gether (Bear & Mumme, 1970a). In α-Zr(SO$_4$)$_2$.H$_2$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 α-Zr(SO₄)₂

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α-Zr(SO$_4$)$_2$ is orthorhombic with space group *Pnma* and unit-cell dimensions, $a=8\cdot61$, $b=5\cdot44_5$, $c=10\cdot89$ 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 γ- and α-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 α-Zr(SO$_4$)$_2$, which contains the dimeric ring common to all the hydrates of Zr(SO$_4$)$_2$ except Zr(SO$_4$)$_2$.4H$_2$O, shows a close relationship to the structures of the γ- and α-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$_4$)$_2$. These included the heptahydrate, α and β-pentahydrates and γ and α-monohydrates, (Bear & Mumme, 1969a,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$_2$SO$_4$ atmospheres consist of three polymorphs two of which, γ and β-Zr(SO$_4$)$_2$, are metastable. Formation of the stable α-form is favoured by high partial pressures of H$_2$SO$_4$ (Bear, 1967, 1969). The metastable anhydrous forms equilibrate to α-Zr(SO$_4$)$_2$ when heated in a sealed tube at temperatures near 650°C or under high partial pressures of H$_2$SO$_4$ at lower temperatures.

Single crystals of γ and β-Zr(SO$_4$)$_2$ have not yet been prepared but well shaped tabular or lens-like crystals of α-Zr(SO$_4$)$_2$ can be grown by evaporating solutions of

Zr(SO$_4$)$_2$.4H$_2$O in strong sulphuric acid at elevated temperatures.

This paper describes the X-ray structure analysis of α-Zr(SO$_4$)$_2$ and discusses it relationship to the structures of the monohydrates.

Experimental

Microcrystalline α-Zr(SO$_4$)$_2$ was prepared by decomposing solid Zr(SO$_4$)$_2$.4H$_2$O in high partial pressures ($\sim$1 atm) of H$_2$SO$_4$ 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$_2$ gas could be passed over the sample to prevent hydration. The microcrystalline material was also used to measure the density of α-Zr(SO$_4$)$_2$ by displacement in CCl$_4$. Unit-cell dimensions and other crystallographic data are given in Table 2.

Single crystals of α-Zr(SO$_4$)$_2$ were obtained by treating one volume of a concentrated solution of Zr(SO$_4$)$_2$.4H$_2$O (1 g.cm^{-3}) with two volumes of concentrated H$_2$SO$_4$ and slowly evaporating the resulting

Table 1. *X-ray data for* α-Zr(SO₄)₂

sin² θ (obs)	sin² θ (calc)	hkl
0·0200	0·0200	001, 200
0·0250	0·0250	101
0·0280	0·0280	011, 210
0·0319	0·0320	020
0·0329	0·0330	111
0·0370	0·0370	120
0·0481	0·0480	211
0·0520	0·0520	021, 220
0·0530	0·0530	310
0·0569	0·0570	121
0·0650	0·0650	301
0·0770	0·0770	130, 320
0·0801	0·0800	002, 400
0·0921	0·0920	031, 230
0·0971	0·0970	131, 321
0·1120	0·1120	420, 022
		231
0·1331	0·1330	140, 312
		510
0·1371	0·1370	331
0·1522	0·1520	032, 430
0·1528	0·1530	141, 511
0·1601	0·1600	402
0·1679	0·1680	241, 412
0·1721	0·1720	232, 431
0·1878	0·1880	013, 610
0·1929	0·1930	113, 341
0·2077	0·2080	042, 213
		440, 611
0·2123	0·2120	023, 620
0·2172	0·2170	123, 531
0·2253	0·2250	151, 303
0·2322	0·2320	223, 432
		621
0·2572	0·2570	133, 323
0·2649	0·2650	351, 701
0·2880	0·2880	060, 442
0·2918	0·2920	423, 622
0·2999	0·3000	252, 451
0·3203	0·3200	004, 800
0·3449	0·3450	551

Table 2. *Crystallographic data for* α-Zr(SO₄)₂

Symmetry	Orthorhombic
Unit-cell dimensions	$a = 8\cdot61 \pm 0\cdot01$ Å
	$b = 5\cdot445 \pm 0\cdot01$
	$c = 10\cdot89 \pm 0\cdot01$
Possible space groups	Pnma
	Pn2₁a
D_x	3·68 g.cm⁻³
D_m	3·71 ± 0·04 g.cm⁻³
Z	4
μ_c	263 cm⁻¹

solution at 350 °C. Alternatively single crystals of either γ and α-Zr(SO₄)₂.H₂O (Bear & Mumme, 1969d) were equilibrated in aqueous 80% H₂SO₄ at approximately 150 °C.

