transition metal chloro and bromo cations[17,18] which are quite stable. In all cases, these cations are polymeric and it would be reasonable to suggest that the fluorovanadium(IV) cation is polymeric, with a structure probably based on the vanadium trifluoride structure. The cation would achieve some degree of stability through polymerization. Even so, the fluorovanadium(IV) cation is not particularly stable, as shown by its formation only with the strongest fluoride ion acceptors.

The reaction between vanadium pentafluoride and carbon disulfide appears to follow a similar path to the reactions of the latter with either molybdenum[2] or uranium[19] hexafluorides; that is, the reaction probably involves the intermediate formation of the trifluoromethylthio radical.[20]

Comparison of the relative fluorinating strength of vanadium pentafluoride with other fluorinating agents that have been treated with carbon disulfide[2,19] is difficult since in the majority of the reactions experimental conditions, particularly temperature, are not the same.

The reactions of vanadium pentafluoride with sulfur, sulfur monofluoride, iodine, molybdenum pentafluoride, and uranium tetrafluoride are all quite simple, resulting in vanadium tetrafluoride and the corresponding higher fluorides.

It has been previously shown that both molybdenum[2] and uranium[4] hexafluorides undergo a number of oxidation–reduction reactions. These reactions readily show that uranium hexafluoride is more easily reduced than molybdenum hexafluoride. The reactions of vanadium pentafluoride with molybdenum pentafluoride and uranium tetrafluoride to form vanadium tetrafluoride and the corresponding hexafluoride thus show that vanadium pentafluoride is a more powerful oxidant than both hexafluorides.

The reactions described above have been found to be most useful in determining relative reactivities and formed part of the basis of the order of reactivities that we previously put forward,[1] that is, $VF_5 > UF_6 > MoF_6 > WF_6 > NbF_5 = TaF_5$, with respect to oxidizing strength.

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Contribution from the Los Alamos Scientific Laboratory,
University of California, Los Alamos, New Mexico

Alkali Fluoride Complexes of Tetravalent Protactinium[1]

By L. B. Asprey, F. H. Kruse, and R. A. Penneman

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Complex fluorides containing tetravalent protactinium and the alkali fluorides (Li, Na, K, Rb) were prepared from MF + PaF_4 starting mixtures and by hydrogen reduction of $MF–PaF_5$ compounds at 400–450°. $LiF \cdot PaF_4$ is tetragonal: $a = 14.96$, $c = 6.58$ A. The three rhombohedral compounds, $7MF \cdot 6PaF_4$ (M = Na, K, and Rb), are isostructural and have the cell dimensions: $a = 9.16$ A, $\alpha = 107° 54'$; $a = 9.44$ A, $\alpha = 107° 09'$; and $a = 9.64$ A, $\alpha = 107° 0'$, respectively. Monoclinic $4NH_4F \cdot PaF_4$ was formed by direct reaction between NH_4F and PaF_4 at temperatures of 25–90°; cell dimensions are $a = 13.18$, $b = 6.71$, $c = 13.22$ A; $\beta = 117° 10'$. PaF_4 is monoclinic with cell dimensions: $a = 12.86$, $b = 10.88$, $c = 8.54$ A; $\beta = 126° 21'$. These protactinium(IV) fluoride compounds are isostructural with their uranium analogs. The absorption spectra of Pa(IV) in $ND_4F–D_2O$ solution and in various solid fluorides are presented. For $7RbF \cdot 6PaF_4$, $3NaF \cdot PaF_4$, and PaF_4, an intense infrared absorption band is observed at $\sim$5485 cm^{-1}, giving a value of $\zeta_{5f} = 1567$ cm^{-1} for Pa(IV).

Although a number of complex fluorides containing other tetravalent actinides are known,[2–7] no such compounds of Pa(IV) have been reported other than in our preliminary communication on $7RbF \cdot 6PaF_4$.[8] (In this paper, formulas of the alkali protactinium fluorides are written $MF \cdot PaF_4$ or $MF \cdot PaF_5$ solely for ease of displaying the valence of protactinium and have no structural implications.) Our previous work on $4NH_4F \cdot UF_4$ and $4NH_4F \cdot AmF_4$,[2,3] plus the very extensive work at the Oak Ridge National Laboratory,[4–6] and earlier work by Zachariasen[7] on compounds in the alkali fluoride–uranium tetrafluoride systems provided X-ray data for the U(IV) fluoride complexes. We anticipated that the analogous Pa(IV) compounds would be isostructural.

