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A Crystalline Fluoride Complex of Tetravalent Americium[1]

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Received October 30, 1961

A stable crystalline complex of tetravalent americium, Rb_2AmF_6, has been obtained from aqueous fluoride solution. It is isostructural with the analogous compound of tetravalent uranium, Rb_2UF_6. Complex fluorides of tetravalent americium prepared from aqueous solution hitherto were unknown. Both compounds are orthorhombic, probable space group $Cmc2_1$, four molecules per unit cell, dimensions: Rb_2AmF_6: $a_0 = 6.98$, $b_0 = 12.09$, $c_0 = 7.56$ Å.; Rb_2UF_6: $a_0 = 6.958$, $b_0 = 12.042$, $c_0 = 7.605$ Å. The crystallographic relation between these orthorhombic compounds and previously known hexagonal fluoride complexes having the same stoichiometry is described.

Introduction

Numerous complex fluorides of the type $R_xM_yF_{4y+x}$ are known where R is an alkali and M is a tetravalent actinide or lanthanide element. Compounds of those elements having a stable (IV) state have been prepared by crystallization both from aqueous solution and from fused salts (Ce,[2] Th,[3-5] U,[3,6,7] Np,[3] and Pu.[3,8,9]) In general, analogous tetravalent compounds of elements whose stable oxidation state is (III), such as Am, Pr, or Tb hitherto have been made by dry preparation techniques involving treatment with fluorine gas at elevated temperatures. This latter method was used to synthesize the only previously known complex fluoride of Am(IV), $KAmF_5$.[10]

Crystals of Rb_2AmF_6 first were noticed as an unknown compound which appeared on standing during attempts to make $RbAmO_2F_2$ by addition of RbF to a solution containing americium in the pentavalent state (AmO_2^+). At that time no compounds of tetravalent americium ever had been obtained from aqueous solution and our first attempts to find the stoichiometry of this new compound by its X-ray properties were inconclusive. The X-ray powder patterns of the compound first were indexed as hexagonal and similar to δ-Na_2ThF_6.[3,11] However, optical examination of Rb_2AmF_6 crystals indicated lower symmetry than hexagonal (biaxial).[12]

The appearance of the data on Rb_2UF_6[7] attracted our attention not only because the powder pattern matched ours but because the same biaxial optical data and contradictory hexagonal X-ray powder pattern data were reported. Our recent single crystal X-ray data show both Rb_2AmF_6 and Rb_2UF_6 to be orthorhombic, pseudo-hexagonal, thus resolving the symmetry as well as stoichiometry questions. Recently,[13,14] it was found that high concentrations of fluoride ion stabilize tetravalent americium; we also have obtained from aqueous solution a crystalline fluoride complex of tetravalent americium, Rb_2AmF_6.

The analogous uranium compound, Rb_2UF_6, was prepared from solution and used to supplement the investigation in order to minimize the handling of hazardous radioactive americium compounds.

Experimental

Technique.—X-Ray powder patterns were obtained using small ground samples sealed in 0.2-mm. diameter glass capillaries. CuKα radiation ($\lambda = 1.5418$ Å.), standard 114.6-mm. Norelco cameras, and Ilford type G or Eastman type AA X-ray film were used. Individual crystals of Rb_2AmF_6 were selected under a microscope and sealed in the tips of small glass capillaries. The capillaries, whose external surfaces were not radioactively contaminated, were mounted on goniometer heads and conventional Weissenberg and precession X-ray photographs were obtained. The rubidium americium complex lasted four

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[1] This work was sponsored by the U. S. Atomic Energy Commission.

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[10] L. B. Asprey, *J. Am. Chem. Soc.*, **76**, 2019 (1954).

[11] F. H. Ellinger, LASL, private communication.

[12] E. Staritzky, LASL, private communication.

[13] L. B. Asprey and R. A. Penneman, *J. Am. Chem. Soc.*, **83**, 2200 (1961).

[14] L. B. Asprey and R. A. Penneman, *Inorg. Chem.*, **1**, 134 (1962).

weeks or longer before the crystals deteriorated due to the americium alpha activity.

Preparation of Rb_2AmF_6 from $RbAmO_2CO_3$.—In a typical preparation, 5 mg. of Am(III) in dil. HNO_3 was precipitated as the hydroxide by NH_3 gas. The pink $Am(OH)_3$ was digested 10 min. in a hot water-bath, centrifuged, washed, and dissolved in 2 ml. of 3 *M* Rb_2CO_3 solution. The carbonate complex then was ozonized at 90° for 1 hr., yielding a light brown precipitate of $RbAmO_2CO_3$. The precipitate was washed with 0.5 ml. of water, dissolved in a minimum amount of 1 *M* HNO_3, and an equal volume of 12 *M* RbF was added. The initial precipitate which forms is a cream-colored fine slurry, $RbAmO_2F_2$.[15] After standing overnight, orange-pink crystals of Rb_2AmF_6 appear.

