The parameter values are:

	u_1	u_2	u_3	x	z
$Ba_3(PO_4)_2$	$0{\cdot}208 \pm 0{\cdot}004$	$0{\cdot}412 \pm 0{\cdot}008$	0·337	0·285	0·742
$Sr_3(PO_4)_2$	$0{\cdot}208 \pm 0{\cdot}004$	$0{\cdot}412 \pm 0{\cdot}008$	0·333	0·279	0·753

Table 2 lists calculated and observed intensities for $Ba_3(PO_4)_2$. The former were obtained using the formula

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

where p is the permutation factor. The observed intensities were measured using the Norelco Spectrometer.

Discussion of the structure

The tetrahedral configuration of four oxygen atoms (one O_I and three O_{II}) about phosphorus with

$$P\text{–}O_I = P\text{–}O_{II} = 1{\cdot}56 \text{ A.}$$

was assumed. The configuration of oxygen atoms about barium and strontium atoms is as follows:

Ba_I–6 O_I = 3·23 A., Ba_I–6 O_{II} = 2·80 A.,
Ba_{II}–1 O_I = 2·71 A., Ba_{II}–3 O_{II} = 2·80 A.,
Ba_{II}–6 O_{II} = 2·83 A.;
Sr_I–6 O_I = 3·10 A., Sr_I–6 O_{II} = 2·63 A.,
Sr_{II}–1 O_I = 2·48 A., Sr_{II}–3 O_{II} = 2·62 A.,
Sr_{II}–6 O_{II} = 2·72 A.

Thus barium or strontium atoms of the first kind show co-ordination number twelve, barium and strontium atoms of the second kind co-ordination number ten. The total strength of the bonds ending on O_I is 1·95 and on O_{II} 2·02.

The observed mean interionic distances and those calculated from ionic radii (Zachariasen, 1931) agree reasonably well as shown below:

	Observed	Calculated
Ba_I–O	3·01 A.	2·96 A.
Ba_{II}–O	2·81	2·90
Ba–O mean	2·88	2·92
Sr_I–O	2·86	2·78
Sr_{II}–O	2·67	2·72
Sr–O mean	2·73	2·74

In view of the close crystal chemical similarity of lead to strontium and barium it was attempted to prepare the isostructural lead compound. These efforts were unsuccessful.

The writer wishes to thank Miss Anne Plettinger for having taken the X-ray diffraction patterns, and Mr H. B. Evans for having made the chemical preparations, the chemical analyses and the direct density determinations.

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Crystal Chemical Studies of the 5*f*-Series of Elements. I. New Structure Types

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The paper gives brief descriptions of new structure types observed for simple compounds of the 5*f*-series of elements and of related elements.

Introduction

In the course of the last five years the writer has determined the crystal structures of a number of compounds of thorium, of uranium, of the transuranic elements, and of the rare elements actinium and protactinium. The work was started in the Manhattan Project and has been continued in the Argonne National Laboratory after the war.

The crystal-structure studies of compounds of the new and rare elements were undertaken for the main purpose of determining the chemical identity of the various micro-preparations, so that the basic chemistry of these elements could be deduced at a time when only microgram amounts were available. In most instances it became necessary to carry out at least a partial crystal-structure determination before the chemical identity of the substance could be ascertained.

This is the first of a series of articles bearing the general title 'Crystal Chemical Studies of the 5*f*-Series of Elements' in which the results of these investigations will be reported. Most of the articles will describe the crystal-structure determination of groups of compounds or of individual compounds. Other articles in the series will contain general discussions of the crystal chemistry of the 5*f*-series of elements. A few of the articles will, like the present one, summarize crystal-structure results which have been obtained.

All the structures described in this article were deduced from X-ray diffraction patterns of crystal powders. Only in two instances, $PuCl_3$ and Na_3UF_7, did single crystals subsequently become available. A number of the structures contain light atoms such as oxygen and fluorine. In some cases it was possible to deduce the positions of the light atoms solely from intensity calculations, in other cases it was necessary to make use of considerations based upon interatomic distances.

The information given about the various structure types include the unit-cell dimensions, the number of stoichiometric molecules per unit cell (n), the space group, the atomic positions and the interatomic distances. In giving the atomic positions the nomenclature of the *International Tables for the Determination of Crystal Structures* is used. A statement such as U–9 Cl = 2·96 A. implies that each uranium atom is bonded to nine chlorine atoms at a mean distance of 2·96 A.