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(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

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Two approaches were taken to prepare the tetravalent protactinium complexes reported in this paper. In the first, anhydrous protactinium tetrafluoride was intimately mixed with alkali (or ammonium) fluoride and heated; in the second, known fluoride complexes of pentavalent protactinium were treated with very pure hydrogen to give tetravalent protactinium complexes.

Experimental Section

The purification of protactinium, the preparation of compounds of pentavalent protactinium, and the techniques for obtaining X-ray diffraction data on compounds containing this radioactive material have been described.[9-11] The alkali fluorides were of analytical reagent grade or equivalent; LiF and NaF were used without treatment. The hygroscopic, heavier alkali fluorides were treated separately with gaseous fluorine prior to use in order to remove traces of water. The resulting anhydrous powders were handled subsequently only in an inert-atmosphere box.

Preparation and Properties of PaF_4.—Amounts of Pa_2O_5 up to 100 mg were placed in a platinum dish in a nickel reactor and heated at 350–500° in a stream of hydrogen and hydrogen fluoride. Details of the nickel reactor were described previously.[9] At 500°, the red-brown PaF_4 was well sintered and appeared to have crept up the sides of the platinum dish during the reaction; some weight loss was observed. When formed at 400°, however, the PaF_4 product showed the expected gain in weight from Pa_2O_5 and had the X-ray powder diffraction pattern typical of anhydrous PaF_4,[10a] isostructural with UF_4.[10b] Some prominent lines of PaF_4 have been published, but the author stated that the data were insufficient to permit determination of lattice constants.[10a] We indexed the data from several of our preparations, using intensities calculated on the basis of the structure of UF_4 recently reported.[10b]

Oxidation of PaF_4 to Pa_2OF_8 occurs very readily, and PaF_4 is an excellent oxygen scavenger. This characteristic of PaF_4 can cause difficulties when heating intimate mixtures of alkali fluoride and PaF_4 on a 20–30-mg scale either in an "inert" gas or in an evacuated metal reactor. While the product obtained is predominantly the desired $MF–PaF_4$ compound, partial oxidation of Pa(IV) is nearly always found. Pure products were produced when such mixtures or the alkali fluoride–protactinium(V) fluoride compounds were pretreated with fluorine in order to obtain a dry, oxygen-free system before reduction with hydrogen. Although sufficiently intimate mixtures were obtained on grinding in a mortar, less of the scarce protactinium material was required if the $MF \cdot PaF_5$ compounds were used. The reduction of $MF–PaF_5$ compounds was the method of choice since the desired ratio of alkali to Pa was already present, thus avoiding both the mixing problem and the separate preparation and handling of PaF_4 and anhydrous alkali fluorides.

Techniques of Hydrogen Reduction.—Compounds for reduction were loaded into sapphire dishes and then placed in a nickel reactor. For the reasons mentioned above, the reactor was evacuated, fluorine was added, and the reactor was kept at 300° for 1 hr or more. After removal of the fluorine by evacuation, pure hydrogen was then added to the reactor. (High-purity hydrogen was prepared by exposing H_2 to uranium hydride at *ca.* 400° for several hours.) It was found that at 350°, reduction of Pa(V) to Pa(IV) is extremely slow. At 400°, the reaction is complete in 15–20 hr while at 450°, only 1–2 hr is necessary. In this study, reductions were carried out at 450° for 2–4 hr.

