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Original Scientific Paper

The Crystal Structure of Anhydrous Mercuric Sulphate

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The crystal structure of anhydrous mercuric sulphate has been determined by X-ray analysis. It is orthorhombic with the space group $Pmn2_1$ (No 31).

The unit cell of dimensions

$$a = 6.58,\ b = 4.78 \text{ and } c = 4.82 \text{ Å}$$

contains two formula units. The parameters of the atoms are determined with the help of Patterson projections and the (001) Fourier projection. Each mercury atom is surrounded tetrahedrally by sulphate-oxygen atoms.

INTRODUCTION

In a previous paper $Pmn2_1$ was proposed[1] as the most probable space group for $HgSO_4$. Cell dimensions and the results of Patterson projections were also reported in the same paper.

The present article is concerned with the crystal structure of $HgSO_4$. The shapes and position of oxygen-atom peaks in all projections appeard to be considerably influenced by diffraction effects from mercury atoms. The effects were especially pronounced in the (100) and (010) projections owing to the smaller number of terms used in the summation. Therefore the study of electron density distribution is based on the (001) projection.

EXPERIMENTAL

Single crystals were obtained by slow evaporation of a solution of mercuric sulphate in dilute sulphuric acid. The X-ray crystallographic data are those as reported in a previous paper[1] *i.e.*

Number of molecules in the unit cell: $z = 2$
(calculated density 6.49 g cm^{-3})
Space group: $Pmn2_1$ (No 31)
Dimensions of the unit cell: $a = 6.58$ Å,
$b = 4.78$ Å, $c = 4.82$ Å

Multiple-film integrated Weissenberg photographs (Ilford-Industrial G, CuKα radiation) were used to record (hk0, 0kl and h0l reflexions and their intensities were determined photometrically. The number of reflexions observed was 42 (possible 46) for hk0 reflexions, 32 (possible 33) for 0kl reflexions, and 26 (possible 26) for h0l reflexions. In order to facilitate application of the absorption corrections, the specimens were made cylindrical by grinding. Corrections for Lorentz and polarization factors were made in the usual way. Structure factors were calculated using values for the atomic scattering factors given in *Internationale Tabellen.*[2]

Isotropic temperature and scaling factors were determined by plotting $\log(F_c/F_o)$ against $\sin^2\Theta$ for the reflexions of each photograph. The mean value of B was 1.5 Å^2. The piezoelectric effect was confirmed by the Bergmann method modified by Yoichi Iitaka.[3]

DETERMINATION OF THE STRUCTURE

The parameters of the mercury atom were obtained from (001) and (100) Patterson projections. A Fourier projection $\varrho(x,y)$ was calculated using the signs given by the coordinates of the mercury atom. Because all the signs of the reflexions were defined by the contribution of the mercury atom alone, the Fourier projections could not be improved with the data available and further refinement of the structure was therefore not possible. The contour map of the Fourier projection (001) is given in Fig. 1.

Two oxygen atoms, O_1 and O_2, lie in the mirror plane. In the case of the centrosymmetric space group Pmmn these two atoms would have the same y coordinate. But the lengthening of the sulphur-atom peak in the mirror plane may be explained only by the projection of one sulphate-oxygen atom O_2 in the neighbourhood of the sulphur-atom peak, the other sulphate-oxygen atom O_1 lying also in the mirror plane of symmetry but with a different y coordinate. Thus we concluded that the tetrahedron is inclined toward the z axis, which allows the space group $Pmn2_1$.

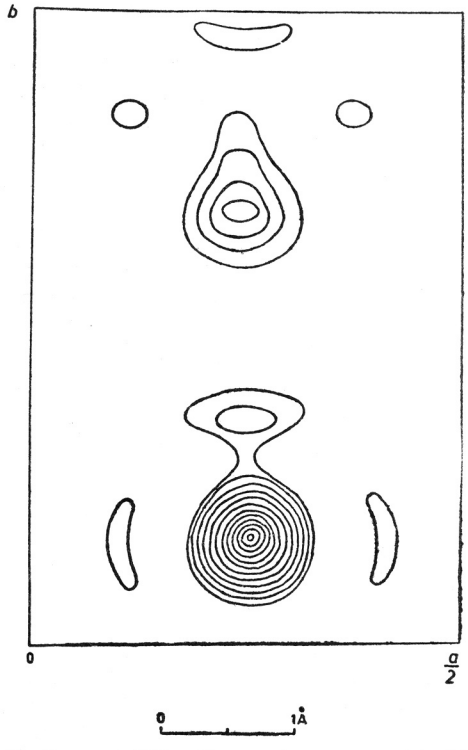

Fig. 1. The Fourier projection on (001). The contours are at arbitrary intervals. For the mercury atom peak every second line is drawn.

