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Synthesis and X-Ray Properties of Alkali Fluoride–Protactinium Pentafluoride Complexes[1]

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Complex fluorides containing pentavalent protactinium and alkali fluoride have been made from aqueous hydrofluoric acid solution and also by fluorine oxidation of intimately ground, stoichiometric mixtures of PaF_4 and alkali fluoride. Formed by these reactions are complexes of the $MPaF_6$ type where M = Li, Na, K, Rb, Cs, and NH_4. The crystalline $MPaF_6$ compounds containing the larger cations (K, Rb, Cs, and NH_4) are orthorhombic, while $NaPaF_6$ is tetragonal. None of the six $MPaF_6$ complexes is isostructural with its tantalum analog. Cell dimensions for these seven compounds are given. Properties of some higher complex fluorides are also given.

A new supply[2,3] of protactinium has caused a resurgence of interest in its chemistry in several of the world's laboratories. In the 30 years since the original atomic weight studies in 1934 by Grosse[4] on K_2PaF_7, there was no further work reported on the characterization of protactinium fluoride complexes. The preparation of hexafluoroprotactinates, $MPaF_6$ (where M = K, Rb, or NH_4), was reported[5] in late 1964, and in early 1965 a description of octafluoroprotactinates, M_3PaF_8 (M = Na or Li), appeared.[6] For other topics see the excellent 1963 protactinium review by Brown and Maddock.[3]

In our preliminary report of the preparation of the $KPaF_6$, $RbPaF_6$, and NH_4PaF_6 complexes,[5] it was noted that these compounds are isostructural with their pentavalent uranium analogs but not with the higher symmetry tantalum compounds. In this paper we confirm these facts and present data on previously unreported $LiPaF_6$, $NaPaF_6$, $CsPaF_6$, Rb_2PaF_7, Cs_2PaF_7, and Rb_3PaF_8.

The isolation of crystalline $MPaF_6$ compounds[5] represented the first preparation of compounds having a fluoride:protactinium ratio of 6:1, a class well-known for pentavalent tantalum[7] and uranium.[8] Historically, the PaF_7^{-2} ion is firmly established in the inorganic literature, primarily as a result of the preparation of K_2PaF_7 by Grosse 30 years ago. Note, however, that Na_3PaF_8 is obtained as the primary solid phase from solutions of NaF and PaF_5 in HF.[6] Information on the fluoride complexes of protactinium(V) is being obtained at the Oak Ridge National Laboratory by Keller and Chetham-Strode, who are investigating them using Raman techniques.[9] Maddock and co-workers reported that PaF_6^{-}, PaF_7^{-2}, PaF_8^{-3} are all observable in fluoride solutions.[10]

Experimental Section

Materials.—Protactinium 231 (α half-life of 32,500 years) was used; milligram quantities of this isotope must be handled with precautions against the radioactivity. Analysis of a 100-mg portion showed our material to contain 2.2% niobium impurity. Two precipitations as K_2PaF_7 followed by precipitation with ammonia and ignition to Pa_2O_5 decreased the niobium to <0.1%.

For conversion to the fluorides, the Pa_2O_5 was reduced with a mixture of H_2 and HF to yield PaF_4. A portion of the PaF_4 was then treated with F_2 yielding PaF_5 without Pa_2OF_8 (which would have been expected if oxygen impurity were present in the fluorine[11]).

Other reagents were prepared as follows: In order to obtain hydrogen of the necessary purity (oxygen and water-free), the gas was passed through UH_3 at 380°. Fluorine was passed through NaF to remove HF. Commercial HF was condensed and hydrogen plus other uncondensed gases were pumped off; after treatment with F_2 (to oxidize possible H_2 and H_2O impurities) the process was repeated. Anhydrous alkali fluorides were of reagent grade and were fluorinated before use to remove traces of moisture.

Equipment.—Anhydrous preparations were carried out on a 10–50 mg scale in a vertical nickel reactor tube (1 in. i.d.) heated by a split tube furnace. The reactor tube was machined from nickel bar stock and no welds were located in the hot zone. Previously we had observed failures upon repeated exposure of welds to hot fluorine. The top of this nickel tube opened into the bottom of an inert atmosphere drybox. Closure was made at the top, water-cooled end of the reactor by a screw cap having a Teflon gasket. The bottom of the reactor had a thermocouple well extending into the center of the hot zone; samples being fluorinated rested in a holder that was supported by the end of the thermocouple well. Other tubes led through the base of the reactor through which H_2, HF, F_2, or He gases could be admitted. The reactor tube could be evacuated to 0.2 μ; a liquid nitrogen trap was used between the pump and the system.

An analytical balance was placed inside the inert atmosphere box in order to weigh the moisture-sensitive materials. The box was kept dry by circulating argon over $Mg(ClO_4)_2$.