Preparation of Pa(V) Compounds as Starting Materials for Reduction.—Since many Pa(V) compounds were used in the preparation of Pa(IV) complexes, a brief description of the preparation of these alkali fluoride–protactinium(V) complexes is given. From aqueous HF solutions of alkali fluoride and protactinium(V), certain crystalline compounds can be obtained readily from solution as pure phases; these are $MF \cdot PaF_5$ (K, Rb, Cs), $2MF \cdot PaF_5$ (K, Rb, Cs), and $3MF \cdot PaF_5$ (Na).[9,11] To prepare the remaining 1:1 compounds, $LiPaF_6$ and $NaPaF_6$, the dried product resulting from evaporation of a solution containing a 1:1 mole ratio of the alkali fluoride and protactinium was heated in F_2 to obtain a pure phase. For 7:6 ratios, a mixture was prepared by weight using MF and PaF_4. The complexes $2MF \cdot PaF_5$ (M = K, Rb, Cs) were prepared from solution as described.[9,11] This 2:1 stoichiometry is not known for lithium– and sodium–protactinium(V) fluorides; consequently starting mixtures were prepared using MF and PaF_4 in 2:1 mole ratio. Only $3NaF \cdot PaF_5$ was prepared from solution. The remaining $3MF \cdot PaF_5$ salts (M = Li, K, Rb, and Cs) were prepared by heating in F_2 the residue from evaporation of a solution containing a 3:1 mole ratio[11] of MF:Pa(V). Alternatively, the mole ratios M:Pa = 3:1 were made by intimately mixing the anhydrous alkali fluoride and PaF_4. In general, hydrolysis of protactinium(V) fluoride complexes, when prepared from solution, is not a problem; they show no OH nor O–Pa bands in the infrared.[12] However, to avoid the possibility of moisture contamination from any inclusions of mother liquor in the crystalline starting materials, all were ground and fluorinated. In all cases, the Pa(V) compounds were identified by their characteristic X-ray powder patterns and by comparison with published results.[9,11]

$LiF–PaF_4$ Compounds.—The pentavalent protactinium compounds[9,11] $LiF \cdot PaF_5$ and $3LiF \cdot PaF_5$, as well as the 2:1 mixture, were treated with hydrogen at 450°. Only one protactinium(IV) reduction product resulted. It was identified by its characteristic X-ray powder pattern to be $LiF \cdot PaF_4$, tetragonal and isostructural with $LiF \cdot UF_4$.[4,5]

$NaF–PaF_4$ Compounds.—In the case of sodium protactinium fluoride complexes, Na:Pa mole ratios of 1:1, 7:6, 2:1, and 3:1 were treated with hydrogen at 450°. With either 1:1 or 7:6 Na:Pa starting ratios, rhombohedral $7NaF \cdot 6PaF_4$, isostructural with $7NaF \cdot 6UF_4$, was obtained.[4,6] Reduction of a 2:1 Na–Pa mixture yielded a product showing the X-ray powder patterns of both 3:1 and 7:6 Na–Pa(IV) compounds. When a number of preparations of the pentavalent protactinium compound, tetragonal[11] $3NaF \cdot PaF_5$, were treated with hydrogen at 450°, the powder pattern of the product was essentially unchanged. The color of the material was altered from white to a pale pinkish tan; its absorption spectrum was different as discussed later.

$KF–PaF_4$ Compounds.—The potassium fluoride–protactinium tetrafluoride system was investigated by treating 1:1, 2:1, and 3:1 $KF–PaF_5$ compounds with hydrogen at 450°. Reduction of $KF \cdot PaF_5$ gave rhombohedral $7KF \cdot 6PaF_4$, isostructural with the analogous uranium compound, $7KF \cdot 6UF_4$.[4,6] Reduction of $2KF \cdot PaF_5$ also gave the same tetravalent compound plus KF. Using $3KF \cdot PaF_5$ as the starting material, a product was obtained upon hydrogen treatment whose powder pattern closely resembled that of the pentavalent starting material.[11] It is to be noted, however, that the pattern also resembled just as closely that of the compound of tetravalent uranium, $3KF \cdot UF_4$.[4,6]

