

Crystal Chemical Studies of the 5f-Series of Elements. XX. The Crystal Structure of Tri-potassium Uranyl Fluoride

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$K_3UO_2F_5$ is tetragonal with $a_1 = 9.160 \pm 0.001$, $a_3 = 18.167 \pm 0.002$ Å and eight stoichiometric molecules per unit cell. The space group is $I4_1/a$. The positions of all light atoms have been determined with considerable accuracy with the aid of precise intensity measurements on a small spherical crystal and a series of generalized Fourier syntheses.

The structure is built up of $(UO_2F_5)^{-3}$ complexes held together by potassium ions. The (UO_2F_5) group has the shape of a pentagonal bipyramid, the five fluorine atoms forming a nearly regular pentagon normal to the axis of the uranyl group. The bond lengths are $U-O = 1.76 \pm 0.03$ Å and $U-F = 2.24 \pm 0.02$ Å.

Introduction

A series of crystal structure studies of uranyl compounds has been undertaken by this writer for the purpose of getting really reliable results concerning the atomic configuration about uranium. In spite of the highly unfavorable situation both as to atomic scattering power and absorption correction, the positions of the light atoms can be determined with appreciable accuracy without the expenditure of an unreasonable amount of time and effort. The present paper reports the results of the first of this series of investigations.

Experimental procedure

Small single crystals of $K_3UO_2F_5$ were prepared by the writer by adding a concentrated KF solution to a concentrated uranyl nitrate solution with subsequent recrystallization from a hot aqueous solution. The composition was verified by means of a chemical analysis which gave the following results:

	Found	Theoretical
UO ₂	56.0 %	56.0 %
F	19.4	19.7
K by difference	24.6	24.3

The crystals were found to be tetragonal body-centered with

$$a_1 = 9.160 \pm 0.001, a_3 = 18.167 \pm 0.002 \text{ Å},$$

and eight stoichiometric molecules per unit cell. The calculated density is $\rho = 4.200 \text{ g.cm.}^{-3}$ as compared with the value 4.263 g.cm.^{-3} reported in the literature (Baker, 1879).

Since the purpose of the investigation was to determine the positions of the light atoms with considerable accuracy, intensity measurements had to be

made with care. The intensities were measured with the General Electric XRD Spectrometer modified for single-crystal work as described earlier (Zachariasen, 1954a). In order to minimize the errors due to absorption correction, all intensity data were taken on a crystal which had been ground in the Bond sphere grinder. The radius of the spherical crystal ranged from 0.0101 to 0.0110 cm., with 0.0107 cm. as the mean value. The calculated linear absorption coefficient for Cu $K\alpha$ radiation is $\mu = 890 \text{ cm.}^{-1}$, giving $\mu R = 9.5$.

The crystal was mounted with the axis a_2 coinciding with the spectrometer axis, and all reflections in the layer lines $H_2 = 0, 1, \text{ and } 2$ were measured. It was felt that these experimental data would suffice if the method of generalized projections was used to the fullest advantage and that the slight improvement in accuracy possible with a complete set of three-dimensional data was not commensurate with the added effort.

The Laue symmetry is $4/m$, but it should be remarked that the intensity differences between reflections $H_1H_2H_3$ and $\bar{H}_1H_2\bar{H}_3$ are small. The following absences occur (in addition to those characteristic of the body-centered translation group): (1) reflections $00H_3$ are absent if $H_3 = 4n+2$, and (2) reflections H_1H_20 are absent if H_1 and H_2 are both odd. The space group is accordingly $I4_1/a-C_{4h}^6$. In giving atomic positions of this space group the origin is chosen in an inversion center.

It is immediately apparent from the observed structure factors that the eight uranium atoms are in positions

$$8(e): \pm(0, \frac{1}{4}, z), (0, \frac{1}{4}, \frac{1}{4}-z).$$

The approximate value of z is 0.396, as is readily deduced. This preliminary value was sufficiently accurate to permit the determination of the algebraic sign for all but the smallest structure factors. The

positions of the light atoms could thus be determined directly by means of suitable Fourier syntheses.

