

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, $Zr(SO_4)_2 \cdot 7H_2O$

(Bear & Mumme, 1969*a*), α -Zr(SO₄)₂·5H₂O (Bear & Mumme, 1969*b*) and now β -Zr(SO₄)₂·5H₂O. All three compounds are dimeric sulphates, and it is now possible to consider their crystal chemistry in relation to the radically different zirconium sulphate tetrahydrate Zr(SO₄)₂·4H₂O (Singer & Cromer, 1959). A section of this paper is therefore devoted to a discussion of those aspects of the chemical and physical behaviour of these compounds which are structure dependent.

Experimental

Single crystals of β -Zr(SO₄)₂·5H₂O were prepared by exposing β - or γ -Zr(SO₄)₂ to a dynamic atmosphere of high relative humidity at room temperature. Under these conditions the uptake of water by the sample was rapid, and almost complete solution of the anhydrous phase was achieved before crystallization of the hydrate commenced. This solution was then aged at an ambient temperature between 15° and 25°C and in an atmos-

phere with partial water vapour pressure close to the saturated solution vapour pressure of β -Zr(SO₄)₂·5H₂O (Bear & Mumme, 1968). Well formed tabular crystals of β -Zr(SO₄)₂·5H₂O generally grew over a period of 24 hours.

To prevent decomposition to the tetrahydrate it was necessary to seal the crystal used for collection of the X-ray data in a quartz capillary. Integrated Weissenberg data $h0l$ to $h4l$ were collected with Cu $K\alpha$ radiation and multiple-film packs from a crystal measuring $0.02 \times 0.02 \times 0.05$ mm. Intensities were measured visually.

Subsequent data handling including interlayer scaling procedures and scattering curves for Zr, S and O were all as described in part I.

The approximate unit-cell parameters obtained from $h0l$ and $0kl$ single crystal data were used in conjunction with Ito's method (Azároff & Buerger, 1958) to index the powder diffraction data which were subsequently refined by least-squares (Table 1) to give the more precise lattice parameters listed in Table 2.

Table 1. X-ray powder diffraction data for β -Zr(SO₄)₂·5H₂O

$\sin^2 \theta_{\text{obs}}$	$\sin^2 \theta_{\text{calc}}$	hkl	I	$\sin^2 \theta_{\text{obs}}$	$\sin^2 \theta_{\text{calc}}$	hkl	I
0.0083	0.0083	100	<i>M</i>	0.0937	0.0937	01 $\bar{3}$	
0.0106	0.0106	001	<i>VS</i>		0.0942	03 $\bar{1}$	<i>W</i>
0.0107	0.0107	010	<i>S</i>		0.0939	11 $\bar{3}$	
0.0161	0.0161	10 $\bar{1}$	<i>W</i>		0.0939	301	
0.0171	0.0171	01 $\bar{1}$	<i>W</i>	0.0961	0.0957	003	<i>W</i>
0.0186	0.0185	$\bar{1}$ 10	<i>M</i>		0.0963	030	
0.0195	0.0195	110	<i>M</i>				
0.0218	0.0218	101	<i>M</i>	0.1001	0.1001	30 $\bar{2}$	<i>M</i>
0.0255	0.0256	011	<i>VS</i>	0.1019	0.1023	022	
0.0282	0.0277	$\bar{1}$ 1 $\bar{1}$	<i>W</i>				
0.0305	0.0305	$\bar{1}$ 11	<i>S</i>	0.1038	0.1037	1 $\bar{3}$ 1	
0.0333	0.0332	200	<i>S</i>		0.1038	1 $\bar{2}$ 2	<i>M</i>
0.0373	0.0373	111	<i>W</i>		0.1039	31 $\bar{2}$	
0.0382	0.0381	20 $\bar{1}$	<i>W</i>	0.1098	0.1100	1 $\bar{1}$ 3	<i>VW</i>
0.0424	0.0428	$\bar{2}$ 10		0.1142	0.1143	$\bar{3}$ 20	
	0.0428	020	<i>VW</i>		0.1139	12 $\bar{3}$	<i>W</i>
	0.0425	002			0.1142	32 $\bar{1}$	
0.0449	0.0451	102		0.1261	0.1263	230	<i>W</i>
	0.0447	01 $\bar{2}$	<i>VS</i>		0.1258	132	
	0.0449	02 $\bar{1}$		0.1289	0.1288	1 $\bar{2}$ 3	<i>W</i>
	0.0450	210			0.1291	32 $\bar{2}$	
0.0479	0.0478	11 $\bar{2}$	<i>W</i>	0.1327	0.1324	131	
0.0498	0.0496	201	<i>VW</i>		0.1327	230	<i>W</i>
	0.0500	1 $\bar{2}$ 0			0.1328	400	
0.0521	0.0520	$\bar{2}$ 11		0.1456	0.1461	203	<i>VW</i>
	0.0521	120	<i>W</i>		0.1457	410	
0.0545	0.0550	$\bar{2}$ 1 $\bar{1}$	<i>W</i>	0.1487	0.1491	222	<i>W</i>
0.0567	0.0566	102	<i>W</i>		0.1484	321	
0.0584	0.0582	1 $\bar{1}$ 2	<i>W</i>				
0.0614	0.0619	021	<i>W</i>	0.1537	0.1538	03 $\bar{3}$	<i>W</i>
	0.0617	012		0.1571	0.1571	32 $\bar{2}$	
					0.1567	322	<i>W</i>
0.0657	0.0656	211	<i>M</i>		0.1569	41 $\bar{2}$	
0.0684	0.0683	022	<i>M</i>	0.1662	0.1662	330	<i>VW</i>
0.0747	0.0745	21 $\bar{1}$	<i>S</i>		0.1665	313	
	0.0747	300		0.1697	0.1695	412	<i>W</i>
0.0816	0.0817	22 $\bar{1}$			0.1701	004	
	0.0813	1 $\bar{2}$ 2	<i>M</i>	0.1726	0.1727	33 $\bar{1}$	
0.0827	0.0824	$\bar{2}$ 12			0.1723	14 $\bar{1}$	<i>W</i>
0.0842	0.0838	310	<i>W</i>		0.1730	233	
0.0877	0.0873	221	<i>W</i>	0.1776	0.1779	223	<i>W</i>
	0.0872	202			0.1773	140	
0.0884	0.0883	$\bar{2}$ 1 $\bar{2}$	<i>W</i>				
0.0921	0.0922	222	<i>W</i>				

