

Supramolecular Interactions in $\text{PuO}_2\text{Cl}_4^{2-}$ and PuCl_6^{2-} Complexes with Protonated Pyridines: Synthesis, Crystal Structures, and Raman Spectroscopy

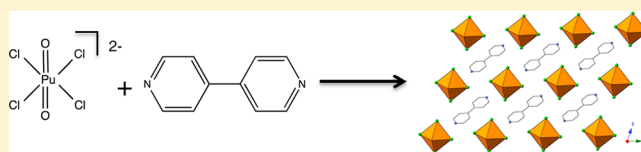
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Supporting Information

ABSTRACT: The synthesis, crystal structures, and Raman spectra of seven plutonium chloride compounds are presented. The materials are based upon $\text{Pu(VI)O}_2\text{Cl}_4^{2-}$ and Pu(IV)Cl_6^{2-} anions that are charge balanced by protonated pyridinium cations. The single crystal X-ray structures show a variety of donor–acceptor interactions between the plutonium perhalo anions and the cationic pyridine groups. Complementary Raman spectra show that these interactions can be probed through the symmetric vibrational mode of the plutonyl moiety. Unlike previously reported studies in similar uranyl(VI) systems, the facile redox chemistry of plutonium in aqueous solution has demonstrated the feasibility of using not only the $\text{An(VI)O}_2\text{Cl}_4^{2-}$ anion with approximate D_{4h} symmetry but also the approximately O_h An(IV)Cl_6^{2-} anion in order to manipulate both the structure and dimensionality of such hybrid materials.



INTRODUCTION

The linear dioxo-cation moiety, $\text{O}=\text{An}=\text{O}^{+2+}$, is a structural feature unique to the early penta- and hexavalent actinide ions U, Np, Pu, and Am. The electronic structure and chemistry of these dioxo-cations has been widely studied from an electronic and synthetic perspective, most frequently for uranium.^{1,2} The dioxo-actinyl ions are chemically robust in aqueous solution and ambient atmosphere thus generally limiting their coordination chemistry under these conditions to the equatorial plane perpendicular to the $\text{O}=\text{An}=\text{O}$ axis.

Synthetic efforts over the past several years have resulted in a significant expansion in the catalog of solid state and hybrid materials containing these linear dioxo-cations. Despite the general tendency toward equatorial coordination, the dimensionality of such materials has not been limited, nor has their structural diversity.³ Indeed, the catalog of U(VI) hybrid materials in particular demonstrates a wide range of dimensionalities influenced by a diverse collection of organic linkers. Carboxylate and phosphonate linkers are perhaps the most representative owing to the affinity of the uranyl cation for these functionalities.^{4–17} Further structural diversity may be attributed to a complex uranyl speciation profile stemming from hydrolysis in aqueous media.¹⁸ Whereas this may be considered an asset for diversity in terms of providing a range of building units, the synthesis of hybrid materials with specific or intended uranyl geometries remains a challenge.¹⁹ Pu bearing hybrid materials, while admittedly less-well developed, demonstrate similar features compared with U systems in terms of extensive speciation profiles and linker affinity. Moreover, the complex redox behavior for Pu^{n+} in aqueous media provides for additional challenges in terms of materials design.^{20–25}

We have recently begun work to investigate the degree to which a more limited speciation profile may be combined with predictable, directional intermolecular interactions, or “synthons”, to enable the rational design of crystalline, uranyl-bearing materials.^{26–28} In these cases, a high concentration of halide ions present in acidic solution effectively prevents hydrolysis and thus limits the speciation profile to mononuclear units, specifically anionic halide $[\text{UO}_2\text{X}_4]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) species, which may engage in hydrogen-bonding interactions with pyridinium based counterions. This is indeed a demonstrated approach as seen in d metal systems, and we thus drew our inspiration from Pd(II) and Pt(II) compounds where square planar geometries may be considered structurally analogous to actinyl complexes with terminal apexes.^{29,30} More generally, the assembly of anionic d metal complexes through directed H-bonding is an active area of inquiry.^{31,32} Beyond these synthesis and crystallographic motivations, however, actinyl compounds in particular are of fundamental interest in terms of providing a forum for the study of actinyl electronic spectra³³ and are relevant to our understanding of radioactive waste disposition in high-halide environments.³⁴

In this study, we have extended the previous synthetic and structural studies of uranyl perhalo complexes of U(VI) to Pu(VI). Herein we report the synthesis of four plutonium(VI) tetrachloride salts and two Pu(IV)Cl_6^{2-} salts crystallized with a series of organic cations. Additionally, we report a rare mixed-valent Pu(IV)/Pu(VI) compound consisting of Pu(IV)Cl_6^{2-} and $\text{PuO}_2\text{Cl}_4^{2-}$ anions. Complementary studies on these and

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Table 1. Crystallographic Parameters for the Reported Complexes

	1	2	3	4
formula	(C ₁₀ H ₁₀ N ₂)PuO ₂ Cl ₄	(C ₁₂ H ₁₂ N ₂)PuO ₂ Cl ₄	(C ₁₃ H ₁₆ N ₂)PuO ₂ Cl ₄	(C ₁₀ H ₁₁ N ₃) ₂ [PuO ₂ Cl ₄]·2Cl(H ₂ O) ₂
MW (g·mol ⁻¹)	574.00	600.04	616.08	869.17
space group	P $\bar{1}$	P $\bar{1}$	C2/c	P $\bar{1}$
a (Å)	5.445(1)	6.900(1)	12.610(1)	7.042(2)
b (Å)	8.538(2)	8.077(2)	11.636(1)	9.828(2)
c (Å)	8.838(2)	8.304(2)	12.252(2)	11.438(2)
α (deg)	71.126(1)	81.327(3)	90.00	72.093(3)
β (deg)	72.806(1)	74.563(3)	101.441(1)	72.116(4)
γ (deg)	86.962(1)	66.512(3)	90.00	77.488(4)
V (Å ³)	371.04(4)	408.62(18)	1762.2(3)	710.3(2)
Z	1	1	4	1
ρ_{calcd} (g·cm ⁻³)	2.569	2.438	2.322	2.032
T (K)	100	100	100	100
λ (Å) [Mo K α]	0.71073	0.71073	0.71073	0.71073
μ (mm ⁻¹)	5.158	4.689	4.353	2.923
S (GOF)	1.044	1.017	1.029	1.081
R(F _o), wR(F _o ²)	0.011, 0.027	0.037, 0.064	0.025, 0.046	0.027, 0.053
	5	6	7	
formula	(C ₁₀ H ₁₀ N ₂) ₂ [PuCl ₆][PuO ₂ Cl ₄]	(C ₁₀ H ₁₀ N ₂) ₃ [PuCl ₆]·4Cl	(C ₁₂ H ₁₄ N ₂)PuCl ₆	
MW (g·mol ⁻¹)	1186.90	1068.15	640.95	
space group	P2 ₁ /c	P $\bar{1}$	P $\bar{1}$	
a (Å)	7.428(1)	7.348(1)	7.929(2)	
b (Å)	16.051(2)	10.981(2)	9.176(2)	
c (Å)	14.172(2)	12.028(2)	13.182(3)	
α (deg)	90.00	83.524(2)	76.270(4)	
β (deg)	113.29(1)	73.930(2)	89.413(4)	
γ (deg)	90.00	88.640(2)	82.040(3)	
V (Å ³)	1552.1(4)	926.69(18)	922.0(3)	
Z	2	1	2	
ρ_{calcd} (g·cm ⁻³)	2.540	1.914	2.309	
T (K)	100	100	100	
λ (Å) [Mo K α]	0.710 73	0.710 73	0.710 73	
μ (mm ⁻¹)	5.0597	2.532	4.437	
S (GOF)	1.032	1.013	1.027	
R(F _o), wR(F _o ²)	0.03, 0.06	0.032, 0.059	0.028, 0.055	

