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Refinement of the Crystal Structure of Mercuric Sulfate Monohydrate*

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The crystal structure of $HgSO_4.H_2O$ was refined using three-dimensional X-ray diffraction data obtained by direct counting. The space group is *Pmcn* with $a=5{\cdot}416$, $b=8{\cdot}964$, $c=7{\cdot}874$ Å (each $\pm 0{\cdot}003$ Å). Each mercury atom is surrounded by five oxygen atoms and a water molecule at the corners of an irregular octahedron. The distances of these neighbors are 2·17 Å, 2·50 Å (twice), 2·51 Å (twice), and 2·24 Å (water molecule), each ±0·01 Å. A hydrogen bond of length 2·83 Å is identified, but no evidence is found for hydrogen bonding by the second hydrogen atom.

Introduction

In making a survey of hydrogen bonding in hydrated sulfate crystals we became interested in the structure of mercuric sulfate monohydrate. This crystal structure was determined by Bonefačić (1961) by analysis of X-ray data for two projections, but the accuracy of this determination is not sufficient to permit the hydrogen bonding to be established with confidence. We have refined this structure on the basis of three-dimensional data obtained by direct counting of diffracted X-ray intensities. We confirm the general features of the atomic arrangement. The atomic positions imply that each water molecule is involved in one hydrogen bond.

Experimental

Well-formed crystals of $HgSO_4.H_2O$ are readily obtained by dissolving anhydrous $HgSO_4$ in 2·5*M* sulphuric acid and allowing the solution to stand at room temperature. We obtained colorless thin plates of $HgSO_4$ if the concentration of acid were too high, and colorless elongated plates like those described by Hoitsema (1895) as $2HgSO_4.HgO.2H_2O$ if the acidity were slightly lower. At still lower acidity a yellow precipitate appeared.

The crystals of $HgSO_4.H_2O$ exhibit orthorhombic holohedral forms {010}, {011}, {100}, {110}, and {102} in several combinations. The habit is often prismatic along [100] or tabular flattened on {010}.

Intensities were measured with a crystal which could be circumscribed by a nearly square prism with dimensions 0·06 × 0·06 × 0·03 mm. The main faces were {100} and {011}, with the short dimension in the **a** direction. An irregular truncation approximately parallel with (010) reduced it almost to triangular shape. Other small faces truncated corners. It was attached to a glass fiber with Glyptal varnish, with no protection from the atmosphere. The goniometer axis was set in the **c** direction. X-ray measurements were made with a scintillation counter with Mo $K\alpha$ radiation ($\lambda=0{\cdot}70926$ Å for $K\alpha_1$) with counting times of 20 seconds for each of the 618 independent reflections permitted by the space group with $2\theta < 60°$, of which 55 were recorded as zero.

The structure was refined by least squares, using the IBM-7090 computer and our version of the Gantzel–Sparks–Trueblood program (unpublished) to minimize the function $\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2$. A modification included the effect of the out-of-phase scattering of Hg in the calculation of $|F_c|$. Atomic form factors were taken for Hg^{2+} from Thomas & Umeda (1957) with $-2{\cdot}5$ and $10{\cdot}3$ for the in-phase and out-of-phase dispersion corrections (Templeton, 1962). For neutral S we took the values of Tomiie & Stam (1958), and for oxygen we took the average of the values for neutral O and for O^- from Freeman (1959). In the final cycles of refinement unit weight was given to each of 547 non-zero reflections with $\sin\theta/\lambda > 0{\cdot}2$, and zero weight was given to low-angle and zero reflections.

