Inorganic Chemistry

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Structural Periodicity in Plutonium(IV) Sulfates

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Supporting Information

ABSTRACT: The chemistry of tetravalent Pu with sulfate is explored in a series of single-crystal X-ray diffraction studies of the alkali metal plutonium sulfate compounds. Five new structures of Pu(IV) sulfates are presented including the structure for the α-phase of $Pu(SO_4)_2(H_2O)_4$, $Na_{10}Pu_2(SO_4)_9(H_2O)_4$, $K_8Pu_2(SO_4)_8(H_2O)_5$, $Rb_8Pu_2(SO_4)_8(H_2O)_4$, and $Cs_4Pu(SO_4)_4(H_2O)_2$. Changes in structure and stoichiometry are seen down the alkali-metal series despite identical reaction conditions for each of the complexes. Comparison to the other known An(IV) sulfates, Group IV sulfates, and Ce(IV) reveals limited similarity in stoichiometry and structure across the actinide series and their homologues. Marked color changes are observed down the series indicating strong interactions between the plutonium ions and the ligands in these complexes.

INTRODUCTION

Since its first production in 1940, unraveling the chemistry of plutonium has focused on its use in processes for energy production and weapons, vis-à-vis chemical separations and metallurgical properties.[1,2] Because of these process and applications-directed studies the fundamental coordination chemistry of this most interesting and important element lags the other early actinide elements as well as other elements in the periodic table. The scarcity of chemical information and the gaps in our chemical knowledge across the early actinide elements hinders the development of a predictive chemical model for 5f chemistry, particularly for plutonium.

Our interest in the chemistry of plutonium is manifold and based on the periodic trends established moving through the actinide series. Transiting from Th to Pu across the actinide series, ionic radius, electron configuration, ion acidity, and consequently trends in coordination chemistry and reactivity are established. These groups of elements and their trends provide a convenient pathway, and a set of chemical systems, to understand the chemistry of the early actinide elements, their structural, electronic, and chemical properties. Of particular interest are their relationships both to each other as actinides and to the remainder of the periodic table, particularly their tetravalent homologues Zr, Hf, and Ce.

Such studies, including crystallographic, aqueous chemical, spectroscopic, and magnetic studies across the early actinides lead to the realization that the 5f series begins with actininium (the actinide series) and not thorium, uranium, neptunium, or even plutonium, at which point significant chemical deviations from their d-element homologues begin to emerge.[3] Central to Seaborg's "Actinide Concept" was the work and observations by Zachariasen on the isomorphism of the binary oxides and halides of the actinides as well as the departure from this isomorphism in a few systems, notably the binary An(III) bromides.[3] These trends were not established with the associated d-group elements. Understanding the chemistry of these elements as an actinide series established the trend of the contracting ionic size consistent with the filling of the 5f electronic shell, analogous to the lanthanides and the lanthanide contraction and was part of a compendium of data used to arrange the modern periodic table.[3]

In aqueous systems trends in coordination chemistry are demonstrated across the early actinides as well. For example, the acidities of the aqua-acids of the tetravalent actinides increases from Th to Pu and similar trends are seen in the coordination of simple ligands such as nitrate, and the halogens.[4] Well-defined trends in the coordination chemistry of the tetravalent actinides do not always exist in aqueous solution. Recent studies by Hennig and co-workers have demonstrated changes in the coordination structure of the tetravalent actinides when moving from Th to Np in aqueous solution.[5−7] This trend is characterized by a change in the distribution between monodentate and bidentate sulfate coordination among the tetravalent actinides. Hennig observed that bidentate coordination was predominant for Np, while a tendency to form monodentate sulfate complexes in solution is seen for Th.[5] These observations were not directly discernible from the stability constants within the An(IV)-SO_4^{2-} system.

