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The Crystal Chemistry of Zirconium Sulphates.

I. The Structure of the Heptahydrate, a Dimer with the Formula $Zr_2(SO_4)_4(H_2O)_8 \cdot 6H_2O$

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Zirconium sulphate heptahydrate is triclinic with space group $P\bar{1}$ and unit-cell dimensions $a=12.04$, $b=6.36$, $c=8.28$ Å, $\alpha=93.0^\circ$, $\beta=92.4^\circ$, $\gamma=95.9^\circ$. The structure has been determined by single-crystal X-ray analysis and refined by least-squares. The main structural unit consists of isolated dimers having the formula $Zr_2(SO_4)_4(H_2O)_8$. Each zirconium atom has eightfold coordination in the form of a dodecahedron with four oxygen atoms from neighbouring sulphate groups and four water molecules. The polyhedra are bridged by two sulphate tetrahedra, two more sulphate groups acting as terminal members. The dimers are held together in three directions by hydrogen bridging through the water molecules, those forming part of the zirconium coordination together with six additional unbonded molecules which lie in sheets parallel to the (001) plane.

Introduction

There is abundant evidence in the literature to show that zirconium in the presence of sulphuric acid can form an unexpectedly large group of compounds (Blumenthal, 1958; Clearfield, 1964). Besides the so-called 'neutral' salts in which the sulphate to zirconium ratio is 2, a number of phases in which the sulphate-zirconium ratio is both greater and less than 2 have been isolated. Although considerable chemical data concerning these compounds have accumulated, there is little real understanding of the reason for this multiplicity of phase formation or of their behaviour in solution. There is also little reliable information available concerning their structures (Clearfield, 1964).

Structures have been reported for $Zr(SO_4)_2 \cdot 4H_2O$, the stable 'neutral' phase under ambient conditions (Singer & Cromer, 1959), and for three basic sulphates $Zr_2(OH)_2(SO_4)_3(H_2O)_4$ and $Zr(OH)_2SO_4$ I and II (McWhan & Lundgren, 1966). $Zr(OH)_2SO_4$ I is isomorphous with the corresponding thorium and uranium salts (Lundgren, 1950, 1952). In these four compounds Zr is present in eightfold coordination. For $Zr(SO_4)_2 \cdot 4H_2O$ and $Zr(OH)_2SO_4$ I the Zr-O coordination is in the form of a square antiprism while in $Zr_2(OH)_2(SO_4)_3(H_2O)_4$ it is a dodecahedron. $Zr(SO_4)_2 \cdot 4H_2O$ is composed of layers of composition $Zr(SO_4)_2 \cdot 4H_2O$ held together by hydrogen bonds. $Zr(OH)_2(SO_4)_3(H_2O)_4$ is built up of sheets of zirconium

and sulphate ions and the zirconium ions of adjacent sheets are connected by double hydroxide bridges.

The $Zr(SO_4)_2$ -hydrate system contains a number of unusual compounds. Several anhydrous forms, a number of lower hydrates, two pentahydrates and a heptahydrate have so far been isolated (Bear, 1966; Bear & Lukaszewski, 1966; Bear, 1967; Bear & Mumme, 1968), in addition to the well known tetrahydrate (Blumenthal, 1958). These compounds, however, do not form a normal series of hydrates, as an increasing degree of hydration cannot be attained by progressively increasing the water vapour pressure over an anhydrous sample at a suitable temperature. For example a zirconium sulphate monohydrate, formed during thermal decomposition of the solid tetrahydrate, could not be prepared by vapour hydration of α - $Zr(SO_4)_2$ (Bear, 1967) while the pentahydrates and the heptahydrate all have lower saturated solution vapour pressures and higher solubilities than the tetrahydrate, and so cannot be formed by vapour phase hydration of the latter compound (Bear & Mumme, 1968).

Parts I to III of this series of papers will describe the structures of $Zr(SO_4)_2 \cdot 7H_2O$, α - $Zr(SO_4)_2 \cdot 5H_2O$ and β - $Zr(SO_4)_2 \cdot 5H_2O$ while the lower hydrates and the anhydrous phases will be reported by us in subsequent papers. A discussion of the chemical and structural relationships between the three highest hydrates and $Zr(SO_4)_2 \cdot 4H_2O$ will be included in part III.

