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**The crystal structure of CsU<sub>6</sub>F<sub>25</sub>\*** By GEORGE BRUNTON, *Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.*

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The complex fluoride CsU<sub>6</sub>F<sub>25</sub> crystallizes with space group *P6<sub>3</sub>/mmc*;  $a_0 = 8.2424(4)$ ,  $c_0 = 16.412(2)$  Å,  $Z = 2$  and the calculated density =  $7.0013$  g.cm<sup>-3</sup>. The U<sup>4+</sup> ion is coordinated by 9F<sup>-</sup> ions at distances of 2.267 (8) to 2.54 (6) Å and the Cs<sup>+</sup> ion by 12F<sup>-</sup> at distances of 3.12 (2) and 3.45 (4) Å. The final *R* value is 0.0685 for 212 reflections  $> 3\sigma$ . The reflections were collected with an automated Picker four-circle goniostat.

### Introduction

The complex fluoride compound CsU<sub>6</sub>F<sub>25</sub> has similar unit cell parameters ( $a_0 = 8.2424(4)$  and  $c_0 = 16.412(2)$  Å) to KU<sub>6</sub>F<sub>25</sub> ( $a_0 = 8.18(1)$  and  $c_0 = 16.42(2)$  Å) and KTh<sub>6</sub>F<sub>25</sub> ( $a_0 = 8.32(1)$  and  $c_0 = 16.78(2)$  Å) which were first described by Zachariasen (1948). The three compounds have the same space group, *P6<sub>3</sub>/mmc*, and with CsTh<sub>6</sub>F<sub>25</sub> (Thoma & Carlton, 1961) and RbU<sub>6</sub>F<sub>25</sub> (Thoma, Insley, Landau, Friedman & Grimes, 1958), probably are isomorphous. Preliminary work on RbTh<sub>6</sub>F<sub>25</sub> indicates that it has a similar structure but a different space group (Brunton, Insley, McVay & Thoma, 1965).

### Experimental

The compound CsU<sub>6</sub>F<sub>25</sub> crystallizes readily as the primary phase in the composition range 60–70 mole per cent UF<sub>4</sub> in a CsF–UF<sub>4</sub> melt. Crystals picked from a cooled ingot of this composition range were ground to approximately spherical shape in an air-driven race. An ellipsoidal crystal of dimensions 0.163 × 0.169 × 0.182 mm was mounted on a computer operated Picker four-circle goniostat equipped with a scintillation counter detector. Independent reflections  $hkl$ ,  $h > k \geq 0$  and  $l \geq 0$  were measured by the  $\theta$ – $2\theta$  scan technique using unfiltered Cu  $K\alpha$  radiation. The 351 reflections were corrected for Lorentz and polarization effects and absorption ( $\mu = 2185.64$  cm<sup>-1</sup>). The conditions for reflection,  $hh2hl$ ,  $l = 2n$ , and the diffraction symmetry, *6/mmm*, are consistent with space groups; *P6<sub>3</sub>mc*, *P6<sub>2</sub>c* and *P6<sub>3</sub>/mmc*. The final structure confirms Zachariasen's (1948) choice of space group *P6<sub>3</sub>/mmc*.

The unit-cell parameters were determined by a least-squares adjustment of 12 high angle (129–135°  $2\theta$ ) Cu  $K\alpha$

reflections (Cu  $K\alpha_1 = 1.5405$  Å),  $Z = 2$  and  $\rho_{\text{cal}} = 7.0013$  g.cm<sup>-3</sup>. The structure was refined by iterative least-squares adjustment using a modification of the Busing, Martin & Levy (1962) computer program. The starting parameters for the uranium atoms were determined from three-dimensional sections of the Patterson function. The parameters of the other ions were determined from Fourier sections computed from the uranium positions. The quantity minimized by the least-squares program was  $\sum w ||F_o| - |F_c||^2$  with weights,  $w$ , equal to the reciprocals of the variances which were estimated from the empirical equation;

$$\sigma^2(F_o^2) = [T + B + (0.03(T - B))^2] / [A(Lp)^2]$$

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 for U and Cs for Cu  $K\alpha$  radiation were taken from Cromer (1965). Anisotropic temperature factors were calculated for U<sup>4+</sup> and Cs<sup>+</sup> and the temperature factors for F<sup>-</sup> were constrained to be isotropic. The final parameters were calculated using the data greater than  $9\sigma^2(F_o^2)$ . The elimination of the statistically poorer weak reflections by this method improves the final discrepancy indices and the F<sup>-</sup>–F<sup>-</sup> distances but does not change the overall discrepancy index for all of the data. The discrepancy indices;