the Pu(VI) containing compounds using Raman spectroscopy have been conducted. The frequency of the symmetric ν_1 mode of the actinyl ion is highly sensitive to the chemical environment about the ion, particularly in the primary equatorial coordination sphere. Prior studies have revealed an empirical correlation between the symmetric stretching frequency of the actinyl and the bond length based on analysis of the symmetric ν_1 and asymmetric ν_3 frequencies, most extensively for uranyl(VI).³⁵ Studies of the compounds reported here reveal a shifting actinyl symmetric vibrational mode that is dependent not only on the immediate inner-sphere equatorial coordination environment but also on the nature of the counteranion–chloride interaction in the crystals.

EXPERIMENTAL METHODS

Caution! ²⁴²Pu is an α -emitting radionuclide. All experiments described here were performed in a laboratory specially designed and designated for the handling of α -emitting radionuclides including radiological fume hoods and gloveboxes under the supervision of health physics personnel.

²⁴²Pu(VI) Stock Solution. A stock solution of ²⁴²Pu was prepared using standard ion-exchange techniques. Briefly, a ²⁴²Pu(IV) solution in 7.5 M HNO₃ was loaded onto a DOWEX anion exchange column conditioned in the nitrate form. The column was then washed with several volumes of 7.5 M HNO₃ to remove cationic and anionic impurities. The plutonium was eluted from the column using 1 M HCl

and subsequently heated with periodic additions of 11 M HCl to drive off residual nitric acid and reduce its volume resulting in a solution of primarily Pu(IV) and Pu(VI). This Pu solution was then bubbled with ozone for three days to fully oxidize the Pu to PuO₂²⁺, as confirmed by UV–vis spectrometry.

Synthetic Protocol. Each of the reported plutonium chloride salts were prepared by mixing stoichiometric quantities of the Pu(VI)/HCl (1 mg, 0.0042 mmol Pu) stock solution with solutions of the organic ligands dissolved in 6 M HCl and allowing these mixtures to crystallize by evaporation at room temperature. All the ligands except 4,4'-dipyridyl amine were purchased from commercial sources without additional purification. 4,4'-Dipyridyl amine was synthesized according to literature methods.³⁶ Crystals suitable for X-ray diffraction studies developed over the course of 2–3 days. Because of the small scale of the reactions, no attempt was made to ascertain the yield of each reaction.

Single Crystal X-ray Diffraction. Single crystals of the reported complexes were mounted on glass fibers and affixed with a quick-drying epoxy. Full spheres of data were collected at 100 K on a Bruker APEX II diffractometer using Mo K α radiation. The data were corrected for absorption using SADABS, and the structures were solved using a Patterson method (SHELXS). Structure refinements were carried out using SHELXL software.³⁷ Hydrogen atoms associated with the carbon and nitrogen atoms were refined using a riding model with rigid group constraints.

Raman Spectroscopy. Raman spectra were collected on randomly oriented single crystals using a Renishaw inVia Raman

microscope using circularly polarized light from a 532 or 785 nm diode laser. Samples were mounted on glass microscope slides with a circular concave depression and covered by a glass coverslip sealed with epoxy. Data were collected from 100 to 1300 cm^{-1} . Data showed no excitation dependence of the Raman shift.

RESULTS AND DISCUSSION

The crystallographic parameters for compounds 1–7 are presented in Table 1. In each of the structures, the plutonium complexes are composed of dianionic complexes with either distorted O_h (PuCl_6^{2-}) or D_{4h} ($\text{PuO}_2\text{Cl}_4^{2-}$) symmetry and are charge balanced by the protonated N-bearing cations that are not directly coordinated to the metal center. Table 2 presents the relevant bond distances about the plutonium metal centers, as well as the site symmetry of the ions as determined by their crystal structures.

Table 2. Selected Bond Distances and Symmetries for the Reported Complexes

compd	Pu=O <i>d</i> (Å)	Pu–Cl <i>d</i> (Å)	Pu–Cl <i>d</i> (avg), Å	sym Pu, sym R^{n+}
1	1.737(2)	2.657(1) 2.665(1)	2.66(1)	C_{2v} C_i
2	1.729(3)	2.646(1) 2.660(1)	2.65(1)	C_{2v} C_i
3	1.747(2)	2.646(1) 2.663(1)	2.65(1)	C_{2v} C_2
4	1.759(2)	2.655(1) 2.676(1)	2.66(2)	C_{2v} C_1
5	1.741(3)	2.642(1), Pu(1) 2.674(1), Pu(1) 2.571(1), Pu(2) 2.614(1), Pu(2)	2.66(2) 2.59(3)	C_{2v} C_1
6		2.580(1) 2.580(1) 2.594(1)	2.58(1)	C_{2v} C_i C_1
7		2.568(1) 2.569(1) 2.586(1) 2.592(1) 2.613(1) 2.616(1)	2.59(2)	C_1 , C_1

Structural Descriptions. Compound 1 contains a single unique $[\text{PuO}_2\text{Cl}_4]^{2-}$ anion that is charged balanced by a 4,4'-bipyridinium dication. The Pu(VI) coordination sphere in this and later structures is typical of those previously reported^{38–40} in terms of bond lengths and angle, and consequently no further discussion of the unit itself will be presented. The plutonyl tetrachloride unit is indeed isostructural with the more well-known uranyl tetrachloride dianion. It follows, therefore,

that compounds 1–4 are isostructural with the corresponding U(VI) materials.²⁶ Because these structures have been described previously, only a brief description of hydrogen-bonding motifs will be included here. The protonated nitrogen atoms on the pyridinium rings in 1 link between metal centers by engaging in asymmetric bifurcated hydrogen bonding to the equatorially bound chloride ligands, forming a chain motif in the $[111]$ direction (Figure 1). Nitrogen to chloride distances are 3.448 Å ($\text{N1}\cdots\text{Cl1}$) and 3.195 Å ($\text{N1}\cdots\text{Cl2}$), the latter of which is just within the sum of the van der Waals radii for N and Cl.

