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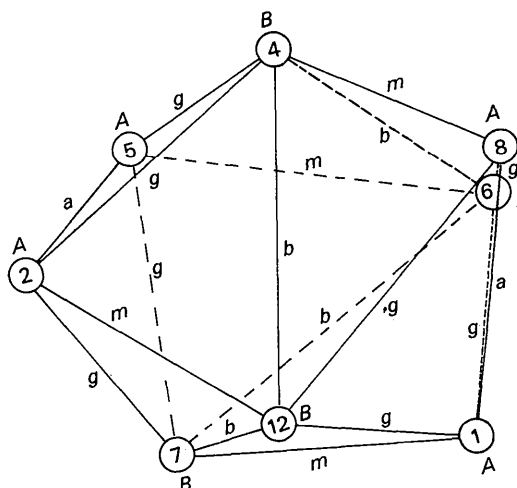


Fig. 5. The coordination of the oxygen atoms around zirconium in $Zr(SO_4)_2 \cdot 7H_2O$. The distances that should be equal, according to the ideal $\bar{4}2m$ symmetry of the $Mo(CN)_4^{4-}$ coordination, are marked according to Hoard & Silverton (1963).

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The Crystal Chemistry of Zirconium Sulphates.

II. The Structure of the α -Pentahydrate, $Zr_2(SO_4)_4(H_2O)_8 \cdot 2H_2O$

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The structure of α - $Zr(SO_4)_2 \cdot 5H_2O$ has been determined by single-crystal X-ray analysis and refined by least-squares. The crystals, which are triclinic with space group $P\bar{1}$, have the unit-cell dimensions $a=11.90$, $b=6.17$, $c=7.57$ Å, $\alpha=106.5^\circ$, $\beta=95.7^\circ$ and $\gamma=104.6^\circ$. The structure of this compound, like that of $Zr(SO_4)_2 \cdot 7H_2O$, contains isolated dimers of composition $Zr_2(SO_4)_4(H_2O)_8$. The Zr-O coordination is again eightfold and the dimeric units are held together by hydrogen bridging through both the coordinated and non-bonded water molecules. In α - $Zr(SO_4)_2 \cdot 5H_2O$, however, there are only two non-bonded water molecules in the unit cell and these lie in sheets parallel to the (101) direction.

Introduction

This is the second paper in a series dealing with chemical-structural aspects of solid phases in the ZrO_2 - SO_3 - H_2O system and in particular with $Zr(SO_4)_2$ -hydrates. Part I (Bear & Mumme, 1969a) described the crystal structure determination of the highest hydrate so far isolated, namely $Zr(SO_4)_2 \cdot 7H_2O$. Its structure, which was shown to be built up from molecular dimers represented by the formula $Zr_2(SO_4)_4(H_2O)_8$, differs markedly from that of the tetrahydrate (Singer &

Cromer, 1959) which is composed of layers of composition $[Zr(SO_4)_2 \cdot 4H_2O]_n$. The present paper describes the structure analysis of one of two pentahydrates in the series, α - $Zr(SO_4)_2 \cdot 5H_2O$ (Bear, 1966), while part III (Bear & Mumme, 1969b), which follows, deals with the other.

Experimental

Microcrystalline α - $Zr(SO_4)_2 \cdot 5H_2O$, free from other hydration products, is readily prepared by allowing a saturated solution of α - $Zr(SO_4)_2$ containing between

eight and eleven moles of water per mole of sulphate to stand at room temperature for several hours (Bear, 1966). However, in order to grow single crystals of the phase it was necessary to use a more dilute solution, approximately twelve moles per mole of sulphate, but under these conditions the surface layers of the large clusters or rosettes of prismatic crystals which grew in about 24 hours were composed of $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$. These crystals were dried over P_2O_5 at approximately 0°C when the $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ decomposed to microcrystalline $\alpha\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ (Bear & Mumme, 1968) but with fragile single crystals of $\alpha\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ in the kernels of the clusters. These were used for the structure analysis. Larger but ill-defined crystals of the phase may also be grown from saturated solutions of γ - and $\beta\text{-Zr}(\text{SO}_4)_2$ at room temperature, when the presence of the more soluble β -pentahydrate (Bear & Lukaszewski, 1966) apparently prevents hydration from proceeding to the heptahydrate stage.

