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Refinement of the Crystal Structure of Beryllium Sulphate Tetrahydrate

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Refinement of the crystal structure of $BeSO_4.4H_2O$ by X-ray methods has confirmed the results of an earlier analysis. The unit cell is tetragonal with $a=7{\cdot}990$ Å, $c=10{\cdot}688$ Å, space-group $I\bar{4}c2$. The lattice is built up from $Be(OH_2)_4^{2+}$ and SO_4^{2-} ions. The bond distances are $S\text{–}O=1{\cdot}465$ and $Be\text{–}OH_2=1{\cdot}610$ Å, with estimated standard deviations 0·004 Å. When corrected for differential thermal vibration, these distances become 1·482 and 1·622 Å, respectively. The tetrahedral $Be(OH_2)_4$ and SO_4 groups both possess slight angular distortions from T_d symmetry. The hydrogen atoms could not be located with precision but the probable geometry of the water molecule can be deduced from the hydrogen-bonding. The crystals exhibit strong diffuse X-ray scattering.

Introduction

The crystal structure of $BeSO_4.4H_2O$ was determined by Beevers & Lipson (1932). The arrangement of the tetrahedral $Be(OH_2)_4^{2+}$ and SO_4^{2+} ions is based on a slightly elongated cesium chloride lattice. Each SO_4^{2+} ion is surrounded by eight $Be(OH_2)_4^{2+}$ ions, and each O(sulphate) atom is hydrogen-bonded to H_2O molecules belonging to two of these.

The purpose of the present refinement was the accurate determination of the dimensions of the sulphate ion. $BeSO_4.4H_2O$ was selected because, as in $Li_2SO_4.H_2O$ (Larson, 1965), the X-ray scattering power is dominated by the contribution of the sulphate ion. Unlike $Li_2SO_4.H_2O$, however, the beryllium salt has a crystal structure in which the sulphate ions are held by forces which cause a minimal perturbation of their symmetry and dimensions. In this sense the present work complements that of Larson (1965).

Procedure

Experimental

The salt ('AnalaR' grade), crystallized from *ca.* 10*N* sulphuric acid solution, was sealed in Lindemann glass capillary tubes for X-ray examination (because of its toxicity). Cu *Kα* radiation was used. The unit-cell dimensions were fitted by Cohen's least-squares method (Buerger, 1942) to the sin *θ* values of 51 high-angle reflexions, measured on powder photographs recorded in the Straumanis mode. The probable errors, after allowing for systematic absorption and eccentricity effects, have been shown to be three times the statistical estimated standard deviations.

BeH_8O_8S F.W. = 177·14
Tetragonal: $a=7{\cdot}990\pm1$, $c=10{\cdot}688\pm6$ Å,
$V=682{\cdot}3$ Å^3, $z=4$, $D_x=1{\cdot}733$ g.cm^{-3},
$D_m=1{\cdot}725$ (Töpsöe, 1872), 1·712 g.cm^{-3}
(Krüss & Moraht, 1890)
$\mu=44{\cdot}5$ cm^{-1}, $\lambda(\text{Cu } K\alpha_1)=1{\cdot}5405$ Å,
$\lambda(\text{Cu } K\alpha_2)=1{\cdot}5443$ Å.

Space-group $I\bar{4}c2$ (Beevers & Lipson, 1932) confirmed by the systematic absences (hkl, $h+k+l=2n+1$; $h0l$, l (and h) $=2n+1$), and structure analysis.

Intensity data for layers $h=0$ through $h=6$ and $l=0$ through $l=3$ were recorded photographically and estimated visually. Of the 229 unique reflexions accessible with Cu *Kα* radiation, one was not recorded and four were unobservably weak. Absorption corrections were applied. The high lattice symmetry of the crystal and the extensive photographic recording resulted in multiple intensity estimates for most reflexions. The standard deviations $\sigma(F_o)$ of the structure factors $|F_o|$ were derived by applying standard statistical formulae (Whittaker & Robinson, 1944; Davies & Pearson, 1934) to three sets of multiple data: (i) the observations of a single reflexion on the films of a film-pack, (ii) the symmetry-related reflexions recorded on each layer, and (iii) symmetry-related reflexions occuring on different layers or recorded about different axes. Observations of types (i) and (ii) were combined to yield an estimated variance σ_1, considered to represent mainly random errors, whereas σ_2 from the less numerous data in class (iii) was regarded as representing both systematic and random errors. The value of $\sigma(F_o)$ was assigned as the larger of σ_1 and σ_2, subjectively adjusted in a few cases where either of these values deviated disproportionately from the general trends.

