Short Communications

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The crystal structure of KU₂**F**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 U⁴⁺ 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 $c_0 = 7.0350$ ± 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⁻³ and Z = 4.

Experimental

Single crystals of KU₂F₉ were selected from an ingot of the composition KF·UF₄ 33 $\frac{1}{2}$ -66 $\frac{2}{3}$ 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, $h \ge 0$, $k \ge 0$ and $l \ge 0$ were measured to $2\theta = 145^{\circ}$ with unfiltered Cu $K\alpha$ radiation by the 2θ scan technique. The 740 reflections were corrected for Lorentz and polarization factors and absorption ($\mu = 1924.07$ cm⁻¹ for Cu $K\alpha$) and reduced to F_{α}^2 .

* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation. 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 $\Sigma w ||sF_o^2| - |F_c^2||^2$ 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 U⁴⁺ scattering factors. Anisotropic temperature factors were calculated for U⁴⁺ and K⁺ and the temperature factors for F⁻ were constrained to be isotropic.

The discrepancy indices are,

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

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

Table 1. The atomic parameters for KU_2F_9 (×103)

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

	x	у	z	β_{11}^*	β_{22}	β_{33}	β_{12}	β_{13}	β_{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)	†	†	†	Ť	†
F(4)	562 (3)	80 (2)	199 (3)	47 (7)	†	Ť	t	†	†
F(5)	321 (3)	250	338 (3)	4 (2)	†	Ť	†	†	Ť

