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Structural and Spectroscopic Studies of Fluoroprotactinates

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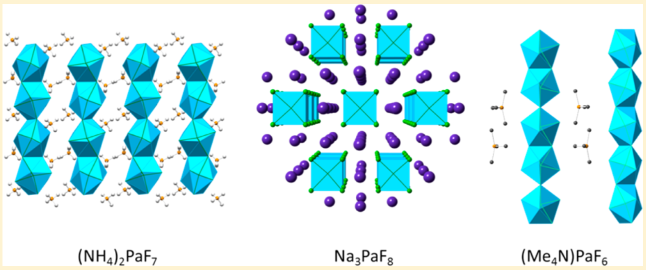
Supporting Information



ABSTRACT: Seven protactinium(V) fluoride compounds have been synthesized, and their crystal structures and Raman spectra are reported. $(NH_4)_2PaF_7$, K_2PaF_7, Rb_2PaF_7, and Cs_2PaF_7 were found to crystallize in the monoclinic space group $P2_1/c$ for the ammonium compound and $C2/c$ for the K^+-, Rb^+-, and Cs^+-containing compounds, with nine-coordinate Pa forming infinite chains through fluorine bridges. Na_3PaF_8 crystallizes in the tetragonal space group $I4/mmm$ with eight-coordinate Pa in tetragonal geometry, while tetramethylammonium fluoroprotactinate shows two different structures: $(Me_4N)_2(H_3O)PaF_8$, an eight-coordinate molecular compound crystallizing in the monoclinic space group $C2/c$, and $(Me_4N)PaF_6$, an eight-coordinate Pa compound forming infinite chains and crystallizing in the orthorhombic space group $Pnnm$. A comparison of solid- and solution-state Raman data indicates that the PaF_8^- anion could be the predominant Pa(V) complex in concentrated solutions of aqueous HF.

■ INTRODUCTION

The observed chemical behavior of the early actinide elements, Th to Am, is exceptionally diverse in comparison to the lighter lanthanide 4f series of elements. This is typified by the multitude of accessible oxidation states in the early actinide elements, trivalent to heptavalent, in contrast to the predominantly trivalent behavior of the lanthanide elements.[1] The differences in oxidation states between the two series can be traced to the relative energetics of the valence orbitals in the 5f and 4f elements. For the lanthanide series the 4f orbitals are generally lower in energy than the 6s and 5d orbitals, giving rise to the predominant +3 oxidation state,[2] while the lowering in energy and contraction of the 5f orbitals versus the 6d and 7s orbitals is less severe in the early actinides, giving rise to a multitude of oxidation states depending on the population of the valence 5f orbitals.[1]

Importantly, the stabilization of the 5f orbitals relative to the 6d orbitals has significant effects on the observed chemistry of these elements. This is best demonstrated by the comparison of gaseous $An^{IV}O_2$ molecules (An = actinide), where $ThO_2(g)$ is bent and $U^{VI}O_2^{2+}(g)$ is linear, a consequence of the predominantly d bonding character in $ThO_2(g)$ versus the dominant f character in U.[3−5] The stabilization of the 5f orbitals relative to the 6d orbitals results in a reversing of these orbitals' relative energies at protactinium, the element between Th and U, making the chemical and spectroscopic properties of Pa of potentially critical importance for understanding 5f electronic structure and bonding and where actinide f and transition metal d chemistries may be observed.[6−9] To explore this hypothesis, we are studying the chemical and spectroscopic properties of protactinium. Because of the paucity of well-characterized complexes of Pa reported in the literature, we are initiating our studies of Pa chemistry by synthesizing and studying a set of simple chemical model systems.

Notwithstanding the potentially critical position in the actinide series occupied by Pa, studying the chemistry of protactinium is important to the development of alternative nuclear fuel cycles, principally those that rely on breeding fissile ^{233}U from fertile ^{232}Th. The principal nuclear reactions relied upon in this breeding process proceed through short-lived ^{233}Pa ($t_{1/2} \approx 27$ days) and its subsequent β^- decay to ^{233}U.[10] However, alternate decay branches and neutron capture pathways also produce longer-lived ^{231}Pa ($t_{1/2} \approx 33000$ years) as a side product. Therefore, understanding the chemistry of this nuclear intermediate in the Th fuel cycle is necessary for the rational and effective design of a nuclear fuel cycle based around ^{232}Th.