Experimental

Well formed prismatic crystals of $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$, some more than 0.5 mm in length, were grown from saturated solutions of either α or β - $\text{Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ at temperatures near 0°C. At these temperatures the crystals are stable in contact with their saturated solution, but decompose if dried at low water vapour pressures. This made chemical analysis of the compound difficult, as samples, whether prepared by vapour hydration of β - $\text{Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ (Bear & Mumme, 1968) or by crystallization from solution, could only be dried in atmospheres with the partial pressure of water vapour, $P(\text{H}_2\text{O})$, just below that of the saturated solution. The water content of preparations dried to constant weight over H_2SO_4 solutions (35–38% w/w) varied by as much as $\pm 0.5\%$, so that compositions ranged between 7.0 and 7.5 moles of water per mole of sulphate. As it was not known whether results tended to be low because of slight decomposition, or high because of inefficient drying, the compound was tentatively considered to have the formula $\text{Zr}(\text{SO}_4)_2 \cdot 7.5\text{H}_2\text{O}$.

For the same reasons the density of the phase could not be obtained by the displacement method, and it was necessary to resort to washing single crystals in benzene and rapidly determining their density by equilibrium flotation in benzene–methylene iodide mixtures. The movement of the crystals in the solution was viewed through an enlarging lens. The average value for a number of experiments was 2.25 g.cm^{-3} but, inevitably, the procedure led to a greater deviation from average than would normally be expected. It should

be noted that any decomposition during measurement would be likely to give a high result.

Because of the instability of the compound it was necessary to take special precautions during collection of the X-ray data. The lattice parameters (Table 1) for $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ were obtained by least-squares refinement of X-ray powder diffraction data (Table 2) collected by slow scanning slightly damp samples, at reduced temperatures, by the use of a Philips proportional-counter diffractometer with a Ni-filter and $\text{Cu } K\alpha_{1,2}$ radiation. Silicon metal powder was used as an internal calibrant. A special sample cover permitted refrigerated nitrogen gas to be blown over the sample continuously during scanning.

Table 1. Crystallographic data for $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$

Symmetry	Triclinic
Unit-cell dimensions (0°C)	$a = 12.04 \pm 0.01 \text{ \AA}$
	$b = 6.36 \pm 0.01$
	$c = 8.28 \pm 0.01$
	$\alpha = 93.0^\circ \pm 0.1^\circ$
	$\beta = 92.4^\circ \pm 0.1^\circ$
	$\gamma = 95.9^\circ \pm 0.1^\circ$
Possible space groups	$P1$ or $P\bar{1}$
D_x	2.16 g.cm^{-3}
D_m	$2.25 \pm 0.1 \text{ g.cm}^{-3}$
Z	2
μ_c	117 cm^{-1}

Integrated Weissenberg intensity data $h0l$ to $h4l$, and $hk0$ were recorded with $\text{Cu } K\alpha$ radiation and multiple film packs, from crystals all measuring approximately $0.1 \times 0.02 \times 0.02 \text{ mm}$, each sealed in a capillary while still wet with mother liquor. Cooling to about -70°C was readily achieved with a Nonius low temperature attachment (Kreuger, 1955) and N_2 gas which was passed through a copper helix immersed in liquid oxygen.

Although the cooling device worked efficiently, there was a considerable problem involved in keeping sufficient liquid oxygen on hand while data were collected. In fact it was possible to collect only one level of data from a particular crystal, and although we tried to use crystals of the same size each time, there was an inevitable variation in their dimensions.

Intensities were measured visually with a standard scale, and the reduction to structure amplitudes, and all subsequent computing was done on the Division's Elliott 803 computer with the use of the computing system devised by Daly, Stephens & Wheatley (1963).

Interlayer scaling for the five levels of data was adjusted after each least-squares refinement cycle, and this scaled observed data and the structure amplitudes calculated from the final model are listed in Table 3. Scattering curves for the atoms Zr^{4+} (corrected for anomalous dispersion, and the presence of 2.0% Hf) and S were taken from Tables compiled by Cromer & Waber (1965). The scattering curve for the O^{2-} ion was that of Suzuki (1960).

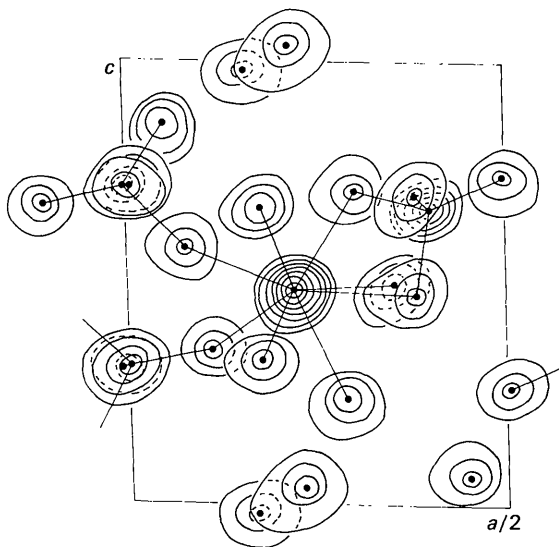


Fig. 1. Composite three-dimensional electron density map selected from sections nearest the atom centres and projected on to (010). The contours are at arbitrary intervals. The small black circles are the atom centres from the least-squares refinement. Bonds are drawn as thin lines.