Correction for absorption

For $HgSO_4.H_2O$ we estimate that the linear absorption coefficient is $\mu=418$ cm^{-1}. After some refinement it was apparent that the largest discrepancies were systematic effects of absorption. For a flat crystal with thickness of the order of μ^{-1} we expect the absorption effect to depend mainly on the angles *P* and *Q* between the incident and diffracted beams respectively and the normal to the crystal plate, in this case the *a* axis. For the reflections at $\chi=90°$ (χ is the setting of the vertical circle of the General Electric Goniostat) it was observed that variation of φ (the spindle axis) caused each intensity to change so that it was approximately proportional to a function:

$$1+1{\cdot}153\exp(-0{\cdot}53/m)$$

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where $m=|\cos P|=|\cos Q|$. The data were corrected for absorption by division of each intensity by the above expression, with m taken in general as the harmonic mean of $|\cos P|$ and $|\cos Q|$. One obtains these variables from the instrument settings by the relations (if φ is set so that $P=0$ when $\theta=\varphi=0$):

$$|\cos P|=|\cos\theta\cos\varphi+\sin\theta\sin\varphi\cos\chi|\ ,$$
$$|\cos Q|=|\cos\theta\cos\varphi-\sin\theta\sin\varphi\cos\chi|\ .$$

This procedure accomplished a considerable reduction of the worst discrepancies between observed and calculated structure factors. It has also been useful in connection with the study of ThI_4 (Zalkin, Forrester & Templeton, 1964) and is expected to be generally useful for thin crystals mounted parallel with the goniometer axis.

Results

Unit cell and space group

For the orthorhombic unit cell we find dimensions:

$$a = 5\cdot416\pm0\cdot003\ \text{Å}\ (5\cdot42\pm0\cdot01\ \text{Å})\ ,$$
$$b = 8\cdot964\pm0\cdot003\quad(8\cdot94\pm0\cdot02)\ ,$$
$$c = 7\cdot874\pm0\cdot003\quad(7\cdot82\pm0\cdot02)\ ,$$

which are in reasonable agreement with the values (in parentheses) which were reported by Bonefačić (1961). The space group is $Pmcn$ (D_{2h}^{16}) with reflections $h0l$ absent if l is odd and $hk0$ absent if $h+k$ is odd. Our structure refinement gives further confirmation of this space group.

Atomic parameters

The refinement by least squares was started with the published coordinates (Bonefačić, 1961) as trial structure. After preliminary calculations with isotropic temperature factors, each atom was assigned an anisotropic temperature factor of the form $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-2\beta_{12}hk-2\beta_{13}hl-2\beta_{23}kl)$. For all atoms except O(2) the parameters β_{12} and β_{13} are zero because of the mirror plane symmetry. With 40 independent parameters, the index $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ was reduced to 0·051 for 547 reflections, excluding zeros and low angle data, and to 0·062 for the entire 618 reflections. The final shifts of parameters were 2×10^{-6} or less. The resulting parameters are listed in Tables 1 and 2, and the observed and calculated structure factors in Table 3. We have retained the setting and choice of origin as given by Bonefačić (1961), which corresponds to the general position 8(d):

$$\pm(x, y, z;\ \tfrac{1}{2}-x, \tfrac{1}{2}-y, \tfrac{1}{2}+z;\ \tfrac{1}{2}+x, \bar{y}, \bar{z};\ \bar{x}, \tfrac{1}{2}+y, \tfrac{1}{2}-z)\,.$$

Some interatomic distances and angles are listed in Tables 4 and 5.

Table 1. *Atomic coordinates in* $HgSO_4.H_2O$

Atom	x	y	z	$\sigma(y)$	$\sigma(z)$
Hg	$\frac{1}{4}$	0·2086	0·1329	0·0001	0·0001
S	$\frac{3}{4}$	0·1421	−0·0955	0·0005	0·0006
O(1)	$\frac{3}{4}$	0·078	0·075	0·002	0·002
O(2)	−0·026*	0·234	−0·120	0·001	0·001
O(3)	$\frac{3}{4}$	0·020	−0·224	0·002	0·002
$O(H_2O)$	$\frac{1}{4}$	0·456	0·094	0·002	0·002

* $\sigma(x)=0\cdot002$.