As for its transition-metal homologues, a hallmark of Pa(V) chemistry is its insolubility in all but the most aggressive and strongly coordinating acids, notably HF and H_2SO_4.[11] In less strongly coordinating acids such as HNO_3, HCl, and $HClO_4$, solutions of Pa are unstable to hydrolysis and precipitation, forming colloidal species of protactinyl, presumably PaO^{3+}, that are far less soluble than the more common dioxo-actinyl cations of U, Np, and Pu. Therefore, a convenient entry point into the study of this chemistry is through the fluoroprotactinates, where a diversity of coordination environments and chemistries may potentially be demonstrated.

Three single-crystal structures have been previously reported for fluoroprotactinate compounds crystallized with alkali metals, namely K_2PaF_7,[12,13] $RbPaF_6$,[14] and Na_3PaF_8.[15] The structures of these compounds are composed of infinite chains

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Table 1. X-ray Crystallographic Data for All Compounds

	$(NH_4)_2PaF_7$	K_2PaF_7	Rb_2PaF_7	Cs_2PaF_7	Na_3PaF_8	$(Me_4N)_2(H_3O)PaF_8$	$(Me_4N)PaF_6$
Z	4	4	4	4	2	4	4
formula wt	400.08	442.20	534.94	629.82	451.97	567.32	419.15
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	tetragonal	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$I4/mmm$ (No. 139)	$C2/c$ (No. 15)	$Pnnm$ (No. 58)
a (Å)	8.1003(10)	13.675(4)	14.1027(12)	14.4439(13)	5.4415(9)	15.1001(5)	8.0330(4)
b (Å)	6.8966(9)	6.6903(19)	6.9361(6)	7.2533(7)	5.4415(9)	9.0563(3)	15.9214(7)
c (Å)	11.8834(15)	8.096(2)	8.1467(7)	8.2150(8)	10.8482(19)	12.9862(4)	7.9958(4)
α (deg)	90	90	90	90	90	90	90
β (deg)	90.606(2)	125.087(3)	124.850(1)	122.870(1)	90	104.920(1)	90
γ (deg)	90	90	90	90	90	90	90
V (Å^3)	663.8(2)	606.1(3)	654.0(1)	722.9(1)	321.2(1)	1716.0(1)	1022.6(1)
T (K)	100	100	100	100	100	100	100
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
D_{calcd} (g cm^{-3})	4.003	4.846	5.433	5.787	4.673	2.196	2.722
μ (cm^{-1})	23.56	27.16	38.69	31.55	24.57	9.167	15.29
R	0.0171	0.0200	0.0349	0.0167	0.0116	0.0184	0.0326
R_w	0.0537	0.0498	0.0950	0.0413	0.0267	0.0439	0.0817

Table 2. Relevant Pa−F Bond Distances and Raman Shifts

	$(NH_4)_2PaF_7$	K_2PaF_7	Rb_2PaF_7	Cs_2PaF_7	Na_3PaF_8	$(Me_4N)_2(H_3O)PaF_8$	$(Me_4N)PaF_6$
Pa−F (Å)	2.138(2) 2.141(2) 2.169(2) 2.193(2) 2.216(2) 2.255(2)[a] 2.348(2)[a] 2.356(2)[a] 2.515(2)[a]	2.153(3) 2.168(3) 2.187(4) 2.287(3)[a] 2.462(3)[a]	2.146(4) 2.170(4) 2.200(6) 2.276(4)[a] 2.481(4)[a]	2.149(3) 2.168(3) 2.210(4) 2.266(3)[a] 2.506(3)[a]	2.198(2)	2.132(2) 2.137(2) 2.190(2) 2.355(2)	2.084(4) 2.085(4) 2.334(3)[a] 2.342(3)[a]
av Pa−F (Å)	2.26(13)	2.26(13)	2.26(13)	2.27(14)	2.198(2)	2.204(8)	2.21(11)
av nonbridging Pa−F (Å)	2.17(10)	2.17(16)	2.17(22)	2.17(16)	2.198(2)	2.204(8)	2.085(4)
av bridging Pa−F (Å)	2.37(10)	2.37(12)	2.38(16)	2.39(12)			2.338(4)
Raman frequency ν_1 (cm^{-1})	549(1)	547(1)	546(1)	543(1)	557(1)	555(1)	581(1)
Pa coordination no.	9	9	9	9	8	8	8