Structure determination

The *b* (and *c*) axis Weissenberg photographs showed that $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ was triclinic, $P1$ or $P\bar{1}$, and from the measured density, $D_m = 2.25 \text{ g.cm}^{-3}$, the number of formula units per cell was calculated to be 2. The space group was assumed to be $P\bar{1}$, and this was confirmed by the satisfactory refinement of the structure. A set of parameters for Zr atom in the general position $2(i)$

was determined from the three-dimensional Patterson function, and 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, $\rho(x, y, z)$. From this it was possible to determine the parameters for the S(1) and S(2) atoms, while later three-dimensional Fourier syntheses revealed the positions of the 30 oxygen atoms, all of which were in the general positions $2(i)$ (Fig. 1).

Table 2. X-ray powder diffraction data for $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$

$\sin^2 \theta_{\text{obs}}$	$\sin^2 \theta_{\text{calc}}$	<i>hkl</i>	<i>I</i>	$\sin^2 \theta_{\text{obs}}$	$\sin^2 \theta_{\text{calc}}$	<i>hkl</i>	<i>I</i>
0.0041	0.0041	100	<i>M</i>	0.0954	0.0954	12 $\bar{2}$	<i>W</i>
0.0087	0.0087	001	<i>VS</i>		0.0950	221	
0.0122	0.0123	10 $\bar{1}$	<i>VW</i>				
0.0149	0.0149	010	<i>VW</i>	0.0974	0.0977	1 $\bar{1}$ 3	<i>VW</i>
0.0166	0.0166	200	<i>M</i>		0.0969	013	
0.0175	0.0174	1 $\bar{1}$ 0	<i>W</i>		0.0978	312	
0.0224	0.0223	01 $\bar{1}$	<i>M</i>				
0.0242	0.0241	201	<i>S</i>	0.1035	0.1036	500	<i>M</i>
0.0255	0.0253	1 $\bar{1}$ 1	<i>W</i>				
0.0283	0.0281	2 $\bar{1}$ 0	<i>M</i>	0.1059	0.1060	2 $\bar{1}$ 3	<i>W</i>
					0.1057	213	
0.0348	0.0348	002	<i>W</i>		0.1056	402	
	0.0347	210					
				0.1095	0.1094	50 $\bar{1}$	<i>W</i>
0.0373	0.0373	300			0.1100	22 $\bar{2}$	
	0.0370	2 $\bar{1}$ 1	<i>M</i>				
	0.0378	10 $\bar{2}$		0.1152	0.1151	501	<i>W</i>
					0.1154	41 $\bar{2}$	
0.0443	0.0443	30 $\bar{1}$	<i>M</i>				
0.0459	0.0458	211	<i>S</i>	0.1206	0.1205	3 $\bar{1}$ 1	<i>W</i>
					0.1210	42 $\bar{1}$	
0.0473	0.0472	3 $\bar{1}$ 0			0.1202	213	
	0.0471	01 $\bar{2}$	<i>M</i>		0.1206	303	
	0.0477	301					
				0.1264	0.1267	3 $\bar{1}$ 3	<i>W</i>
0.0491	0.0491	2 $\bar{0}$ 2	<i>S</i>		0.1264	313	
					0.1267	510	
0.0537	0.0536	1 $\bar{1}$ 2	<i>W</i>				
	0.0536	202		0.1299	0.1300	02 $\bar{3}$	<i>VW</i>
					0.1296	412	
0.0559	0.0563	3 $\bar{1}$ 1	<i>M</i>				
	0.0555	3 $\bar{1}$ 1		0.1330	0.1327	502	<i>W</i>
					0.1326	1 $\bar{2}$ 3	
0.0572	0.0571	310	<i>W</i>		0.1330	130	
					0.1329	32 $\bar{2}$	
0.0594	0.0595	020	<i>VW</i>		0.1327	50 $\bar{2}$	
	0.0591	112					
				0.1392	0.1391	004	<i>W</i>
0.0663	0.0663	400	<i>W</i>		0.1389	420	
					0.1395	511	
0.0688	0.0686	30 $\bar{2}$	<i>W</i>				
	0.0688	311		0.1426	0.1429	130	<i>W</i>
					0.1428	42 $\bar{1}$	
0.0747	0.0746	4 $\bar{1}$ 0	<i>W</i>				
	0.0743	212		0.1483	0.1481	3 $\bar{1}$ 2	<i>M</i>
					0.1479	422	
0.0754	0.0755	302	<i>M</i>		0.1488	01 $\bar{4}$	
0.0830	0.0828	3 $\bar{1}$ 2	<i>VW</i>	0.1507	0.1511	20 $\bar{4}$	<i>M</i>
	0.0826	220					
				0.1528	0.1524	11 $\bar{4}$	<i>M</i>
0.0845	0.0843	4 $\bar{1}$ 1	<i>VW</i>		0.1525	421	
	0.0841	103			0.1532	521	
0.0878	0.0876	22 $\bar{1}$	<i>VW</i>	0.1562	0.1558	4 $\bar{1}$ 3	<i>W</i>
	0.0877	410			0.1563	330	
					0.1560	131	
0.0928	0.0929	41 $\bar{1}$	<i>VW</i>				