Refinement of the structure

The sulphur and beryllium atoms lie in special positions (*b*) and (*c*) with point symmetry $\bar{4}$ – the S atoms at $(0,0,0)$, $(0,0,\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},0)$ and the Be atoms at $(0,\frac{1}{2},\frac{1}{4})$, $(0,\frac{1}{2},\frac{3}{4})$, $(\frac{1}{2},0,\frac{1}{4})$, $(\frac{1}{2},0,\frac{3}{4})$. The tetrahedra are formed by sets of oxygen atoms in 16-fold general positions.

F_o and (F_o-F_c) Fourier syntheses confirmed the approximate atomic positions obtained by Beevers &

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Table 1. *Positional and vibrational parameters*

The standard deviations (in parentheses) refer to the two least significant digits in the preceding quantities. B_{iso} is the isotropic vibrational parameter for the hydrogen atoms.
The anisotropic atomic temperature factors are:

$$T=\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2klb^*c^*U_{23}+2lhc^*a^*U_{31})\right].$$

	x (σ_x)	y (σ_y)	z (σ_z)	B_{iso} (Å^2)	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{23} (Å^2)	U_{31} (Å^2)
S	0 —	0 —	0 —	—	0·0148 (13)	0·0148 (13)	0·0235 (09)	0	0	0
Be	0 —	0·50000 (—)	0·25000 (—)	—	0·0200 (56)	0·0200 (56)	0·0158 (37)	0	0	0
O(1)	0·12591 (45)	0·08405 (45)	0·07737 (36)	—	0·0281 (21)	0·0219 (19)	0·0506 (20)	0·0058 (16)	−0·0106 (16)	−0·0201 (19)
O(2)	0·13799 (50)	0·39686 (47)	0·17182 (33)	—	0·0340 (23)	0·0205 (19)	0·0398 (18)	−0·0085 (16)	−0·0112 (15)	0·0179 (17)
H(1)	0·225	0·465	0·130	2·5	—	—	—	—	—	—
H(2)	0·109	0·281	0·125	2·5	—	—	—	—	—	—

Lipson (1932), and indicated markedly anisotropic thermal motions for the sulphur and oxygen atoms. The initial refinements of the positional parameters of the oxygens and the anisotropic thermal parameters of all the atoms were made by Fourier methods. The residual R was reduced to 0·075. Diffuse regions of positive electron density appeared in the expected vicinities of the hydrogen atoms, which were therefore assigned tentative positions and isotropic thermal parameters $B=2{\cdot}5$ Å^2.

In the full-matrix least-squares refinement, the reflexions were given individual weights $w=1/\sigma^2(F_o)$, and the function minimized was $\Sigma\, w||F_o|-|F_c||^2$. The atomic scattering factors used were those of Dawson (1960) for sulphur, Berghuis, Haanappel, Potters, Loopstra, MacGillavry, & Veenendaal (1955) for oxygen, Ibers (1957) for beryllium and McWeeny (1951) for hydrogen. Dispersion corrections were applied to the sulphur scattering curve (*International Tables for* X-*ray Crystallography*, 1962). All except the hydrogen atom parameters were refined. Appropriate constraints were imposed on the thermal parameters of atoms in special positions. The refinement converged after four cycles ($R=0{\cdot}072$).

