Dimeric Sulphate Hydrates of Zirconium: $Zr(SO_4)_2,7H_2O$ and α-$Zr(SO_4)_2,5H_2O$

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CRYSTAL structure analyses of a new hydrate of zirconium sulphate, $Zr(SO_4)_2,7H_2O$, and of the previously reported α-$Zr(SO_4)_2,5H_2O$ show that both are built up from similar dimeric groups and can best be represented by the formulae $[Zr_2(SO_4)_4(H_2O)_8],6H_2O$ and $[Zr_2(SO_4)_4(H_2O)_8],2H_2O$ respectively.

The new hydrate of zirconium sulphate, $Zr(SO_4)_2,7H_2O$, has been prepared by crystallization, at *ca* 0°, from saturated solutions of any one of the anhydrous or pentahydrate phases[1] or from solutions of the tetrahydrate, which have been supersaturated by concentration under vacuum; the vapour pressure curves of the hydrates

Crystallographic data for zirconium sulphate hydrates

Compound	*a*	*b*	*c*	α	β	γ	Volume (Å^3)	Density	*Z*
$Zr(SO_4)_2,7H_2O$	12·04	6·36	8·28	93·0	92·4	95·9	629	2·25 ± 0·05	2
α-$Zr(SO_4)_2,5H_2O$	11·89	6·17	7·56	106·5	95·7	104·6	507	2·41 ± 0·03	2
$Zr(SO_4)_2,4H_2O$	25·92	5·53	11·62	90·0	90·0	90·0	1666	2·80	8

(Figure 1) explain the need for supersaturation of the tetrahydrate.

The heptahydrate is metastable under ambient conditions being converted directly into $Zr(SO_4)_2,4H_2O$. It is stable, however, in contact with its saturated solution near 0° but decomposes either to α-$Zr(SO_4)_2,5H_2O$, if dried over P_2O_5, or to $Zr(SO_4)_2,4H_2O$, if equilibrated in atmospheres of higher $P(H_2O)$, up to that of the saturated solution vapour pressure of β-$Zr(SO_4)_2,5H_2O$ (Figure 1).

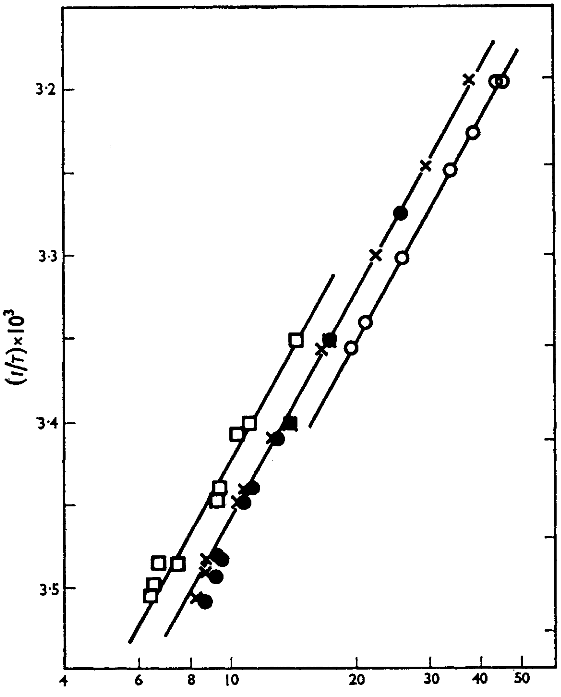

FIGURE 1. *Saturated solution vapour pressures of* $Zr(SO_4)_2$ *hydrates*; ○, $Zr(SO_4)_2,4H_2O$; ×, α-$Zr(SO_4)_2,5H_2O$; □, β-$Zr(SO_4)_2,5H_2O$; ●, $Zr(SO_4)_2,7H_2O$.

The heptahydrate cannot be dried at very low $P(H_2O)$, but preparations obtained by vapour hydration of β-$Zr(SO_4)_2,5H_2O$ to constant weight over 35—38% H_2SO_4 (w/w), or by evaporation of saturated solutions of the new phase over acid of similar concentration, gave compositions containing between 7·0 and 7·5 moles of water per mole of $Zr(SO_4)_2$. Because the *X*-ray crystal structure analysis of the compound gave evidence of only 7 molecules of water, it has been concluded that the new phase is a heptahydrate of zirconium sulphate.