The main problem in determining the structure arose from the uncertainty of composition. On the initial assumption that the composition was $Zr(SO_4)_2 \cdot 7.5H_2O$ there had to be one oxygen atom in a single-fold position (assuming PT), but two other possibilities of composition $Zr(SO_4)_2 \cdot 7H_2O$ and $Zr(SO_4)_2 \cdot 8H_2O$ were also kept in mind.

The arrangement of the oxygen atoms in the sulphate groups was quickly determined. However, inter-

layer scaling errors doubtless caused by the use of many different crystals in data collection, manifested themselves in spurious peaks close to the zirconium atom in projection, of comparable height to the oxygen atom peaks and at reasonable bond distances above and below it. This, coupled with the uncertainty of composition, made the determination of the oxygen coordination around the zirconium atom a lengthy and complicated procedure. To this end the data $hk0$ were col-

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

H	K	L	F _o	F _c	H	K	L	F _o	F _c	H	K	L	F _o	F _c	H	K	L	F _o	F _c
0	0	0	1251	-1277	8	0	0	0	0	7	0	0	1353	1369	11	0	0	1071	-1086
0	0	1	251	189	0	0	0	1	0	0	0	1	1071	1071	0	0	1	712	-725
0	0	2	377	289	0	0	0	2	0	0	0	2	1942	1942	0	0	2	1425	-1477
0	0	3	1019	853	0	0	0	3	0	0	0	3	2897	2897	0	0	3	2115	-2203
0	0	4	1929	1593	0	0	0	4	0	0	0	4	4316	4316	0	0	4	3197	-3345
0	0	5	2655	2159	0	0	0	5	0	0	0	5	5711	5711	0	0	5	4247	-4465
0	0	6	3219	2619	0	0	0	6	0	0	0	6	6984	6984	0	0	6	5167	-5417
0	0	7	3681	2979	0	0	0	7	0	0	0	7	8145	8145	0	0	7	5977	-6267
0	0	8	3957	3159	0	0	0	8	0	0	0	8	9196	9196	0	0	8	6687	-6997
0	0	9	4089	3219	0	0	0	9	0	0	0	9	10147	10147	0	0	9	7307	-7627
0	0	10	4105	3219	0	0	0	10	0	0	0	10	11000	11000	0	0	10	7827	-8147
0	0	11	4005	3089	0	0	0	11	0	0	0	11	11763	11763	0	0	11	8247	-8567
0	0	12	3705	2759	0	0	0	12	0	0	0	12	12436	12436	0	0	12	8567	-8887
0	0	13	3219	2219	0	0	0	13	0	0	0	13	12920	12920	0	0	13	8787	-9127
0	0	14	2579	1579	0	0	0	14	0	0	0	14	13225	13225	0	0	14	8907	-9267
0	0	15	1819	939	0	0	0	15	0	0	0	15	13450	13450	0	0	15	8927	-9307
0	1	0	1071	1071	0	1	0	1071	1071	0	1	0	1071	1071	0	1	0	1071	1071
0	1	1	1942	1942	0	1	1	1942	1942	0	1	1	1942	1942	0	1	1	1942	1942
0	1	2	2897	2897	0	1	2	2897	2897	0	1	2	2897	2897	0	1	2	2897	2897
0	1	3	4316	4316	0	1	3	4316	4316	0	1	3	4316	4316	0	1	3	4316	4316
0	1	4	5711	5711	0	1	4	5711	5711	0	1	4	5711	5711	0	1	4	5711	5711
0	1	5	6984	6984	0	1	5	6984	6984	0	1	5	6984	6984	0	1	5	6984	6984
0	1	6	8145	8145	0	1	6	8145	8145	0	1	6	8145	8145	0	1	6	8145	8145
0	1	7	9196	9196	0	1	7	9196	9196	0	1	7	9196	9196	0	1	7	9196	9196
0	1	8	10147	10147	0	1	8	10147	10147	0	1	8	10147	10147	0	1	8	10147	10147
0	1	9	11000	11000	0	1	9	11000	11000	0	1	9	11000	11000	0	1	9	11000	11000
0	1	10	11763	11763	0	1	10	11763	11763	0	1	10	11763	11763	0	1	10	11763	11763
0	1	11	12436	12436	0	1	11	12436	12436	0	1	11	12436	12436	0	1	11	12436	12436
0	1	12	12920	12920	0	1	12	12920	12920	0	1	12	12920	12920	0	1	12	12920	12920
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0	4	0	1071	1071	0	4	0	1071	1071	0	4	0	1071	1071	0	4	0	1071	1071
0	4	1	1942	1942	0	4	1	1942	1942	0	4	1	1942	1942	0	4	1	1942	1942
0	4	2	2897	2897	0	4	2	2897	2897	0	4	2	2897	2897	0	4	2	2897	2897
0	4	3	4316	4316	0	4	3	4316	4316	0	4	3	4316	4316	0	4	3	4316	4316
0	4	4	5711	5711	0	4	4	5711	5711	0	4	4	5711	5711	0	4	4	5711	5711
0	4	5	6984	6984	0	4	5	6984	6984	0	4	5	6984	6984	0	4	5	6984	6984
0	4	6	8145	8145	0	4	6	8145	8145	0	4	6	8145	8145	0	4	6	8145	8145
0	4	7	9196	9196	0	4	7	9196	9196	0	4	7	9196	9196	0	4	7	9196	9196
0	4	8	10147	10147	0	4	8	10147	10147	0	4	8	10147	10147	0	4	8	10147	10147
0	4	9	11000	11000	0	4	9	11000	11000	0	4	9	11000	11000	0	4	9	11000	11000
0	4	10	11763	11763	0	4	10	11763	11763	0	4	10	11763	11763	0	4	10	11763	11763
0	4	11	12436	12436	0	4	11	12436	12436	0	4	11	12436	12436	0	4	11	12436	12436
0	4	12	12920	12920	0	4	12	12920	12920	0	4	12	12920	12920	0	4	12		