[a] Bridging fluorine atom.

of fluoride-bridged polyhedra, PaF_9^{4-} (C_{4v}), corrugated infinite chains of PaF_8^{3-} (C_{2v}), and molecular units of PaF_8^{3-} (D_{4h}), respectively. Among the pentavalent actinides and their transition-metal homologues these compounds share few common structural features.[16−20]

In this paper we present our study of the homoleptic fluoride complexes of Pa(V), reporting on their synthesis, structures, and Raman spectra, as well as Raman spectra on Pa in aqueous hydrofluoric acid solution in order to determine the speciation of the protactinium fluoride complex by correlating the solution- and solid-state Raman spectra. Reported here are seven structures, five of which are new fluoroprotactinate compounds, Rb_2PaF_7, Cs_2PaF_7, $(NH_4)_2PaF_7$, $(Me_4N)_2(H_3O)PaF_8$, and $(Me_4N)PaF_6$, along with the Raman spectra and our analysis of the series of alkali-metal (Na^+, K^+, Rb^+, Cs^+) and ammonium fluoroprotactinates demonstrating four coordination environments about the Pa(V) ion.

■ EXPERIMENTAL METHODS

Caution! ^{231}Pa is a naturally occurring α- and γ-emitting radionuclide with a half-life of 32760 years. Along with its decay daughters from the ^{235}U chain, ^{227}Ac ($t_{1/2} \approx 22$ years), ^{227}Th ($t_{1/2} \approx 19$ days), ^{223}Ra ($t_{1/2} \approx 11$ days), ^{219}Rn ($t_{1/2} \approx 4$ s), and ^{215}Po ($t_{1/2} \approx 1.8$ ms), ^{231}Pa poses a significant radiological risk. All experiments described were conducted in laboratories specially designed for the handling of α-emitting radionuclides and under strict radiological and engineering controls. HF is highly toxic and corrosive even when diluted and must be handled with great care.

Synthesis. The compounds reported were all synthesized similarly. A ^{231}Pa solution in 5 M HF, recently separated from its decay daughters, was used for all syntheses. The compounds were synthesized using 55 μL of 79 mM ^{231}Pa(V) (1 mg, 4.3 μmol) in 5 M HF, 8.6 μL (8.6 μmol) of 1 M XF (X = Me_4N, NH_4, Na, K, Rb, Cs), and 100 μL of 48% HF(aq). The solutions were stored in a desiccator over Drierite in PTFE dishes for a few days, except for one reaction using tetramethylammonium solution, which was left out in the air. All syntheses resulted in the deposition of crystals suitable for X-ray diffraction and Raman studies. The sodium- and tetramethylammonium-containing compounds showed a sensitivity to atmospheric moisture. The remaining compounds synthesized were stable in air.

Single-Crystal X-ray Diffraction. Crystal structures for all Pa compounds were determined using a Bruker AXS SMART diffractometer equipped with an APEX II CCD detector using Mo Kα radiation from either a Bruker Quazar or Bruker Triumph X-ray source. Data were collected at 100 K under a stream of nitrogen. Corrections for absorption were applied, and structure solutions were performed using direct methods with SHELXS and structural refinements using SHELXL.[21,22] The structure solutions and refinements proceeded routinely except as noted below.