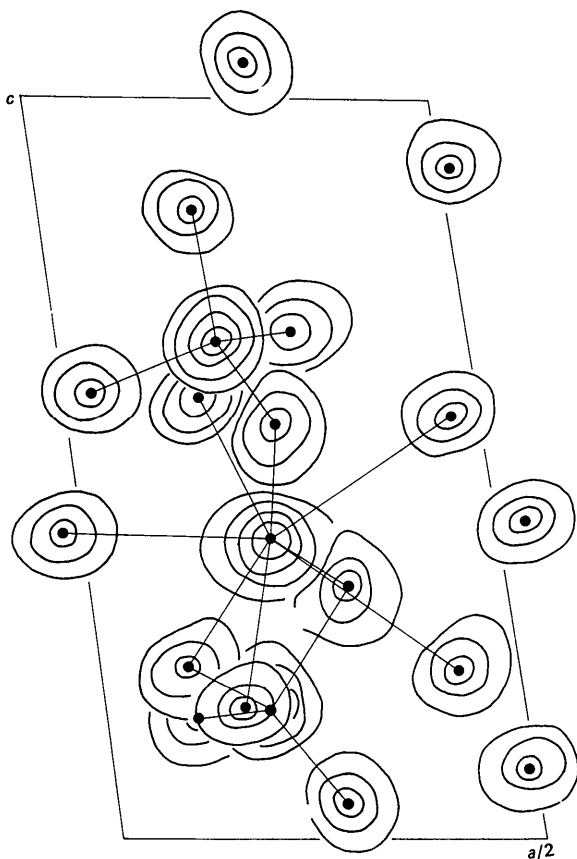


Fig. 1. The electron density distribution indicated by sections $\rho_o(xyz)$ selected near the atom centres and projected on to (010). The contours are at arbitrary intervals.

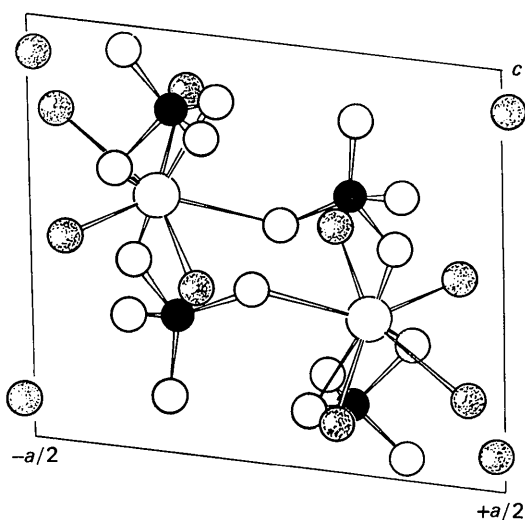


Fig. 2 The structure of $\beta\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ projected on to (010). Large open circles, zirconium atoms; full black circles, sulphur atoms; medium open circles, oxygen atoms; stippled circles, water molecules.

The morphological cell was preferred for collection of the single-crystal data as the six faces of the crystal were $\{100\}$ $\{001\}$ $\{001\}$ pinacoids for the crystallographic axes given in Table 2. In addition these axes defined a more orthogonal unit cell.

The positions of the zirconium atoms, assuming the space group $P\bar{1}$, were determined from a three-dimensional Patterson function $P(uvw)$ 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, $\rho(xyz)$ (Fig. 1). 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 28 oxygen atoms, all occupying the general positions $2(i)$.

Refinement of the structure was carried on with a number of least-square cycles, with isotropic temperature factors for each atom, until R dropped to 12.2% for the 754 observed reflexions. The weighting scheme and matrix inversion were those used in part I (Bear & Mumme, 1969a). The scaled observed data and structure amplitudes calculated from the final model are given in Table 3.

