The Crystal Structure of Mercuric Sulphate Monohydrate

By A. Bonefačić

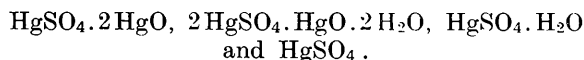*Rudjer Bošković Institute and Physical Institute of the Faculty of Science, University, Zagreb, Yugoslavia*

The structure of mercuric sulphate monohydrate has been determined by X-ray analysis. It is orthorhombic with the space group D_{2h}^{16}-*Pmcn*. The unit cell of dimensions

$$a = 5\cdot42, \quad b = 8\cdot94, \quad c = 7\cdot82 \text{ Å}$$

contains four formula units. The parameters of the atoms were determined with the help of Patterson and Fourier–Bragg projections. Each mercury atom is surrounded by five oxygen atoms and a water molecule in octahedral coordination.

Introduction

A number of authors have worked on the mercuric sulphates. Hoitsema (1895) has listed the following compounds:

$$\text{HgSO}_4.2\text{HgO}, \quad 2\text{HgSO}_4.\text{HgO}.2\text{H}_2\text{O}, \quad \text{HgSO}_4.\text{H}_2\text{O}$$
$$\text{and HgSO}_4 .$$

Some authors did not agree completely with Hoitsema's results, but they were confirmed by Paić (1933), who used X-ray powder diagrams. The same author studied also the dehydratation of mercuric sulphate hydrates.

With the intention of finding out the role of a water molecule in these sulphates, we started our work on the crystal structures of the compounds mentioned above. In the present article the result of the crystal analysis of $\text{HgSO}_4.\text{H}_2\text{O}$ is reported. Work on the structures of the remaining sulphates is in progress.

Experimental

Well-formed, colourless, transparent single crystals were prepared by slow evaporation of a solution of mercuric sulphate in dilute sulphuric acid. The crystals obtained were orthorhombic and had already been described and examined crystallographically by Hoitsema (1895).

All X-ray diffraction data were obtained from oscillation and Weissenberg diagrams taken with nickel-filtered Cu K radiation. The diagrams gave

$$a = 5\cdot42 \pm 0\cdot01, \quad b = 8\cdot94 \pm 0\cdot02, \quad c = 7\cdot82 \pm 0\cdot02 \text{ Å} .$$

The pycnometrically measured density of the crystals was 5·52 g.cm.$^{-3}$; that calculated with four formula units in the elementary cell is 5·36 g.cm.$^{-3}$.

The observed reflexions are: hkl: no conditions, $hk0$: $h + k = 2n$, $0kl$: no conditions, $h0l$: $l = 2n$. It thus follows, taking also into account the holohedral appearance of the crystals, that D_{2h}^{16}-*Pmcn* is the most probable space group.

Multiple-film Weissenberg diagrams were used to obtain intensity data for $0kl$ and $hk0$ reflexions. The relative intensities were determined from the optical densities measured at the centre of each spot by means of a microdensitometer. In order to facilitate the absorption correction, the specimen was made cylindrical by grinding. The linear absorption coefficient was 825 cm.$^{-1}$. Corrections for Lorentz and polarization factors were made in the usual way.

Determination of the structure

There are for the space group *Pmcn* eightfold general positions and, since the unit cell contains four formula units, the mercury, sulphur and oxygen (from a water molecule) atoms must occupy special positions. Because of the absence of the extra conditions of extinctions for hkl reflexions it follows that these atoms lie in the plane of symmetry m at $\frac{1}{4}$ and $\frac{3}{4}$ of a period a.

The parameters of the mercury atom were obtained from [100] and [001] Patterson projections. The contour map of the Patterson projection on (100) is given in (Fig. 1(a)). For the first Fourier synthesis the signs of the structure factors $F(0kl)$ and $F(hk0)$ were determined using only mercury-atom contributions. Later the signs were recalculated taking also the sulphur-atom contributions into account. Only five structure factors changed sign owing to the inclusion of the sulphur atom. The maxima of all atoms (except the hydrogen atom) are well resolved. In both projections the diffraction rings around the mercury atoms influenced appreciably the position of the maximum