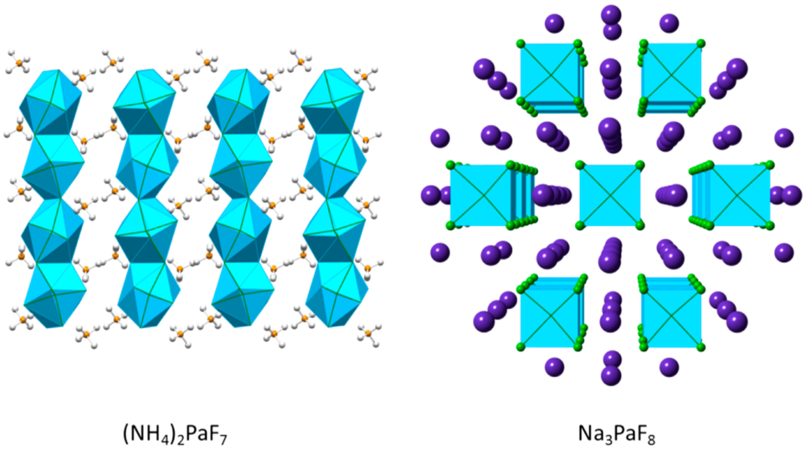

Figure 1. Polyhedral representations depicting two different coordination environments around the Pa: PaF_9 and PaF_8 units, blue; F, green; N, orange; H, white; Na, violet.

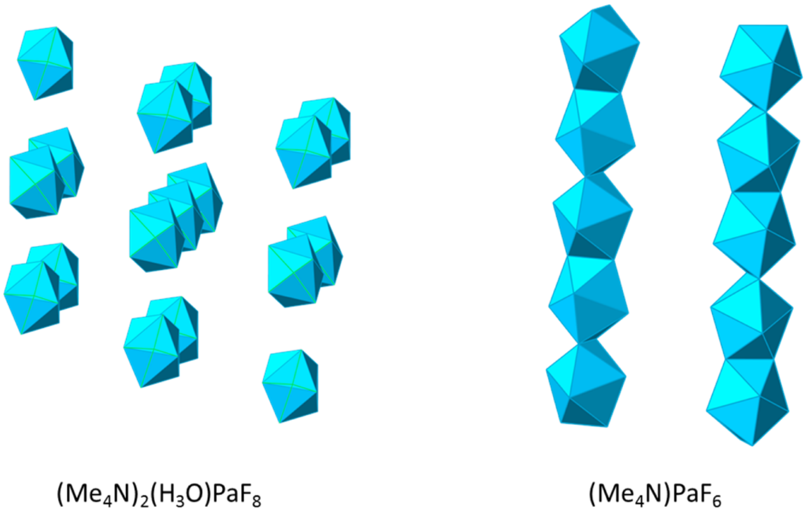

Figure 2. Polyhedral representations depicting two different structures obtained upon crystallization from tetramethylammonium fluoride solution. The hydronium and tetramethylammonium cations have been omitted for clarity in both representations.

Cs_2PaF_7 was solved and refined as a nonmerohedral twin with two domains rotated by about 180°.

The tetramethylammonium cation in the $(Me_4N)PaF_6$ structure was disordered and was modeled and refined by restraining the anisotropic displacement parameters of the carbon and the nitrogen atoms to be the same. Hydrogen atoms were generated for each carbon as two idealized disordered CH_3 groups, rotated from one another by 60°, each hydrogen position having 50% occupancy. A summary of crystallographic details for the reported compounds are found in Table 1. Definitions of the R and R_w factors are those defined by the International Union of Crystallography.

Raman Spectra. Solutions studied using Raman spectroscopy were prepared by the precipitation of protactinium from HF solution using ammonium hydroxide with subsequent washing with deionized water. The protactinium precipitate, presumably $Pa_2O_5 \cdot xH_2O$, was redissolved in the appropriate volume and concentration of HF(aq) to prepare the sample (1 M ^{231}Pa: 5 mg of ^{231}Pa/22 μL of 48% HF(aq)). Nb and Ta samples were prepared by the dissolution of either their oxides M_2O_5 in HF or by dissolution of K_2NbF_7 or K_2TaF_7 (>99% AlfaAesar). The solutions were transferred to sapphire (Al_2O_3) tubes and further encapsulated in 5 mm NMR tubes for radiological containment in the case of Pa. For the solids, single crystals of the compounds were placed on glass slides and covered using a glass coverslip affixed with an epoxy. Raman spectra were recorded using a Renishaw inVia Raman microscope with an excitation line of 532 nm. Polarized Raman spectra were collected by adjusting the polarization of the incident and scattered light using a series of waveplates and polarization filters.

■ RESULTS AND DISCUSSION

In all cases, the reported synthetic protocols produced single crystals suitable for single-crystal X-ray diffraction measurements. The measured crystallographic parameters and results of the single-crystal refinements for all of the compounds are presented in Table 1. A summary of the relevant bond distances is provided in Table 2.

