

A Neutron Diffraction Study of Barium Thiosulphate Monohydrate, $\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}^*$

BY LJUBICA MANOJLOVIĆ-MUIR†

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, U.S.A.

(Received 18 July 1974; accepted 8 August 1974)

A three-dimensional neutron diffraction analysis of barium thiosulphate monohydrate was based on 615 intensity data. The structure was refined by full-matrix least squares to R (based on F^2) of 0.034. The crystals are built of Ba^{2+} cations, $\text{S}_2\text{O}_3^{2-}$ anions and H_2O molecules. The Ba-S distances are 3.355 (4) and 3.424 (4) Å, and the Ba-O distances range from 2.775 (4) to 3.428 (4) Å. In the tetrahedral $\text{S}_2\text{O}_3^{2-}$ anion the S-S and S-O bond lengths are 1.979 (3) Å and 1.472 (3)–1.483 (3) Å, respectively. One hydrogen atom is disordered, thus giving rise to two statistically distributed orientations of the water molecule. The O-H bond lengths are 0.960 (5), 0.987 (6) and 0.997 (6) Å and the H-O-H angles are 101.5 (5)° and 102.4 (4)°. Each water molecule forms three hydrogen bonds, two of the type O-H...O, involving the disordered hydrogen atom, and one of the type O-H...S.

Introduction

The X-ray crystal structure analysis of barium thiosulphate monohydrate, carried out by Nardelli & Fava (1962), revealed the positions of all atoms except hydrogens. Steric and symmetry requirements indicated a disordered distribution of the hydrogen atoms, and a reasonable hydrogen-bonding scheme, involving an O-H...S interaction between the water molecule and a sulphur atom of the thiosulphate ion, was suggested on the basis of Donohue's (1952) angular criterion. Although the existence of O-H...S hydrogen bonding in solids has also been inferred from the results of other X-ray diffraction studies (e.g. Nardelli, Fava & Giraldi, 1962; Manojlović & Edmunds, 1965), definitive evidence, based on determination of the complete geometry around the hydrogen atom in an O-H...S bond, has been lacking. In view of this, we have undertaken a neutron diffraction analysis of the title compound.

The results of this work, briefly reported earlier (Manojlović-Muir, 1969), have confirmed the existence of an O-H...S bond in $\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Experimental

A crystal of prismatic b habit, with the {100} form predominating, was used in this analysis. Its volume was 3.5 mm³.

Crystal data

$\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$, F.W. = 267.5. Orthorhombic, space group $Pbcn$, $a = 20.07$ (1), $b = 7.19$ (1), $c = 7.37$ (1) Å, $Z = 8$ (Nardelli & Fava, 1962). The absorption coefficient for 1 Å neutrons, calculated from the true ab-

sorption cross sections and the incoherent scattering cross sections of the atomic species present, is 0.56 cm⁻¹.

Intensity measurements

The intensity data were collected at Brookhaven National Laboratory high-flux beam reactor, using a computer-controlled (Bednowitz, Coppens & Hamilton, 1966) Multi-Spectrometer Control System (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & van Norton, 1966). A θ - 2θ scan technique was applied. To avoid second-order contamination ($\lambda/2$) in the incident neutron beam, a germanium monochromator was used. The neutron wavelength was 1.050 Å. The integrated intensities were measured for all independent reflexions with $\theta \leq 35^\circ$, and also for some reflexions in the 35–40° θ range; in the outer θ range only a small number of reflexions were significantly above background and the data collection was therefore not completed.

The intensities were corrected for Lorentz and absorption effects. A set of 615 independent reflexions, for which $F_o^2 \geq 2\sigma(F_o^2)$, was used in the analysis.

