Braun, P. B., Hornstra, J., Knobler, C., Rutten, E. W. M. & Romers, C. (1973). *Acta Cryst.* **B29**, 463–469.
Bucourt, R. (1964). *Bull. Soc. Chim. Fr.* pp. 2080–2091.
Buys, H. R. & Geise, H. J. (1968). *Tetrahedron Lett.* **54**, 5619–5624.
Drew, M. G. B., Templeton, D. & Zalkin, A. (1969). *Acta Cryst.* **B25**, 261–267.
Geise, H. J., Buys, H. R. & Mijlhoff, F. (1971). *J. Mol. Struct.* **9**, 447–453.
Ingen Schenau, A. D. van, Verschoor, G. C. & Romers, C. (1974). *Acta Cryst.* **B30**, 1686–1694.
Johnson, C. K. (1967). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
Karle, I. L. & Karle, J. (1966). *Acta Cryst.* **21**, 860–868.
Kennard, O., Isaacs, N. W., Motherwell, W. D. S., Coppola, J. C., Wampler, D. L., Larson, A. C. & Watson, D. G. (1971). *Proc. Roy. Soc.* **A325**, 401–436.
Kitaigorodsky, A. I. (1961). *Organic Chemical Crystallography*, p. 99. New York: Consultants Bureau.
Knobler, C., Romers, C., Braun, P. B. & Hornstra, J. (1972). *Acta Cryst.* **B28**, 2097–2103.
Motherwell, W. D. S. & Isaacs, N. W. (1971). *Acta Cryst.* **A27**, 681–682.
Romers, C., Altona, C., Jacobs, H. J. C. & de Graaff, R. A. G. (1974). *Specialist Periodical Reports*, *Terpenoids and Steroids*, Vol. 4. London: The Chemical Society.
Romers, C., de Graaff, R. A. G., Hoogenboom, F. J. M. & Rutten, E. W. M. (1974). *Acta Cryst.* **B30**, 1063–1071.
Sanders, G. M., Pot, J. & Havinga, E. (1969). *Fortschr. Chem. org. Naturst.* **27**, 131–157.
Tables of Interatomic Distances and Configuration in Molecules and Ions (1965). Special Publication No. 18. London: The Chemical Society.

Acta Cryst. (1974). **B30**, 1701

The Structures of Fluorides. VIII. The Crystal Structure of β-Uranium Oxide Tetrafluoride

By J. C. Taylor and P. W. Wilson

AAEC Research Establishment, Private Mail Bag, Sutherland, New South Wales, Australia 2232

(*Received* 7 *January* 1974; *accepted* 12 *February* 1974)

UOF_4 is the first actinide oxide tetrahalide to be characterized. β-UOF_4, formed by slow crystallization from HF solution, is tetragonal, with $a=11\cdot4743$ (11) and $c=5\cdot2043$ (5) Å, and the space group $I\bar{4}2d$ (D_{2d}^{12}), and is of the β-UF_5 structure type. The structure was refined by a least-squares analysis with 272 independent $F(hkl)$ values collected on an automatic single-crystal X-ray diffractometer, and the final weighted and unweighted R values were 0·089 and 0·110. The U and O atoms are in positions $8(d)$ with $x_U=0\cdot0861$ (2) and $x_O=0\cdot249$ (12). The fluorine atoms F(1) and F(2) are at [0·142 (2), 0·077 (2), 0·003 (7)] and [0·036 (4), 0·181 (3), 0·442 (11)], in positions $16(e)$. The configuration around the uranium is a pentagonal bipyramid, the oxygen atom being in the pentagonal ring; this is the first example of this type of coordination polyhedron for uranium. The four F(1) atoms in the ring form asymmetric bridges to neighbouring uranium atoms. The F(2) and O atoms are terminal, and there is possible O, F disorder in the terminal positions.

Introduction

Recently, the preparation of the important compound UOF_4 was described (Wilson, 1973). Although transition metal oxide tetrafluorides of the second and third transition series such as $MoOF_4$, WOF_4 and $ReOF_4$ have been prepared and their structures determined, UOF_4 is the first actinide oxide tetrahalide to be discovered. Because of the uniqueness of this compound, it was felt that a study of its structure would be interesting and could possibly reveal new bonding patterns for uranium.