Multiple weak hydrogen bonds, such as $\text{CH}\cdots\text{O}$ and $\text{CH}\cdots\text{Cl}$, are involved in the packing of these chains (Figure 2).

Compound 2 is formed from a single unique $[\text{PuO}_2\text{Cl}_4]^{2-}$, which is charged balanced by a diprotonated *trans*-1,2-bis(pyridyl)ethylene unit. The protonated nitrogen atoms on the pyridinium rings link between metal centers by engaging in bifurcated hydrogen bonding to the equatorially bound chloride ligands, forming a chain motif in the $[21\bar{1}]$ direction (Figure 3). Nitrogen to chloride distances are 3.233 Å ($\text{N1}\cdots\text{Cl1}$) and 3.258 Å ($\text{N1}\cdots\text{Cl2}$) and are just within the sum of the van der Waals radii for N and Cl. As in 1, weak hydrogen bonds are involved in the packing of these chains (Figure 4)

Compound 3 contains a single unique $[\text{PuO}_2\text{Cl}_4]^{2-}$ unit, which is charged balanced by a doubly protonated 4,4'-trimethylene dipyridinium cation (Figure 5). The protonated nitrogen atoms on the pyridinium rings link between metal centers by hydrogen bonding to a single chloride ligand, Cl1 ($\text{N1}\cdots\text{Cl1} = 3.174$ Å) to form a distorted chain motif.

In this structure, as in those previously described, $\text{CH}\cdots\text{A}$ hydrogen bonds and other weak intermolecular interactions, notably π -stacking with a ring–ring separation of 3.532 Å, are involved in the packing of these chains.

Compound 4 also contains a single unique $[\text{PuO}_2\text{Cl}_4]^{2-}$ anion, along with a free chloride anion, which are charge-balanced by a single crystallographically distinct diprotonated 4,4'-dipyridylamine. In addition to this, there is also a single solvent water molecule present. In this structure there are no significant interactions directly between the plutonyl tetrachloride unit and the pyridinium unit. Instead, the protonated aromatic nitrogen atoms, N1 and N3, engage in hydrogen-bonding to the free chloride Cl3 to form chains that propagate in the $[01\bar{1}]$ direction (Figure 6). The metal-bound chloride ligand Cl1 hydrogen bonds to the solvent water molecule (O2, protons omitted from diagrams for clarity), which in turn acts as a hydrogen bond donor to Cl3 and a hydrogen bond acceptor from the secondary amine N2 present in the organic base. The water molecules may therefore be considered to bridge between the metal centers and the pyridinium–chloride chains.

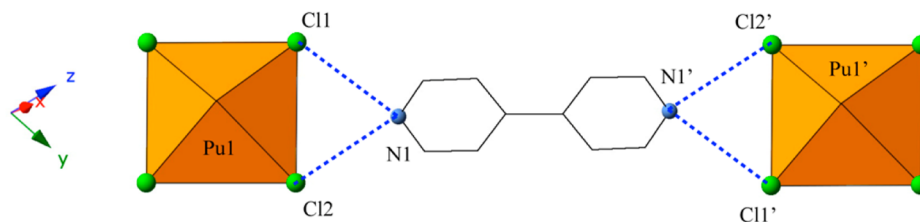


Figure 1. The bifurcated hydrogen bonding in 1; a partial numbering scheme is used in this and subsequent figures. Superscript indicates symmetry equivalent atoms.

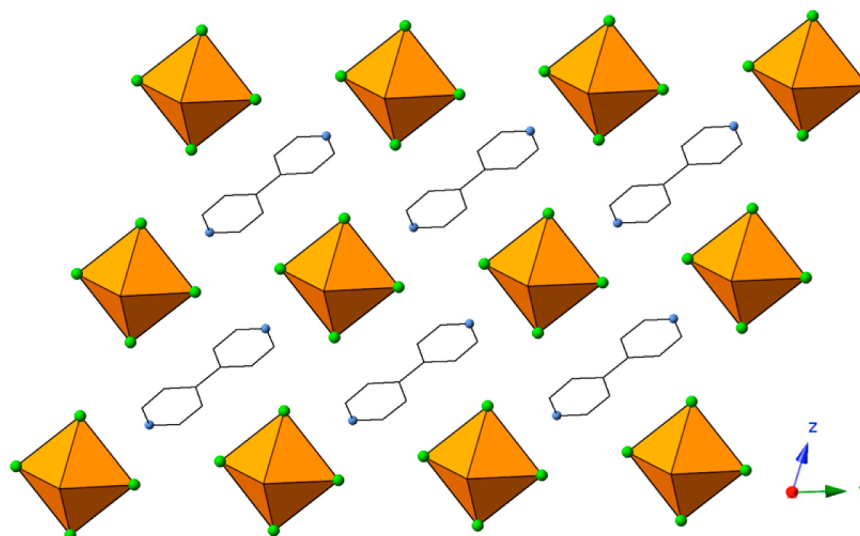


Figure 2. The extended structure of **1**, showing the packing of the chains.

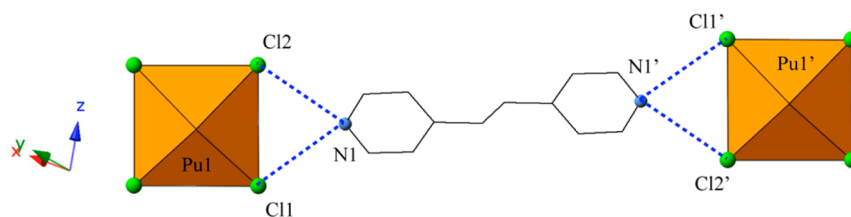


Figure 3. The bifurcated hydrogen bonding in **2**.

