

The observed O–H distance is consistent with the curve given by Pimentel & McClellan (1971) relating O–H distance as a function of O···O distance. In addition, the O–H and O···O distances are very close to recent neutron results presented (Fig. 1.4) by Speakman (1972).

A neutron study of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Curry & Jones, 1971) showed that HPO_4^{2-} ions are linked together by hydrogen bonds forming a chain $\cdots\text{HOPO}_3^{2-}\cdots\text{HOPO}_3^{2-}\cdots$. The O···O distance in this chain is 2.678 Å, which is significantly longer than the distance of 2.560 Å for the HPO_4^{2-} dimers in SnHPO_4 .

Some characteristics of the HPO_4^{2-} ion have been tabulated by Baur (1974). These were obtained from nine published structures in which the dimeric configuration does not occur. Baur gives an average value of 1.590 Å for the P–O(H) distance compared to our value of 1.566 Å. This is to be expected because the H atom in SnHPO_4 is participating in a moderately short, strong hydrogen bond. Baur's data show that P–O(H) distances shorten even more (1.516 Å) when the H is involved in a symmetrical hydrogen bond. Thus, the O···O distance of 2.560 Å, the O–H···O angle of 178.1°, and the P–O(H) distance of 1.566 Å in SnHPO_4 all indicate that the asymmetric hydrogen bond in dimeric $(\text{HPO}_4^{2-})_2$ is quite strong.

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Single-Crystal X-ray Study of β -Uranium Pentafluoride. The Eight Coordination of U^{V}

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Abstract. β - UF_5 , tetragonal, $I\bar{4}2d$; $a=11.456$ (2), $c=5.195$ (1) Å; $Z=8$. The structure of β - UF_5 has been solved by a three-dimensional X-ray diffraction study, with counter techniques. Rather than seven-coordinated as originally proposed on the basis of powder data, the U is found to be eight-coordinated, with coordination geometry intermediate between a dodecahedron and a square antiprism.

Introduction. Isolated seven-coordinated fluoride anions of the d transition elements are well established in NbF_7^{2-} and TaF_7^{2-} by X-ray (Hoard, 1939) and neutron (Brown & Walker, 1966) diffraction. In these K_2MF_7 compounds the anion coordination polyhedron is that of a capped trigonal prism [but distorted towards a capped octahedron (Penneman, Ryan & Rosenzweig, 1973)]. In $(\text{NH}_4)_3\text{ZrF}_7$ there is evidence for a

pentagonal bipyramid coordination unit (Hurst & Taylor, 1970), first proposed for this compound and for K_3UF_7 by Zachariassen (1954*a,b*). In both these latter structures there is disorder.

It is interesting to note that there are several actinide elements with radii relatively larger than the d elements mentioned, but whose structures are thought to contain coordination polyhedra of both the above types (see Penneman *et al.*, 1973). However, to date there are no single-crystal studies to substantiate such geometry. Thus, when crystals of β - UF_5 were prepared the opportunity of establishing one of these, *i.e.* the pentagonal bipyramid geometry for an actinide bound only to fluorine, arose. The dioxopentafluorouranyl case with five equatorial fluorines is well established (Zachariassen, 1954*a*). The structure of β - UF_5 had been deduced by Zachariassen (1949) and has remained a

curiosity in that it is the only pentavalent uranium fluoride compound for which the pentagonal-bipyramidal geometry (our interpretation) has been suggested.

Pale-green crystals of β -UF₅ resulted when a solution of UF₆ in anhydrous HF was allowed to stand for several weeks at room temperature under fluorescent illumination in a closed Kel-F tube.

A powder pattern from a single crystal of β -UF₅ agreed exactly with the published data for tetragonal β -UF₅ and with data from a bulk preparation of analyzed β -UF₅. Optical examination of the crystals confirmed uniaxial symmetry. Typical shapes are prisms elongated along *c* and truncated tetragonal pyramids, the latter giving a centered uniaxial (+) optic figure. The crystals are pale-green in bulk, at the usual size of 100 μ m in this preparation. They are pleochroic (pale yellow-green to green) and cleave readily, perpendicular to *c*.

Slow decomposition, resulting in a mottled appearance, is observed when the crystals are left under mineral oil and exposed to room air. Catastrophic decomposition occurs when unprotected crystals are exposed to moisture. Single crystals immobilized by fluocarbon grease in a sealed glass capillary were stable for many days. A crystal of approximate dimensions 0.086 \times 0.086 \times 0.130 mm was selected for single-crystal investigation (mounted on the *c* axis) and the space group was confirmed by precession techniques. With the exceptions noted below, the cell parameters, room-temperature intensity measurements, data reduction and structure refinements were carried out as reported previously (Ryan & Swanson, 1974). Data were collected for *h, k, \pm l* and $2\theta \leq 60^\circ$, resulting in 466 reflections, for which $I \geq 3\sigma(I)$ after averaging equivalent observations. Although the data were corrected for absorption (Coppens, de Meulenaer & Tompa, 1967; with a modification of L. Templeton), the calculated transmission factors are, in general, small and comparison of equivalent reflections resulted in an average deviation from the mean of 3.9% based on the structure factors after application of the absorption correction. Least-squares refinements were carried out

with neutral-atom scattering factors (Cromer, 1976) and anomalous scattering corrections for U (Cromer & Liberman, 1970).

