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Crystal Chemical Studies of the 5*f*-Series of Elements. XXII. The Crystal Structure of K_3UF_7

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K_3UF_7 can be prepared in an ordered and in a disordered form. The ordered form is tetragonal and isostructural with the compound $K_3UO_2F_5$. The unit-cell dimensions are $a_1 = 9{\cdot}22$ Å, $a_3 = 18{\cdot}34$ Å. The structure contains complexes $(UF_7)^{-3}$ having the shape of pentagonal bipyramids with U–F= 2·26 Å.

The disordered form is cubic face-centered with $a = 9{\cdot}22 \pm 0{\cdot}02$ Å and four molecules per unit cube. It is proposed that the structure contains UF_7 complexes of the same shape and dimensions as observed in the ordered form, but that there is some randomness as to the orientation of these complexes.

The compounds $(NH_4)_3ZrF_7$ and K_3ZrF_7 are isostructural with the disordered form of K_3UF_7.

Introduction

A study of the system KF–UF_4 (Zachariasen, 1948) showed the existence of the compound K_3UF_7. This substance could be prepared in either of two closely related forms. By slow cooling of the melt the compound was found to be tetragonal body-centered with $a_1 = 9{\cdot}20 \pm 0{\cdot}02$ Å, $a_3 = 18{\cdot}40 \pm 0{\cdot}06$ Å and with eight molecules in the unit cell. Rapidly cooled preparations of K_3UF_7 were on the other hand cubic face-centered with $a = 9{\cdot}21 \pm 0{\cdot}01$ Å and four molecules per unit cube. The X-ray diffraction patterns of the two phases are strikingly similar. All of the diffraction lines of the cubic phase correspond to lines of the tetragonal phase. However, the diffraction pattern of the latter phase contains a number of superstructure lines which require the choice of the larger, tetragonal unit cell. Furthermore, at larger angles the pseudo-cubic lines show multiplet structure, indicating that a_3 is not exactly twice the length of a_1.

Single crystals were not obtained of either modification of K_3UF_7. As far as the tetragonal form goes

Table 1. *Powder diffraction data for* $K_3UO_2F_5$ *and* K_3UF_7

	$K_3UO_2F_5$		Tetragonal K_3UF_7		Cubic K_3UF_7		
$H_1H_2H_3$	I	$\sin^2\theta$	I	$\sin^2\theta$	I	$\sin^2\theta$	$H_1H_2H_3$
112	*s*	0·0224	*s*–	0·0211	*s*	0·0214	111
103	Trace	0·0244					
200, 004	*m*	0·0297	*m*	0·0283	*m*	0·0285	200
211	*vvw*	0·0388	Trace	0·0369			
105, 213	*w*	0·0534	*vw*	0·0514			
220, 204	*vs*	0·0587	*s*	0·0567	*vs*	0·0566	220
312, 116	*ms*	0·0800 }	*w*	0·0776	*m*	0·0778	311
215, 303	*vw*	0·0824 }					
224	*vw*	0·0876	*vw*–	0·0839	*vw*	0·0844	222
107	*w*	0·0972	*vw*	0·0947			
305, 323	*vw*–	0·1108					
400	*s*	0·1153 }	*w*	0·1118	*m*	0·1124	400
008	*vw*	0·1182 }					
217	*w*	0·1258	*vw*	0·1217			
332, 316	*w*–	0·1378 }	*w*	0·1340	*w*	0·1342	331
325, 413	*w*	0·1392 }					
420, 404, 208	*m*	0·1444	*w*	0·1403	*w*	0·1411	420
109, 307	*w*	0·1549	*vw*	0·1502			
415	*vw*–	0·1680	Trace	0·1638			
424, 228	*s*	0·1734	*s*–	0·1687	*s*–	0·1686	422
219, 327	*m*	0·1832	*w*	0·1784			
512, 336, 1,1,10	*m*	0·1944	*w*	0·1896	*w*	0·1901	333, 511
309, 417	*w*	0·2118	*vw*	0·2067			
1,0,11, 435, 505, 523	*w*–	0·2246	*vw*	0·2190			
440	*vw*	0·2296 }	*w*–	0·2249	*w*	0·2251	440
408	*vw*	0·2315 }					

it would under the circumstances not seem feasible to get much information about its structure. However, the situation is altered by the observation that the tetragonal form of K_3UF_7 is isostructural with $K_3UO_2F_5$, the detailed structure of which has recently been deduced (Zachariasen, 1954*b*). The conclusion on the basis of the available experimental evidence is inescapable that the cubic K_3UF_7 is to be regarded as a disordered form of the tetragonal modification.

