An X-ray and Neutron Diffraction Study of Mercury(II) Sulphate Monohydrate

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Abstract

The structure of $HgSO_4.H_2O$ has been reinvestigated with both X-ray and neutron diffraction methods and refined to $R = 0.040$ (X-rays) and $R = 0.032$ (neutrons). The crystals are orthorhombic, space group *Pnma*, with $a = 7.8796$ (9), $b = 5.4209$ (4), $c = 8.9704$ (7) Å, $Z = 4$. The Hg atom is coordinated to one sulphate O atom and one water molecule forming discrete $HgSO_4.H_2O$ groups, connected by hydrogen bonds to form a three-dimensional structure. Four more distant O atoms of different sulphate tetrahedra complete an irregular octahedron around Hg. In the water molecule the O—H distances are 0.931 (9) and 0.955 (5) Å and the angle is 108.0 (6)°.

Introduction

This investigation is part of a structural study of inorganic Hg^{II} hydrates. The structures of $HgCrO_4.\frac{1}{2}H_2O$, $Hg_3(OH)_2(SO_4)_2.H_2O$, $HgCl_2.2KCl.H_2O$ and $HgSeO_4.H_2O$ (Aurivillius & Stålhandske, 1975, 1976*a,b*; Stålhandske, 1978) have been refined from neutron diffraction data. The present structure, $HgSO_4.H_2O$, has been the subject of several crystallographic studies (Bonefačić, 1961; Arivillius, 1964; Templeton, Templeton & Zalkin, 1964). In the last refinement, which was performed by least squares from diffractometer data, the authors concluded that the water molecule was involved in only one hydrogen bond. As this is rather rare the present study was started to reveal the hydrogen-bonding system in the compound.

Experimental

Colourless single crystals were obtained by dissolving anhydrous $HgSO_4$ in 2.0–2.5 *M* H_2SO_4 and slowly evaporating the solution in a desiccator with concentrated H_2SO_4 as drying agent. A prismatic crystal of volume 27 mm^3 was chosen for the neutron work and mounted in a thin-walled silica sphere to protect the crystal from the air. The intensity measurements were carried out on a Hilger & Watts computer-controlled four-circle diffractometer at the R2 reactor, Studsvik,

Sweden. Some details of the crystal data, the collection of intensities and the refinement are given in Table 1. The neutron flux at the specimen was about 10^4 n mm^{-2} s^{-1}. Three standard reflexions were measured at regular intervals. No significant fluctuations in their intensities were observed. The values of I and $\sigma_c(I)$, where $\sigma_c(I)$ is the standard deviation based on counting statistics, were corrected for Lorentz and absorption effects.

The linear absorption coefficient was measured as 0.359 mm^{-1}, corresponding to a value of 5.5×10^3 fm^2 for the incoherent scattering cross section for H. In the earlier structure determinations the refinements were performed in space group *Pnma*. In the neutron data set a few reflexions were found with $I > 3\sigma_c(I)$ for both *hk0*: $h \neq 2n$ and $0kl$: $l \neq 2n$, the systematic absences in space group *Pnma*. If these reflexions are real, the correct space group should be $P2_12_12_1$. A set of X-ray intensities was then collected to check the systematic absences and to compare refinement based on the neutron data with that of X-ray. Reflexions were measured in one quadrant of reciprocal space from a crystal mounted in a capillary of Lindemann glass, with Zr-filtered Mo *K* radiation. This data set, however,

Table 1. *Crystal data, collection and reduction of intensities and least-squares refinement*

Formula	$HgSO_4.H_2O$	a	7.8796 (9) Å	V	383.17 $Å^3$
FW	314.66	b	5.4209 (4)	Z	4
Space group	*Pnma*	c	8.9704 (7)	D_x	5.45 Mg m^{-3}

	Neutron diffraction	X-ray diffraction
Crystal size (mm)	5.6 × 2.6 × 1.8	0.36 × 0.25 × 0.14
λ (Å)	1.210	0.7107
θ interval ($°$)	2–57	3–32.5
$\Delta\omega$ ($°$) (ω–2θ scan)	2.5–2.7	0.75 + 1.0 tan θ
Maximum recording time (min)	~12	4
μ (mm^{-1})	0.359	41.4
Range of transmission factor	0.38–0.53	0.004–0.050
Number of measured reflexions	729	1582
Number of reflexions used in the final refinement, m	499	1182*
Number of parameters refined, n	56	41
$R = \sum \lVert F_o\rvert - \lvert F_c\rVert/\sum \lvert F_o\rvert$	0.032	0.040
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.032	0.051
$S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m-n)]^{1/2}$	1.05	1.05
a (weighting function)	0.004	0.040
b (weighting function)	0.008	1.0
$g(\times 10^{-4})$ (extinction)	0.56 (3)	0.37 (2)

* *hkl* and −*hkl*.

showed no reflexions inconsistent with space group *Pnma*. Thus if the symmetry of the H atom positions is the same as of the other atoms, the correct space group is *Pnma*. The X-ray intensities were corrected for Lorentz–polarization and absorption effects. Symmetry-related reflexions were not averaged as the mean path lengths varied considerably.