The lattice parameters for $\text{Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ (Table 1) were obtained from X-ray powder diffraction data (Table 2) prior to any single-crystal investigations. The powder data were indexed by Ito's method, reduced by Delaunay's procedure (Azároff & Buerger, 1958) to yield a triclinic unit cell, which was then refined by a least-squares procedure.

As $\alpha\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ decomposes to tetrahydrate in the presence of moisture it was necessary to seal any crystal in a quartz capillary for the collection of X-ray data. It proved quite difficult to get a suitable crystal for recording data however, one was finally obtained

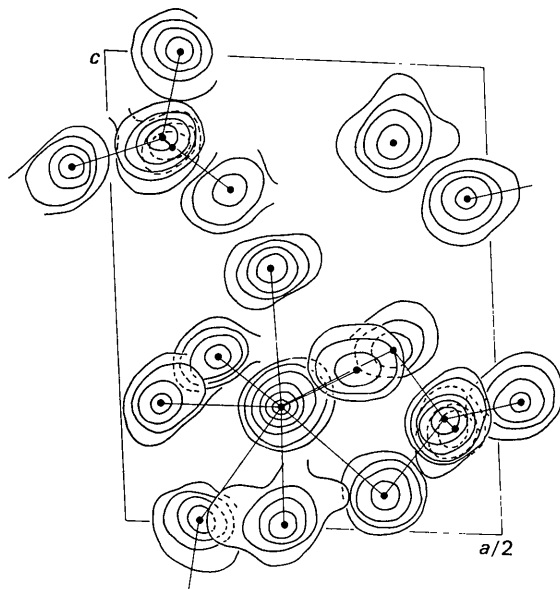


Fig. 1. Composite three-dimensional electron density map selected from sectors near the atom centres, and projected onto (010). The contours are at arbitrary intervals. The small black circles are the atom centres from the least-squares refinement. Bonds are drawn as thin lines.

Table 1. Crystallographic data for $\alpha\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$

Symmetry	Triclinic
Unit-cell dimensions	$a = 11.90 \pm 0.01 \text{ \AA}$ $b = 6.17 \pm 0.01$ $c = 7.57 \pm 0.01$ $\alpha = 106.5^\circ \pm 0.1^\circ$ $\beta = 95.7^\circ \pm 0.1$ $\gamma = 104.6^\circ \pm 0.1$
Possible space groups	$P1$ or $P\bar{1}$
D_x	2.45 g.cm^{-3}
D_m	$2.41 \pm 0.03 \text{ g.cm}^{-3}$
Z	2
μ_c	141 cm^{-1}

for which the values of a^* , b^* , c^* , and β^* measured from the $h0l$ Weissenberg photograph and b axis rotation photograph agreed closely with those previously determined from the powder data.

Integrated Weissenberg data $h0l$ to $h4l$ were recorded about this axis with $\text{Cu } K\alpha_{1,2}$ radiation and multiple-film packs. The crystal measured $0.1 \times 0.02 \times 0.02 \text{ mm}$. Further attempts to obtain data around axes other than this failed, but there was little doubt that this was the b axis of the standard Delaunay cell obtained from the powder data. Measurement of intensities, subsequent data handling, including interlayer scaling procedures, and scattering curves for Zr, S and O atoms were all as described in part I.

Structure determination

The number of formula units, $Z=2$, was calculated from the density measured by displacement in CCl_4 . Of the alternatives $P1$ and $P\bar{1}$ the space group was assumed to be $P\bar{1}$, and this was later confirmed by refinement of the structure.