$RbF–PaF_4$ Compounds.—The rhombohedral compound $7RbF \cdot 6PaF_4$ resulted when either the compound $RbF \cdot PaF_5$ or the mixture $RbF–PaF_4$ in a 7:6 mole ratio was heated in hydrogen for 4 hr at 450°.[8] It is isostructural with $7RbF \cdot 6UF_4$.[4,6] We have cycled back and forth several times between orthorhombic[9] $RbF \cdot PaF_5$, the *pentavalent* protactinium compound, and rhombohedral[8] $7RbF \cdot 6PaF_4$, the *tetravalent* compound, by alternate use of hydrogen and fluorine. When the 2:1 complex[9] $2RbF \cdot PaF_5$ was treated with hydrogen, a mixture of $7RbF \cdot 6PaF_4$ and unreduced $2RbF \cdot PaF_5$ was obtained. Starting with $3RbF \cdot PaF_5$, the reduction product was a buff color and showed only slight

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differences in its X-ray powder pattern from that of the pentavalent starting material.[9,11]

CsF–PaF$_4$ Compounds.—In the cesium fluoride–protactinium fluoride system, only unidentified, complex X-ray powder patterns were obtained from the products of hydrogen treatment of CsF–PaF$_5$ compounds.

Preparation of NH$_4$F–PaF$_4$ Compounds.—Weighed amounts of PaF$_4$ were ground both with stoichiometric (4:1) quantities of NH$_4$F and with excess NH$_4$F in a Mullite mortar in a dry argon atmosphere. Portions were heated to 90° in a Teflon bomb. Both the heated and unheated products gave the same X-ray diffraction pattern which could be indexed as $4NH_4F \cdot PaF_4$, isostructural with $4NH_4F \cdot UF_4$. (The latter is the highest complex in the NH$_4$F–UF$_4$ system,[3] which also can be prepared readily by direct, low-temperature synthesis using anhydrous reagents.) On standing in an open dish in the inert-atmosphere box, slow growth of PaF$_4$ was observed (confirmed by X-ray) as NH$_4$F was lost from the compound.

Absorption Spectra of MF–PaF$_4$ Compounds.—Tetravalent protactinium should have a $5f^1$ (or $6d^1$) electron and, therefore, show visible and infrared absorption significantly different from that of pentavalent protactinium which has none. Calcium fluoride dishes made from optical flats were used to mount the samples as a Fluorocarbon mull. Auxiliary containers with quartz windows were used to protect the sample from the atmosphere and to prevent the spread of radioactivity. A Cary Model 14MR was used to measure the absorption spectra.

The absorption spectrum of the reduction product obtained by hydrogen treatment of $3NaF \cdot PaF_5$ gave a strong peak at 18,220 A and a main ultraviolet peak at 3550 A. The spectrum of $3NaF \cdot PaF_5$ before reduction had neither of these absorption peaks. The well-characterized compound $7RbF \cdot 6PaF_4$ was chosen for detailed study of the absorption spectrum which is given in Figure 1. Table I lists the main absorption peaks due to Pa(IV); these peaks disappear on fluorine oxidation to Pa(V).

The measurements on the solid protactinium(IV) fluorides indicated that strong absorption from Pa(IV) in fluoride solution should occur at wavelengths longer than those investigated by Haissinsky, *et al.*, who covered the range from 2000 to 6000 A.[13] To extend this range, Pa(IV) in a saturated solution of ND$_4$F in D$_2$O was investigated. The results are also given in Table I. Unfortunately, the long-wavelength region where the main absorption peak of Pa(IV) is located (18,300 A) was obscured by solvent absorption but the peak at ~12,600 A was observed. The absorption spectrum of solid PaF$_4$ is given for comparison.

Discussion

X-Ray Properties.—Work reported herein shows that protactinium in the tetravalent state forms complex fluorides similar to those previously established for other tetravalent actinides. The data for the Pa(IV) complex fluorides are given in Tables II–IV. These characteristic X-ray powder patterns were used to establish the presence of a complex as the major phase, even in reactions in which more than one component is present in the product, *e.g.*, excess KF in the reduction of $2KF \cdot PaF_5$ to $7KF \cdot 6PaF_4$ or excess PaF$_4$ in the reduction of $RbF \cdot PaF_5$ to $7RbF \cdot 6PaF_4$. Conclusive evidence for the preparation of the complex fluorides of tetravalent protactinium rests primarily on the X-ray data and its consistency with the data for similar compounds for the rest of the actinides. This is amply demonstrated in Figure 2 in which molecular volume data are collected for the seven actinides (Th–Cm) for which tetravalent compounds are known. A plot of molecular volume *vs.* atomic number for the 1:1 Li–Pa(IV) and the 7:6 Na–, K–, and Rb–Pa(IV) complexes is given in Figure 2. (Note; It has been established by complete structure determinations that the 1:1 stoichi-