Integrated Weissenberg data h0l to h3l were collected around the b axis of a crystal fragment measuring 0·2 × 0·2 × 0·5 mm using Cu Kα radiation and multiple-film packs. Measurement of intensities, subsequent data handling including interlayer scaling procedures and the scattering curves for Zr, S and O are as

described in part I (Bear & Mumme, 1969a). As the crystal was deliquescent it was sealed in a quartz capillary during collection of the X-ray data.

Structure determination

From the measured density and the unit-cell volume, the number of formula units per cell was found to be 4. The systematic absences defined the space group alternatives as Pnma and Pn2₁a.

With the b axis of 5·445 Å it was expected that most atoms should be resolved in the (010) projection, and the structure determination was initially confined to the h0l data. A sharpened Patterson function $P(u,w)$ was used to determine a set of parameters for Zr and

Table 3. *Observed and calculated structure amplitudes*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c

Fig.1. Electron density distribution indicated by sections $\varrho_0(x,y,z)$ selected 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. The atom numbering corresponds to Table 4. The levels of atoms are indicated.
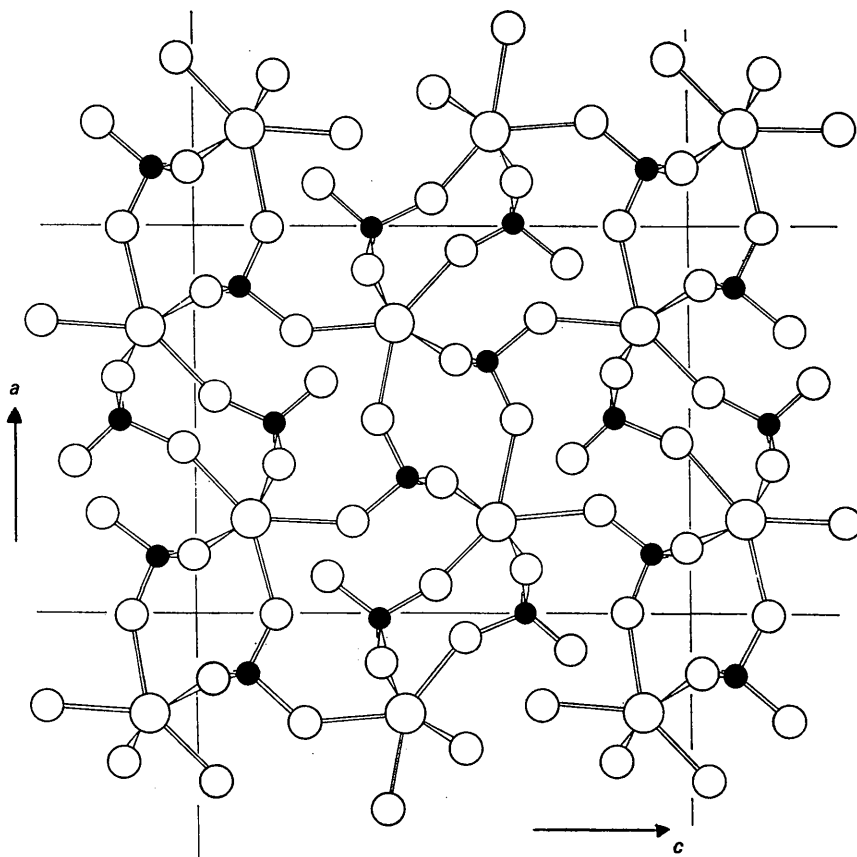
Fig. 2. The structure of α-Zr(SO₄)₂ projected on to (010). Large open circles, zirconium atoms, full black circles, sulphur atoms, medium open circles, oxygen atoms. A bond in the $z=\frac{1}{4}$, or $z=\frac{3}{4}$, plane is represented by a pair of parallel lines.

S(1) and S(2), which were all assumed to be on the mirror planes at $y=\frac{1}{4}$, or $y=\frac{3}{4}$ at the position 4(c), space group $Pnma$. The positions of the oxygen atoms were located by reiteration of electron density and structure factor calculations based on the $h0l$ data. It was found that the sulphate tetrahedra were being viewed exactly down one edge and four oxygen atoms were in positions 4(c) on the mirror planes while the other four were in two pairs in positions 8(d). The stereochemistry of the sulphate group allowed the assignment of y parameters for the oxygen atoms at 8(d) and their positions were confirmed by three-dimensional Fourier syntheses coinciding with, and on either side of, the mirror planes (Fig. 1).