Parameters for the Zr atom in the general position $2(i)$ were determined from a three-dimensional Patterson map $P(uvw)$. The signs of the structure factors, calculated for these zirconium atom positions, were used with the observed structure factors to calculate a three-dimensional Fourier synthesis, $\rho(xyz)$, from which it was possible to determine the parameters for the S(1) and S(2) atoms, both also in twofold general positions.

In later three-dimensional Fourier syntheses (Fig. 1) the eight oxygen atoms in the sulphate groups were readily located. The disposition of these sulphate groups quickly led to the recognition of a dimeric unit, similar to that in $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$. Once the orientation of the dimer was recognized the locations of the remaining four oxygen atoms completing the dodecahedral coordination of the zirconium atom in the asymmetric unit were readily found, as was a further atom which was obviously that of a non-bonded water molecule.

The presence of only two non-bonded water molecules in the unit cell of the α -pentahydrate, as distinct

from the six found in the heptahydrate, reinforces the arguments used in part I for locating the water molecules in the latter compound. In the present case the assumption that the 16 atoms in the unit cell constituting the sulphur ligands are oxygen atoms, while the remaining eight-bonded atoms completing the coordination of the zirconium atoms, and the two non-bonded atoms, are the oxygen atoms of water molecules,

leads to a structural formula $Zr(SO_4)_2 \cdot 5H_2O$ confirming the earlier chemical evidence (Bear, 1966).

Refinement of the structure was continued with a number of least-squares cycles with isotropic temperature factor for each atom, until R dropped to 13.4% for the 867 observed reflexions. The weighting scheme of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) was used and the matrix inversion involved the block-