The parameter determination

The most general Fourier synthesis which can be evaluated with the available experimental data is

$$\int_0^1 \rho \{1 + A_1 \cos 2\pi y + B_1 \sin 2\pi y + A_2 \cos 2\pi 2y + B_2 \sin 2\pi 2y\} dy. \quad (1)$$

Owing to the fact that Cu $K\alpha$ radiation was used the termination-of-series error is considerable. For this reason all parameter determinations were based on difference syntheses of the type given above, i.e. ρ represents the electron density with uranium atoms or with uranium atoms and potassium atoms removed.

The ordinary projection, $\int_0^1 \rho dy$, is not suited for parameter determination because of considerable overlapping of atoms. With the aid of generalized projection it is, however, possible to eliminate the superposition by suitable choice of the coefficients A_1, B_1, A_2, B_2 . Suppose, as an example, that four atoms were in exact superposition, their y values being $1/12, 1/3, 7/12, 5/6$. The choice $A_1 = 1/3, B_1 = 1, A_2 = 1/2, B_2 = 1/3$ would bring out the first atom and eliminate the other three since the weight factor for ρ in the integral

above is large for the first atom and vanishes for the others. The three suppressed atoms would, of course, give small contributions to the integral since the weight factor is made to vanish only at the atomic centers. These contributions are, however, so small as to be negligible because the weight factor is a slowly varying function of y .

Since there is at least one atom of each equivalent set in each y quadrant, the coefficients A_1, B_1 and B_2 may be restricted to positive values so as to enhance the atom in the first quadrant. If the y coordinate lies in the range $0 \leq y \leq \frac{1}{8}$, a positive value for A_2 will provide the greatest enhancement, whereas a negative value should be used if the atom of interest has $\frac{1}{8} \leq y \leq \frac{1}{4}$.

The following procedure was used in determining the parameter values. Using the preliminary value $z_U = 0.396$, and preliminary values for the normalization and uranium temperature factors, generalized difference syntheses were carried out corresponding to $A_1 = B_1 = B_2 = 1, A_2 = \pm 1$. These syntheses revealed the approximate location of all potassium, oxygen and fluorine atoms. The coefficients were next adjusted for enhancement at the uranium site at $y = \frac{1}{4}$ and suppression of superimposed potassium and oxygen atoms. Residual electron density at the uranium site was observed. The uranium parameter and temperature factor and the normalization factor were next adjusted until no trace remained of residual