The NH_4^+, Rb^+, and Cs^+ compounds are isostructural with the previously reported structure of K_2PaF_7, despite ambiguity in the literature regarding differences in the interpretation of X-ray powder photographs in earlier work.[12,13,23,24] However, the NH_4^+-containing structure crystallizes in $P2_1/c$, instead of $C2/c$ as found for the K^+-, Rb^+-, and Cs^+-containing structures. Attempts to solve and refine the structure in $C2/c$ were unsuccessful.

The $P2_1/c$ structure of $(NH_4)_2PaF_7$ is representative of this structure type and is presented in Figure 1. The protactinium is nine-coordinate, with four of the F atoms bridging with neighboring Pa atoms forming infinite chains parallel to the a axis. The Pa−F distances range from 2.138(2) to 2.216(2) Å for nonbridging F bonds and from 2.255(2) to 2.515(2) Å for the bridging bonds.

The compounds K_2PaF_7, Rb_2PaF_7, and Cs_2PaF_7 are isostructural in $C2/c$. In these compounds, the protactinium has the same nine-coordinate environment as in $(NH_4)_2PaF_7$, but the infinite chains of fluorine-bridged Pa are parallel to the crystallographic c axis. The mean distance of the Pa−F bridging bonds in these complexes increases slightly with the size of the charge-compensating cation, whereas the mean distance for the nonbridging Pa−F bonds remains the same (Table 2).

In contrast to the heptafluoro complexes found for the other alkali metals in our syntheses, Na_3PaF_8 crystallizes as an eight-coordinate molecular complex (Figure 1). This compound has been previously reported.[15,23−25] Briefly, each Pa atom is surrounded by eight fluorine atoms in an approximate cubic geometry, with D_{4h} site symmetry. The Pa−F bond distance is 2.198(2) Å. This compound was synthesized under the same conditions as for the other compounds but results in the higher symmetry molecular structure presented. Observations from the literature suggest that a cubic phase of fluoroprotactinates with larger cations or the heavier alkali metals may exist.[23,25] In order to explore this hypothesis, we attempted the synthesis of a series of fluoroprotactinates using tetramethylammonium, added as $Me_4NF(aq)$. The existence of such cubic phases would be useful to synthesize for further study because of their high symmetry, simplifying studies of their electronic properties.

Two different compounds were obtained upon crystallization with tetramethylammonium fluoride depending on the conditions of the crystallization method (Figure 2). The evaporation of the solution stored in a desiccator resulted in the deposition of $(Me_4N)PaF_6$ crystallizing in the space group $Pnnm$. Each protactinium is surrounded by eight fluorine atoms in a dodecahedral arrangement with four of the fluorides bridging neighboring Pa atoms forming infinite chains parallel to the c axis. This structure is similar to the previously reported structure of $RbPaF_6$, which shows the same eight-coordinate complexes with four bridging fluorides.[14] $RbPaF_6$ crystallizes in $Cmma$ with the infinite chains along the a axis. The mean Pa−F distance in $(Me_4N)PaF_6$ for the bridging fluorides corresponding to the shared edges of the polyhedra is 2.34 Å, while the Pa−F mean distance for nonbridging fluorines is 2.08 Å. These distances are similar to those reported for $RbPaF_6$, which are 2.34 and 2.09 Å, respectively.[14]

The crystals obtained after evaporation outside of the desiccator in air produced a structure different from that of the crystals grown in the desiccator, with the formula $(Me_4N)_2(H_3O)PaF_8$. They crystallize in $C2/c$ as eight-coordinate molecular complexes charge-balanced with two tetramethylammonium cations and a hydronium cation. The mean distance for the Pa−F bond in this compound is 2.20 Å. Two of the Pa−F bonds in this complex are considerably longer with a value of 2.35 Å, similar to the value of Pa−F bridging bonds observed in the M_2PaF_7 compounds. The inclusion of the hydronium ion in the structural model satisfies the charge balance requirements for the compound, but its identification on the basis of the crystallography alone is ambiguous. The Raman spectra of this compound (Figure 3 and Figure S8 (Supporting Information)) and the preparative method used to prepare the compound do not support the inclusion of any other cation such as ammonium or H_2F^+.