Table 2. *X-ray powder diffraction data for α - $Zr(SO_4)_2 \cdot 5H_2O$*

$\text{Sin}^2 \theta_{\text{obs}}$	$\text{Sin}^2 \theta_{\text{calc}}$	<i>hkl</i>	<i>I</i>	$\text{Sin}^2 \theta_{\text{obs}}$	$\text{Sin}^2 \theta_{\text{calc}}$	<i>hkl</i>	<i>I</i>
0.0046	0.0046	100	<i>W</i>	0.0880	0.0881	31 $\bar{2}$	<i>W</i>
0.0117	0.0117	001	<i>VW</i>		0.0880	3 $\bar{1}\bar{2}$	
0.0136	0.0136	10 $\bar{1}$	<i>VS</i>	0.0895	0.0896	120	<i>VW</i>
0.0178	0.0177	1 $\bar{1}\bar{0}$	<i>W</i>	0.0935	0.0932	12 $\bar{2}$	<i>M</i>
					0.0932	3 $\bar{1}\bar{2}$	
0.0186	0.0185	010	<i>M</i>	0.0951	0.0953	01 $\bar{3}$	<i>W</i>
	0.0185	200					
0.0190	0.0190	101	<i>M</i>	0.0992	0.0996	112	<i>VW</i>
0.0207	0.0208	0 $\bar{1}\bar{1}$	<i>VS</i>		0.0992	40 $\bar{2}$	
0.0227	0.0227	1 $\bar{1}\bar{1}$	<i>VW</i>				
0.0263	0.0262	2 $\bar{1}\bar{0}$	<i>VW</i>	0.1016	0.1016	10 $\bar{3}$	<i>W</i>
0.0280	0.0281	1 $\bar{1}\bar{1}$	<i>S</i>		0.1018	21 $\bar{1}$	
0.0286	0.0286	110	<i>S</i>				
0.0357	0.0361	1 $\bar{1}\bar{1}$	<i>VW</i>	0.1048	0.1047	021	
	0.0356	201			0.1050	003	<i>M</i>
					0.1046	302	
					0.1048	4 $\bar{2}\bar{0}$	
0.0397	0.0396	011	<i>M</i>	0.1089	0.1085	21 $\bar{3}$	<i>W</i>
0.0417	0.0419	2 $\bar{1}\bar{1}$	<i>W</i>				
	0.0417	300					
0.0440	0.0439	3 $\bar{1}\bar{0}$	<i>S</i>	0.1241	0.1244	1 $\bar{2}\bar{3}$	<i>VW</i>
0.0468	0.0467	002	<i>S</i>		0.1243	212	
	0.0464	01 $\bar{2}$			0.1245	4 $\bar{2}\bar{1}$	
0.0509	0.0510	11 $\bar{2}$	<i>M</i>	0.1302	0.1300	12 $\bar{3}$	<i>W</i>
	0.0510	1 $\bar{1}\bar{2}$					
0.0525	0.0524	111	<i>M</i>	0.1356	0.1356	2 $\bar{2}\bar{3}$	
					0.1354	4 $\bar{2}\bar{2}$	<i>VW</i>
					0.1355	502	
					0.1356	5 $\bar{2}\bar{0}$	
0.0543	0.0543	3 $\bar{1}\bar{1}$	<i>W</i>	0.1462	0.1466	22 $\bar{3}$	<i>W</i>
	0.0544	20 $\bar{2}$			0.1464	411	
0.0571	0.0567	10 $\bar{2}$	<i>W</i>	0.1512	0.1514	3 $\bar{2}\bar{2}$	<i>W</i>
	0.0569	3 $\bar{1}\bar{1}$			0.1510	3 $\bar{3}\bar{1}$	
0.0615	0.0615	301	<i>VW</i>	0.1526	0.1527	2 $\bar{3}\bar{0}$	
0.0668	0.0669	02 $\bar{1}$	<i>M</i>		0.1529	3 $\bar{1}\bar{3}$	<i>M</i>
0.0711	0.0709	2 $\bar{2}\bar{0}$			0.1526	5 $\bar{2}\bar{1}$	
	0.0707	31 $\bar{1}$	<i>M</i>		0.1527	6 $\bar{1}\bar{0}$	
	0.0709	4 $\bar{1}\bar{0}$					
0.0742	0.0741	020		0.1560	0.1560	3 $\bar{2}\bar{3}$	<i>W</i>
	0.0745	211	<i>VW</i>	0.1658	0.1659	3 $\bar{3}\bar{2}$	<i>W</i>
	0.0741	400					
0.0747	0.0745	211	<i>W</i>	0.1668	0.1668	030	
	0.0750	40 $\bar{1}$			0.1668	11 $\bar{4}$	<i>W</i>
					0.1668	600	
0.0812	0.0809	2 $\bar{1}\bar{2}$	<i>W</i>				
	0.0812	4 $\bar{1}\bar{1}$		0.1679	0.1675	01 $\bar{4}$	<i>W</i>
					0.1675	4 $\bar{2}\bar{2}$	
0.0843	0.0841	012	<i>M</i>	0.1800	0.1801	4 $\bar{1}\bar{3}$	<i>W</i>
	0.0841	3 $\bar{2}\bar{1}$			0.1803	50 $\bar{3}$	
	0.0840	4 $\bar{1}\bar{1}$					

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 and the bond lengths in Table 5.

Description

The structure of α-Zr(SO4)2·5H2O, viewed in projection, is shown in Fig. 2. For convenience, the origin in this diagram has been moved to (1/2, 0, 0) and the structure is referred to the axes [001̄] and [101]. By doing this it is possible to compare it readily with the structure of Zr(SO4)2·7H2O (Fig. 3, part I).