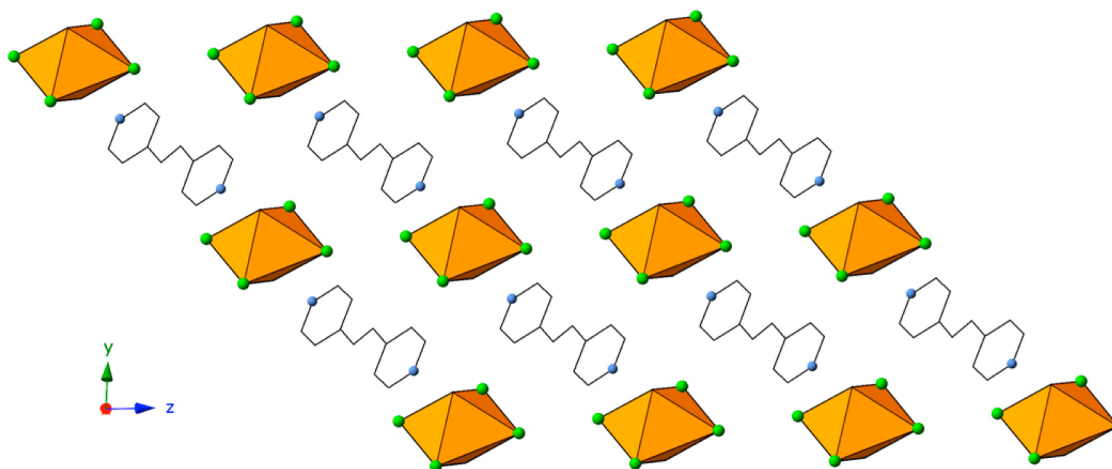


Figure 4. The extended structure of **2**, showing the packing of the chains.

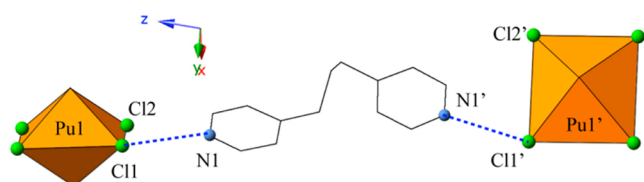


Figure 5. The structure of compound **3** with H-bonding shown as dashed line.

As each metal center hydrogen bonds to two solvent water molecules (via Cl1 and Cl1', omitted for clarity from Figure 6), the overall structure may be considered to be formed of

“bilayers”, between which there are relatively few significant interactions (Figure 7).

Compound **5** (Figure 8) is the first to deviate from the aforementioned uranyl tetrachloride family as it contains two distinct metal centers. Pu1 is an octahedral plutonium(IV) hexachloride, with Pu–Cl bond distances of approximately 2.6 Å, typical for the PuCl_6^{2-} unit.⁴¹ Pu2 is a $[\text{PuO}_2\text{Cl}_4]^{2-}$ similar to those described for compounds **1–4**. The two metal centers form an alternating Pu(IV)/Pu(VI) chain motif, which propagates in the [001] direction. The chain is held together by hydrogen bonding to a single crystallographically unique 2,4'-bipyridinium cation where the 4-functionalized pyridinium hydrogen bonds to a Pu(IV)-bound chloride ligand ($\text{N1}\cdots\text{Cl8} =$

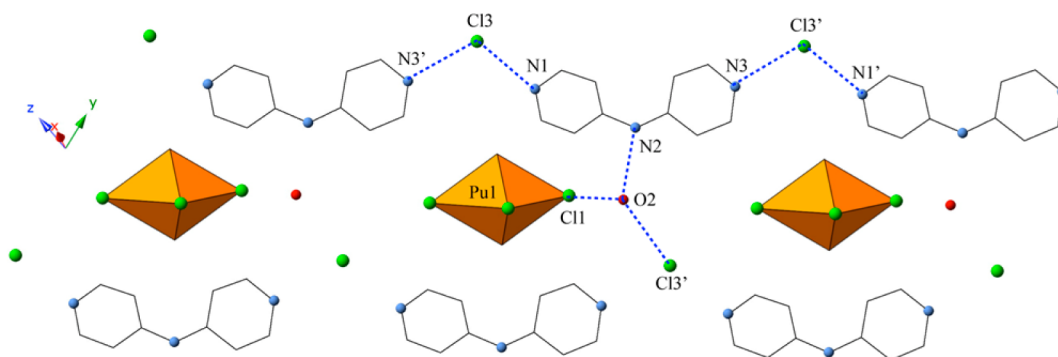


Figure 6. The structure of **4** highlighting the pyridinium–chloride chains, as well as their interactions with the $[\text{PuO}_2\text{Cl}_4]^{2-}$ centers via bridging solvent water molecules. All H atoms are omitted for clarity.

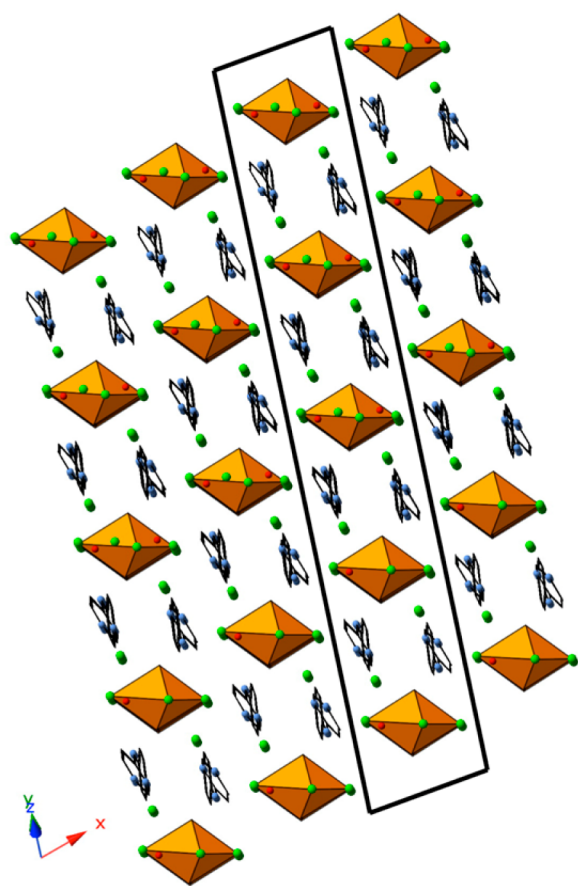


Figure 7. The packing of **4** shown down the pyridinium–chloride chains. An individual “bilayer” is outlined.

3.183 Å) and the 2-functionalized pyridinium hydrogen bonds to the equatorial chloride ligand of the plutonyl ($\text{N}2 \cdots \text{Cl}1 = 3.076$ Å). As with previous structures bearing a chain motif, packing of the chains involves numerous weak intermolecular interactions and may be considered to form an overall layered motif (Figure 9).

Compound **6** is formed of a single crystallographically unique PuCl_6^{2-} unit and two crystallographically unique free chloride ions, all of which are charge balanced by two crystallographically unique, diprotonated 4,4'-dipyridinium units (Figure 10).