Location of the hydrogen atoms and refinement

The starting structural model was that of Nardelli & Fava, involving the non-hydrogen atoms only. The structure was refined by full-matrix least-squares, using *LINUS* – a Brookhaven version of the program *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w\Delta^2$, where $\Delta = |F_o|^2 - |F_c|^2$ and $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. The weights, w , were determined from the counting statistics variances, $\sigma^2(\text{count})$, using the relationships $w = 1/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = \sigma^2(\text{count}) + (pF_o^2)^2$. The $\sigma^2(\text{count})$ was derived on the assumption of standard Poisson statistics, and the empirical factor p was initially taken as 0.05. The coherent neutron scat-

* Research performed under the auspices of the U.S. Atomic Energy Commission.

† Present address: Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland.

tering amplitudes, s , were 5.2, 2.8, 5.77 and -3.72 fm,* for barium, sulphur, oxygen and hydrogen atoms, respectively (Neutron Diffraction Commission, 1969). The scale factor was varied throughout refinement.

A refinement of the positional and isotropic thermal parameters of all atoms, except hydrogens, led to R 0.32 and R_w 0.45, where $R = \sum \Delta / \sum F_o^2$ and $R_w = (\sum w \Delta^2 / \sum w F_o^4)^{1/2}$. The F_o map displayed only three negative peaks significantly below background. The positions of these peaks, relative to that of the water oxygen atom, were compatible with the known geometry of the water molecule; they were also compatible with the distribution of the disordered hydrogens suggested by Nardelli & Fava. The peak heights however did not indicate clearly whether both, or only one, of the hydrogen atoms were disordered. Hence the model proposed by Nardelli & Fava, which assumes that the two hydrogen atoms are equally distributed over three available sites (s_H fixed at -2.48 fm) was first tested. The refinement of this model, A , with isotropic thermal parameters of atoms brought R to 0.120 and R_w to 0.186. With allowance for the anisotropic thermal vibrations of all atoms the refinement terminated at R 0.086 and R_w 0.123. The resulting thermal parameters for oxygen and one hydrogen atom of the water molecule were, however, non-positive definite.

In the model subsequently examined, the three available positions were assigned to three hydrogen atoms with full scattering power (s_H fixed at -3.72 fm), but their occupancy factors were allowed to vary. The refinement of this model, with isotropic thermal parameters for all atoms, terminated at R 0.091 and R_w 0.123. The final values of the occupancy factors for H(1), H(2a) and H(2b) atoms (Fig. 2) were 0.995, 0.479 and 0.473 respectively. Accordingly, the occupancy factor for H(1) was fixed at 1.0 and those for H(2a) and H(2b) at 0.5. The refinement of this model, B , converged with physically meaningful anisotropic thermal parameters for all atoms and with the agreement indices, R 0.077 and R_w 0.102, significantly lower than for model A . Model B was therefore chosen as the correct one and used in all subsequent calculations.

Parameters which allowed for the effects of extinction were then added to the list of least-squares variables. In the treatment of anisotropic extinction each of Zachariasen's (1967) two extreme crystal types was considered separately, and the six independent elements of a symmetrical tensor, G_{ij} , were used to define first the mosaic spread (type I) and then the particle size (type II) in the crystal (Coppens & Hamilton, 1970). The results of this refinement are summarized in Table 1. The parameters of anisotropic type I extinction, which led to the lowest R and R_w values, were varied through further refinement.

An analysis-of-variance test (with W. C. Hamilton's program *NANOVA*) revealed some dependence of $\Delta/\sigma(F_o^2)$ values on F_o^2 . The weighting scheme was there-

Table 1. *Effect of extinction on refinement*

Extinction parameters refined	R	R_w
None	0.077	0.102
Isotropic	0.041	0.073
Anisotropic, type I	0.036	0.071
Anisotropic, type II	0.037	0.072

fore adjusted by varying the parameter p (see above); for each value of p the $\sigma(F_o^2)$ and w quantities were recalculated. The best results were obtained when p was assigned the unusually low value of 0.01. This suggested that the dominant factor in the $\sigma(F_o^2)$ values was the contribution of the counting statistics. The refinement finally converged at R 0.034 and R_w 0.038. The corresponding agreement indices based on F , rather than F^2 , were R' 0.033 and R'_w 0.022.