All atom positions, together with individual isotropic temperature factors, were refined by a number of least-squares cycles, with all data included. Refinement was stopped when the shift of each variable was less than one quarter of its standard deviation. No attempt was made to reduce the symmetry to $Pn2_1a$ since the final R value of 11·8% appeared satisfactory for the 285 observed reflexions. A comparison between F_o and F_c is given in Table 3, and the atomic parameters, the temperature factors, and their estimated standard deviations are given in Table 4.

Description and discussion

The structure of α-Zr(SO$_4$)$_2$ viewed in (010) projection is shown in Fig. 2. Each zirconium atom is in sevenfold coordination, with bonds to one oxygen atom of each of seven sulphate tetrahedra forming seven Zr–O–S linkages. The sulphate groups are of two types. One, centred around S(2), is bonded to four zirconium atoms while the other centred around S(1), is bonded to three zirconium atoms and has one terminal oxygen atom. Six of the sulphate groups attached to a zirconium atom act as double bridges to six zirconium

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

E.s.d.'s are given in parentheses.

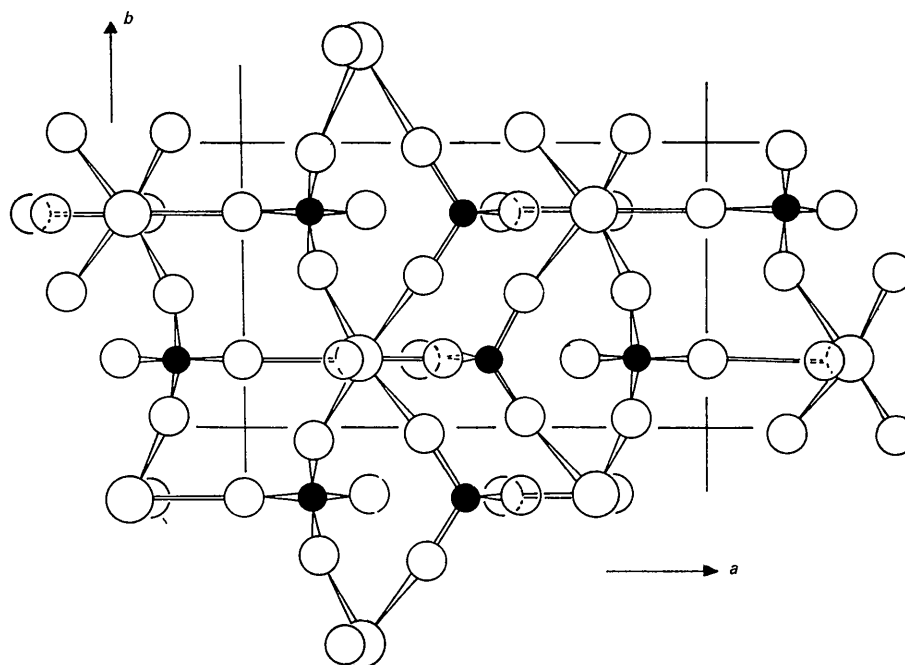|	x	y	z	B
Zr	0·2547 (4)	$\frac{1}{4}$	0·1033 (3)	0·27 (6)
S(1)	0·5009 (12)	$\frac{3}{4}$	0·1554 (9)	0·22 (17)
S(2)	0·3543 (11)	$\frac{1}{4}$	0·4098 (9)	0·07 (16)
O(1)	0·1042 (41)	$\frac{3}{4}$	0·2513 (32)	1·38 (68)
O(2)	0·0720 (39)	$\frac{3}{4}$	0·4665 (29)	0·99 (59)
O(3)	0·2402 (34)	$\frac{1}{4}$	0·3043 (26)	0·39 (48)
O(4)	0·5140 (36)	$\frac{1}{4}$	0·3508 (29)	0·99 (58)
O(5)	0·3929 (24)	0·5323 (50)	0·1573 (19)	0·79 (40)
O(6)	0·3359 (25)	0·4755 (52)	0·4801 (19)	0·54 (41)

Fig. 3. The structure of α-Zr(SO$_4$)$_2$ centred at $x=0$ as viewed along the c axis. Designation of the atoms and bonds is the same as in Fig. 2.