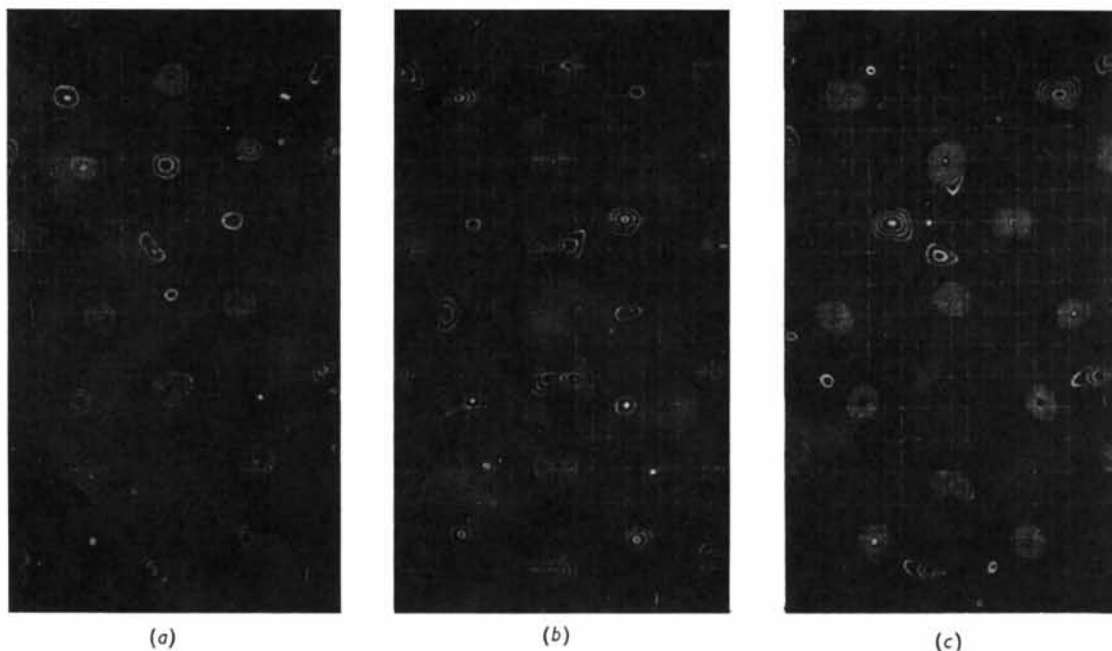


Fig. 1. (a) The XRAC photograph of the generalized difference synthesis corresponding to $A_1 = 2.0, B_1 = 2.5$ and $A_2 = B_2 = 1.0$. The uranium atoms have been removed. The orientation of the photograph corresponds to that of the projection of the structure shown in Fig. 2(a).

(b) The XRAC photograph of the generalized synthesis with $A_1 = 1.28, B_1 = 0, A_2 = B_2 = 1$ and uranium and potassium atoms removed.

(c) The XRAC photograph corresponding to $A_1 = 1.0, B_1 = 1.6, A_2 = -1.0, B_2 = 1.0$ with uranium and potassium atoms removed.

Table 1. *Final parameters*

		<i>x</i>	<i>y</i>	<i>z</i>
4K _I	4(<i>a</i>)	0	$\frac{1}{4}$	$\frac{1}{8}$
4K _{II}	4(<i>b</i>)	0	$\frac{1}{4}$	$\frac{1}{8}$
16K _{III}	16(<i>f</i>)	0.210 ± 0.001	-0.009 ± 0.001	0.0113 ± 0.0005
8U	8(<i>e</i>)	0	$\frac{1}{4}$	0.3960 ± 0.0004
16O	16(<i>f</i>)	0.043 ± 0.002	0.062 ± 0.002	0.397 ± 0.001
8F _I	8(<i>e</i>)	0	$\frac{1}{4}$	0.273 ± 0.001
16F _{II}	16(<i>f</i>)	0.359 ± 0.001	0.232 ± 0.001	0.005 ± 0.001
16F _{III}	16(<i>f</i>)	0.271 ± 0.001	0.202 ± 0.002	0.143 ± 0.001