Structure type: UCl_3

Hexagonal; $n=2$; space group: $C6_3/m$–C_{6h}^2.
2 U in 2(a).
6 Cl in 6(h), with $x=0·375$, $y=0·292$.
U–9 Cl = 2·96 A.

The unit-cell dimensions are:

	a_1 (kX.)	a_3 (kX.)
$AcCl_3$	7·62 ± 0·02	4·55 ± 0·02
UCl_3	7·428 ± 0·003	4·312 ± 0·003
$NpCl_3$	7·405 ± 0·010	4·273 ± 0·005
$PuCl_3$	7·380 ± 0·001	4·238 ± 0·001
$AmCl_3$	7·37 ± 0·01	4·24 ± 0·01
$LaCl_3$	7·468 ± 0·003	4·366 ± 0·003
$CeCl_3$	7·436 ± 0·004	4·304 ± 0·004
$PrCl_3$	7·41 ± 0·01	4·25 ± 0·01
$NdCl_3$	7·381 ± 0·004	4·231 ± 0·003
$AcBr_3$	8·06 ± 0·04	4·68 ± 0·02
UBr_3	7·926 ± 0·002	4·432 ± 0·002
α-$NpBr_3$	7·917 ± 0·005	4·382 ± 0·005
$LaBr_3$	7·951 ± 0·003	4·501 ± 0·003
$CeBr_3$	7·936 ± 0·003	4·435 ± 0·003
$PrBr_3$	7·92 ± 0·01	4·38 ± 0·01
$La(OH)_3$	6·510 ± 0·005	3·843 ± 0·005
$Pr(OH)_3$	6·47 ± 0·03	3·76 ± 0·03
$Nd(OH)_3$	6·42 ± 0·02	3·74 ± 0·02

Structure type: $PuBr_3$

Orthorhombic; $n=4$; space group: $Ccmm$–D_{2h}^{17}.
4 Pu in 4(c), with $x=0·25$.
4 Br_I in 4(c), with $x=-0·07$.
8 Br_{II} in 8(f), with $x=0·36$, $z=-0·05$.
Pu–8 Br = 3·08 A.

This is a layer structure with layers normal to a_1.

The unit-cell dimensions are:

	a_1 (kX.)	a_2 (kX.)	a_3 (kX.)
β-$NpBr_3$	12·65 ± 0·05	4·11 ± 0·03	9·15 ± 0·04
$PuBr_3$	12·62 ± 0·05	4·09 ± 0·03	9·13 ± 0·04
$AmBr_3$	12·6 ± 0·1	4·10 ± 0·04	9·10 ± 0·05
$NdBr_3$	12·63 ± 0·05	4·10 ± 0·03	9·15 ± 0·04
$SmBr_3$	12·62 ± 0·05	4·03 ± 0·03	9·06 ± 0·04
UI_3	13·98 ± 0·06	4·31 ± 0·03	9·99 ± 0·05
NpI_3	14·00 ± 0·06	4·29 ± 0·03	9·93 ± 0·05
PuI_3	14·00 ± 0·06	4·29 ± 0·03	9·90 ± 0·05
AmI_3	14·0 ± 0·1	4·30 ± 0·05	9·9 ± 0·1
LaI_3	14·1 ± 0·1	4·33 ± 0·05	10·05 ± 0·10

Structure type: Ce_2S_3

Cubic; $n=16/3$; space group: $I\bar{4}3d$–T_d^6.
$10\frac{2}{3}$–12 Ce in 12(a).
16 S in 16(c), with $x=0·083$.
Ce–8 S = 2·98 A.

The ideal composition is Ce_3S_4 with $n=4$.

The unit-cell dimensions are:

	a (kX.)
Ac_2S_3	8·97 ± 0·01
Pu_2S_3	8·4373 ± 0·0005
Am_2S_3	8·428 ± 0·002
La_2S_3	8·706 ± 0·001
Ce_2S_3	8·6173 ± 0·0005
Ce_3S_4	8·6076 ± 0·0005

Structure type: β_2-Na_2ThF_6

Hexagonal; $n=1$; space group: $C32$–D_3^2.
2 Na in 2(d), with $z=0·385$.
1 Th in 1(a).
3 F in 3(e), with $x=0·600$.
3 F in 3(f), with $x=0·250$.
Na–6 F = 2·33 A., Th–9 F = 2·41 A.

