The Crystal Chemistry of Zirconium Sulphates.
IV. The Structure of the γ-Monohydrate, $Zr(SO_4)_2.H_2O$, a Layer Compound with the Zirconium Atom in Sevenfold Coordination

BY I. J. BEAR AND W. G. MUMME

Division of Mineral Chemistry, C.S.I.R.O., Melbourne, Australia

γ-$Zr(SO_4)_2.H_2O$ is triclinic, space group $P\bar{1}$, with unit-cell dimensions $a=7\cdot89$, $b=5\cdot21$, $c=8\cdot96$ Å, $\alpha=95\cdot2°$, $\beta=99\cdot8°$, $\gamma=109\cdot2°$. The structure, determined by single-crystal X-ray analysis, consists of layers of composition $Zr(SO_4)_2.H_2O$, 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, ZrO_2.

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 hepta- and the two pentahydrates are all built up from isolated dimeric groups of composition $Zr_2(SO_4)_4(H_2O)_8$ which

Table 1. *X-ray powder diffraction data for* γ-$Zr(SO_4)_2.H_2O$

d_{obs}	$\sin^2 \theta_{obs}$	$\sin^2 \theta_{calc}$	hkl	I	d_{obs}	$\sin^2 \theta_{obs}$	$\sin^2 \theta_{calc}$	hkl	I
8·70	0·0078	0·0078	001	w	2·485	0·0961	0·0961	1$\bar{1}$3	w
7·29	0·0112	0·0112	100	vs			0·0959	112	
6·28	0·0150	0·0150	10$\bar{1}$	m					
4·90	0·0247	0·0251	010	w	2·424	0·1010	0·1007	1$\bar{2}\bar{1}$	w
		0·0245	1$\bar{1}$0				0·1007	300	
4·37	0·0311	0·0312	002	w	2·355	0·1070	0·1069	2$\bar{2}\bar{1}$	w
4·32	0·0318	0·0319	1$\bar{1}$1	m			0·1068	3$\bar{1}$2	
4·24	0·0332	0·0329	1$\bar{1}\bar{1}$	w					
4·151	0·0344	0·0345	10$\bar{2}$	m	2·342	0·1081	0·1085	013	w
3·985	0·0374	0·0373	011	s			0·1081	30$\bar{2}$	
3·644	0·0447	0·0447	200	m	2·219	0·1205	0·1202	10$\bar{4}$	vw
		0·0446	20$\bar{1}$				0·1203	301	
3·576	0·0464	0·0464	2$\bar{1}$0	w	2·096	0·1350	0·1350	120	w
3·512	0·0481	0·0480	110	w			0·1354	3$\bar{2}\bar{1}$	
		0·0507	2$\bar{1}\bar{1}$				0·1353	30$\bar{3}$	
3·418	0·0508	0·0503	102	vw	2·072	0·1381	0·1379	20$\bar{4}$	w
							0·1384	3$\bar{1}\bar{3}$	
3·290	0·0548	0·0549	1$\bar{1}$2	m	2·048	0·1415	0·1415	3$\bar{2}$1	vw
3·214	0·0574	0·0577	2$\bar{1}$1	w	1·967	0·1533	0·1535	4$\bar{1}\bar{1}$	w
3·137	0·0603	0·0601	20$\bar{2}$	m	1·942	0·1573	0·1571	2$\bar{1}\bar{4}$	w
		0·0606	201				0·1571	4$\bar{1}$0	
3·084	0·0624	0·0625	11$\bar{2}$	w–m	1·822	0·1787	0·1785	40$\bar{2}$	m
3·025	0·0648	0·0651	012	m			0·1790	400	
2·925	0·0693	0·0695	10$\bar{3}$	w–m					
2·910	0·0701	0·0702	003	w	1·789	0·1853	0·1853	2$\bar{1}$4	
		0·0705	2$\bar{1}$2				0·1855	3$\bar{1}$4	w
							0·1850	311	
2·686	0·0823	0·0821	01$\bar{3}$	w			0·1855	4$\bar{2}$0	
2·650	0·0845	0·0846	2$\bar{1}$2	w					
2·594	0·0882	0·0881	1$\bar{2}$0	w–m	1·753	0·1930	0·1931	4$\bar{1}\bar{3}$	w–m
2·554	0·0910	0·0911	1$\bar{2}$1	w–m	1·721	0·2003	0·2004	1$\bar{3}$1	w
		0·0912	20$\bar{3}$				0·2002	2$\bar{3}$0	
		0·0909	3$\bar{1}\bar{1}$				0·2002	20$\bar{3}$	
		0·0906	3$\bar{1}$0				0·2004	213	
							0·2003	4$\bar{2}$1	
2·522	0·0933	0·0935	1$\bar{1}$3	w	1·713	0·2022	0·2018	1$\bar{3}$0	w
		0·0933	103				0·2026	4$\bar{2}\bar{2}$	
		0·0932	11$\bar{3}$				0·2017	40$\bar{3}$	
		0·0933	210				0·2026	401	

