The Crystal Chemistry of Zirconium Sulphates. IV. The Structure of the γ-Monohydrate, Zr(SO₄)₂.H₂O, a Layer Compound with the Zirconium Atom in Sevenfold Coordination

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 γ -Zr(SO₄)₂. H₂O is triclinic, space group *P*T, with unit-cell dimensions a = 7.89, b = 5.21, c = 8.96 Å, $\alpha = 95.2^\circ$, $\beta = 99.8^\circ$, $\gamma = 109.2^\circ$. The structure, determined by single-crystal X-ray analysis, consists of layers of composition Zr(SO₄)₂. H₂O, probably held together by hydrogen bonding. Each zirconium atom is bonded to six oxygen atoms of bridging sulphate tetrahedra, while the hydrate oxygen atom forms a seventh ligand. The coordination of the zirconium atom is sevenfold and is similar to that found in baddeleyite, ZrO₂.

Introduction

Parts I–III of this series of papers (Bear & Mumme, 1969a, b, c) described the structural and chemical relationships between the four higher hydrates:

 $Zr(SO_4)_2.7H_2O$, α - $Zr(SO_4)_2.5H_2O$, β - $Zr(SO_4)_2.5H_2O$ and $Zr(SO_4)_2.4H_2O$. In all of these compounds hydrogen bonding plays an important role. The heptaand the two pentahydrates are all built up from isolated dimeric groups of composition $Zr_2(SO_4)_4(H_2O)_8$ which

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Table	1.	л-ruy	powaer	allraction	aata jor	γ - $Lr(SO_4)_2$. п ₂ 0

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4.37 0.0311 0.0312 002 w 2.355 0.1070 0.1069	271	w
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3.512 0.0481 0.0480 110 w 0.1354	371	~
0.0507 211 0.1353	303	
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0.1384	313	~
3.290 0.0548 0.0549 1 $\overline{12}$ m 2.048 0.1415 0.1415	371	<i>m</i> w
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3.137 0.0603 0.0601 202 m 1.942 0.1573 0.1571	214	w
0.0606 201 0.1571	410	"
3.084 0.0624 0.0625 117 w-m 1.822 0.1787 0.1785	402	m
3.025 0.0648 0.0651 012 m 0.1790	400	
2.925 0.0693 0.0695 103 w-m	400	
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0.1855	314	w
0.1850	311	"
2.686 0.0823 0.0821 0.13 w 0.1855	470	
2.650 0.0845 0.0846 212 w	120	
2.594 0.0882 0.0881 170 w-m 1.753 0.1930 0.1931	413	w_m
2.554 0.0910 0.0911 171 w-m 1.771 0.2003 0.2004	131	w
0.0912 203 0.2002 0.2002	230	
0.0909 311 0.2002	205	
0.0906 310 0.2004	213	
0.2003	471	
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0.0933 103 0.2022 0.2026	477	~~
0.0932 113 0.2017	403	
0.0933 210 0.2017	401	

in all three cases are held together in several directions by hydrogen bonds through the coordinated and nonbonded water molecules. The tetrahydrate is composed of infinite layers of composition $Zr(SO_4)_2.4H_2O$ held together by hydrogen bonding through the coordinated water molecules.

Parts IV and V of the series deal with three monohydrates of zirconium sulphate. In contrast to the higher hydrates which are all essentially hydration products either of a lower hydrate or of one of the three anhydrous zirconium sulphates (Bear & Mumme, 1968), γ - and β -Zr(SO₄)₂. H₂O have only been obtained by thermal decomposition of the higher hydrates (Bear & Mumme, 1969d). Both phases are metastable and equilibrate to α -Z4(SO₄)₂. H₂O under suitable conditions. The stable α -phase can be prepared either as a decomposition product or by vapour hydration of the anhydrous sulphates at 120°C (Bear & Mumme, 1969d).

This paper describes the structure of γ -Zr(SO₄)₂. H₂O. Part V (Bear & Mumme, 1970) which follows, reports that of α -Zr(SO₄)₂. H₂O and presents unit-cell parameters and powder data for β -Zr(SO₄)₂. H₂O. It also includes a discussion of the structural inter-relationships between the three monohydrates and the higher hydrates.

Experimental

 γ -Zr(SO₄)₂. H₂O was prepared as a microcrystalline powder by thermal decomposition of solid Zr(SO₄)₂. 4H₂O at 200 °C for one hour. The compound is extremely hygroscopic under ambient conditions.

