

## Short Communications

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**The crystal structure of  $KU_2F_9$ .**\* BY GEORGE BRUNTON, *Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U. S. A.*

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The compound  $KU_2F_9$  crystallizes with space group  $Pnma$  and with lattice constants  $a_0 = 8.7021$  (9),  $b_0 = 11.4769$  (4) and  $c_0 = 7.0350$  (3) Å. The  $U^{4+}$  ions are coordinated by  $9F^-$  at distances 2.292 (1) to 2.39 (3) Å and the  $K^+$  ions are coordinated by  $10F^-$  at distances 2.62 (2) to 3.21 (2) Å.

The complex fluoride compound  $KU_2F_9$  is an equilibrium phase in the fused salt system  $KF \cdot UF_4$  and it melts incongruently to  $UF_4$  + liquid at 765°C (Thoma, Insley, Landau, Friedman & Grimes, 1958). The lattice parameters and space group for  $KU_2F_9$  were first determined by Zachariasen (1948) but he did not determine its structure. This paper presents the values for refined lattice parameters;  $a_0 = 8.7021 \pm 0.0009$ ,  $b_0 = 11.4769 \pm 0.0004$  and  $c_0 = 7.0350 \pm 0.0003$  Å (Cu  $K\alpha_1 = 1.54050$ ), at 23°C and the atomic parameters for  $KU_2F_9$  determined from three-dimensional Cu  $K\alpha$  X-ray data (Tables 1 and 2). The calculated density is 6.4851 g.cm<sup>-3</sup> and  $Z = 4$ .

### Experimental

Single crystals of  $KU_2F_9$  were selected from an ingot of the composition  $KF \cdot UF_4$  33½–66½ mole per cent. The single crystals were ground to nearly spherical shape in an air driven race and one crystal of ellipsoidal shape (0.182 × 0.182 × 0.195 mm) was mounted on a computer operated Picker four-circle goniostat equipped with a scintillation counter detector. Independent reflections  $hkl$ ,  $h \geq 0$ ,  $k \geq 0$  and  $l \geq 0$  were measured to  $2\theta = 145^\circ$  with unfiltered Cu  $K\alpha$  radiation by the  $2\theta$  scan technique. The 740 reflections were corrected for Lorentz and polarization factors and absorption ( $\mu = 1924.07$  cm<sup>-1</sup> for Cu  $K\alpha$ ) and reduced to  $F_o^2$ .

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The conditions for reflection,  $hkl$ , no conditions,  $0kl$ ,  $k + l = 2n$  and  $hk0$ ,  $h = 2n$  and the diffraction symmetry,  $mmm$  are consistent with space groups  $Pna2_1$  (33) and  $Pnma$  (62). The final structure confirms the choice of  $Pnma$  (Zachariasen, 1948).

The structure was refined by iterative least squares with a modification of the Busing, Martin & Levy (1962) computer program. The starting parameters were determined from three-dimensional sections of the Patterson function. The quantity minimized by the least-squares program was  $\sum w| |sF_o^2| - |F_c^2| |^2$  with weights,  $w$ , equal to the reciprocals of the variances which were estimated from the empirical equation:

$$\sigma^2(F_o^2) = [T + B + (0.05(T - B))^2] / [A(Lp)^2]$$

where  $T$  = total counts,  $B$  = background counts,  $A$  = absorption correction, and  $Lp$  = Lorentz and polarization corrections (Brown & Levy, 1964). The scattering factors for the ions were taken from Cromer & Waber (1965) and the anomalous dispersion terms,  $\Delta f' = -5$  and  $\Delta f'' = 15$  electrons (Dauben & Templeton, 1955), were included in the  $U^{4+}$  scattering factors. Anisotropic temperature factors were calculated for  $U^{4+}$  and  $K^+$  and the temperature factors for  $F^-$  were constrained to be isotropic.

The discrepancy indices are,

$$R_1 = \sum ||F_o^2| - |F_c^2| | / \sum |F_o^2| = 0.1228$$

$$R_2 = \sum ||F_o| - |F_c| | / \sum |F_o| = 0.0682$$

Table 1. *The atomic parameters for  $KU_2F_9$  ( $\times 10^3$ )*

Standard errors in parentheses, corresponding to the last significant digit, are given by the variance-covariance matrix.

	$x$	$y$	$z$	$\beta_{11}^*$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
U	325.3 (1)	449.58 (6)	346.8 (2)	2.8 (2)	1.18 (8)	4.3 (3)	-0.04 (6)	-0.3 (1)	-0.02 (5)
K	463 (2)	250	857 (2)	5 (2)	1.8 (5)	10 (2)	0	4 (2)	0
F(1)	-4 (2)	598 (2)	76 (2)	25 (6)	†	†	†	†	†
F(2)	290 (2)	96 (2)	29 (3)	47 (8)	†	†	†	†	†
F(3)	283 (3)	607 (2)	145 (3)	45 (8)	†	†	†	†	†
F(4)	562 (3)	80 (2)	199 (3)	47 (7)	†	†	†	†	†
F(5)	321 (3)	250	338 (3)	4 (2)	†	†	†	†	†

\* Coefficients in the temperature factor;  $\exp [ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) ]$ .