Re-inspection of the data showed that there was a systematic trend in the remaining discrepancies due to extinction, for which corrections were applied according to the method of Pinnock, Taylor & Lipson (1956). An analysis of the weighting scheme at this stage showed that the mean value of $w^{\frac{1}{2}}\Delta$ was 2·0, and independent of the magnitude of $|F_o|$. Individual $w^{\frac{1}{2}}\Delta$ values, however, deviated strongly from the mean, the standard deviation of the mean value 2·0 for the population being 1·8. This indicated that the $\sigma(F_o)$ had been assessed with insufficient precison to validate their use in assigning weights to the F_o. The least-squares refinement was therefore completed with a weighting derived from the variation of root mean squares $||F_o|-|F_c||$ in ranges of $|F_o|$. Three cycles were necessary, converging with $\Sigma\, w\Delta^2/(m-n)=1{\cdot}046$ and residuals R(unweighted $=$ 0·048 and R'(weighted)$=0{\cdot}069$. The most significant features in a final (F_o-F_c) Fourier synthesis, the hydrogen contributions having been omitted from the F_c's, were broad peaks in the regions of the hydrogen atoms. This observation and the failure of further refinement to reduce the residual R led to the conclusion that the X-ray diffraction data could not yield the hydrogen positions with errors smaller than 0·1 Å.

The atomic parameters and their calculated standard deviations are given in Table 1, and the final structure factors are listed in Table 2. We use the symbols O and O_w or O(1) and O(2) for the O(sulphate) and O(water) atoms, respectively. The two independent H(water) atoms are H(1) and H(2).

Description of the structure

It follows from the special positions occupied by the S and Be atoms that the tetrahedral SO_4^{2-} and

Table 2. *Calculated and observed structure factors*

$F(000)=172$. Unobservably weak reflexions are indicated by *X*.