Powder diffractometer data were collected from this material using a Philips proportional-counter diffractometer with a Ni filter and Cu $K\alpha_{1,2}$ radiation. A continuous stream of dry N₂ gas was passed over the sample to delay rehydration.

Well-formed crystals of γ -Zr(SO₄)₂. H₂O suitable for structural analysis can be prepared either by evaporation of an aqueous solution of Zr(SO₄)₂.4H₂O or by the thermal decomposition of solid Zr(SO₄)₂.4H₂O as a slurry in 10 molar sulphuric acid at 120–140 °C. The crystals were long blade-like needles up to a millimetre in length, but unfortunately many of these were twinned. As with the microcrystalline material these

Fable 2.	Crystal	data foi	r y-Zr(SO ₄)	$_2.H_2C$
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Symmetry	Triclinic
Unit-cell dimensions	$a = 7 \cdot 89 \pm 0.01 \text{ Å}$ $b = 5 \cdot 21 \pm 0.01$ $c = 8 \cdot 96 \pm 0.01$ $\alpha = 95 \cdot 2 \pm 0.1^{\circ}$ $\beta = 99 \cdot 8 \pm 0.1$ $\gamma = 109 \cdot 2 \pm 0.1$
Possible space groups D_x D_m Z μ_c	P1 or PT 2.95 g.cm ⁻³ 2.93 \pm 0.03 g.cm ⁻³ 2 200 cm ⁻¹

crystals were extremely hygroscopic, so that it was necessary to seal the crystal used for collection of X-ray data in a quartz capillary. This procedure was carried out inside a glove box purged with dry N_2 gas.

Weissenberg data collected around the needle axis, b, gave values of a^* , b, c^* and β^* . Although upper level data indicated that the crystals were triclinic, it was not possible to confirm this by indexing the powder diffractometer data, from the approximate lattice parameters obtained by the vector shift method. Considerable time had been spent in obtaining an untwinned crystal, so that the data about other axes necessary for indexing the powder data were sought by the precession method, rather than by attempting to



Fig. 1. Patterson function P(u, w) projected on to (010). The cross is the Zr-Zr vector across the origin.



Fig. 2. Electron density distribution indicated by sections $\rho_0(x, y, z)$ selected near the atom centres and projected on to (010). The contours are at arbitrary intervals.

remount the crystal, already aligned, about either **a** or **c**. A zero-level precession film was obtained which contained [$\overline{1}10$] and [$20\overline{1}$] as the axes, and with the additional reciprocal lattice dimensions obtained from it, the powder data (Table 1) were indexed, reduced, and refined to give the lattice parameters of γ -Zr(SO₄)₂. H₂O given in Table 2.

Integrated Weissenberg data h0l to h3l were recorded about the needle axis, using Cu $K\alpha_{1,2}$ radiation and multiple-film packs, from a crystal measuring $0.2 \times 0.2 \times 0.5$ mm. Measurement of intensities, subsequent data handling, including interlayer scaling procedures, and the scattering curves for Zr, S, and O are as described in part I (Bear & Mumme, 1969a).

Table 3. Observed and calculated structure factors

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Structure determination

The number of formula units Z=2 was calculated from the density, 2.93 g.cm⁻³, obtained by displacement in CCl₄. The space group was assumed to be $P\overline{1}$ rather than the alternative P1, and this was later confirmed by the satisfactory refinement of the structure.

With the *b* axis dimension only 5.21 Å it was expected that most atoms should be resolved in projection, so initially the structure determination by Fourier methods was confined to the h0l level alone.

The Patterson projection P(u, w) shown in Fig.1 contained many well resolved peaks, but one of the smallest at (0.25, 0.54) eventually proved to be the Zr-Zr interaction across the origin. Using the signs of the structure factors calculated for these zirconium atom positions it was possible to determine the approximate parameters for S(1) (0.85, 0.10) and S(2) (0.75, 0.47) from a Fourier synthesis. In subsequent Fourier syntheses, five peaks corresponding to oxygen atoms became well resolved at (0.4, 0.25), (0.16, 0.06), (0.67, 0.12), (0.60, 0.35) and (0.93, 0.42) together with two broader less well resolved peaks at (0.19, 0.24) and (0.93, 0.17). It soon became clear that in this (010)projection both sulphate tetrahedra were being viewed almost down one of their edges, so that the two broader peaks in each case corresponded to two oxygen atoms almost overlapping. Thus the zirconium atom was probably in sevenfold coordination and if it were assumed that the six ligands to the six attached sulphate groups closest to each zirconium atom were oxygen atoms, the one further ligand was an oxygen atom of a water molecule, and the overall composition became $Zr(SO_4)_2$. H₂O, confirming the chemical analysis.