The ring nitrogen atoms in the pyridinium units have no interaction with the metal-bound chloride ligands and instead

form a network with the free chloride anions by engaging in both monofurcated and bifurcated hydrogen bonding. This network is arranged as a “broad-chain” motif, which propagates in the $[10\bar{1}]$ direction. The PuCl_6^{2-} units are situated in the voids of this network (Figure 10), forming weak hydrogen bonds between the chloride ligands and the pyridine ring H atoms. The PuCl_6^{2-} centers are situated both above and below the plane of the “broad-chain”, and each engage in hydrogen bonding to two chains to result in an overall “stepped sheet” topology (Figure 11). These sheets then interact by weak hydrogen bonding, similar to the interaction of chains in previous structures.

Compound **7** is formed of a single, crystallographically unique PuCl_6^{2-} unit, which is charge-balanced by a single, crystallographically unique, diprotonated 4,4'-dipyridyl ethane. The organic cation links between metal centers by engaging in asymmetric bifurcated hydrogen bonding from N1 to Cl3 and Cl6 (3.361 and 3.235 Å, respectively) and monofurcated hydrogen bonding from the other pyridinium group ($\text{N}2 \cdots \text{Cl}2 = 3.131$ Å), to result in a chain motif that propagates in the $[001]$ direction (Figure 12). As in previous structures, multiple (weaker) hydrogen bonds are involved in the packing of these chains.

Structural Discussion. Compounds **1** and **2** are based on the $\text{MX}_2 \cdots \text{HN}$ synthon described first by Brammer and Orpen.^{29,42} In these structures, the pyridinium group forms bifurcated hydrogen bonds to two halide ligands on the metal. This occurs on both sides of the $[\text{PuO}_2\text{Cl}_4]^{2-}$ unit, and it is this second sphere coordination number of two, combined with the covalent linkage between pyridinium groups, that results in the formation of an infinite 1-D “ribbon motif”. In compound **3**, an extended aliphatic linker between pyridinium groups adds flexibility between the pyridinium groups. As a result of this, the bifurcated hydrogen-bonding motif is no longer observed; instead the pyridinium units hydrogen bond to a single chloride ligand. Despite this difference, the symmetry of the organic cation generated a 1-D structure. In compound **4**, the presence of a secondary amine linker between the pyridinium units resulted in a nonlinear dicationic species with an additional hydrogen bond donor atom. As a result of these factors, the ribbon motif was not observed, and indeed there was no direct interactions at all between the metal center and the organic.

Compounds **5–7** all display an additional or alternative metal center, Pu(IV)Cl_6^{2-} , and as such are distinct from any previously reported structures. In compound **5**, the organic linker, 2,4'-bipyridinium, hydrogen bonds via the protonated nitrogen groups to chloride ligands on two metal centers,

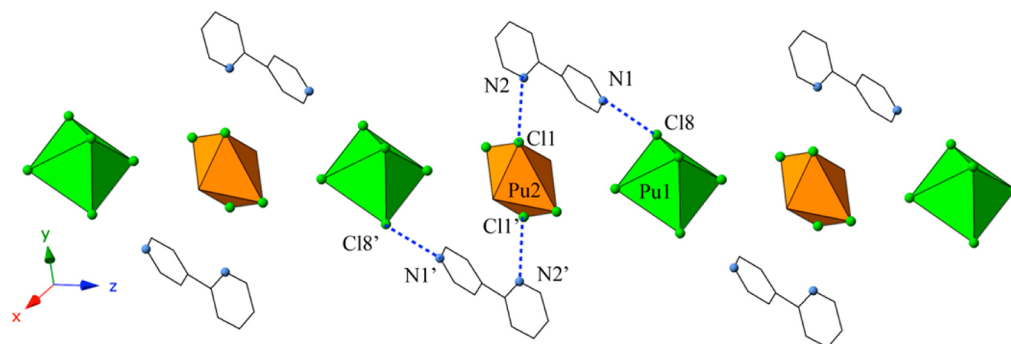


Figure 8. The structure of **5** highlighting the alternating chain motif along $[001]$. $[\text{PuCl}_6]^{2-}$ anions are shown in green whereas $[\text{PuO}_2\text{Cl}_4]^{2-}$ species are orange.

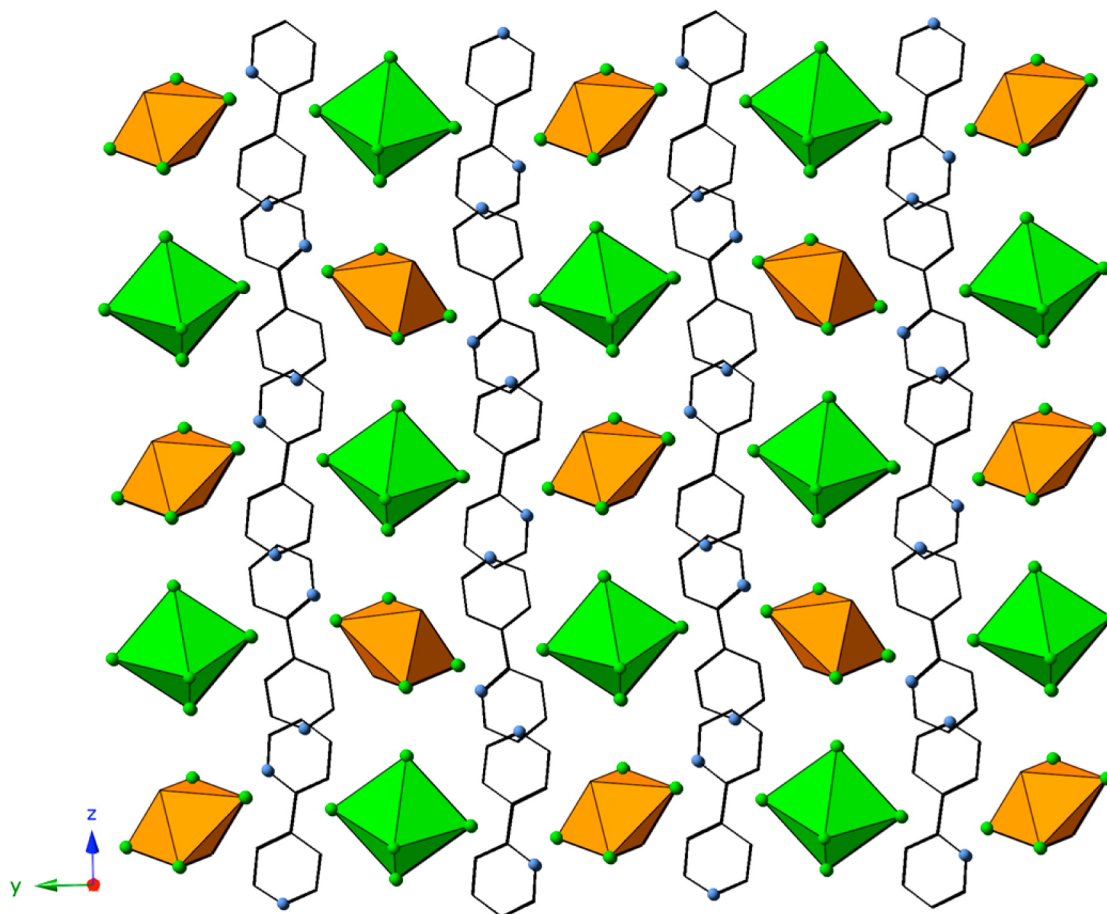


Figure 9. An extended view of **5**.