In the final cycle of refinement all parameters shifted by $<0.1\sigma$. The standard deviation of an observation of unit weight was 1.48. The observed and calculated structure amplitudes and the extinction correction factors are listed in Table 2. The final positional and vi-

Table 2. *The observed and calculated structure amplitudes and the extinction corrections (y)*

The columns are: $h, k, l, |F_o|/y^{1/2}, |F_c|$ and y , where $y = F_o^2/F_c^2$. Values of $y > 0.999$ are omitted.

h	k	l	$ F_o /y^{1/2}$	$ F_c $	y
002	0.02	0.02	0.02	0.02	0.02
004	0.04	0.04	0.04	0.04	0.04
006	0.06	0.06	0.06	0.06	0.06
008	0.08	0.08	0.08	0.08	0.08
010	0.10	0.10	0.10	0.10	0.10
012	0.12	0.12	0.12	0.12	0.12
014	0.14	0.14	0.14	0.14	0.14
016	0.16	0.16	0.16	0.16	0.16
018	0.18	0.18	0.18	0.18	0.18
020	0.20	0.20	0.20	0.20	0.20
022	0.22	0.22	0.22	0.22	0.22
024	0.24	0.24	0.24	0.24	0.24
026	0.26	0.26	0.26	0.26	0.26
028	0.28	0.28	0.28	0.28	0.28
030	0.30	0.30	0.30	0.30	0.30
032	0.32	0.32	0.32	0.32	0.32
034	0.34	0.34	0.34	0.34	0.34
036	0.36	0.36	0.36	0.36	0.36
038	0.38	0.38	0.38	0.38	0.38
040	0.40	0.40	0.40	0.40	0.40
042	0.42	0.42	0.42	0.42	0.42
044	0.44	0.44	0.44	0.44	0.44
046	0.46	0.46	0.46	0.46	0.46
048	0.48	0.48	0.48	0.48	0.48
050	0.50	0.50	0.50	0.50	0.50
052	0.52	0.52	0.52	0.52	0.52
054	0.54	0.54	0.54	0.54	0.54
056	0.56	0.56	0.56	0.56	0.56
058	0.58	0.58	0.58	0.58	0.58
060	0.60	0.60	0.60	0.60	0.60
062	0.62	0.62	0.62	0.62	0.62
064	0.64	0.64	0.64	0.64	0.64
066	0.66	0.66	0.66	0.66	0.66
068	0.68	0.68	0.68	0.68	0.68
070	0.70	0.70	0.70	0.70	0.70
072	0.72	0.72	0.72	0.72	0.72
074	0.74	0.74	0.74	0.74	0.74
076	0.76	0.76	0.76	0.76	0.76
078	0.78	0.78	0.78	0.78	0.78
080	0.80	0.80	0.80	0.80	0.80
082	0.82	0.82	0.82	0.82	0.82
084	0.84	0.84	0.84	0.84	0.84
086	0.86	0.86	0.86	0.86	0.86
088	0.88	0.88	0.88	0.88	0.88
090	0.90	0.90	0.90	0.90	0.90
092	0.92	0.92	0.92	0.92	0.92
094	0.94	0.94	0.94	0.94	0.94
096	0.96	0.96	0.96	0.96	0.96
098	0.98	0.98	0.98	0.98	0.98
100	1.00	1.00	1.00	1.00	1.00
102	1.02	1.02	1.02	1.02	1.02
104	1.04	1.04	1.04	1.04	1.04
106	1.06	1.06	1.06	1.06	1.06
108	1.08	1.08	1.08	1.08	1.08
110	1.10	1.10	1.10	1.10	1.10
112	1.12	1.12	1.12	1.12	1.12
114	1.14	1.14	1.14	1.14	1.14
116	1.16	1.16	1.16	1.16	1.16
118	1.18	1.18	1.18	1.18	1.18
120	1.20	1.20	1.20	1.20	1.20
122	1.22	1.22	1.22	1.22	1.22
124	1.24	1.24	1.24	1.24	1.24
126	1.26	1.26	1.26	1.26	1.26
128	1.28	1.28	1.28	1.28	1.28
130	1.30	1.30	1.30	1.30	1.30
132	1.32	1.32	1.32	1.32	1.32
134	1.34	1.34	1.34	1.34	1.34
136	1.36	1.36	1.36	1.36	1.36
138	1.38	1.38	1.38	1.38	1.38
140	1.40	1.40	1.40	1.40	1.40
142	1.42	1.42	1.42	1.42	1.42
144	1.44	1.44	1.44	1.44	1.44
146	1.46	1.46	1.46	1.46	1.46
148	1.48	1.48	1.48	1.48	1.48
150	1.50	1.50	1.50	1.50	1.50
152	1.52	1.52	1.52	1.52	1.52
154	1.54	1.54	1.54	1.54	1.54
156	1.56	1.56	1.56	1.56	1.56
158	1.58	1.58	1.58	1.58	1.58
160	1.60	1.60	1.60	1.60	1.60
162	1.62	1.62	1.62	1.62	1.62
164	1.64	1.64	1.64	1.64	1.64
166	1.66	1.66	1.66	1.66	1.66
168	1.68	1.68	1.68	1.68	1.68
170	1.70	1.70	1.70	1.70	1.70
172	1.72	1.72	1.72	1.72	1.72
174	1.74	1.74	1.74	1.74	1.74
176	1.76	1.76	1.76	1.76	1.76
178	1.78	1.78	1.78	1.78	1.78
180	1.80	1.80	1.80	1.80	1.80
182	1.82	1.82	1.82	1.82	1.82
184	1.84	1.84	1.84	1.84	1.84
186	1.86	1.86	1.86	1.86	1.86
188	1.88	1.88	1.88	1.88	1.88
190	1.90	1.90	1.90	1.90	1.90
192	1.92	1.92	1.92	1.92	1.92
194	1.94	1.94	1.94	1.94	1.94
196	1.96	1.96	1.96	1.96	1.96
198	1.98	1.98	1.98	1.98	1.98
200	2.00	2.00	2.00	2.00	2.00