At this point a three-dimensional Patterson function P(u, v, w) was calculated from which the parameters of Zr, S(1) and S(2), were determined. These were confirmed by a three-dimensional Fourier analysis shown in Fig.2.

Refinement of the structure was continued with a number of least-squares cycles using isotropic temper-

ature factors for each atom, until R dropped to 12.6%, for the 708 observed reflexions. The weighting scheme of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) was used and the matrix inversion involved the blockdiagonal approximation. The scaled observed data, and structure amplitudes calculated from the final model are given in Table 3. Atomic parameters and individual isotropic temperature factors are listed in Table 4 (Fig. 3) and bond lengths in Table 5.



Fig. 3. The structure of γ -Zr(SO₄)₂. H₂O projected on to (010). Large open circles, zirconium atoms; full black circles, sulphur atoms; medium open circles, oxygen atoms; stippled circles, water molecules.

Table 4. Fractional atomic parameters and thermal parameters for γ -Zr(SO₄)₂. H₂O

Estimated standard deviations are given in parentheses.

	· x	у	Z	В
Zr	0.1200(3)	0.3025 (6)	0.2719 (2)	0·60 (4) Ų
S(1)	0.8424 (8)	0.6368 (19)	0.1025 (7)	0.74 (12)
S(2)	0.7586 (7)	0.0971 (18)	0.4726 (7)	0.44 (11)
O(W1)	0.3951 (27)	0.3325 (57)	0.2402 (27)	3.21 (49)
O(2)	0.6714 (26)	0.6534 (55)	0.1230 (26)	2.95 (47)
O(3)	0.6004 (23)	0.0475 (49)	0.3527 (23)	1.97 (39)
O(4)	0.9335 (22)	0.1850 (48)	0.4191(22)	1.85 (39)
O(5)	0.2554(21)	0.1462(45)	0.4559 (20)	1.52 (36)
O(6)	0.2314 (24)	0.6851 (50)	0.4070 (23)	2.19 (40)
O(7)	0.1593 (22)	0.4452 (49)	0.0588 (22)	1.85 (38)
O(8)	0.8848 (22)	0.4192 (49)	0.1886 (23)	1.83 (39)
0(9)	-0.0072(25)	-0.1058(53)	0.1530(24)	2.58 (44)

Description and discussion of structure

The structure of γ -Zr(SO₄)₂. H₂O viewed in (010) projection is shown in Fig. 3. It is made up of layers of composition Zr(SO₄)₂. H₂O which extend infinitely along [001]. One such layer centred at x = 0 is shown in Fig. 4.

Each zirconium atom is in sevenfold coordination. Each has six ligands being the oxygen atoms of six attached sulphate tetrahedra, and the seventh being the oxygen atom of the hydrate group. Sulphate groups bridge between the zirconium polyhedra in such a way that each zirconium atom is in contact with six sulphate groups, and each sulphate group is in contact with three zirconium atoms. This provides for the double bridging of sulphate groups between zirconium atoms and for the building up of each layer both along [010] and [001]. Hydrogen bonding may be assumed to be between the coordinated water molecules and the free ligands of the sulphate groups and presumably serves to hold the layers together.

Sevenfold coordination for zirconium has previously been found in a variety of compounds such as ZrO_2 (monoclinic form), ZrOS (McCullough, Brewer & Bromley, 1948) and $Na_5Zr_2F_{13}$ (Herak, Malcic & Manojlovic, 1965). The range of metal-oxygen bonds in γ -Zr(SO₄)₂. H₂O (Table 5 and Fig. 3) is between 2.07 and 2.19 Å, which differs only slightly from the range of 2.04 to 2.26 Å found in ZrO₂ (monoclinic).



Fig.4. The layer centred at x=0 as viewed along the *a* axis. Designation of the atoms is the same as in Fig.3.



Fig. 5. The representation of sevenfold coordination of zirconium, (1) as a trigonal base-tetragonal base combination; (2) as a capped trigonal prism; (3) as a capped octahedron.