Table 2. *Anisotropic thermal parameters and standard deviations*

Atom	β_{11}	β_{22}	β_{33}	β_{23}	$\sigma(\beta_{11})$	$\sigma(\beta_{22})$	$\sigma(\beta_{33})$	$\sigma(\beta_{23})$
	(each multiplied by 10^4)							
Hg	115	38	53	1	3	1	1	1
S	68	32	46	6	12	4	6	4
O(1)	191	64	59	10	54	19	22	16
O(2)*	70	49	100	−1	25	11	16	12
O(3)	143	28	77	−2	48	15	22	15
$O(H_2O)$	278	28	86	−10	63	15	25	16

* For O(2), $10^4\beta_{12}=-25\pm15$; $10^4\beta_{13}=4\pm20$.

Our refinement shifted O(1) and $O(H_2O)$ about 0·2 and 0·3 Å, respectively, and other atoms smaller amounts. Some circumstantial evidence for the correctness of the structure comes from the dimensions we find for the sulfate ion, which deviates from regular tetrahedral by less than a standard deviation. The average S–O bond length is 1·48 Å. We estimate that thermal motion, if oxygen rides on sulfur, requires a correction of 0·01 Å. The corrected average, 1·488 Å, is to be compared with the corrected average value 1·486 Å found in $Mg(NH_4)_2(SO_4)_2.6H_2O$ (Margulis & Templeton, 1962) and in $MgSO_4.6H_2O$ (Zalkin, Ruben & Templeton, 1964).

Environment of mercury

Each mercury atom has two close ligands, O(3) at 2·17 Å and $O(H_2O)$ at 2·24 Å, which are approximately colinear with a bond angle 169°. The other four neighbors, O(2) at 2·50 or 2·51 Å, are at the corners of a rectangle whose shorter sides are perpendicular to the mirror plane containing Hg, O(3), and $O(H_2O)$. The Hg atom is 0·37 Å from the plane of this rectangle, on the side toward O(3). The six neighbors thus are the corners of an octahedron which is considerably distorted. The octahedra share edges (Fig. 1).

The tendency toward twofold coordination is prevalent among mercuric compounds (Wells, 1962), but frequently is more extreme. For example, in the two forms of HgO (Aurivillius, 1956; Aurivillius & Carlsson, 1958) each Hg has two oxygen neighbors at 2·03 Å and four others at distances 2·79 Å or more. In these cases, of course, the oxygen atoms are unhampered by other bonds.

Hydrogen bonding

Each water molecule has one neighbor, O(1) at 2·83 Å, at a suitable distance for a hydrogen bond. The angle that this bond makes with the $O(H_2O)$–Hg vector (105°) is in the range in which such angles

Table 3. *Observed* (FOB) *and calculated* (FCA) *structure factor magnitudes*

The calculated structure factors are complex because of the out-of-phase scattering by mercury, and the sign given FCA is the sign of the real part. Reflections marked with an asterisk were given zero weight in the refinement