Table 2. *Calculated and observed structure factors, F_c and F_o*

<i>H</i> ₁ <i>O</i> <i>H</i> ₃	<i>F_c</i>	<i>F_o</i>	<i>H</i> ₁ <i>O</i> <i>H</i> ₃	<i>F_c</i>	<i>F_o</i>	<i>H</i> ₁ <i>O</i> <i>H</i> ₃	<i>F_c</i>	<i>F_o</i>
004	-57.7	57.9	19	-15.9	16.1	3	-21.1	23.2
8	90.2	92.8	21	8.7	7.7	5	13.7	14.2
12	9.3	11.7				7	18.9	18.7
16	-12.7	13.4	400	112.4	112.7	9	-33.7	33.2
20	33.2	33.2	2	-15.5	16.2	11	-34.3	33.7
			4	-54.8	52.3	13	22.5	22.9
101	-3.4	5.4	6	-13.0	11.2	15	18.3	18.2
3	-20.4	22.7	8	53.6	51.7	17	-19.4	18.5
5	31.2	33.5	10	-8.7	8.4			
7	43.9	46.3	12	-0.5	0	800	55.4	57.0
9	-43.4	45.6	14	-5.2	4.8	2	-7.4	7.3
11	-41.0	42.6	16	-14.5	14.6	4	-33.1	36.3
13	33.3	36.3	18	-3.1	3.6	6	-5.2	5.8
15	29.2	31.9	20	26.7	26.5	8	28.5	28.3
17	-24.6	25.9	22	-1.2	1.3	10	-5.2	3.9
19	-16.4	16.4				12	-0.9	1.1
21	7.3	6.4	501	6.8	6.6	14	-2.3	2.5
23	0.5	1.5	3	-3.5	5.2	16	-10.8	10.9
			5	35.2	34.2			
200	80.2	78.0	7	42.7	39.7	901	-1.0	0
2	-1.1	8.1	9	-30.1	27.9	3	-3.1	3.7
4	-91.2	89.2	11	-26.5	25.4	5	20.1	20.5
6	-20.0	22.7	13	32.1	32.5	7	23.6	22.9
8	31.8	30.8	15	29.0	29.4	9	-21.9	21.3
10	8.5	7.9	17	-21.3	20.4	11	-18.5	18.0
12	-14.1	14.6	19	-12.6	10.9	13	21.7	20.6
14	-11.0	10.4	21	7.1	6.1	15	21.4	17.4
16	-20.8	22.9						
18	2.1	1.9	600	63.7	65.1	10,0,0	38.5	38.9
20	25.1	24.7	2	6.2	6.7	2	4.2	3.6
22	-2.2	2.3	4	-53.4	52.8	4	-32.1	32.8
			6	5.0	4.7	6	5.5	4.4
301	-7.9	9.9	8	29.3	27.2	8	18.9	18.3
3	-16.0	17.2	10	3.6	3.8	10	1.2	1.3
5	29.4	28.6	12	-5.3	6.1	12	-2.8	2.6
7	35.2	32.2	14	1.7	0			
9	-38.3	37.5	16	-15.3	16.1	11,0,1	-1.8	2.6
11	-37.9	37.2	18	0.9	1.2	3	-10.4	10.2
13	32.0	32.9	20	23.0	19.1	5	14.0	14.0
15	27.1	28.4				7	18.5	15.6
17	-20.6	21.2	701	-13.3	13.7			

electron density at the uranium site. The results for the uranium parameter and for the exponent B_U in the temperature factor for uranium, $\exp(-B_U \sin^2 \theta / \lambda^2)$ are:

$$z_U = 0.3960 \pm 0.0004, B_U = 0.735 \pm 0.06 \text{ \AA}^2.$$

There was no evidence of significant anisotropy in the thermal vibrations of the uranium atoms.

Fig. 1(*a*) shows the generalized difference synthesis corresponding to $A_1 = 2.0$, $B_1 = 2.5$, $A_2 = B_2 = 1.0$. The highest peaks represent potassium atoms as follows:

$$4K_I \text{ in } \pm(0, \frac{1}{4}, \frac{1}{8}), 4K_{II} \text{ in } \pm(0, \frac{1}{4}, \frac{5}{8})$$

and 16K_{III} in general positions 16(*f*) with

$$x = 0.21 \quad y = -0.01 \quad z = 0.01.$$

With these parameter values there is superposition of K_{III} atoms in the (010) projection. For example, Fig. 1(*a*) shows a K_{III} atom at $x = 0.24$, $z = 0.26$ for which $y = 0.04$. By symmetry there is another K_{III} atom at $x = 0.26$, $z = 0.24$ with $y = 0.46$. However, the coefficients of the generalized projection shown in Fig. 1(*a*) have been adjusted so as to get no contribution from

the second K_{III} atom, and hence the x, z coordinates for the electron-density maximum under consideration are those of the K_{III} atom at $y = 0.04$. The result of the parameter determination for the K_{III} atoms is

$$x_K = 0.210 \pm 0.001, \quad y_K = -0.009 \pm 0.001, \\ z_K = 0.0113 \pm 0.0005.$$

Fig. 1(b) shows the result of the generalized difference synthesis with $A_1 = 1.28, B_1 = 0, A_2 = B_2 = 1$ and uranium and potassium atoms removed. Fig. 1(c) corresponds to $A_1 = 1.0, B_1 = 1.6, A_2 = -1.0, B_2 = 1.0$ with uranium and potassium atoms removed.

