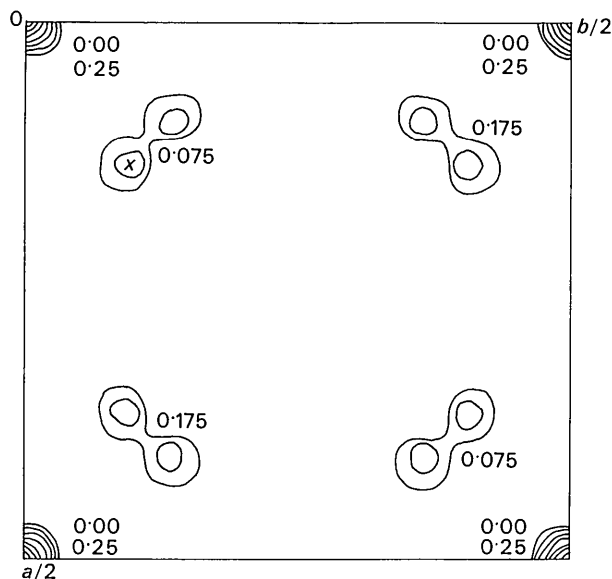


Fig. 1. Composite map of the symmetry minimum function  $Q(x, y, z)$ . The decimal fractions indicate the  $z$  coordinates of the levels from which the contoured portions were taken. The cross indicates the atom which was chosen for the calculation of the minimum function. Zero contours are omitted.

metry minimum function involved testing each grid point  $(x, y, z)$  in the asymmetric unit for possible atomic positions by taking the minimum of the Patterson values at the ends of the vectors between this point and points related to it by the space group symmetry. The form of the symmetry minimum function was the following:

$$Q(x, y, z) = \min [0.25P(2x, 0, \frac{1}{2}), 0.25P(0, 2y, \frac{1}{2}), \\ 0.5P(2x, 2y, 0), 0.5P(x-y, x+y, 2z), \\ 0.5P(x+y, x-y, 2z), 0.5P(x-y, x-y, \frac{1}{2}+2z), \\ 0.5P(x+y, x+y, \frac{1}{2}+2z)].$$

The Patterson function was not sharpened. The resultant map for the asymmetric unit is shown in Fig. 1. This map contains maxima, corresponding to each of eight  $\bar{4}$  centres  $(000, 00\frac{1}{2}, \frac{1}{2}\frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{1}{2}0, 0\frac{1}{2}\frac{1}{2}\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}\frac{1}{2})$  all of which are possible origins of the  $I\bar{4}c2$  space group and thus give rise to an eightfold ambiguity in the choice of origin. The peak marked X was then selected for the calculation of the 16-fold Buerger minimum function:

$$S(x, y, z) = \min [P(x-x_0, y-y_0, z-z_0), \\ P(x+x_0, y+y_0, z-z_0), \text{ etc.}],$$

where  $(x_0, y_0, z_0)$  are the coordinates of the chosen atomic position and the minimum was taken of all the sixteen Patterson values at the ends of the vectors between  $(x, y, z)$  and sixteen equivalent positions  $(x_0, y_0, z_0; -x_0, -y_0, z_0; \text{etc.})$ . The function  $S(x, y, z)$  (Fig. 2) contained only four definite maxima in the asymmetric unit and these were assigned to S, Be, O(1) and O(2) from peak height and symmetry considerations. The hydrogen atoms did not show up in this map. At this stage, a Fourier synthesis of the nuclear scattering density calculated with phases based on the contributions of S, Be, O(1) and O(2), omitting terms for which  $|F_o| \geq 2|F_c|$  failed to show the hydrogen peaks. However a 'weighted' nuclear scattering density synthesis clearly revealed sizable negative peaks corresponding to the hydrogen positions. In this synthesis the coefficients used were  $\omega|F_o|$  where  $\omega = I_1(x)/I_0(x)$  (Sim, 1961);  $I_0(x)$  and  $I_1(x)$  are respectively the zero-order and first-order Bessel functions of the first kind and  $x = 2|F_o| |F_c| / \sum b_H^2$  ( $\sum b_H^2$  is the sum of the squares of the scattering amplitudes of the hydrogen atoms in the unit cell). The  $R$  value ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ) at this stage was 0.283.

