Sulphate Hydrates of Zirconium: Three Polymorphs of $Zr(SO_4)_2,H_2O$

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THE wide variety of zirconium sulphate hydrates[1-3] is extended by three polymorphs of $Zr(SO_4)_2,H_2O$ which we have prepared. Crystal structure analyses of two of these, designated the γ- and α-forms, show that both have layer structures, but unlike $Zr(SO_4)_2,4H_2O$[3] the layers are built up from dimeric units similar to those present in the hepta- and penta-hydrates. Unit cell parameters and other relevant data for the three phases are given in the Table.

The metastable γ-$Zr(SO_4)_2,H_2O$ is formed by the thermal decomposition of solid $Zr(SO_4)_2,4H_2O$ in air between 120° and 220°.[4] It crystallizes in long blade-like needles suitable for single-crystal diffraction studies when an aqueous solution of $Zr(SO_4)_2,4H_2O$ or a slurry of solid $Zr(SO_4)_2,4H_2O$ in 10M-H_2SO_4 is heated at 120°—140°. Microcrystalline γ-$Zr(SO_4)_2,H_2O$ ages at room temperature to give a second metastable polymorph, the β-phase. The mechanism of this transformation is still being studied, and while single crystals of this β-phase have not yet been obtained, the unit cell dimensions have been provisionally derived from *X*-ray powder data by Ito's procedure.

When heated in a sealed tube, both γ- and β-$Zr(SO_4)_2,H_2O$ give α-$Zr(SO_4)_2,H_2O$, while single crystals of the latter can be grown by equilibration in aqueous (75%, *w/w*) H_2SO_4. These crystals have been observed in two different morphological forms, as well shaped rhombs and as elongated crystals with two sets of pinacoid and well developed terminal faces. The α-form has also been prepared by vapour hydration of α- and β-$Zr(SO_4)_2$ over 75% H_2SO_4 at 120°.

For the structure analyses the initial co-ordinates for the

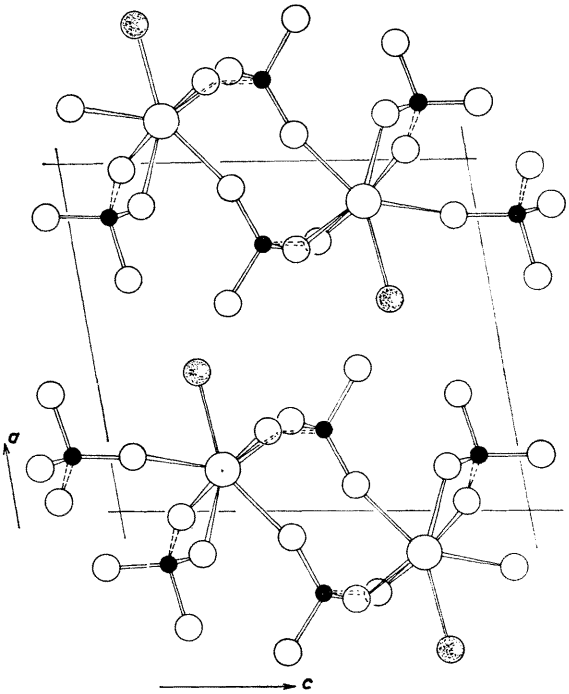


FIGURE 1. *Structure of* γ-$Zr(SO_4)_2,H_2O$. *Small full circles sulphur atoms, large open circles zirconium atoms, medium open circles oxygen atoms, medium stippled circles oxygen atoms of water molecules.*