the oxygen atom of a free water molecule occupying one of the special single-fold positions in the space group $P\bar{1}$. However, no such peak could be found and it was therefore concluded that the compound was in fact a heptahydrate.

Refinement of the structure was continued with a number of least-squares cycles by the use of isotropic temperature factors for each atom, until R dropped to 15.9% for the 1219 observed reflexions. The weighting scheme of Cruickshank, Pilling, Bujosa, Lovell & Truter, (1961) was adopted, and the matrix inversion involved the block-diagonal approximation. This relatively high R value is considered reasonable in view of the difficulties experienced in data collection.

The atomic parameters and individual isotropic temperature factors are listed in Table 4, and the bond lengths in Table 5. The positions of the hydrogen atoms

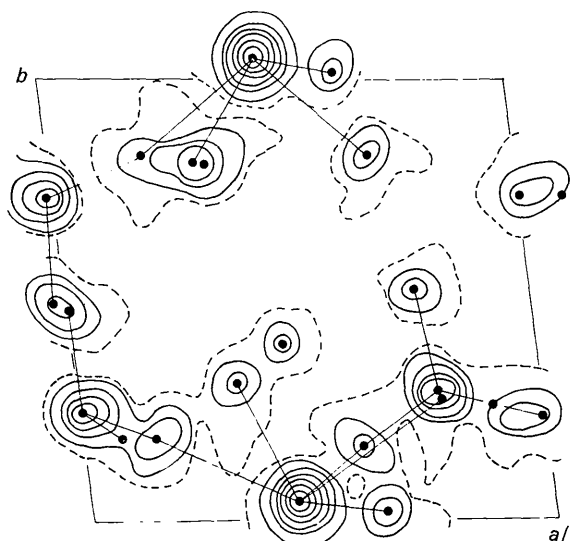


Fig. 2. The electron density projection on to (001), contoured at arbitrary intervals. For notation see caption for Fig. 1.

could not be determined directly, but as we have discussed above, the only initial doubt concerning the decomposition of the compound was its degree of hydration. This was resolved by the Fourier analysis since the oxygen atoms constituting the sulphate groups were easily recognizable and all other peaks of the same height were water molecules. Intramolecular distances between water oxygen atoms and all possible donors and acceptors were calculated and only those with bond distances between the limits 2.50 and 3.20 Å were considered in the hydrogen bonding scheme.