Because of a lack of information on solid state An(IV) sulfate complexes, trends in aqueous solution cannot be easily correlated with observations in the solid state, and building conceptual frameworks to understand the chemistry, origin, and importance of these trends is difficult. Furthermore, the lack of solid and solution state structures hinders the development of accurate

Received: February 23, 2011
Published: May 18, 2011

Table 1. Crystallographic Parameters for the Reported Plutonium Sulfate Complexes

	$Pu(SO_4)_4(H_2O)_4$	$Na_{10}Pu_2(SO_4)_9(H_2O)_4$	$K_8Pu_2(SO_4)_8(H_2O)_5$	$Rb_8Pu_2(SO_4)_8(H_2O)_4$	$Cs_4Pu(SO_4)_4(H_2O)_2$
space group	*Fddd*	*Pbcn*	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	5.601(2)	27.162(2)	12.364(1)	12.490(3)	18.642(3)
b (Å)	12.032(1)	6.892(1)	11.109(1)	11.360(2)	10.488(1)
c (Å)	26.525(4)	17.646(1)	13.450(1)	13.480(3)	20.445(3)
α /deg, β /deg, γ/deg	90, 90, 90	90, 90, 90	90, 111.68(1), 90	90, 109.36(3), 90	90, 91.61(1), 90
V (Å^3)	1787.6(4)	3303.2(3)	1717.0(1)	1804.5(6)	3995.9(1)
Z	8	4	2	2	8
M.W. ($g \cdot mol^{-1}$)	502.15	1650.50	1655.36	2008.30	1193.91
ρ ($g \cdot cm^{-3}$)	3.732	3.319	3.202	3.696	3.969
T (K)	100	100	100	100	100
λ (Å) [Mo K_α]	0.71073	0.71073	0.71073	0.71073	0.71070
μ (mm^{-1})	7.902	4.802	5.389	14.922	10.978
S (GoF)	1.181	1.036	1.021	1.028	1.004
$R(F_o)$, $wR(F_o^2)^a$	0.021, 0.049	0.046, 0.096	0.032, 0.055	0.042, 0.073	0.063, 0.086

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR^2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$, F on all data. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o^2, 0)]/3$.

Table 2. Relevant Bond Distances and Coordination Metrics for the Five Reported Compounds

	$Pu(SO_4)_4(H_2O)_4$	$Na_{10}Pu_2(SO_4)_9(H_2O)_4$		$K_8Pu_2(SO_4)_8(H_2O)_5$		$Rb_8Pu_2(SO_4)_8(H_2O)_4$		$Cs_4Pu(SO_4)_4(H_2O)_2$	
C.N. Pu	8	9		9		9		9	
R (Å) Pu$-OH_2$	2.351(2)	2.450(5)		na^a		na^a		Pu(1)	Pu(2)
								2.362(6)	2.347(6)
								2.395(6)	2.413(6)
R (Å) Pu-OSO_3 monodentate	2.286(2)	2.247(5)	2.296(5)	2.324(2)		2.300(4)		Pu(1)	Pu(2)
		2.325(5)	2.428(5)					2.270(6)	2.301(6)
R (Å)Pu$-O_2SO_2$ bidentate	na^a	2.379(5)	2.396(5)	2.359(2)	2.369(2)	2.362(4)	2.368(4)	Pu(1)	Pu(2)
		2.464(5)	2.481(5)	2.371(2)	2.381(2)	2.369(4)	2.387(4)	2.340(6)	2.333(6)
				2.393(2)	2.400(2)	2.398(4)	2.409(4)	2.380(6)	2.374(6)
				2.433(2)	2.437(2)	2.419(4)	2.443(4)	2.390(6)	2.397(6)
								2.420(6)	2.408(6)
								2.439(6)	2.422(6)
								2.440(6)	2.439(6)

[a] na: bond-type does not exist in the compound.

chemical models and calculations within these complex electronic systems.

Inspired by the utility of the periodic system established in the early actinide elements we have undertaken an investigation of the solid state structures of the Pu(IV) sulfates, an important end member of the early actinide elements. Following Zachariasen's approach, we are interested in the relationship among the structures of the early actinides and their transition metal and lanthanide homologues in the solid state. Herein we report the single crystal structures and synthesis of five new Pu(IV) sulfate complexes synthesized in the presence of alkali metal cations in dilute sulfuric acid. The structures are presented in the context of the known structures of An(IV) sulfates and other tetravalent metals, notably Ce(IV) and the Group IV metals, often used as chemical surrogates for tetravalent actinides.