* 1 fm = 1 Fermi = 10^{-13} cm.

brational parameters of atoms are shown in Tables 3 and 4.

Table 3. *Final fractional coordinates with corresponding e.s.d.'s*

	<i>x</i>	<i>y</i>	<i>z</i>
Ba	0.16419 (6)	0.2208 (2)	0.0449 (2)
S(1)	0.15904 (11)	0.7280 (3)	0.0432 (3)
S(2)	0.08356 (11)	0.6086 (3)	0.1708 (3)
O(1)	0.19969 (6)	0.8337 (2)	0.1760 (1)
O(2)	0.13494 (6)	0.8592 (2)	-0.0954 (1)
O(3)	0.20192 (6)	0.5864 (1)	-0.0423 (1)
O(<i>W</i>)	0.02640 (8)	0.1619 (3)	0.0749 (3)
H(1)	-0.00003 (16)	0.2512 (4)	0.0101 (4)
H(2 <i>a</i>)	0.01066 (29)	0.0439 (8)	0.0214 (9)
H(2 <i>b</i>)	0.00649 (31)	0.1658 (7)	0.1988 (6)

Discussion

The crystal structure, built of Ba²⁺ and S₂O₃²⁻ ions and of water molecules, was discussed in detail by Nardelli & Fava. This analysis has produced shifts of up to 0.13 Å in Nardelli & Fava's coordinates of the non-hydrogen atoms.

The effects of extinction

In the crystal used in the analysis, extinction was large and appreciably anisotropic. The extinction correction factors for F_o^2 (Table 2) range from 1.00 to

0.57 (for the reflexion 400). The final values of the extinction tensor elements,* G_{ij} ($\times 10^{-3}$), are: G_{11} 1.99 (20), G_{22} 0.63 (5), G_{33} 0.71 (12), G_{12} 0.27 (11), G_{13} -0.03 (15) and G_{23} 0.20 (9). The corresponding mosaic spread parameters are 1.3, 2.3 and 2.2''.