Technique.—For the aqueous preparations, a 48% HF solution containing an alkali (or ammonium) fluoride and protactinium(V) was evaporated in air and then finely ground, all within a Berkeley-type glove box. At $MF:PaF_5$ = 1:1, the M_2PaF_7 complex containing the heavier alkali fluorides (not Li or Na) was sufficiently insoluble so that the first few crystals gave the most

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] D. A. Collins, J. J. Hillary, J. S. Nairn, and G. M. Phillips, *J. Inorg. Nucl. Chem.*, **24**, 441 (1962).

[3] D. Brown and A. G. Maddock, *Quart. Rev.* (London), **17**, 289 (1963).

[4] A. V. Grosse, *J. Am. Chem. Soc.*, **56**, 2501 (1934); *Proc. Roy. Soc.* (London), **A150**, 363 (1935).

[5] L. B. Asprey and R. A. Penneman, *Science*, **146**, 924 (1964).

[6] D. Brown and J. F. Easey, *Nature*, **205** (4971) 589 (1965).

[7] R. D. W. Kemmitt, D. R. Russell, and D. W. A. Sharp, *J. Chem. Soc.*, 4408 (1963); B. Cox, *ibid.*, 876 (1956).

[8] G. D. Sturgeon, R. A. Penneman, F. H. Kruse, and L. B. Asprey, *Inorg. Chem.*, **4**, 748 (1965); **3**, 727 (1964); **3**, 126 (1964).

[9] O. L. Keller and A. Chetham-Strode, Oak Ridge National Laboratory, private communication, 1965. Proceedings of Protactinium Conference, Orsay, France, July 1965.

[10] N. Bukhsh, J. Flegenheimer, F. M. Hall, A. G. Maddock, and C. F. de Miranda, presented at the Protactinium Conference, Orsay, France, July 1965.

[11] L. Stein, *Inorg. Chem.*, **3**, 995 (1964).

intense X-ray lines characteristic of the heptafluoride. Subsequent crystals obtained by further evaporation were pure $MPaF_6$ free from M_2PaF_7. With M_2PaF_7, an excess of alkali is needed to avoid contamination with $MPaF_6$.

A representative sample was taken for X-ray and optical identification. The remainder of the sample was ground, transferred into the nickel reactor, and heated at 400° in F_2 at 1–1.5 atm. After this treatment, the whole sample was then crushed and a powder diffraction photograph was again taken to find whether any change had occurred.

Anhydrous preparations were made by intimately grinding weighed amounts of alkali fluoride and protactinium tetrafluoride (in 1:1, 2:1, and 3:1 stoichiometric ratios) within the inert atmosphere box. The mixture was then fluorinated (in a sapphire dish) at 400° and 1.5 atm. Temperatures of $\sim$400° were satisfactory, but some loss of PaF_5 was noted at 500°.

X-Ray powder diffraction photographs were taken using a 114.6-mm Debeye–Scherrer camera, Ilford-G film, and filtered Cu radiation, (λ 1.5418 A). Contamination was avoided on the exterior of the 0.2-mm Lindemann glass capillaries by mounting the empty capillary within a protective test tube with only the larger, open end of the capillary exposed above a test tube stopper. Transfer of the fine α-active powder from the capillary mouth to the tip was facilitated by agitating the capillary with a Vibrograver. The capillary was then temporarily sealed by a drop of viscous fluorocarbon oil, transported to a hood, removed from the test tube, and sealed with a microtorch. Thereafter, X-ray data were obtained in the normal manner without additional precautions (other than care to avoid capillary breakage).

The complex protactinium(V) fluorides containing alkali or ammonium ions are white, crystalline solids.

LiF–PaF_5 System.—Two compounds were observed in the lithium–protactinium(V) fluoride system. $LiPaF_6$ was obtained by evaporation of a solution containing Li and Pa in 1:1 mole ratio in 48% HF followed by fluorination of the dried residue. Without fluorination, the dried product contained both $LiPaF_6$ and Li_3PaF_8. A starting mole ratio of 2:1 Li:Pa in aqueous HF gave a mixture of $LiPaF_6$ and Li_3PaF_8 while a 3:1 Li:Pa mole ratio yielded only Li_3PaF_8.

NaF–PaF_5 System.—Two preparative methods gave $NaPaF_6$: The first involved evaporation to dryness of a 48% HF solution containing Na and Pa(V) in 1:1 mole ratio followed by grinding and fluorination of the product. Fluorination of the dried residue is necessary to obtain good X-ray powder patterns of $NaPaF_6$, free of Na_3PaF_8. A second approach is to grind together and then fluorinate an equimolar ratio of NaF and PaF_4. When higher ratios of Na to Pa were employed, no Na_2PaF_7 was detected, but Na_3PaF_8 formed readily and was identified as being isostructural with Na_3UF_8.[12]

KF–PaF_5 System.—Simple evaporation of an HF solution containing a 1:1 K:Pa(V) ratio yielded $KPaF_6$ crystals. Fluorination of the $KPaF_6$ caused no change in the X-ray pattern. With either 2:1 or 3:1 K:Pa starting ratios, the characteristic X-ray pattern of K_2PaF_7 was the only phase observed.