$$R_1 = \frac{\sum ||F_o^2| - |F_c^2||}{\sum |F_o^2|} = 0.1329 \text{ for 212 reflections } > 3\sigma$$

$$= 0.1385 \text{ for all reflections}$$

$$R_2 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.0685 \text{ for 212 reflections } > 3\sigma$$

$$= 0.0936 \text{ for all reflections.}$$

The standard deviation of an observation of unit weight  $[\sum w(F_o - F_c)^2 / (n_o - n_v)]^{1/2}$  is 2.708 where  $n_o$  is the number of reflections, 212, and  $n_v$  the number of variables. An extinction correction was applied to  $F_c$  by the method suggested by Zachariasen (1967, 1968),  $r^* = 0.006(2)$  Å.

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Table 1. *Atomic parameters and temperature factors for CsU<sub>6</sub>F<sub>25</sub>(× 10<sup>3</sup>)*

Wyckoff notation	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
12( <i>k</i> )	U	173.7 (2)	2 <i>x</i>	111.46 (9)	0.9 (4)	7.7 (4)	0.6 (1)	0.0	-0.12 (8)	<i>b</i>
2( <i>d</i> )	Cs	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{2}$	7.2 (9)	<i>c</i>	1.9 (4)	<i>c</i>	0.0	0.0
12( <i>j</i> )	F(1)	184 (3)	2 <i>x</i>	$\frac{1}{2}$	1 (2)	<i>d</i>				
12( <i>k</i> )	F(2)	485 (3)	2 <i>x</i>	144 (2)	7 (2)					
12( <i>i</i> )	F(3)	678 (4)	0.0	0.0	6.7 (9)					
4( <i>f</i> )	F(4)	$\frac{1}{2}$	$\frac{2}{3}$	68 (7)	23 (5)					
4( <i>e</i> )	F(5)	0.0	0.0	76 (18)	68 (15)					
12( <i>k</i> )	F(6)	121 (5)	2 <i>x</i>	649 (5)	25 (3)					

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

*b*  $\beta_{23} = 2\beta_{13}$

*c*  $\beta_{22} = 2\beta_{12} = \beta_{11}$

*d* All of the *F* temperature factors were constrained to be isotropic:  $\beta_{22} = \beta_{11}$ ,  $\beta_{33} = c^*2\beta_{11}/a^{*2}$ ,  $\beta_{12} = b^* \cos \gamma^* \beta_{11}/a^*$  and  $\beta_{23} = \beta_{13} = 0$ , where  $a^*$ ,  $b^*$ ,  $c^*$  and  $\gamma^*$  are the reciprocal parameters. Standard errors in parentheses, corresponding to the last significant digit, are given by the variance-covariance matrix.

Results

The atomic parameters and temperature factors for CsU<sub>6</sub>F<sub>25</sub> are listed in Table 1; the interatomic distances in Table 2 and the observed and calculated structure factors and the square root of  $\sigma^2(F_o^2)$  in Table 3. The U<sup>4+</sup> ion is coordinated by 9F<sup>-</sup> at the corners of a trigonal prism with pyramids on each of the prism faces. The U-F polyhedron is distorted with U-F distances ranging from 2.267 (8) to 2.54 (6) Å, Fig. 1. The Cs<sup>+</sup> ion is coordinated by 12F<sup>-</sup> at distances of 3.12 (2) and 3.45 (4) Å. The result of the 12F<sup>-</sup> coordination around Cs is a double ring of U-F polyhedra around each Cs ion—a ring of 6 polyhedra on each side. Within each ring the polyhedra link by sharing edges, F(2)-F(4) and F(6)-F(5) alternately and these are the short F-F distances. The rings on each side of Cs are linked by corner sharing through the F(1) ion, Fig. 2. The sets of double rings are joined in three dimensions by one pair of adjacent polyhedra sharing edges [F(3)-F(3)] with another pair of polyhedra in another double ring.