H,K	L	FOB	FCA
0, 0	2	11	-6*
	4	267	-280
	6	0	-10*
	8	124	125
	10	25	-25
0, 1	1	86	89*
	2	155	-192*
	3	61	-63*
	4	50	53
	5	33	-34
	6	128	132
	7	20	19
	8	62	-63
	9	11	17
	10	67	-63
	11	17	-15
0, 2	0	223	-246*
	1	64	-62*
	2	12	10*
	3	39	-38
	4	204	215
	5	78	78
	6	50	-51
	7	0	8*
	8	104	-109
	9	63	-60
	10	34	35
0, 3	1	175	-172*
	2	125	123
	3	132	135
	4	49	-46
	5	108	109
	6	97	-97
	7	80	-83
	8	36	32
	9	31	-34
	10	52	54
0, 4	0	144	140
	1	148	142
	2	39	-36
	3	79	79
	4	89	-88
	5	122	-125
	6	38	36
	7	42	-42
	8	59	60
	9	79	85
	10	29	-30
0, 5	1	135	130
	2	79	-76
	3	160	-157
	4	22	-24
	5	72	-67
	6	44	39
	7	112	112
	8	0	8*
	9	39	33
	10	0	-7*
0, 6	0	0	-7*
	1	133	-130
	2	0	-9*
	3	116	-113
	4	12	13
	5	122	121
	6	0	-8*
	7	50	52
	8	11	-2
	9	76	-73
0, 7	1	102	-99
	2	60	-58
	3	120	116
	4	0	-3*
	5	52	54
	6	44	41
	7	102	-102
	8	0	-6*
	9	12	-16
0, 8	0	54	-53
	1	116	112
	2	0	4*
	3	90	85
	4	50	50
	5	82	-75
	6	21	-21
	7	49	-45
	8	36	-31
0, 9	1	71	70
	2	121	117
	3	80	-78
	4	0	-5*
	5	46	-42
	6	71	-70
	7	59	58
0,10	0	77	74
	1	31	-25
	2	15	-19
	3	15	-18
	4	69	-66
	5	47	44
	6	36	35
0,11	1	35	-30
	2	107	-99
	3	28	27
	4	12	11
	5	24	23
0,12	0	94	-90
	1	0	-6*
	2	0	7*
	3	24	-21
1, 0	2	298	-327*
	4	38	33
	6	184	173
	8	28	-22
	10	90	-82
1, 1	0	199	-215*
	1	71	-74*
	2	38	40*
	3	11	-10
	4	169	180
	5	40	41
	6	66	-69
	7	26	26
	8	106	-110
	9	20	-24
	10	50	52
1, 2	1	24	-23*
	2	206	218*
	3	80	81
	4	24	-23
	5	14	11
	6	135	-141
	7	77	-83
	8	38	43
	9	0	-7*
	10	60	62
1, 3	0	201	204*
	1	142	140
	2	16	-12
	3	150	147
	4	138	-137
	5	109	-107
	6	19	19
	7	58	-59
	8	78	73
	9	53	52
	10	21	-25
1, 4	1	144	146
	2	101	-100
	3	136	-139
	4	34	35
	5	67	-73
	6	52	58
	7	90	94
	8	30	-32
	9	25	26
	10	38	-41
1, 5	0	82	-80
	1	155	-158
	2	13	-13
	3	95	-98
	4	67	71
	5	113	120
	6	13	8
	7	47	48
	8	24	-28
	9	78	-83
	10	12	-5
1, 6	1	130	-128
	2	21	-20
	3	133	135
	4	12	-15
	5	85	86
	6	0	-4*
	7	96	-101
	8	16	16
	9	33	-32
1, 7	0	50	-48
	1	95	92
	2	12	-8
	3	59	59
	4	45	47
	5	114	-117
	6	0	-4*
	7	27	-25
	8	23	-21
	9	85	85
1, 8	1	101	102
	2	53	52
	3	96	-101
	4	20	-19
	5	61	-63
	6	49	-47
	7	63	65
	8	24	24
1, 9	0	114	110
	1	73	-74
	2	10	-11
	3	52	-51
	4	80	-84
	5	59	63
	6	16	8