NH_4F–PaF_5 System.—Evaporation of an HF solution containing NH_4 and Pa(V) in a 1:1 mole ratio gave NH_4PaF_6. Heating this compound under vacuum gave PaF_5 containing some Pa_2OF_8. HF solutions containing NH_4 and Pa(V) in ratios of 2:1 and 3:1 yielded $(NH_4)_2PaF_7$, which is isostructural with K_2PaF_7 and Rb_2PaF_7.

RbF–PaF_5 System.—Crystals of $RbPaF_6$ resulted when a solution of 48% HF containing Rb and Pa(V) in 1:1 mole ratio was evaporated. Fluorination of precipitated $RbPaF_6$ did not alter its X-ray properties. Fluorination of finely ground mixtures of RbF and PaF_4 in 1:1 mole ratio also yielded $RbPaF_6$. At 2:1 and 3:1 ratios of Rb:Pa(V), Rb_2PaF_7 was the major phase precipitated from aqueous HF; traces of $RbPaF_6$ could be detected. From an HF solution containing Rb and Pa(V) at 10:1, a new phase, Rb_3PaF_8, was formed; no lines due to Rb_2PaF_7 were observed in the X-ray powder photograph of this preparation.

CsF–PaF_5 System.—As in the case of the rest of the heavier alkalis the $MPaF_6$ compound is of low solubility and a 1:1 Cs:Pa(V) ratio in aqueous 48% HF precipitated $CsPaF_6$. At 2:1 Cs:Pa(V) ratios, Cs_2PaF_7, apparently not isostructural with Rb_2PaF_7, was precipitated. Fluorinating a 2:1 Cs:Pa(V) mixture at 275° also yielded Cs_2PaF_7; however, at 400° $CsPaF_6$ was the major phase observed.

Results and Discussion

X-Ray Results. (A) $MPaF_6$ Compounds.—In the cases of $LiPaF_6$ and $NaPaF_6$ only microcrystalline powders could be obtained *via* the fluorination route. Therefore, cell dimensions and symmetry were assigned on the basis of powder data only. No acceptable results have been obtained for $LiPaF_6$. However, using the straight-line graphical solution method of Coleman and McInteer,[13] $NaPaF_6$ could be indexed on the basis of a tetragonal cell, $a_0 = 5.35$, $c_0 = 3.98$ A. These cell dimensions give a rather small molecular volume of 114 A^3 per formula unit.

The rest of the $MPaF_6$ compounds (M = K, Rb, NH_4, and Cs) were obtained as orthorhombic crystals. Crystals of the three isostructural uranium(V) compounds were also obtained from anhydrous HF and both optical and X-ray measurements were made on them.[8] Because of the high radioactivity, the optic figure (but not refractive index data) was obtained on the protactinium compounds. Optical measurements on the four $MPaF_6$ compounds show that they are biaxial, requiring symmetry of orthorhombic or lower. The X-ray powder data could be indexed satisfactorily for a unimolecular orthorhombic cell.

Our powder diffraction data for the three analogous uranium(V) compounds[8] has been interpreted by Charpin[14] as compatible with an orthorhombic unit cell with a_0 and b_0 of similar size at about 5.8 A and c_0 about 4.0 A. Brown and Easey[15] find corresponding dimensions for $KPaF_6$. Charpin further suggested, based on geometrical considerations, that the c axis length should be doubled. Burns and Keller[16] have recently found for $RbPaF_6$ that the unit cell is tetramolecular rather than unimolecular.

Our single crystal data obtained for the analogous uranium compounds, NH_4UF_6, KUF_6, and $RbUF_6$, show that in these compounds also the b and c axes must be doubled. The cell of quadruple volume as first observed by Burns and Keller for $RbPaF_6$ was confirmed for all three compounds and, thus, in all likelihood is valid for all the orthorhombic members of this series. Systematic absences of reflections indicate the space group to be Abm2 or Abmm (Cmma). Reflections of the type hkl for which k and l are odd are extremely weak, while those with k and l even are generally quite strong. The intensity distribution of

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[12] W. Ruedorff and H. Leutner, *Ann. Chem.*, **622**, 1 (1960).

[13] J. S. Coleman and B. B. McInteer, "Los Alamos Straight Line Indexing Diagram," to be published.

[14] P. Charpin, *Compt. Rend.*, **260**, 1914 (1965).

[15] D. Brown and J. F. Easey, *J. Chem. Soc.*, in press.