Preparation of Rb_2AmF_6 from $Am(OH)_4$.—A slurry of dark brown $Am(OH)_4$ precipitate was prepared by the method of Penneman, *et al.*,[16] washed twice with 0.01 *M* Rb_2CO_3 solution, and then was treated with a solution of nearly saturated RbF in 1 *M* HF. The dark brown color of $Am(OH)_4$ disappeared coincident with the appearance of a precipitate. The microcrystalline pink precipitate thus obtained was washed with three small portions of water and then three portions of acetone. An X-ray powder diffraction pattern of this product showed it to be identical with Rb_2AmF_6 as prepared above.

Preparation of Rb_2UF_6.—Dissolution of UF_4 in strong solutions of RbF followed by evaporation gives green crystalline products such as $RbUF_5$, Rb_3UF_7, and $Rb_7U_6F_{31}$ as well as Rb_2UF_6. Large crystals of nearly pure Rb_2UF_6 are more readily prepared from solution by the following method used by Zachariasen.[3]

In a typical preparation, 0.2 g. $UO_2(NO_3)_2 \cdot 6H_2O$ and 7.0 g. RbF were dissolved in 16 ml. H_2O in a polyethylene beaker. To this solution was added 2.0 g. formic acid and the solution was irradiated under a mercury lamp for 6 to 12 hr. The product sometimes is contaminated by a small amount of RbF but this is removed easily by water washing. Chemical analysis gives: U, 45.9 ± 0.5% obsd., 45.5% calcd.; Rb, 29.0 ± 4.0% obsd., 32.7% calcd.

TABLE I

PRINCIPAL PEAKS IN THE SOLID ABSORPTION SPECTRA OF Rb_2AmF_6 AND Rb_2UF_6

Peak, Å.	Comment[a]	Peak, Å.	Comment[a]
Rb_2AmF_6		Rb_2UF_6	
4309	wk.	4059	med., bd.
4457	str.	4259	med.
4477	doublet	4564	str.
4712	med.	4683	med. str., bd.
4741	med.	4953	med.
4865	med., bd.	5091	med.
5018	med. str.	5189	med.
5141	med. wk.	5336	med. str.
5226	wk.	5618	wk.
5335	med. str.	6067	str., on bd. pk.
5453	wk.	6332	med. str., bd.
5647	wk., bd.	6530	str.
5735	med. str.		
5995	wk.		
6273	med.		
6424	med., bd.		

[a] wk. = weak, med. = medium, str. = strong, bd. = broad. Peaks are relatively sharp unless otherwise designated.

Absorption Spectra.—Absorption spectra for solid Rb_2AmF_6 and Rb_2UF_6 were obtained using a Cary Model 14 recording spectrophotometer. The samples were ground to a fine slurry in Fluorolube "S"[17] oil before being mounted in a thin cell. The data are given in Table I.

Crystallographic Data.—The optical properties of Rb_2AmF_6 and Rb_2UF_6 are given in Table II. The Rb_2AmF_6 data were obtained by E. Staritzky of this Laboratory and most of the Rb_2UF_6 data first were published by Thoma, *et al.*[7] All crystallographic data in this paper were collected from samples prepared from aqueous solutions and agree in detail with data from fused salt studies.

TABLE II

OPTICAL PROPERTIES OF Rb_2AmF_6 AND Rb_2UF_6

Rb_2AmF_6[a]

Biaxial + $2V = 33°$

$\eta_\alpha = 1.495$, $\eta_\gamma = 1.523$, $\eta_\beta = 1.499$

Color: light pink, weak dichroism

Strong dispersion, $r > V$

Twinning essentially 100%, usually polysynthetic

Rb_2UF_6[7]

Biaxial + $2V = 70°$

$\eta_\alpha = 1.473$, $\eta_\gamma = 1.487$, $\eta_\beta = 1.477$

Dichroic: X = light green, Z = light violet

Strong dispersion, $r > V$

Twinning essentially 100%, usually polysynthetic

[a] Optical data for Rb_2AmF_6 obtained by E. Staritzky, Los Alamos Scientific Laboratory.

Though highly twinned, sufficient single crystal specimens of Rb_2UF_6 were obtained and photographed by X-ray methods to determine unit cell dimensions and space group. Also, single crystals of Rb_2AmF_6 yielded patterns which confirmed the isostructural character of these two complexes.

Space group: Diffraction symmetry allows Cmcm, $Cmc2_1$, or C2cm.

Cell dimensions in Å.:

Rb_2AmF_6: $a_0 = 6.98 \pm 0.02$ $b_0 = 12.09 \pm 0.02$ $c_0 = 7.56 \pm 0.02$

Rb_2UF_6: $a_0 = 6.958 \pm 0.005$ $b_0 = 12.042 \pm 0.005$ $c_0 = 7.605 \pm 0.005$

Four formula weights per cell

Rb_2UF_6 density: 5.36 g. per cc. (X-ray)

5.3 g. per cc. (obsd.)