Atomic parameters, and individual temperature factors are listed in Table 4. Bond lengths are given in Table 5.

Description

The structure of $\beta\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ viewed in the (010) projection is shown in Fig. 2, where the origin has been moved to the point $(\frac{1}{2}, 0, 0)$. Although less obvious in this projection, the main structural unit of $\beta\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ is the same as that found in $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ and $\alpha\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$, consisting of the two zirconium dodecahedra which, with the four tetrahedral sulphate groups, form the dimer with composition $\text{Zr}_2(\text{SO}_4)_4(\text{H}_2\text{O})_8$. There are four water molecules bonded to each zirconium atom, while the two non-bonded water molecules in the unit cell lie in sheets almost normal to [100]. The formula of the compound, as with $\alpha\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$, is best expressed as $\text{Zr}_2(\text{SO}_4)_4(\text{H}_2\text{O})_8 \cdot 2\text{H}_2\text{O}$.

It is more satisfactory to compare this structure with those of the two previously described compounds $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ and $\alpha\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$, by viewing it in the (001) projection, as is done in Fig. 3. In this projection the differences between α - and β - $\text{Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ are easily seen. The disposition of the free water molecules is considerably changed, for in $\beta\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ they lie in sheets running obliquely with respect to the dimer, while in the α form they are parallel to it. The other notable difference lies in the orientation of the terminal sulphate groups, which in $\beta\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ are seen to lie at a different orientation with respect to the Zr-Zr direction than they do in $\alpha\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$. This results in a more distorted arrangement of the dimeric group than is found in either $\text{Zr}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ or $\alpha\text{-Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$.

Bond distances in the ZrO_8 dodecahedra (Fig. 4) are given in Table 5 in accordance with the nomenclature of Hoard & Silverton (1963), where the mean distances are compared with those of $Zr(SO_4)_2 \cdot 7H_2O$ and α - $Zr(SO_4)_2 \cdot 5H_2O$. The tetrahedral sulphate groups (Table 5) are considerably distorted from the ideal, but once again the mean distances and angles are not very different from those of other sulphates (Baur, 1964).

β - $Zr(SO_4)_2 \cdot 5H_2O$ may simply be described as a more closely packed, and therefore a denser form, of the α - $Zr(SO_4)_2 \cdot 5H_2O$ structure. The decrease in unit-cell volume is 4.14%. Fig. 5 shows the probable hydrogen bonding scheme. Bonding to overlying and underlying dimers is through the two oxygen atoms O(2) and O(3) in each of the bridging sulphate groups, and the one oxygen atom O(9) in the terminal group. This is a different arrangement from both $Zr(SO_4)_2 \cdot 7H_2O$ and α - $Zr(SO_4)_2 \cdot 5H_2O$, where only one oxygen atom from each of the bridging and terminal groups takes part in the three-dimensional linkage of the dimeric groups. The bridging sulphate groups, as in α - $Zr(SO_4)_2 \cdot 5H_2O$ also enter into the lateral bonding. In this case however they provide bonds O(2)–O(W10), O(6)–O(W11) and O(1)–O(W12) to two adjacent dimers. This is a direct consequence of the closer packing of the dimeric groups into the structure.

The coordination of the free water molecule is best described as a square pyramid in which the water molecule is moved considerably from the centre of the base.

Discussion

(a) Chemical and structural relationships of the higher hydrates of $Zr(SO_4)_2$

The chemical inter-relationship of the hydrates $Zr(SO_4)_2 \cdot 4H_2O$, $Zr(SO_4)_2 \cdot 7H_2O$, α - $Zr(SO_4)_2 \cdot 5H_2O$ and β - $Zr(SO_4)_2 \cdot 5H_2O$, and the various anhydrous $Zr(SO_4)_2$ phases (Bear, 1967) is shown in Fig. 6. From this it is evident that the chemical behaviour of the latter three hydrates is anomalous. They do not form a normal hydration series with the tetrahydrate, which is the

stable phase at all vapour pressures within the temperature interval $+40^\circ$ to $-5^\circ C$.

These differences are reflected in their crystal structures. In all four hydrates the zirconium atom has eightfold coordination. While in the heptahydrate and the two pentahydrates it is dodecahedral the symmetry in the tetrahydrate is an antiprism. The tetrahydrate is composed of infinite layers of composition $Zr(SO_4)_2 \cdot 4H_2O$ (Fig. 7) but we have shown that the three higher hydrates are all built up from isolated dimeric groups of composition $Zr_2(SO_4)_4(H_2O)_8$. In the tetrahydrate the layers are held together by hydrogen bonding through the coordinated water molecules, while the isolated molecular groups in the other three hydrates are hydrogen bonded in several directions through both the coordinated and non-bonded water molecules.