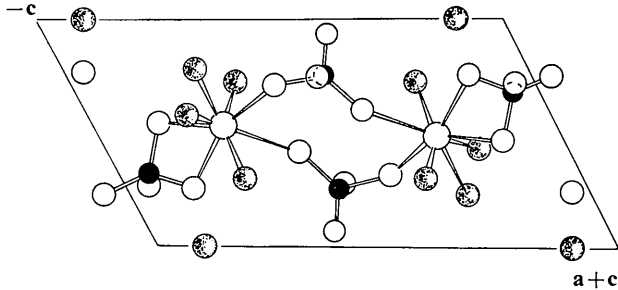


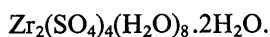
Fig. 2. The structure of α-Zr(SO4)2·5H2O projected onto (010). Large open circles, zirconium atoms; Full black circles, sulphur atoms; Medium open circles, oxygen atoms; Stippled circles, water molecules. The solitary free water molecule in the asymmetric unit appears to lie on the axis [101].

In α-Zr(SO4)2·5H2O, the zirconium atoms have dodecahedral coordination. The main structural unit is the same as that in Zr(SO4)2·7H2O, and consists of two zirconium polyhedra and four tetrahedral sulphate groups forming the dimeric group with composition Zr2(SO4)4(H2O)8. Each zirconium dodecahedron contains four bonded water molecules while the remaining two non-bonded water molecules in the unit cell lie in

Table 3. Observed and calculated structure factors on an absolute scale

Table with multiple columns labeled H, K, L, F0, Fc, H, K, L, F0, Fc, H, K, L, F0, Fc, H, K, L, F0, Fc, H, K, L, F0, Fc, H, K, L, F0, Fc, H, K, L, F0, Fc. Each column contains numerical values for structure factors.

sheets parallel to the [101] direction. The formula of the compound is therefore best expressed as



Following Hoard & Silverton (1963) the interatomic distances in the ZrO_6 dodecahedron are divided into the six groups that should be equal according to the ideal $4\bar{2}m$ symmetry. These groups $M-A$, $M-B$, a , b , g and m are given in Table 5 (cf. Fig. 3) and their averages are compared with those found in $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$. The sulphate groups (Table 5) are distorted from the ideal tetrahedral symmetry as in the heptahydrate, the maximum and minimum values for S-O distances being 1.52 and 1.42 Å and for the O-S-O angle, 113° and 101°. The mean bond length and angle are 1.48 and 109.5° just as in the case of the heptahydrate.

From Figs. 2 and 3 of part I it is apparent that transformations between the α -pentahydrate and the heptahydrate are accompanied by only a slight alteration in shape of the dimeric groups and the gain or loss of two non-bonded water molecules.

Again, as in $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$, it is the hydrogen bonding (Table 5), in this case corresponding to the three general directions [101], [010] and [001], which provides the cohesion of the compound. The probable scheme is shown in Fig. 4, and it should be noted that in this case much of the lateral hydrogen bonding between adjacent dimers is through bonded oxygen atoms and water molecules. In fact none of the hydrogen bonding through the free water molecule is essential to the stability of the α -pentahydrate as was the case for $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$. The bond from O(W13) to O(8) and O(9) is in all probability a bifurcated one. This means that the hydrogen atom has the coordination number three and takes up the position between the two acceptor oxygen atoms, O(8) and O(9), which is electrostatically most favourable. Hydrogen atoms forming bifurcated bonds have been reported for a number of hydrates and have been discussed by Baur (1965). The coordination of the free water molecule, O(W13), assuming a resultant direction for this bifurcated bond,

approximates to a flattened tetrahedron, which may account for the observation that it is quite strongly bound into the structure.

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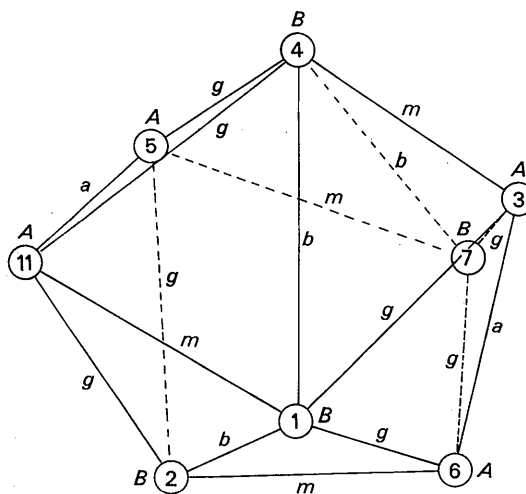


Fig. 3. Coordination of the oxygen atoms around the zirconium atom in α - $\text{Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$. The distances that should be equal, according to the ideal $4\bar{2}m$ symmetry of the $\text{Mo}(\text{CN})_6^{3-}$ coordination, are marked according to Hoard & Silverton (1963).