$[\text{PuO}_2\text{Cl}_4]^{2-}$ and $[\text{Pu(IV)Cl}_6]^{2-}$, to form a mixed-valence 1-D chain motif. In the compound previously formed by combining this organic cation with the isostructural uranyl tetrachloride, the pyridinium groups did not hydrogen bond to the metal center; instead alternative hydrogen bond acceptors (Cl^- , H_2O) were incorporated, similar to compound **4** (described above) and its U(VI) analogue.²⁶ It appears that a material in which $[\text{AnO}_2\text{Cl}_4]^{2-}$ is charge-balanced with a single 2,4'-bipyridinium unit is not stable or at least is less stable than incorporating additional species from the environment.

The preference of the 2-substituted pyridinium to hydrogen bond to the $[\text{PuO}_2\text{Cl}_4]^{2-}$ whereas the 4-substituted pyridinium hydrogen bonds to the $[\text{Pu(IV)Cl}_6]^{2-}$ unit is likely due to sterics. Because the 2-substituted pyridinium is more sterically

hindered, it hydrogen bonds to the plutonyl species, which is more compact due to the short Pu(VI)–O bonds.

In compound **6**, the $[\text{Pu(IV)Cl}_6]^{2-}$ is the only metal species present, and it does not receive hydrogen bonds from the protonated nitrogen present on the 4,4'-bipyridinium group. Instead, this anion resides in voids formed by a pyridinium–chloride hydrogen bonding network. The reason for this is unclear. Octahedral species have been known to form hydrogen bonds to protonated nitrogen atoms, with monofurcated, bifurcated, and trifurcated motifs known. Indeed, 4,4'-bipyridinium has been reported to form hydrogen bonding networks with octahedral Os(IV) and Pt(IV) hexachlorides.⁴³ In these cases, however, the M–Cl bond lengths were significantly shorter (approximately 2.3 Å compared with 2.6

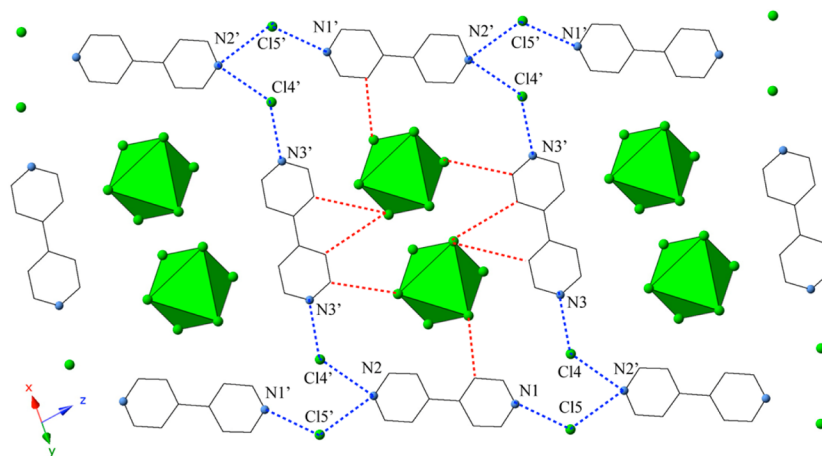


Figure 10. The structure of **6** highlighting the hydrogen bonding of the pyridinium–chloride network (blue) and the hydrogen bonding to the PuCl_6^{2-} “guest” units (red) in a single “broad chain” motif.

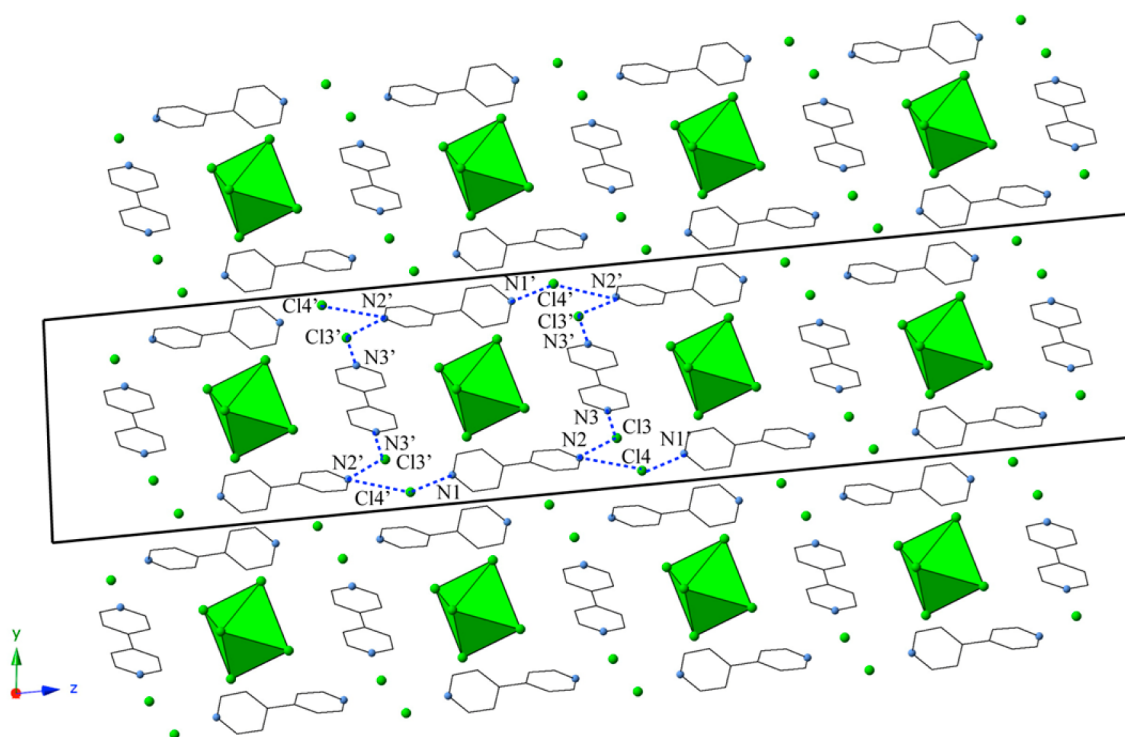


Figure 11. The hydrogen bonding in a single “stepped sheet” (outlined), viewing down the plane of the PuCl_6^{2-} units in **6**.