in all three cases are held together in several directions by hydrogen bonds through the coordinated and non-bonded 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 mono-hydrates 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-$Zr(SO_4)_2.H_2O$ have only been obtained by thermal decomposition of the higher hydrates (Bear & Mumme, 1969d). Both phases are metastable and equilibrate to α-$Z4(SO_4)_2.H_2O$ 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-$Zr(SO_4)_2.H_2O$. Part V (Bear & Mumme, 1970) which follows, reports that of α-$Zr(SO_4)_2.H_2O$ and presents unit-cell param-eters and powder data for β-$Zr(SO_4)_2.H_2O$. It also includes a discussion of the structural inter-relation-ships between the three monohydrates and the higher hydrates.

Experimental

γ-$Zr(SO_4)_2.H_2O$ was prepared as a microcrystalline powder by thermal decomposition of solid $Zr(SO_4)_2.4H_2O$ 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 diffrac-tometer with a Ni filter and Cu $K\alpha_{1,2}$ radiation. A continuous stream of dry N_2 gas was passed over the sample to delay rehydration.

Well-formed crystals of γ-$Zr(SO_4)_2.H_2O$ suitable for structural analysis can be prepared either by evapora-tion of an aqueous solution of $Zr(SO_4)_2.4H_2O$ or by the thermal decomposition of solid $Zr(SO_4)_2.4H_2O$ 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 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. Con-siderable time had been spent in obtaining an un-twinned 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
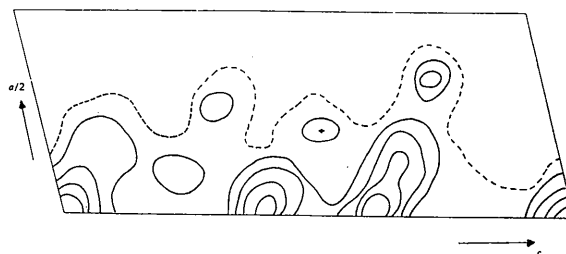

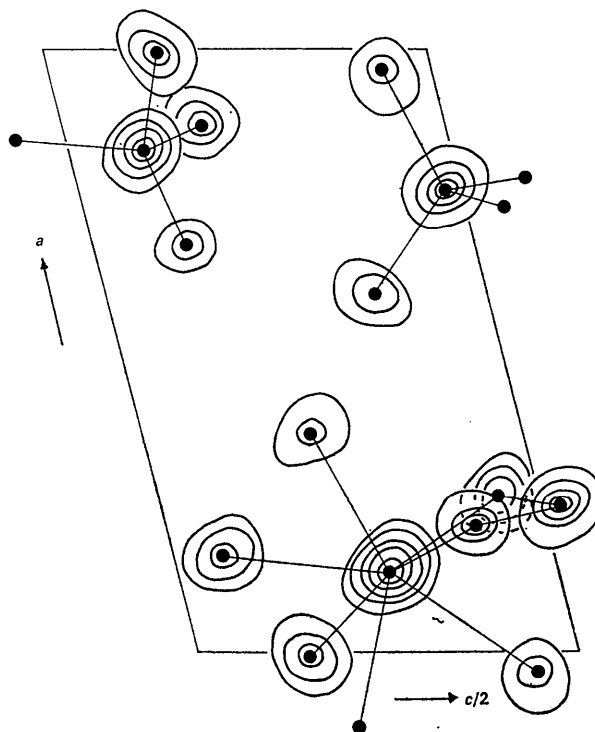Fig. 1. Patterson function $P(u,w)$ projected on to (010). The cross is the Zr–Zr vector across the origin.