Table 5. *Interatomic distances and angles,*
and their e.s.d.'s

(a) Within the ZrO₇ polyhedron

	Number	Metal–oxygen distance
Zr–O(4)	1	2·13 ± 0·02 Å
–O(3)	1	2·19 ± 0·02
–O(2)	1	2·11 ± 0·02
–O(5)	2	2·03 ± 0·02
–O(6)	2	2·16 ± 0·02
	Average	2·12

	Number	Oxygen–oxygen distance
O(2)–O(6)	2	2·73 ± 0·03 Å
O(2)–O(5)	2	2·60 ± 0·03
O(5)–O(6)	2	2·76 ± 0·03
O(6)–O(6')	1	2·99 ± 0·03
O(5)–O(5')	1	3·07 ± 0·03
O(4)–O(6)	2	2·70 ± 0·03
O(3)–O(5)	2	2·60 ± 0·03
O(3)–O(4)	1	2·58 ± 0·03

	Number	Angle
O(2)–Zr–O(5)	2	78°
O(2)–Zr–O(6)	2	79
O(5)–Zr–O(6)	2	82
O(5)–Zr–O(5)	1	98
O(6)–Zr–O(6)	1	88
O(4)–Zr–O(6)	2	78
O(3)–Zr–O(5)	2	75
O(4)–Zr–O(3)	1	73

(b) Within sulphate groups

	Number	Distance
S(1)–O(1)	1	1·35 ± 0·02 Å
–O(2)	1	1·46 ± 0·02
–O(5)	2	1·51 ± 0·02
	Average	1·46

	Number	Angle
O(1)–S(1)–O(2)	1	114°
O(1)–S(1)–O(5)	2	113
O(5)–S(1)–O(5')	1	104
O(2)–S(1)–O(5)	2	106
	Average	109

	Number	Distance
S(2)–O(3)	1	1·51 ± 0·02 Å
–O(4)	1	1·52 ± 0·02
–O(6)	2	1·46 ± 0·02
	Average	1·49

	Number	Angle
O(3)–S(2)–O(4)	1	105°
O(3)–S(2)–O(6)	2	109
O(6)–S(2)–O(6)	1	115
O(4)–S(2)–O(6)	2	109
	Average	109

atoms giving rise to three pairs of non-equivalent dimeric rings. These rings form sheets normal to [001] (Fig. 3), and are held together by the seventh Zr–O–S linkage which is through the sulphate group that is in contact with four zirconium atoms.

Sevenfold coordination for zirconium has previously been found in α- and γ-$Zr(SO_4)_2$.H_2O. It is more regular in α-$Zr(SO_4)_2$ where there are two pairs of Zr–O bonds of equal length (Table 5). The range of

Zr–O separations is 2·03 to 2·19 Å. Similarly the sulphate groups, while not ideal tetrahedra, are more regular than have previously been found in this series of compounds (Bear & Mumme, 1969c), as both types contain one pair of equal bonds.

α-$Zr(SO_4)_2$ can be prepared under high partial pressures of H_2SO_4 from either the tetrahydrate or the γ- or α-monohydrates (Bear, 1967, 1969). These three hydrates all have layer structures with the water molecules directed out from the layers, presumably providing hydrogen bonding between them. On dehydration, the coordinated water molecules are liberated and the hydrogen bonds are severed but, as the easiest diffusion path would be between the layers, the escaping water molecules are unlikely to disrupt other bonds within the layers. Therefore, although some bonds may have to break and be reformed in order to maintain the sevenfold coordination of the zirconium atom and to link the layers of the parent hydrate into a three dimensional network, it can be expected that there will be a relationship between the structure of the layers of the parent and that of the anhydrate.

It is found, in fact, that a particularly striking relationship exists in the case of the monohydrates. In the structure of α-$Zr(SO_4)_2$ the manner of crosslinking of the sheets of dimeric rings formed normal to the [010] direction (Fig. 2) is similar to the mode of crosslinking of the chains of dimeric rings in a layer of α-monohydrate (Bear & Mumme, 1970b). On the other hand the double sulphate bridging within these sheets in