For the isomorphous compounds $NaPuF_4$, $NaLaF_4$, $NaCeF_4$, $n=\frac{3}{2}$ with 1·5 Na + 0·5 Pu in 2(d) and 1 Pu in 1(a).

The unit-cell dimensions are:

	a_1 (kX.)	a_3 (kX.)
β_2-Na_2ThF_6	5·977 ± 0·005	3·827 ± 0·005
β_2-K_2UF_6	6·53 ± 0·02	4·04 ± 0·01
β_2-Na_2UF_6	5·94 ± 0·01	3·74 ± 0·01
$NaPuF_4$	6·117 ± 0·006	3·746 ± 0·004
$NaLaF_4$	6·167 ± 0·001	3·819 ± 0·002
$NaCeF_4$	6·140 ± 0·001	3·770 ± 0·001

Structure type: β_1-K_2UF_6

Hexagonal; $n=1$; space group: $C\bar{6}2m$–D_{3h}^3.
2 K in 2(d).
1 U in 1(a).
3 F in 3(f), with $x=0·640$.
3 F in 3(g), with $x=0·220$.
K–9 F = 2·73 A., U–9 F = 2·36 A.

$n=\frac{3}{2}$ for isomorphous compounds KXF_4 with 1·5 K + 0·5 X in 2(d) and 1 X in 1(a).

The unit-cell dimensions are:

	a_1 (kX.)	a_3 (kX.)
β_1-K_2ThF_6	6·565 ± 0·002	3·815 ± 0·001
β_1-K_2UF_6	6·53 ± 0·01	3·77 ± 0·01
β_1-$KLaF_4$	6·524 ± 0·001	3·791 ± 0·001
β_1-$KCeF_4$	6·496 ± 0·001	3·750 ± 0·001

Structure type: Ce_2O_2S

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

2 Ce in 2(*d*), with z = 0·208.
1 S in 1(*b*).
2 O in 2(*d*), with z = −0·137.
Ce–3 S = 3·04 A., Ce–4 O = 2·36 A.

The structure is closely related to that of La_2O_3.

The unit-cell dimensions are:

	a_1 (kX.)	a_3 (kX.)
Pu_2O_2S	3·919 ± 0·003	6·755 ± 0·010
La_2O_2S	4·03 ± 0·02	6·88 ± 0·04
Ce_2O_2S	4·00 ± 0·01	6·82 ± 0·03

Structure type: $Ca(UO_2)O_2$

Rhombohedral; $n=1$; space group: $R\bar{3}m$–D^5_{3d}.

1 Ca in 1(*b*).
1 U in 1(*a*).
2 O_I in 2(*c*), with x = 0·109.
2 O_{II} in 2(*c*), with x = 0·361.
Ca–8 O = 2·45 A., U–2 O_I = 1·91 A., U–6 O_{II} = 2·29 A.

The structure contains linear uranyl groups O–U–O.

The unit-cell dimensions are:

	a (kX.)	α
$CaUO_4$	6·254 ± 0·001	36° 2′ ± 1′
$SrUO_4$	6·53 ± 0·03	35° 32′ ± 20′

Structure type: UO_2F_2

Rhombohedral; $n=1$; space group: $R\bar{3}m$–D^5_{3d}.

a = 5·764 ± 0·001 kX., α = 42° 43′ ± 3′.

1 U in 1(*a*).
2 O in 2(*c*), with x = 0·122.
2 F in 2(*c*), with x = 0·294.
U–2 O = 1·91 A. (assumed), U–6 F = 2·50 A.

This is a typical layer structure. There is stacking disorder.

Structure type: U_2F_9

Cubic; $n=4$; space group: $I\bar{4}3m$–T^3_d.

8 U in 8(*c*), with x = 0·187.
12 F in 12(*e*), with x = 0·225.
24 F in 24(*g*), with x = 0·20, z = 0·46.
U–9 F = 2·31 A.

In the isomorphous compound $NaTh_2F_9$ the six holes 6(*b*) are occupied by four sodium atoms.