Cell dimensions were determined from powder photographs taken in a Guinier–Hägg focusing camera at 295 K with Cu $K\alpha_1$ radiation ($\lambda = 1.54056$ Å) and KCl ($a = 6.2928$ Å) as an internal standard.

Structure refinement

In the refinement of the X-ray data, the starting parameters were taken from Templeton, Templeton & Zalkin (1964). The calculations were performed by full-matrix least squares (Table 1). The function minimized was $\sum w_i(|F_o| - |F_c|)^2$; weights were $w_i^{-1} = \sigma_c^2(|F_o|^2)/4|F_o|^2 + a|F_o|^2 + b$. The values of a and b were varied to give constant values of $\langle w_i(|F_o| - |F_c|)^2\rangle$ in different $|F_o|$ and $\sin\theta$ intervals. Spurious peaks interpreted as H atoms were found in the difference maps, but they could not be refined. In the final refinement all non-hydrogen atoms were assigned anisotropic thermal movements and a parameter was included to correct for secondary extinction (Zachariasen, 1967). The scattering factors were those of Doyle & Turner (1968) and the anomalous-dispersion corrections for Hg and S were taken from Cromer & Liberman (1970).

The final X-ray parameters were used at the start of the refinement with the neutron data. Difference maps showed that one of the H atoms was statistically distributed across the mirror plane. Refinement with anisotropic thermal parameters for all atoms gave lower R and R_w values than with the X-ray data and the e.s.d.'s for all atoms except Hg were now 2–3 times smaller. The coherent scattering amplitudes were those of Bacon (1972). A refinement of the neutron data set in $P2_12_12_1$ converged with higher R, R_w and S values than in *Pnma*. As no improvements were obtained and the disordering of the water molecule still remained, $P2_12_12_1$ was considered incorrect and the reflexions inconsistent with *Pnma* were rejected. The corrections

applied to $|F_o|$ due to the isotropic extinction were >1.10 for 6% of the X-ray and 13% of the neutron reflexions. The atomic coordinates are given in Table 2,* selected interatomic distances and angles in Table

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* Lists of structure factors and anisotropic thermal parameters from both determinations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34783 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Interatomic distances* (Å) *and angles* ($^\circ$)

	Neutron	X-ray
(*a*) Around Hg		
Hg–O(3)	2.179 (2)	2.191 (6)
–O(*W*)	2.228 (2)	2.233 (7)
–O($2^{i,ii}$)	2.501 (1)	2.503 (5)
–O($2^{iii,iv}$)	2.514 (1)	2.507 (5)
O(3)–Hg–O(*W*)	168.75 (8)	169.3 (3)
O(2^{ii})–Hg–O(2^i)	73.71 (6)	73.4 (2)
O(2^i)–Hg–O(2^{iv})	103.89 (5)	104.0 (2)
O(2^{iv})–Hg–O(2^{iii})	73.27 (6)	73.3 (2)
O(2^{iii})–Hg–O(2^{ii})	103.89 (5)	104.0 (2)
(*b*) In the SO$_4$ group		
S–O(1)	1.456 (4)	1.462 (7)
–O($2,2^v$)	1.481 (2)	1.484 (5)
–O(3)	1.496 (4)	1.486 (6)
O(1)–S–O($2,2^v$)	109.7 (2)	109.6 (2)
O(1)–S–O(3)	110.3 (2)	110.4 (4)
O(2)–S–O(2^v)	109.6 (2)	109.9 (4)
O(3)–S–O($2,2^v$)	108.8 (2)	108.6 (2)
(*c*) In the water molecule and the hydrogen bonds		
O(*W*)–H(1)	0.955 (5)	
O(*W*)–H(2)	0.931 (9)	
H(1)$\cdots$O(1^{vi})	1.902 (5)	
H(2)$\cdots$O(W^{vii})	2.264 (9)	
O(*W*)$\cdots$O(1^{vi})	2.849 (3)	2.862 (9)
O(*W*)$\cdots$O(W^{vii})	3.184 (2)	3.168 (8)
H(1)–O(*W*)–H(2)	108.0 (6)	
O(*W*)–H(1)$\cdots$O(1^{vi})	170.6 (5)	
O(*W*)$\cdots$H(2)$\cdots$O(W^{vii})	170.0 (8)	
O(1^{vi})$\cdots$O(*W*)$\cdots$O(W^{vii})	108.6 (1)	108.3 (3)