A further difference in the two types of structure lies in the symmetry of the sulphate tetrahedra. Although in the tetrahydrate there is a significant departure from the ideal tetrahedral symmetry, this is small compared with the distortion in both the non-equivalent sulphate groups of the dimeric units of the higher hydrates. The effect of this increase in distortion in the pentahydrates is reflected in the enrichment of the 950 – 1250 cm^{-1} region of their infrared spectra. In the tetrahydrate the

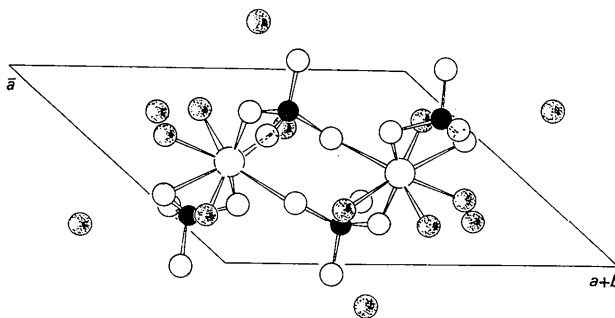


Fig. 3. The structure of β - $Zr(SO_4)_2 \cdot 5H_2O$ projected on to (001). Notation is the same as in Fig. 2.

Table 4. Fractional atomic parameters and thermal parameters for β - $Zr(SO_4)_2 \cdot 5H_2O$

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Zr(1)	0.2211 (3)	0.1989 (5)	0.3848 (3)	0.99 (0.04) Å ²
S(1)	0.1918 (9)	0.4700 (15)	0.1755 (9)	1.41 (0.13)
S(1)	0.1864 (8)	0.9030 (14)	0.6704 (8)	1.00 (0.12)
O(1)	0.1931 (27)	0.0224 (40)	0.8447 (29)	1.97 (0.43)
O(2)	0.2866 (26)	0.7469 (39)	0.6774 (27)	1.72 (0.41)
O(3)	0.0204 (21)	0.8532 (33)	0.5886 (22)	0.59 (0.31)
O(4)	0.2468 (25)	−0.00005 (37)	0.5425 (26)	1.48 (0.40)
O(W5)	0.1518 (24)	0.4063 (36)	0.5976 (25)	1.46 (0.39)
O(6)	0.3067 (22)	0.4642 (33)	0.3381 (23)	1.01 (0.34)
O(7)	0.2676 (31)	0.4801 (42)	0.0254 (33)	2.75 (0.52)
O(8)	0.0989 (31)	0.2979 (44)	0.1594 (33)	2.74 (0.52)
O(9)	0.0951 (28)	0.6229 (42)	0.2274 (30)	2.28 (0.47)
O(W10)	0.4226 (29)	0.1213 (41)	0.2266 (31)	2.63 (0.49)
O(W11)	0.4461 (24)	0.2828 (37)	0.5734 (25)	1.37 (0.37)
O(W12)	0.1520 (30)	0.9553 (43)	0.1645 (31)	2.65 (0.52)
O(W13)	0.4863 (38)	0.7732 (51)	0.0907 (39)	3.72 (0.67)

inequalities in bond lengths and angles reduce the molecular symmetry of the group from T_d to C_2 , with the result that some resolution of the triply degenerate

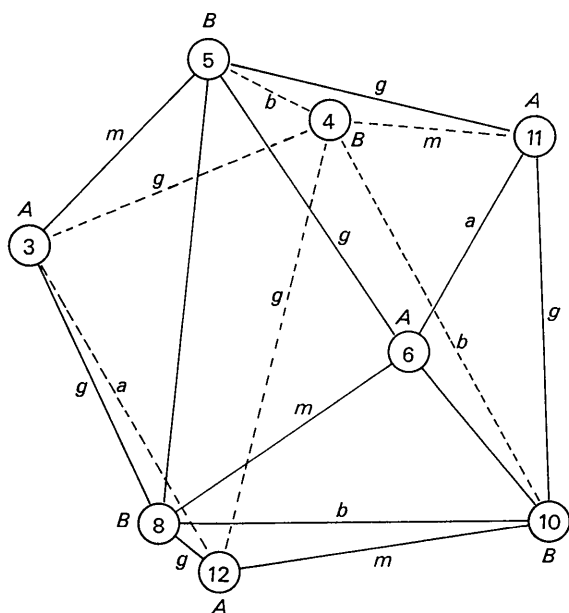


Fig. 4. The coordination of the oxygen atoms around zirconium in β - $Zr(SO_4)_2 \cdot 5H_2O$ seen in projection down (010). The distances that should be equal according to the ideal $\bar{4}2m$ symmetry of the dodecahedron are marked according to Hoard & Silverton (1963).

ν_3 stretching frequency occurs at 1140 and 1090 cm^{-1} [Table 6 and Fig. 8(a)]. With C_2 symmetry the ν_1 stretching frequency also becomes active in the infrared region and Adler (1965) has assigned the sharp band at 1030 cm^{-1} to this mode. However, this frequency is rather higher than generally found for the ν_1 absorptions (Adler & Kerr, 1965; Hezel & Ross, 1966) and it seems more likely that this is either a ν_3 or a combination band. It is also of note that Evstaf'era, Molodkin, Dvoryantseva, Ivanova & Struchkova (1966) have attributed a weak band at ~ 970 cm^{-1} to the ν_1 stretching mode in $Th(SO_4)_2 \cdot 4H_2O$ which they state is isomorphous with $Zr(SO_4)_2 \cdot 4H_2O$.