Table 1. *Atomic parameters in* $\text{HgSO}_4.\text{H}_2\text{O}$

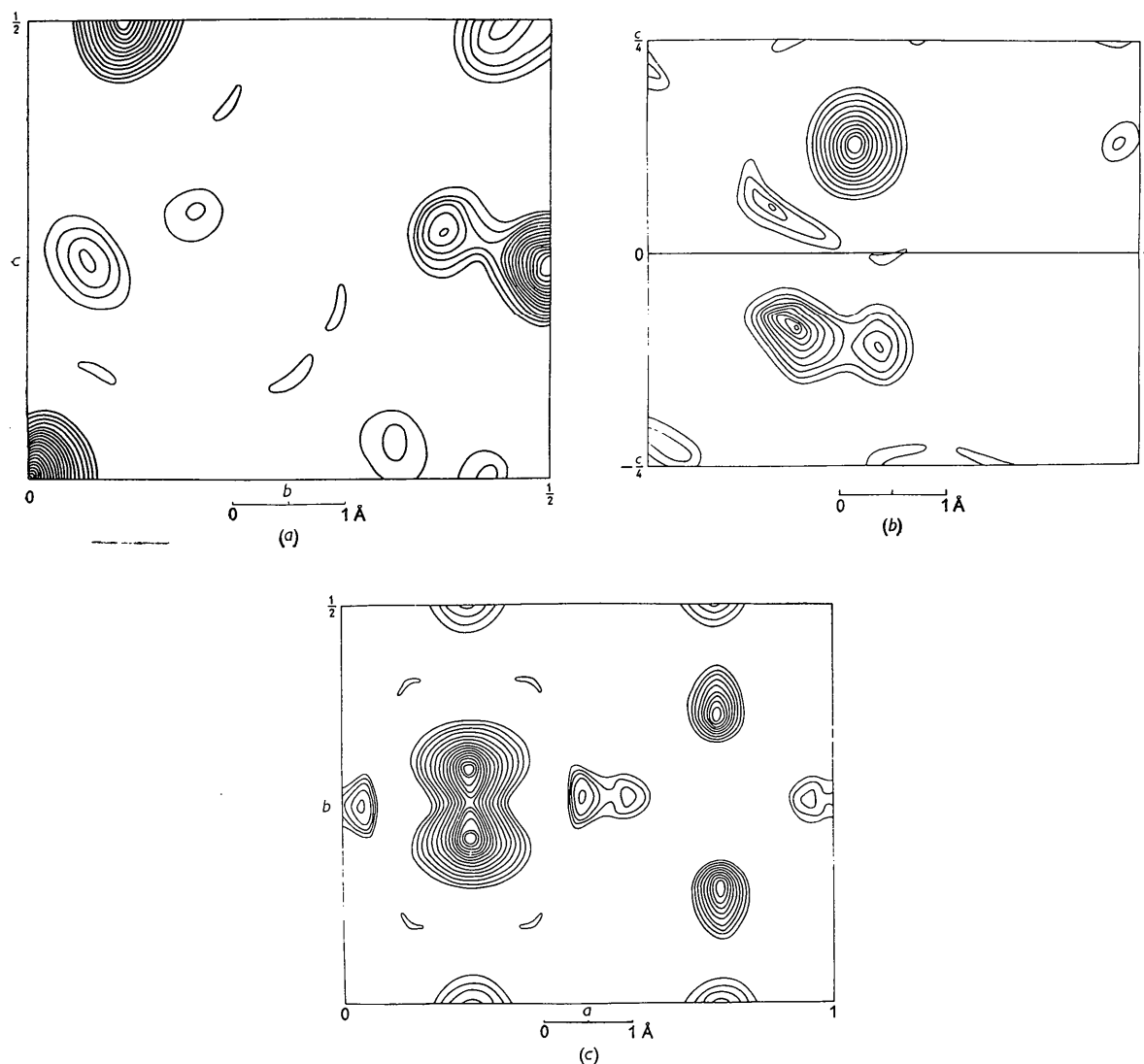| Atom	x	y	z
4 Hg	$\frac{1}{4}$	0·208	0·133
4 S	$-\frac{1}{4}$	0·145	$-0\cdot094$
4 O(I)	$-\frac{1}{4}$	0·087	0·048
8 O(II)	$-0\cdot017$	0·241	$-0\cdot116$
4 O(III)	$-\frac{1}{4}$	0·019	$-0\cdot228$
4 O(H$_2$O)	$\frac{1}{4}$	0·470	0·130

Fig. 1. (a) The contour map of the Patterson projection on (100). (b) Fourier projection on (100). By the mercury atom peak each seventh line is drawn. (c) Fourier projection on (001). By the mercury atom peak each third line is drawn. The contours are at arbitrary intervals.

of the oxygen atom which fell near the mercury atom. These peaks appeared also distorted and lengthened (Fig. 1(b) and (c)).

Subtracting the contributions of mercury and sulphur atoms to each reflexion, we could readjust somewhat the positions of the oxygen atoms. The final atomic coordinates are given in Table 1 and the comparison between F_o and F_c is given in Table 2.