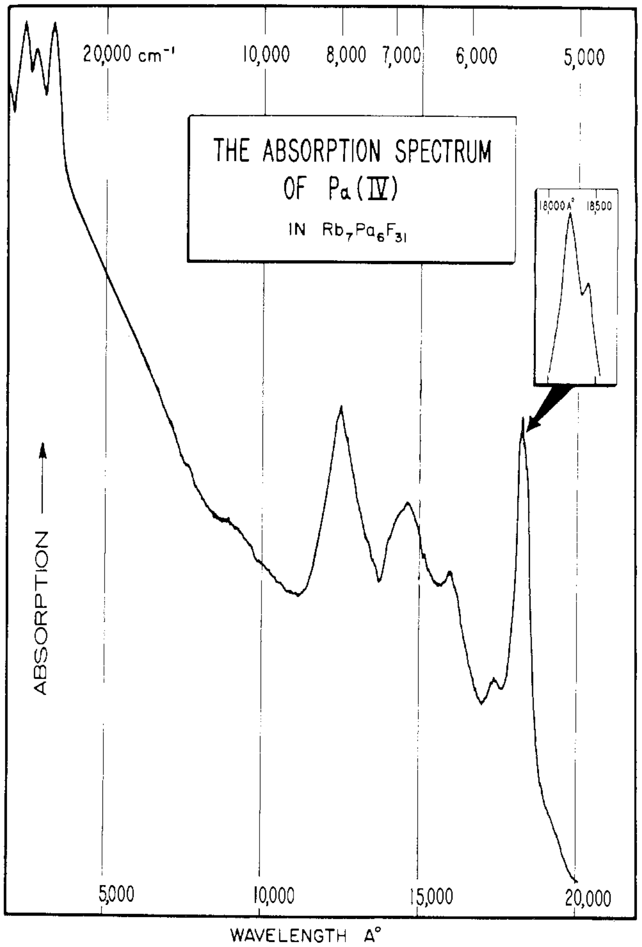

Figure 1.—Absorption spectrum of $7RbF \cdot 6PaF_4$ as fluorocarbon mull.

Table I

Absorption Spectra of Tetravalent Protactinium Fluorides

Compound	Peak Maxima A	Remarks
$7RbF \cdot 6PaF_4$	2580	M
	2920	W
	3500	M
	12600	S
	14700	W, broad
	16000	VW, broad
	17400	VW
	18270	VS, narrow
	18510	M, shoulder
$3NaF \cdot PaF_4$	3550	M
	18220	S
PaF$_4$ saturated ND$_4$F–D$_2$O solution	2470	M
	3475	S
	12700	W
PaF$_4$, solid	~ 2400	M
	3500	W
	12600 – 12900	M, broad
	17200	W
	18200	S

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TABLE II

X-RAY CRYSTALLOGRAPHIC DATA FOR PaF_4 AND SOME ALKALI FLUORIDE–PaF_4 COMPLEXES

Compound	Crystal System	Structure Type	Unit Cell Dimensions, A
PaF_4	Monoclinic	UF_4	a_o = 12.86 b_o = 10.88 c_o = 8.54 β = 126°21′
$LiF{:}PaF_4$	Tetragonal	$LiF \cdot UF_4$	a_o = 14.96 c_o = 6.58
$7NaF \cdot 6PaF_4$	Rhombohedral	$7NaF \cdot 6ZrF_4$	a_o = 9.16 {a_o = 14.81 * α = 107°54′ c_o = 9.85}
$7KF \cdot 6PaF_4$	Rhombohedral	$7NaF \cdot 6ZrF_4$	a_o = 9.44 {a_o = 15.18 * α = 107°9′ c_o = 10.47}
$7RbF \cdot 6PaF_4$	Rhombohedral	$7NaF \cdot 6ZrF_4$	a_o = 9.64 {a_o = 15.49 * α = 107°0′ c_o = 10.75}
$4NH_4F \cdot PaF_4$	Monoclinic	$4NH_4F \cdot UF_4$	a_o = 13.18 b_o = 6.71 c_o = 13.22 β = 117°10′