h	k	l	F_{calc}	F_{obs}
0	0	2	39.89	45.86
		4	24.38	24.14
		6	29.46	31.39
		8	11.77	10.69
		10	16.28	14.40
		12	35.33	38.06
0	2	0	97.46	92.51
		2	60.31	64.23
		4	29.64	34.71
		6	16.85	18.18
		8	27.58	27.64
		10	19.67	17.55
		12	20.99	22.28
0	4	0	66.94	64.01
		2	36.76	37.40
		4	64.57	65.57
		6	17.41	15.44
		8	54.50	55.73
		10	17.23	16.66
		12	3.76	2.74
0	6	0	6.21	5.97
		2	35.67	35.77
		4	43.91	45.02
		6	28.15	27.42
		8	25.04	24.58
		10	19.10	18.68
0	8	0	42.83	44.06
		2	20.62	21.49
		4	21.08	21.88
		6	21.18	20.68
		8	9.52	9.52
0	10	0	24.64	26.63
		2	17.32	17.91
1	1	0	53.17	52.94
		2	126.51	127.33
		4	33.76	35.25
		6	19.39	16.96
		8	18.17	18.67
		10	30.78	30.30
		12	6.03	11.30
1	2	1	34.75	37.05
		3	75.79	75.74
		5	34.24	34.86
		7	12.71	11.56
		9	17.51	16.38
		11	10.17	9.34
		13	1.32	1.18 X
1	3	0	48.01	51.21
		2	14.31	14.92
		4	34.65	36.29
		6	58.57	63.47
		8	20.62	19.08
		10	23.91	23.33
		12	14.12	13.73
1	4	1	16.94	15.74
		3	22.49	20.11
		5	19.01	17.45
		7	18.07	17.69
		9	3.76	2.97
		11	1.89	1.50 X
1	5	0	20.24	18.48
		2	13.27	12.49
		4	27.02	26.12
		6	57.16	59.89
		8	20.99	18.21
		10	13.75	13.38
		12	8.47	10.86
1	6	1	17.69	16.21
		3	21.08	20.25
		5	6.49	6.11
		7	2.26	2.44 X
		9	7.72	7.39
		11	6.87	7.52
1	7	0	13.93	13.19
		2	33.80	34.38
		4	30.21	31.23
		6	20.53	19.19
		8	19.10	19.15
		10	12.05	12.78
1	8	1	9.42	8.25
		3	11.67	10.49
		5	10.45	10.18
		7	11.86	11.98
1	9	0	13.46	14.38
		2	25.96	27.64
		4	16.57	15.78
		6	9.42	9.45
1	10	1	8.19	8.19
		3	2.92	2.84
2	2	0	48.57	45.78
		2	37.16	36.64
		4	41.44	45.63
		6	21.28	22.09
		8	30.97	29.84
		10	18.26	16.15
		12	17.60	17.89
2	3	1	54.31	55.78
		3	64.24	60.27
		5	22.12	20.02
		7	4.89	3.01
		9	24.19	23.65
		11	10.26	10.32
2	4	0	26.45	26.97
		2	28.43	28.19
		4	40.74	42.46
		6	27.86	26.75
		8	28.80	28.02
		10	15.82	15.66
		12	12.24	12.53
2	5	1	22.10	20.66
		3	22.78	21.22
		5	26.15	26.84
		7	14.21	12.74
		9	4.33	3.84
		11	3.20	3.36
2	6	0	33.71	34.32
		2	22.69	21.26
		4	31.44	31.24
		6	19.96	19.93
		8	17.32	17.71
		10	11.49	10.32
2	7	1	20.33	19.50
		3	17.69	16.22
		5	9.42	8.61
		7	6.40	6.63
		9	15.06	14.64
2	8	0	29.18	29.90
		2	20.24	21.18
		4	20.60	19.98
		6	12.61	11.63
		8	16.38	15.39
2	9	1	16.57	16.33
		3	6.03	5.80
		5	12.33	12.35
2	10	0	15.06	15.20
		2	11.02	13.58
3	3	0	10.73	11.34
		2	55.15	55.43
		4	29.46	29.78
		6	22.97	20.89
		8	25.70	23.67
		10	18.73	18.24
		12	9.04	7.94
3	4	1	16.00	15.46
		3	17.89	15.73
		5	12.14	11.15
		7	17.51	17.13
		9	4.05	3.48
		11	4.05	3.29
3	5	0	16.83	17.42
		2	51.30	51.00
		4	34.74	34.15
		6	9.60	8.54
		8	17.41	17.65
		10	19.39	18.40
3	6	1	25.51	25.33
		3	20.42	19.49
		5	4.62	3.84
		7	4.05	4.40
		9	10.45	10.25
3	7	0	28.62	29.22
		2	29.18	27.69
		4	20.14	18.82
		6	20.42	18.76
		8	9.42	9.40
3	8	1	7.53	7.40
		3	7.72	7.28
		5	5.94	6.74
		7	13.18	12.52
3	9	0	19.67	20.84
		2	16.48	16.77
		4	13.09	13.27
4	4	0	90.62	90.53
		2	20.33	18.77
		4	17.69	16.71
		6	26.43	27.12
		8	4.89	4.70
		10	10.83	9.77
4	5	1	9.22	8.49
		3	11.95	11.38
		5	12.61	13.59
		7	9.22	8.66
		9	2.45	2.25 X
4	6	0	44.65	45.79
		2	34.17	35.41
		4	18.17	16.92
		6	12.80	12.35
		8	17.60	16.64
4	7	1	7.24	7.32
		3	6.12	6.18
		5	3.76	4.96
		7	8.85	9.45
4	8	0	12.99	13.94
		2	21.18	21.56
		4	23.35	22.79
		6	6.49	6.44
4	9	1	2.07	2.48
		3	5.17	5.15
5	5	0	27.02	27.17
		2	40.61	40.48
		4	19.96	17.74
		6	4.62	4.45
		8	10.26	10.40
		10	16.45	23.08
5	6	1	9.04	9.74
		3	9.22	8.62
		5	9.79	9.51
		7	3.58	3.67
		9	4.05	4.86
5	7	0	22.49	22.86
		2	17.60	17.74
		4	22.31	21.97
		6	25.32	23.38
5	8	1	6.58	6.44
		3	8.66	7.48
		5	10.54	11.02
5	9	0	10.54	12.58
6	6	0	19.39	18.73
		2	17.51	17.84
		4	19.39	18.93
		6	10.54	9.92
6	7	1	11.86	11.39
		3	7.63	6.38
		5	2.45	1.38
6	8	0	11.39	11.58
		2	14.97	15.08
7	7	0	7.81	7.60

Table 3. *Interatomic distances and angles with their estimated standard deviations* (*in parentheses*)

