X-Ray Crystal Structure of β-UOF_4

By JOHN C. TAYLOR and PAUL W. WILSON*
(*Chemical Technology Division, AAEC, Private Mail Bag, Sutherland, 2232, N.S.W. Australia*)

Summary β-UOF_4 is tetragonal and is isostructural with β-UF_5, having, around each uranium atom, a pentagonal bipyramid, which consists of six fluorine atoms and one oxygen atom.

THE preparation of α-UOF_4 has only recently been described.[1,2] A second crystal form of UOF_4, β-UOF_4, which is isostructural with β-UF_5,[3] has now been prepared by slow growth of crystals from a solution of UOF_4 in anhydrous

hydrogen fluoride. The crystals were yellow and very hygroscopic.

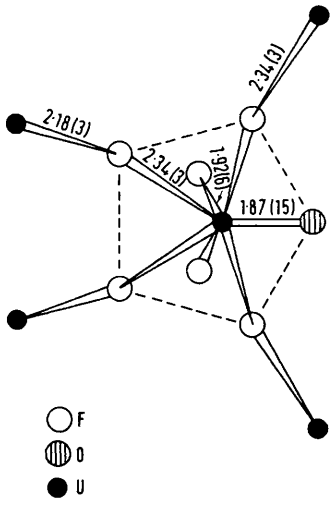

FIGURE. Structure of β-UOF_4 as seen down the *c*-axis.

The crystal used for structure analysis was coated with a thin film of Kel-F oil and placed in a glass capillary. β-UOF_4 is tetragonal, space group $I\bar{4}2d$ (D_{2d}^{12}; No 122), $a = 11{\cdot}4743(11)$, $c = 5{\cdot}2043(5)$ Å, $U = 685{\cdot}20$ Å^3, $D_m = 6{\cdot}40$ g cm^{-3}, $Z = 8$, $M = 330{\cdot}02$, μ(Mo-K_α) = 580 cm^{-1}.

The intensities of 637 independent reflexions in the range $0 < 2\theta < 57°$ were measured with an automatic *X*-ray diffractometer with Mo-K_α radiation. After averaging equivalents, 272 independent reflexions remained for structure analysis. The data were corrected for absorption by the crystal. Since the above cell dimensions were close to those of β-UF_5, the starting co-ordinates for a least-squares refinement were those given by Zachariasen[3] for β-UF_5. Although oxygen could not be distinguished from fluorine from the *X*-ray data alone, symmetry requires the oxygen atom to be in the F(1) position of the β-UF_5 structure, in positions 8(d) as shown in the Figure. There may, however, be some O,F disorder. The weighted and unweighted *R*-factors on F were 0·089 and 0·110.

The configuration around the uranium atom is a pentagonal bipyramid of six fluorine atoms and one oxygen atom, and the observed interatomic distances are shown in the Figure. This appears to be the first such arrangement observed for uranium. The analysis has thus confirmed the existence of a β-UF_5-type structure for β-UOF_4. Since the i.r. spectrum of β-UOF_4 (ν_{max} 880, 655, and 550 cm^{-1}) is similar to that of α-UOF_4,[1,2] the crystal structure and i.r. spectrum are consistent.

(*Received, 24th September* 1973; *Com.* 1335.)

[1] P. W. Wilson, *J. Inorg. Nuclear Chem.*, 1973, **35**, in the press.
[2] P. W. Wilson, *J.C.S. Chem. Comm.*, 1972, 1241.
[3] W. H. Zachariasen, *Acta Cryst.*, 1949, **2**, 296.