Rb_2AmF_6: 5.44 g. per cc. (X-ray)

The partial X-ray powder diffraction data are presented in Table III.

Discussion

Five structure types have been reported for various phases of sodium or potassium fluoride complexes of thorium and uranium where the ratio of alkali to actinide is two. Rb_2UF_6 and Rb_2AmF_6 form a new structure type resulting from

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[15] L. B. Asprey, F. H. Ellinger, and W. H. Zachariasen, *J. Am. Chem. Soc.*, **76**, 5235 (1954).

[16] R. A. Penneman, J. S. Coleman, and T. K. Keenan, *J. Inorg. & Nuclear Chem.*, **17**, 138 (1961).

[17] Hooker Electrochemical Co., Niagara Falls, N. Y.

TABLE III

PARTIAL POWDER PATTERNS

	Rb_2UF_6		Rb_2AmF_6	
hkl[a]	*d*	I/I_0[b]	*d*	*I*[b]
020, 110	6.018	75	5.982	S
021, 111	4.710	50	4.666	W
002	3.837	5	3.829	VW
130, 200	3.477	100	3.448	S
022, 112	3.223	75	3.193	W
131	3.162	15	3.149	W
040, 220	3.011	10	2.979	W
041, 221	2.808	15	2.788	VW
042, 222 023, 113	2.362	40 B	2.337	VW
310	2.276	10	2.253	VW
151, 241	2.181	60	2.159	W
133	2.053	8	...	...
060, 330	2.006	20	1.988	W
152, 242, 312	1.964	12	1.945	VW
043, 061	1.944	15	1.924	W
004	1.910	10	1.886	VW

[a] Due to the pseudo-hexagonal nature of these orthorhombic crystals there are a number of coincident lines for which the indices of the stronger lines are given. [b] Visual estimates of intensity, I/I_0 is scaled to 100 max. and I is based on strong, medium, and weak. B = broad line.

TABLE IV

ACTINIDE FLUORIDE COMPLEXES RELATED TO Rb_2AmF_6[3]

Complex	Symmetry	Cell Dimensions, Å. a_0	b_0	c_0
β_1-K_2UF_6	Hexagonal $P\bar{6}2m$	6.54		3.76
β_2-K_2UF_6	Hexagonal $P3_2$	6.52		4.03
δ-Na_2ThF_6	Hexagonal . .	6.13		7.34
γ-Na_2UF_6	Orthorhombic Immm	5.54	4.01	11.69
α-K_2UF_6	Cubic (Fluorite) Fm3m	5.934		

the presence of the Rb^+ ion, which distorts the hexagonal symmetry of the β_1-Na_2UF_6 or β_2 K_2UF_6 types. Table IV lists some of the structures most closely related to Rb_2UF_6. In the case of Rb_2UF_6 the distorting influence is weak so that the crystals tend to revert to higher symmetry by frequent twinning to produce a pseudo-hexagonal pattern. Aragonite, $CaCO_3$, is a classic example of such a pseudo-hexagonal orthorhombic structure.

In order to correlate the hexagonal structure types with the Rb_2UF_6 structure, powder patterns were synthesized numerically by carrying out the following transformation: (1) the hexagonal c_0 dimension usually was doubled, (2) the enlarged hexagonal cell was converted to the related orthorhombic cell dimensions, and (3) Na^+ or K^+ was replaced by Rb^+ in a systematic order conforming to the allowed positions in the orthorhombic space group. We have calculated powder patterns from the proposed orthorhombic model using only rubidium and uranium since the fluorine atoms contribute weakly to most of the line intensities. The space group, $Cmc2_1$, permits use of two sets of fourfold positions which yield acceptable line intensities and also reasonable interatomic distances. The other two allowable orthorhombic space groups do not give compatible sets of eightfold or fourfold positions for Rb^+. To obtain accurate fluorine atomic parameters, a detailed analysis using small untwinned crystals is required. This structure will be reported in a separate paper when suitable crystals are prepared. The parameters giving best relative agreement between observed and calculated patterns are for $Cmc2_1$: U (*a*) 0, 0, 0; Rb_1 (*a*) 0, 0.33, 0.21; Rb_2 (*a*) 0, 0.67, 0.29.

Coördination of nine fluorines about each uranium (or americium) should be conserved although somewhat distorted in the hexagonal to orthorhombic transformation. The same should hold true in the sixfold coördination of fluorine about rubidium.

Acknowledgments.—The authors would like to acknowledge the help of Dr. John H. Burns, Oak Ridge National Laboratory, in supplying samples of Rb_2UF_6; Dr. Bruno Morosin, Sandia Corporation, who aided in americium preparations and X-ray analysis; Dr. R. A. Penneman of this Laboratory, who prepared Rb_2UF_6 from solution; and Mr. Edward G. Bosier of this Laboratory, who collected many of the X-ray data.