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## The Crystal Chemistry of Zirconium Sulphates. V. The Structure of $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O

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$\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, the stable modification of the three monohydrates of zirconium sulphate that are formed by thermal decomposition of Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, is monoclinic with space group  $P2_1/C$ , and unit-cell 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(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O]<sub>n</sub> 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  $\gamma$ -monohydrate and in ZrO<sub>2</sub> (monoclinic form). Powder data for a third monohydrate  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O are also presented, and it is deduced from this and infrared data that the  $\beta$ -form is, most probably, closely related to the structure of the  $\gamma$ -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<sub>4</sub>)<sub>2</sub>·7H<sub>2</sub>O,  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O,  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O and Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O. Part IV (Bear & Mumme, 1970a) described the structure of  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, one of the three forms of zirconium sulphate monohydrate obtained by thermal decomposition of Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (Bear & Mumme, 1969d).  $\gamma$  and  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O are metastable, and equilibrate to the stable  $\alpha$  form when heated in a sealed tube at temperatures between 150 and 210°C or in an atmosphere provided by 75% (w/w) H<sub>2</sub>SO<sub>4</sub> at 150–160°C. In keeping with the equilibrium nature of the phase,  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O can also be obtained by vapour hydration of the anhydrous zirconium sulphates at 120°C in atmospheres provided by 75% H<sub>2</sub>SO<sub>4</sub>.

This paper describes the structure of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and also presents powder data and unit-cell parameters

for  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. Part VII (Bear & Mumme, 1970b) discusses the structural relationships between the hydrates of Zr(SO<sub>4</sub>)<sub>2</sub>. Skeletal structural correspondences between them are used to postulate mechanisms of transformation.

#### Experimental

Microcrystalline  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O was prepared by aging  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (Bear & Mumme, 1969d) at room temperature while  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O was obtained by equilibration of the  $\gamma$ -phase over 75% H<sub>2</sub>SO<sub>4</sub> at 155°C. Powder X-ray diffraction data for  $\beta$  and  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>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<sub>2</sub> gas to be passed over the specimens. The powder data for the two compounds were indexed by

Ito's method, reduced by Delaunay's procedure and refined to give the unit-cell parameters in Table 3.

So far single crystals of  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, suitable for X-ray structure analysis have not been obtained but crystals of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O were grown by equilibrating microcrystalline  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O in aqueous 75% (w/w) H<sub>2</sub>SO<sub>4</sub> at 120–150°C. The crystals of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O were mostly in the form of rhombs but among them were observed a limited number of an elongated variety with two well developed sets of pinacoid and terminating faces. Powder data of both crystals were identical, so that they represent two morphological forms of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. A single-crystal investigation of the elongated form proved it to be monoclinic with, in this case, the long growth direction along *c* and with clino- and basal-pinacoids de-

fining *a* and *b*. Single crystals of the rhomb-like form had six faces formed by the ortho-pinacoids {100} and the clino-domes {011} and {01 $\bar{1}$ }.

Integrated Weissenberg data *h*0*l* to *h*6*l* and 0*kl* were recorded, using Cu *K* $\alpha$  radiation and multiple-film packs, from part of an elongated crystal, as its morphology permitted the positions of the *a* and *b* axes to be determined more easily. Measurement of intensities, subsequent data handling, including interlayer sealing procedures, and the scattering curves for Zr, S, and O are as described in part I (Bear & Mumme, 1969*a*). Crystals used for collecting X-ray data were sealed in quartz capillaries to prevent hydration.

The number of formula units, *Z*=4, was calculated from the measured density, *D*<sub>*m*</sub>=2.84 g.cm<sup>-3</sup>, obtained by displacement in CCl<sub>4</sub>.

Table 1. X-ray powder data for  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O