Tetragonal K_3UF_7

A re-examination of the original diffraction patterns of the tetragonal form of K_3UF_7 has led to improved values for the lattice periods, namely:

$$a_1 = 9{\cdot}22 \pm 0{\cdot}02\ \text{Å},\ a_3 = 18{\cdot}34 \pm 0{\cdot}04\ \text{Å}\ .$$

With eight stoichiometric molecules per unit cell this gives a calculated density of 4·15 g.cm.$^{-3}$.

Except for small shifts in line positions due to the small differences in unit-cell dimensions, the powder diffraction patterns of $K_3UO_2F_5$ and K_3UF_7 are hardly distinguishable. Table 1, which gives a limited amount of diffraction data for $K_3UO_2F_5$ and for the two forms of K_3UF_7, gives an entirely inadequate illustration of the near identity, extending to large scattering angles, of the intensity distribution in the two tetragonal patterns. This close intensity agreement is proof not only that tetragonal K_3UF_7 is isostructural with $K_3UO_2F_5$, but also that the parameter values are very nearly the same for the two compounds.

An immediate consequence of this observation is that the K_3UF_7 structure must contain $(UF_7)^{-3}$ complexes and that these complexes must be nearly isostructural with the $(UO_2F_5)^{-3}$ groups. The replacement of the two uranyl oxygens by fluorine atoms may be expected to be accompanied by an appreciable increase in the length of these bonds so as to make all seven bond lengths within the bipyramidal $(UF_7)^{-3}$ group approximately equal.

Let the fluorine atoms in the K_3UF_7 structure which take the place of the uranyl oxygens in the $K_3UO_2F_5$ structure be denoted as F_{IV} atoms. In accordance with the discussion given above, it is suggested that all parameters of the K_3UF_7 structure are the same as for $K_3UO_2F_5$ except as regards the O–F_{IV} parameters. The proposed structure for K_3UF_7 is accordingly based upon the space group $I4_1/a$ with the parameter values as given in Table 2.

Table 2. *Parameter values for tetragonal* K_3UF_7

		x	y	z
4 K_I	4(*a*)	0	$\frac{1}{4}$	$\frac{1}{8}$
4 K_{II}	4(*b*)	0	$\frac{1}{4}$	$\frac{5}{8}$
16 K_{III}	16(*f*)	0·210	−0·009	0·011
8 U	8(*e*)	0	$\frac{1}{4}$	0·396
8 F_I	8(*e*)	0	$\frac{1}{4}$	0·273
16 F_{II}	16(*f*)	0·359	0·232	0·005
16 F_{III}	16(*f*)	0·271	0·202	0·143
16 F_{IV}	16(*f*)	0·100	0·025	0·396

The interatomic distances of the proposed structure are:

U–2 F_{II}	2·24 Å	K_{III}–1 F_{II}	2·62 Å
–1 F_I	2·25	–1 F_{III}	2·64
–2 F_{IV}	2·27	–1 F_{IV}	2·73
–2 F_{III}	2·28	–1 F_{II}	2·76
K_I–2 F_I	2·71	–1 F_{IV}	2·81
–4 F_{III}	2·56	–1 F_{III}	2·94
K_{II}–4 F_{II}	2·72	–1 F_I	2·96
–4 F_{IV}	2·72	–1 F_{III}	3·14

Interatomic distances predicted from ionic radii (Zachariasen, 1954*a*) are, for comparison:

$$U^{IV}\text{–}7\ F = 2{\cdot}30\ \text{Å},\ K\text{–}6\ F = 2{\cdot}66\ \text{Å},\ K\text{–}8\ F = 2{\cdot}74\ \text{Å}.$$

It is felt that the main features of the proposed structure are beyond doubt; a detailed structural study based upon single-crystal measurements probably will lead to only minor parameter adjustments.

Cubic K_3UF_7

The cubic form of K_3UF_7 is face centered. The best value for the cube edge is

$$a = 9{\cdot}22 \pm 0{\cdot}02\ \text{Å}\ ,$$

and there are four stoichiometric molecules per unit cube.

The observed intensities, some of which are listed in Table 1, show that the metal atoms are at or near the following sites:

$$4\ U\ \text{in}\ (0, 0, 0),\ \ 4\ K_I\ \text{in}\ (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}),\ \ 8\ K_{II}\ \text{in}\ (\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4})\ .$$

The structure of $K_3UO_2F_5$ and of tetragonal K_3UF_7 shows a pronounced pseudo-cubic character as far as the metal positions are concerned. Indeed, the metal atoms of these tetragonal compounds are displaced by small amounts of 0·4 Å or less from the cubic sites given above.

It is proposed that the cubic form of K_3UF_7 is in reality a disordered form of the tetragonal modification. This suggestion does not rest on direct evidence, but is made probable by a series of arguments. In the first place the cubic structure seems to form only under conditions of rapid cooling. Second, the observed close structural relationship between the two forms may be regarded as supporting evidence. Lastly, there is no way of obtaining a reasonable structure by assigning positions to the fluorine atoms in accordance with cubic face-centered space group symmetry.