Description of the structure

The structure of $Zr(SO_4)_2 \cdot 7H_2O$ viewed in projection is shown in Fig. 3. The coordination of the zirconium atoms is eightfold, the ligands forming a dodecahedron. The main structural unit consists of two of these polyhedra and four tetrahedral sulphate groups forming a dimeric molecular group of composition $Zr_2(SO_4)_4(H_2O)_8$. The two zirconium atoms in the dimer are bridged by two of the sulphate groups forming an eight-membered ring structure, while each of the other two forms a bidentate complex with one zirconium atom, and these act as terminal groups to the unit. The dimer has a centre of symmetry.

In view of the difficulties, the refinement of the structure may be deemed satisfactory. The stereochemistry of the dimer was subsequently substantiated when an essentially similar unit was found in a parallel study of the structures of the two pentahydrates (parts II and III), and refinement in the alternative space group $P1$ in the present instance was therefore not considered.

Apart from the four water molecules bonded to each zirconium atom in the dimer, six more are non-bonded and lie in sheets parallel to (001), so that the compound can best be represented by the formula

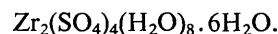


Table 4. Fractional atomic parameters and thermal parameters for $Zr(SO_4)_2 \cdot 7H_2O$

All atoms occupy general positions $2(i)$, $\pm(x, y, z)$.

	x	y	z	B
Zr(1)	0.2233 (2)	0.0515 (6)	0.4758 (3)	0.58 (3) Å ²
S(1)	0.3919 (6)	0.3150 (13)	0.6629 (8)	0.77 (11)
S(2)	0.0117 (5)	0.2530 (13)	0.7002 (7)	0.57 (10)
O(W1)	0.2940 (16)	0.0081 (35)	0.2356 (21)	0.96 (32)
O(2)	0.0784 (19)	0.1824 (36)	0.5696 (26)	1.89 (41)
O(3)	0.0408 (19)	0.1891 (42)	0.8571 (25)	1.77 (40)
O(4)	0.2911 (16)	0.1785 (40)	0.7154 (22)	1.05 (33)
O(W5)	0.1694 (16)	0.8158 (36)	0.6610 (21)	0.90 (32)
O(W6)	0.3480 (16)	0.8250 (35)	0.4901 (22)	0.99 (33)
O(7)	0.1085 (17)	0.8293 (37)	0.3394 (22)	1.19 (34)
O(8)	0.3797 (17)	0.2871 (37)	0.4806 (22)	1.26 (35)
O(W9)	0.4437 (21)	0.2629 (44)	0.0722 (28)	2.42 (46)
O(10)	0.4935 (20)	0.2365 (43)	0.7317 (26)	1.92 (40)
O(W11)	0.1721 (16)	0.8144 (35)	0.9831 (21)	0.92 (32)
O(W12)	0.1686 (18)	0.3058 (35)	0.3203 (25)	1.63 (39)
O(W13)	0.2246 (21)	0.4059 (40)	0.0272 (28)	2.31 (45)
O(14)	0.0082 (25)	0.4940 (49)	0.7032 (33)	3.35 (57)
O(15)	0.3819 (19)	0.5385 (42)	0.7089 (26)	1.84 (40)

The overall stability of this compound evidently depends on the hydrogen bridging between the non-bonded water molecules and the adjacent layers consisting of $Zr_2(SO_4)_4(H_2O)_8$ groups. A possible system of hydrogen bonding is shown in Fig. 4 although some of the O—O distances lie just outside the

limits of 2.6 to 3.0 Å suggested by Baur (1965). These bonds may be divided into a number of groups which effect the cohesion of the molecule in the three general directions [100], [010] and [001] [Table 5(c)]. Bonds between the oxygen atoms of the terminal sulphate groups of one dimer and the bonded water molecules

Table 5. *Interatomic distances and e.s.d.'s (Å) and angles (°)*

(a) Within the ZrO_8 polyhedra

M—A		M—B	
Zr—O(W1)	2.21 ± 0.02	Zr—O(4)	2.19 ± 0.02
Zr—O(2)	2.16 ± 0.02	Zr—O(W6)	2.19 ± 0.02
Zr—O(W5)	2.27 ± 0.02	Zr—O(7)	2.12 ± 0.02
Zr—O(8)	2.28 ± 0.02	Zr—O(W12)	2.25 ± 0.02
Av.	2.23	Av.	2.19
Basic salt*	2.20	Basic salt	2.19
a		m	
O(W1)—O(8)	2.72 ± 0.03	O(W1)—O(7)	2.60 ± 0.03
O(2)—O(W5)	2.80 ± 0.03	O(2)—O(W12)	2.50 ± 0.03
		O(W5)—O(W6)	2.62 ± 0.03
		O(4)—O(8)	2.36 ± 0.03
Av.	2.76	Av.	2.52
Basic salt	2.78	Basic salt	2.40
* $Zr_2(OH)_2(SO_4)_3(H_2O)_4$.			
g		b	
O(4)—O(W5)	2.61 ± 0.03	O(7)—O(W12)	3.06 ± 0.03
O(2)—O(4)	2.79 ± 0.03	O(7)—O(W6)	3.10 ± 0.03
O(W5)—O(7)	2.74 ± 0.03	O(4)—O(W12)	3.70 ± 0.03
O(2)—O(7)	2.93 ± 0.03	O(4)—O(W6)	3.00 ± 0.03
O(8)—O(W12)	2.83 ± 0.03		
O(W1)—O(W6)	2.55 ± 0.03		
O(W6)—O(8)	2.93 ± 0.03		
O(W1)—O(W12)	2.63 ± 0.03		
Av.	2.78	Av.	3.21
Basic salt	2.72	Basic salt	3.21