The allowance for extinction led to a considerably improved refinement (Table 1). The changes in R and R_w on going from isotropic to anisotropic extinction were small, though statistically significant (Hamilton, 1965). It proved immaterial, however, whether anisotropic extinction is ascribed predominantly to mosaic spread (type I) or to particle size (type II). The refinement of extinction produced considerable changes in the thermal parameters; the positional parameters were not affected, but their accuracy was significantly improved. Thus the effects of extinction on the least-squares refinement were similar in character to those observed in several other crystal structure analyses where an analogous treatment was applied (Coppens & Hamilton, 1970).

The environment of the barium ion

The coordination number of the Ba²⁺ ion is eleven. As shown by Nardelli & Fava, the coordination polyhedron can be described as a distorted octahedron

* The tensor elements refer to the crystallographic axes *a*, *b* and *c*.

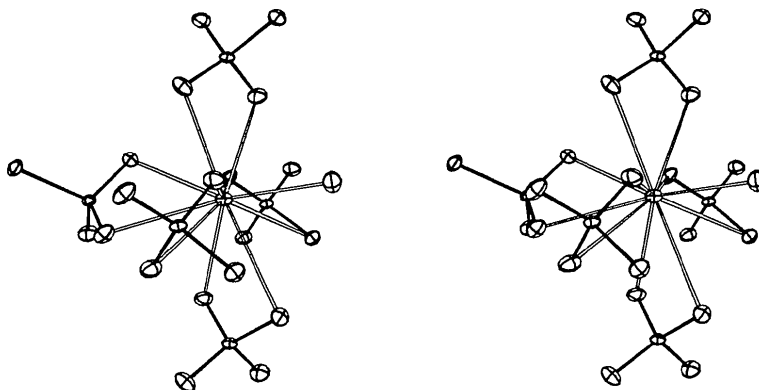


Fig. 1. A stereoscopic view of the coordination geometry around the barium ion. The bonds involving barium are indicated by double lines, and those in the thiosulphate ion by full lines.

Table 4. *Thermal parameters with corresponding e.s.d.'s* ($\times 10^5$)

The atoms were assigned anisotropic temperature factors of the form: $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	83 (3)	418 (24)	526 (24)	2 (7)	23 (7)	-12 (19)
S(1)	65 (6)	308 (38)	311 (38)	-10 (14)	23 (13)	5 (34)
S(2)	73 (6)	652 (47)	699 (38)	-36 (13)	44 (13)	169 (37)
O(1)	118 (4)	822 (23)	538 (19)	-108 (8)	-25 (7)	-133 (19)
O(2)	130 (3)	642 (20)	577 (21)	3 (8)	-16 (7)	171 (20)
O(3)	88 (3)	553 (22)	1013 (21)	2 (7)	91 (8)	-169 (19)
O(<i>W</i>)	94 (4)	986 (36)	1093 (36)	-23 (12)	-32 (11)	94 (33)
H(1)	217 (6)	1740 (54)	1997 (57)	100 (19)	-78 (17)	442 (57)
H(2 <i>a</i>)	173 (25)	1862 (256)	1661 (162)	-107 (51)	-71 (48)	-134 (160)
H(2 <i>b</i>)	197 (18)	1688 (102)	1376 (180)	49 (37)	101 (62)	19 (84)

(Fig. 1) with three vertices occupied by O–O edges, and another two by S–O edges, of five different S₂O₃²⁻ tetrahedra; the octahedron is completed by the oxygen atom of a water molecule.