McCullough & Trueblood (1959) visualize the coordination polyhedron in ZrO₂ as being derived from a cube. Four oxygen atoms are at the base, and one at one of the upper corners and the remaining two are at the mid points of the cube edges connecting the unoccupied corners, which is a distortion of the ideal tetragonal base – trigonal base form. Earlier McCullough et al. (1948) likened the coordination of the zirconium atom in ZrOS to a capped octahedron. The similarity of these two forms of coordination with the capped trigonal prism, another idealized form of sevenfold coordination (the fourth being the pentagonal-bipyramid) has been pointed out by Mumme & Wadsley (1968) (Fig. 5) in a discussion of the sevenfold coordination polyhedron as a structure building block in oxide systems.

While mean bond lengths and angles for the sulphate groups are close to those expected for the ideal tetrahedron the variation of 1.39 to 1.52 Å for the tetrahedron around S(1) represents a considerable distortion. The second group is also distorted but the varia-

Table 5. Interatomic distances and angles, and their e.s.d.'s

(a) Within the ZrO_7 polyhedron

Å

Å

Metal-oxygen	
distances	
Zr-O(W1)	2.19 ± 0.03
O(7)	2.15 ± 0.02
O(9)	2.12 ± 0.02
O(8)	2.17 ± 0.02
O(4)	2.12 ± 0.02
O(5)	2.18 ± 0.02
O(6)	2.07 ± 0.02
Average	2.14
Oxygen-oxygen	
distances	
O(5)—O(6)	2.94 + 0.03
000000	2.91 ± 0.03
O(8)O(9)	3.12 ± 0.03
O(5)O(9)	3.02 + 0.03
O(W1)-O(7)	2.51 ± 0.03
O(7)O(8)	2.59 ± 0.03
O(7)O(9)	3.01 ± 0.03
O(Ŵ1)–O(6)	2.99 ± 0.03
$O(W_1) - O(5)$	2.50 ± 0.03
O(4)O(8)	2.53 ± 0.03
O(4)O(9)	2.90 ± 0.03
O(4)O(6)	2.91 ± 0.03
O(4)—-O(5)	2.58 + 0.03
Angles	
Augles	
O(4) - Zr - O(8)	$72 \pm 1^{\circ}$
O(4) - Zr - O(9)	86 ± 1
O(4) = Zr - O(6)	88 ± 1
$O(4) = -Z_{1} = O(3)$	74±1 02±1
O(9) - Zr - O(6)	93 ± 1
$O(9) - Z_1 - O(3)$	09 ± 1 98 ± 1
O(5) = -21 - O(0)	$\frac{00 \pm 1}{97 \pm 1}$
$O(0) = Z_1 = O(0)$	07 ± 1
O(7) = 7r = O(8)	70 ± 1
$O(W_1)_7_0(6)$	20 ± 1
$O(W_1) - Z_1 - O(0)$	$\frac{0}{2} \pm 1$
$O(W_1) - Z_1 - O(3)$	70 ± 1 71 + 1
O(m 1) = 21 = O(7)	/1 ± 1

Table 5 (cont.)

(b) Within the	sulphate groups
S(1)-O(8)	$1.52 \pm 0.02 \text{ Å}$
O(2)	1.42 ± 0.03
O(9)	1.39 ± 0.02
O(7)	1.49 ± 0.02
Average	1•46
S(2)-O(3)	1.44 ± 0.02 Å
O(4)	1.48 ± 0.02
O(5)	1.46 ± 0.02
O(6)	1.47 ± 0.02
Average	1.46
O(7)-S(1)-O(9)	$108 \pm 1^{\circ}$
O(7) - S(1) - O(2)	113 ± 1
O(7) - S(1) - O(8)	103 ± 1
O(9)-S(1)-O(8)	106 ± 1
O(9)-S(1)-O(2)	116 ± 1
O(8) - S(1) - O(2)	110 ± 1
Average	109
O(4)-S(2)-O(3)	$113 \pm 1^{\circ}$
O(4) - S(2) - O(5)	109 ± 1
O(4) - S(2) - O(6)	107 ± 1
O(6)-S(2)-O(5)	106 ± 1
O(6)-S(2)-O(3)	110 ± 1
O(5)-S(2)-O(3)	111 ± 1
Average	109

(c) Possible hydrogen bonding between the water molecule and its neighbours

± 0.03 ± 0.03 ± 0.03 ± 0.03
1° 1 1 1
±1 ±1 ±1 ±1

tion of 1.44 to 1.48 Å is much less. Again the variation of angle for the first tetrahedron of 106 to 116° is more extreme than that of the second where it is 106 to 113°.