(b) Within sulphate groups

S(1)—O(8)	1.51 ± 0.02	S(2)—O(2)	1.45 ± 0.02
S(1)—O(4)	1.51 ± 0.02	S(2)—O(3)	1.42 ± 0.02
S(1)—O(10)	1.47 ± 0.02	S(2)—O(7)	1.50 ± 0.02
S(1)—O(15)	1.47 ± 0.02	S(2)—O(14)	1.54 ± 0.02
Av.	1.49	Av.	1.48
O(15)—S(1)—O(8)	108°	O(7)—S(2)—O(14)	102°
O(15)—S(1)—O(4)	110	O(3)—S(2)—O(14)	111
O(15)—S(1)—O(10)	114	O(2)—S(2)—O(14)	111
O(10)—S(1)—O(8)	114	O(3)—S(2)—O(7)	108
O(8)—S(1)—O(4)	103	O(3)—S(2)—O(2)	116
O(4)—S(1)—O(10)	109	O(7)—S(2)—O(2)	108
Av.	110	Av.	109

(c) Possible hydrogen bonding between water molecules and their neighbours

(a) Bonds directed along [100]	
O(15)—O(W9)	2.86 ± 0.03
O(W9)—O(W1)	2.74 ± 0.03
O(10)—O(W1)	3.14 ± 0.03
O(10)—O(W6)	2.74 ± 0.03
(b) Bonds directed along [010]	
O(14)—O(W5)	2.72 ± 0.03
O(14)—O(W12)	2.60 ± 0.03
O(15)—O(W6)	2.68 ± 0.03
(c) Bonds directed along [001]	
O(7)—O(W11)	3.08 ± 0.03
O(W12)—O(W13)	2.64 ± 0.03
O(W11)—O(W13)	2.78 ± 0.03
O(W11)—O(W5)	2.67 ± 0.03
O(W13)—O(4)	3.07 ± 0.03
O(W13)—O(W9)	2.90 ± 0.03
O(W13)—O(3)	2.77 ± 0.03
O(W11)—O(3)	3.19 ± 0.03
O(W9)—O(10)	2.91 ± 0.03
O(W1)—O(W11)	2.67 ± 0.03

of a neighbour help bridge the ends of the dimers. Lateral bridging of adjacent dimers is achieved between the bonded oxygen atom and water molecules *via* the non-bonded water molecules, while each dimer is bonded to the dimers immediately above and below it, mainly by bridging between bonded oxygen atoms and bonded water molecules.

The distances in ZrO_8 polyhedra given in Table 5 (*cf.* Fig. 5) are divided into six groups ($M-A$, $M-B$, a , b ,

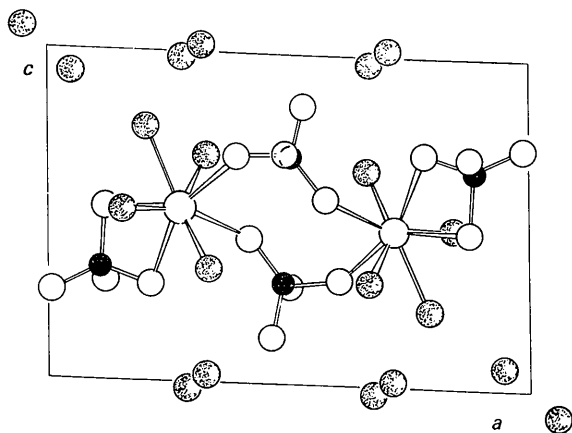


Fig. 3. The structure of $Zr(SO_4)_2 \cdot 7H_2O$ projected on to (010). Large open circles, zirconium atoms; full black circles, sulphur atoms; medium open circles, oxygen atoms; stippled circles, water molecules.

g and m) in accordance with the nomenclature of Hoard & Silverton (1963) for the $42m$ symmetry of the ideal $Mo(CN)_8^{4-}$ coordination, and do not differ greatly from the average values found by McWhan & Lundgren (1966) for the basic salt $Zr_2(OH)_2(SO_4)_3(H_2O)_4$, which are also given in the same Table.