The Ba–O(S₂O₃), Ba–S and Ba–O(water) distances, shown in Table 5, reveal no unexpected features. They are comparable with appropriate distances found in other compounds containing eleven-coordinate Ba²⁺ ions. Thus in BaFe₂O₄, for example, the Ba–O distances range from 2.74 to 3.34 Å (Mitsuda, Mori & Okazaki, 1971), and in BaS₄·H₂O the Ba–S distances are 3.250 (2)–3.618 (2) Å and the Ba–O(water) distances are 2.764 (6) and 2.792 (6) Å (Abrahams & Bernstein, 1969).

Table 5. *Interatomic distances in the coordination polyhedron around a barium ion*

Ba···S(2)	3.355 (4) Å	Ba···O(2 ^{III})	2.775 (4) Å
Ba···S(2 ^{II})	3.424 (4)	Ba···O(3)	2.810 (4)
Ba···O(1 ^I)	3.031 (4)	Ba···O(3 ^{III})	3.428 (4)
Ba···O(1 ^{II})	2.838 (4)	Ba···O(3 ^{I*})	2.927 (2)
Ba···O(1 ^{IV})	3.009 (2)	Ba···O(W)	2.806 (2)
Ba···O(2 ^I)	2.859 (4)		

The atoms belonging to the asymmetric unit are at *x, y, z*. Superscripts refer to positions at:

i	<i>x, y-1, z</i>	v	$-x, -y, -z$
ii	$x, 1-y, z-\frac{1}{2}$	vi	$-x, y, \frac{1}{2}-z$
iii	$x, 1-y, \frac{1}{2}+z$	vii	$-x, 1-y, -z$
iv	$\frac{1}{2}-x, y-\frac{1}{2}, z$		

The structure of the thiosulphate ion

The geometry and bonding in the S₂O₃²⁻ ion (Table 6) are similar to those observed in two other ionic thiosulphates, MgS₂O₃·6H₂O (Baggio, Amzel & Becka, 1969) and Na₂S₂O₃·5H₂O (Padmanabhan *et al.*, 1971). Thus the bond angles subtended at the central sulphur atom, which range from 108.1 (2)° to 110.9 (2)°, reveal only slight distortions from ideal tetrahedral symmetry, and the bond lengths indicate considerable π bonding character in both S–O and S–S bonds. The S–O distances [1.472 (3)–1.483 (3) Å] are in agreement with those in the magnesium salt, [1.465 (5) and 1.471 (5) Å], which is the only other ionic thiosulphate where the dimensions of the S₂O₃²⁻ ion have been determined with comparable accuracy. The S–S distance of 1.979 (3) Å is, however, significantly shorter than that of 2.013 (3) Å in the magnesium salt. This could be ascribed to different environments of the thiosulphate ion, and perhaps also to different effects of thermal vibrations of atoms, in the crystal structures of the two compounds.

Table 8. *Hydrogen-bonding distances and angles*

The O–H bond distances are shown in Table 7. The significance of the roman numerals is as shown in Table 5.

O(W)···O(W ^v)	2.786 (5) Å	O(W)–H(2a)···O(W ^v)	174.2 (5)°
O(W)···O(W ^{vi})	2.790 (5)	O(W)–H(2b)···O(W ^{vi})	176.8 (5)
O(W)···S(2 ^{III})	3.298 (4)	O(W)–H(1)···S(2 ^{III})	163.0 (3)
H(2a)···O(W ^v)	1.802 (5)	O(W ^v)···O(W ^{vi})···O(W ^{vi})	102.8 (1)
H(2b)···O(W ^{vi})	1.794 (4)	S(2 ^{III})···O(W ^v)···O(W ^v)	86.9 (1)
H(1)···S(2 ^{III})	2.367 (4)	S(2 ^{III})···O(W ^v)···O(W ^{vi})	104.7 (1)

Table 6. *Geometry of the thiosulphate group*

S(1)–S(2)	1.979 (3) Å	O(1)–S(1)–O(2)	108.1 (2)°
S(1)–O(1)	1.483 (3)	O(1)–S(1)–O(3)	108.3 (2)
S(1)–O(2)	1.472 (3)	O(2)–S(1)–O(3)	109.7 (2)
S(1)–O(3)	1.475 (3)	S(2)–S(1)–O(1)	109.3 (2)
		S(2)–S(1)–O(2)	110.9 (2)
		S(2)–S(1)–O(3)	110.5 (2)