The removal of the potassium atoms was first carried out on the assumption that the temperature factor for potassium is the same as for uranium. However, this assumption led to deep minima at the potassium sites, showing $B_K \gg B_U$. The actual value obtained is $B_K = 2.04 \text{ \AA}^2$.

The fluorine and oxygen parameters were deduced from the syntheses shown in Fig. 1(b) and (c) and from similar syntheses corresponding to different sets of coefficients A_1, B_1, A_2, B_2 . Oxygen atoms can be distinguished from fluorine atoms not only by virtue of the unique role played by the oxygen atoms in the structure, but also by means of their lower electron-density maxima.

The final results of the parameter determination are given in Table 1.

Table 2 shows the degree of agreement between observed and calculated structure factors for reflections $F_{H_10H_3}$. The calculated values were obtained using the parameter values given in Table 1. The f values for uranium and potassium were taken from the *International Tables* except that the uranium values were reduced by $\Delta = 5.4$, which is Hönl's (1933) value for the oscillator strength of the K electrons. The experimental values $B_U = 0.735 \text{ \AA}^2$ and $B_K = 2.04 \text{ \AA}^2$ were used. McWeeny's (1951) f curves were used for oxygen and fluorine. It was assumed that $B_O = B_F = B_K$.

The agreement shown in Table 2 corresponds to $R = 0.05$. It is seen, however, that there are systematic deviations between observed and calculated F values.

Table 3. *Calculated and observed structure factors for reflections $41H_3$ and $\bar{4}1\bar{H}_3$*

H_3	$41H_3$		$\bar{4}1\bar{H}_3$		Ratio $41H_3 : \bar{4}1\bar{H}_3$	
	F_c	$ F_o $	F_c	$ F_o $	Calc.	Obs.
1	6.6	8.8	6.0	8.0	1.10	1.10
3	-17.5	18.9	15.3	15.2	1.14	1.24
5	-14.5	16.3	27.1	27.2	0.54	0.60
7	36.4	32.4	-37.8	34.0	0.96	0.95
9	43.2	38.8	-29.9	26.4	1.44	1.47
11	-29.8	29.6	34.9	32.4	0.85	0.91
13	-23.2	23.0	32.9	32.8	0.71	0.70
15	28.9	27.6	-24.3	24.4	1.19	1.13
17	26.6	27.1	-19.1	18.8	1.39	1.44
19	-16.2	11.0	16.6	15.4	0.62	0.72
21	-3.9	2.6	9.5	8.6	0.41	0.30

These deviations can be attributed to the departure of the crystal from the assumed spherical shape.

Tables of calculated and observed structure factors for H_11H_3 and H_12H_3 reflections are omitted, but the agreement is equally satisfactory. Table 3 illustrates the agreement for the H_11H_3 reflections, in particular