* Hexagonal dimensions

TABLE III

X-RAY POWDER DIFFRACTION DATA FOR PaF_4 AND $LiF \cdot PaF_4$

Monoclinic PaF_4			
h k ℓ	$d_{obs.}$	$d_{calc.}$	$I_{obs.}$
1 1 0	7.45	7.50	4
1 1 $\bar{1}$	6.66	6.70	4
0 2 0	5.44	5.44	1
2 0 0	5.14	5.18	4
0 2 1, 0 2 $\bar{1}$ 1 1 1	4.224	4.268 4.244	10
2 2 $\bar{1}$	4.122	4.119	1
3 1 $\bar{1}$	3.969	3.967	8
2 2 0	3.737	3.751	8
3 1 $\bar{2}$	3.596	3.604	6
0 0 2	3.477	3.441	2
1 3 0	3.381	3.422	1
2 2 $\bar{2}$ 1 3 $\bar{1}$	3.334	3.351 3.336	6
3 1 0	3.264	3.291	3
3 1 $\bar{3}$ 4 2 $\bar{2}$ 1 1 2	2.721	2.745 2.728 2.720	4 broad
1 3 2	2.214	2.219	2
6 0 $\bar{2}$, 1 5 0 2 2 2	2.130	2.130 2.122	7

Tetragonal $LiF \cdot PaF_4$			
h k ℓ	$d_{obs.}$	$d_{calc.}$	$I_{obs.}$
1 0 1	6.02	6.02	4
2 2 0	5.28	5.29	9
1 2 1	4.685	4.691	10
3 0 1	3.973	3.973	7
0 4 0	3.729	3.741	>1
3 2 1	3.509	3.510	7
2 4 0	3.344	3.346	8
4 1 1	3.178	3.178	7
2 0 2	3.007	3.010	7
2 2 2	2.788	2.793	4
5 0 1	2.722	2.724	4
2 5 1	2.558	2.560	3
2 6 0	2.363	2.366	2
6 1 1	2.301	2.304	2
4 5 1	2.193	2.190	1
3 6 1	2.111	2.113	4
2 1 3 4 6 0	2.077	2.083 2.075	4
4 4 2	2.060	2.061	6

ometry occurs with $LiF \cdot UF_4$, while the 7:6 stoichiometry occurs with the heavier alkali fluoride–actinide tetrafluorides.[5,6]

For $4NH_4F \cdot PaF_4$, the X-ray powder diffraction data show that the compound is monoclinic and isostructural with the rest of the $4NH_4F \cdot XF_4$ compounds (X = U, Np, Pu, and Am).[3] The cell volume of $4NH_4F \cdot PaF_4$ is slightly larger than that of $4NH_4F \cdot UF_4$, a complete structure determination of which is in progress.[14] In the cases of the $3MF \cdot PaF_4$ compounds (M = Na, K, and Rb), X-ray data were not reported here since the amount of Pa(IV) present was not determined. The presence of Pa(IV) could be demonstrated by absorption spectra, but the *absence* of Pa(V) could not be established in this manner. It would be anticipated that there would be little difference in the $3MF \cdot PaF_4$ and $3MF \cdot PaF_5$ X-ray powder diffraction patterns, since similarity was observed for $3NaF \cdot UF_4$ and $3NaF \cdot UF_5$.[15] Indeed, this close structural similarity has now been shown to include compounds containing *three different valence states* of uranium—$3MF \cdot UF_3$, $3MF \cdot UF_4$, and $3MF \cdot UF_5$.[16,17] In these compounds there must be

TABLE IV

X-RAY POWDER DIFFRACTION DATA FOR $7MF \cdot 6PaF_4$ COMPOUNDS (M = Na, K, Rb)