A comparison of the four structure types presented here with those of the pentavalent actinides and the group V transition metals shows limited similarity in both dimensionality and coordination geometry. For the Nb and Ta salts X_2MF_7, the transition-metal salts are molecular, with seven-coordinate fluoroniobate and tantalate anions.[17,18,26] Among comparable pentavalent actinide compounds, there are no known single-crystal structures of these types. Earlier studies based on X-ray powder photographs of these compounds suggested that the heptafluoroprotactinates are not isostructural with their uranium(V) homologues.[20,24] Among the known octafluoro complexes of Nb and Ta, there is only Na_3TaF_8, which crystallizes in $C2/c$ with a distorted-square-antiprismatic arrangement of the fluoride ions about the Ta center,[16] in contrast to the tetragonally distorted cubic geometry in Na_3PaF_8 or the distorted dodecahedron in $(Me_4N)_2(H_3O)PaF_8$. X-ray powder photographs showed that Na_3UF_8 may be isostructural with Na_3PaF_8; however, no single-crystal structures are available.[19]

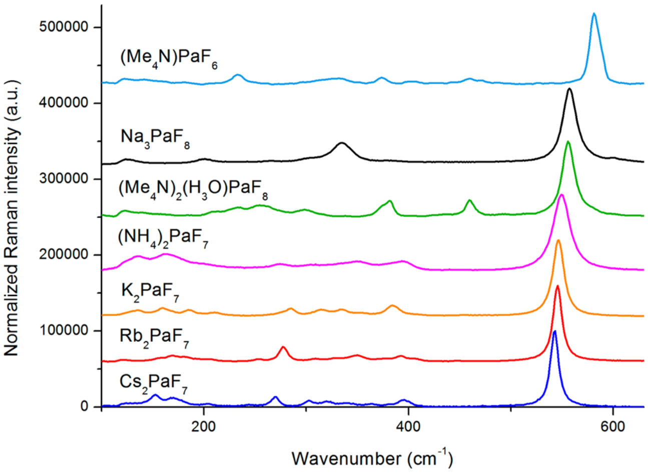

Figure 3. Raman spectra of fluoroprotactinate crystals.

The Raman spectra collected on single crystals of the fluoroprotactinate compounds are shown in Figure 3. The most intense band in these spectra (545−590 cm^{-1}) is assigned to the symmetric Pa−F vibration.[27] For the isostructural compounds K_2PaF_7, Rb_2PaF_7, and Cs_2PaF_7, this band undergoes a slight red shift as the size of the countercation increases from K to Cs. Less straightforward is the dependence of this band on the increasing Pa−F bond distance within the complexes when considering only the fluoride bonds on the shared edges of the polyhedra.

In the ammonium compound, the symmetric Pa−F vibration is broadened and slightly higher in frequency than for the other isostructural compounds. The observed shift for the $(NH_4)_2PaF_7$ compound may be explained by a difference in the crystal packing rather than by an effect of the cation size, where NH_4^+ is approximately the same size as Rb^+: about 1.50 Å for both cations.[27−29] In $P2_1/c$, the Pa is on a general position, in contrast to the compounds crystallized in $C2/c$, where the Pa is on a special position of C_2 symmetry. This is consistent with the broadened nature of the Pa−F symmetric stretching frequency and distribution of bond distances. Broad and less intense bands are observed at lower frequencies in all of these complexes and are likely associated with Pa−F bending modes.

The corresponding symmetric stretching frequency in the Raman spectra of Na_3PaF_8 and $(Me_4N)_2(H_3O)PaF_8$ are at 557 and 555 cm^{-1}, respectively. The observed higher frequencies are consistent with the lower coordination number about the Pa center: 8 instead of 9. Molecular site group analysis for the Na_3PaF_8 compound demonstrates that there should be 21 active vibrational modes for the PaF_8^{3-} anion. In D_{4h} symmetry only the four gerade modes (A_{1g}, B_{1g}, B_{2g}, and E_g) are Raman active. The spectrum presented is consistent with D_{4h} symmetry and four observed bands. Symmetry analysis demonstrates that the degeneracy of the E_g mode is conserved. Preliminary studies of the polarization dependence of the Na_3PaF_8 compound suggest that the two lower frequency bands between 100 and 200 cm^{-1} are of B_{2g} and E_g symmetry and the band at 325 cm^{-1} is of B_{1g} symmetry (see the Supporting Information). However, a high degree of confidence cannot be placed in this assignment, absent a precisely oriented single-crystal study.