Table 2. Interatomic distances for CsU<sub>6</sub>F<sub>25</sub>

2[U-F(3)]	2.267 (8) Å	U-F(5)	2.54 (6) Å
U-F(1)	2.279 (2)	6[Cs-F(2)]	3.12 (2)
2[U-F(6)]	2.29 (5)	6[Cs-F(6)]	3.45 (4)
2[U-F(2)]	2.29 (2)	F(1)-F(2)	2.76 (3)
F(1)-F(6)	2.85 (6)	F(2)-F(3)	2.79 (4)
F(2)-F(6)	2.84 (4)	F(2)-F(4)	2.50 (6)
F(3)-F(3)	2.65 (4)	F(3)-F(6)	2.84 (7)
F(5)-F(6)	2.1 (2)	F(5)-F(5)	2.5 (6)

Table 3. Observed and calculated structure factors for CsU<sub>6</sub>F<sub>25</sub>

L	F <sub>obs</sub>	F <sub>calc</sub>	SIGMA	L	F <sub>obs</sub>	F <sub>calc</sub>	SIGMA	L	F <sub>obs</sub>	F <sub>calc</sub>	SIGMA	L	F <sub>obs</sub>	F <sub>calc</sub>	SIGMA	
1	1017	1010	209	8	116	124	34	14	361	-373	85	18	16	25	16	20
2	470	410	108	9	37	-11	32	10	7	1	18	16	25	16	20	4
3	976	877	219	10	146	-150	37	0	90	-89	27	1	131	-113	37	6
4	260	234	61	11	171	194	41	2	20	24	24	3	289	-260	67	9
5	149	136	61	12	101	113	36	10	29	25	3	277	270	63	4	8
6	139	148	16	13	86	103	19	4	47	42	23	6	137	132	39	1
7	193	149	91	14	86	86	29	6	50	-59	21	9	48	50	26	1
8	399	379	93	15	117	-124	30	11	18	8	85	0	221	-29	37	6
9	116	116	0	16	171	194	41	2	20	24	24	3	289	-260	67	9
10	976	877	219	17	146	-150	37	0	90	-89	27	1	131	-113	37	6
11	260	234	61	18	101	113	36	10	29	25	3	277	270	63	4	8
12	149	136	61	19	86	103	19	4	47	42	23	6	137	132	39	1
13	139	148	16	20	117	-124	30	11	18	8	85	0	221	-29	37	6
14	193	149	91	21	146	-150	37	0	90	-89	27	1	131	-113	37	6
15	399	379	93	22	101	113	36	10	29	25	3	277	270	63	4	8
16	116	116	0	23	86	103	19	4	47	42	23	6	137	132	39	1
17	193	149	91	24	117	-124	30	11	18	8	85	0	221	-29	37	6
18	399	379	93	25	146	-150	37	0	90	-89	27	1	131	-113	37	6
19	116	116	0	26	101	113	36	10	29	25	3	277	270	63	4	8
20	193	149	91	27	86	103	19	4	47	42	23	6	137	132	39	1
21	399	379	93	28	117	-124	30	11	18	8	85	0	221	-29	37	6
22	116	116	0	29	146	-150	37	0	90	-89	27	1	131	-113	37	6
23	193	149	91	30	101	113	36	10	29	25	3	277	270	63	4	8
24	399	379	93	31	86	103	19	4	47	42	23	6	137	132	39	1
25	116	116	0	32	117	-124	30	11	18	8	85	0	221	-29	37	6
26	193	149	91	33	146	-150	37	0	90	-89	27	1	131	-113	37	6
27	399	379	93	34	101	113	36	10	29	25	3	277	270	63	4	8
28	116	116	0	35	86	103	19	4	47	42	23	6	137	132	39	1
29	193	149	91	36	117	-124	30	11	18	8	85	0	221	-29	37	6
30	399	379	93	37	146	-150	37	0	90	-89	27	1	131	-113	37	6
31	116	116	0	38	101	113	36	10	29	25	3	277	270	63	4	8
32	193	149	91	39	86	103	19	4	47	42	23	6	137	132	39	1
33	399	379	93	40	117	-124	30	11	18	8	85	0	221	-29	37	6