The atomic coordinates, with the origin at the screw axis halfway between two mercury atoms, are given in Table I. The x and the y coordi-

TABLE I

Atomic Coordinates in $HgSO_4$

Atom	x	y	z
2 Hg	1/4	0.175	1/4
2 S	1/4	0.681	3/4
2 O_1	1/4	0.370	0.683
2 O_2	1/4	0.800	0.033
4 O_3	0.070	0.833	0.650

nates are determined from the Fourier (001) projection, the z coordinates of mercury and sulphur atoms are obtained from the Patterson projection and z coordinates of oxygen atoms are assumed from known distances in the sulphate ion.[4]

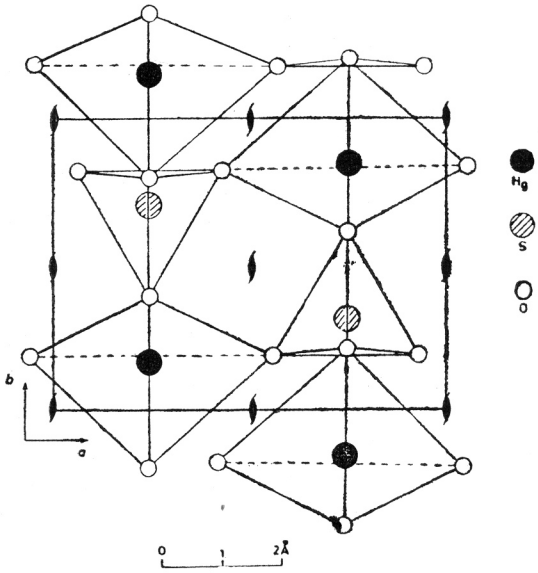

Fig. 2. Projection of the unit cell on (001).

The comparison between F_o and F_c is given in Table II. The reliability index: $R = \Sigma||F_o| - |F_c||/|F_o|$ has the value 0.13 for hk0 reflexions, 0.15 for 0kl and 0.11 for h0l reflexions.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The mercury atom lies at the centre of a distorted tetrahedron of four oxygen atoms from sulphate ions (Fig. 2.). Mercury and oxygen atoms are connected through SO_4 groups in zig-zag chains. One chain lies in the mirror plane, the other is perpendicular to it, as shown in Fig. 3. The interatomic

TABLE II

Observed (F_o) and Calculated (F_c) Structure Amplitudes

h k 0	F_o	F_c	h k 0	F_o	F_c
0 1 0	64	62	4 1 0	39	45
0 2 0	115	—111	4 2 0	55	— 76
0 3 0	94	—101	4 3 0	46	— 75
0 4 0	45	— 27	4 4 0	29	— 21
0 5 0	39	48	4 5 0	32	40
0 6 0	56	55	5 1 0	61	— 69
1 1 0	93	—106	5 2 0	66	— 71
1 2 0	108	—104	5 3 0	0	1
1 3 0	0	— 1	5 4 0	57	68
1 4 0	86	92	5 5 0	31	37
1 5 0	43	48	6 0 0	111	— 90
1 6 0	14	— 24	6 1 0	33	— 32
2 0 0	193	—168	6 2 0	55	50
2 1 0	37	— 33	6 3 0	50	48
2 2 0	67	86	6 4 0	24	12
2 3 0	60	72	7 1 0	50	46
2 4 0	38	17	7 2 0	56	49
2 5 0	28	— 39	7 3 0	0	— 2
2 6 0	48	— 44	8 0 0	75	74
3 1 0	90	95	8 1 0	19	23
3 2 0	82	80	8 2 0	45	41
3 3 0	0	0			
3 4 0	74	— 73			
3 5 0	36	— 34			
4 0 0	151	152			

0 k l	F_o	$\lvert F_c \rvert$	A_c	B_c
0 1 0	72	66	66	0
0 2 0	113	106	—106	0
0 3 0	89	100	—100	0
0 4 0	43	36	— 36	0
0 5 0	45	45	45	0
0 6 0	49	53	53	0
0 1 1	125	149	—149	— 3
0 2 1	87	103	—103	6
0 3 1	43	21	21	2
0 4 1	69	68	68	— 1
0 5 1	61	64	64	— 3
0 6 1	10	15	— 14	— 5
0 0 2	117	150	—146	34
0 1 2	45	41	— 41	6
0 2 2	70	67	66	— 11
0 3 2	76	74	73	— 11
0 4 2	42	28	28	— 5
0 5 2	35	30	— 29	7
0 1 3	84	93	92	— 13
0 2 3	61	64	61	— 20
0 3 3	24	18	— 17	6
0 4 3	44	48	— 47	11
0 5 3	39	33	— 32	7
0 0 4	75	80	80	— 8
0 1 4	32	26	26	2
0 2 4	51	43	— 43	0
0 3 4	50	53	53	— 2

