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MERCURIC SULFATE MONOHYDRATE

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UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
Contract No. W-7405-eng-48

REFINEMENT OF THE CRYSTAL STRUCTURE OF MERCURIC SULFATE MONOHYDRATE

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August 1963

Refinement of the Crystal Structure of Mercuric Sulfate Monohydrate*

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The crystal structure of $\text{HgSO}_4 \cdot \text{H}_2\text{O}$ was refined using three-dimensional x-ray diffraction data obtained by direct counting. The space group is Pmcn with a = 5.416, b = 8.964, c = 7.874 Å (each \pm 0.003 Å). Each Hg 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 \pm 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

*Work done in part under the auspices of the U. S. Atomic Energy Commission.

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 $\text{HgSO}_4 \cdot \text{H}_2\text{O}$ are readily obtained by dissolving anhydrous HgSO_4 in 2.5 M H_2SO_4 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 $2\text{HgSO}_4 \cdot \text{HgO} \cdot 2\text{H}_2\text{O}$ if the acidity were slightly lower. At lower acidity a yellow precipitate appeared.

The crystals of $\text{HgSO}_4 \cdot \text{H}_2\text{O}$ 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 $0.06 \times 0.06 \times 0.03$ 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 $\text{MoK}\alpha$ radiation ($\lambda = 0.70926 \text{ \AA}$ for $\text{K}\alpha_1$) with counting times of 20 seconds for each of the 618 independent reflections permitted by the space group with $2\theta < 60^\circ$, 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 $\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$. 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^{++} from Thomas and Umeda (1957) with -2.5 and 10.3 for the in-phase and out-of-phase dispersion corrections (Templeton, 1962). For neutral S we took the values of Tommie and 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 $\sin\theta/\lambda > 0.2$, and zero weight was given to low-angle and zero reflections.

Correction for absorption

For $\text{HgSO}_4 \cdot \text{H}_2\text{O}$ we estimate that the linear absorption coefficient is $\mu = 418 \text{ cm}^{-1}$. 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 \underline{P} and \underline{Q} between the incident and diffracted beams respectively and the normal to the crystal plate, in this case the \underline{a} axis. For the reflections at $\chi = 90^\circ$ (χ is the setting of the vertical circle of the General Electric Coniostat) it was observed that variation of ϕ (the spindle axis) caused each intensity to change so that it was approximately proportional to a function:

$$1 + 1.153 \exp(-0.53/\underline{m})$$

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

$$|\cos\underline{P}| = |\cos\theta\cos\phi + \sin\theta\sin\phi\cos\chi|,$$

$$|\cos\underline{Q}| = |\cos\theta\cos\phi - \sin\theta\sin\phi\cos\chi|.$$

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 and Templeton, 196x) 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:

$$\underline{a} = 5.416 \pm 0.003 \text{ \AA} (5.42 \pm 0.01 \text{ \AA}),$$

$$\underline{b} = 8.964 \pm 0.003 \text{ \AA} (8.94 \pm 0.02 \text{ \AA}),$$

$$\underline{c} = 7.874 \pm 0.003 \text{ \AA} (7.82 \pm 0.02 \text{ \AA}),$$

which are in reasonable agreement with the values (in parentheses) which were reported by Bonefačić (1961). The space group is $\underline{Pm\bar{c}n}$ (\underline{D}_{2h}^{16}) with reflections $\underline{h0\ell}$ absent if $\underline{\ell}$ is odd and $\underline{hk0}$ absent if $\underline{h} + \underline{k}$ 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 $\exp(-\beta_{11}\underline{h}^2 - \beta_{22}\underline{k}^2 - \beta_{33}\underline{\ell}^2 - 2\beta_{12}\underline{hk} - 2\beta_{13}\underline{h\ell} - 2\beta_{23}\underline{k\ell})$. 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 $\underline{R} = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ 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):

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

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

Our refinement shifted O(1) and O(H₂O) 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 $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Margulis and Templeton, 1962) and in $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ (Zalkin, Ruben and Templeton, 196x).

Environment of mercury

Each mercury atom has two close ligands, O(3) at 2.17 Å and O(H₂O) 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(H₂O). 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 two-fold coordination is prevalent among mercuric compounds (Wells, 1962), but frequently is more extreme. For example, in the two forms of HgO (Aurivillius, 1956; Aurivillius and 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(H₂O)-Hg vector (105°) is in the range in which such angles 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(H₂O)-Hg vector (109°) is acceptable, but the angle O(3)-O(H₂O)-O(1) = 116° 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 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 electron/Å³ 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 electron/Å³ 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.

We thank Dr J. D. Forrester for assistance in this research.

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Table 1. Atomic coordinates in $\text{HgSO}_4 \cdot \text{H}_2\text{O}$

Atom	x	y	z	$\sigma(y)$	$\sigma(z)$
Hg	1/4	0.2086	0.1329	0.0001	0.0001
S	3/4	0.1421	-0.0955	0.0005	0.0006
O(1)	3/4	0.078	0.075	0.002	0.002
O(2)	-0.026 ^a	0.234	-0.120	0.001	0.001
O(3)	3/4	0.020	-0.224	0.002	0.002
O(H ₂ O)	1/4	0.456	0.094	0.002	0.002

^a $\sigma(x) = 0.002$.

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) ^a	70	49	100	-1	25	11	16	12
O(3)	143	28	77	-2	48	15	22	15
O(H ₂ O)	278	28	86	-10	63	15	25	16

^a For O(2), $10^4\beta_{12} = -25 \pm 15$; $10^4\beta_{13} = 4 \pm 20$.

Table 3. Observed and calculated structure factor magnitudes, FOB and FCA.

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.