sin <sup>2</sup> $\theta_{\text{obs}}$	sin <sup>2</sup> $\theta_{\text{calc}}$	<i>hkl</i>	<i>I</i>	sin <sup>2</sup> $\theta_{\text{obs}}$	sin <sup>2</sup> $\theta_{\text{calc}}$	<i>hkl</i>	<i>I</i>
0.0077	0.0077	001	<i>w</i>	0.1052	0.1055	221	<i>vw</i>
0.0112	0.0113	100	<i>vs</i>	0.1092	0.1095	30 $\bar{2}$	<i>vw</i>
0.0152	0.0152	10 $\bar{1}$	<i>m</i>	0.1196	0.1192	104	<i>vw</i>
0.0226	0.0227	101	<i>vw</i>	0.1196	0.1197	2 $\bar{2}\bar{2}$	
0.0237	0.0236	010	<i>w</i>				
0.0237	0.0237	1 $\bar{1}\bar{0}$		0.1230	0.1230	004	<i>vw</i>
				0.1270	0.1271	12 $\bar{1}$	<i>vw</i>
0.0307	0.0307	002	<i>w</i>	0.1311	0.1314	2 $\bar{2}\bar{2}$	<i>w</i>
0.0330	0.0329	1 $\bar{1}\bar{1}$	<i>m</i>	0.1311	0.1313	2 $\bar{1}\bar{3}$	
0.0333	0.0336	011	<i>s</i>				
0.0345	0.0345	10 $\bar{2}$	<i>m</i>	0.1371	0.1374	014	
0.0452	0.0452	20 $\bar{1}$	<i>m</i>	0.1371	0.1368	203	<i>m</i>
0.0452	0.0450	200		0.1371	0.1366	30 $\bar{3}$	
0.0465	0.0464	2 $\bar{1}\bar{0}$	<i>m</i>	0.1437	0.1438	121	<i>w</i>
0.0475	0.0476	11 $\bar{1}$	<i>m</i>	0.1437	0.1433	3 $\bar{2}\bar{1}$	
0.0491	0.0495	102	<i>w</i>	0.1499	0.1497	02 $\bar{3}$	<i>vw</i>
0.0491	0.0488	2 $\bar{1}\bar{1}$		0.1499	0.1500	1 $\bar{2}\bar{3}$	
0.0576	0.0574	1 $\bar{1}\bar{2}$	<i>w</i>	0.1554	0.1557	014	
0.0589	0.0589	012	<i>m</i>	0.1554	0.1549	1 $\bar{2}\bar{3}$	<i>w</i>
0.0589	0.0593	2 $\bar{1}\bar{1}$		0.1554	0.1552	2 $\bar{2}\bar{3}$	
0.0645	0.0646	11 $\bar{2}$	<i>m</i>	0.1729	0.1728	2 $\bar{2}\bar{3}$	
0.0671	0.0666	21 $\bar{2}$	<i>w</i>	0.1729	0.1731	3 $\bar{2}\bar{2}$	<i>w</i>
0.0693	0.0692	003	<i>w</i>	0.1729	0.1728	40 $\bar{1}$	
0.0693	0.0691	10 $\bar{3}$					
0.0836	0.0833	1 $\bar{2}\bar{0}$	<i>w</i>	0.1774	0.1772	023	<i>w</i>
0.0859	0.0858	01 $\bar{3}$	<i>w</i>	0.1802	0.1797	4 $\bar{1}\bar{1}$	<i>m</i>
0.0882	0.0885	1 $\bar{1}\bar{3}$	<i>m</i>	0.1802	0.1802	400	
0.0906	0.0901	1 $\bar{2}\bar{1}$					
0.0906	0.0909	202	<i>w</i>	0.1869	0.1867	31 $\bar{3}$	<i>w</i>
0.0906	0.0909	210		0.1994	0.1995	20 $\bar{5}$	<i>w</i>
0.0906	0.0902	3 $\bar{1}\bar{1}$		0.2079	0.2079	11 $\bar{5}$	<i>w</i>
				0.2269	0.2272	015	
				0.2269	0.2267	031	<i>w</i>
				0.2269	0.2270	1 $\bar{3}\bar{2}$	
				0.2269	0.2269	314	
0.0917	0.0918	1 $\bar{2}\bar{1}$					
0.0917	0.0917	103	<i>m</i>				
0.0917	0.0916	20 $\bar{3}$		0.2377	0.2372	4 $\bar{2}\bar{2}$	<i>w</i>
0.0917	0.0916	3 $\bar{1}\bar{0}$		0.2499	0.2498	1 $\bar{3}\bar{3}$	<i>vw</i>
				0.2499	0.2495	5 $\bar{1}\bar{0}$	
0.0940	0.0943	020	<i>w</i>				
0.0973	0.0974	02 $\bar{1}$					
0.0973	0.0973	1 $\bar{1}\bar{3}$	<i>w</i>	0.2605	0.2606	03 $\bar{3}$	<i>w</i>
0.0973	0.0969	11 $\bar{3}$					
0.0973	0.0977	30 $\bar{1}$		0.2657	0.2654	10 $\bar{6}$	
				0.2657	0.2661	1 $\bar{3}\bar{2}$	<i>vw</i>
				0.2657	0.2653	41 $\bar{3}$	
0.1014	0.1014	300	<i>w</i>				

## Structure determination

The systematic absent reflexions,  $h0l$  with  $l=2n+1$  and  $0k0$  with  $k=2n+1$ , define the space group uniquely as  $P2_1/C$ , and there are four zirconium, eight sulphur and 36 oxygen atoms in the unit cell. It seemed unlikely that any of the metal atoms would occupy special positions, so only the general  $4(e)$  positions were considered in determining the Zr and S positions. From the Patterson projections  $P(u, w)$  and  $P(v, w)$  a set of parameters for Zr, S(1) and S(2) was found. The signs of the structure factors calculated for these zirconium and sulphur positions were used with the observed

structure factors to calculate the electron density projections  $\rho(x, z)$  and  $\rho(y, z)$ . However it was immediately obvious that there was considerable overlap of many of the oxygen atoms in both of these projections, and for this reason a three-dimensional electron density map was calculated from the  $b$  axis data.

As in previous analyses, it was possible to recognize the disposition of the eight oxygen atoms attached to the two sulphur atoms. This left the position of one further oxygen atom to be determined; fortunately it was one of the well resolved oxygen atoms identifiable in the Fourier syntheses.

The zirconium atom was recognized as having seven-

Table 2. X-ray powder diffraction data for  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O