Table 4. Fractional atomic parameters and temperature factors

Space group $P\bar{1}$. All atoms in point position $2(i)$, $\pm(x, y, z)$.

	x	y	z	B
Zr(1)	0.2062 (2)	0.1704 (5)	0.2519 (3)	0.71 (4) Å ²
S(1)	0.4234 (6)	0.0654 (14)	0.2440 (10)	1.0 (0.1)
S(2)	0.0710 (6)	0.7406 (15)	0.8102 (10)	1.1 (0.1)
O(W1)	0.1274 (22)	0.8575 (45)	0.3391 (33)	2.4 (0.5)
O(2)	0.0544 (21)	0.2734 (43)	0.2675 (32)	2.2 (0.5)
O(3)	0.3576 (18)	0.1072 (38)	0.4020 (28)	1.2 (0.4)
O(4)	0.3406 (19)	0.0843 (39)	0.0909 (29)	1.5 (0.4)
O(W5)	0.2092 (21)	0.3442 (42)	0.0333 (32)	2.3 (0.5)
O(W6)	0.2027 (23)	0.3096 (45)	0.5566 (35)	2.7 (0.5)
O(W7)	0.3279 (24)	0.5239 (49)	0.3570 (37)	3.4 (0.6)
O(8)	0.4386 (24)	0.8203 (47)	0.1940 (36)	3.0 (0.6)
O(9)	0.4622 (17)	0.7663 (36)	0.7183 (26)	1.1 (0.4)
O(10)	0.1540 (22)	0.8436 (45)	0.7046 (34)	2.5 (0.5)
O(11)	0.0946 (17)	0.8862 (36)	0.0084 (26)	0.9 (0.4)
O(12)	0.0726 (21)	0.5032 (44)	0.7964 (32)	2.3 (0.5)
O(W13)	0.3766 (20)	0.3814 (42)	0.8335 (30)	1.8 (0.4)

Table 5. *Interatomic distances (Å) and angles (°)*

M-A, *M-B*, *a*, *b*, *g* and *m* are the six groups of interatomic distances that should be equal according to the ideal $\bar{4}2m$ symmetry of $\text{Mo}(\text{CN})_8^{4-}$ coordination. Their averages are compared with those previously found for $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$.

(a) Within the ZrO_8 polyhedra

	<i>M-A</i>		<i>M-B</i>
Zr-O(3)	2.21 (2)	Zr-O(W1)	2.23 (3)
O(W5)	2.21 (3)	O(2)	2.06 (3)
O(W6)	2.23 (3)	O(4)	2.18 (2)
O(11)	2.18 (2)	O(W7)	2.16 (3)
Average	2.20	Average	2.16
Average for $\text{Zr}_2(\text{SO}_4)_4(\text{H}_2\text{O})_8 \cdot 6\text{H}_2\text{O}$	2.23	Average for $\text{Zr}_2(\text{SO}_4)_4(\text{H}_2\text{O})_8 \cdot 6\text{H}_2\text{O}$	2.19