† Constrained to be isotropic.

Table 2. Observed and calculated structure factors for  $KU_2F_9$

L	F <sub>obs</sub>	F <sub>calc</sub>	L	F <sub>obs</sub>	F <sub>calc</sub>	L	F <sub>obs</sub>	F <sub>calc</sub>	L	F <sub>obs</sub>	F <sub>calc</sub>	L	F <sub>obs</sub>	F <sub>calc</sub>	L	F <sub>obs</sub>	F <sub>calc</sub>
0	-7.0	1.1	0	152	152	0	152	152	0	152	152	0	152	152	0	152	152
1	174	152	1	39	39	1	39	39	1	39	39	1	39	39	1	39	39
2	193	152	2	223	211	2	223	211	2	223	211	2	223	211	2	223	211
3	15	15	3	57	57	3	57	57	3	57	57	3	57	57	3	57	57
4	113	113	4	107	107	4	107	107	4	107	107	4	107	107	4	107	107
5	13	13	5	103	103	5	103	103	5	103	103	5	103	103	5	103	103
6	53	53	6	26	26	6	26	26	6	26	26	6	26	26	6	26	26
7	15	15	7	115	115	7	115	115	7	115	115	7	115	115	7	115	115
8	17	17	8	13	13	8	13	13	8	13	13	8	13	13	8	13	13
9	13	13	9	138	138	9	138	138	9	138	138	9	138	138	9	138	138
10	3	3	10	107	107	10	107	107	10	107	107	10	107	107	10	107	107
11	13	13	11	107	107	11	107	107	11	107	107	11	107	107	11	107	107
12	13	13	12	107	107	12	107	107	12	107	107	12	107	107	12	107	107
13	13	13	13	107	107	13	107	107	13	107	107	13	107	107	13	107	107
14	13	13	14	107	107	14	107	107	14	107	107	14	107	107	14	107	107
15	13	13	15	107	107	15	107	107	15	107	107	15	107	107	15	107	107
16	13	13	16	107	107	16	107	107	16	107	107	16	107	107	16	107	107
17	13	13	17	107	107	17	107	107	17	107	107	17	107	107	17	107	107
18	13	13	18	107	107	18	107	107	18	107	107	18	107	107	18	107	107
19	13	13	19	107	107	19	107	107	19	107	107	19	107	107	19	107	107
20	13	13	20	107	107	20	107	107	20	107	107	20	107	107	20	107	107
21	13	13	21	107	107	21	107	107	21	107	107	21	107	107	21	107	107
22	13	13	22	107	107	22	107	107	22	107	107	22	107	107	22	107	107
23	13	13	23	107	107	23	107	107	23	107	107	23	107	107	23	107	107
24	13	13	24	107	107	24	107	107	24	107	107	24	107	107	24	107	107
25	13	13	25	107	107	25	107	107	25	107	107	25	107	107	25	107	107
26	13	13	26	107	107	26	107	107	26	107	107	26	107	107	26	107	107
27	13	13	27	107	107	27	107	107	27	107	107	27	107	107	27	107	107
28	13	13	28	107	107	28	107	107	28	107	107	28	107	107	28	107	107
29	13	13	29	107	107	29	107	107	29	107	107	29	107	107	29	107	107
30	13	13	30	107	107	30	107	107	30	107	107	30	107	107	30	107	107

for all reflections and the standard deviation of an observation of unit weight,  $[\sum W(F_o - F_c)^2 / (n_o - n_v)]^{1/2}$  is 2.596 where  $n_o$  is the number of observations and  $n_v$  the number of variables. The interatomic distances are listed in Table 3 and the observed and calculated structure factors in Table 2. An extinction correction was applied to  $F_c$  by the method suggested by Zachariasen (1967).

Table 3. The interatomic distances for  $KU_2F_9$

The numbers in parentheses are the standard errors in terms of the last significant digit.

U—F(5)	2.292 (1) Å	2[K—F(2)]	2.62 (2) Å
U—F(1)	2.30 (2)	2[K—F(1)]	2.66 (2)
U—F(2)	2.32 (2)	2[K—F(3)]	2.75 (2)
U—F(1)	2.32 (2)	2[K—F(3)]	3.09 (2)
U—F(3)	2.32 (2)	2[K—F(4)]	3.21 (2)
U—F(4)	2.33 (2)	F(1)—F(1)	2.49 (3)
U—F(4)	2.34 (2)	F(1)—F(3)	2.55 (3)
U—F(2)	2.34 (2)	F(1)—F(2)	2.60 (3)
U—F(3)	2.39 (2)	F(1)—F(4)	2.65 (3)
F(1)—F(3)	2.70 (3)	F(1)—F(4)	2.71 (3)
F(1)—F(5)	2.89 (3)	F(2)—F(3)	2.47 (3)
F(2)—F(4)	2.66 (3)	F(2)—F(4)	2.76 (3)
F(2)—F(4)	2.78 (3)	F(2)—F(5)	2.82 (3)
F(2)—F(4)	2.89 (3)	F(3)—F(4)	2.79 (3)
F(3)—F(5)	2.86 (3)	F(4)—F(5)	2.99 (3)