34	116	116	0	41	146	-150	37	0	90	-89	27	1	131	-113	37	6
35	193	149	91	42	101	113	36	10	29	25	3	277	270	63	4	8
36	399	379	93	43	86	103	19	4	47	42	23	6	137	132	39	1
37	116	116	0	44	117	-124	30	11	18	8	85	0	221	-29	37	6
38	193	149	91	45	146	-150	37	0	90	-89	27	1	131	-113	37	6
39	399	379	93	46	101	113	36	10	29	25	3	277	270	63	4	8
40	116	116	0	47	86	103	19	4	47	42	23	6	137	132	39	1
41	193	149	91	48	117	-124	30	11	18	8	85	0	221	-29	37	6
42	399	379	93	49	146	-150	37	0	90	-89	27	1	131	-113	37	6
43	116	116	0	50	101	113	36	10	29	25	3	277	270	63	4	8
44	193	149	91	51	86	103	19	4	47	42	23	6	137	132	39	1
45	399	379	93	52	117	-124	30	11	18	8	85	0	221	-29	37	6
46	116	116	0	53	146	-150	37	0	90	-89	27	1	131	-113	37	6
47	193	149	91	54	101	113	36	10	29	25	3	277	270	63	4	8
48	399	379	93	55	86	103	19	4	47	42	23	6	137	132	39	1
49	116	116	0	56	117	-124	30	11	18	8	85	0	221	-29	37	6
50	193	149	91	57	146	-150	37	0	90	-89	27	1	131	-113	37	6
51	399	379	93	58	101	113	36	10	29	25	3	277	270	63	4	8
52	116	116	0	59	86	103	19	4	47	42	23	6	137	132	39	1
53	193	149	91	60	117	-124	30	11	18	8	85	0	221	-29	37	6
54	399	379	93	61	146	-150	37	0	90	-89	27	1	131	-113	37	6
55	116	116	0	62	101	113	36	10	29	25	3	277	270	63	4	8
56	193	149	91	63	86	103	19	4	47	42	23	6	137	132	39	1
57	399	379	93	64	117	-124	30	11	18	8	85	0	221	-29	37	6
58	116	116	0	65	146	-150	37	0	90	-89	27	1	131	-113	37	6
59	193	149	91	66	101	113	36	10	29	25	3	277	270	63	4	8
60	399	379	93	67	86	103	19	4	47	42	23	6	137	132	39	1
61	116	116	0	68	117	-124	30	11	18	8	85	0	221	-29	37	6
62	193	149	91	69	146	-150	37	0	90	-89	27	1	131	-113	37	6
63	399	379	93	70	101	113	36	10	29	25	3	277	270	63	4	8
64	116	116	0	71	86	103	19	4	47	42	23	6	137	132	39	1
65	193	149	91	72	117	-124	30	11	18	8	85	0	221	-29	37	6
66	399	379	93	73	146	-150	37	0	90	-89	27	1	131	-113	37	6
67	116	116	0	74	101	113	36	10	29	25	3	277	270	63	4	8
68	193	149	91	75	86	103	19	4	47	42	23	6	137	132	39	1
69	399	379	93	76	117	-124	30	11	18	8	85	0	221	-29	37	6
70	116	116	0	77	146	-150	37	0	90	-89	27	1	131	-113	37	6
71	193	149	91	78	101	113	36	10	29	25	3	277	270	63	4	8
72	399	379	93	79	86	103	19	4	47	42	23	6	137	132	39	1
73	116	116	0	80	117	-124	30	11	18	8	85	0	221	-29	37	6
74	193	149	91	81	146	-150	37	0	90	-89	27	1	131	-113	37	6
75	399	379	93	82	101	113	36	10	29	25	3	277	270	63	4	8
76	116	116	0	83	86	103	19	4	47	42	23	6	137	132	39	1
77	193	149	91	84	117	-124										