In the zirconium sulphate pentahydrates the symmetry of both non-equivalent sulphates is further reduced to C_1 , so that up to six vibrations corresponding to the ν_3 mode and two to ν_1 could be observed. In fact this is the number of peaks present in the spectrum of β - $Zr(SO_4)_2 \cdot 5H_2O$ [Table 6, Fig. 8(c)] but in common with $Zr(SO_4)_2 \cdot 4H_2O$ at least one of these peaks may prove to be a combination band. Fewer absorptions are observed in the ν_3 region for α - $Zr(SO_4)_2 \cdot 5H_2O$ [Table 6, Fig. 8(b)] and we conclude that in this case not all the vibrational components from the two non-equivalent sulphate groups are resolved.

(b) Lattice stability

Hoard & Silverton (1963) have studied the stereochemistry of discrete eightfold coordination, and have concluded that the energies of direct bonding inter-

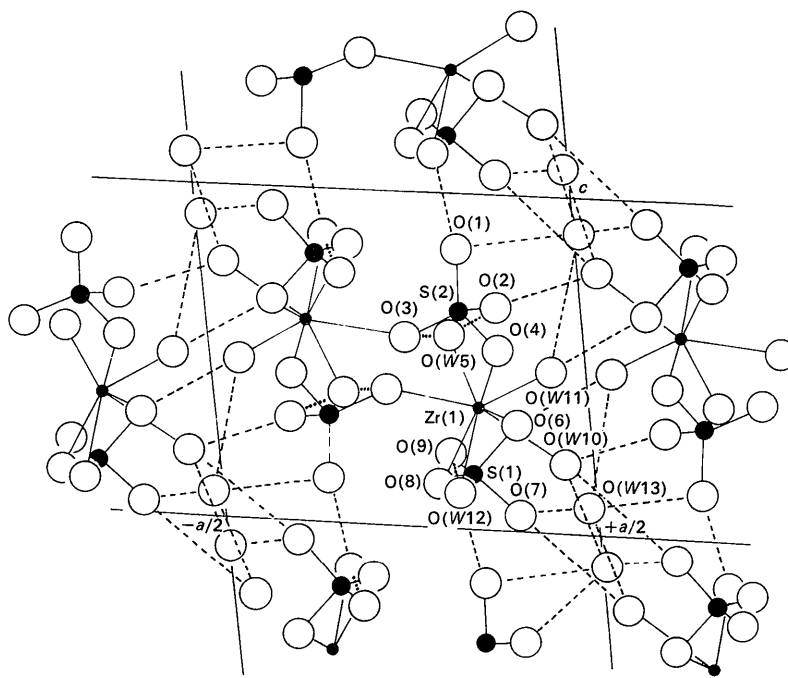


Fig. 5. Schematic projection on to (010) illustrating the possible hydrogen bonding scheme. Atoms are numbered according to Table 5. Small full black circles, zirconium atoms; medium full black circles, sulphur atoms; large open circles, oxygen atoms and water molecules. Dotted lines and dashed lines represent probable hydrogen bonding. Dotted lines are confined to bonding along [010].

action must differ so little for the dodecahedral and square anti-prism configurations that the choice between the two is usually decided by other factors. Their conclusions have been supported by the structure studies of McWhan & Lundgren (1966), who examined

several basic zirconium sulphates in which both types of symmetry occur. It seems, therefore, that energy differences between the dodecahedral zirconium coordination in the dimeric sulphates, and the square anti-prism coordination of the tetrahydrate, are unlikely to

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

(a) Within the ZrO_8 polyhedra			
	<i>M-A</i>		<i>M-B</i>
Zr(1)-O(3)	2.15 (2)	Zr(1)-O(W5)	2.19 (2)
O(W11)	2.24 (2)	O(W10)	2.27 (3)
O(W12)	2.26 (2)	O(4)	2.11 (2)
O(6)	2.26 (2)	O(8)	2.16 (3)
Av.	2.23	Av.	2.18
I*	2.23	I	2.19
II†	2.20	II	2.16
	<i>a</i>		<i>m</i>
O(3)-O(W12)	2.77 (3)	O(3)-O(W5)	2.52 (3)
O(6)-O(W11)	2.64 (3)	O(4)-O(W11)	2.70 (3)
Av.	2.71	O(8)-O(6)	2.29 (4)
I	2.76	O(W12)-O(W10)	2.57 (4)
II	2.71	Av.	2.52
		I	2.52
		II	2.48
	<i>g</i>		<i>b</i>
O(3)-O(4)	2.69 (3)	O(8)-O(W10)	3.09 (4)
O(3)-O(8)	2.76 (3)	O(W5)-O(8)	3.28 (4)
O(8)-O(W12)	2.65 (4)	O(4)-O(W5)	3.15 (3)
O(4)-O(W12)	2.86 (4)	O(4)-O(W10)	3.32 (4)
O(W5)-O(6)	2.66 (3)	Av.	3.18
O(W5)-O(11)	2.70 (3)	I	3.21
O(6)-O(W10)	2.81 (3)	II	3.18
O(W10)-O(W11)	2.69 (4)		
Av.	2.73		
I	2.78		
II	2.71		
(b) Within sulphate groups			
S(1)-O(6)	1.48 (2)	S(2)-O(2)	1.47 (3)
O(7)	1.42 (3)	O(3)	1.48 (2)
O(8)	1.51 (3)	O(1)	1.46 (3)
O(9)	1.45 (3)	O(4)	1.49 (3)
Av.	1.465	Av.	1.475
O(6)-S(1)-O(7)	112.3	O(1)-S(2)-O(2)	112.6
O(6)-S(1)-O(8)	100.1	O(1)-S(2)-O(3)	110.9
O(6)-S(1)-O(9)	104.8	O(1)-S(2)-O(4)	109.8
O(7)-S(1)-O(9)	113.7	O(2)-S(2)-O(3)	113.1
O(7)-S(1)-O(8)	114.7	O(2)-S(2)-O(4)	106.0
O(8)-S(1)-O(9)	110.1	O(3)-S(2)-O(4)	104.0
Av.	109.3	Av.	109.4
(c) Hydrogen bonds			
(a) Vertical			
O(2)-O(W5)	2.75 (3)		
O(3)-O(W5)	2.52 (3)		
O(9)-O(W12)	2.72 (3)		
(b) Lateral			
O(1)-O(W12)	2.69 (3)		
O(2)-O(W10)	2.63 (3)		
O(6)-O(W11)	2.64 (3)		
O(7)-O(W13)	2.83 (3)		
O(1)-O(W13)	3.08 (3)		
O(W11)-O(W13)	2.76 (3)		
O(W10)-O(W13)	2.73 (3)		