$\sin^2 \theta_{\text{obs}}$	$\sin^2 \theta_{\text{calc}}$	$hkl$	$l$	$\sin^2 \theta_{\text{obs}}$	$\sin^2 \theta_{\text{calc}}$	$hkl$	$l$	
0.0119	0.0120	100	<i>vs</i>	0.1079	0.1082	311	<i>w</i>	
0.0184	0.0184	002	<i>m</i>		0.1079	0.1079	300	
0.0201	0.0201	110	<i>s</i>					
0.0206	0.0206	$\bar{1}\bar{1}1$	<i>m</i>	0.1118	0.1118	132	<i>w</i>	
	0.0207	101		0.1159	0.1160	310	<i>w</i>	
0.0222	0.0222	$\bar{1}02$	<i>m</i>	0.1211	0.1206	$\bar{3}\bar{1}3$		
0.0265	0.0265	012	<i>s</i>		0.1212	0.1212	224	<i>w</i>
0.0288	0.0288	111	<i>m</i>		0.1213	0.1213	230	
0.0303	0.0303	$\bar{1}12$	<i>vs</i>	0.1326	0.1328	311		
0.0326	0.0326	020	<i>m</i>		0.1327	0.1327	$\bar{3}21$	<i>w</i>
0.0449	0.0446	120	<i>vs</i>	0.1326	0.1323	$\bar{3}04$		
	0.0449	$\bar{1}21$						
0.0466	0.0467	112	<i>w</i>	0.1342	0.1342	$\bar{3}22$		
0.0480	0.0479	200	<i>w</i>		0.1345	0.1345	124	<i>m</i>
0.0494	0.0492	$\bar{1}13$	<i>s</i>		0.1342	0.1341	231	
	0.0494	013						
0.0533	0.0532	121	<i>w</i>	0.1425	0.1427	$\bar{1}41$		
0.0547	0.0547	$\bar{1}22$	<i>s</i>		0.1425	0.1424	$\bar{1}34$	<i>w</i>
0.0560	0.0561	210	<i>m</i>		0.1425	0.1422	$\bar{1}40$	
0.0691	0.0691	$\bar{1}04$	<i>w</i>	0.1507	0.1509	141	<i>w</i>	
	0.0691	211			0.1507	0.1508	302	
0.0712	0.0711	122	<i>m</i>	0.1544	0.1543	$\bar{2}25$	<i>w</i>	
					0.1544	0.1542	204	
0.0738	0.0736	$\bar{1}23$		0.1647	0.1648	$\bar{3}24$	<i>w</i>	
	0.0738	004	<i>m</i>		0.1647	0.1643	$\bar{2}06$	
	0.0738	023		0.1737	0.1734	$\bar{3}31$	<i>w</i>	
	0.0738	113			0.1737	0.1736	016	
0.0775	0.0770	$\bar{2}\bar{2}1$		0.1778	0.1774	$\bar{4}02$	<i>w</i>	
	0.0775	$\bar{1}14$	<i>m</i>		0.1778	0.1780	$\bar{2}40$	
	0.0775	031						
	0.0804	0.0805	220		<i>w</i>			
0.0826	0.0825	$\bar{2}20$	<i>s</i>	0.1803	0.1800	$\bar{4}01$		
	0.0826	202			0.1800	0.1800	$\bar{2}42$	<i>m</i>
0.0853	0.0853	130	<i>w</i>		0.1803	0.1799	$\bar{1}35$	
	0.0853	$\bar{1}31$			0.1803	0.1799	125	
	0.0916	0.0916	032	<i>m</i>	0.1855	0.1855	$\bar{4}12$	
	0.0930	0.0931	221	<i>w</i>		0.1855	0.1856	$\bar{3}33$
				0.1855	0.1854	$\bar{1}26$		
0.0968	0.0968	$\bar{2}14$	<i>m</i>	0.1967	0.1967	$\bar{2}26$	<i>w</i>	
	0.0968	$\bar{2}23$		0.2052	0.2053	334	<i>m</i>	
0.1019	0.1017	$\bar{3}02$		0.2320	0.2321	$\bar{4}24$		
	0.1019	$\bar{1}24$	<i>m</i>		0.2320	0.2323	$\bar{3}26$	<i>w</i>
	0.1019	104			0.2320	0.2316	$\bar{3}42$	
					0.2320	0.2321	144	

fold coordination similar to that in the  $\gamma$ -monohydrate. If it were assumed that the six ligands of the attached sulphate groups were oxygen atoms and the one additional ligand the oxygen atom of the hydrate group, the overall composition became  $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ , as determined by chemical analysis.

Refinement of the structure was continued with the  $b$ -axis data, and after a number of least-squares cycles using isotropic temperature factors for each atom,  $R$  dropped to 13.1% for the 807 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 cal-

culated from the final model are given in Table 4. Atomic parameters and individual isotropic temperature factors with their estimated standard deviations are listed in Table 5, and bond lengths and angles in Table 6.

### Description

The structure is composed of layers, of composition  $[\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}]_n$ , lying in the (100) plane and extending infinitely in the  $b$  and  $c$  directions. Figs. 1(a) and 2 show these layers in the (010) projection while Fig. 1(b) is one such layer centred about  $x=0$ .

Each zirconium atom is in sevenfold coordination, six ligands being the oxygen atoms of the sulphate