Symmetry code

None x,y,z

(i) $-x, -\frac{1}{2} + y, -z$

(ii) $-x, 1 - y, -z$

(iii) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$

(iv) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z$

(v) $-x, \frac{1}{2} - y, z$

(vi) $\frac{1}{2} + x, y, \frac{1}{2} - z$

(vii) $-x, -y, 1 - z$

Table 2. *Positional coordinates* ($\times 10^4$; *for* Hg $\times 10^5$) *for* HgSO$_4$.H$_2$O *with e.s.d.'s in parentheses*

	Neutron			X-ray		
	x	y	z	x	y	z
Hg	13273 (10)	$\frac{1}{4}$	20851 (9)	13287 (4)	$\frac{1}{4}$	20850 (4)
S	951 (4)	$\frac{1}{4}$	–1423 (3)	957 (3)	$\frac{1}{4}$	–1426 (2)
O(1)	–753 (2)	$\frac{1}{4}$	–795 (2)	–754 (8)	$\frac{1}{4}$	–793 (9)
O(2)	1194 (2)	4733 (2)	–2351 (1)	1199 (5)	4740 (10)	–2352 (6)
O(3)	2248 (2)	$\frac{1}{4}$	–205 (2)	2250 (7)	$\frac{1}{4}$	–219 (7)
O(*W*)	925 (3)	$\frac{1}{4}$	4543 (2)	903 (9)	$\frac{1}{4}$	4547 (8)
H(1)	1980 (7)	$\frac{1}{4}$	5067 (5)			
H(2)	291 (12)	1160 (16)	4876 (9)			

3. Distances and angles in Figs. 1 and 3 and in the discussion are from the neutron work.

Description and discussion of the structure

The fractional coordinates of the non-hydrogen atoms in the present investigation (Table 2) are in good agreement with those obtained by Templeton, Templeton & Zalkin (1964) who from their X-ray measurements predicted the position of H(1) but were unable to find H(2) (Table 2). The e.s.d.'s are now, however, considerably lower.

In $HgSO_4.H_2O$ each Hg atom has two close ligands: one water molecule and one sulphate group. Four more distant O atoms of different sulphate groups complete an irregular octahedron around Hg (Fig. 1, Table 3). The structure can thus be described as built up either of discrete $HgSO_4.H_2O$ molecules linked by hydrogen bonds into a three-dimensional structure (Fig. 2) or, as suggested in the earlier works, by edge-sharing HgO_6 octahedra forming columns, parallel to [100], connected by the sulphate groups.
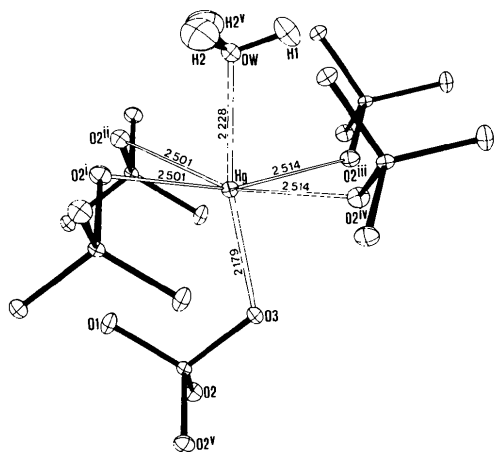
Hg^{II} is, in the coordination to O, in most cases bonded to two atoms at the short distances 2·0–2·2 Å, with 3–5 more neighbours closer than 2·9 Å, the sum of the van der Waals radii (Grdenić, 1965). In $HgSO_4.H_2O$ the two short Hg—O bonds are 2·179 (2) and 2·228 (2) Å with an angle of 168·8 (1)° and with four weaker bonds of 2·50–2·51 Å (Fig. 1, Table 3). The bond between Hg and O(W) of 2·228 Å is long for two-coordination; no shorter Hg^{II}—O(W) distance has hitherto been found, however. This bond is in the same range as found for three-coordinated Hg in $HgTiO_3$ (Sleight & Prewitt, 1973) [Hg—O 2·20 (4) Å] and for four-coordination in $Hg(OHg)_4Br_2$ (Aurivillius, 1968) [Hg—O 2·24 (3) Å]. Longer Hg—O bonds for two-coordination are only found in $HgCu(OH)_2$-$(NO_3)_2.2H_2O$ (Kamenar, 1969) with Hg linearly bonded to O at 2·30 (4) Å and with four more O neighbours at 2·54–2·78 Å, forming an irregular octahedron.