X-Ray data for the heptahydrate were collected at *ca.* −70°. Crystals of $Zr(SO_4)_2,7H_2O$ and α-$Zr(SO_4)_2,5H_2O$ are both triclinic with the space group $P\bar{1}$. The unit-cell parameters and related information for the two compounds are listed in the Table together with those for $Zr(SO_4)_2,4H_2O$.[2] In both cases the initial co-ordinates for the zirconium and sulphur atoms were obtained from three dimensional Patterson syntheses, and all the light atoms, other than hydrogen, were located by three-dimensional Fourier and difference Fourier syntheses. Refinement was by least-squares with the matrices inverted by the block diagonal approximation and individual isotropic temperature factors assigned to each atom (except hydrogen). The final *R* value for the heptahydrate was 15·9% with 1214 reflections, while that for the pentahydrate was 13·4% with 867 reflections.

The structures of $Zr(SO_4)_2,7H_2O$ and of α-$Zr(SO_4)_2,5H_2O$, viewed in projection are shown in Figures (2a and b) respectively. The co-ordination of the zirconium atom in each case is eightfold forming a dodecahedron. The main structural unit which is common to the two compounds consists of two of these zirconium co-ordination polyhedra and four tetrahedral sulphate groups. These units are joined together through the bonded and non-bonded water molecules. The overall composition of both phases, and the reasonable assumption that the atoms constituting the sulphate groups are oxygens, make it possible to determine unambiguously the position of all the water molecules in the two structures. In $Zr(SO_4)_2,7H_2O$ four are co-ordinated to each zirconium atom while the remaining six are non-bonded and lie in sheets along (001). In α-$Zr(SO_4)_2,5H_2O$ (Figure 2b) there are again eight bonded but only two non-bonded water molecules in the unit cell.

The loss of two of the three non-bonded water

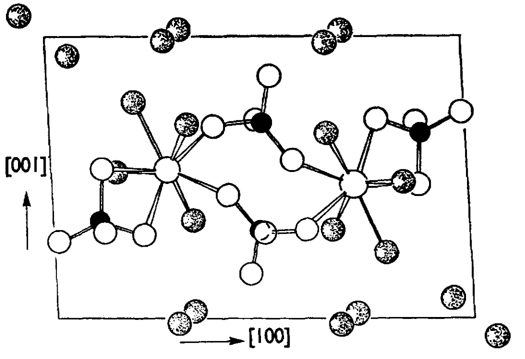

FIGURE 2a. *Structure of* $Zr(SO_4)_2,7H_2O$.

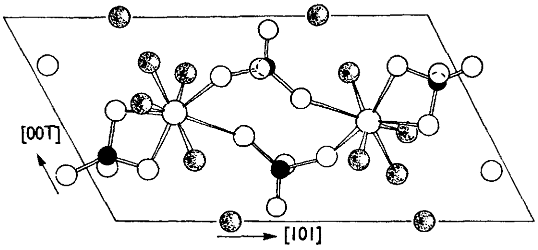

FIGURE 2b. *Structure of* α-$Zr(SO_4)_2,5H_2O$; Large open circles, zirconium atoms; ●, sulphur atoms; Medium open circles, oxygen atoms; ◍, water molecules.

molecules during decomposition of the heptahydrate over P_2O_5 results in the formation of the pentahydrate, while removal of the third, during equilibration of the latter phase, is accompanied by a complete reconstruction of the molecular unit to give the tetrahydrate. Thus the stability of both dimeric structures evidently depends upon the hydrogen bridging between the non-bonded water molecules and adjacent layers of $Zr_2(SO_4)_4(H_2O)_8$ groups. Bonding between dimers in the [010] direction is probably again due to hydrogen bridging, this time through the bonded water molecules. This aspect of the structures will be discussed in detail elsewhere.

The similarity in the saturated solution vapour pressures of the two compounds (Figure 1) and the fact that these phases not only crystallize from near-saturated solutions of the equilibrium anhydrous phase[3] but also from supersaturated solutions of the tetrahydrate suggest strongly that the $Zr(SO_4)_4(H_2O)_8$ molecular group is the preferred species in concentrated solutions of zirconium sulphate.

The structure of β-$Zr(SO_4)_2,5H_2O$ is also being investigated and will be reported in due course. We acknowledge helpful discussion with Dr. A. D. Wadsley.

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