### Refinement

Isotropic refinement using the program *ORFLS* (Busing, Martin & Levy, 1962) based on  $|F|^2$ , starting from the parameters obtained in the last section and weights based on counting statistics, immediately indicated the presence of severe extinction. Corrections for extinction were made by the method described elsewhere (Sikka, Momin, Rajagopal & Chidambaram,

1967), in which it can be approximated by the expression:\*

$$E \approx \frac{|F_o|^2}{|F_c|^2} \approx 1 - G \cdot \frac{|F_c|^2}{\sin 2\theta} \cdot \frac{\frac{1}{V} \int_V T e^{-\mu T} dV}{A(\mu)}$$

Here  $G$  is a constant,  $A(\mu)$  the absorption factor and  $T$  the sum of the path lengths of the incident and reflected beams inside the crystal for the element of volume  $dV$ .  $F_c$  is the calculated structure factor following an anisotropic refinement in which the reflexions suffering from extinction have been omitted.

For applying the correction to  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  data, an anisotropic refinement in which 41 parameters – one scale factor, 12 positional and 28 temperature parameters – were varied was carried out omitting reflexions with  $|F_o|^2 / \sin 2\theta \geq 20$ . This converged at an  $R$  value of 0.130. The constant  $G$  was estimated by a least-squares fit of the values for which  $|F_o|^2 / |F_c|^2 \geq 0.70$ . The corrections beyond this range were read directly from the plot by extending it visually. After application of this correction the  $R$  value became 0.105. Two further cycles of refinement lowered the  $R$  value to 0.095. An error analysis at this stage indicated that the errors based on counting statistics were underestimated. The new weighting scheme was derived from the expression:

$$\omega^{-1} = \langle |A(F^2)| \rangle_{av} \approx 1.3 + 0.022 \frac{|F_o|^2}{\sin 2\theta}$$

After two more cycles of refinement, the  $R$  value was 0.073. The extinction correction† was repeated at this stage with new values of  $F_c$ 's and with a better value

\* It should be pointed out here that an extinction correction based on the more approximate expression

$$E \approx 1 - G' \frac{|F_c|^2}{\sin 2\theta}$$

leads to essentially the same positional and thermal parameters and gives nearly the same  $R$  value.

† To give an idea of the extinction correction, it may be mentioned that the most severely affected reflexion was 112 for which  $E \approx |F_o|^2 / |F_c|^2 = 0.56$ . The number of reflexions in various ranges of  $E$  were: 3 in 0.56 to 0.59, 5 in 0.60 to 0.69, 9 in 0.70 to 0.79, 17 in 0.80 to 0.89 and 217 in 0.9 and above.

of  $G$ . The various discrepancy factors defined by  $R_x = [\sum ||F_o|^x - |F_c|^x| / \sum |F_o|^x]$  computed from the final refinement are as follows:

Set	1	2
$x=1$	0.071	0.066
$x=2$	0.082	0.080
Number of data	251	237

where set 1 includes all data and set 2 data which have  $|F_o|^2 > \omega^{-1}$ .

The final positional and temperature parameters are given in Table 1. The observed and calculated squared structure factors are compared in Table 2. Some of the bond distances and bond angles calculated by the program *ORFFE* (Busing, Martin & Levy, 1964) are presented in Table 3. These have not been corrected for thermal motion because of the somewhat unreasonable temperature factors of H(2) and S. A composite Fourier synthesis of the structure calculated using the program *FORDAP* (Zalkin, 1962) is presented in Fig. 3.