The highest observed frequency for the Pa−F stretching corresponds to $(Me_4N)PaF_6$ at 581 cm^{-1}. This large blue shift is consistent with the reported value for the isostructural $RbPaF_6$ at 590 cm^{-1}.[27] Generally, as the coordination number about the metal center changes, one expects a shift in frequency; generally, higher coordination numbers result in lower vibrational frequencies.[30] However, because of the bridging fluoride ions present resulting in infinite chains of Pa−F polyhedra, a direct correlation between the observed vibrational frequencies and the coordination number is less straightforward.

The polarized Raman spectra of 1 M Pa in 48% HF are shown in Figure 4. The broad band observed at 563 cm^{-1} is characteristic of the Pa−F stretching vibration. The remaining bands in the spectrum can be assigned to the sapphire cell. The Pa−F vibrational mode at 563 cm^{-1} is fully polarized as expected. Unfortunately, the sapphire bands obscure the lower frequency vibrational modes that would be diagnostic of the symmetry about the Pa ion: for example, D_{4h} or C_{2v}.

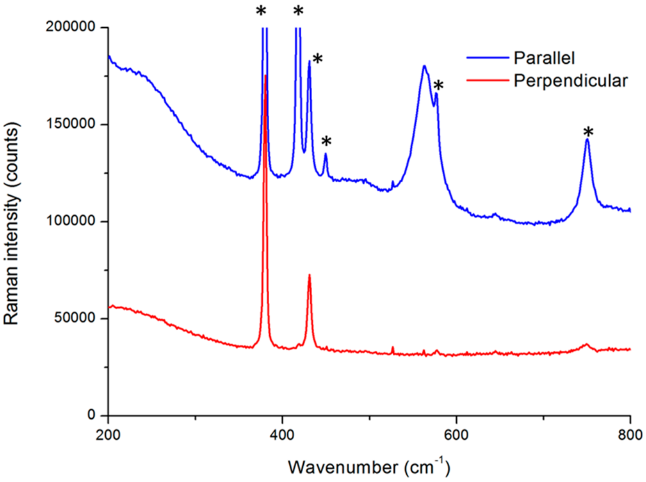

Figure 4. Polarized Raman spectra of 1 M Pa in 48% HF. Asterisks indicate sapphire bands.

Raman spectroscopy has been used previously to study the speciation of Nb and Ta in aqueous fluoride solutions.[31,32] By comparing Raman spectra of crystals of known structure ($CsNbF_6$, K_2NbF_7, $CsTaF_6$, K_2TaF_7, and Na_3TaF_8) and Raman spectra of solutions containing fluoride complexes of Nb and Ta in various HF concentrations, it was possible to identify the main fluoride species present in solution, TaF_6^- and NbF_6^- in 48% HF. The Raman frequency of the symmetric M−F stretching vibration ν_1 (M = Nb, Ta) undergoes a large red shift when the anion coordination is increased from 6 to 8 in the crystals (Table 3). Raman spectra of $RbPaF_6$ and Rb_2PaF_7 crystals, along with Raman spectra of Pa solutions in HF, were also recorded but the full single-crystal structures were not known at that time, preventing the authors from further identification of the Pa species in solution.[27]

Table 3. Comparison of ν_1 Raman Shifts in Crystals and Solution for Nb, Ta, and Pa Fluoride Complexes

<table>
<tr><th></th><th colspan="5">crystal</th></tr>
<tr><th></th><th>$CsNbF_6$</th><th>K_2NbF_7</th><th>$CsTaF_6$</th><th>K_2TaF_7</th><th>Na_3TaF_8</th></tr>
<tr><td>Raman frequency ν_1 (cm^{-1})</td><td>683[31]</td><td>630[31]</td><td>692[32]</td><td>640[32]</td><td>614[32]</td></tr>
<tr><td>coordination no.</td><td>6</td><td>7</td><td>6</td><td>7</td><td>8</td></tr>
<tr><th></th><th colspan="5">solution</th></tr>
<tr><th></th><th colspan="2">Nb in 48% HF</th><th colspan="2">Ta in 48% HF</th><th>Pa in 48% HF</th></tr>
<tr><td>Raman frequency ν_1 (cm^{-1})</td><td colspan="2">685,[31] 687[a]</td><td colspan="2">697,[32] 697[a]</td><td>563</td></tr>
</table>

[a] Measurement conducted in this work (see the Supporting Information).