The disorder and structure of the water molecule

The disorder of the water molecule involves one hydrogen atom only (model *B*), rather than both (model *A*), as suggested by Nardelli & Fava. It can be rationalized in terms of two different and statistically distributed orientations of the water molecule. One orientation is determined by H(1) and H(2a), and the other by H(1) and H(2b) positions of the hydrogen atoms (Fig. 2).

The dimensions of the water molecule are equal, within the limits of experimental error, for both orientations (Table 7). They are in the ranges of O–H distances [0.86 (3)–1.03 (1) Å] and H–O–H angles [101 (1)–115.2 (5)°] observed in some 90 water molecules in 41 crystalline hydrates, investigated by neutron diffraction and surveyed by Ferraris & Franchini-Angela (1972). According to these authors, the dimensions of the 'average' water molecule are: O–H 0.96 Å and H–O–H 108°. The O–H distances in BaS₂O₃·H₂O

Table 7. *Geometry of the water molecule*

O(W)–H(1)	0.960 (5) Å	H(1)···H(2a)	1.508 (6) Å
O(W)–H(2a)	0.987 (6)	H(1)···H(2b)	1.526 (6)
O(W)–H(2b)	0.997 (6)	H(1)–O(W)–H(2a)	101.5 (5)°
		H(1)–O(W)–H(2b)	102.4 (4)

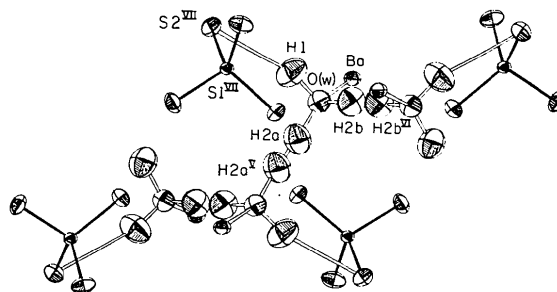


Fig. 2. A chain of water molecules, with the hydrogen-bonding network and the coordination geometry around water oxygen illustrated by double lines. The thermal vibration ellipsoids enclose 50% probability. The significance of the roman numerals is as shown in Table 5.

are close to the corresponding average value, but the H-O-H angles, of 101.5 (5)° and 102.4 (4)°, are among the smallest found in crystalline hydrates. However, as pointed out by Ferraris & Franchini-Angela, the geometry of the water molecule and of its environment in crystal structures exhibits considerable flexibility, which enables water to act as a 'strain-absorber'.

Each O(*W*) atom is in a distorted tetrahedral environment (Fig. 2), the coordination polyhedron being completed by a Ba²⁺ ion and a hydrogen atom from a symmetry-related water molecule [H(2a^v) or H(2b^v)], depending on the orientation of water molecules]. Thus this compound can be assigned to class 2, type *H* crystalline hydrates (Ferraris & Franchini-Angela, 1972; Chidambaram, Sequeira & Sikka, 1964).

The hydrogen bonding

The hydrogen-bonding network proposed by Nardelli & Fava has been confirmed. Each water molecule forms two O-H...O bonds, one with the water molecule (*W*^v) related by a symmetry centre and the other with the water molecule (*W*^{vi}) related by a twofold axis (Fig. 2). Both of these bonds involve the disordered hydrogen atoms. Thus the hydrogen atom in the O(*W*)...O(*W*^v) bond is statistically distributed between the positions H(2a) and H(2a^v), and that in the O(*W*)...O(*W*^{vi}) bond is distributed between the positions H(2b) and H(2b^{vi}).

The dimensions of the O-H...O bonds, the O...O, O-H and H...O distances and the O-H...O and O...O...O angles (Tables 7 and 8), are in agreement with those found in other crystalline hydrates, and the correlations between these dimensions are in accordance with those established by Ferraris & Franchini-Angela.