It is further proposed that the disordered structure of K_3UF_7 contains $(UF_7)^{-3}$ complexes of the same shape and dimensions as in the ordered structure (i.e. pentagonal bipyramids with U–F = 2·26 Å), and that there is disorder in respect to the orientation of these complexes. In the ordered structure the pentagonal axis of the UF_7 group (the F_{IV}–U–F_{IV} axis) lies in the *xy* plane and makes an angle of 24° with the *x* or *y* axis, while the U–F_I bond is parallel to the *z* axis.

The atomic positions of the F_I and F_{IV} atoms when referred to the cubic axes of the disordered structure with the uranium at the origin become:

$$F_I \text{ in } (0, 0, 0{\cdot}245),\ F_{IV} \text{ in } (0{\cdot}100, 0{\cdot}225, 0)\,.$$

It is suggested that this orientation of the UF_7 group is but one of a number of statistically equivalent orientations to be found in the disordered structure. The various possibilities for the orientation of the UF_7 group may be described as follows. Choosing the origin in a uranium atom, the F_I atom is at any one of the six equivalent sites $\pm(0, 0, 0{\cdot}245)$ while the pentagonal axis of the UF_7 group is normal to the U–F_I bond and makes an angle of 24° with a cube axis. Accordingly, there are 24 statistically equivalent orientations for the UF_7 complex. In order that reasonable interatomic distances be obtained it becomes necessary to assume small local displacements of the metal atoms from the mean sites given at the beginning of this section. Thus, if the F_I atom is at (0, 0, 0·245), the K_I may be expected to be at (0, 0, 0·549) rather than at the ideal site of (0, 0, $\frac{1}{2}$).

If these local displacements of the metal atoms from the ideal sites are disregarded, the average structure as regards the fluorine positions may be described in the following manner:

Space group: *Fm*3*m*.
4 U in 4(*a*);
4 K_I in 4(*b*), 8 K_{II} in 8(*c*);
4 F_I in 24(*e*);
8 F_{II} in 192(*l*), 8 F_{III} in 192(*l*), 8 F_{IV} in 96(*j*);

with the fluorine parameters having the values

	x	*y*	*z*
F_I	0·245	0	0
F_{II}	−0·199	0·132	−0·059
F_{III}	0·076	0·212	−0·095
F_{IV}	0	0·100	0·225

On the $(NH_4)_3ZrF_7$ structure

The crystal structure of $(NH_4)_3ZrF_7$ and the isostructural hafnium compound was first investigated by Hassel & Mark (1924). These writers concluded that the structure contained ZrF_6^{-2} ions and F^- ions rather than complexes ZrF_7^{-3}. The validity of the structure proposed by Hassel & Mark was subsequently questioned by Hampson & Pauling (1938), who pointed out that some of the interatomic distances were impossibly small. As a consequence Hampson & Pauling reinvestigated the structure and came to the conclusion that $(NH_4)_3ZrF_7$ and the analogous potassium compound contained ZrF_7^{-3} complexes. However, they demonstrated that the space-group theory provided no way of placing all of the atoms in definite positions in the unit cell. Hampson & Pauling therefore proposed a structure involving some randomness in the orientation of the ZrF_7-complexes. The shape of the ZrF_7 complex was assumed to be such that it could be obtained from an octahedral ZrF_6 group by adding a seventh fluorine atom to be situated on the threefold axis and by distorting the octahedron such as to make the twelve small F–F distances equal, with the seven Zr–F distances also equal.

All the compounds in question are, like the disordered form of K_3UF_7, cubic face-centered with four stoichiometric molecules per unit cube, and the intensities show that the metal atoms are at or near the ideal sites deduced in the preceding section. The values for the unit-cube edges are, according to Hampson & Pauling, 9·382 Å for the NH_4–Zr compound and 8·969 Å for the K–Zr compound. On the basis of the experimental evidence, the conclusion seems inescapable that the whole series of cubic compounds, the NH_4–Zr, NH_4–Hf, K–Zr and K–U salts, are isostructural.

The shape which Hampson & Pauling suggested for the ZrF_7 complex is reasonable from the point of view of interatomic distances, but there was otherwise no indication of its correctness. In view of the arguments presented in the preceding sections it seems likely that proposed shape of the ZrF_7 complex is incorrect, and that the complex, instead, has the form of a pentagonal bipyramid as was found for the UF_7 complex. Except for the different conclusions as to the shape of the XF_7 complex, this writer agrees with the conclusions of Hampson & Pauling that the structure of the crystal is disordered as a consequence of some randomness in the orientation of the XF_7 complexes.

The powder diffraction patterns used in this study were all taken by Miss Anne Plettinger.

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