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

Table 2. Observed and calculated structure factors for KU₂F₉

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-7 0 L	8 82 78	1 503 -450	8 142 -141 8	15 20 8	217 211	3 37 -34 7	202 - 196 1 76 78
ັ-7ີາ ເຼົ	8 41 39	5 308 340	1 28 -30 0	508 474 1	208 - 187	5 128 128 1	48 - 46 7 0 L
°-7°2 L	8 223 211	/ 138 -138 0 4 L	3 17 21 2	316 291 2	160 169	5 14 -20 2 4 SL 3	76 66 1 93 105 97 92 2 927 911
5 113 97 -7 3 L	7 57 57	0 113 101 2 107 -108	4 102 108 3 5 26 24 4	91 101 4	19 13	0 507 -480 4	40 - 35 3 85 - 76
6 17 -13	-3 6 L	122 -133	6 49 52 5	243 -257 6	18 -6	165 162	5 7 5 30 24
6 63 53	-3 7 L	8 26 26	' i ' i '' '	79 78 '	103 -97 3 5 L	3 49 41 1 4 271 275 2	125 -111 7 1 L 207 -191 1 56 57
-76L 517-13	7 15 15 -3 BL	0 5 L 1 499 - 483	1 211 201	2,5 1	56 -48	5 130 -124 3	208 197 2 19 -5
-7 7 L	6 37 38	3 84 -98	3 234 -248 1	104 -92 3	77 73	4 6 L S	23 -24 4 4 15
-7 8 L	6 30 -30	7 150 -152	5 24 32 5	47 -47 5	14 10	1 200 190 1	146-134 7 2 L
-6 0 L	5 20 20	0 410 -389	6 31 30 4 7 184 182 5	35 - 37 6 91 93 7	147 - 147 -	2 47 -38 2 3 44 40 3	227 208 1 54 52
7 47 -37 -6 1 L	-311L 1 70 71	2 55 58	1 8 L 6	70 74	3 6 L	4 0 -10 4	126 -122 3 61 -51
7 45 43	-3 12 L	6 119 -122	2 298 - 302	271 2	¥Õ - 39	6 35 33 1	63 -57 5 0 11
7 32 -23	3 196 -203	1 371 - 363	4 171 180 1	309 290 3 166 159 4	176 - 185	7 58 59 2 4 7 L 3	95 -89 7 31. 108 104 1 198 184
6 54 -44	-3 13 L 1 16 -17	3 124 -131 5 303 327	5 0 4 2	114 - 112 5	11 24	0 359 - 329 5	16 -15 2 41 -30
-6 4 L 6 102 94	5 515 -556	7 88 -85	7 118 -116 4	103 -191 7	101 103	2 135 125 1	149 -138 4 55 52
ັ-6ີ 5 ເຼິ	8 17 -14	0 334 - 320	1 75 75 6	172 175 1	17 -22	4 243 245 4	215 204 5 26 23 135 -136 7 4 L
-661	8 45 -41	4 185 199	2 109 -108 7	28132	21 13	5 70 -66 4 BL 2	5 11 L 1 37 -36 78 81 2 141 129
6 74 -64 -6 7 L	-23L 837-31	6 204 -210	4 44 43 0	227 211 4	189 - 198	0 154 137 3	88 -88 3 21 -11
5 230 211	-2,4 60	1 80 -73	6 22 17 2	60 -58 6	126 - 123	2 44 -35 1	95 -95 7 5 L
5 82 -77	ໍ-2ິ6 ເ	5 87 87	1 82 -76 4	143 - 149	14 - 14 3 B L	3 53 56 2 4 90 -84	165 174 1 222 202 6 0 L 2 85 -63
-69L ₩₩6₩5	7 39 37 -27L	0 10 L 0 385 - 374	2 351 -357 5	219 229 1	202 191	5 227 -223 0	372 459 3 346 -323
-6 10 L	7 55 53	2 169 166	4 193 203 7	78 -76 3	283 -288	ູ ຟີ 9 ເຼື ຊໍ	121 -115 7 6 L
ັ-6 ໍ້ 1 ເ	7 76 77	6 258 -269	6 125 126 0	136 131 5	28 30	U /6 -65 3 1 37 33 4	314 - 292 2 147 - 138
-5 0 L	6 73 -71	1 122 117	1 65 -61 2	94, 93 6 58 -58	37 - 37	2 35 32 5	96 -88 3 35 27 275 245 H 88 82
7 168 155 -5 1 L	-210L 5246-248	3 25 26	2 83 77 3	8 4 1	44 - 36	73 72	5 1 L 7 7 L
7 80 76	-2 11 L	0 12 L	1 27 -25 5	91 - 94 4	61 -63	410L 1	100 -102 2 67 -60
7 157 144	5 91 91	2 88 86	1 15 1	2 10 1 6	27 - 30	1 301 288 3	9 4 3 273 -250 25 -16 7 8 L
7 151 136	3 50 46	4 164 17D 0 13 L	2 203 -207 1	206 205	3 10 L 277 266	2 22 -23 4	31 - 32 1 26 - 18
7 79 75	4 121 -122	1 229 239	3 130 135 2	80 74 2	64 60	¥ 70 -69 6	39 36 8 0 L
-5 51	0 191 201	DIVL	1 13 1	135 - 139 4	20-25	4 11 L 0	289 322 1 119 152
-5°6 i	2 72 -73	1 0 L	2 95 103	5 11 L	ນີ້ແດ້	2 52 -47 2	110 102 2 132 124 107 -96 3 37 29
ີ-5°7 ເ	3 8 -14 -1 0 L	2 479 513	3 185 197 0	126 -113 1	22 13 92 -86	36-53 469-704	55 51 4 214 191
6 60 57 -5 8 L	8 252 -246	3 161 -171	1 18 -17 2	36 37 3	18 -9	ู้ พูโอ เ รี	106 -95 0 70 94
5 18 -12	8 65 -63	5 20 -2N	0 397 358	83 84	3 12 L	1 160 167	6 3 6 2 51 -41
່ມີຮ	8 199 - 192	7 116 112	2 84 84	5 15 1 5	55 55	2 23 -20 0	50 50 3 34 31 261 - 243 4 87 - 74
5 17 16 -5 10 L	a 108 -106	8 252 247 1 1 L	3 143 142 0	186 187 3	195 -203	4 13 L 2	17 21 8 2 L 81 -56 0 198 -227
3 213 215	a 105 -100	1 132 102	5 325 -345 2	66 -63 1	20 18	1 47 46 4	33 -26 1 146 152
-s ii i	-1 5 L	3 209 -217	7 127 125	155 -155	N O L	1 181 180	6 4 L 3 54 43
5 92 89	-1 6 L	5 18 10	211	192 -200 1	545 -559	2 312 -292 0 3 320 -307 1	139 132 4 167 145 7 -7 8 3 L
1 96 -95	-17L	7 91 91	1 153 125 2	104 - 106 2	111 95 138 -128	4 177 169 2	70 -61 0 141 147
2 166 -172 -% 0 L	7 186 -181 -1 B L	8 67 -63	2 43 -35 3	16 -14 4	70 71	6 130 116 4	94 -83 2 81 -73
8 9 -6	7 118 -116	1 213 165	4 96 -101 1	296 -273 6	103 - 102	1 91 -85	6 5 1 4 133 -112
8 0 -3	6 22 17	3 188 -203	6 95 97	548 571 8	11 -6	3 114 106 1	160 153 8 4 L 342 - 314 0 90 - 98
7 39 31	5 37 -37	5 14 -15	7 31 30 4	55 -60 0	4 1 L 156 - 173	4 102 99 2 5 17 -2 3	42 -37 1 56 51
7 41 32	6 126 -127 -1 11 L	6 124 -127	2 2 1 6	49 40 1	105 93	6 65 60 4	108 -106 3 22 12
-4 5 L	5 23 17	8 195 193	1 369 318 8	ເຊີ ສີ	45 45	1 173 157	6 6 L 0 239 255
-4 6 L	3 130 135	1 279 231	5 109 106 1	25 - 27 5	68 -58	2 254 - 264 0	152 -137 1 256 234 11 -15 2 88 -75
7 62 -58 -4 7 L	4 118 -122 -1 13 L	2 76 - 78	4 184 191 2 5 263 -276 3	18-2 184 6	93 -86 17 A	4 152 148 3	19 23 3 68 65
6 214 207	1 137 142	4 95 106	6 166 -169	92 - 96 8	io i	6 120 107 4	101 95 0 114 104
6 75 72	3 182 -196	6 77 79	8 40 -41 6	57 -46 0	133-126	1 138 -125	0 14 1 43 -33 6 7 L 2 50 -48
5 38 -38	1 10 -17	9 106 -106	0 342 315 6	7 38 -36 L 3 83 78 2	345 - 318 61 61	2 231 -212 0	82 72 8 7 L 258 - 237 0 145 131
-4 10 L 4 72 -69	2 206 -213	1 1 1	1 168 138	3 2 1 3	80 -74	ų 199 188 ž	46 -41 1 175 154
5 265 294	4 390 -441	\$ 212 2 <u>15</u>	3 97 106	56 -58 5	268 267	5 109 104 4	68 -63 1 109 -167
3 14 -5	8 47 39	4 79 -89	5 107 -111	342 355 6 34 31 7	89 -85	1 73 65 0	6 8 1 2 122 -114
N 68 71 -N 12 L	1 244 -132	5 42 42	6 187 194 9 7 67 6	5 48 -43 5 47 44 n	4 3 L	2 71 -62 1	78 -68 9 1
0 95 99	3 28 20	7 36 37	8 35 32	218 -211 1	130 120	¥ 56 53 5	x 8 2 9 8
5 51 -20	7 69 -67	1 5 1	0 62 -51	, vi -36 2 3 3 L 3	137 124 52 47	5 26 29	5 9 L 3 73 65
3 53 -54 -413 L	0 719 707	2 261 -254	1 118 106	1 14 10 4 9 456 1179 5	222 222	5 5 1	104 -92 1 127 -133
0 221 -235	2 138 -139	3 387 - 134	3 17 8	¥\$ 50 6	246 235	2 313 -298	6 10 1 9 3 1
ໍ-3 <u>ີ</u> 0 ເືື	6 238 250	5 37 43	5 89 -92 1	4 222 -232 5 27 34 0	100 -96	3 308 300 0 4 187 180 1	352 -310 1 53 -52 60 -56 2 213 199
8 86 8	8 27 22	6 103 10w	6 25 -22 (5 161 - 156 1	112 -117	6 33	