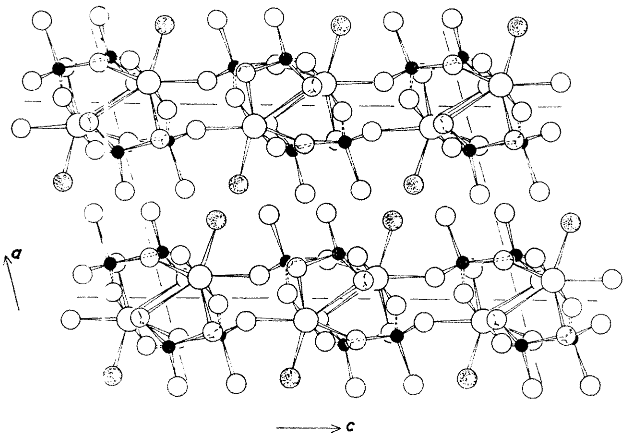
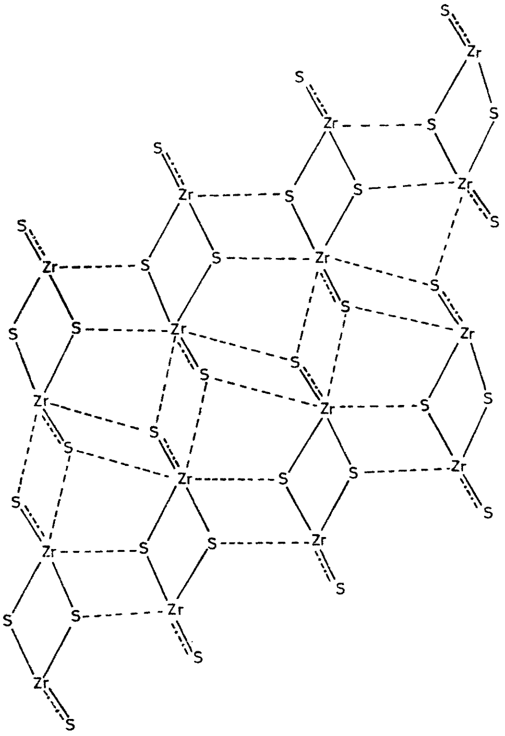
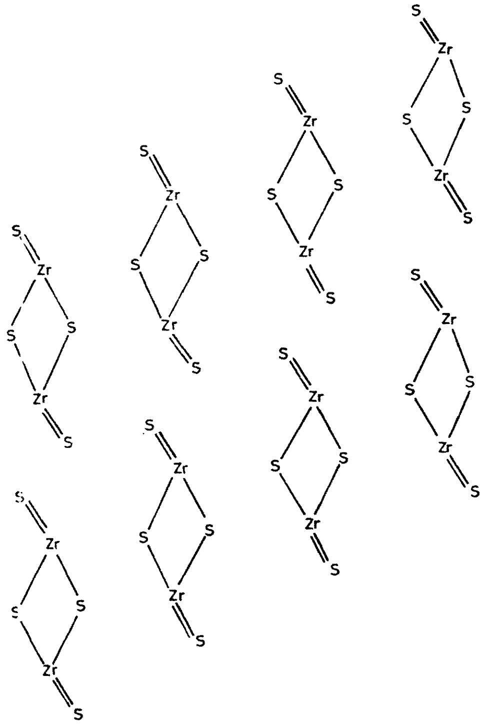


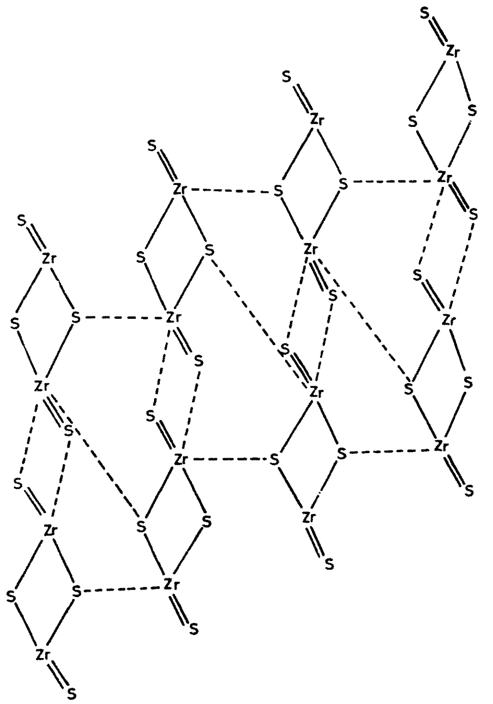
FIGURE 2. *Structure of* α-$Zr(SO_4)_2,H_2O$ *with the notation of Figure* 1.