* $I = Zr_2(SO_4)_4(H_2O)_8 \cdot 6H_2O$.

† $II = \alpha-Zr_2(SO_4)_4(H_2O)_8 \cdot 2H_2O$.

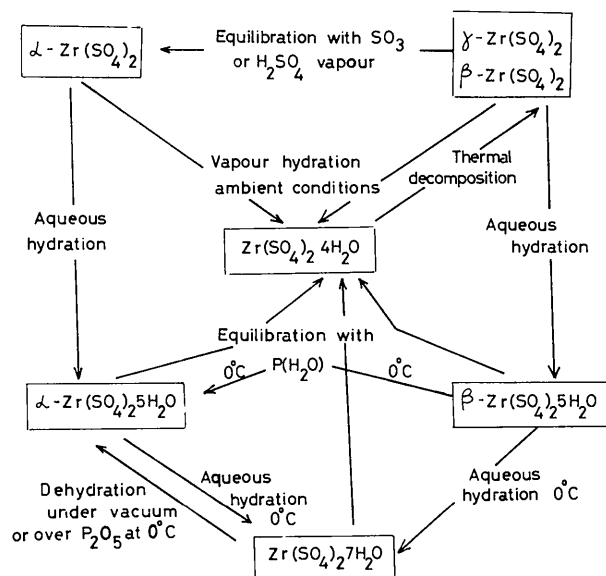
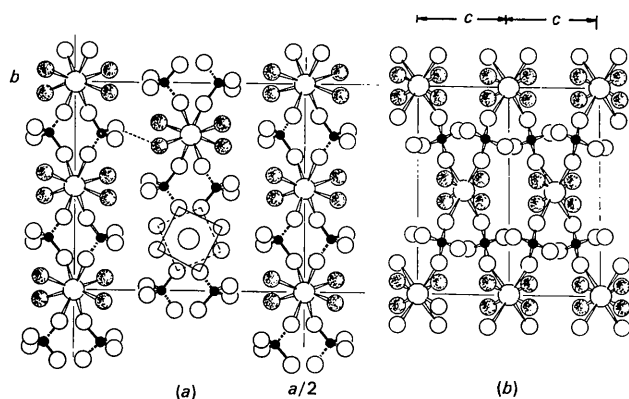


Fig. 6. Chemical inter-relationship of zirconium sulphate phases.

Fig. 7. The structure of $Zr(SO_4)_2 \cdot 4H_2O$. (a) Projected on (001). (b) The layer centred at $x=0$ as viewed along the a axis. Notation is the same as in Fig. 2.

influence markedly the stability of the two types of structures. From consideration of the structural data, there can be little doubt that the differences in chemical behaviour between zirconium sulphate tetrahydrate, and the three higher hydrates, are attributable to the radical difference between the polymerized layer type structure of the former compound and the completely hydrogen bonded molecular dimers in the other three.