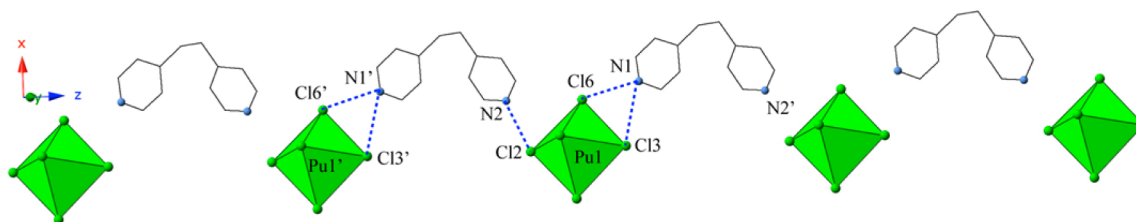


Figure 12. The chain motif in compound **7**. The pyridinium cations engage in both mono- and bifurcated H-bonding.

Å). Whether the sterics of the PuCl_6^{2-} octahedron or the hydrogen bond accepting abilities of the more weakly bound chloride ligands is the key to the difference in structure is unclear.

In compound **7**, the bipyridinium unit displays both bifurcated and monofurcated hydrogen bonding to chloride

ligands on a $[\text{Pu(IV)Cl}_6]^{2-}$ unit. It is possible that the flexibility of the aliphatic linker prevents both bipyridinium units from forming bifurcated hydrogen bonding, similar to compound **3**.

Raman Spectroscopy. Raman spectra of the reported complexes are presented in Figure 13. Our primary interest in these spectra are the vibrational modes associated with the

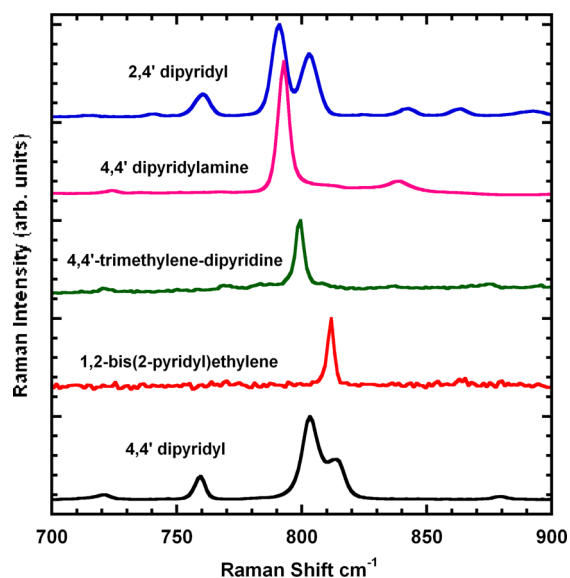


Figure 13. Raman spectra of the Pu(VI) bearing complexes highlighting the symmetric stretching frequency of the plutonyl ion.

linear dioxo-plutonyl moiety. The vibrational modes arising from the organic cations will not be discussed in this analysis. In idealized D_{4h} symmetry, one expects the presence of 15 vibrational modes. Of these modes, six of them are Raman active in D_{4h} symmetry ($2A_{1g}$, B_{1g} , B_{2g} , E_g). Reduction of the idealized symmetry by incorporation into the crystalline state often results in the lifting of the degeneracies associated with the vibrational modes and relaxation of the selection rules where inversion symmetry is lost. In the case of the vibrational modes arising principally from the symmetric stretch of the dioxo-moiety, the band is not degenerate and should appear as a single band assuming one plutonyl in the unit cell and no coupling of vibrational modes from other modes of the same symmetry. Characteristic frequencies for the vibrational modes associated with the Pu–O actinyl bonds are known from previous studies. Generally, the vibrations attributable to the plutonyl moiety occur between 750 and 850 cm^{-1} . The symmetric stretching frequencies observed in the Pu(VI)- $\text{O}_2\text{Cl}_4^{2-}$ bearing complexes reported here are listed in Table 3.

Table 3. Observed Vibrational Frequencies and Bond Distances for the Reported $\text{PuO}_2\text{Cl}_4^{2+}$ Bearing Complexes

compound	ν_1 (cm^{-1}) PuO ₂ ²⁺ symmetric stretch	Pu–O bond length (Å)
[4,4'-bipyridine]PuO ₂ Cl ₄ , 1	803, 813	1.737(2)
[1,2-bis(4-pyridyl)ethylene]PuO ₂ Cl ₄ , 2	811	1.729(3)
[4,4'-trimethylene dipyridine]PuO ₂ Cl ₄ , 3	800	1.747(2)
[4,4'-dipyridylamine]PuO ₂ Cl ₄ , 4	793	1.759(2)
[2,4'-dipyridyl](PuO ₂ Cl ₄)(PuCl ₆), 5	791, 803	1.741(3)

The spectral features attributable to the PuO₂²⁺ stretching modes are prominent in all of the spectra near 800 cm^{-1} . Previous studies of Pu(VI)O₂²⁺ complexes using Raman spectroscopy have shown that the symmetric stretching frequency for Pu(VI)O₂²⁺ in aqueous perchloric acid solution is observed at 835 cm^{-1} , in solid $[\text{PuO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ at 844 cm^{-1} , and in PuO₂(IO₃)₂·H₂O at 856 cm^{-1} .^{25,44,45} The lower frequency vibrations attributable to the bending modes of

the plutonyl unit and the Pu–Cl modes are not easily assigned. A reliable assignment of these bands would require a polarized Raman study of oriented single crystals since the low frequency region of the spectrum is populated by several bands that may also be assigned to the ligand modes.