Preparation

The crystals of UOF_4 were grown from solution in anhydrous HF and took several months to grow sufficiently large for analysis. The starting UOF_4 powder was prepared as described previously (Wilson, 1973).

The crystals grown were orange-yellow and were very hygroscopic. Some of these crystals were ground, and a Debye–Scherrer powder photograph was taken with Cu $K\alpha$ radiation. The pattern was similar to that of β-UF_5 reported by Zachariasen (1949), but differed from the powder pattern of the initial UOF_4 precipitate. Thus the larger crystals appeared to be a second polymorphic form of UOF_4. Because of their structural similarity to β-UF_5, the larger UOF_4 crystals, grown slowly from HF solution, were designated β-UOF_4, while the UOF_4 as prepared in the original way (Wilson, 1973) was designated α-UOF_4.

In view of the above difference between the powder patterns of the starting material and the large crystals, there was initially some doubt if the crystals were actually UOF_4. It was clearly demonstrated that the compound was UOF_4 by the subsequent crystal study, and the similarity of the infrared spectra of the crystals and the UOF_4 starting product (Wilson, 1973), as outlined later.

Several β-UOF_4 crystals were mounted in a 0·063 cm diameter quartz capillary in a dry-box; the crystals were separated by 0·2 cm intervals. Mounting of more than one crystal reduced hydrolysis and permitted some choice in the selection of a suitable crystal for data collection.

To reduce hydrolysis further and to cause adhesion to the capillary wall, the crystals were coated with a thin film of dry Kel-F oil before being mounted.

Crystal data and intensity-data collection

Generally, the crystals did not have well defined faces. The crystal chosen for the X-ray data collection gave extinction positions in the polarizing microscope and was roughly square-pyramidal in shape with [001] normal to the pyramid base. The base was about $0{\cdot}018\times0{\cdot}018$ cm and the height 0·018 cm. The base adhered to the tube wall, with [100] approximately along the length of the tube. For the purpose of absorption correction, the shape was approximated with {001}, {401} and {221} faces; the calculated crystal volume was 12×10^{-7} cm^3.

Rotation and (0–2) layer Weissenberg photographs taken with Cu $K\alpha$ radiation about the a axis indicated a body-centred tetragonal cell, with $a=11{\cdot}45$ and $c=5{\cdot}18$ Å, and reflexions hhl present for $2h+l=4n$. Thus both the cell dimensions and symmetry seemed analogous to β-UF_5 (Zachariasen, 1949), the latter compound having the cell dimensions $a=11{\cdot}4729$ (20), $c=5{\cdot}2084$ (10) Å and the space group $I\bar{4}2d$ (D_{2d}^{12}). Although the reflexions persisted to high angles, indicating a low temperature factor of the uranium atom, the low-angle reflexions on the films were all weak, indicating high absorption of the Cu $K\alpha$ radiation by the glass and oil. The analysis was thus continued with the harder Mo $K\alpha$ radiation, on a computer-controlled four-circle X-ray diffractometer equipped with a solid-state detector. After alignment of the crystal, the extinctions for D_{2d}^{12} were carefully checked by measuring intensities at the reciprocal lattice positions which should be extinguished by the above space group up to $2\theta=20°$. No significant intensity above background was found at any of these positions. A similar search failed to produce any evidence for doubling of the short c axis. Thus, the β-UOF_4 cell was in agreement with the β-UF_5 cell.

All hkl intensities in the range $5°<2\theta<50°$ were measured at least twice in different, equivalent reciprocal lattice locations with ω scans of range 2°. The reflexions were broad in ω. The counting time per reflexion was about 9 min. Most of the reflexions in the range $50°<2\theta<57°$ were also measured (once only). The reflexions were weak and the highest integrated intensity, corrected for background, was 25 000 counts. A standard, 600, was measured every 20 reflexions. Slow, but significant sliding movements of the crystal within the capillary were detected over 24 h periods by observing the standard; consequently it was necessary to redetermine the UB orientation matrix every day. No decomposition of the crystal during the experiment was observed. In all, 637 intensities were measured, and each intensity was normalized to the preceding standard.