	7	27	26
1,10	1	31	-32
	2	78	-73
	3	42	38
	4	35	31
	5	20	19
	6	56	60
1,11	0	105	-100
	1	27	27
	2	0	-2*
	3	26	27
	4	85	90
	5	21	-19
1,12	1	12	-12
	2	89	91
	3	12	-1
2, 0	0	297	-320*
	2	15	12
	4	203	195
	6	11	-11
	8	105	-99
	10	26	26
2, 1	1	69	-65
	2	240	242
	3	53	50
	4	45	-42
	5	32	29
	6	159	-148
	7	11	-16
	8	57	54
	9	19	-15
	10	83	77
2, 2	0	129	134
	1	65	67
	2	14	-14
	3	41	43
	4	142	-145
	5	76	-75
	6	52	50
	7	0	-10*
	8	82	85
	9	54	57
	10	35	-35
2, 3	1	129	129
	2	164	-172
	3	108	-109
	4	32	33
	5	86	-89
	6	109	113
	7	73	73
	8	27	-25
	9	29	28
	10	61	-58
2, 4	0	62	-64
	1	138	-139
	2	34	34
	3	83	-85
	4	41	45
	5	116	120
	6	41	-38
	7	42	45
	8	40	-43
	9	74	-81
	10	28	31
2, 5	1	97	-100
	2	104	106
	3	125	129
	4	23	24
	5	51	51
	6	51	-54
	7	95	-99
	8	16	-11
	9	27	-26
2, 6	0	27	-29
	1	134	135
	2	0	4*
	3	120	118
	4	13	13
	5	119	-118
	6	10	11
	7	59	-56
	8	12	-8
	9	69	70
2, 7	1	77	75
	2	31	29
	3	93	-95
	4	0	-1*
	5	37	-39
	6	24	-26
	7	90	90
	8	17	8
2, 8	0	67	66
	1	112	-115
	2	0	-3*
	3	88	-91
	4	58	-59
	5	72	77
	6	19	18
	7	47	50
	8	33	35
2, 9	1	55	-52
	2	92	-95
	3	62	63
	4	0	5*
	5	30	29
	6	60	58
	7	49	-50
2,10	0	80	-78
	1	32	33
	2	19	17
	3	25	27
	4	66	69
	5	46	-47
	6	30	-31
2,11	1	20	19
	2	88	86
	3	21	-18
	4	12	-11
2,12	0	87	88
	1	12	-2
3, 0	2	224	222
	4	24	-25
	6	143	-136
	8	18	20
	10	71	68
3, 1	0	204	187
	1	56	53
	2	32	-28
	3	24	17
	4	172	-157
	5	33	-33
	6	64	56
	7	18	-22
	8	107	98
	9	15	20
	10	51	-44
3, 2	1	27	28
	2	157	-154
	3	70	-66
	4	26	20
	5	0	-11*
	6	117	110
	7	72	70
	8	39	-37
	9	14	6
	10	56	-52
3, 3	0	168	-172
	1	107	-106
	2	12	8
	3	105	-111
	4	118	124
	5	79	86
	6	0	-15*
	7	46	49
	8	64	-67
	9	47	-45
3, 4	1	110	-112
	2	62	64
	3	112	115
	4	35	-31
	5	60	60
	6	44	-43
	7	81	-82
	8	32	29
	9	18	-23
3, 5	0	76	78
	1	117	122
	2	13	10
	3	76	78
	4	64	-67
	5	93	-100
	6	11	-9
	7	43	-39
	8	24	27
	9	70	71
3, 6	1	112	112
	2	23	26
	3	110	-115
	4	14	13
	5	74	-76
	6	0	-3*
	7	81	87
	8	21	-15
3, 7	0	30	31
	1	76	-75
	2	0	5*
	3	45	-47
	4	33	-33
	5	94	97
	6	0	4*
	7	21	20
	8	13	16
3, 8	1	85	-89
	2	47	-50
	3	84	88
	4	19	16
	5	54	57
	6	43	44
	7	51	-57
3, 9	0	85	-90
	1	58	60
	2	0	9*
	3	39	41
	4	69	69
	5	48	-53
	6	0	-7*
3,10	1	28	30