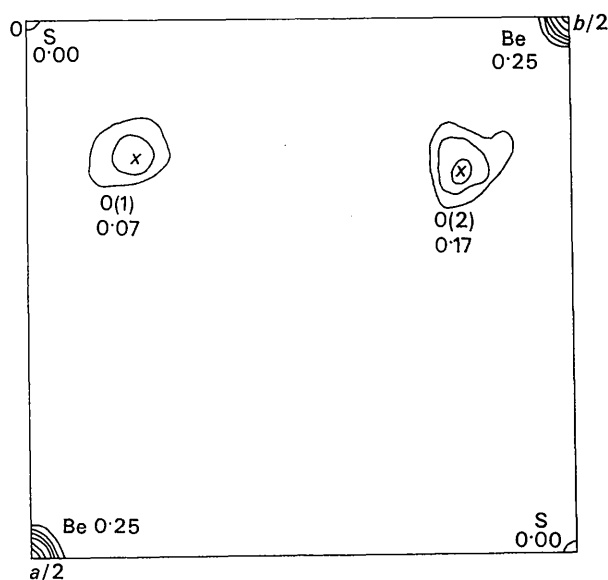


Fig. 2. Composite map of the minimum function  $S(x, y, z)$ . The decimal fractions indicate the  $z$  coordinate of the levels from which the contoured portions were taken. The contours are at equal arbitrary intervals. Zero contours are omitted.

Table 1. Positional and thermal parameters

The expression for the temperature factor is

$$\exp[-2\pi^2(h^2a^*2U_{11} + k^2b^*2U_{22} + l^2c^*2U_{33} + 2hka^*b^*U_{12} + 2hlc^*a^*U_{13} + 2klb^*c^*U_{23})]$$

The least-squares standard errors are given in parentheses.

	Fractional coordinate ( $\times 10^5$ )			Thermal parameter ( $\text{\AA}^2 \times 10^4$ )					
	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
S	0	0	0	28 (25)	$U_{11}$	421 (62)	0	0	0
Be	0	50000	25000	136 (12)	$U_{11}$	151 (17)	0	0	0
O(1)	12563 (50)	8408 (49)	7733 (49)	313 (20)	163 (16)	452 (19)	48 (15)	-221 (18)	-81 (16)
O(2)	13758 (57)	39560 (47)	17093 (49)	358 (21)	148 (18)	446 (21)	-73 (16)	216 (18)	-114 (16)
H(1)	22729 (105)	45696 (96)	13106 (82)	416 (43)	319 (32)	511 (40)	-26 (27)	240 (39)	4 (30)
H(2)	12290 (82)	28418 (57)	13628 (65)	327 (30)	108 (30)	423 (33)	-21 (18)	8 (27)	-70 (24)

## Discussion

## Comparison with X-ray structure

It appears that the X-ray structure determined by Beevers & Lipson (1932) is basically correct. The errors in the coordinates are, however, significant, the maximum being 0.13 Å in the  $y$  coordinate of O(1). As a consequence, the hydrogen bonds are not as strong as indicated by Beevers & Lipson's structure – 2.62 and 2.68 Å instead of 2.56 Å. The positional parameters of O(1) and O(2), as determined from our neutron study, have been compared in Table 4 with the values found in the X-ray study of Dance & Freeman (1969); the differences in the two sets of bond lengths and bond angles (not involving hydrogen atoms) are given in Tables 5 and 6. It is noticed that no coordinate, bond length or bond angle differs by more than 1.86 times the 'pooled' error. The agreement between the two structures should be considered excellent.\* The differences with respect to the positional parameters of the hydrogen atoms, *viz.* 0.07 and 0.17 Å, are not bad considering the well known difficulty in locating hydrogen atoms by X-ray methods. The thermal parameters of O(1) and O(2) in the two structures are in reasonable agreement. In view of the scattering amplitudes of the various atoms in the structure for X-rays and neutrons, our values for the thermal parameters of Be

\* It may be noted that a deviation of up to  $\pm 1.96\sigma$  lies inside a 95% confidence interval, assuming a normal distribution of errors (Hamilton, 1964).