The reflexions were sorted with the program *VARISORT* into sets of equivalents, and corrected for absorption with the program *DRACULA* (Elcombe, Cox, Pryor & Moore, 1971), the linear absorption coefficient μ(Mo $K\alpha$) being 580 ± 30 cm^{-1}.

Absorption by the crystal was high, as the transmission factors A^{-1} lay between 0·009 and 0·039. Thus the absorption problem in the present analysis was very severe. Corrections were not applied for the absorption by the capillary walls and oil film. After the crystal absorption corrections were applied, sets of equivalent reflexions were averaged, giving 272 independent $F_o(hkl)$ values. The $F_o(hkl)$ values of 12 weak reflexions, where the average background-corrected intensity was slightly negative, were set at zero by the program. These were considered 'unobservably weak' and their $F_o(hkl)$ values were reset during the following least-squares refinement to the mean of the $F_c(hkl)$ values for those reflexions. Standard deviations $\sigma[F_o(hkl)]$ were obtained as follows:

$$\begin{aligned} Q(hkl)&=AI\\ \sigma^2(Q)&=\sigma_1^2+\sigma_2^2\\ \sigma_1&=\sigma(I)A\\ \sigma_2^2&=(10+0{\cdot}05I)^2A^2+I^2\sigma^2(A) \end{aligned}$$

where $Q(hkl)$ was the absorption-corrected intensity, σ_1 was based on the counting statistics and σ_2 was introduced to allow for systematic, noncounting errors. The computed errors may be underestimated for some low-angle reflexions with the largest A values.

Accurate cell dimensions were obtained by identifying high-angle reflexions on a powder photograph taken with a 114·6 mm diameter Philips powder camera and Cu $K\alpha$ radiation. Thirty-six 2θ values in the range 62–166° were measured, and, after correction for shrinkage, lattice constants obtained with the least-squares program of Mueller, Heaton & Miller (1960) [$\cos^2\theta$ extrapolation function and $(\sin^2 2\theta)^{-1}$ weights] were: $a=11{\cdot}4743$ (11) and $c=5{\cdot}2043$ (5) Å. The cell dimensions were close to the β-UF_5 dimensions with possibly a slight difference in the length of the c axis. The crystal data for β-UOF_4 are collected in Table 1.

Table 1. *Crystal data for* β-UOF_4

β-UOF_4, F.W. 330·0
Tetragonal, $Z=8$, $a=11{\cdot}4743$ (11), $c=5{\cdot}2043$ (5) Å
Unit-cell volume 685·2 Å^3, $D_x=6{\cdot}40$ g cm^{-3}
Space group $I\bar{4}2d$ (D_{2d}^{12}), $\lambda=0{\cdot}7107$ Å (Mo $K\bar{\alpha}$)
μ(Mo $K\alpha$) = 580 (30) cm^{-1}
$F(000)$ = 1088 e

Trial structure and least-squares refinement

The starting point for the β-UOF$_4$ structure analysis was the β-UF$_5$ structure of Zachariasen (1949), the coordinates for which are given in Table 2. The only change in going from β-UF$_5$ structure to the β-UOF$_4$ trial structure was that the F(1) atom in the former was changed to an oxygen atom in the latter. This was the only position for oxygen which preserved the stoichiometry. The F(2) and F(3) β-UF$_5$ locations were therefore labelled F(1) and F(2) in the β-UOF$_4$ model.