Code for symmetry-related atoms

Superscript	Atom at		
–	x	y	z
′	$\bar{x}$	$\bar{y}$	z
″	$\bar{x}$	$1-y$	z
‴	$\frac{1}{2}-x$	$\frac{1}{2}+y$	z
iv	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	z
v	y $\bar{y}$	$\bar{x}$ x	$\bar{z}$ $\bar{z}$
vi	$\frac{1}{2}-y$ $-\frac{1}{2}+y$	$\frac{1}{2}+x$ $\frac{1}{2}-x$	$\frac{1}{2}-z$ $\frac{1}{2}-z$

Atoms	Distance l (Å)
S———O(1)	1·465 (4)
O(1)···O(1′)	2·419 (7)
O(1)···O(1^{v})	2·379 (7)
Be———O(2)	1·610 (4)
O(2)···O(2″)	2·753 (7)
O(2)···O(2^{vi})	2·566 (7)
O(2)···O(1‴)	2·610 (5)
O(1)···O(2^{iv})	
O(2)···O(1)	2·697 (5)
O(2)——H(1)	0·99 (10)
O(2)——H(2)	1·08 (10)
H(1)···O(1‴)	1·63 (10)
H(2)···O(1)	1·66 (10)

Atoms	Angle (°)
O(1)———S———O(1′)	111·3 (3)
O(1)———S———O(1^{v})	108·6 (3)
O(2)———Be———O(2″)	117·5 (3)
O(2)———Be———O(2^{vi})	105·6 (3)
S————O(1)···O(2)	131·3 (3)
S————O(1)···O(2^{iv})	116·9 (3)
O(2) ····O(1)···O(2^{iv})	111·1 (3)
S————O(1)···H(1^{iv})	115
S————O(1)···H(2)	122
Be————O(2)···O(1‴)	113·7 (3)
Be————O(2)···O(1)	130·1 (3)
O(1‴)···O(2)···O(1)	114·3 (3)
Be————O(2)——H(1)	116
Be————O(2)——H(2)	122
H(1)———O(2)——H(2)	114
O(1‴)——O(2)···H(1)	4
O(1) ····O(2)——H(2)	12
O(2)———H(1)···O(1‴)	173
O(2)———H(2)···O(1)	160

$Be(OH_2)_4^{2+}$ ions are arranged in alternating layers separated by $c/4$ [see Fig. 1(*a*)]. Each $Be(OH_2)_4^{2+}$ ion is then surrounded by eight SO_4^{2-} ions lying at the corners of a square prism ($5{\cdot}65 \times 5{\cdot}65 \times 5{\cdot}34$ Å^3), and *vice versa* [Fig. 1(*b*)]. Every H_2O molecule of the aquo-cation is hydrogen-bound to two oxygen atoms having equal z coordinates but belonging to different sulphate ions; conversely, each O(sulphate) atom is the acceptor of two hydrogen bonds.

The tetrahedra are contracted parallel to the tetragonal axis, the crystallographic symmetry being S_4 for the total $Be(OH_2)_4^{2+}$ group and D_{2d} for SO_4^{2-}. Starting from an idealized structure in which the top and bottom edges of each tetrahedron are perpendicular to **c** and lie at 45° to **a** and **b**, we obtain the real structure by rotating the tetrahedra through *ca.* 9° about axes parallel to **c**. Adjacent tetrahedra of each type are rotated in opposite senses. The bond lengths and angles are listed in Table 3. The standard deviations were computed by assuming r.m.s. isotropic errors for the atomic positions (Cruickshank & Robertson, 1953). The shortest non-bonded contact between oxygen atoms is 3·47 Å.

The ellipsoids representing the thermal parameters (restricted to spheroids in the cases of atoms in special positions) are shown in Fig. 2. Numerical details are listed in Table 4. With the usual reservation that the thermal parameters may include contributions from systematic error sources, we conclude that the vibrations of Be are isotropic, that S has a marginally larger amplitude along the S_4 axis than perpendicular to it, and that the vibrational ellipsoids of both alpha O atoms are prolate spheroids whose major axes are about twice the minor axes. The maximum displacements of the O and O_w atoms occur in directions at $83 \pm 2°$ and $78 \pm 2°$ to the S–O and Be–O bonds, respectively. We note that the anisotropic thermal parameters provide the only significant differences between the present results and those of a neutron diffraction study of $BeSO_4.4H_2O$ (Chidambaram, 1969).