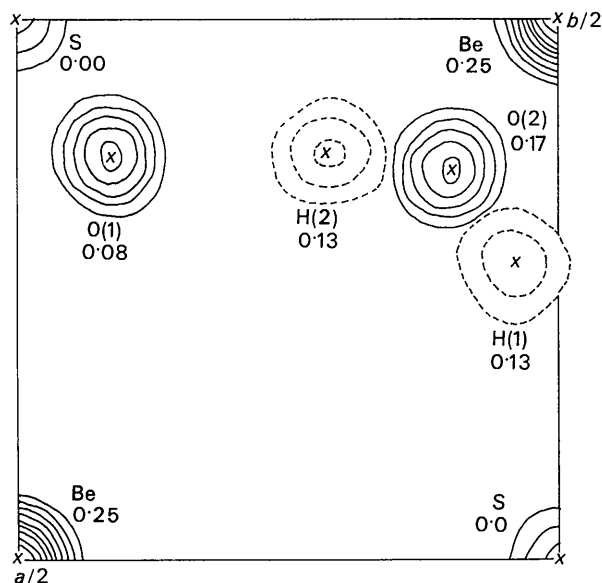


Fig. 3. Composite map of the final three-dimensional nuclear scattering density of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ . The positive and the negative contours (shown by broken lines) are at intervals of  $0.46 \text{ cm} \times 10^{-12} \text{ \AA}^{-3}$ . The zero contours have been omitted. The decimal fractions indicate the  $z$  coordinates of the levels from which the contoured portions were taken.

and those of Dance & Freeman for S are perhaps relatively more reliable.

Table 2. Observed and calculated squared structure factors for  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$

The nuclear scattering lengths used are (in units of  $10^{-12} \text{ cm}$ ): oxygen 0.581, beryllium 0.774; sulphur 0.284; and hydrogen – 0.378.

The five columns in each set contain respectively the Miller indices  $h, k, l$ ,  $100|F_o|^2$  and  $100|F_c|^2$ .

0 0 2	43	29	5 2 1	468	156	7 4 1	542	534
4	6125	6496	3	2994	3295	3	217	95
6	2026	2247	5	2171	1950	5	358	312
8	12163	12232	7	1851	2113	7	555	509
12	12276	12169	9	171	146	7 5 0	938	676
14	1044	1014	11	151	12	2	408	345
1 1 0	36	40	13	637	609	4	4126	4229
2	8794	8919	5 3 0	783	604	6	2840	2459
4	1133	1271	2	6595	6585	8	680	756
6	1584	1574	4	2512	2610	7 6 1	830	944
8	244	202	6	1345	942	3	900	640
10	1926	1897	8	613	731	5	72	322
14	1693	1462	10	1071	1043	7	519	550
2 0 0	9591	9477	12	444	623	7 7 0	2245	2318
2	333	262	5 4 1	1444	1151	2	114	270
6	1271	1289	3	768	627	6	1580	1864
8	2031	2026	5	3042	2759	8 0 0	4818	5027
10	1913	1628	7	926	1058	2	569	467
12	848	905	9	552	541	4	2631	2554
14	73	72	11	269	234	6	125	311
2 1 1	346	284	5 5 0	912	599	8	603	605
3	2466	2254	2	4260	4252	8 1 1	1148	1377
5	4187	4575	6	682	864	3	663	630
7	389	456	8	1938	1955	5	872	983
9	2188	2077	10	3722	3622	7	939	997
11	1662	1745	6 0 0	285	83	9	257	15
2 2 0	7898	7468	2	5731	5866	8 2 0	2262	2266
2	507	498	4	2105	2339	2	1237	1326
6	84	151	6	744	792	4	541	554
8	4038	3962	8	2269	2299	6	692	582
10	497	535	10	2537	2070	8	517	533
12	426	165	12	199	66	10	280	248
3 1 0	968	926	6 1 1	3099	3561	8 3 1	1440	1303
2	146	138	3	2761	3561	3	922	1058
4	1511	1577	5	2894	2720	5	301	290
6	6071	6407	7	330	331	7	1253	1252
8	1754	1759	9	1061	1207	8 4 2	1576	1441
10	1233	1088	11	329	349	4	1822	2238
12	336	29	6 2 0	2825	2413	6	1581	1717
3 2 1	7061	6829	2	127	417	8	1277	1355
3	10105	9047	4	1351	1197	8 5 1	796	277
5	492	274	6	153	87	3	1573	1159
7	495	521	8	677	481	5	564	481
9	2814	2661	10	840	666	7	362	522
11	602	751	12	92	443	8 6 2	1606	1276
13	253	241	6 3 1	5703	5896	4	1804	1684
3 3 0	1644	1328	3	4987	4721	6	126	120
2	3108	3056	5	326	376	8 7 3	416	425
10	222	191	7	289	104	9 1 2	2501	2484
12	513	580	9	654	528	4	767	897
4 0 0	14814	14737	11	297	352	6	92	47
2	672	459	6 4 0	6306	5838	9 2 1	1991	1984
4	11608	11576	2	2100	2122	3	191	284
6	1584	1719	4	177	107	5	1079	1079
8	6779	6720	6	1564	1510	7	948	904
10	434	441	8	776	457	9 3 2	681	453
4 1 1	670	491	10	1686	1732	4	882	662
3	1200	1168	6 5 1	585	619	6	1818	1678
5	852	676	3	617	780	9 4 3	285	343
7	1340	1461	5	903	948	5	147	319
9	98	44	7	195	157	7	278	241
11	106	21	9	491	407	9 5 0	389	247
4 2 0	180	122	6 6 0	525	375	2	666	751
2	6436	6463	2	118	87	4	85	152
4	5356	5749	4	281	486	9 6 1	456	846
6	981	1058	6	578	638	3	820	637
8	638	578	8	2116	2456	10 0 0	3543	3668
12	436	530	7 1 0	3857	4144	2	1665	1737
4 3 1	799	676	2	2484	2716	4	299	356
3	1360	1572	4	3025	2762	6	741	635
5	1465	1524	6	330	315	10 1 3	88	180
7	3535	3421	8	1055	1153	10 2 0	210	250
9	742	848	10	384	395	2	282	307
11	1033	691	7 2 1	3004	3154	4	1265	1061
13	58	107	3	2150	1800	6	519	279
4 4 0	21806	22587	5	299	363	10 3 1	1352	1211
2	1059	799	9	1499	1551	3	369	109
4	463	77	7 3 2	2641	2755	5	419	536
6	199	81	4	899	893	10 4 2	572	539
10	920	1010	6	953	930	4	1446	857
12	2608	2811	8	917	1088	10 5 1	273	96
5 1 4	2199	2275	10	856	887	11 1 0	516	462
6	10201	10478				11 2 1	719	441
8	98	145						
12	763	746						