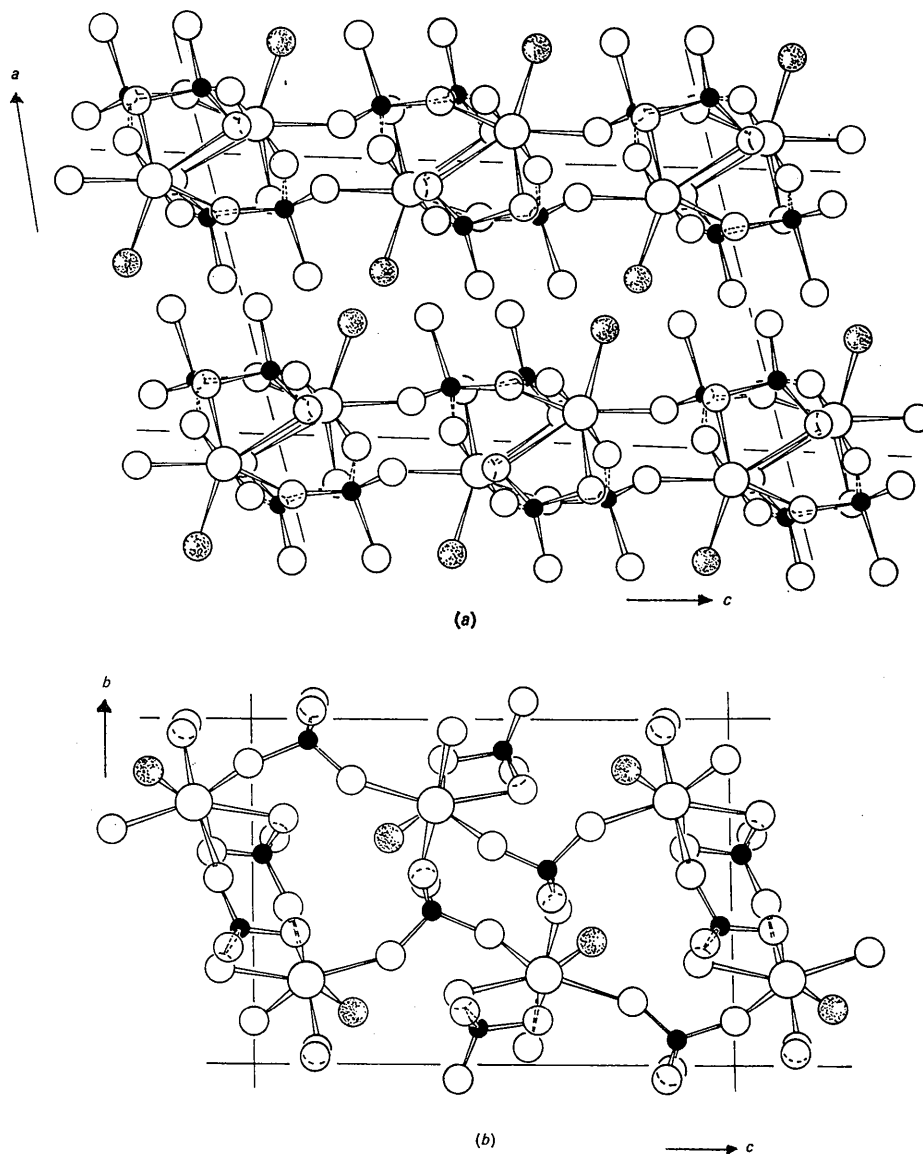
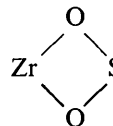


Fig. 1. (a) The structure of  $\alpha\text{-Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  projected on to (010). (b) A layer centred at  $x=0$  as viewed along the  $a$  axis. Large open circles, zirconium atoms; full black circles, sulphur atoms; medium open circles, oxygen atoms; stippled circles, water molecules.

groups and one the oxygen atom of the water molecule. Although all sulphate groups have three oxygen atoms bridging to zirconium atoms and one terminal oxygen atom which is directed out of the (100) plane, two types of sulphate tetrahedra can be recognized. One type connects three zirconium atoms by single oxygen bridges each of the form Zr-O-S [Fig. 3(a)], the other type connects two zirconium atoms by one single oxygen bridge, Zr-O-S, and one double oxygen

bridge, Zr-O-S, [Fig. 3(b)]. Each type of sulphate group, in addition, takes part in double sulphate

bridging of two zirconium atoms to give rise in turn to two forms of dimeric ring (Bear & Mumme, 1969c), as shown schematically in Fig. 3(c) and (d) respectively. In these diagrams the lines joining zirconium and sulphur atoms represent oxygen bridges so that in Fig. 3(c) the zirconium-sulphur linkages are all of the Zr-O-S type while in Fig. 3(d) there are two Zr-O-S and two



Zr-O-S linkages. These dimeric rings are joined

alternately to form zigzag chains of double sulphate bridge zirconium polyhedra [Fig. 3(e)] extending in the [010] direction. The two additional Zr-O-S bridges

Table 3. Crystallographic data for zirconium sulphate monohydrates

	(a) $\alpha$ -Zr(SO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O Monoclinic	(b) $\beta$ -Zr(SO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O Triclinic	(c) $\gamma$ -Zr(SO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O* Triclinic
Symmetry			
Unit-cell dimensions			
<i>a</i>	7.32 ± 0.01 Å	7.86 ± 0.01 Å	7.89 ± 0.01 Å
<i>b</i>	8.54 ± 0.01	5.34 ± 0.01	5.21 ± 0.01
<i>c</i>	11.82 ± 0.01	8.97 ± 0.01	8.96 ± 0.01
$\alpha$	90.0°	91.0 ± 0.1°	95.2 ± 0.1°
$\beta$	106.0 ± 0.1	100.7 ± 0.1	99.8 ± 0.1
$\gamma$	90.0	109.4 ± 0.1	109.2 ± 0.1
Unit-cell volume	710 Å <sup>3</sup>	348 Å <sup>3</sup>	339 Å <sup>3</sup>
Possible space groups	<i>P</i> 2 <sub>1</sub> / <i>C</i>	—	<i>P</i> 1 or <i>P</i> $\bar{1}$
<i>D<sub>x</sub></i>	2.82 g.cm <sup>-3</sup>	—	2.95 g.cm <sup>-3</sup>
<i>D<sub>m</sub></i>	2.84 ± 0.02 g.cm <sup>-3</sup>	—	2.93 ± 0.03 g.cm <sup>-3</sup>
<i>Z</i>	4	—	2
$\mu_e$	191 cm <sup>-1</sup>	—	200 cm <sup>-1</sup>
$\mu_r$	0.19	—	—

\* Bear & Mumme (1969d).