■ EXPERIMENTAL METHODS

Caution! *^{242}Pu is an alpha-emitting isotope of Pu. All experiments described were performed in specially designed laboratories with negative pressure fume hoods and gloveboxes, using strict radiological controls.*

^{242}Pu Stock Solution. A solution of ^{242}Pu was prepared by precipitation of a Pu(IV) solution in nitric acid using NaOH, washing the precipitate with water and dissolution of the precipitate with conc. HNO_3. This solution was loaded on a Dowex anion exchange column conditioned in the nitrate form. Five free column volumes of 7.5 M HNO_3 were used to wash the column, and the Pu was eluted using 1 M HCl. The elutriant was concentrated by boiling, at which time $NaNO_2$ was added to place the Pu in the tetravalent state. The plutonium was precipitated with NaOH, the precipitate washed three times with water, and dissolved in 5 mL of concentrated H_2SO_4 (18 M). The plutonium sulfate solution was carefully brought to a fume where a finely divided pink precipitate, presumably that of $Pu(SO_4)_2 \cdot xH_2O$ was formed during the fuming. The solution was fumed until the volume of the solution reached approximately 1 mL, and the supernatant was colorless to the eye. The solution and precipitate were cooled and collected in a centrifuge cone. The pink powder was washed several times with methanol to remove residual sulfuric acid, dried in air, and dissolved in 20 mL of 0.5 M H_2SO_4 providing a Pu stock solution of 15 mM Pu(IV) as determined by liquid scintillation counting.

Synthetic Protocol for all Compounds. In a 3 mL cone, 0.250 mL of 0.5 M M_2SO_4 (M = Na, K, Rb, Cs) was mixed with 0.250 mL of ^{242}Pu in 0.5 M H_2SO_4 (0.900 mg Pu; 3.75 μmol).

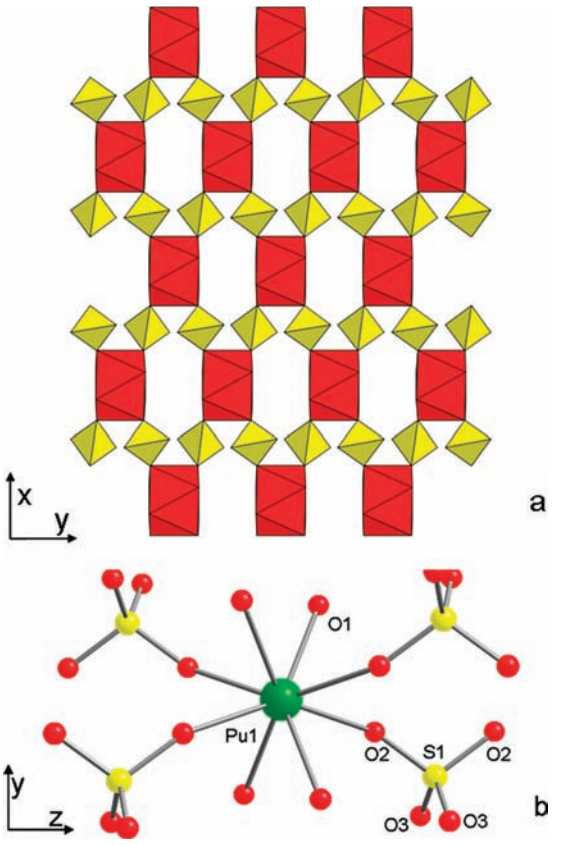

Figure 1. (a) Polyhedral representation of $Pu(SO_4)_2(H_2O)_4$ highlighting the square antiprismatic Pu coordination (red), linked through sulfate tetrahedra (yellow). (b) Ball and stick model of the local Pu coordination in $Pu(SO_4)_2(H_2O)_4$.

Approximately 1 mL of ethanol was carefully layered onto each solution, the cones sealed with a stopper and allowed to stand at room temperature. Crystals began developing within 24−48 h in each vessel. Slow evaporation of the Pu stock solution (15 mM Pu in 0.5 M H_2SO_4) at room temperature and without the addition of any other reagents produced crystals of $Pu(SO_4)_2(H_2O)_4$.

Single Crystal Diffraction. Crystals were sorted under oil and secured on a glass fiber using a five minute curing epoxy as required for contamination control, not because of chemical instability of the complexes. Full spheres of diffraction data were collected using a Bruker SMART diffractometer equipped with an APEXII detector. All data were collected at 100 K using an Oxford Cryosystems cryostat. The structures were solved using direct methods with subsequent full matrix least-squares refinements on F^2. Structure solutions and refinements were completed using the SHELXTL suite.[8] No hydrogen atoms were located in the difference maps of the data and were not refined or included in the final data treatment.