Table 3. Bond distances (Å) and bond angles (°) uncorrected for thermal motion

The standard deviations are given in parentheses\*

SO <sub>4</sub> tetrahedron			
S—O(1)	1.464 (4)	O(1)—S—O(1 <sup>i</sup> )	111.2 (2)
O(1)—O(1 <sup>i</sup> )†	2.416 (8)	O(1)—S—O(2 <sup>v</sup> )	108.6 (2)
O(1)—O(1 <sup>v</sup> )	2.377 (7)		
Be(H <sub>2</sub> O) <sub>4</sub> tetrahedron			
Be—O(2)	1.618 (4)	O(2)—Be—O(2 <sup>ii</sup> )	117.0 (2)
O(2)—O(2 <sup>vi</sup> )	2.582 (8)	O(2)—Be—O(2 <sup>vi</sup> )	105.8 (2)
O(2)—O(2 <sup>iii</sup> )	2.760 (9)		
Water molecule and the hydrogen bonds			
O(2)—H(1)	0.967 (6)	H(1)—O(2)—H(2)	112.7 (8)
O(2)—H(2)	0.971 (8)	O(1)—O(2)—O(1 <sup>iii</sup> )	114.6 (2)
O(2)—O(1)	2.684 (5)	O(2)—H(1)—O(1 <sup>iii</sup> )	171.7 (8)
O(2)—O(1 <sup>iii</sup> )	2.617 (5)	O(2)—H(2)—O(1)	172.3 (6)
H(1)—O(1 <sup>iii</sup> )	1.656 (8)	Be—O(2)—H(1)	118.2 (5)
H(2)—O(1)	1.719 (6)	Be—O(2)—H(2)	126.2 (5)
H(1)—H(2)	1.614 (10)	Be—O(2)—O(1)	130.4 (3)
		Be—O(2)—O(1 <sup>iii</sup> )	113.2 (2)

\* The errors given here have been calculated from the variance-covariance matrix of the final least-squares refinement and do not include the cell-constant errors.