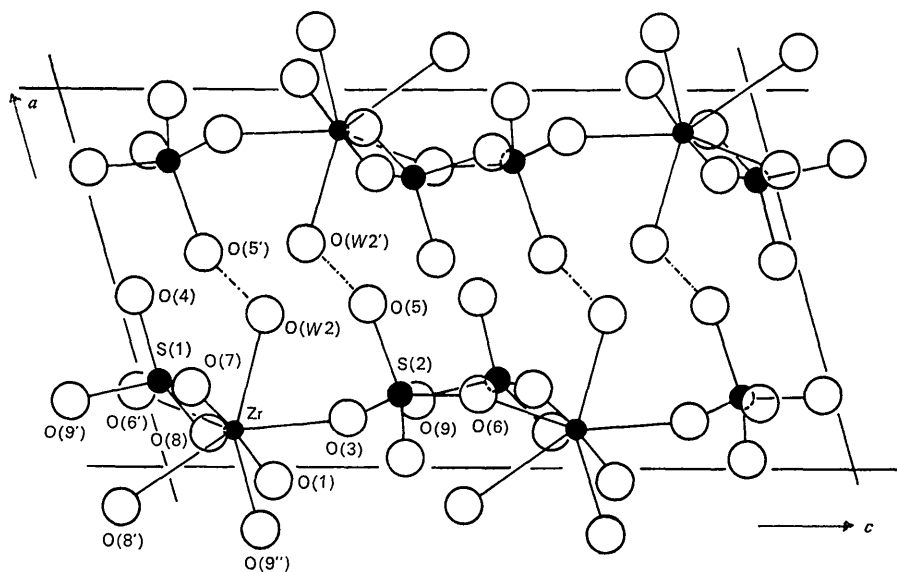


Fig. 2. Crystallographic sites in  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. The numbers in the asymmetric unit correspond to Table 5. Small black circles, zirconium atoms; medium black circles, sulphur atoms; large open circles, oxygen atoms and water molecules; dot and dashed lines, postulated hydrogen bonds.



Table 5. *Fractional atomic parameters and thermal parameters for  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O*E.s.d.'s are given in parentheses.  
(Origin at  $\bar{1}$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Zr	0·1031 (3)	0·2539 (4)	0·1110 (2)	0·77 (3) Å <sup>2</sup>
S(1)	0·2412 (9)	0·6144 (10)	0·0234 (6)	0·87 (11)
S(2)	0·1591 (9)	0·4468 (9)	0·3774 (6)	0·63 (10)
O(1)	-0·0278 (31)	0·0487 (32)	0·1394 (19)	1·66 (40)
O( <i>W</i> 2)	0·3748 (30)	0·1622 (31)	0·2088 (18)	1·55 (38)
O(3)	0·1392 (29)	0·3184 (30)	0·2868 (18)	1·46 (38)
O(4)	0·4334 (29)	0·6657 (32)	0·0532 (18)	1·78 (39)
O(5)	0·3591 (33)	0·5218 (33)	0·3712 (20)	2·16 (46)
O(6)	0·2197 (24)	0·3734 (26)	0·4920 (15)	0·67 (32)
O(7)	0·2350 (31)	0·4563 (31)	0·0790 (19)	1·74 (40)
O(8)	0·1056 (27)	0·7196 (29)	0·0633 (17)	1·26 (35)
O(9)	0·1553 (25)	0·8944 (26)	0·3954 (16)	0·92 (33)

Table 6. *Interatomic distances and bond angles, and their e.s.d.'s*(a) Within the ZrO<sub>7</sub> polyhedron

	Metal-oxygen distance
Zr-O(7)	2·07 (2) Å
O( <i>W</i> 2)	2·15 (2)
O(3)	2·09 (2)
O(6)	2·13 (2)
O(1)	2·07 (2)
O(8)	2·21 (2)
O(9)	2·22 (2)
Average	2·13
	Oxygen-oxygen distance
O(6)---O(7)	2·99 (3) Å
O(7)---O(9)	3·00 (3)
O(9)---O(1)	3·09 (3)
O(1)---O(6)	2·91 (3)
O( <i>W</i> 2)-O(3)	2·55 (3)
O( <i>W</i> 2)-O(7)	2·97 (3)
O( <i>W</i> 2)-O(6)	2·51 (3)
O(3)---O(1)	2·94 (3)
O(3)---O(9)	2·67 (3)
O(8)---O(6)	2·64 (3)
O(8)---O(7)	3·00 (3)
O(8)---O(1)	3·04 (3)
O(8)---O(9)	2·33 (3)
	Angle
O(8)---Zr-O(6)	75 ± 1°
O(8)---Zr-O(7)	89 ± 1
O(8)---Zr-O(1)	90 ± 1
O(8)---Zr-O(9)	63 ± 1
O(7)---Zr-O(6)	91 ± 1
O(6)---Zr-O(1)	88 ± 1
O(1)---Zr-O(9)	92 ± 1
O(9)---Zr-O(7)	89 ± 1
O( <i>W</i> 2)-Zr-O(7)	90 ± 1
O( <i>W</i> 2)-Zr-O(6)	72 ± 1
O(3)---Zr-O(1)	90 ± 1
O(3)---Zr-O(9)	76 ± 1
O(3)---Zr-O( <i>W</i> 2)	74 ± 1

(b) Within sulphate groups

	Distance
S(1)-O(4)	1·42 (2) Å
O(8)	1·51 (2)
O(7)	1·51 (2)
O(9)	1·47 (2)
Average	1·48

Table 6 (cont.)