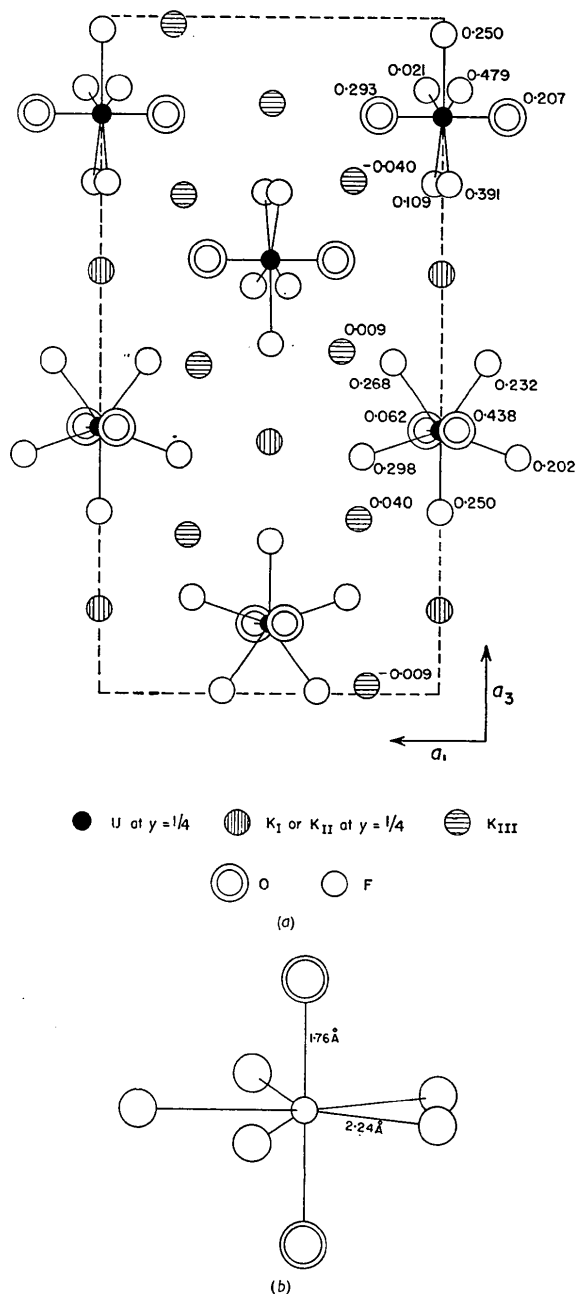


Fig. 2. (a) View of the structure along a_2 . Only half of the atoms in the unit cell are shown, the whereabouts of the omitted atoms being obvious since the lattice is body-centered.

(b) The UO_2F_5 complex. The oxygen and fluorine atoms are at the corners, the uranium atom at the center of a pentagonal bipyramid. The uranyl group forms the axis of the bipyramid.

the numerical differences between reflections $41L$ and $41\bar{L}$ which are due only to K_{III} , O, F_{II} and F_{III} atoms.

Discussion of the structure

A view of the structure along the a_2 axis is shown in Fig. 2(a). Only half the atoms in the unit cell are shown. The uranium atoms and the K_I and K_{II} atoms at the level $y = \frac{3}{4}$ have been omitted, together with the oxygen and fluorine atoms bonded to these uranium atoms. The K_{III} atoms with y coordinates near $\frac{1}{2}$ have also been removed.

The structure is built up of complexes $(UO_2F_5)^{-3}$ and potassium ions. The UO_2F_5 group has the shape of a pentagonal bipyramid, as shown in Fig. 2(b). The uranyl group O-U-O is discernible within the complex, the oxygen atoms being at the apices of the bipyramid. The uranyl group is found to be collinear within the experimental error. The U-O distance of 1.76 ± 0.03 Å is much smaller than the value 1.91 ± 0.10 Å found in the $Ca(UO_2)O_2$ structure (Zachariasen, 1948) and the value 1.92 ± 0.03 Å in the $Mg(UO_2)O_2$ structure (Zachariasen, 1954b), these being the only direct determinations of the size of the uranyl group. The significance of these seemingly contradictory results for the length of the uranyl bond is discussed in the following paper, to which the reader is referred.