Table 5(c) gives the distance between O(W1) and possible acceptor oxygen atoms for hydrogen bonds. The O-O(W1)-O angles are also included. It seems likely that hydrogen bridging occurs between O(W1)and O(2) and O(W1) and O(3) as at least one of these contacts is essential for cohesion between the layers. The O(2)-O(W1)-O(3) angle of 92° is small but Baur (1964) has pointed out that there appears to be no correlation between the magnitudes of the angles H-O-H and O-O(W)-O. Nevertheless the possibility that one of the hydrogen atoms makes a long contact to O(6) instead of O(3) cannot be discounted. Bonding between O(W1) and O(5) or O(7) seems unlikely as an O(W)-O distance of 2.51 Å is rather shorter than is generally found for hydrogen bonding in hydrates

1130

(Singer & Cromer, 1959). A Fourier difference synthesis failed to reveal the positions of the hydrogen atoms but a study of the lengths of the bonds by spectroscopic methods is in progress.

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The Crystal Chemistry of Zirconium Sulphates. V. The Structure of a-Zr(SO₄)₂. H₂O

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 α -Zr(SO₄)₂. H₂O, the stable modification of the three monohydrates of zirconium sulphate that are formed by thermal decomposition of Zr(SO₄)₂. 4H₂O, is monoclinic with space group P₂₁/C, and unitcell dimensions a = 7.32, b = 8.54, c = 11.8 Å, $\beta = 106.0^{\circ}$. It crystallizes in two differing morphologies. The structure, as determined by single-crystal X-ray analysis, consists of layers of composition [Zr(SO₄)₂. H₂O]_n aligned in sheets parallel to the (100) plane. These layers appear to be held together by hydrogen bonds. Within the layers zirconium is bonded by six oxygen atoms to bridging sulphate tetrahedra, and to one additional oxygen atom belonging to the water molecule. The resulting sevenfold coordination for zirconium is similar to that previously found in the γ -monohydrate and in ZrO₂ (monoclinic form). Powder data for a third monohydrate β -Zr(SO₄)₂. H₂O are also presented, and it is deduced from this and infrared data that the β -form is, most probably, closely related to the structure of the γ -form.

Introduction

Parts I-III of this series of papers (Bear & Mumme, 1969a, b, c) have described the structural and chemical relationships between the four higher hydrates $Zr(SO_4)_2$, $7H_2O$, α - $Zr(SO_4)_2$, $5H_2O$, β - $Zr(SO_4)_2$, $5H_2O$ and Zr(SO₄)₂.4H₂O. Part IV (Bear & Mumme, 1970a) described the structure of γ -Zr(SO₄)₂. H₂O, one of the three forms of zirconium sulphate monohydrate obtained by thermal decomposition of Zr(SO₄)₂.4H₂O (Bear & Mumme, 1969d). γ and β -Zr(SO₄)₂. H₂O are metastable, and equilibrate to the stable α form when heated in a sealed tube at temperatures between 150 and 210 °C or in an atmosphere provided by 75% (w/w) H_2SO_4 at 150–160 °C. In keeping with the equilibrium nature of the phase, α -Zr(SO₄)₂. H₂O can also be obtained by vapour hydration of the anhydrous zirconium sulphates at 120°C in atmospheres provided by 75% H₂SO₄.

This paper describes the structure of α -Zr(SO₄)₂. H₂O and also presents powder data and unit-cell parameters

for β -Zr(SO₄)₂. H₂O. Part VII (Bear & Mumme, 1970b) discusses the structural relationships between the hydrates of Zr(SO₄)₂. Skeletal structural correspondences between them are used to postulate mechanisms of transformation.

Experimental

Microcrystalline β -Zr(SO₄)₂. H₂O was prepared by aging γ -Zr(SO₄)₂. H₂O (Bear & Mumme, 1969*d*) at room temperature while α -Zr(SO₄)₂. H₂O was obtained by equilibration of the γ -phase over 75% H₂SO₄ at 155°C. Powder X-ray diffraction data for β and α -Zr(SO₄)₂. H₂O (Tables 1 and 2 respectively) were collected from these microcrystalline samples with a Philips proportional counter diffractometer using a Ni filter and Cu K α radiation. As both compounds are deliquescent under ambient conditions a special sample holder was fitted to the diffractometer which permitted dry N₂ gas to be passed over the specimens. The powder data for the two compounds were indexed by