	<i>a</i>		<i>m</i>
O(3)—O(W6)	2.66 (3)	O(W1)—O(11)	2.55 (3)
O(W5)—O(11)	2.76 (3)	O(2)—O(W6)	2.59 (4)
		O(3)—O(4)	2.30 (3)
		O(W5)—O(W7)	2.49 (4)
Average	2.71	Average	2.48
Average for $\text{Zr}_2(\text{SO}_4)_4(\text{H}_2\text{O})_8 \cdot 6\text{H}_2\text{O}$	2.76	Average for $\text{Zr}_2(\text{SO}_4)_4(\text{H}_2\text{O})_8 \cdot 6\text{H}_2\text{O}$	2.52

	<i>g</i>		<i>b</i>
O(W1)—O(W6)	2.67 (4)	O(W1)—O(2)	3.08 (4)
O(W1)—O(3)	2.70 (3)	O(W1)—O(4)	3.54 (3)
O(2)—O(W5)	2.72 (4)	O(2)—O(W7)	3.14 (4)
O(2)—O(11)	2.81 (3)	O(4)—O(W7)	2.93 (4)
O(3)—O(W7)	2.79 (4)		
O(4)—O(W5)	2.59 (3)		
O(4)—O(11)	2.80 (3)		
Average	2.71	Average	3.18
Average for $\text{Zr}_2(\text{SO}_4)_4(\text{H}_2\text{O})_8 \cdot 6\text{H}_2\text{O}$	2.78	Average for $\text{Zr}_2(\text{SO}_4)_4(\text{H}_2\text{O})_8 \cdot 6\text{H}_2\text{O}$	3.21

(b) Within sulphate groups

S(1)—O(3)	1.49 (2)	S(2)—O(2)	1.52 (3)
O(4)	1.49 (2)	O(10)	1.46 (3)
O(8)	1.52 (3)	O(11)	1.47 (2)
O(9)	1.44 (2)	O(12)	1.44 (3)
Average	1.48	Average	1.48
O(3)—S(1)—O(4)	101.0 ± 1.5	O(2)—S(2)—O(11)	105.6 ± 1.5
O(3)—S(1)—O(9)	113.4 ± 1.5	O(2)—S(2)—O(12)	107.4 ± 1.5
O(3)—S(1)—O(8)	110.8 ± 1.5	O(2)—S(2)—O(10)	110.4 ± 1.5
O(4)—S(1)—O(9)	112.5 ± 1.5	O(12)—S(2)—O(11)	109.7 ± 1.5
O(4)—S(1)—O(8)	110.7 ± 1.5	O(12)—S(2)—O(10)	111.3 ± 1.5
O(8)—S(1)—O(9)	108.3 ± 1.5	O(10)—S(2)—O(11)	112.3 ± 1.5
Average	109.5	Average	109.4

(c) Hydrogen bonds

(1) Along [101]			
O(W7)—O(9)	2.80 (3)		
O(W6)—O(W13)	2.65 (3)		
(2) Along [010]			
O(W1)—O(12)	2.68 (3)		
O(W5)—O(12)	2.84 (3)		
O(W7)—O(8)	2.64 (3)		
(3) Along [001]			
O(12)—O(W6)	2.71 (3)		
O(10)—O(W1)	2.78 (3)		
O(W13)—O(W5)	2.62 (3)		
O(W13)—O(4)	3.02 (3)		
O(W13)—O(9)	2.75 (3)	} Bifurcated bond	
O(8)	2.78 (3)		