	Angle
O(7)-S(1)-O(8)	107 ± 1°
O(7)-S(1)-O(4)	108 ± 1
O(7)-S(1)-O(9)	110 ± 1
O(8)-S(1)-O(9)	103 ± 1
O(8)-S(1)-O(4)	115 ± 1
O(4)-S(1)-O(9)	113 ± 1
Average	109
	Distance
S(2)-O(3)	1·51 (2) Å
O(5)	1·38 (2)
O(1)	1·47 (2)
O(6)	1·46 (2)
Average	1·46
	Angle
O(3)-S(2)-O(5)	112 ± 1°
O(3)-S(2)-O(1)	106 ± 1
O(3)-S(2)-O(6)	107 ± 1
O(6)-S(2)-O(1)	105 ± 1
O(6)-S(2)-O(5)	111 ± 1
O(5)-S(2)-O(1)	115 ± 1
Average	109

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

	Distance
O( <i>W</i> 2)-O(5')	2·67 Å
-O(6)	2·51
-O(3)	2·55
-O(7)	2·97
	Angle
O(5')-O( <i>W</i> 2)-O(3)	175°
O(5')-O( <i>W</i> 2)-O(7)	112
O(5')-O( <i>W</i> 2)-O(6)	76

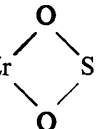
attached to each dimeric ring, which contains only Zr-O-S linkages [Fig. 3(c)], join the chains together in the [001] direction to form layers. This arrangement, which is represented schematically in Fig. 3(f), results in each zirconium atom being in contact with five sulphate tetrahedra.

The two non-equivalent sulphate groups are both distorted from the ideal tetrahedral symmetry (Table 6 and Fig. 2) but the mean bond-lengths and angles are close to those found for other sulphates in this series.

From the oxygen–oxygen distances shown in Table 6, it may be assumed that there is hydrogen bonding between the coordinated water molecule, O(W2), and the terminal oxygen atom, O(5'), of the sulphate group which makes Zr–O–S linkages with three zirconium atoms (Fig. 2). This bond presumably serves to hold the layers together. Of the other three possible hydrogen contacts [Table 6(c)] that to O(7), a distance of 2.97 Å, would appear the most likely as the other two of 2.51 and 2.55 Å respectively are rather shorter than is generally found for hydrogen bonds in hydrates (Singer & Cromer, 1959).

### Discussion

The sevenfold coordination of zirconium in  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O is similar to that found in ZrO<sub>2</sub> (monoclinic form) and  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, and the range of metal–oxygen separations between 2.07 and 2.22 Å is only marginally different from those found in these compounds (Bear & Mumme, 1970*a*). The disposition of the water molecule within the coordination sphere is similar to that in  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, but the positions of the Zr–O–S linkages between the double sulphate bridged chains in the two compounds are not the same

and only in  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O is there a Zr  S form

of attachment to a zirconium atom. A comparison of individual bond lengths and angles in the four crystallographically distinguishable sulphate tetrahedra does not reveal any significant difference arising from this one special form of attachment in the case of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. Differences do appear, however, in the 900–1250 cm<sup>-1</sup> region of the infrared absorption spectra of the  $\gamma$  and  $\alpha$ -phases [Fig. 4(a) and (c)]. In both cases the inequalities in the bond lengths and angles reduce the molecular symmetry of the two non-equivalent sulphate groups to C<sub>1</sub>, permitting observation of up to six vibrations corresponding to the  $\nu_3$  mode and two to the  $\nu_1$  mode (Bear & Mumme, 1969*c*). While the spectra are not well resolved, it can be seen that the vibrational components produced by this loss of symmetry do not have the same frequencies in the two compounds.

The third monohydrate polymorph,  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, has as yet, an undetermined structure. However, its lattice parameters are very similar to those of  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (Table 3). The changes in the *b* and  $\alpha$  lattice parameters and in the volume of  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O are towards those of the equilibrium  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O so that it seems that the transformation of  $\gamma$ - to  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O may only involve a relaxation of the  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O structure in the [010] direction. This tends to be supported by the absorption bands attributable to the sulphate vibrations in the infrared spectrum of  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O [Fig. 4(b)]. These

correspond more closely to the absorption spectrum of  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O than to that of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, suggesting that there is little difference in the symmetry