The β-UOF$_4$ model was refined by least-squares calculations with the program *LINUS* (Coppens & Hamilton, 1970). The X-ray scattering factors for neutral U, O and F were used (*International Tables for X-ray Crystallography*, 1962), and the anomalous dispersion terms (Cromer, 1965) $\Delta f' = -9$e and $\Delta f'' = 9$e were included for uranium. The oxygen atoms were initially assigned isotropic Debye–Waller factors B of 2·0 Å^2. The uranium temperature factor was first refined isotropically and finally anisotropically with the form $\exp[-(\beta_{11}h^2 + 2\beta_{12}hk + \ldots)]$. An isotropic extinction correction factor g' was also refined, bringing the total number of variables to 14. The least-squares weights were: $w_{hkl} = [\sigma^2(F_{(hkl)})]^{-1}$. In the latter stages of the refinement, 8 reflexions were given reduced weights as their $|F_o - F_c|/\sigma$ values were greater than 3. These larger $|\Delta|/\sigma$ values were probably due to absorption effects.

The refinement converged to weighted and unweighted R values $R_w = [\sum w(F_o - S|F_c|)^2/\sum wF_o^2]^{1/2}$ and $R_u = \sum(F_o - S|F_c|)/F_o$ of 0·089 and 0·110 and a value of $\chi = [\sum w(F_o - S|F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$ of 1·08, where NO is the number of observations, NV the number of variables and S is the scale factor. The g' value of 0·00 (3) was low, indicating that extinction effects were negligible. The structural parameters for β-UOF$_4$ are given in Table 2, and the bond lengths and angles in Table 3.* The parameters based on spatial considerations by Zachariasen in β-UF$_5$, Table 2, are in good agreement with the β-UOF$_4$ parameters, except that the terminal atoms O and F(2) in the present structure have moved closer to the uranium atom.

Table 2. *Crystal structure parameters for* β-UOF$_4$

(a) Positional parameters in β-UOF$_4$, compared with the coordinates suggested by Zachariasen (1949) for β-UF$_5$

	Crystal	x	y	z
U in 8(d)	β-UOF$_4$	0·0861 (2)	$\frac{1}{4}$	$\frac{1}{8}$
	β-UF$_5$	0·083	$\frac{1}{4}$	$\frac{1}{8}$
O in 8(d)	β-UOF$_4$	0·249 (12)	$\frac{1}{4}$	$\frac{1}{8}$
F(1) in 8(d)	β-UF$_5$	0·273	$\frac{1}{4}$	$\frac{1}{8}$
F(1) in 16(e)	β-UOF$_4$	0·142 (2)	0·077 (2)	0·003 (7)
F(2) in 16(e)	β-UF$_5$	0·15	0·07	0·05
F(2) in 16(e)	β-UOF$_4$	0·036 (4)	0·181 (3)	0·442 (11)
F(3) in 16(e)	β-UF$_5$	0·05	0·14	0·46

Table 2 (*cont.*)

(b) Thermal vibration parameters in β-UOF$_4$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	0·00170 (17)	0·00182 (17)	0·0243 (11)	0	0	−0·0033 (5)
O(1)	B = 6·4 (13) Å^2					
F(1)	B = 1·6 (5)					
F(2)	B = 5·8 (11)					

Table 3. *Interatomic distances and angles in* β-UOF$_4$

U–O	1·87 (15) Å
U–F(1)	2·18 (3)
U–F(1)	2·34 (3)
U–F(2)	1·92 (6)
U–F(2)	3·68 (6)
O–O	2·60 (1)
U–U	4·574 (3)
U–U	4·483 (1)

U—F(1)–U (bridging)	165·0 (15)°
U—F(2)–U	134·1 (22)

Angles in U coordination polyhedron

F(2)–U—F(2) (axial)	145·3 (27)
F(2)–U—F(1)	77·7 (18)
F(2)–U—F(1)	74·7 (15)
F(2)–U—F(1)	102·2 (18)
F(2)–U—F(1)	87·9 (16)
F(2)–U—O	107·3 (14)

O–F and F–F contacts in polyhedron

F(2)–O	3·09 (8) Å
F(2)–F(1)	3·19 (6)
F(2)–F(1)	2·60 (5)
F(2)–F(1)	2·69 (7)
F(2)–F(1)	2·85 (7)

Possible O, F disorder in the terminal positions O(1) and F(2)

