Crystal Structure of Dicopper Octafluorozirconate Dodecahydrate, $Cu_2ZrF_8,12H_2O$

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IN order to determine the stereochemistry of Zr in the hydrated fluorozirconate complexes,[1] we have resolved the structure of $Cu_2ZrF_8 12H_2O$ by *X*-ray methods. Crystals of $Cu_2ZrF_8,12H_2O$ were prepared by Marignac's method,[2] from a solution of $Cu_3Zr_2F_{14},16H_2O$ and an excess of CuF_2 in H_2O. An *X*-ray study, using Cu-K_α radiation (λ = 1·5418 Å), led to the following results:

$Cu_2ZrF_8,12H_2O$, M = 586·49, monoclinic, a = 15·895 ± 0·013, b = 9·652 ± 0·01, c = 11·921 ± 0·012 Å, β = 121° 47′ ± 15′, U = 1555·77 Å^3, D_o = 2·46, Z = 4, D_c = 2·50, space group $C2/c$ (No. 15).

The intensities of 774 independent non-zero reflexions were recorded by film techniques using a Weissenberg camera and Mo-K_α radiation. Intensities were measured with a microdensitometer. The crystal used was a cylinder of axis [010], having a mean radius of 0·15 mm. (μ = 14·41 cm.$^{-1}$). Absorption corrections were made using the tables of Bond.[3] A trial structure, determined from the three-dimensional Patterson function, was refined by isotropic, full-matrix

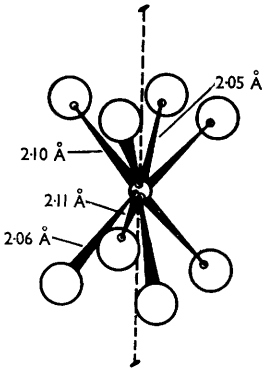

FIGURE 1

least-squares analysis to an R-value of 0·090.[4] Allowance was made for the anomalous dispersion of copper and zirconium. Standard deviations of Zr–F and Cu–H_2O distances are estimated as 0·02 and 0·03 Å.

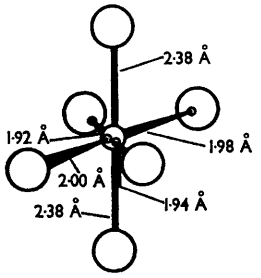

FIGURE 2

Each zirconium atom is eight-co-ordinated to fluorine atoms, the co-ordination polyhedron being a square antiprism. The mean value of the Zr–F distances is 2·08 Å. Figure 1 illustrates the $[ZrF_8]^{4-}$ anion and gives individual Zr–F distances.

The copper atoms are octahedrally co-ordinated to six water molecules. The octahedron presents an orthorombic distortion as in $Cu(NH_4)_2(SO_4)_2$, $6H_2O$;[5] the three mean Cu–H_2O distances are 1·93, 1·99, and 2·38 Å. Figure 2 illustrates this cation and gives the individual Cu–H_2O distances.

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