	2	65	67
	3	35	-35
	4	24	-26
	5	22	-19
3,11	0	84	83
	1	21	-21
	2	0	2*
	3	22	-22
4, 0	0	247	251
	2	0	-6*
	4	176	-175
	6	0	8*
	8	95	90
4, 1	1	49	48
	2	134	-128
	3	38	-39
	4	45	38
	5	26	-27
	6	102	95
	7	23	14
	8	48	-47
	9	15	14
4, 2	0	159	-148
	1	43	-43
	2	0	8*
	3	25	-23
	4	149	137
	5	60	55
	6	32	-32
	7	0	6*
	8	90	-78
	9	46	-45
4, 3	1	106	-101
	2	103	97
	3	92	88
	4	25	-24
	5	78	74
	6	80	-72
	7	64	-59
	8	25	22
	9	26	-25
4, 4	0	70	75
	1	90	91
	2	29	-22
	3	55	54
	4	51	-55
	5	87	-88
	6	27	28
	7	29	-30
	8	45	43
4, 5	1	84	87
	2	55	-55
	3	102	-106
	4	19	-15
	5	43	-48
	6	27	30
	7	81	82
	8	0	6*
4, 6	0	0	3*
	1	92	-95
	2	0	-3*
	3	81	-83
	4	11	4
	5	82	87
	6	12	-8
	7	42	40
4, 7	1	68	-67
	2	36	-37
	3	79	82
	4	0	-1*
	5	38	38
	6	30	29
	7	77	-76
4, 8	0	40	-38
	1	75	80
	2	0	4*
	3	61	62
	4	38	37
	5	51	-57
	6	13	-17
4, 9	1	47	50
	2	87	85
	3	58	-57
	4	0	-3*
	5	29	-30
4,10	0	56	57
	1	17	-20
	2	18	-14
	3	13	-14
5, 0	2	166	-170
	4	11	14
	6	108	109
	8	14	-14
5, 1	0	104	-103
	1	36	-37
	2	19	21
	3	16	-20
	4	92	93
	5	21	23
	6	44	-43
	7	13	18
	8	66	-66
5, 2	1	20	-19
	2	133	126
	3	45	44
	4	13	-13
	5	0	8*
	6	98	-90
	7	53	-50
	8	26	25
5, 3	0	110	98
	1	86	78
	2	0	-6*
	3	84	79
	4	81	-76
	5	70	-63
	6	14	12
	7	37	-38
5, 4	1	75	70
	2	60	-56
	3	85	-78
	4	27	22
	5	46	-39
	6	43	40
	7	66	61
5, 5	0	46	-41
	1	90	-88
	2	0	-6*
	3	59	-59
	4	32	37
	5	75	76
	6	0	6*
	7	36	31
5, 6	1	74	-79
	2	0	-6*
	3	79	81
	4	0	-9*
	5	52	54
	6	0	-5*
5, 7	0	34	-32
	1	59	59
	2	12	-3
	3	36	38
	4	32	31
	5	71	-75
5, 8	1	63	61
	2	28	28
	3	58	-62
	4	13	-13
5, 9	0	76	76
	1	45	-48
	2	0	-5*
6, 0	0	131	-138
	2	12	5
	4	99	103
	6	0	-8*
6, 1	1	26	-31
	2	84	98
	3	17	24
	4	22	-25
	5	13	19
	6	64	-74
6, 2	0	80	83
	1	30	30
	2	0	-6*
	3	13	16
	4	78	-79
	5	38	-39
	6	20	23
6, 3	1	60	63
	2	82	-82
	3	55	-56
	4	19	12
	5	49	-47
	6	64	59
6, 4	0	34	-33
	1	68	-64
	2	14	15
	3	43	-41
	4	29	27
	5	71	63
6, 5	1	53	-53
	2	54	47
	3	72	67
	4	15	11
	5	27	29
6, 6	0	21	-13
	1	74	72
	2	0	-0*
	3	69	64
	4	0	6*
6, 7	1	44	39
	2	21	18
7, 0	2	83	92
	4	0	-9*
7, 1	0	69	79
	1	18	23
	2	13	-12
	3	13	15
	4	67	-71
7, 2	1	13	14
	2	60	-65
	3	23	-29
	4	0	10*
7, 3	0	72	-77
	1	43	-47
	2	0	3*
	3	50	-48
7, 4	1	47	-46
	2	25	22