The parameter B of the temperature factor was determined from calculated and observed structure amplitudes, the straight line being determined by the least-squares method. We found by this procedure $B = 2.35$ Å² for the projection along [100] and $B = 2.70$ Å² for the projection along [001]. The reliability index $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ has the values 0.18 and 0.15 for $F(0kl)$ and $F(hk0)$ respectively.

Description and discussion of the structure

The mercury atom lies at the centre of a distorted octahedron of five oxygen atoms from a sulphate ion and an oxygen atom from a water molecule.

In the [001] direction the coordination octahedra are arrayed in zigzag chains by sharing one edge (Fig. 2). This common edge of two linked octahedra is the shortest O–O distance in the octahedron. Neighbouring chains of octahedra are connected through SO_4 groups, one connection along [100] by O(II), the other one by O(II) and O(III). The O(I) atom is included in the sulphate tetrahedra only. This oxygen atom is nearer to sulphur (1.24 Å) than the other atoms of oxygen in the sulphate ion.

The interatomic distances between the nearest atoms

Table 2. *Observed and calculated structure amplitudes*

| 0kl	F_o	F_c		0kl	F_o	F_c		0kl	F_o	F_c		hk0	F_o	F_c
002	0	−5		038	31	30		074	0	3		600	73	−91
004	194	−251		039	24	−20		075	42	34		110	259	−215
006	16	19		040	141	135		076	32	28		310	144	164
008	85	92		041	138	150		077	60	76		510	66	−81
0,0,10	42	−25		042	46	−27		078	0	11		020	227	−245
011	106	91		043	78	63		080	48	−52		220	127	114
012	172	−189		044	83	−86		081	94	93		420	111	−119
013	62	−45		045	102	−120		082	0	9		620	46	45
014	47	34		046	36	29		083	73	36		130	198	190
015	34	−25		047	37	−27		084	41	38		330	155	−145
016	96	112		048	46	42		085	54	−64		530	64	69
017	16	9		049	50	65		086	16	−20		040	140	142
018	48	−67		051	122	114		087	26	−25		240	69	−50
019	18	7		052	70	−60		091	56	39		440	62	67
0,1,10	35	−49		053	143	−142		092	88	89		640	17	−20
020	251	−250		054	28	20		093	55	−52		150	85	−66
021	89	−64		055	63	−55		094	0	16		350	75	56
022	0	−5		056	38	23		095	32	−22		550	31	−22
023	40	−39		057	79	110		096	34	−48		060	0	5
024	162	188		058	0	−2		0,10,0	54	49		260	36	−37
025	66	75		059	27	21		0,10,1	19	35		460	0	5
026	43	−35		060	0	6		0,10,2	14	−12		170	51	−43
027	0	3		061	123	−117		0,10,3	14	−26		370	30	26
028	76	−78		062	0	−5		0,10,4	38	44		570	20	−20
029	40	−26		063	102	−98		0,10,5	32	39		080	51	−52
0,2,10	16	24		064	16	−6		0,11,1	19	−16		280	58	69
031	195	−140		065	94	93		0,11,2	50	−74		480	26	−30
032	132	120		066	8	−13		0,11,3	22	14		190	90	73
033	125	131		067	38	30						390	62	−53
034	50	−68		068	0	−1		hk0	F_o	F_c		0,10,0	60	39
035	92	88		071	91	−86		200	267	−295		2,10,0	57	−51
036	77	−95		072	58	−52		400	164	223		1,11,0	58	−65
037	63	−75		073	98	95								
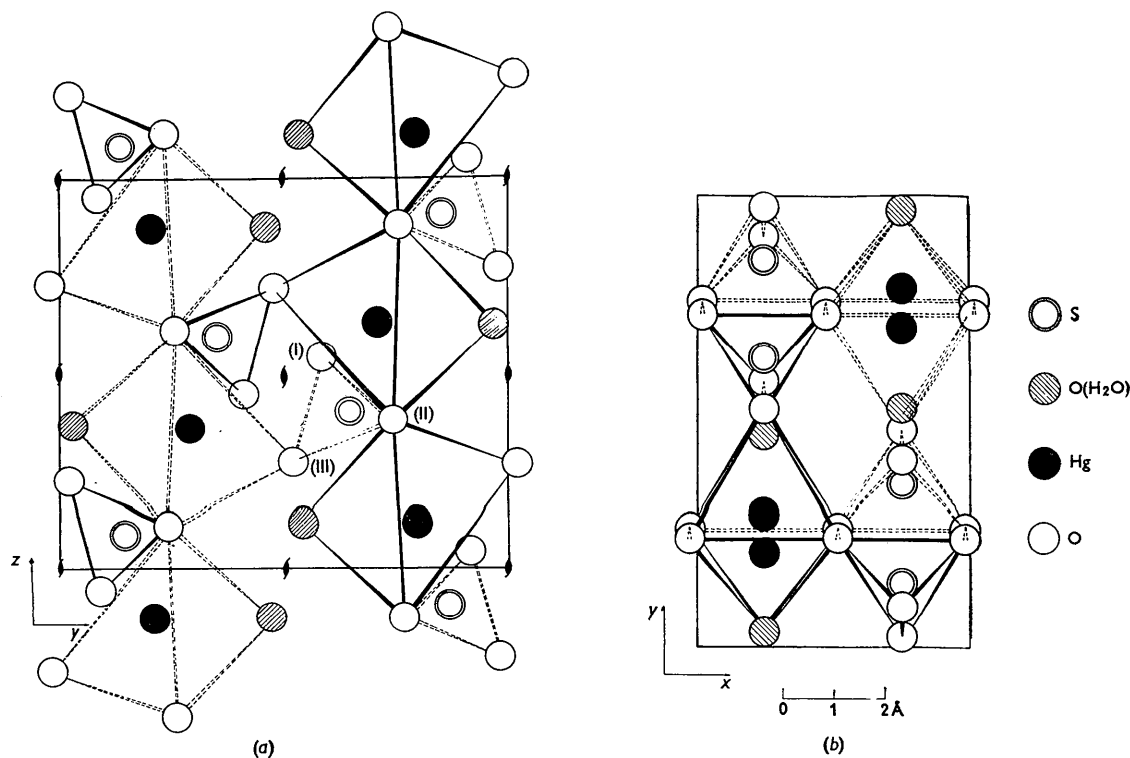
Fig. 2. Projection of the unit cell.   (a) On (100). The origin is in the centre of the Fig.   (b) On (001) Polyhedra in the rear are drawn in the broken lines.