Initial refinements confirmed the position of the U atom [8(*d*)] and of two of the three crystallographically independent F atoms proposed by Zachariassen. The third F atom was located by Fourier techniques and refinement, including anisotropic thermal motion for the U atom and a secondary extinction parameter, con-

Table 1. *Crystallographic data*

| | |
|-------------------------|---|
| Diffractometer: | Picker FACS-1 |
| Radiation: | Mo <i>K</i> α , graphite monochromator |
| Data collection: | 2° θ -2 θ scans |
| Background: | 20 s at each end of the scan |
| Bounding planes: | {100}, {00 $\bar{1}$ } and \sim {021} |
| Extinction coefficient: | 709 cm ⁻¹ |

Table 2. *Atomic coordinates ($\times 10^4$) and temperature factors*

β are reported as $\beta \times 10^4$ and defined by:
 $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{23}kl)]$.

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> |
|----------------|--------------|--------------|--------------|----------|
| U | 876 (1) | 2500 | 1250 | * |
| F(1) | 391 (20) | 1686 (21) | 4389 (44) | 2.2 (4) |
| F(2) | -2736 (27) | 2500 | 1250 | 2.3 (5) |
| F(3) | 1456 (18) | 757 (20) | 36 (39) | 1.6 (3) |
| * β_{11} | β_{22} | β_{33} | β_{23} | |
| 7 (1) | 9 (1) | 157 (6) | -21 (4) | |

Extinction parameter, $g = 6 (2) \times 10^{-6}$.

Table 3. *Selected distances (\AA) within the inner coordination sphere of uranium*

| | | | |
|-----------------------|-----------|-----------|----------|
| U-F(1) ^(a) | 1.96 (2) | U-F(3) | 2.32 (2) |
| U-F(2) | 2.285 (4) | U-F'(3) | 2.20 (2) |
| F(1)-F(2) | 2.53 (2) | F(2)-F(2) | 2.65 (1) |
| F(1)-F(3) | 2.66 (3) | | |
| F(1)-F(3) | 2.68 (3) | F(3)-F(3) | 2.74 (4) |
| F(1)-F(3) | 2.78 (3) | F(3)-F(3) | 2.66 (3) |

(a) See Fig. 1.

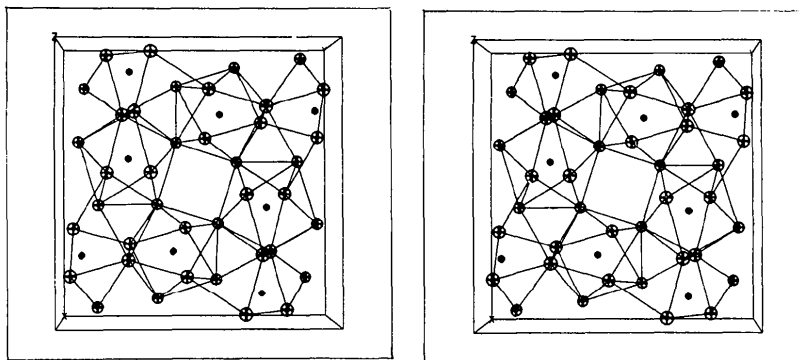


Fig. 1. Stereo view of the contents of the unit cell.

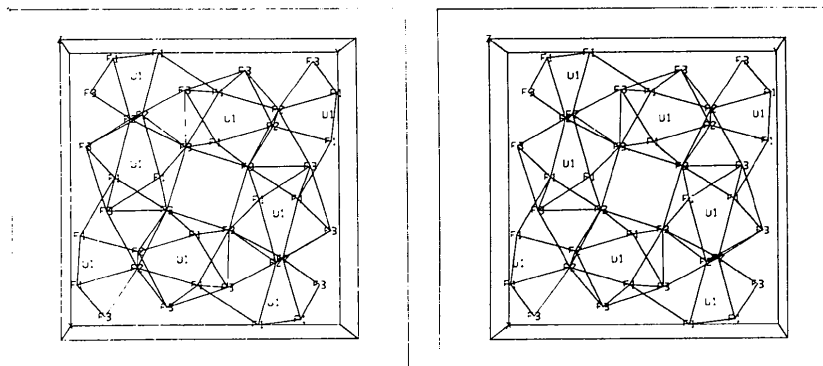


Fig. 2. Stereo view of the U coordination polyhedron.

verged to a crystallographic R value of 0.073.* All the features of a final difference map could be rejected due to their proximity to existing atom positions. Crystallographic data are given in Table 1, atomic and thermal parameters in Table 2, and selected bond lengths in Table 3.

Discussion. A stereo view of the contents of the unit cell is shown in Fig. 1. The U atom is seen to be eight-coordinate with a coordination polyhedron which may be described as intermediate between the idealized dodecahedral and square-antiprism polyhedra. The observed polyhedron (Fig. 2) is similar to that found in many eight-coordinate U structures (see Penneman *et al.*, 1973).

Finally, we notice that the terminal U–F(1) bond distance of 1.96(2) Å is the shortest such distance to be reported for a uranium(V) complex, although it is within about 2σ of the predicted U–F distance of 2.01 Å obtained

from bond length–bond strength relationships. (Zachariasen, 1954*b*; Zachariasen & Plettinger, 1959)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31940 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.