Structure type: U_3Si_2

Tetragonal; $n=2$; space group: $P4/mbm\text{–}D_{4h}^5$.

$a_1=7{\cdot}3151\pm0{\cdot}0004$ kX., $a_3=3{\cdot}8925\pm0{\cdot}0005$ kX.

$2\,U_I$ in $2(a)$.
$4\,U_{II}$ in $4(h)$, with $x=0{\cdot}181$.
4 Si in $4(g)$, with $x=0{\cdot}389$.
$U_I\text{–}4\,Si=2{\cdot}96$ A., $U_I\text{–}8\,U_{II}=3{\cdot}32$ A.,
$U_{II}\text{–}6\,Si=2{\cdot}92$ A., $U_{II}\text{–}4\,U_I=3{\cdot}32$ A.,
$Si\text{–}1\,Si=2{\cdot}30$ A.

The structure contains pairs of Si atoms.

Structure type: U_3Si

Tetragonal; $n=4$; space group: $I4/mcm\text{–}D_{4h}^{18}$.

$a_1=6{\cdot}017\pm0{\cdot}002$ kX., $a_3=8{\cdot}679\pm0{\cdot}003$ kX.

$4\,U_I$ in $4(a)$.
$8\,U_{II}$ in $8(h)$, with $x=0{\cdot}231$.
4 Si in $4(b)$.
$U_I\text{–}4\,Si=3{\cdot}01$ A., $U_I\text{–}8\,U_{II}=3{\cdot}04$ A.,
$U_{II}\text{–}2\,Si=2{\cdot}92$ A., $U_{II}\text{–}2\,Si=3{\cdot}17$ A.,
$U_{II}\text{–}4\,U_{II}=3{\cdot}02$ A., $U_{II}\text{–}4\,U_I=3{\cdot}04$ A.

The structure is closely related to that of $AuCu_3$.

Structure type: α-UO_3

Hexagonal; $n=1$; space group: $C\bar{3}m\text{–}D_{3d}^3$.

$a_1=3{\cdot}963\pm0{\cdot}004$ kX., $a_3=4{\cdot}160\pm0{\cdot}008$ kX.

1 U in $1(a)$.
$1\,O_I$ in $1(b)$.
$2\,O_{II}$ in $2(d)$, with $z=0{\cdot}17$.
$U\text{–}2\,O_I=2{\cdot}08$ A., $U\text{–}6\,O_{II}=2{\cdot}39$ A.

There are endless chains $\text{–}O_I\text{–}U\text{–}O_I\text{–}U\text{–}$ along a_3.

The orthorhombic U_3O_8 structure is closely related.

Remarks

The compounds of actinium, neptunium, plutonium and americium referred to in this paper were first prepared by various investigators as follows:

Sherman Fried and F. Hagemann: $AcCl_3$, $AcBr_3$, Ac_2S_3.
Sherman Fried: $AmCl_3$, α-$NpBr_3$, $AmBr_3$, NpI_3, AmI_3, Am_2S_3.
Sherman Fried and N. R. Davidson: $NpCl_3$.
I. Sheft: β-$NpBr_3$.
F. Hagemann: $PuCl_3$, PuI_3.
N. R. Davidson: Pu_2O_2S, Pu_2S_3.
E. K. Hyde: $PuBr_3$.
H. L. Baumbach: $NaPuF_4$.

With the single exception of $PuBr_3$ all of the compounds listed above were first identified by the writer through interpretation of the X-ray diffraction patterns.

Miss Anne Plettinger gave valuable aid by taking all of the powder diffraction patterns.

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Crystal Chemical Studies of the 5*f*-Series of Elements. II. The Crystal Structure of Cs_2PuCl_6

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Cs_2PuCl_6 is trigonal and has the K_2GeF_6-type of structure. The unit-cell dimensions are:

$$a_1=7{\cdot}43\pm0{\cdot}01\ \text{kX.},\quad a_3=6{\cdot}03\pm0{\cdot}01\ \text{kX.},$$

giving a calculated density of $\rho=4{\cdot}10$ g.cm.$^{-3}$ Plutonium is bonded to six chlorine atoms at the corners of an octahedron with $Pu\text{–}Cl=2{\cdot}62$ A. Cesium is bonded to twelve chlorine atoms with $Cs\text{–}Cl=3{\cdot}71$ A.

The compound Cs_2PuCl_6 was first prepared by Herbert H. Anderson,* who also established the identity of the substance by direct chemical analysis. The results given below were obtained using a micro-sample of the original preparation kindly lent to the writer by Dr Anderson.

The sample consisted of a small amount of powdered material in a sealed, thin-walled glass capillary. The powder diffraction photographs were taken with Cu *K* radiation filtered through nickel foil.

Table 1 gives a portion of the diffraction data (up to $\sin^2\theta=0{\cdot}310$). The observed sine squares correspond to a hexagonal unit cell with dimensions

$$a_1=7{\cdot}43\pm0{\cdot}01\ \text{kX.},\qquad a_3=6{\cdot}03\pm0{\cdot}01\ \text{kX.}$$

In this cell there is room for but one molecule Cs_2PuCl_6, giving a calculated density $\rho=4{\cdot}10$ g.cm.$^{-3}$.