† Code for symmetry-related atoms:

Superscript	Atom at			Superscript	Atom at		
—	x	y	z	v	y	$\bar{x}$	$\bar{z}$
i	$\bar{x}$	$\bar{y}$	z	vi	$\bar{y}$	x	$\bar{z}$
ii	$\bar{x}$	1-y	z		$\frac{1}{2}-y$	$\frac{1}{2}+x$	$\frac{1}{2}-z$
iii	$\frac{1}{2}-x$	$\frac{1}{2}+y$	z		$-\frac{1}{2}+y$	$\frac{1}{2}-x$	$\frac{1}{2}-z$
iv	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	z				

Table 4. Differences in coordinates obtained from neutron and X-ray studies

Atom	Parameter	Difference  (Δ)	Pooled error (σ)	* Δ/σ
O(1)	x	0.0003	0.0007	0.43
	y	0	0.0007	0.00
	z	0.0001	0.0006	0.17
O(2)	x	0.0004	0.0008	0.50
	y	0.0012	0.0007	1.71
	z	0.0009	0.0006	1.50

\* The 'pooled' error is  $\sigma = (\sigma^2_{\text{neutron}} + \sigma^2_{\text{X-ray}})^{1/2}$

Table 5. Differences in bond distances obtained from neutron and X-ray studies

Bond	Difference  (Δ)	'Pooled' error (σ)	Δ/σ
S—O(1)	0.001 Å	0.006 Å	0.17
O(1)—O(1 <sup>i</sup> )	0.003	0.010	0.30
O(1)—O(1 <sup>iv</sup> )	0.002	0.010	0.20
Be—O(2)	0.008	0.006	1.33
O(2)—O(2 <sup>vi</sup> )	0.016	0.010	1.60
O(2)—O(2 <sup>iii</sup> )	0.007	0.011	0.64
O(2)—O(1)	0.013	0.007	1.86
O(2)—O(1 <sup>iii</sup> )	0.007	0.007	1.00

Table 6. Differences in bond angles obtained from neutron and X-ray studies

Angle	Difference  (Δ)	'Pooled' error (σ)	Δ/σ
O(1)—S—O(1 <sup>i</sup> )	0.1°	0.3°	0.33
O(1)—S—O(1 <sup>iv</sup> )	0.0	0.3	0.00
O(2)—Be—O(2 <sup>ii</sup> )	0.5	0.3	1.67
O(2)—Be—O(2 <sup>vi</sup> )	0.2	0.3	0.67
Be—O(2)—O(1)	0.3	0.4	0.75
Be—O(2)—O(1 <sup>iii</sup> )	0.5	0.3	1.67
O(1)—O(2)—O(1 <sup>iii</sup> )	0.3	0.3	1.00

#### Water molecule and hydrogen bonding

The environment of the oxygen atom of the water molecule is illustrated in Fig. 4. The sum of the three angles Be—O(2)—H(1), Be—O(2)—H(2) and H(2)—O(2)—H(1) is 357°. Thus, the lone-pair coordination of the water molecule in the structure is almost planar trigonal

and is of type *D* in the classification of Chidambaram, Sequeira & Sikka (1964). The two O—H orbitals of each water oxygen are utilized to form hydrogen bonds: O(2)—H(1)---O(1<sup>iii</sup>) and O(2)—H(2)---O(1) where O(1) and O(1<sup>iii</sup>) belong to two different SO<sub>4</sub> tetrahedra. Each sulphate oxygen atom acts as the negative end of two hydrogen bonds from two different water mol-