Discussion

Dimensions of the SO_4^{2-} *ion*

The S–O bond length is $1{\cdot}465 \pm 0{\cdot}004$ Å. Baur (1964*c*) and Larson (1965) have tabulated twenty crystallo-

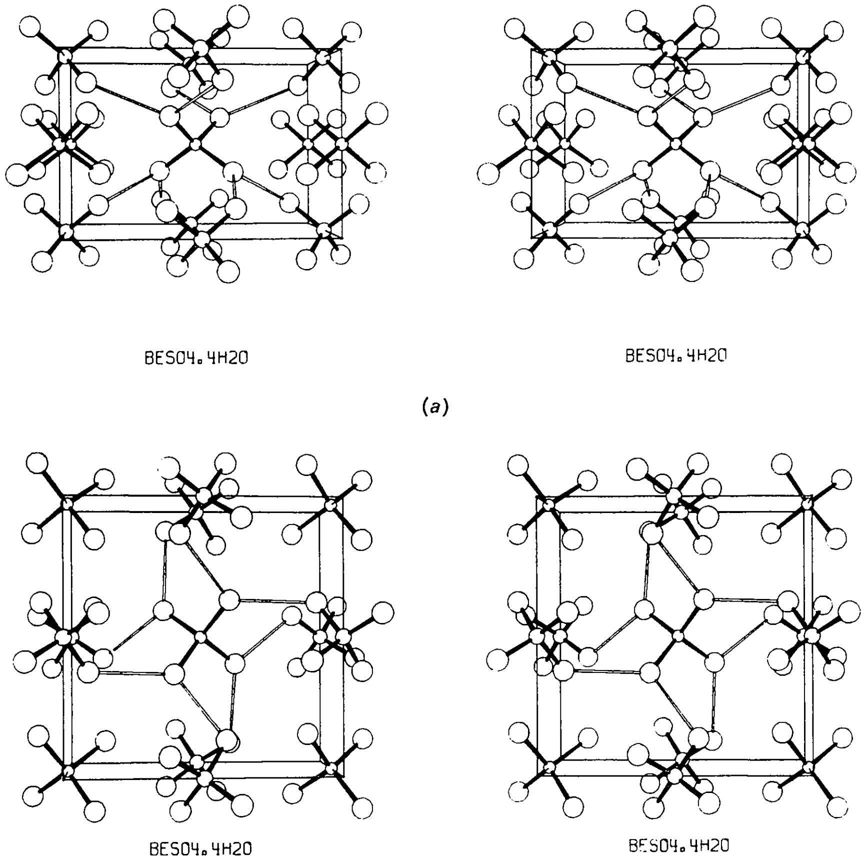

Fig. 1. Stereoscopic diagrams of a portion of the $BeSO_4.4H_2O$ unit-cell ($0 \le z \le \frac{1}{2}$). (*a*) z Axis vertical, x axis into paper. (*b*) x Axis vertical, z axis out of paper.

graphically independent sulphate S–O bonds in five different structures in which S–O bond lengths were reported with standard deviations <0·01 Å. The pattern which emerges from these compilations is that the fewer metal ions and hydrogen-bond donors an O(sulphate) atom has around it, and the more distant such neighbours are, the shorter the S–O bond will be (Larson, 1965). The shortest S–O bond recorded by Baur and by Larson is 1·459 Å, the smallest mean of the four in any individual structure is 1·471 Å, and the mean of their twenty examples is 1·473 Å. According to Baur (1964*c*), the S–O bond length to be expected when the O(sulphate) atom makes only two hydrogen-bonded contacts is 1·464 Å – exactly the value found in $BeSO_4.4H_2O$. These values may be corrected for in-phase differential thermal motion (Busing & Levy, 1958). The correction involves the assumptions (i) that the sulphate ions behave as rigid bodies, and (ii) that the vibrational parameters represent only vibrational effects. We are therefore reluctant to attach a physical interpretation to the equality of the corrected S–O distance in the present crystal (1·482 Å) and the similarly corrected mean value (1·483 Å) found in Baur's and Larson's surveys.