in the unit cell, calculated with the values of parameters listed in Table 1, are given in Table 3.

Table 3. *Interatomic distances in* $HgSO_4 . H_2O$

Atom	Neighbour	Coordination number	Interatomic distances
Hg	O(II)	2	2·44 Å
	O(II)	2	2·47
	O(III)	1	2·10
	O(H₂O)	1	2·34
S	O(I)	1	1·24
	O(II)	2	1·53
	O(III)	1	1·53
O–O distances in tetrahedron			
O(I)	O(II)	—	1·95
	O(III)	—	2·24
O(II)	O(II)	—	2·53
	O(III)	—	2·51
O–O distances in octahedron			
O(II)	O(II)	—	3·91
	O(II)	—	2·89
	O(H₂O)	—	3·09
	O(H₂O)	—	3·18
	O(III)	—	3·85
	O(III)	—	3·14

The values for the distances from mercury to the sulphate–oxygen atoms O(II) (2·44 and 2·47 Å) are nearly equal to the sum of ionic radii (2·45 Å), if the values of 1·10 Å, the generally accepted value for the radius of the mercuric ion, and 1·35 Å for oxygen are used. Distances of nearly the same length (2·40 and 2·42 Å) are found to exist also in crystals of mercurous nitrate dihydrate, between mercury and the nitrate-oxygen atoms (Grdenić, 1956).

Shorter distances between the mercury atom and the water molecule (2·34 Å) are found. It may be compared with the distances between the mercury atom and the water molecule in mercurous nitrate dihydrate (2·15 Å). A short coordination Hg–O bond has been shown to exist also in mercury diethylene oxide (2·21 Å) by Grdenić (1952), and much shorter (2·03 Å) in trichlormercury oxonium chloride (Šćavničar & Grdenić, 1955) and in mercuric oxide (Aurivilius, 1954).

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The Crystal Structure of URe₂

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The intermetallic compound URe₂ has two allotropic forms. Up to 180 °C. it has an orthorhombic structure, space group *Cmca*; above this temperature a C14 structure is formed by a simple dilation of the unit cell. The lattice parameters at 20 °C. are

$$a = 5·600, \quad b = 9·180, \quad c = 8·460 \text{ Å} .$$

For the hexagonal modification at 213 °C. $a = 5·433$, $c = 8·561$ Å. In both modifications the thermal expansion coefficients are positive along c and negative along a.

Introduction

During an investigation of the uranium–rhenium phase diagram an intermetallic compound URe₂ was observed (Brook & Hatt, 1954). An alloy of composition uranium 66·7 at.% rhenium appeared single-phased when examined microscopically and by the X-ray Debye–Scherrer powder method, whereas alloys with higher rhenium content showed free rhenium, and those of lower rhenium content free uranium. Spacing measurements indicated a negligible solubility of either rhenium or uranium in URe₂.

Structure determination

Alloys of URe₂ were prepared from uranium bar