The comparison of the Raman spectra reported in Figures 3 and Figure 4 does not show a clear relationship between the protactinium complexes in the solid and solution states, as no Raman shift in the solid state matches exactly the Raman shift observed at 563 cm^{-1} for the Pa in 48% HF solution. However, the closest frequencies observed at 557 and 555 cm^{-1} in the solid state, corresponding to Na_3PaF_8 and $(Me_4N)_2(H_3O)PaF_8$ complexes, respectively, suggest that the main species in concentrated HF solution could be the PaF_8^{3-} molecular anion. Moreover, the large red shift in ν_1 observed for Nb and Ta should also be observed when the coordination number around the Pa is increased from 6 to 8. Therefore, the expected frequencies corresponding to PaF_7^{2-} and PaF_6^- molecular anions should be higher than 590 cm^{-1}, which corresponds to the eight-coordinate crystal $RbPaF_6$.[27] Finally, the only homoleptic molecular anion observed to date in single-crystal structures is PaF_8^{3-} in Na_3PaF_8 and $(Me_4N)_2(H_3O)PaF_8$, suggesting that this anion may be present in solutions of 48% HF.

The existence of the PaF_8^{3-} anion was already suggested in the literature by NMR, ion-exchange, and conductometric titration experiments for moderate HF concentrations (0.1−1.42 M),[33] suggesting an equilibrium between seven- and eight-coordinate complexes. DFT calculations combined with EXAFS measurements suggested the existence of the PaF_7^{2-} anion in the range 0.05−0.5 M HF,[34] which is far less concentrated than the solutions studied in this work (48% HF ≈ 27 M HF). Therefore, additional experiments are required to conclusively comment on the speciation of the protactinium fluoride complexes in aqueous HF solutions.

■ CONCLUSION

Seven protactinium(V) fluoro compounds were synthesized, and among them five new single-crystal structures were reported. $(NH_4)_2PaF_7$, Rb_2PaF_7, and Cs_2PaF_7 were found to be isostructural with the previously reported K_2PaF_7,[12,13] crystallizing in the monoclinic crystal system in space group $C2/c$, with nine-coordinate Pa forming infinite chains through fluorine bridges. However, $(NH_4)_2PaF_7$ crystallizes in the space group $P2_1/c$, in contrast to the aforementioned compounds. This difference is reflected in the Raman spectra of these crystals, the Pa–F symmetric stretching band ν_1 of $(NH_4)_2PaF_7$ being blue-shifted and broader in comparison to those for the other $XPaF_7$ (X = K, Cs, Rb) compounds. Two molecular complexes containing the PaF_8^{3-} anion were obtained: Na_3PaF_8, which crystallizes in the tetragonal space group *I*4/*mmm* with eight-coordinate Pa in an approximate cubic geometry, and $(Me_4N)_2(H_3O)PaF_8$, which crystallizes in the monoclinic space group *C*2/*c*. Finally, $(Me_4N)PaF_6$ forms an eight-coordinate Pa compound of infinite chains in the orthorhombic space group *Pnnm*. A comparison of the solid- and solution-state Raman data indicates that the PaF_8^- anion could be the predominant Pa(V) complex in 48% HF solutions, a hypothesis consistent with our observations and previous observations.

Further studies will focus on investigating the coordination number around the Pa in various HF solutions with other techniques, such as high-energy X-ray scattering. At low acidity, the occurrence of a monooxo bond as suggested by some authors[34,35] should be studied by EXAFS and vibrational spectroscopy. The synthesis of Pa monooxo-containing complexes would be useful both for comparative studies with the heavier dioxo-containing actinides U, Np, and Pu and for spectroscopic comparison to protactinium's transition-metal homologues.

■ ASSOCIATED CONTENT

S Supporting Information

CIF files and figures giving X-ray crystallographic data, additional crystallographic details, thermal ellipsoid plots, and Raman spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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