	Na		K		Rb	
h k ℓ	$d_{obs.}$	$I_{obs.}$	$d_{obs.}$	$I_{obs.}$	$d_{obs.}$	$I_{obs.}$
1 0 1	7.79	3	8.19	5	8.35	4
1 1 0	7.40	1	7.65	2	7.72	1
0 2 1	5.37	3	5.57	2	5.69	3
0 1 2	4.60	4	4.86	3	4.98	4
2 1 1	4.34	5	4.51	4	4.58	6
3 0 0	4.26	2	4.37	2	4.46	3
2 0 2	3.904	1	4.107	1	4.195	1
2 2 0	3.704	2	3.811	2	3.870	2
1 2 2	3.453	2	3.604	2	3.697	2
1 3 1	3.342	10	3.453	10	3.508	10
0 0 3	3.278	2			3.577	5
4 0 1	3.048	3	3.143	3	3.200	3
3 1 2	2.880	6	2.998	5	3.049	7
3 2 1	2.803	8	2.903	2	2.933	3
4 1 0			2.854	3		
0 4 2	2.675	1	2.788	1	2.838	2
3 0 3	2.601	3	2.730	2	2.791	3
2 3 2	2.528	1	2.691	1	2.653	2
2 2 3	2.455	3	2.561	2	2.627	1
2 4 1	2.353	2	2.440	2	2.463	1
0 2 4	2.303	2				
5 1 1	2.237	3	--	-	2.370	2
2 1 4	2.197	3	2.316	2		
4 2 2	2.174	2	2.244	2	2.290	2

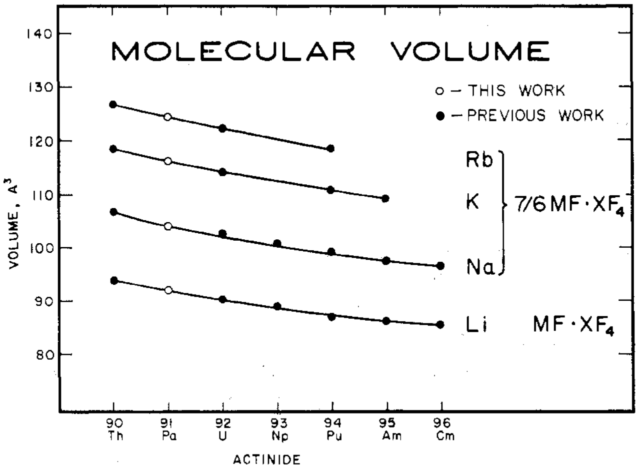

Figure 2.—Molecular volume of alkali fluoride–actinide(IV) complexes, thorium through curium. The stoichiometry is 1:1 for $LiF \cdot XF_4$ and 7:6 for $^7/_6$ $MF \cdot XF_4$ (M = Na, K, Rb; X = actinide).

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[14] D. T. Cromer and A. Rosenzweig, unpublished work (1966).

[15] W. Ruedorff and H. Leutner, *Ann. Chem.*, **632**, 1 (1960).

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[17] R. E. Thoma, H. A. Friedman, and R. A. Penneman, *J. Am. Chem. Soc.*, **88**, 2046 (1966).

slight differences in line intensities since the numbers of fluorines differ, but the positions of the alkali and actinide atoms are the same and their scattering dominates the X-ray intensities. In our experience with 3:1 alkali fluoride–actinide fluoride compounds, there are no obvious differences in the X-ray powder diffraction film data as the actinide valence is changed.

Absorption Spectra of Pa(IV) in Solution.—Previous observations of the absorption spectra of aqueous Pa(IV) in different media show three ultraviolet absorption peaks at about 2250–2350, 2550–2600, and 2800–2900 A in chloride, perchlorate, bromide, and sulfate solution.[18] In strong NH_4F solution, the most intense absorption is reported[13] to be at 3525 A. (We find it at 3475 A in saturated ND_4F solution.)