Differences in the stability of the skeletal dimer structure can be noted within the dimeric sulphates themselves. From the chemistry of the two pentahydrates of $Zr(SO_4)_2$ it can be concluded that the β phase is less stable than the α form. Thus $\beta-Zr(SO_4)_2 \cdot 5H_2O$ has a lower saturated solution vapour pressure than $\alpha-Zr(SO_4)_2 \cdot 5H_2O$ (Bear & Mumme, 1968). On equilibration at temperatures between 0° and $+5^\circ C$ in atmospheres of controlled water vapour pressure (provided by NaOH solutions) conversion of the β to the α form occurs before both pentahydrates finally decompose to tetrahydrate. Complete equilibration of the β to the α phase can also be achieved indirectly by way of the heptahydrate. Despite the fact that during transformation of $\beta-Zr(SO_4)_2 \cdot 5H_2O$ to the heptahydrate the dimer has to undergo greater structural reorientation, the β phase hydrates much more rapidly than does the α form, suggesting there is less resistance to the diffusion of water into the lattice. Further, on dehydration of the heptahydrate product over P_2O_5 at $0^\circ C$ it is the α -pentahydrate which is formed and not the β form. Clearly therefore there is a marked difference between the lattice energies of the two pentahydrates. As we have seen however, both compounds are built up from similar dimeric units, both contain Zr in eightfold dodecahedral coordination and in both the dimers are bonded through the coordinated water molecules and two non-bonded water molecules. It seems, therefore, that the individuality of the two phases must result from small differences in the relative orientation within the unit cell, both of the Zr-O polyhedra and of the

Table 6. Infrared data

$Zr(SO_4)_2 \cdot 4H_2O$	$\alpha-Zr(SO_4)_2 \cdot 5H_2O$	$\beta-Zr(SO_4)_2 \cdot 5H_2O$	Assignment
		1250 <i>m</i>	} ν_3
	1240 <i>m</i>	1225 <i>m</i>	
	1180 <i>m</i>	1165 <i>s</i>	
1140 <i>s(b)</i>		1115 <i>m</i>	
1090 <i>s(b)</i>	1085 <i>s</i>	1075 <i>s</i>	} ν_1
1030 <i>m(shp)</i>	1030 <i>m(shp)</i>	1015 <i>m</i>	
	1010 <i>m(shp)</i>	990 <i>m</i>	
	975 <i>m(shp)</i>	960 <i>m</i>	

s = strong
m = medium
(shp) = sharp
(b) = broad

sulphate tetrahedra, as well as in the symmetry of the latter. Fig. 9 is a diagram of the 'ring' structure common to the three dimeric sulphates, and Table 7 contains the Zr-Zr, S-S and O-O distances across the centre of the unit and the relevant angles for all three compounds. It can be seen that in β -Zr(SO₄)₂·5H₂O the Zr-Zr distance is longer, while the two O-O and the S-S distances are shorter than in the other two sulphates. Furthermore, the sums of the bond angles subtended at the centre of the 'rings' vary from 365.3° for the heptahydrate, through 365.8° for the α -pentahydrate, to 367.0° for the β -pentahydrate, indicating an increasing departure from planarity.

While this structural arrangement apparently contributes to a more efficient packing, resulting in the higher density for the β -pentahydrate, the repulsion between the O(1) (see Fig. 9) oxygen atoms would be expected to decrease the stability of the dimeric rings. Thus the lower lattice energy of α -Zr(SO₄)₂·5H₂O is most probably achieved by contraction of the ring in the Zr-Zr direction with an accompanying lateral expansion in the O-O and S-S directions. At the same time some reorientation of the terminal sulphate groups takes place with the non-bonded water molecules migrating to a new position.

(c) Hydrogen bonding

Regardless of the relative energies of the skeletal Zr₂(SO₄)₄(H₂O)₈ structure, the dimeric sulphates owe their existence as crystalline solids to the three-dimensional hydrogen bridging of the isolated units by the bonded and non-bonded water molecules. In Zr(SO₄)₂·7H₂O two of the non-bonded water molecules are weakly held, as may be seen by their ready removal over P₂O₅ or under vacuum. When this occurs the structure collapses with only small change in the orientation of the dimer to give the α -pentahydrate. In the latter compound the remaining non-bonded water molecule is relatively strongly held, as is indicated by the hydrogen bonding scheme (part II), and cannot be removed by P₂O₅ or by pumping under moderately high vacuum. However, when the dry sample is exposed, even at low temperatures, to atmospheres containing a significant partial pressure of water vapour (but below the saturated solution vapour pressure of the phase), the presence of

the highly polar water molecules may weaken the hydrogen bonding so that the non-bonded water molecules are free to migrate to the surface where they are lost. This process is accompanied by a rearrangement of the structure to that of the stable tetrahydrate, where the dimers have polymerized into sheets of Zr(SO₄)₂·4H₂O.

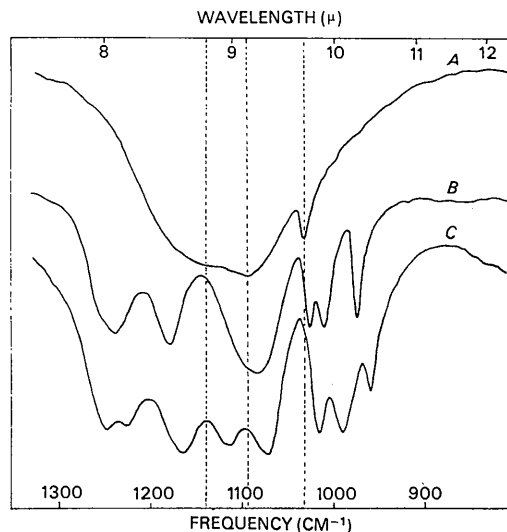


Fig. 8. Portions of the infrared spectra of (a) Zr(SO₄)₂·4H₂O, (b) α -Zr(SO₄)₂·5H₂O, (c) β -Zr(SO₄)₂·5H₂O.