[16] J. H. Burns and O. L. Keller, Oak Ridge National Laboratory, private communication, 1965; ORNL-3913, Annual Report of Reactor Chemistry Division, 1965.

TABLE I

1:1 ALKALI FLUORIDE:PROTACTINIUM(V) AND URANIUM(V) FLUORIDE COMPLEXES

	a_0, A	b_0, A	c_0, A	Vol. of empirical formula unit, A^3
NH_4PaF_6	5.84	11.90	8.03	139.5
NH_4UF_6	5.83	11.89	8.03	139.2
$KPaF_6$	5.64	11.54	7.98	129.8
KUF_6	5.61	11.46	7.96	127.9
$RbPaF_6$	5.86	11.97	8.04	140.9
$RbUF_6$	5.82	11.89	8.03	139.0
$CsPaF_6$	6.14	12.56	8.06	155.3
$CsUF_6$[a]	8.04		8.39	156.4

[a] Rhombohedral, hexagonal lattice dimensions.

TABLE II

PARTIAL X-RAY POWDER DIFFRACTION DATA FOR $RbPaF_6$ AND $RbUF_6$

$RbPaF_6$		$RbUF_6$	
d, A	I/I_0[a]	d, A	I/I_0[b]
6.00	s	5.96	66
5.85	s	5.78	14
4.18	vs	4.15	97
4.02	m	4.01	40
3.66	w	3.64	12
3.46	w	3.40	9
3.33	vs	3.31	100
3.00	m	2.97	19
2.91	m	2.89	13
2.67	mw	2.64	9
2.63	w	2.61	3
2.39	vw	2.38	6
2.23	s	2.21	37
2.20	s	2.18	18
2.10	m	2.07	14
2.01	m	2.00	24
1.90	m	1.89	11
1.86	m	1.87	11
1.81	m	1.81	28
1.79	w	1.79	8

[a] Visual estimate of intensity. [b] Peak height from diffractometer scan, normalized to 100.

the strong reflections suggest that at least the actinide atoms are in such special positions as to produce a psuedo-cell of one-quarter the volume of the true cell. Lattice dimensions derived from powder diffraction data are listed in Table I. The observed *d* spacings and intensities for $RbPaF_6$ (and $RbUF_6$ for comparison) are given in Table II. A complete single crystal study of the $RbPaF_6$ structure is being made by Burns and Keller, Oak Ridge National Laboratory, and will provide details of bonding in these orthorhombic compounds.

NH_4UF_6 was described[8] as biaxial positive with $n_z = 1.520$, $n_y = 1.490$, $n_x = 1.488$. The optical orientation has now been determined relative to the unit cell translations as $Z = c$, $Y = b$, $X = a$. Thus, the two nearly equal indices correspond to the nearly equal axes (a_0 and $b_0/2$) of the pseudo-cell.

(B) **M_2PaF_7 Compounds.**—No evidence was found for Li_2PaF_7 or Na_2PaF_7. We find K_2PaF_7, Rb_2PaF_7, and $(NH_4)_2PaF_7$ have the same structure, whereas Cs_2PaF_7 does not. The partial powder pattern typical of Rb_2PaF_7 is listed in Table III for comparison with the Cs_2PaF_7 pattern. (Note: The structure of K_2PaF_7 is being worked on by Smith and Brown.[17])

TABLE III

Rb_2PaF_7–Cs_2PaF_7 PARTIAL X-RAY POWDER PATTERNS

Rb_2PaF_7		Cs_2PaF_7	
d, A	I/I_0	d, A	I/I_0
...	...	6.23	m
...	...	6.04	w
5.97	s	...	...
5.81	m	...	...
...	...	3.63	s
...	...	3.54	vs
3.47	m	3.46	vs
3.38	vs	3.36	s
2.54	vw	2.467	m, br
2.406	m	...	...
2.373	mw	2.331	vw
2.226	m	...	...
2.200	w	2.175	vw
2.090	w	2.080	m
2.040	vw	2.055	m, br
...	...	2.027	mw
1.988	m	1.987	m
1.961	mw	1.971	mw
1.931	m	1.949	m
1.813	vw	1.81	m, br
1.789	vw	1.771	m

(C) **M_3PaF_8 Compounds.**—In agreement with Brown and Easey, we find that Na_3PaF_8 and Na_3UF_8 are isostructural.[6] However, we were unable to obtain their reported phase of Li_3PaF_8. A new compound, Rb_3PaF_8, was found at high Rb:Pa(V) ratios in 48% HF: the crystalline precipitate was indexed as fcc, $a_0 = 9.6$ A, and did not contain Rb_2PaF_7.

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(17) A. J. Smith and D. Brown, presented at the Protactinium Conference, Orsay, France, July 1965; *Chem. Commun.* (London), 554 (1965).