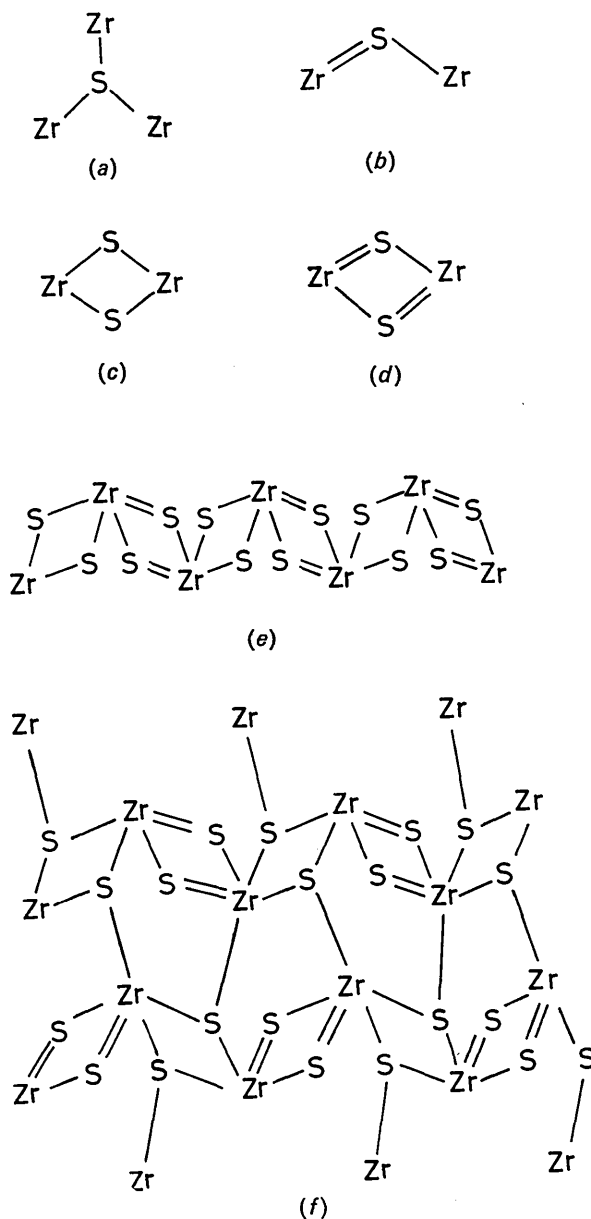


Fig. 3. Schematic representation of the mode of sulphate bridging of zirconium atoms in the structure of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. Lines joining zirconium and sulphur atoms represent oxygen bridges. (a) Manner in which a sulphate group forms single oxygen bridges to three zirconium atoms. (b) Manner in which a sulphate group forms one single and one double oxygen bridge between two zirconium atoms. (c) and (d) Two types of dimeric rings formed by the two crystallographically distinguishable sulphate tetrahedra. (e) A zigzag chain of double sulphate bridged zirconium polyhedra formed from the ring structures in (c) and (d). (f) Manner of cross-linking of chains in (e) to form a layer of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O.



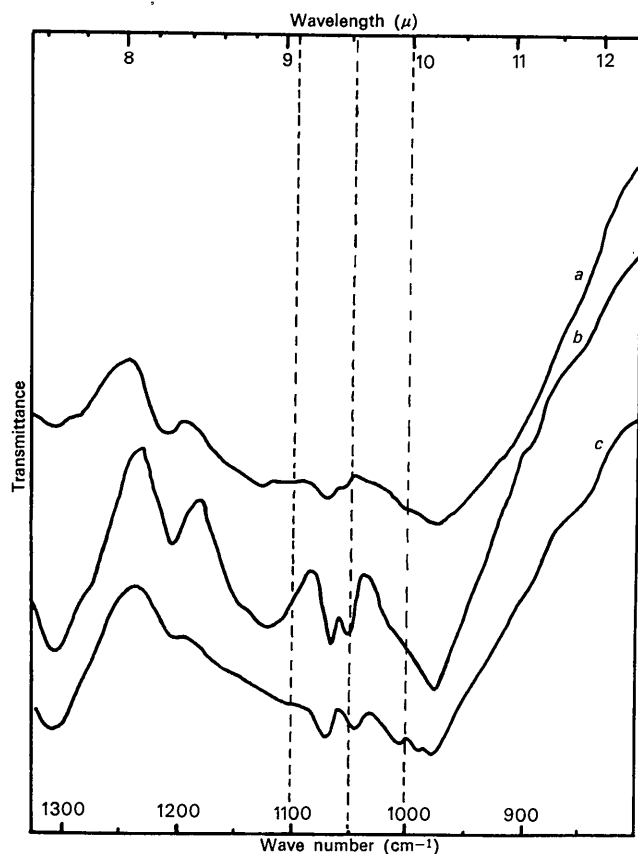


Fig. 4. Section of the infrared spectrum of (a)  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, (b)  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, (c)  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O.

and form of attachment of the sulphate groups in  $\beta$  and  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O.

The relationship between the two monohydrates  $\gamma$ - and  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and the previously discussed higher hydrates (Bear & Mumme, 1969*c*, 1970*a*) is most simply illustrated by Fig. 5. Fig. 5(a) is a schematic representation of the isolated dimeric units Zr<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>8</sub> which were the basic structural unit of the three compounds Zr(SO<sub>4</sub>)<sub>2</sub>·7H<sub>2</sub>O,  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O and  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O. There are two outstanding features of this unit. One is the bidentate nature of the two terminal sulphate groups; the second is the manner in which the other two groups act as double bridges between the two zirconium atoms to form dimeric rings (Bear & Mumme, 1969*c*). This is a completely different type of structural arrangement than is present in Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O where the layers are composed of a network of singly bridged zirconium atoms (Bear & Mumme, 1969*c*).

A close examination of the structures of the metastable  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and the stable  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O reveals that with the addition of suitable terminal and crosslinking the layers in both compounds are built up of dimeric rings in which, however, the zirconium has sevenfold coordination as distinct from the eightfold coordination found in the Zr(SO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>8</sub> units. Fig. 5(b) illustrates schematically the way zirconium atoms are doubly bridged by sulphate groups to make up a layer of the  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O structure. In fact, each layer of the structure may be regarded as a planar network of three chains of cross-linked dimeric rings. Hydrogen bonding presumably holds the layers to-