The unit-cell dimensions are:

	a (kX.)
U_2F_9	8·4545 ± 0·0005
$NaTh_2F_9$	8·705 ± 0·001

Structure type: α-UF_5

Tetragonal; $n=2$; space group: $I4/m$–C^5_{4h}.

a_1 = 6·512 ± 0·001 kX., a_3 = 4·463 ± 0·001 kX.

2 U in 2(*a*).
2 F_I in 2(*b*).
8 F_{II} in 8(*h*), with x = 0·32, y = 0·11.
U–2 F_I = 2·23 A., U–4 F_{II} = 2·20 A.

There are strings of UF_6 octahedra along a_3.

Structure type: β-UF_5

Tetragonal; $n=8$; space group: $I\bar{4}2d$–D^{12}_{2d}.

a_1 = 11·450 ± 0·002 kX., a_3 = 5·198 ± 0·001 kX.

8 U in 8(*d*), with x = 0·083.
8 F_I in 8(*d*), with x = 0·278.
16 F_{II} in 16(*e*), with x = 0·167, y = 0·083, z = 0.
16 F_{III} in 16(*e*), with x = 0·042, y = 0·125, z = 0·445.
U–7 F = 2·23 A.

Structure type: γ-Na_2UF_6

Orthorhombic; $n=2$; space group: $Immm$–D^{25}_{2h}.

a_1 = 5·54 ± 0·01 kX., a_2 = 4·01 ± 0·01 kX.,
a_3 = 11·67 ± 0·02 kX.

2 U in 2(*a*).
4 Na in 4(*i*), with $z=\frac{1}{3}$.
4 F_I in 4(*f*), with $x=\frac{1}{4}$.
8 F_{II} in 8(*m*), with $x=\frac{1}{4}$, $z=\frac{1}{6}$.
Na–8 F = 2·38 A., U–8 F = 2·38 A.

Structure type: Na_3UF_7

Tetragonal; $n=2$; space group: $I4/mmm$–D^{17}_{4h}.

a_1 = 5·448 ± 0·007 kX., a_3 = 10·896 ± 0·014 kX.

2 U in 2(*a*).
2 Na_I in 2(*b*).
4 Na_{II} in 4(*d*).
14 F in 16(*m*), with $x=\frac{1}{4}$, $z=\frac{1}{8}$.
Na–7 F = 2·36 A., U–7 F = 2·36 A.

The structure is closely related to that of fluorite.

Structure type: UCl_6

Hexagonal; $n=3$; space group: $C\bar{3}m$–D^3_{3d}.

a_1 = 10·95 ± 0·02 kX., a_3 = 6·03 ± 0·01 kX.

1 U_I in 1(*a*).
2 U_{II} in 2(*d*), with $z=\frac{1}{2}$.
6 Cl_I in 6(*i*), with x = 0·10, $z=\frac{1}{4}$.
6 Cl_{II} in 6(*i*), with x = 0·43, $z=\frac{1}{4}$.
6 Cl_{III} in 6(*i*), with x = 0·77, $z=\frac{1}{4}$.
U–6 Cl = 2·42 A.

This is a typical molecular structure.

Structure type: U_3Si_2

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

$a_1=7{\cdot}3151\pm0{\cdot}0004$ 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–4 Si = 2·96 A., U_I–8 U_{II} = 3·32 A.,
U_{II}–6 Si = 2·92 A., U_{II}–4 U_I = 3·32 A.,
Si–1 Si = 2·30 A.

The structure contains pairs of Si atoms.

Structure type: U_3Si

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

$a_1=6{\cdot}017\pm0{\cdot}002$ 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–4 Si = 3·01 A., U_I–8 U_{II} = 3·04 A.,
U_{II}–2 Si = 2·92 A., U_{II}–2 Si = 3·17 A.,
U_{II}–4 U_{II} = 3·02 A., U_{II}–4 U_I = 3·04 A.

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

Structure type: α-UO_3

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

$a_1=3{\cdot}963\pm0{\cdot}004$ 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–2 O_I = 2·08 A., U–6 O_{II} = 2·39 A.

There are endless chains $-O_I-U-O_I-U-$ 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–Cl = 2·62 A. Cesium is bonded to twelve chlorine atoms with Cs–Cl = 3·71 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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