Each water molecule also forms an ordered hydrogen bond of the type O-H...S, involving the terminal sulphur atom of the S₂O₃²⁻ ion (Fig. 2). The dimensions of this bond, the O(*W*)...S(2^{vi}), O(*W*)-H(1) and H(1)...S(2^{vi}) distances of 3.298 (4), 0.960 (5) and 2.367 (4) Å respectively, and the O(*W*)-H(1)...S(2^{vi}) angle of 163.0 (3)°, are compatible with hydrogen-bonding interactions. The H(1)...S(2^{vi}) distance is 0.43 Å shorter than the sum of van der Waals radii of sulphur, 1.80 Å, and hydrogen, 1.0 Å (Bondi, 1964; Baur, 1972). The operational criterion of Hamilton & Ibers (1968) for the detection of hydrogen bonding is therefore fulfilled. Thus this analysis has produced the first definitive geometrical evidence for the existence

of hydrogen bonding of the type O-H...S in solids (Manojlović-Muir, 1969). More recently Padmanabham *et al.* (1971) have confirmed, also by neutron diffraction analysis, the existence of three O-H...S bonds in Na₂S₂O₃·5H₂O. For these bonds the O...S, O-H and H...S distances and the O-H...S angle are, respectively, 3.13 (2)-3.40 (2) Å, 0.92 (2)-0.96 (2) Å, 2.38 (2)-2.59 (2) Å and 143 (1)-145 (1)°.

Helpful discussions with the late Dr W. C. Hamilton are gratefully acknowledged. Thanks are also due to the U.S. Atomic Energy Commission for the financial support.

References

- ABRAHAM, S. C. & BERNSTEIN, J. L. (1969). *Acta Cryst.* **B25**, 2365-2370.
- BAGGIO, S., AMZEL, L. M. & BECKA, L. N. (1969). *Acta Cryst.* **B25**, 2650-2653.
- BAUR, W. H. (1972). *Acta Cryst.* **B28**, 1456-1465.
- BEAUCAGE, D. R., KELLEY, M. A., OPHIR, D., RANKOWITZ, S., SPINRAD, R. J. & VAN NORTON, R. (1966). *Nucl. Instrum. Meth.* **40**, 26.
- BEDWNOWITZ, A. L., COPPENS, P. & HAMILTON, W. C. (1966). *Abstracts of the Pittsburgh Diffraction Conference*, Pittsburgh, Pennsylvania.
- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441-451.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CHIDAMBARAM, R., SEQUEIRA, A. & SIKKA, S. K. (1964). *J. Chem. Phys.* **41**, 3616-3622.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71-83.
- DONOHUE, J. (1952). *J. Phys. Chem.* **56**, 502-510.
- FERRARIS, G. & FRANCHINI-ANGELA, M. (1972). *Acta Cryst.* **B28**, 3572-3583.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502-510.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*, pp. 14-16. New York: Benjamin.
- MANOJLOVIĆ, LJ. & EDMUNDS, I. G. (1965). *Acta Cryst.* **18**, 543-548.
- MANOJLOVIĆ-MUIR, LJ. (1969). *Nature, Lond.* **224**, 686-687.
- MITSDA, H., MORI, S. & OKAZAKI, C. (1971). *Acta Cryst.* **B27**, 1263-1269.
- NARDELLI, M. & FAVA, G. (1962). *Acta Cryst.* **15**, 477-484.
- NARDELLI, M., FAVA, G. & GIRALDI, G. (1962). *Acta Cryst.* **15**, 227-231.
- NEUTRON DIFFRACTION COMMISSION (1969). *Acta Cryst.* **A25**, 391-392.
- PADMANABHAN, V. M., YADAVA, V. S., NAVARRO, Q. O., GARCIA, A., KARSONO, L., SUH, I.-H. & CHIEN, L. S. (1971). *Acta Cryst.* **B27**, 253-257.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558-564.