0 k l	F_o	$\lvert F_c \rvert$	A_c	B_c
0 4 4	23	15	— 14	7
0 1 5	59	52	— 52	— 5
0 2 5	37	32	— 31	2
0 0 6	51	27	— 27	— 1
0 1 6	20	22	— 20	— 2
h 0 l				
0 0 2	141	148	—148	31
0 0 4	89	82	82	— 6
0 0 6	59	42	— 42	1
1 0 1	103	96	— 95	15
1 0 3	82	79	79	8
1 0 5	55	53	— 53	— 1
2 0 0	175	180	—180	0
2 0 2	123	111	111	6
2 0 4	89	87	— 87	— 2
2 0 6	47	44	44	— 4
3 0 1	93	102	101	— 15
3 0 3	59	63	63	0
3 0 5	46	43	43	1
4 0 0	100	133	133	0
4 0 2	90	99	— 99	7
4 0 4	73	63	63	— 6
5 0 1	64	57	— 58	— 3
5 0 3	57	52	51	12
5 0 5	35	28	28	— 2
6 0 0	91	95	95	0
6 0 2	73	72	72	— 7
6 0 4	46	49	49	2
7 0 1	50	64	64	— 3
7 0 3	25	44	— 46	— 2
8 0 0	40	53	53	4
8 0 2	39	47	47	— 3

distances between the nearest atoms in the unit cell, calculated with the values of parameters listed in Table I, are given in Table III.

TABLE III

Interatomic Distances and Angles in $HgSO_4$

S — O_1 = 1.49 Å	Hg — O_1 = 2.28 Å
S — O_2 = 1.48 Å	Hg — O_2 = 2.08 Å
S — O_3 = 1.48 Å	Hg — O_3 = 2.14 Å

O . . . O Distances in Sulphate Tetrahedron

$O_1 \ldots O_2$ = 2.66 Å
$O_1 \ldots O_3$ = 2.51 Å
$O_2 \ldots O_3$ = 2.21 Å
$O_3 \ldots O_3$ = 2.37 Å

O . . . O Distances in Tetrahedron Around Mercuric Atom

$O_1 \ldots O_2$ = 4.15 Å	O_1 — Hg — O_2 = 144°
$O_1 \ldots O_3$ = 3.32 Å	O_3 — Hg — O_3 = 159°
$O_2 \ldots O_3$ = 2.78 Å	
$O_3 \ldots O_3$ = 4.21 Å	

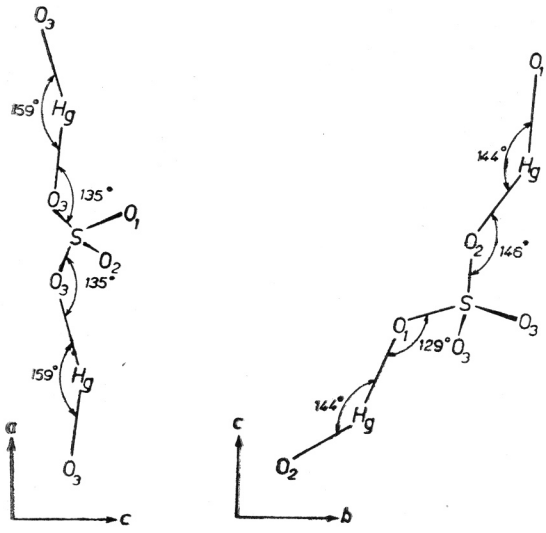

Fig. 3.

As the z coordinates of oxygen atoms were not determined, S — O distances are to some extent assumed. In other recently determined sulphate structures[4] S — O distances vary from 1.47 to 1.51 Å, therefore the assumed S — O distances (1.48 and 1.49 Å) induce an uncertainty of about ± 0.02 Å on Hg — O, and ± 0.04 Å on O — O distances.

The positions of the light atoms obtained define the structure in a satisfactory way. The distances and the coordinates of atoms are consistent with known crystallochemical facts. The distance from mercury to the sulphate-oxygen atom O_3 (2.14 Å) is equal to the sum of covalent radii for mercury (1.48 Å) and oxygen (0.66 Å). The shorter distance Hg — O_2 (2.08 Å) may be compared with distances in trichlormercury oxonium chloride[5] and in mercuric oxide.[6] The distance Hg — O_1 (2.28 Å) is smaller than the sum of ionic radii (2.45 Å). The coordination polyhedron of the mercury atom in this structure may be compared with that in the crystal structure of trimercuric oxychloride ($HgCl_2 \cdot 2HgO$), where each mercury atom in general position is surrounded by three oxygen atoms and one chlorine atom in a distorted tetrahedron[7].

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IZVOD

Kristalna struktura bezvodnog merkurisulfata

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Redgenskom strukturnom analizom određena je kristalna struktura bezvodnog merkurisulfata. Kristali su rompski i pripadaju prostornoj grupi $Pmn2_1$ (No 31). Elementarna ćelija s

$$a = 6{,}58\ \text{Å},\quad b = 4{,}78\ \text{Å},\quad c = 4{,}82\ \text{Å}$$

sadrži dvije stehiometrijske jedinice. Parametri atoma određeni su na temelju Pattersonovih projekcija i Fourierove (001) projekcije. Atomi žive koordinirani su tetraedrijski s atomima kisika od sulfatnog iona.

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