Generally, upon coordination of a ligand to the equatorial plane, a nearly ionic bond is formed between the An(VI)O₂²⁺ ion and the equatorial ligand or ligands.⁴⁶ Despite the ionic interaction of the ligand with actinide ion, it has been demonstrated that the symmetric and asymmetric vibrational frequencies of the actinyl cations vary depending on both the ligands and coordination number in the equatorial plane.^{35,47} Because of the shifting of the vibrational modes of the actinyl unit with equatorial coordination, these frequencies are used as indicators of actinide–ligand interactions, as well as spectroscopic probes of actinyl speciation in solution. Empirical relationships have been determined to correlate the actinyl bond length with both the symmetric and asymmetric frequencies of actinyl complexes using Badger's rules relating the shifting vibrational frequency with a lengthening of the actinyl bond.⁴⁸

As seen in Table 3, there is a general correlation between the symmetric stretching frequency and the Pu–O_{y1} bond length as measured using single crystal X-ray diffraction, in agreement with Badger's rules and prior experiments with uranyl(VI) Raman; less straightforward are complexes 1 and 5 that show at least two peaks where the plutonyl symmetric stretching mode is expected to be observed. Compounds 1 and 5 both contain one crystallographically unique plutonyl(VI) cation in the asymmetric unit. Therefore, the observation of two bands in the symmetric stretching region of plutonyl is not expected. Molecular site group analysis for both 1 and 5 reveals that the plutonyl resides on a special position with inversion symmetry in both cases and the space groups are centrosymmetric. Correlating this symmetry with the space group maintains the Raman and IR selection rules; thus we do not expect to observe any extra bands in the Raman occurring as a result of its incorporation in the crystal for these compounds. However, correlation splitting or coupling of other vibrational modes with these modes may give rise to extra observed bands in the spectra.

Similar analysis of the molecular units in these crystals reveals that in 1, the 4,4'-bipyridine molecule of idealized D_{2h} symmetry is centered on a special position with inversion symmetry; thus the descent in symmetry to C_i for the site symmetry and imposition of the space group symmetry C_i results in conservation of the selection rules for the idealized 4,4'-bipyridine molecule. Similar analysis for 5 is trivial, revealing that the 2,4'-bipyridine, with C_s idealized symmetry where all modes are IR and Raman active, resides on a general position of C_1 symmetry. In the IR spectra of these bipyridine molecules, strong bands associated with C–H stretching modes are observed in this region, which are Raman active because of the symmetry in 5.

Comparison of the two spectra (Figure 13) reveals that the peak arising from the bipyridines at 760 cm^{-1} appears in both Raman spectra with a peak at 803 cm^{-1} equally spaced higher in energy in both spectra providing some guidance to the assignments. Based on these spectral features and the general trend established in uranyl Raman studies, where the ν_1 frequency should correlate with an increasing actinyl bond distance, we cautiously assign the peak at 813 cm^{-1} to the ν_1 mode in 1 and the peak at 791 cm^{-1} to the ν_1 mode in 5. We

further highlight that compound **5** does not correlate with the predicted trends of bond distance and frequency. We caution that at this level of analysis we cannot rule out the coupling of modes of similar symmetry resulting in the observation of these multiple peaks, particularly in **5** where there are two plutonyl molecules per unit cell instead of one in **1**.

The lowering of the vibrational frequency generally correlates with a lengthening of the actinyl bond. This is widely believed to result from the donation of electron density from the ligand to the actinide metal center.^{1,49,50} In the case of the complexes reported here, the same $\text{PuO}_2\text{Cl}_4^{2-}$ complex is present in all of the structures that were studied using Raman spectroscopy with the exception of the mixed-valence compound **5**. Thus, the change in both the observed bond distance and the vibrational frequency may be due to second sphere interactions within these complexes. As highlighted in the discussion of the structural data, the donor–acceptor interactions between the protonated nitrogen groups and the chloride anions vary among the different complexes. For compounds **1** and **2**, the interaction between the equatorial chlorine atoms and the protonated bipyridine cations occurs as a bifurcation of the equatorially coordinated chloride ions. Thus, we might qualitatively expect that the total electron density that would be donated to the Pu(VI) center would be decreased as a result of the secondary interaction between the protonated nitrogen atoms on the pyridine rings and the chloride ions in the primary coordination sphere. These two compounds can be grouped together with regard to Raman frequency and bond lengths. The remainder of the compounds interact with only one (**3** and **5**) or none (**4**) of the organic cations. While these observations are preliminary, they are qualitatively consistent with the concept that the bond length and Raman frequency of the actinyl units changes with the degree of electron donation to the metal center or the basicity of the coordinating ligands. Therefore, more numerous or stronger interactions in second sphere donor–acceptor interactions may offset the total electron density donated from the equatorial chloride ligands to the plutonyl(VI) center.

A similar effect has been observed before for uranyl perhalo complexes crystallized with alkali-metal salts of crown ethers.⁵¹ The Raman shift of the uranyl unit displays a similar trend between the geometry of the alkali–crown ether interaction and the ν_1 frequency. Within these uranyl perhalo complexes, the frequency of the Raman bands was lowest for the bifurcated interaction where the alkali metal cation interacted with either both the –yl oxygen and the halide or just the halide and higher in the case where the interaction was through only one of the halide ions. While our compounds do not show donor–acceptor interactions between the cations and the –yl oxygen atoms, these plutonyl data are consistent with the previously studied uranyl perhalo complexes that demonstrate donor–acceptor interactions between the equatorial halides and the charge compensating second coordination sphere cations.

CONCLUSIONS

Seven plutonium chloride compounds have been synthesized from acidic aqueous solution, and their structures have been determined using single crystal X-ray diffraction. Five of the structures contain the $\text{PuO}_2\text{Cl}_4^{2-}$ anion as a building unit either exclusively or in the case of one of the compounds, coexisting with the PuCl_6^{2-} anion in a mixed valence complex. The two remaining structures contain only the PuCl_6^{2-} anion. Counterbalancing the anionic plutonium complexes are a variety of

protonated organic containing pyridine or amine groups. These anionic metal complexes coupled with the cationic organic linkers create a variety of donor–acceptor interactions resulting in a variety of one-dimensional structures, similar to what was observed with the uranyl perhalo complexes reported previously. Unlike the U(VI) systems, the facile redox chemistry of Pu has resulted in the observation of a mixed valence Pu(VI)/Pu(IV) complex in one of the reported structures, **5**.

The Raman spectra of **1–5** reported for the complexes suggest that the vibrational frequency of the ν_1 mode of these complexes is sensitive to the second coordination sphere donor–acceptor interactions in these systems. Though additional work is needed to quantify and understand these effects at the electronic level, they have been suggested to be important in understanding metal ion speciation and ion-pairing and may prove useful in the design of functional materials.

ASSOCIATED CONTENT

Supporting Information

Crystallographic information in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic information also has been deposited at the Cambridge Crystallographic Database Centre and may be obtained from <http://www.ccdc.cam.ac.uk> by citing reference codes 976623–976629 for compounds **1–7**, respectively.

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Notes

The authors declare no competing financial interest.

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