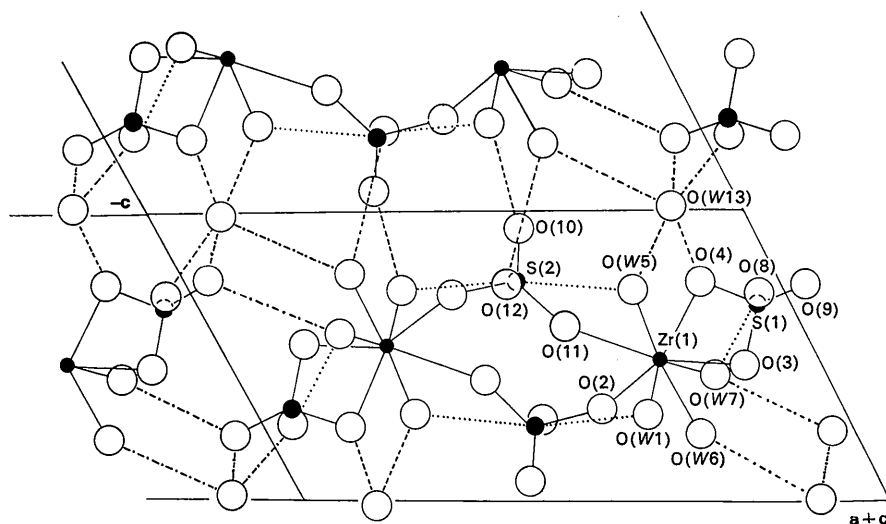


Fig. 4. Schematic projection on to (010) illustrating the possible hydrogen bonding scheme. Atoms are numbered according to Table 4. Small full black circles, zirconium atoms; Medium full black (and cross hatched) circles, sulphur atoms; Large open circles, oxygen atoms and water molecules. Dots and dashes represent bonding between ends of dimers: dashes represent bonding between dimers; dots represent bonding between overlying and underlying dimers.

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The Crystal Chemistry of Zirconium Sulphates. III. The Structure of the β -Pentahydrate, $Zr_2(SO_4)_4(H_2O)_8 \cdot 2H_2O$, and the Inter-relationship of the Four Higher Hydrates

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The structure of β - $Zr(SO_4)_2 \cdot 5H_2O$ has been determined by single-crystal X-ray analysis. It is triclinic with space group $P\bar{1}$, and the dimensions of the primitive unit cell are $a=8.55$, $b=7.60$, $c=7.71$ Å, $\alpha=101.4^\circ$, $\beta=98.6^\circ$, $\gamma=89.9^\circ$. The structure is similar to those of $Zr(SO_4)_2 \cdot 7H_2O$ and α - $Zr(SO_4)_2 \cdot 5H_2O$, being built up of isolated dimers of composition $Zr_2(SO_4)_4(H_2O)_8$. These dimeric units are held together by hydrogen bridging through both the coordinated and non-bonded water molecules. β - $Zr(SO_4)_2 \cdot 5H_2O$ is a closer-packed version of α - $Zr(SO_4)_2 \cdot 5H_2O$, with the free water molecules taking up a different disposition with respect to the dimeric groups. The dimeric group itself, when compared with those of $Zr(SO_4)_2 \cdot 7H_2O$ and α - $Zr(SO_4)_2 \cdot 5H_2O$ is seen to have undergone some distortion.

Chemico-structural relationships between the three dimeric sulphates, $Zr(SO_4)_2 \cdot 7H_2O$, α - $Zr(SO_4)_2 \cdot 5H_2O$ and β - $Zr(SO_4)_2 \cdot 5H_2O$, and the tetrahydrate are discussed.

Introduction

Several forms of anhydrous $Zr(SO_4)_2$ can be prepared by thermal decomposition of $Zr(SO_4)_2 \cdot 4H_2O$ in atmospheres of controlled sulphuric acid vapour pressure (Bear, 1967). Two of these forms, β - and γ - $Zr(SO_4)_2$, are metastable and equilibrate to α - $Zr(SO_4)_2$ under suitable conditions. On hydration the latter

phase yields the dimeric α - $Zr(SO_4)_2 \cdot 5H_2O$ described in part II (Bear & Mumme, 1969*b*), while γ - and β - $Zr(SO_4)_2$ both yield a second form of the pentahydrate β - $Zr(SO_4)_2 \cdot 5H_2O$ (Bear & Lukaszewski, 1966), the structure of which is described in this paper.

With the latter work we have completed structural analyses of the three highest hydrates of $Zr(SO_4)_2$ that have so far been isolated, namely, $Zr(SO_4)_2 \cdot 7H_2O$