The temperature factor of the uranium atom was low, its anisotropic temperature coefficients in Table 2 being equivalent to $B_U \simeq 1·5$ Å^2. The thermal parameter of the bridging fluorine atoms F(1) was also low, 1·6 (5) Å^2. However, the thermal parameters of the terminal atoms O(1) and F(2) were higher [6·4 (13) and 5·8 (11) Å^2]. This suggested the possibility of O, F disorder in the terminal positions. The diffuseness of the terminal peaks could then be explained on the basis of the different lengths of the U–O and U–F vectors appearing superposed in these peaks. It was known from other transition metal oxide tetrafluoride structures that oxygen atoms were not likely to enter the bridges; this was in agreement with the normal temperature factor of the bridging F(1) atom.

To investigate this point further, refinements were made with (a) (0·7 oxygen + 0·3 fluorine) in the O(1) peak and with the corresponding (O, F) mixture in the

---

* The list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30376 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

F(2) peak (the starting U–O and U–F distances were 1·8 and 2·0 Å and $B_O = B_F$ values of 2·0 Å^2 were assumed) and (*b*) (0·6 oxygen + 0·4 fluorine) in the O(1) peak. The *x* parameters for the light atom 8(*d*) site were refined only. The results (Table 4) gave two minima in the *x* direction at about 1·8 and 2·3 Å from the uranium atom, and tended to support the disorder hypothesis. Refinements of occupancy factors suggested about $\frac{2}{3}$ oxygen and $\frac{1}{3}$ fluorine in the O(1) peak. Similar refinements failed to locate two minima at F(2); here the assumed oxygen–fluorine ratio was necessarily lower than at O(1). The *R* index was found to be insensitive to the possible order–disorder, and difference maps were inconclusive. Andersson & Galy (1969) also found that the *R* index was not a sensitive test for order–disorder in their X-ray study of $NaNbO_2F_2$.

Table 4. *Refinements with assumed* O, F *disorder in the* O(1) *peak*

(*a*) 70% O, 30% F
(*b*) 60% O, 40% F

Refinement	$x_{(\text{partial O})}$	$x_{(\text{partial F})}$	U–O$_{(\text{partial})}$	U–F$_{(\text{partial})}$
(*a*) 70% O, 30%F	0·245 (8)	0·294 (11)	1·82 (9) Å	2·38 (13) Å
(*b*) 60% O, 40%F	0·242 (10)	0·282 (10)	1·78 (12)	2·24 (12)

Evidence for disorder in β-UOF_4 thus rested solely on the refinement behaviour of partial O and F atoms in the O(1) peak and the high apparent thermal parameters at the terminal positions. This evidence however could not be considered conclusive since the disorder model gave no improvement in the *R* value. The following discussion of the structure is therefore based on the ordered model refinement with complete oxygen occupancy at the O site. The U–O distance derived from the ordered model (Table 3) may be high if disorder of the above type occurs.

Discussion

The structure of β-UOF_4, shown in Fig. 1, is of the β-UF_5 type (Zachariasen, 1949), one fluorine atom being replaced by oxygen. As mentioned above, there is possible O, F disorder in the terminal atoms, O(1) and F(2). The configuration around the uranium atom is a pentagonal bipyramid and the oxygen atom is part of the pentagonal ring. This $[UOF_2F_{4/2}]$ bipyramid is the first one of its type to be observed; the UO_2F_5 bipyramid, as found in $K_3UO_2F_5$ (Zachariasen, 1954), is more common. The distances and angles in β-UOF_4 are given in Table 3. The terminal bonds U–O(1) and U–F(2) are 1·87 (15) and 1·92 (6) Å (the former distance may be shorter if O, F disorder is present), and the four F(1) atoms in the pentagonal ring form asymmetric bridges with neighbouring uranium atoms of length 2·34 (3) and 2·18 (3) Å. The bridge bonds appear largely ionic, while the terminal bonds have covalent character as the predicted ionic distances for U^{6+}–O^{2-} and U^{6+}–F^- are 2·23 and 2·17 Å (Shannon & Prewitt, 1969). As in other oxide tetrafluorides (Edwards & Jones, 1968*a*), the longer bridge bonds are *trans* to the shorter U–O bond.