In $BeSO_4.4H_2O$ there are four O–S–O angles of 108·6° and two of 111·3°. These values lie in the ranges found in other sulphates (Table 5). While they are consistent with Baur's (1964*c*) observation that SO_4^{2-} groups in crystalline sulphates are usually distorted from T_d symmetry, the data in Table 5 do not support his predicted correlation between the degree of dis-

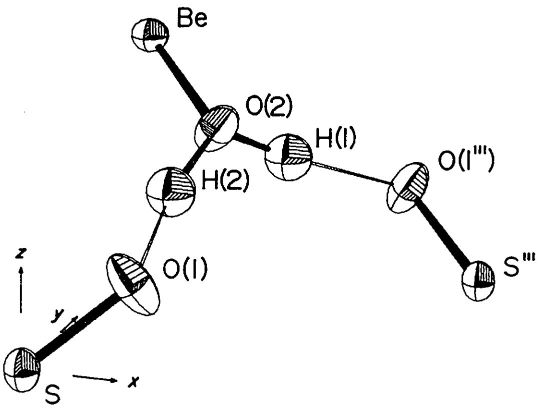

Fig. 2. Thermal vibration ellipsoids in $BeSO_4.4H_2O$.

Table 4. *Vibrational ellipsoids*

	Ellipsoid principal axis	r.m.s. displacement (Å)	Inclination to unit-cell axis (°) *x*	*y*	*z*
S	*A*	0·122±0·003	0	90	90
	B	0·122±0·003	90	0	90
	C	0·153±0·003	90	90	0
Be	*A*	0·141±0·010	0	90	90
	B	0·141±0·010	90	0	90
	C	0·126±0·015	90	90	0
O(1)	*A*	0·128±0·007	33	82	58
	B	0·136±0·008	105	72	81
	C	0·256±0·005	119	105	56
O(2)	*A*	0·124±0·007	87	23	68
	B	0·138±0·007	143	101	55
	C	0·245±0·005	53	110	44

Table 5. O–S–O *angles in sulphate groups* (*e.s.d.'s in parentheses*)

Crystal	Angular range (°)	Bonding of four O(sulphate) atoms	Reference
$MgSO_4.4H_2O$	108·2–111·8 (0·2)	One accepts 3 H-bonds	Baur, 1962
$FeSO_4.4H_2O$		One accepts 2 H-bonds One accepts 1 H-bond & coordinates M^{2+} One coordinates M^{2+}	Baur, 1964*a*
$Li_2SO_4.H_2O$	108·4–110·9 (0·1)	Three have 2 Li^+ neighbours One has 1 Li^+ neighbour & accepts 1 H-bond	Larson, 1965
$FeSO_4.7H_2O$	108·4–110·1 (0·3)	Three accept 3 H-bonds One accepts 2 H-bonds	Baur, 1964*b*
$MgSO_4.7H_2O$	108·6–110·2 (0·3)	Two accept 3 H-bonds Two accept 2 H-bonds	Baur, 1964*c*
$[CH_3SC(NH_2)_2]_2SO_4$	109·0–109·9 (0·4)	Each accepts 2 H-bonds	Stam, 1962
$BeSO_4.4H_2O$	108·6–111·3 (0·3)	Each accepts 2 H-bonds	Present work

tortion and the extent to which the environments of O(sulphate) atoms are unequal.

The $Be(OH_2)_4^{2+}$ *ion*

The length of the H_2O–Be bond is 1·610 ± 0·004 Å. Differential vibrational correction, on the assumption that the water molecule is riding upon Be^{2+}, leads to a distance of 1·622 Å. This distance agrees with the Be–O(acetate) distance found in $Be_4O(CH_3COO)_6$, 1·624 Å (Tulinsky & Worthington, 1959). It is significantly shorter than the Be–O distances 1·655 and 1·647 Å in BeO (Jeffrey, Parry & Mazzi, 1956) and the average lengths 1·636, 1·650 Å for Be–O and Be–(OH) bonds reported in a review by Ross (1964).

There is significant angular distortion in the coordination tetrahedron, the two different O_w–Be–O_w angles being 117·5 and 105·6°. There are no strong external bonding forces acting to perturb the shape of the ion from the regular tetrahedron expected for sp^3 hybridization of the Be orbitals.