Table 2. *Crystal data for* γ-$Zr(SO_4)_2.H_2O$

Symmetry	Triclinic
Unit-cell dimensions	$a = 7\cdot89 \pm 0\cdot01$ Å
	$b = 5\cdot21 \pm 0\cdot01$
	$c = 8\cdot96 \pm 0\cdot01$
	$\alpha = 95\cdot2 \pm 0\cdot1°$
	$\beta = 99\cdot8 \pm 0\cdot1$
	$\gamma = 109\cdot2 \pm 0\cdot1$
Possible space groups	$P1$ or $P\bar{1}$
D_x	2·95 g.cm^{-3}
D_m	2·93 ± 0·03 g.cm^{-3}
Z	2
μ_c	200 cm^{-1}

Fig. 2. Electron density distribution indicated by sections $\varrho_0(x,y,z)$ 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 [Ī10] and [20Ī] 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(SO$_4$)$_2$.H$_2$O 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*

H	K	L	F_O	F_C

Structure determination

The number of formula units $Z = 2$ was calculated from the density, 2·93 g.cm^{-3}, obtained by displacement in CCl$_4$. The space group was assumed to be $P\bar{1}$ 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$_4$)$_2$.H$_2$O, 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 block-diagonal 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.
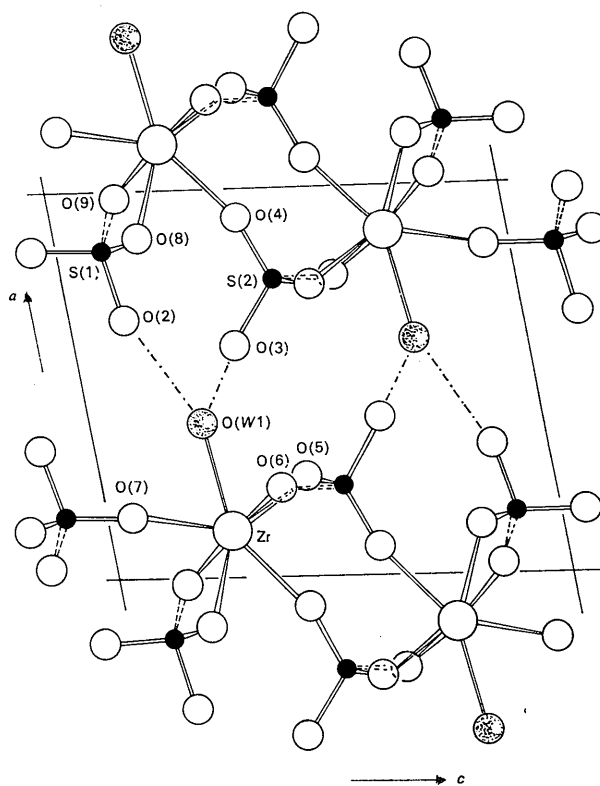
Fig. 3. The structure of γ-Zr(SO$_4$)$_2$.H$_2$O projected on to (010). Large open circles, zirconium atoms; full black circles, sulphur atoms; medium open circles, oxygen atoms; stippled circles, water molecules.

Table 4. *Fractional atomic parameters and thermal parameters for* γ-Zr(SO$_4$)$_2$.H$_2$O

Estimated standard deviations are given in parentheses.

	x	y	z	B
Zr	0·1200 (3)	0·3025 (6)	0·2719 (2)	0·60 (4) Å^2
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)
O(9)	−0·0072 (25)	−0·1058 (53)	0·1530 (24)	2·58 (44)