3(*b*)



3(*a*)



3(*c*)

FIGURE 3. *A schematic representation illustrating the* ***relationship*** *between* α-$Zr(SO_4)_2,5H_2O$ *and layers of the* γ- *and* α-$Zr(SO_4)_2,H_2O$ *structures.*

(*a*) *Original dimeric units of* α-$Zr(SO_4)_2,5H_2O$. (*b*) *A layer of the* γ-$Zr(SO_4)_2,H_2O$ *structure.* (*c*) *A layer of the* α-$Zr(SO_4)_2,H_2O$ *structure. Full lines represent original oxygen linkages in the dimers; dots and dashes, broken linkages in the dimers; and dashes, new linkages between dimers.*

Crystallographic data for zirconium monohydrates

Compound	Symmetry and space group	*a*	*b*	*c*	α	β	γ	Volume (Å^3)	Density g.cm.$^{-1}$	*Z*
γ-Zr(SO$_4$)$_2$,H$_2$O	Triclinic, $P\bar{1}$	7·89	5·21	8·96	95·2	99·8	109·2	339	2·93	2
β-Zr(SO$_4$)$_2$,H$_2$O	Triclinic	7·86	5·34	8·97	91·0	100·7	109·4	348		
α-Zr(SO$_4$)$_2$,H$_2$O	Monoclinic, $P2_1/c$	7·32	8·54	11·82	90·0	106·0	90·0	710	2·84	4

zirconium and sulphur atoms in the γ- and α-forms were obtained from the three-dimensional Patterson functions, and all the light atoms, other than hydrogen, were located by three-dimensional Fourier and difference Fourier syntheses. Refinement was performed by least-squares with the matrices inverted by the block-diagonal approximation and individual isotropic temperature factors assigned to each atom (except hydrogen). *R*-Value for γ-Zr(SO$_4$)$_2$,H$_2$O 12·6%, 708 reflections; for α-Zr(SO$_4$)$_2$,H$_2$O 13·1%, 807 reflections.

The structures of γ- and α-Zr(SO$_4$)$_2$,H$_2$O, viewed in projection are shown in Figures 1 and 2 respectively. In γ-Zr(SO$_4$)$_2$,H$_2$O each zirconium atom is in seven-fold co-ordination, six ligands being the oxygens of six attached sulphate tetrahedra, and the seventh being the oxygen of the hydrate group. Sulphate groups bridge the zirconium polyhedra in such a way that each zirconium atom is in contact with six sulphate groups, and each sulphate group is in contact with three zirconium polyhedra. This arrangement [Figure 3(b)] provides for the double bridging of sulphate groups between zirconium atoms and for the building up of each layer along (010) and (001). Hydrogen bonding may be assumed to be between the co-ordinated water molecules and the free ligands of the sulphate groups, and presumably serves to hold the layers together.

Each zirconium atom in α-Zr(SO$_4$)$_2$,H$_2$O is also in seven-fold co-ordination, with six bonds to sulphate tetrahedra and one to a water molecule. Within the layers the sulphate groups fall into two categories: those which are in contact with three zirconium atoms and those which are in contact with only two but form a bidentate complex with one of these. This arrangement results in the formation of "strings" of doubly bridged zirconium polyhedra extending along (010), which are joined by S–O–Zr linkages directed along (100) to form the layers [Figure 3(c)]. Once again hydrogen bonding between the co-ordinated water molecules and the free ligand of one of the sulphate groups presumably holds the layers together.

In both cases the structures are built up of "condensed" dimeric units much the same as those previously reported for the zirconium sulphate hepta- and penta-hydrates.[1] Figure 3 illustrates the relationship between isolated dimers of α-Zr(SO$_4$)$_2$,5H$_2$O and the layers in the γ- and α-monohydrates. The zirconium co-ordination in the real dimers is eight-fold dodecahedral, with four oxygen atoms from the neighbouring sulphate groups, and four co-ordinated water molecules, while in the γ- and α-monohydrates it is seven-fold, with only one co-ordinated water molecule in each case.

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