$5f^1$ Absorption of Pa(IV) in Solid Fluorides.—The fluoride complexes of Pa(IV) are an off-white to pale tan; their main absorption occurs in the ultraviolet and infrared. The position of the main absorption bands in the solid tetravalent protactinium complex fluorides can be roughly compared with the data of Axe, who observed the absorption of dilute Pa(IV) in a Cs_2ZrCl_6 matrix.[19]

Ultraviolet Region.—Axe observed a very strong, broad band centered at about 5400 A and suggested that this intense absorption could arise either from crystal field stabilization of the 6d orbital states or from charge-transfer mechanisms. He also reported two minor peaks at 3320 and 3650 A which were not discussed. In $7RbF\cdot6PaF_4$ three ultraviolet peaks occur at 3500, 2980, and 2580 A or, alternatively, 28.6, 34.2, and 38.8 kK, respectively (1 kK = 1000 cm^{-1}). This discrete absorption in the ultraviolet region (Figure 1) can reasonably be ascribed to $5f^1$–6d transitions. Jørgensen[20] has reported values for such transitions in U^{3+} at 25.5, 28.6, and 31.2 kK, and for U^{4+} at 31.8, 33.0, 35.8, and 40.0 kK, while Reisfeld and Crosby give values for the $5f^1$–6d transition in U^{5+} at 36.2, 40.0, and 44.0 kK.[21] Also in our spectrum at ~5000 A (20 kK) there is evidence of very broad, relatively weak absorption on which are superimposed the extremely intense f–d bands just discussed. It seems reasonable to ascribe this absorption to a charge-transfer mechanism involving electron transfer to the nonbonding ligand orbitals.

Infrared Region.—In the case of $5f^1$ Pa(IV), it would be anticipated that a $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition should appear as a strong band in the ~18,000-A region. This is based on the trend in ζ_{5f} values for the actinides as given by Reisfeld and Crosby (ζ_{5f} for Pa^{4+} is ~1600 cm^{-1}) and using $^7/_2\zeta_{5f}$ for the transition energy.[21] In comparable situations, strong absorption in fluoride complexes occurs at the position estimated as above; *e.g.*, $5f^1$ uranium(V) at ~14,000 A yields ζ_{5f}[uranium(V)] ~ 2000 cm^{-1} and $4f^1$ praseodymium(IV) at ~35,000 A yields ζ_{4f}[praseodymium(IV)] ~ 825 cm^{-1}.[21,22] In $7RbF\cdot6PaF_4$ we observe a narrow, strong infrared band at 18,300 A (see Figure 1) near its estimated position.

For the compounds $7RbF\cdot6PaF_4$, $3NaF\cdot PaF_4$, and PaF_4, itself, this sharp, intense absorption lies at an average value of 5485 cm^{-1}, leading to a value for protactinium(IV) of ζ_{5f} = 1567 cm^{-1}. The true location of the parent transition might be 100 cm^{-1} lower since the observed peaks probably are a combination of the f–f transition with a vibrational mode. Axe, by comparison, gives a value of $\zeta_{5f}[Pa(IV)] = 1490 \pm 60$ cm^{-1}.[19]

For $5f^1$ Pa(IV), octahedrally coordinated as $PaCl_6^{2-}$, Axe reported near-infrared bands at about 12,000, 14,000, and 18,500 A, which he assigned to the Γ_6, $\Gamma_8{}^1$, and $\Gamma_7{}^1$ transitions, respectively, originating in the Γ_7 level. The spectra are largely vibronic, giving rise to several components in each band (five components in Axe's 18,500-A band). For the fluoride compounds reported in our study, there are several absorption bands in addition to the strong one at 18,300 A, and the gross features of our spectrum roughly correspond to those found by Axe. However, the origin of the levels (though undoubtedly crystal field in nature) cannot be designated as identical with those of Axe because of the different site symmetry of Pa(IV) in the two different environments.[23]

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(22) L. B. Asprey, J. S. Coleman, and M. J. Reisfeld, Abstracts of Papers, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966; to be published in Advances in Chemistry Series, American Chemical Society, Washington, D. C.

(23) Note Added in Proof.—After submission of this paper, preparations and unit cell data were reported by Keller and Schmutz[24] for $7KF\cdot6NpF_4$ and $7RbF\cdot6NpF_4$. The same compounds also have been prepared in the Los Alamos Scientific Laboratory by T. K. Keenan. Molecular volumes calculated from either set of data supply the neptunium data missing from the curves in Figure 2.

(24) C. Keller and H. Schmutz, *Inorg. Nucl. Chem. Letters*, **2**, 355 (1966).