Reflections H_1H_20 are missing if $H_1-H_2=3n\pm1$. Reflections $H_1H_2H_3$ for which $H_1-H_2=3n$ are strong when $H_3=0$ or 4, weak when $H_3=1$ or 3, and missing when $H_3=2$. These observations require the cesium positions to be $\pm(\frac{2}{3},\frac{1}{3},u)$ with $u\approx\frac{1}{4}$.

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* Report ANL-4056 of the Argonne National Laboratory.

The calculated intensities due to the metal atoms alone explain the main features of the observed intensity distribution. There are, however, a series of discrepancies which must be ascribed to the effect of the chlorine atoms. The most symmetrical space group compatible with the deduced metal positions is $C\bar{3}m$–D_{3d}^3. An attempt was therefore made to remove the discrepancies by placing the chlorine atoms in accordance with the space group symmetry $C\bar{3}m$.

Table 1. *Diffraction data for* Cs_2PuCl_6

$\sin^2\theta$	I	$H_1H_2H_3$	$\sin^2\theta$	I	$H_1H_2H_3$
0·0169	*wm**	001	0·1678	*m*	212
0·0315	*s*	101	0·1732	*w*+	220
0·0437	*m*	110	0·1919	*m*	221+113
0·0604	*vw*	111	0·2058	*s*−	311+203
0·0670	*vw*	002	0·2476	*w*	213+401
0·0750	*s*	201	0·2524	*w*	312
0·0815	*s*−	102	0·2636	*m*−	004
0·1179	*m*−	211	0·2778	*m*	104+303
0·1244	*m*+	202	0·2898	*vw*	321
0·1307	*vw*	300	0·2963	*vw*+	402
0·1484	*vw*	301+003	0·3026	*vvw*	410
0·1632	*w*−	103	0·3066	*m*	114

* *s* = strong, *m* = medium, *w* = weak, *vw* = very weak.

This attempt led to the following structure:

1 Pu in (0, 0, 0);
2 Cs in $\pm(\frac{2}{3}, \frac{1}{3}, u)$ with $u = 0{\cdot}25 \pm 0{\cdot}03$;
6 Cl in $\pm(x, \bar{x}, z)\ (x, 2x, z)\ (2\bar{x}, \bar{x}, z)$ with $x = 0{\cdot}17 \pm 0{\cdot}03$ and $z = 0{\cdot}25 \pm 0{\cdot}04$.

Since only powder photographs were available reflections $H_1H_2H_3$ and $H_2H_1H_3$ could not be separated. Hence, the parameter values could not be determined with accuracy.

Table 2 shows a comparison of observed and calculated intensities. The latter were calculated by the formula

$$I \propto |F|^2 p \frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta},$$

where p is the permutation factor. It is seen that the agreement in Table 2 is fairly satisfactory except that the reflections $H_1H_2H_3$ appear with enhanced intensity when $H_3^2/(H_1^2+H_1H_2+H_2^2)$ is large. This enhancement would result if the crystallites were tabular parallel to (001). Because of the extremely high absorption coefficient only the crystallites near the inner wall of the capillary would contribute to the scattering. These crystallites would, because of their tabular shape, tend to line up parallel to the glass wall and thus give rise to the observed enhancement.

The deduced structure is of the K_2GeF_6-type (Hoard & Vincent, 1939). Each plutonium atom is bonded to six chlorine atoms at the corners of a nearly perfect octahedron. The interatomic distance is Pu–Cl = 2·62 A.

Table 2. *Observed and calculated intensities*

	Intensity			Intensity	
$H_1H_2H_3$	Calc.	Obs.	$H_1H_2H_3$	Calc.	Obs.
100	0·6	Nil	103	1·6	*w*−
001	3·5	*wm**	212	4·0	*m*
101	14·3	*s*	220	4·1	*w*+
110	10·6	*m*	310	0·3	Nil
200	0·1	Nil	221	0·8	*m*
111	4·2	*vw*	113	0·8	
002	0·8	*vw*	302	0	Nil
201	12·6	*s*	311	3·6	*s*
102	5·7	*s*−	203	2·8	
210	0·7	Nil	400	0	Nil
112	0·1	Nil	222	0·4	Nil
211	5·2	*m*−	401	1·9	*w*
202	6·1	*m*+	213	1·6	
300	2·4	*vw*	312	1·9	*w*
301	1·2	*vw*	004	0·6	*m*−
003	0·2				

* *s* = strong, *m* = medium, *w* = weak, *vw* = very weak.

Each cesium atom is bonded to twelve chlorine atoms, six of them at a distance Cs–Cl = 3·70 A., and six at Cs–Cl = 3·72 A.

The interionic distances calculated with the aid of the ionic radii of the writer (Zachariasen, 1931, 1948) are Pu^{+4}–Cl^- = 2·67 A. and Cs^+–Cl^- = 3·74 A., in satisfactory agreement with the observed values.

The writer wishes to express his gratitude to Dr Herbert H. Anderson for the loan of the microsample and to Miss Anne Plettinger for having taken the powder photograph.

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