Discussion

Fig. 1 is a stereoscopic pair of drawings showing the nearest neighbor fluoride anions around  $U^{4+}$  and  $K^+$  which in turn are the nearest neighbor cations to F(5) at  $x=0.321$ ,  $y=1/2$ ,  $Z=0.338$ . The uranium ion is coordinated by  $9F^-$  at the corners of a polyhedron which resembles a trigonal prism with a pyramid on each of the three faces. The  $K^+$  ion is coordinated by  $6F^-$  at about  $2.7\text{Å}$  and by two  $F^-$  at  $3.09\text{Å}$  forming a distorted cube around it. Two additional fluoride ions, F(4), are at  $3.21\text{Å}$  on the same side of the cube and nearly coplanar with each set of four fluoride ions forming the top and bottom of the cube. The  $U^{4+}$  and  $K^+$  polyhedra each form alternating layers perpendicular to the  $b_0$  axis with the  $K^+$  polyhedra centered at  $b_0 = 1/2$  and  $3/2$ . The  $U^{4+}$  polyhedra share edges with each other within a layer and edges with  $K^+$  polyhedra in adjacent layers. The  $K^+$  polyhedra also share edges with one another within a layer.

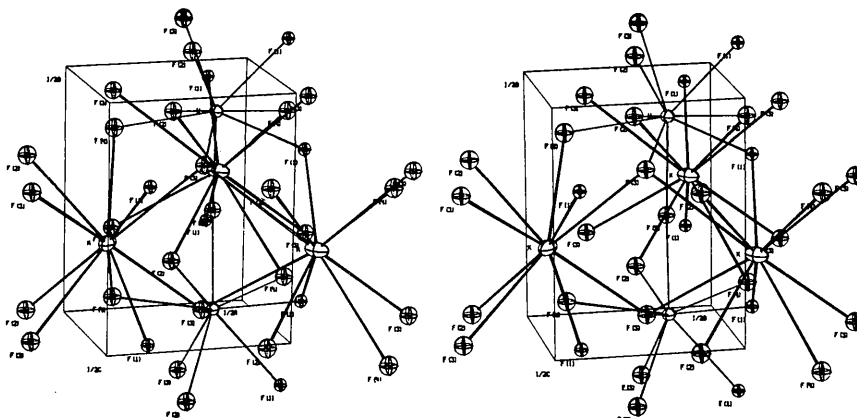


Fig. 1. A stereoscopic view of the structure of  $KU_2F_9$  with one fourth unit cell outlined.

The fluorine ion F(5) is shared only by U<sup>4+</sup> ions across the K<sup>+</sup> layers but is too distant, 4Å, to be considered shared by K<sup>+</sup> ions.

The interatomic distances F(1)–F(1), 2.49(3)Å and F(1)–F(3), 2.55(3)Å are considerably shorter than twice 1.36Å, the usual ionic radius for F<sup>-</sup> (Pauling, 1960). Recent structure determinations show that F<sup>-</sup>–F<sup>-</sup> interatomic distances may be as short as 2.241(11)Å in Na<sub>7</sub>Zr<sub>6</sub>F<sub>31</sub> (Burns, Ellison & Levy, 1968) and 2.40(3)Å in RbPaF<sub>6</sub> (Burns, Levy & Keller, 1968). These two compounds are similar to KU<sub>2</sub>F<sub>9</sub> in that they are complex fluorides with similar sizes and kinds of ions. The Zr–8F antiprism in Na<sub>7</sub>Zr<sub>6</sub>F<sub>31</sub> has F<sup>-</sup>–F<sup>-</sup> distances as short as 2.504(3)Å and the 2.40(3)Å distances observed for RbPaF<sub>6</sub> occur in the Pa–8F dodecahedron. In KU<sub>2</sub>F<sub>9</sub> the six K–F distances and the nine U–F distances are equal to the sum of the ionic radii so that the bonding is primarily ionic. The application of Hannay & Smyth's (1946) formula for the calculation of percentage of ionic character indicates that the K–F bond is 88% ionic while the U–F bond should have 55% ionic character. It is evident that most of the F<sup>-</sup>–F<sup>-</sup> distances in these complex fluorides reflect the ionic nature of the bonding but that some covalent bonding occurs in the same compound.

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**The crystal structure of calcium 1,3-diphosphorylimidazole hexahydrate (revised title).** By L. NEEL BEARD and P. GALEN LENHERT, *Department of Physics, Vanderbilt University, Nashville, Tennessee 37203, U.S.A.*

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A paper on the structure of the title compound was published (Beard & Lenhart, 1968) under the title *The Crystal Structure of 1,3-Diphosphorylimidazole*. This title should be

replaced by *The Crystal Structure of Calcium 1,3-Diphosphorylimidazole Hexahydrate* in order to reflect the actual composition of the substance studied.

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