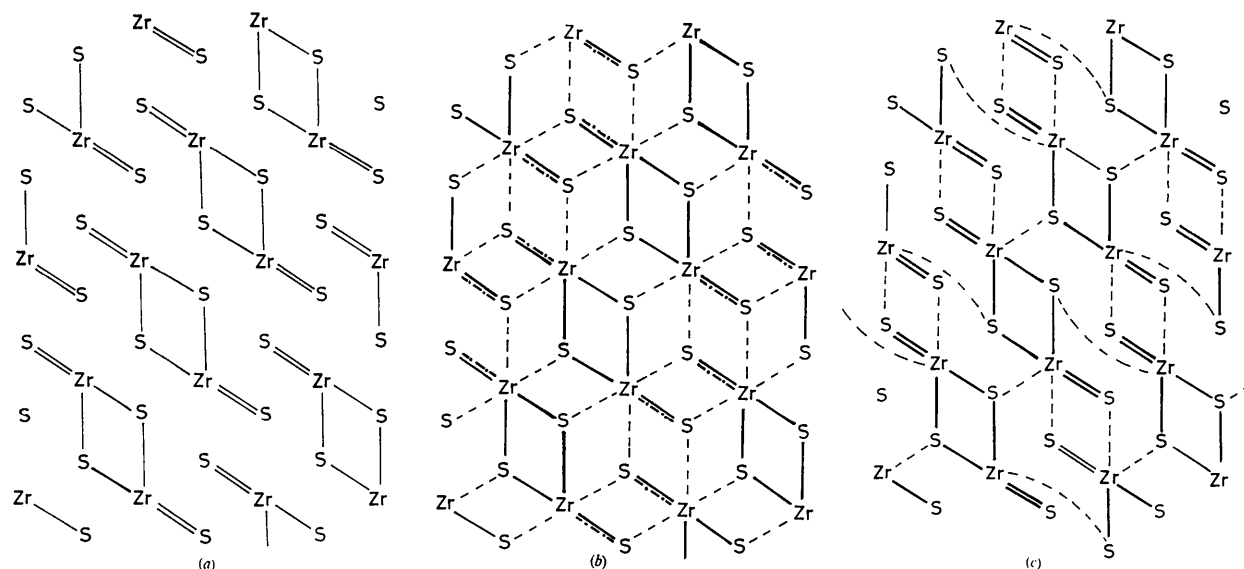


Fig. 5. Schematic representations of the skeletal sulphate lattices of zirconium sulphate-hydrates. Oxygen atoms are omitted but lines joining zirconium and sulphur atoms represent oxygen bridges. (a) An array of isolated dimeric units which are common to the structures of Zr(SO<sub>4</sub>)<sub>2</sub>·7H<sub>2</sub>O and  $\alpha$  and  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O. (b) A layer of  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. (c) A layer of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. Full lines represent original oxygen linkages in the dimers; dots and dashes, broken linkages in the dimers; dashes, new linkages between dimers.

gether (Bear & Mumme, 1970*a*). In  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O [Fig. 5(c)] the dimers are more evident for in building up this structure even the bidentate nature of the terminal sulphate group is retained. Dimeric units are joined end to end to form the chains of dimeric rings already discussed in this paper.

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## The Crystal Chemistry of Zirconium Sulphates.

### VI. The Structure of $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>

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$\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub> is orthorhombic with space group *Pnma* and unit-cell dimensions,  $a=8.61$ ,  $b=5.445$ ,  $c=10.89$  Å and  $Z=4$ . The structure, determined by single-crystal X-ray analysis, consists of a three-dimensional network of sulphate-bridged zirconium atoms. Each zirconium atom is bonded to oxygen atoms of seven sulphate groups giving it sevenfold coordination as previously found for the  $\gamma$ - and  $\alpha$ -zirconium sulphate monohydrates. There are two environments for sulphate tetrahedra: either bonded to four zirconium atoms or bonded to three, leaving one terminal oxygen atom. The structure of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>, which contains the dimeric ring common to all the hydrates of Zr(SO<sub>4</sub>)<sub>2</sub> except Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, shows a close relationship to the structures of the  $\gamma$ - and  $\alpha$ -monohydrates.

### Introduction

Zirconium forms a particularly large number of hydrated and anhydrous sulphates. The present work is directed towards elucidating the crystal chemistry of the so-called 'neutral' salts in which the sulphate-to-zirconium ratio is two. Previous papers in this series have described the crystal structure of hydrates of Zr(SO<sub>4</sub>)<sub>2</sub>. These included the heptahydrate,  $\alpha$  and  $\beta$ -pentahydrates and  $\gamma$  and  $\alpha$ -monohydrates, (Bear & Mumme, 1969*a, b, c*, 1970 *a, b*).

The anhydrous products which result from the dehydration of zirconium sulphate hydrates at temperatures between 250 and 500°C in controlled H<sub>2</sub>SO<sub>4</sub> atmospheres consist of three polymorphs two of which,  $\gamma$  and  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>, are metastable. Formation of the stable  $\alpha$ -form is favoured by high partial pressures of H<sub>2</sub>SO<sub>4</sub> (Bear, 1967, 1969). The metastable anhydrous forms equilibrate to  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub> when heated in a sealed tube at temperatures near 650°C or under high partial pressures of H<sub>2</sub>SO<sub>4</sub> at lower temperatures.

Single crystals of  $\gamma$  and  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub> have not yet been prepared but well shaped tabular or lens-like crystals of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub> can be grown by evaporating solutions of

Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O in strong sulphuric acid at elevated temperatures.

This paper describes the X-ray structure analysis of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub> and discusses its relationship to the structures of the monohydrates.

### Experimental

Microcrystalline  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub> was prepared by decomposing solid Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O in high partial pressures (~1 atm) of H<sub>2</sub>SO<sub>4</sub> at 350°C, (Bear, 1967). X-ray powder diffraction data (Table 1) were collected from this material using a Philips proportional counter diffractometer and Ni filtered Cu *K* $\alpha$  radiation. A special sample holder was fitted to the diffractometer so that dry N<sub>2</sub> gas could be passed over the sample to prevent hydration. The microcrystalline material was also used to measure the density of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub> by displacement in CCl<sub>4</sub>. Unit-cell dimensions and other crystallographic data are given in Table 2.

Single crystals of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub> were obtained by treating one volume of a concentrated solution of Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (1 g.cm<sup>-3</sup>) with two volumes of concentrated H<sub>2</sub>SO<sub>4</sub> and slowly evaporating the resulting