β-UOF_4 is not isostructural with any of the pentafluorides or oxide tetrafluorides of the second and third row transition metals, which have three main classes of structure (Edwards & Jones, 1969):

(i) the tetrameric NbF_5 type where four octahedra are fused by sharing corners;

(ii) a distorted monoclinic version of the NbF_5 type as shown by RuF_5;

(iii) the orthorhombic VF_5 type where octahedra are joined in endless chains.

The lack of similarity between β-UOF_4 and these structures is due to the occurrence of pentagonal bipyramids in the former, rather than octahedra. As the crystals being investigated were isostructural with β-UF_5, and it is difficult to distinguish between fluorine and oxygen in the presence of uranium by X-ray methods, the possibility that they were actually β-UF_5 and not β-UOF_4 was considered. This, however, was dismissed on the following grounds:

(*a*) The crystals were yellow, whereas UF_5 is colourless.

(*b*) The infrared spectrum had a band at 880 cm^{-1}, corresponding to an asymmetric U–O stretching frequency for a U–O bond approaching uranyl strength. Other bands at 655 cm^{-1} and 550 cm^{-1} corresponded to U–F (terminal) and U–F–U (bridging).

(*c*) Under the conditions of the preparation, the U^V oxidation state was unlikely.

The possibility that O, F disorder occurs in β-UOF_4 may have some implications concerning doubts surrounding the structure of WOF_4. An X-ray analysis

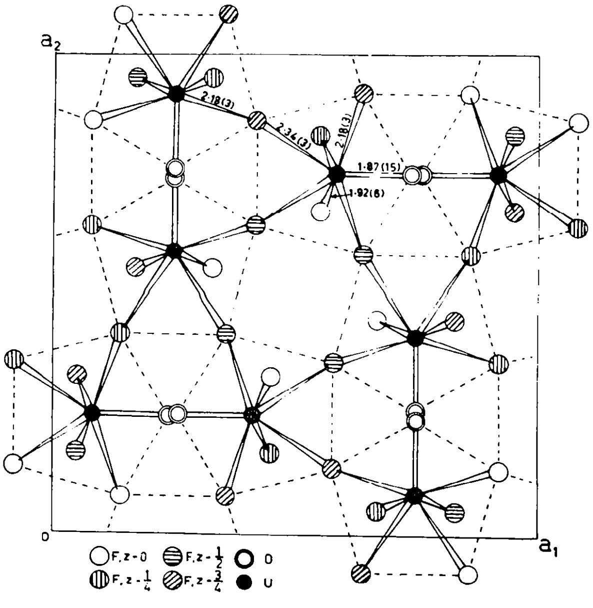

Fig. 1. The crystal structure of β-UOF_4.

(Edwards & Jones, 1968*b*) of WOF_4 found the structural unit to be a tetramer, $[WF_4O_{2/2}]_4$, with the tungsten atoms approximately at the corners of a square and bridging W–O–W bonds. However the infrared and Raman spectra strongly suggest terminal W=O bonds and bridging fluorine atoms (Beattie, Livingston, Reynolds & Ozin, 1970; Beattie & Reynolds, 1968; Winfield, 1972). The X-ray result is clearly a 'correct' structure in the sense that the centres of the electron density distribution were located. On close examination, it appears that it is impossible to propose an ordered structure with fluorine bridging and satisfy the valence requirements of W within the symmetry of the possible space groups, $C_{2/m}$, C_2 and C_m. This, together with the spectral evidence, enforces the conclusion that there must be O, F disorder in the WOF_4 crystal studied by Edwards & Jones (1968*b*). By analogy with ordered $ReOF_4$ (Edwards & Jones, 1968*a*), which X-ray analysis indicates is fluorine-bridged, the O–F disorder is probably mainly in the shorter in-plane terminal bonds. We have refined a disordered model with the published X-ray data for WOF_4, but failed to obtain a significantly lower *R* value for the disordered model. Difference maps were also inconclusive, and more accurate data would appear necessary for a clear demonstration of the possible disorder in WOF_4.