Description and discussion of structure

The structure of γ-Zr(SO$_4$)$_2$.H$_2$O viewed in (010) projection is shown in Fig.3. It is made up of layers of composition Zr(SO$_4$)$_2$.H$_2$O 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$_5$Zr$_2$F$_{13}$ (Herak, Malcic & Manojlovic, 1965). The range of metal–oxygen bonds in γ-Zr(SO$_4$)$_2$.H$_2$O (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 ZrO$_2$ (monoclinic).
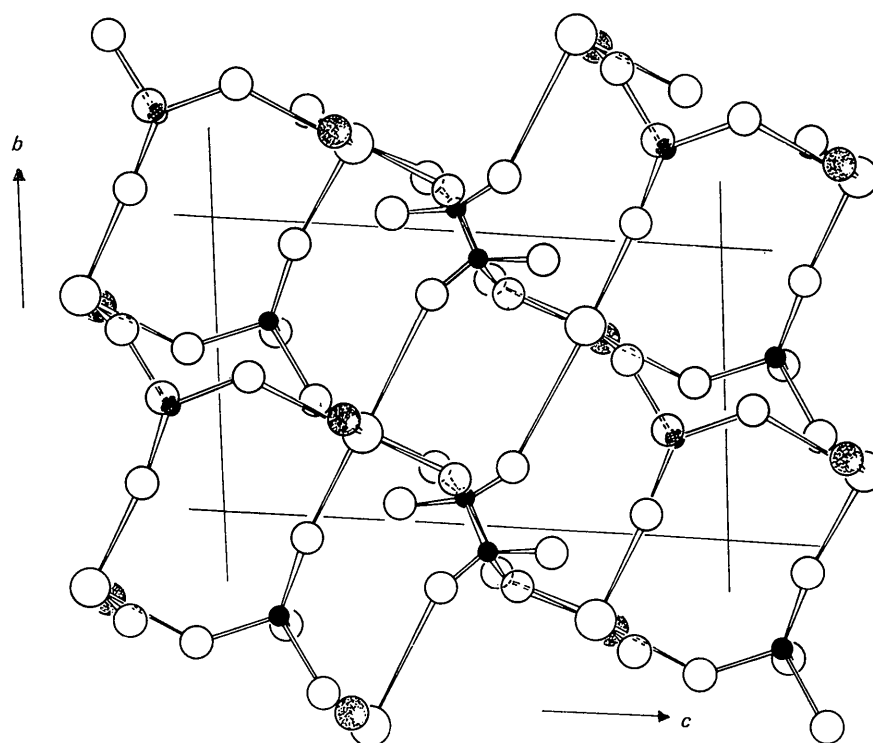

Fig.4. The layer centred at $x=0$ as viewed along the a axis. Designation of the atoms is the same as in Fig.3.
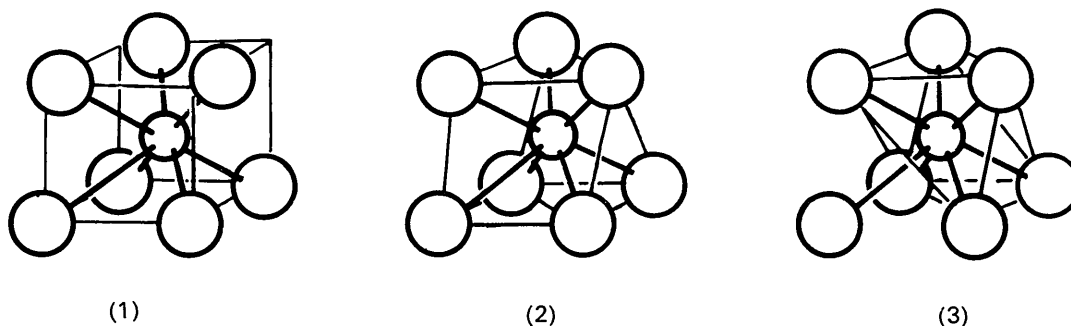

(1) (2) (3)

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 co-ordination polyhedron in ZrO_2 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

Metal–oxygen distances

Zr–O(W1)	2·19 ± 0·03 Å
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 Å
O(6)——O(8)	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(W1)–O(6)	2·99 ± 0·03
O(W1)–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

O(4)——Zr–O(8)	72 ± 1 °
O(4)——Zr–O(9)	86 ± 1
O(4)——Zr–O(6)	88 ± 1
O(4)——Zr–O(5)	74 ± 1
O(9)——Zr–O(8)	93 ± 1
O(9)——Zr–O(5)	89 ± 1
O(5)——Zr–O(6)	88 ± 1
O(6)——Zr–O(8)	87 ± 1
O(7)——Zr–O(9)	90 ± 1
O(7)——Zr–O(8)	74 ± 1
O(W1)–Zr–O(6)	89 ± 1
O(W1)–Zr–O(5)	70 ± 1
O(W1)–Zr–O(7)	71 ± 1

Table 5 *(cont.)*

(b) Within the sulphate groups

S(1)–O(8)	1·52 ± 0·02 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 ± 1 °
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 ± 1 °
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

Distances

O(W1)–O(2)	2·71 ± 0·04 Å
O(3)	2·67 ± 0·03
O(5)	2·50 ± 0·03
O(6)	2·99 ± 0·03
O(7)	2·51 ± 0·03

Angles

O(3)–O(W1)–O(6)	129 ± 1 °
O(5)	76 ± 1
O(2)	92 ± 1
O(7)	159 ± 1
O(2)–O(W1)–O(3)	92 ± 1
O(7)	91 ± 1
O(6)	110 ± 1
O(5)	153 ± 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

(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.