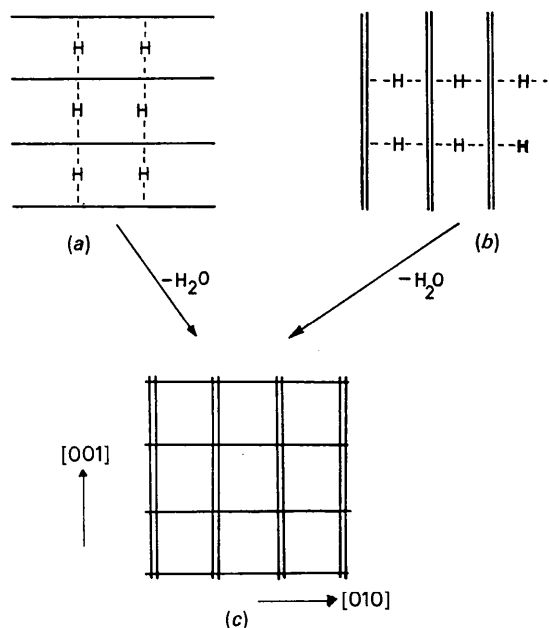Fig. 4. Schematic diagram showing the formation of α-$Zr(SO_4)_2$ from the monohydrates. (a) γ-monohydrate with layers represented by single horizontal lines, (b) α-monohydrate with layers represented by double vertical lines, (c) α-$Zr(SO_4)_2$.

α-Zr(SO$_4$)$_2$ gives rise to a planar network in which each zirconium atom is situated at the intersection of three chains of dimeric rings (Fig. 3), similar to the network found in a layer of γ-monohydrate (Bear & Mumme, (1970a). Thus the structure of α-Zr(SO$_4$)$_2$ may be visualized as being built up from layers of α-monohydrate, lying normal to the [010] direction in α-Zr(SO$_4$)$_2$, which are cross-linked in the [010] direction so that the chains of dimeric rings in the layers of monohydrate are joined to form the planar network of rings in the anhydrate structure. Alternatively the α-Zr(SO$_4$)$_2$ structure may be viewed as being derived from layers of the γ-monohydrate, lying normal to the [001] direction in α-Zr(SO$_4$)$_2$, which are cross-linked in the [001] direction to give the three dimensional network of the anhydrate structure.

It can be seen therefore, that although the structure of α-Zr(SO$_4$)$_2$ can be described as being made up of sheets of dimeric rings held together by Zr–O–S cross-linkages, it is in effect an intermeshing of the two distinct forms of layers found in the γ and α-monohydrates. In the removal of the water molecules from either one of these two monohydrates and the subsequent linking up of the layers, the anhydrate retains in its structure the characteristic form of the layers already present in the parent monohydrate and gains through the cross-linking the characteristic form of the layers of the other monohydrate. This effect is shown diagrammatically in Fig. 4 and supports the argument put forward above that both these transformations proceed with little breaking of the bonds within the layers of the parent compound.

Throughout this investigation we were fortunate to have the support and guidance of the late Dr A. D. Wadsley. His great enthusiasm for all aspects of the solid state was a continuing source of encouragement to us.

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The Crystal Structure of Quinone–Resorcinol Molecular Complex

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The crystal structure of p-benzoquinone–resorcinol molecular complex C$_6$H$_4$O$_2$.C$_6$H$_4$(OH)$_2$ has been determined from three-dimensional X-ray diffraction data. The crystal is orthorhombic, space group Pnca, with $a = 14 \cdot 653$, $b = 5 \cdot 976$, $c = 11 \cdot 529$ Å, $Z = 4$. Quinone and resorcinol molecules are alternatively linked side by side by hydrogen bonds (O$\cdots$O = 2·747 Å) to form infinite molecular chains. These chains are packed plane-to-plane by the charge transfer force to form a molecular sheet. The molecular planes of quinone and resorcinol in a sheet are almost parallel, the perpendicular distance between the molecular planes being about 3·1 Å. Overlap of the six-membered carbon rings of quinone and resorcinol is very small. This pattern of molecular arrangement is very similar to those of quinhydrones reported thus far.

Introduction

This is the third report of a series of crystal structure analyses of the charge transfer complexes between p-benzoquinone (electron acceptor) and hydroxybenzenes (electron donors); the structure of triclinic quinhydrone (β-form) and the refinement of the structures

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of phenoquinone and monoclinic quinhydrone (α-form) have already been reported (Sakurai, 1965, 1968).

Hydroquinone, the donor component of quinhydrones, is a *para* isomer, whereas resorcinol is a *meto* isomer, of dihydroxybenzenes. It will be interesting to see the effect of this isomerism on the molecular arrangements in these complexes. Preparation of crystals of quinone–resorcinol complex was reported by Michaelis & Granick (1944). Charge transfer absorption bands of this complex were observed by Amano (1969).