Polymorphism has been found in other oxide tetrafluorides. $TcOF_4$ has a blue monoclinic form (Edwards, Jones & Sills, 1968) with a structure similar to VF_5 and a green hexagonal form comprising the cyclic tetramers $[TcOF_3F_{2/2}]$. $MoOF_4$ also has a similar dimorphism (Edwards, Jones & Sills, 1968) but the hexagonal form changes to the monoclinic form in a few days. The structure of α-UOF_4 is presently being studied in this laboratory.

References

Andersson, S. & Galy, J. (1969). *Acta Cryst.* **B25**, 847–850.
Beattie, I. R., Livingston, K. M. S., Reynolds, D. J. & Ozin, G. A. (1970). *J. Chem. Soc.* (*A*), pp. 1210–1216.
Beattie, I. R. & Reynolds, D. J. (1968). *Chem. Commun.* pp. 1531–1532.
Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.
Edwards, A. J. & Jones, G. R. (1968*a*). *J. Chem. Soc.* (*A*), pp. 2511–2515.
Edwards, A. J. & Jones, G. R. (1968*b*). *J. Chem. Soc.* (*A*), pp. 2074–2078.
Edwards, A. J. & Jones, G. R. (1969). *J. Chem. Soc.* (*A*), pp. 1651–1654.
Edwards, A. J., Jones, G. R. & Sills, R. J. C. (1968). *Chem. Commun.* pp. 1177–1178.
Elcombe, M. M., Cox, G. W., Pryor, A. W. & Moore, F. H. (1971). Report AAEC/TM578.
International Tables for X-ray Crystallography (1962). Vol. III, p. 201. Birmingham: Kynoch Press.
Mueller, M. H., Heaton, L. & Miller, K. T. (1960). *Acta Cryst.* **13**, 828–829.
Shannon, R. D. & Prewitt, C. T. (1969). *Acta Cryst.* **B25**, 925–946.
Wilson, P. W. (1973). *J. Inorg. Nucl. Chem.* **36**, 303–305.
Winfield, J. M. (1972). *MTP Int. Rev. Sci.* **5**, chap. 7, p. 279. London: Butterworths.
Zachariasen, W. H. (1949). *Acta Cryst.* **2**, 296–298.
Zachariasen, W. H. (1954). *Acta Cryst.* **7**, 783–787.

Acta Cryst. (1974). **B30**, 1705

A Powder Neutron-Diffraction Determination of the Structure of $Ba_4Sb_3LiO_{12}$: the Preparation and Structure of the Perovskite-Related Compounds $Ba_4M_3LiO_{12}$ (M=Sb, Bi) and $Ba_5M_3Li_2O_{15-x}$ (M=Te, U)

By A. J. Jacobson, B. M. Collins and B. E. F. Fender
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, England

(*Received* 23 *February* 1974; *accepted* 27 *February* 1974)

The structure of the ordered perovskite-like compound $Ba_4Sb_3LiO_{12}$ has been determined by profile analysis of powder neutron-diffraction data. The preparation of the compounds $Ba_4Sb_3LiO_{12}$ and $Ba_5M_3Li_2O_{15-x}$ (M=Te, U) and X-ray evidence for their structures is described. All are found to contain only cubic stacking of AO_3 layers in contrast to the behaviour of the analogous Nb, Ta and W compounds.

Introduction

In three recent reports the preparation and structure of some lithium-containing perovskites has been described (Negas, Roth, Parker & Brower, 1973; Collins, Jacobson & Fender, 1974; Jacobson, Collins & Fender, 1974). We find that in $Ba_4Ta_3LiO_{12}$, $Ba_4Nb_3LiO_{12}$ and $Ba_5W_3Li_2O_{15}$ both the transition metal ion and the lithium ion can coexist on the *B* site of the perovskite but that the stacking sequence of BaO_3 layers is modified by cation ordering with the result that Nb^{5+} Ta^{5+} or W^{6+} and Li^+ ions are brought