## References

- BROWN, G. M. & LEVY, H. A. (1964). *J. Phys.* **25**, 497.  
 BRUNTON, G. D., INSLEY, H., MCVAY, T. N. & THOMA, R. E. (1965). USAEC Report ORNL-3761, Oak Ridge National Laboratory, Oak Ridge, Tennessee.  
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.  
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.  
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.  
 THOMA, R. E. & CARLTON, T. S. (1961). *J. Inorg. Nucl. Chem.* **17**, 88.  
 THOMA, R. E., INSLEY, H., LANDAU, B. S., FRIEDMAN, H. A. & GRIMES, W. R. (1958). *J. Amer. Ceram. Soc.* **41**, 538.  
 ZACHARIASEN, W. H. (1948). *J. Amer. Chem. Soc.* **70**, 2147.  
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558.  
 ZACHARIASEN, W. H. (1968). *Acta Cryst.* **A24**, 212.

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**The unit cell and space group of L-tyrosine.** By RITA BOGGS and JERRY DONOHUE, *Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104, U. S. A.*

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The space group of L-tyrosine is  $P2_12_12_1$ , and there are four molecules in a unit cell having  $a = 6.921 \pm 0.002$ ,  $b = 21.146 \pm 0.006$ ,  $c = 5.835 \pm 0.001$  Å.

The space group  $Pnam$  was assigned to L-tyrosine by Khawas & Krishna Murti (1969*a*) on the basis of indexing of powder photographs, and of fiber patterns obtained from clusters of very fine acicular crystals: they had been unable to obtain good single crystals. The unit-cell dimensions were given as  $a = 13.89$ ,  $b = 21.08$ , and  $c = 5.842$  Å, with  $Z = 8$ . After it was pointed out to them by Dr Gerald Strahs that a centric space group was not possible for L-tyrosine, they (Khawas & Krishna Murti, 1969*b*) withdrew  $Pnam$  and remarked 'No acentric space group can be assigned to L-tyrosine satisfying the apparent systematic extinctions of X-ray reflection. Presumably the extinctions are accidental,' the implication being that the space group is thus  $P222$ , the one assigned by them in the same communication to L-tryptophan. Because we considered this space group unlikely, and because of continuing interest in these laboratories in amino acid structures, we undertook a reinvestigation of the space group.

After numerous attempts, one single crystal was obtained by evaporation of saturated aqueous solutions. It proved to be orthorhombic, and the only systematic absences observed on precession photographs are  $h00$  with  $h$  odd,  $0k0$  with  $k$  odd, and  $00l$  with  $l$  odd. The space group is thus uniquely determined as the ubiquitous  $P2_12_12_1$ . These photographs also showed that the  $a$  axis of Khawas & Krishna Murti must be halved, giving 4 molecules per unit cell, a not unusual number for this space group. Unfortunately, shortly after the precession photographs had been obtained, the crystal became detached from the glass fiber and was lost.

We recorded the powder pattern of L-tyrosine in a Philips 11.46 cm camera using  $CrK\alpha$  radiation. This pattern matches that published by Khawas & Krishna Murti (1969*a*), except that we did not observe a line at  $d = 6.237$  Å ( $vw$ ), which they indexed as 130, nor at  $2.336$  Å ( $vvw$ ), which they indexed as 332. Of the 39 other  $hkl$  having  $h$  odd in their Table 1 only 7 do not have spacings coinciding with other  $hkl$  having  $h$  even. These 7 are 1.10.0, 720, 581-731, 313, 760, and 513. However, these may be indexed

as 291, 490, 602-233-043-0.11.1, 472, 4.10.1-810, and 273 respectively, which had been overlooked by the previous authors. The powder pattern is accordingly consistent with the halving of  $a$ .

The fiber pattern, Table 2 of Khawas & Krishna Murti, includes 14  $hkl$  having  $h$  odd, 5 of which do not coincide with  $h$  even reflections. These are 360, 111, 171, 361, and 142, which may be indexed as 470, 021, 441, 271, and 232 respectively, likewise previously overlooked. The fiber pattern is thus also consistent with the halving of  $a$ .

We have obtained revised values of the lattice constants by least-squares treatment of 42 resolved lines in our powder pattern. If there was any suspicion that a line was composite it was omitted from the calculations. The results are  $a = 6.921 \pm 0.002$ ,  $b = 21.146 \pm 0.006$ , and  $c = 5.835 \pm 0.001$  Å, where the stated uncertainties are 10 times those obtained from the least-squares calculations, which we feel are unrealistic.

If we succeed in obtaining another crystal suitable for recording intensity data a full structure determination will be initiated.

It is worth mentioning that the danger of basing a unit cell on powder data only has recently been pointed out by Lester & Lipson (1970).

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## References

- KHAWAS, B. F. & KRISHNA MURTI, G. S. R. (1969*a*). *Acta Cryst.* **B25**, 1006.  
 KHAWAS, B. F. & KRISHNA MURTI, G. S. R. (1969*b*). *Acta Cryst.* **B25**, 2663.  
 LESTER, K. M. & LIPSON, H. (1970). *J. Appl. Cryst.* **3**, 92.