(Table submitted as a photographic print)

Table 4. Interatomic distances in $\text{HgSO}_4 \cdot \text{H}_2\text{O}$

Atom	Neighbor	Number	Distance
Hg	O(2)	2	$2.50 \pm 0.01 \text{ \AA}$
	O(2)	2	2.51 ± 0.01
	O(3)	1	2.17 ± 0.01
	O(H ₂ O)	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 ₂ O)	Hg	1	2.24 ± 0.01
	O(1) ^a	1	2.83 ± 0.02
	O(3)	1	2.96 ± 0.02
	O(2) ^b	2	3.00 ± 0.02
	O(2)	2	3.04 ± 0.02
	O(3)	2	3.07 ± 0.02
	O(H ₂ O)	2	3.18 ± 0.02
	O(2) ^b	2	3.20 ± 0.02

^aNeighbor connected by hydrogen bond

^bNeighbor in same octahedron

Table 5. Angles in $\text{HgSO}_4 \cdot \text{H}_2\text{O}^{\text{a}}$

$\text{O}(\text{H}_2\text{O})-\text{Hg}-\text{O}(3)$	169°
$\text{O}(\text{H}_2\text{O})-\text{Hg}-\text{O}(2)$	$78^\circ, 85^\circ$
$\text{O}(3)-\text{Hg}-\text{O}(2)$	$86^\circ, 111^\circ$
$\text{O}(2)-\text{Hg}-\text{O}(2)$	$73^\circ, 73^\circ, 104^\circ, 163^\circ$
$\text{O}(1)-\text{S}-\text{O}(2)$	110°
$\text{O}(1)-\text{S}-\text{O}(3)$	109°
$\text{O}(2)-\text{S}-\text{O}(2)$	110°
$\text{O}(2)-\text{S}-\text{O}(3)$	109°
$\text{Hg}-\text{O}(\text{H}_2\text{O})-\text{O}(1)$	105°
$\text{O}(1)-\text{O}(\text{H}_2\text{O})-\text{O}(3)^{\text{b}}$	146°
$\text{O}(1)-\text{O}(\text{H}_2\text{O})-\text{O}(3)^{\text{c}}$	63°
$\text{O}(1)-\text{O}(\text{H}_2\text{O})-\text{O}(2)^{\text{d}}$	65°

^aStandard deviations are 1° or less.

^b $\text{O}(3)$ at 2.96 Å

^c $\text{O}(3)$ at 3.07 Å

^d $\text{O}(2)$ at 3.04 Å

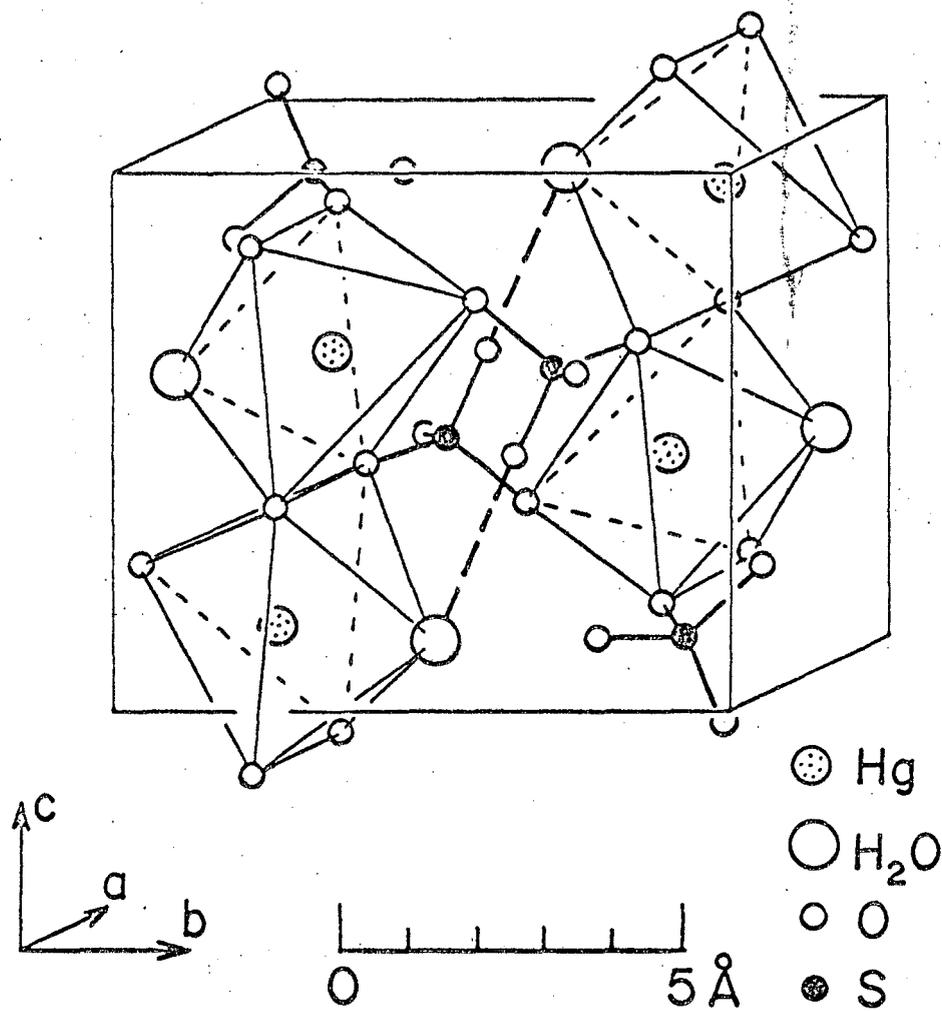


Fig. 1. Crystal structure of $\text{HgSO}_4 \cdot \text{H}_2\text{O}$. A heavy broken line indicates the hydrogen bond.

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