Hydrogen bonds

The direct $O_w \cdots O$ distances for the two hydrogen bonds formed by each water molecule are 2·697 and 2·610 Å, at angles of 130° and 114° with the Be–O_w direction, respectively. The angle between the Be–O_w bond and the $O \cdots O_w \cdots O$ plane is 13°. A more detailed description of the hydrogen-bonding cannot be given without more precise values for the H atom positions. We note, however, that all the hydrogen-bonds would be *shortened* if either the SO_4 or $Be(O_w)_4$ tetrahedra (or both) were given perfect T_d symmetry, the S and Be atoms remaining where they are. In the case of the $Be(O_w)_4$ tetrahedra, this would involve shifting the O_w atoms by 0·113 Å and would make the Be–O_w and two $O_w \cdots O$ bonds coplanar. It appears that the actual structure represents a compromise between the tendencies of the Be and O(water) atoms to have tetrahedral bond distributions.

Additional observations

We record here two observations which have not yet been fully explored and between which no relationship has been found. They do not appear to have affected the structure analysis.

(1) All of the X-ray powder photographs (see *Experimental*) showed lines of weaker intensity which could not be attributed to the $BeSO_4.4H_2O$ lattice, and which did not correspond with the published patterns of the di-, mono- and anhydrate of $BeSO_4$ (Petersen, Rinn & Sutton, 1964). The spacings of these extra lines are listed in Table 6.

Table 6. *Unidentified lines on the* X-ray *powder photographs of* $BeSO_4.4H_2O$ (Cu $K\alpha$ radiation)

$\sin\theta$	$\sin\theta$	$\sin\theta$
0·12773	0·21547	0·28164
0·15008	0·21826	0·28505
0·15339	0·24387	0·32958
0·18684	0·25325	0·44690
0·20310	0·26208	

(2) On the single-crystal photographs, diffuse X-ray scattering was associated with the more intense reflexions. By use of a crystal monochromator this scattering was separated from the effects of impure radiation, and a qualitative determination of the shape of the equal-diffusion surfaces in reciprocal space was made from a series of closely adjacent stationary-crystal photographs. The most intense region, which lay around the (112) reflexion, was examined in greatest detail; here the equal-diffusion surface appeared to be a thin plate, normal to the reciprocal lattice vector and with its maximum possibly slightly displaced from the reciprocal lattice point along that vector.

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A Neutron Diffraction Determination of the Structure of Beryllium Sulphate Tetrahydrate, $BeSO_4.4H_2O$

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The crystal structure of $BeSO_4.4H_2O$ (space group $I\bar{4}c2$; $a=7\cdot990$ Å, $c=10\cdot688$ Å; $Z=4$) has been directly determined from the intensities of 251 independent three-dimensional single-crystal neutron reflexions with $\sin\theta/\lambda \le 0\cdot7$ $Å^{-1}$. 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 $1\cdot464 \pm 0\cdot004$ Å. Four sulphate oxygens form a tetrahedron around beryllium with a Be–O distance of $1\cdot618 \pm 0\cdot004$ Å. The structure contains two hydrogen bonds from the water molecule to the sulphate oxygens of length $2\cdot684 \pm 0\cdot005$ Å and $2\cdot617 \pm 0\cdot005$ Å, the O–H distances being $0\cdot971 \pm 0\cdot006$ Å and $0\cdot967 \pm 0\cdot006$ Å (both uncorrected for thermal motion); the H–O–H angle is $112\cdot7 \pm 0\cdot8$°.

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 SO_4 and tetrahedral $Be(H_2O)_4$ groups. Beevers & Lipson (1932) reinvestigated the structure and showed that the true space group is $I\bar{4}c2$; the postulated structure had tetrahedral SO_4 and $Be(H_2O)_4$ groups linked together by strong hydrogen bonds of length 2·56 Å 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 φ 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 $\sin\theta/\lambda = 0\cdot70$ $Å^{-1}$ were then measured at a wavelength of 1·031 Å using the θ–2θ scan technique. The orientation angles, 2θ, χ, φ, 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 ($\mu = 1\cdot78$ cm^{-1}, as measured experimentally). The