for all reflections and the standard deviation of an observation of unit weight, $[\Sigma W(F_o-F_c)^2/(n_o-n_v)]^{1/2}$ 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 KU₂F₉

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

	· · · · · · · · · · · · · · · · ·		·- ·
UF(5)	2·292 (1) A	2[K –F(2)]	2·62 (2) A
U - F(1)	2.30(2)	2[K - F(1)]	2.66(2)
UF(2)	2.32(2)	2[K - F(3)]	2.75 (2)
UF(1)	2.32 (2)	2[K -F(3)]	3.09 (2)
U - F(3)	2.32 (2)	2[K - F(4)]	3.21 (2)
UF(4)	2.33(2)	F(1) - F(1)	2.49 (3)
UF(4)	2.34 (2)	F(1) - F(3)	2.55(3)
UF(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 U4+ and K+ which in turn are the nearest neighbor cations to F(5) at x = 0.321, $y = \frac{1}{2}$, 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 2.7Å and by two F- at 3.09Å forming a distorted cube around it. Two additional fluoride ions, F(4), are at 3.21 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 U⁴⁺ and K⁺ polyhedra each form alternating layers perpendicular to the b_0 axis with the K⁺ polyhedra centered at $b_0 = \frac{1}{4}$ and $\frac{3}{4}$. The U⁴⁺ 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 KU₂F₉ with one fourth unit cell outlined.

The fluorine ion F(5) is shared only by U⁴⁺ ions across the K⁺ layers but is too distant, 4Å, to be considered shared by K⁺ 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- (Pauling, 1960). Recent structure determinations show that F^--F^- interatomic distances may be as short as 2.241(11)Å in Na₇Zr₆F₃₁ (Burns, Ellison & Levy, 1968) and 2.40(3)Å in RbPaF₆ (Burns, Levy & Keller, 1968). These two compounds are similar to KU₂F₉ in that they are complex fluorides with similar sizes and kinds of ions. The Zr-8F antiprism in Na₇Zr₆F₃₁ has F⁻-F⁻ distances as short as 2.504(3)Å and the 2.40(3)Å distances observed for RbPaF₆ occur in the Pa-8F dodecahedron. In KU₂F₉ 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^--F^- 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.

(Received 13 March 1969)

A correction of the title of Acta Cryst. (1968), B24, 1529.

Structure of 1,3-Diphosphorylimidazole. This title should be composition of the substance studied.

A paper on the structure of the title compound was pub- replaced by The Crystal Structure of Calcium 1,3-Diphoslished (Beard & Lenhert, 1968) under thetitle The Crystal phorylimidazole Hexahydrate in order to reflect the actual

Reference

BEARD, L. N. & LENHERT, P. G. (1968). Acta Cryst. B24, 1529.