The authors are grateful to Mr C. Anderson for taking the precession data.

References

BAUR, W. H. (1964). Acta Cryst. 17, 863.
BEAR, I. J. & MUMME, W. G. (1968). Chem. Comm. p. 609.
BEAR, I. J. & MUMME, W. G. (1969a). Acta Cryst. B25, 1558.
BEAR, I. J. & MUMME, W. G. (1969b). Acta Cryst. B25, 1566.
BEAR, I. J. & MUMME, W. G. (1969c). Acta Cryst. B25, 1572.
BEAR, I. J. & MUMME, W. G. (1969d). Chem. Comm. p. 230
BEAR, I. J. & MUMME, W. G. (1970). Acta Cryst. B26, 1131.
CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In Computing Methods and the Phase Problem in X-ray Crystal Analysis, p. 32. Oxford: Pergamon Press.
HERAK, R. M., MALCIC, S. S. & MANOJLOVIC, L. M. (1965). Acta Cryst. 18, 520.
McCULLOUGH, J. D., BREWER, L. & BROMLEY, L. A. (1948). Acta Cryst. 1, 287.
McCULLOUGH, J. D. & TRUEBLOOD, K. N. (1959). Acta Cryst. 12, 507.
MUMME, W. G. & WADSLEY, A. D. (1968). Acta Cryst. B24, 1327.
SINGER & CROMER, D. T. (1959). Acta Cryst. 12, 719.

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

BY I. J. BEAR AND W. G. MUMME

Division of Mineral Chemistry, C.S.I.R.O., Melbourne, Australia

α-Zr(SO$_4$)$_2$.H$_2$O, the stable modification of the three monohydrates of zirconium sulphate that are formed by thermal decomposition of Zr(SO$_4$)$_2$.4H$_2$O, is monoclinic with space group $P2_1/C$, and unit-cell dimensions $a = 7 \cdot 32$, $b = 8 \cdot 54$, $c = 11 \cdot 8$ Å, $\beta = 106 \cdot 0°$. It crystallizes in two differing morphologies. The structure, as determined by single-crystal X-ray analysis, consists of layers of composition [Zr(SO$_4$)$_2$.H$_2$O]$_n$ 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 ZrO$_2$ (monoclinic form). Powder data for a third monohydrate β-Zr(SO$_4$)$_2$.H$_2$O 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$_2$O, α-Zr(SO$_4$)$_2$.5H$_2$O, β-Zr(SO$_4$)$_2$.5H$_2$O and Zr(SO$_4$)$_2$.4H$_2$O. Part IV (Bear & Mumme, 1970a) described the structure of γ-Zr(SO$_4$)$_2$.H$_2$O, one of the three forms of zirconium sulphate monohydrate obtained by thermal decomposition of Zr(SO$_4$)$_2$.4H$_2$O (Bear & Mumme, 1969d). γ and β-Zr(SO$_4$)$_2$.H$_2$O 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$_2$SO$_4$ at 150–160°C. In keeping with the equilibrium nature of the phase, α-Zr(SO$_4$)$_2$.H$_2$O can also be obtained by vapour hydration of the anhydrous zirconium sulphates at 120°C in atmospheres provided by 75% H$_2$SO$_4$.

This paper describes the structure of α-Zr(SO$_4$)$_2$.H$_2$O and also presents powder data and unit-cell parameters

for β-Zr(SO$_4$)$_2$.H$_2$O. Part VII (Bear & Mumme, 1970b) discusses the structural relationships between the hydrates of Zr(SO$_4$)$_2$. Skeletal structural correspondences between them are used to postulate mechanisms of transformation.

Experimental

Microcrystalline β-Zr(SO$_4$)$_2$.H$_2$O was prepared by aging γ-Zr(SO$_4$)$_2$.H$_2$O (Bear & Mumme, 1969d) at room temperature while α-Zr(SO$_4$)$_2$.H$_2$O was obtained by equilibration of the γ-phase over 75% H$_2$SO$_4$ at 155°C. Powder X-ray diffraction data for β and α-Zr(SO$_4$)$_2$.H$_2$O (Tables 1 and 2 respectively) were collected from these microcrystalline samples with a Philips proportional counter diffractometer using a Ni filter and Cu $K\alpha$ radiation. As both compounds are deliquescent under ambient conditions a special sample holder was fitted to the diffractometer which permitted dry N$_2$ gas to be passed over the specimens. The powder data for the two compounds were indexed by