The structure of $HgSO_4.H_2O$ is different from $CdSO_4.H_2O$ (Brégeault & Herpin, 1970) and $CdSeO_4.H_2O$ (Stålhandske, 1980), both isomorphous with $HgSeO_4.H_2O$ (Stålhandske, 1978). Dehydration of $HgSO_4.H_2O$ and $CdSO_4.H_2O$ gives the isomorphous compounds $HgSO_4$ and $CdSO_4$, in which the polyhedra around the metal atoms are distorted tetrahedra (Kokkoros & Rentzeperis, 1963; Aurivillius & Stålhandske, 1980). $HgSeO_4.H_2O$ is built up of distorted HgO_6 octahedra (Hg—O 2·26–2·50 Å) with four O atoms from different selenate groups and two water molecules.

The S—O distances for the sulphate group in $HgSO_4.H_2O$ are 1·456–1·496 Å and the O—S—O angles 108·8–110·3°. As expected, the longest S—O bond is to O(3) which is also bonded to Hg at 2·179 Å, and the shortest to O(1), not coordinated to Hg.

In the water molecule, O(W) and H(1) are located in the mirror plane whereas H(2) is statistically distributed across the plane. The O—H distances are 0·955 (5) and 0·931 (9) Å and the angle H—O—H is 108·0 (6)°. In a survey of water-molecule geometry in crystalline hydrates determined by neutron diffraction, Ferraris & Franchini-Angela (1972) have found the
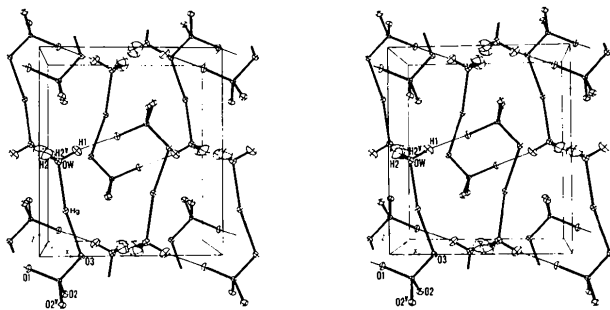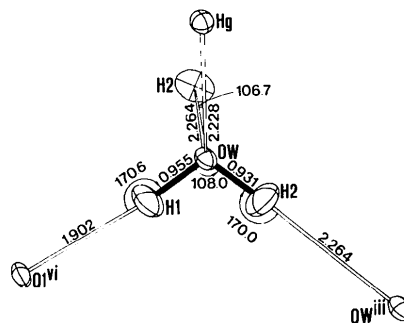

Fig. 1. The coordination around the Hg atom.

Fig. 2. The unit-cell contents. Bonds within the $HgSO_4.H_2O$ molecules, including the statistically distributed H(2) atoms, are drawn with heavy lines, acceptor distances H(1)···O(1) with thin lines.

Fig. 3. The environment of the water molecule.

average values 0·956 Å for the O—H length and 107·8° for the H—O—H angle. In the present study only the O(W)—H(2) bond of 0·931 Å deviates from the average water molecule.

There are only two possible O acceptor atoms (O···H < 2·4 Å) to the water H atoms: O(1) at 1·90 and O(W) at 2·26 Å. The corresponding O···O distances are 2·85 and 3·18 Å with O—H···O angles of 171 and 170°. Brown (1976) has, from a bond-valence analysis of the repulsion between the O atoms in an O—H···O bond, predicted a correlation between the O···H distance and the O—H···O angles. The angle 171° is somewhat larger than calculated from the O···H distance of 1·90 Å and for an acceptor distance of 2·26 Å a much more bent hydrogen bond is suggested than that found in the present structure. A weak hydrogen bond with a similar geometry is however found in $Na_2H_2SiO_4.5H_2O$ (Williams & Dent Glasser, 1971) with an O···O hydrogen bond of 3·13 Å, an acceptor distance of 2·24 Å and an O—H···O angle of 175°. The hydrogen bond of normal strength, O(W)···O(1), connects the $HgSO_4.H_2O$ molecules in chains running in the xz plane (Fig. 2), linked in the y direction by the very weak hydrogen bond O(W)··· O(W). The environment of the water molecule in $HgSO_4.H_2O$ is tetrahedral (Fig. 3), including the two hydrogen-bonded atoms O(1) and O(W) and, in the directions of the lone pairs, Hg and H(2). The hydrate thus belongs to class $2H$ according to Ferraris & Franchini-Angela (1972).

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The Crystal Structure of a New Polytype 12R of Cadmium Bromide

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Abstract

The crystal structure of a new rhombohedral polytype, 12R, of cadmium bromide, $CdBr_2$, has been determined. It is found to be (13)$_3$ in the Zhdanov notation with space group $R\bar{3}m1$. Its formation has been explained by a layer-transformation mechanism.

Introduction

Only two reports (Mitchell, 1962; Agrawal & Trigunayat, 1970) are available on polytypism in $CdBr_2$

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