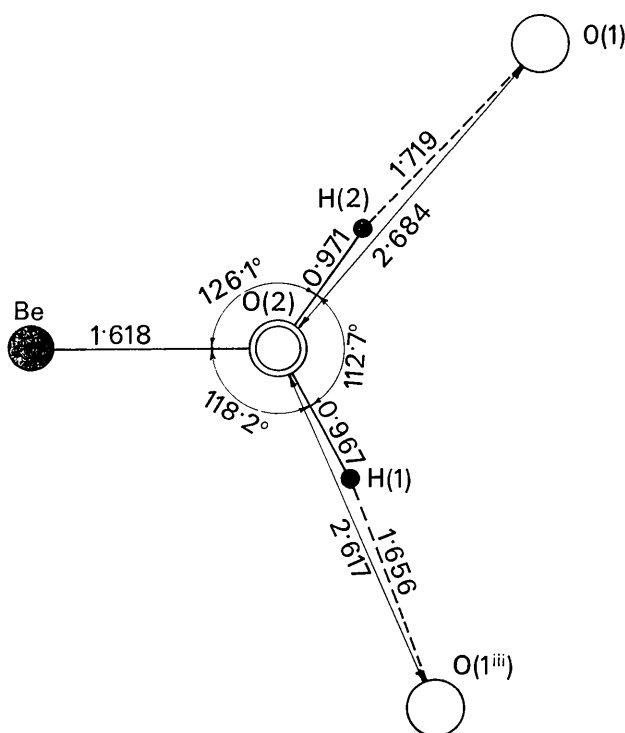


Fig. 4. The environment of the water oxygen in the structure of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ .

ecules. The lengths of the hydrogen bonds are 2.617 and 2.684 Å. The former is one of the shortest distances found in hydrates. The O-H distances, 0.971 and 0.967 Å (both uncorrected for thermal motion) are close to the O-H distance in water vapour.

The angles  $\text{H}(1)\text{-O}(2)\text{---O}(1^{\text{iii}})$  and  $\text{H}(2)\text{-O}(2)\text{---O}(1)$  are  $5.3^\circ$  and  $4.9^\circ$  and the dihedral angle between

the  $\text{H}(1)\text{-O}(2)\text{-H}(2)$  and  $\text{O}(1)\text{---O}(2)\text{---O}(1^{\text{iii}})$  planes is  $4.2^\circ$ . The H-O-H angle of  $112.7^\circ$  is significantly larger than the vapour value of  $104.5^\circ$ ; it has been noted earlier that the H-O-H angles for the type D coordinated water molecule are generally high (Chidambaram, Sequeira & Sikka, 1964; Baur, 1965; Pietrzak, 1966). This effect is probably more than usually pronounced in  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  because of the short Be-O(2) contact of 1.618 Å.

The lengths and orientations of interproton vectors as obtained from the proton magnetic resonance technique (Pietrzak, 1965) and from this study are compared in Table 7. The agreement between the two results is satisfactory.

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Table 7. The length and orientation of the interproton vectors of the water molecules

Parameter*	Neutron diffraction	Proton magnetic resonance† (Pietrzak, 1965)
$r$ ‡	$1.614 \pm 0.010$ Å	$1.63 \pm 0.01$ Å
$\alpha$	$58.9 \pm 0.4^\circ$	$57^\circ$
$\beta$	$31.2 \pm 0.4$	33
$\gamma$	$92.0 \pm 0.4$	90

\*  $r$  is the length of the inter-proton vector and  $\alpha, \beta, \gamma$  are the angles which this vector makes with the crystallographic axes,  $a, b, c$  respectively. By symmetry there are four non-parallel vectors at  $\alpha, \beta, \gamma$ ;  $\alpha, \beta, 180 - \gamma$ ;  $\beta, 180 - \alpha, \gamma$ ; and  $\beta, 180 - \alpha, 180 - \gamma$ .

† The values of the angles given by Pietrzak are  $102^\circ, 12^\circ, 90^\circ$ . The values in the above table have been recalculated assuming that his values are with respect to a pseudo-cell of dimensions,  $a' = a/2$  and  $c' = c/2$  referred to by him. This pseudo-cell is rotated by  $45^\circ$  about the  $c$  axis from the normal unit cell.

‡ The neutron diffraction value has not been corrected for thermal motion while the proton magnetic resonance value has been corrected for thermal motion by the method given by Pedersen (1964).