commonly fall in other hydrated salts. The fact that O(1) is the only oxygen atom not adjacent to a mercury atom makes it the most appropriate one to accept a hydrogen bond.

The next nearest oxygen neighbor of water is O(3) at 2·96 Å. Such a distance is near the upper limit for a hydrogen bond. The angle with respect to the O(H_2O)–Hg vector (109°) is acceptable, but the angle O(3)–O(H_2O)–O(1) = 146° is incompatible with a normal H–O–H angle.

All other neighbors occur in pairs related by the mirror plane. Thus bonding to one of them must

Table 4. *Interatomic distances in* $HgSO_4.H_2O$

Atom	Neighbor	Number	Distance
Hg	O(2)	2	2·50 ± 0·01 Å
	O(2)	2	2·51 ± 0·01
	O(3)	1	2·17 ± 0·01
	$O(H_2O)$	1	2·24 ± 0·01
S	O(1)	1	1·46 ± 0·02
	O(2)	2	1·48 ± 0·01
	O(3)	1	1·49 ± 0·02
$O(H_2O)$	Hg	1	2·24 ± 0·01
	O(1)*	1	2·83 ± 0·02
	O(3)	1	2·96 ± 0·02
	O(2)†	2	3·00 ± 0·02
	O(2)	2	3·04 ± 0·02
	O(3)	2	3·07 ± 0·02
	$O(H_2O)$	2	3·18 ± 0·02
	O(2)†	2	3·20 ± 0·02

* Neighbor connected by hydrogen bond.
† Neighbor in same octahedron.

Table 5. *Angles in* $HgSO_4.H_2O$*

$O(H_2O)$–Hg–O(3)	169°
$O(H_2O)$–Hg–O(2)	78, 85
O(3)–Hg–O(2)	86, 111
O(2)–Hg–O(2)	73, 73, 104, 163
O(1)–S–O(2)	110
O(1)–S–O(3)	109
O(2)–S–O(2)	110
O(2)–S–O(3)	109
Hg–$O(H_2O)$–O(1)	105
O(1)–$O(H_2O)$–O(3)†	146
O(1)–$O(H_2O)$–O(3)‡	63
O(1)–$O(H_2O)$–O(2)§	65

* Standard deviations are 1° or less.
† O(3) at 2·96 Å.
‡ O(3) at 3·07 Å.
§ O(2) at 3·04 Å.

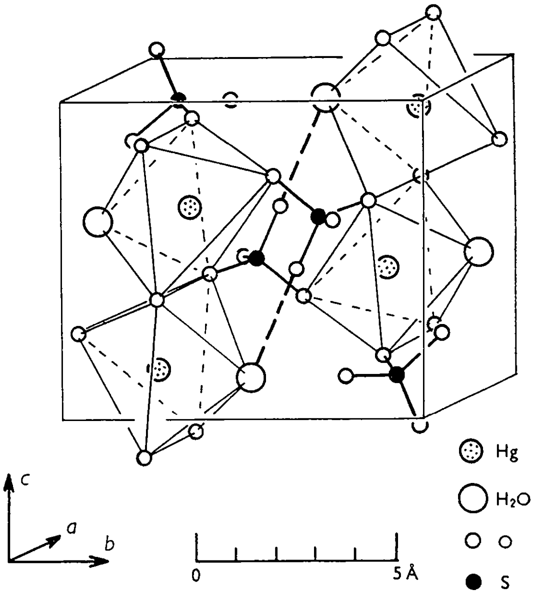

Fig. 1. Crystal structure of $HgSO_4.H_2O$.
A heavy broken line indicates the hydrogen bond.

involve disorder or change of the space group, unless the bond to O(1) is discarded. With disorder one can shorten somewhat the distances which otherwise are too long, but the angles are unsatisfactory as long as the bond to O(1) is retained. It is in principle impossible to prove that any crystal has a mirror plane beyond some limiting experimental accuracy, but in the present case we have no evidence of the absence of such a plane. Thus from the present evidence we conclude that there is only one hydrogen bond.

We calculated an electron density difference function in the section at $x = 0·25$ as an attempt to locate the hydrogen atoms. The result showed spurious peaks as high as 1·2 e.$Å^{-3}$ in locations distant from the water molecule and therefore cannot be considered to be reliable for the hydrogen atoms. However, a peak of height 0·8 e.$Å^{-3}$ appeared at 0·25, 0·51, 0·20, which is very close to the expected position for a hydrogen atom in the bond to O(1). No peak appeared at a reasonable position for the second hydrogen atom. We expect a non-bonded hydrogen atom to have large thermal motion and therefore to be difficult to see.

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