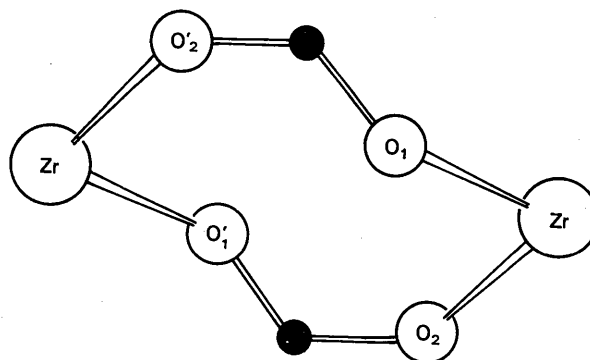


Fig. 9. Dimeric 'ring' structure consisting of two zirconium atoms joined by two O-S-O bridges. Notation is the same as in Fig. 2.

Table 7. Bond distances (Å) angles (°) in dimeric 'ring'

	β -Zr(SO ₄) ₂ ·5H ₂ O	α -Zr(SO ₄) ₂ ·5H ₂ O	Zr(SO ₄) ₂ ·7H ₂ O
Atomic notation is the same as in Fig. 9.			
Distances			
Zr-Zr	5.55	5.53	5.38
S-S	4.28	4.46	4.47
O ₁ -O ₁	2.78	2.95	2.98
O ₂ -O ₂	4.16	4.29	4.45
Angles			
O ₁ -Zr-O ₂	77.5	82.9	92.9
O ₁ -S-O ₂	102.9	105.6	108.4
Zr-O ₁ -S	150.0	151.8	153.1
Zr-O ₂ -S	151.9	153.1	147.4

The question of why a dimeric tetrahydrate does not form should be asked. It may be that such a metastable polymorph does indeed exist, but has not yet been isolated or recognized. On the other hand it may be that in the absence of any non-bonded water molecules, the hydrogen bonding through the coordinated waters alone is not strong enough to hold the isolated units together, although it should be remembered that hydrogen bridging through the water molecule in both pentahydrates is not essential to their stability.

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New Families of ZnS Polytypes

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Seven ZnS polytypes belonging to hitherto unknown families, namely 44L–132R; 38L–114R and 18L–54R have been found. The polytypes are 44L (37 7) and 44L (17 4 17 6) of the family 38L–132R; 114R (29 9)₃, 114R (35 3)₃, 114R (21 9 6 2)₃ and 114R (13 5 2 2 6 2 6 2)₃ of the family 38L–114R and 54R (10 8)₃ of the family 18L–54R. Eighteen further new polytypes are reported: 12H (6 6), 12L (9 3) and 36R (8 4)₃ of the family 12L–36R; 42R (12 2) of the family 14L–42R; 20H (10 10), 20L (2 3 8 7), 20L (3 4 7 6), 60R (9 3 6 2)₃, 60R (17 3)₃, 60R (9 4 5 2)₃, 60R (10 3 5 2)₃, 60R (5 4 5 2 2 2)₃, 60R (6 3 3 3 3 2)₃, 60R (8 4 2 2 2 2)₃ of the family 20L–60R; and 28L (23 5), 28L (2 2 21 3), 84R (25 3)₃ and 84R (11 8 4 5)₃ of the family 28L–84R. X-ray oscillation photographs of their (10.l) or (40.l) row line are shown, and the calculated and observed intensities are compared.

During an investigation of ZnS polytypes, new polytypes were found, some of them belonging to hitherto unknown families (Steinberger & Mardix, 1967). The crystals investigated were ZnS platelets grown by sublimation at about 1200 C. Each crystal contains a large number of polytype regions having a common *c* axis. Most of the polytype regions investigated are wider than 0.1 mm. X-ray oscillation photographs about the *c* axis were taken with Cu *K* radiation. Photographs of the (10.l), or in some cases of (40.l) row line are given in Figs. 1 to 7. The structure was determined by a method given in a previous publication (Mardix, Alexander, Brafman & Steinberger, 1967). For the identification of the higher order polytypes an improved

method was used (to be published). The observed and calculated intensities are given in Table 1.

In a few cases the width of the polytype region was smaller than 0.1 mm and a number of different regions were simultaneously in the X-ray beam. Thus spots appearing in a certain row line of the X-ray photograph may belong to two or three neighbouring regions. At first glance, the photograph may be thought to belong to a polytype of higher periodicity. An example is seen in Fig. 1(a), which is a photograph of the (40.l) row line of the polytype regions 12H (6 6) together with the two polytype regions 36R (8 4)₃ and 36R (2 10)₃. More examples are seen in Fig. 3; in Fig. 4 (f) which is a photograph of the (10.l) row line of the polytype regions 60R (9 4 5 2)₃ and 60R (5 4 5 2 2 2)₃; and in Fig. 5(b) where the two polytype regions 28L (23 5) and 84R (11 8 4 5)₃ are photographed simultaneously. However, the reflexions from different regions can be readily

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