The five fluorine atoms of the UO_2F_5 complex form a nearly plane pentagon which is nearly normal to the uranyl group. The individual U-F distances (Table 4) range from 2.22 Å to 2.26 Å. As to the orientation of

the UO_2F_5 groups in the crystal lattice, the uranyl axis is normal to a_3 and makes an angle of 13° with the a_1 or a_2 axes. The U-F_I bond coincides with the vertical twofold axis of the crystal, so that this twofold axis is the only symmetry element imposed on the UO_2F_5 complex by the space group.

Each potassium atom K_I is bonded to six fluorine atoms, K_{II} to four fluorine and four oxygen atoms, and each K_{III} atom to six fluorine and two oxygen atoms. The individual bond lengths are listed in detail in Table 4. The K-F distances are in good agreement with those predicted from ionic radii (2.66 Å for six and 2.74 Å for eight coordination). The K-O distances are appreciably larger than the value 2.87 Å expected for eight coordination from ionic radii.

There is a pronounced pseudo-cubic character to the structure of $K_3UO_2F_5$. Were the axial ratio $a_3:a_1 = 2.000$ instead of 1.984, the parameters $z_U = \frac{3}{8}$ instead of 0.3960, $x_K = \frac{1}{4}$ instead of 0.210, $y_K = 0$ instead of -0.009, $z_K = 0$ instead of 0.011, then the potassium and uranium atoms would be in a face-centered cubic structure with $a = 9.13$ Å and with atomic positions as follows:

$$4U \text{ in } (0, 0, 0), 4K \text{ in } (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), 8K \text{ in } (\frac{1}{4}, \frac{1}{4}, \frac{1}{4});$$

These are precisely the positions of zirconium atoms and ammonium groups in the cubic face-centered structure of $(NH_4)_3ZrF_7$. The structural relationship between $K_3UO_2F_5$, $(NH_4)_3ZrF_7$ and K_3UF_7 will be discussed in a subsequent article.

The chemical analysis was carried out by Mr B. Holt and Miss C. Carter. Miss Anne Plettinger ground the crystal sphere used in the investigation, and also made some of the intensity measurements. Their aid is gratefully acknowledged.

The Fourier syntheses were made on XRAC in the course of several visits to Pennsylvania State College. The writer is deeply indebted to Prof. Ray Pepinsky for the use of XRAC and for his hospitality, and to the XRAC staff members for their kind help.

References

- BAKER, H. (1879). *J. Chem. Soc.* **35**, 763.
 HÖNL, H. (1933). *Z. Phys.* **84**, 1.
 MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
 ZACHARIASEN, W. H. (1948). *Acta Cryst.* **1**, 281.
 ZACHARIASEN, W. H. (1954a). *Acta Cryst.* **7**, 305.
 ZACHARIASEN, W. H. (1954b). *Acta Cryst.* **7**, 788.

Table 4. *Interatomic distances*

$K_I-4F_{III} = 2.54$ Å	$O-1U = 1.76$ Å
$-2F_I = 2.69$	$-1K_{II} = 2.92$
	$-1K_{III} = 3.07$
$K_{II}-4F_{II} = 2.70$ Å	$-1K_{III} = 3.10$
$-4O = 2.92$	
$K_{III}-1F_{II} = 2.60$ Å	$F_I-1U = 2.23$ Å
$-1F_{III} = 2.62$	$-1K_I = 2.69$
$-1F_{II} = 2.74$	$-2K_{III} = 2.94$
$-1F_{III} = 2.92$	
$-1F_I = 2.94$	$F_{II}-1U = 2.22$ Å
$-1F_{III} = 3.12$	$-1K_{III} = 2.60$
$-1O = 3.07$	$-1K_{II} = 2.70$
$-1O = 3.10$	$-1K_{III} = 2.74$
$U-2O = 1.76$ Å	$F_{III}-1U = 2.26$ Å
$-2F_{II} = 2.22$	$-1K_I = 2.54$
$-1F_I = 2.23$	$-1K_{III} = 2.62$
$-2F_{III} = 2.26$	$-1K_{III} = 2.92$
	$-1K_{III} = 3.12$