While the sulphate groups show quite a significant departure from the ideal tetrahedral symmetry (Table 5), the mean bond distances and angles for each group are close to the values Bauer (1964) found for several other sulphates. It is possible that the very short bond of 1.42 Å for S(2)–O(3) indicates that this oxygen atom does not enter into the hydrogen bonding scheme (Baur, 1964). The very long bond 1.54 Å for S(2)–O(14) on the other hand suggests that the main hydrogen bonding along [010] is *via* this oxygen atom.

The outstanding feature of this structure is of course the dimer and its existence as an isolated unit. Hydrogen bridging in layer structures such as γ -FeO(OH) (Ewing, 1935) is well documented and $Zr(SO_4)_2 \cdot 4H_2O$ is a pertinent example of this type of bonding in sulphate-hydrates. Isolated metal and sulphate groups held together by hydrogen bonds are found in $NiSO_4 \cdot 7H_2O$ (Beever & Schwartz, 1935) and $BeSO_4 \cdot 4H_2O$ (Beever & Lipson, 1932), while Baur (1962) found isolated $Mg_2(SO_4)_2(H_2O)_8$ rings linked by hydrogen bonds in $MgSO_4 \cdot 4H_2O$. There is little doubt that the hydrogen bonding of the somewhat larger molecular unit in $Zr(SO_4)_2 \cdot 7H_2O$ contributes to its abnormal chemical behaviour. This will be discussed in part III.

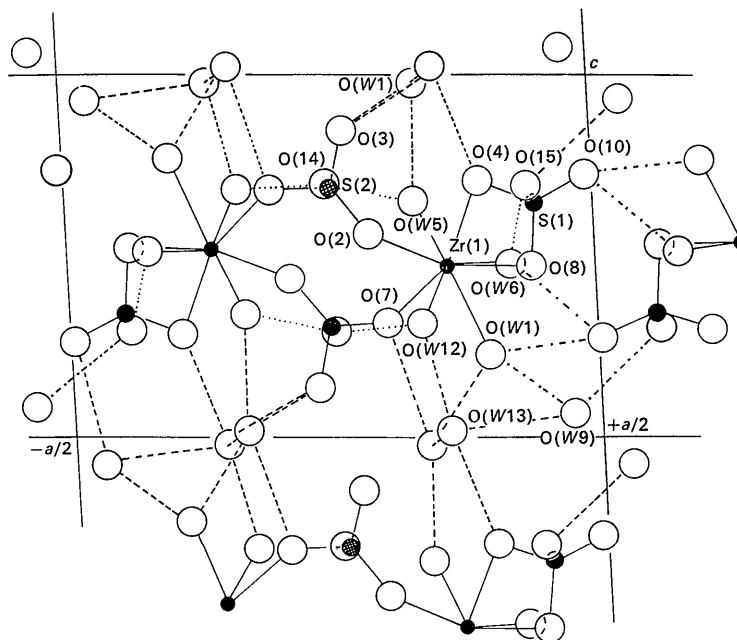


Fig. 4. Schematic projection on to (010) illustrating the possible hydrogen bonding scheme. Atoms are numbered according to Table 4. Small full black circles, zirconium atoms; medium full black (and cross hatched) circles, sulphur atoms; large open circles, oxygen atoms and water molecules. Dots and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

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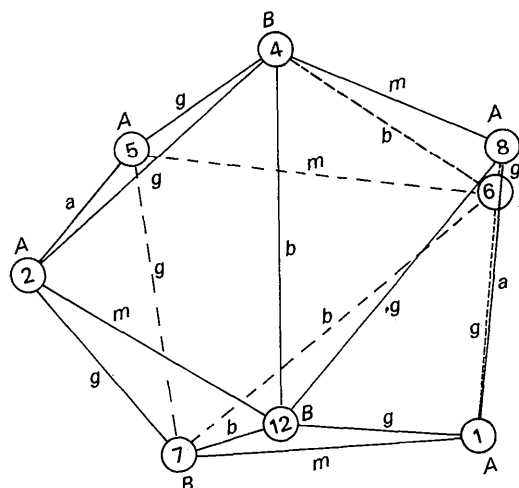


Fig. 5. The coordination of the oxygen atoms around zirconium in $Zr(SO_4)_2 \cdot 7H_2O$. The distances that should be equal, according to the ideal $42m$ symmetry of the $Mo(CN)_4^{4-}$ coordination, are marked according to Hoard & Silverton (1963).

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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