RESULTS

The compound $Pu(SO_4)_2(H_2O)_4$ crystallizes in the orthorhombic space group *Fddd*, $a = 5.601(2)$ Å, $b = 12.032(2)$ Å, and $c = 26.525(4)$ Å, the crystals are a brick red color. Detailed crystallographic parameters are provided in Tables 1 and 2. The structure consists of eight-coordinate Pu(IV) in a square antiprismatic arrangement of water and sulfate anions. Two dimensional sheets of the complexes stack along the *c*-axis, Figure 1a. The plutonium atom position has 222 site symmetry and D_{2h} point symmetry. The four sulfate oxygen atoms are coordinated at 2.286(2) Å from the Pu atom on the corners of the square antiprism maintaining the rotational symmetry. The remaining four water molecules are coordinated at 2.351(2) Å from the Pu atom. The sulfate anions form corner sharing tetrahedra linking the Pu antiprisms. The local coordination environment of the Pu in $Pu(SO_4)_2(H_2O)_4$ is shown in Figure 1b.

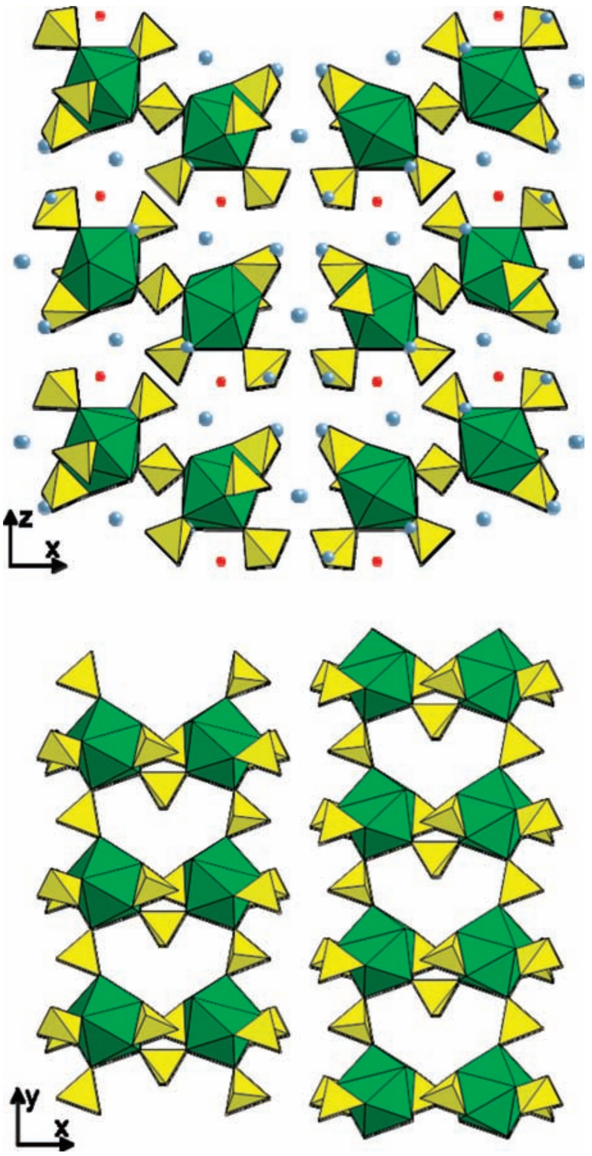

Figure 2. Polyhedral representation of $Na_{10}Pu_2(SO_4)_9(H_2O)_4$ projected down the *y*-axis (top panel), and down the *z*-axis (bottom panel) highlighting the connectivity of the dimeric units through corner sharing sulfate tetrahedra to form infinite chains. The interstitial water molecules and sodium cations have been omitted for clarity.

The structure of this plutonium sulfate compound is different from the previously reported plutonium sulfate, β-$Pu(SO_4)_2(H_2O)_4$, of the same stoichiometry, which crystallizes in the orthorhombic space group *Pnma*.[9] The β-phase structure is isostructural with the β-$Ce(SO_4)_2(H_2O)_4$, structure type and has been isolated for U(IV), Np(IV), and Pu(IV), but not Th(IV).[10] Interestingly, the currently known structure for Th(IV) is a 10 coordinate octa-hydrate with exclusively bidentate coordination with respect to the sulfate anions.[11] The total

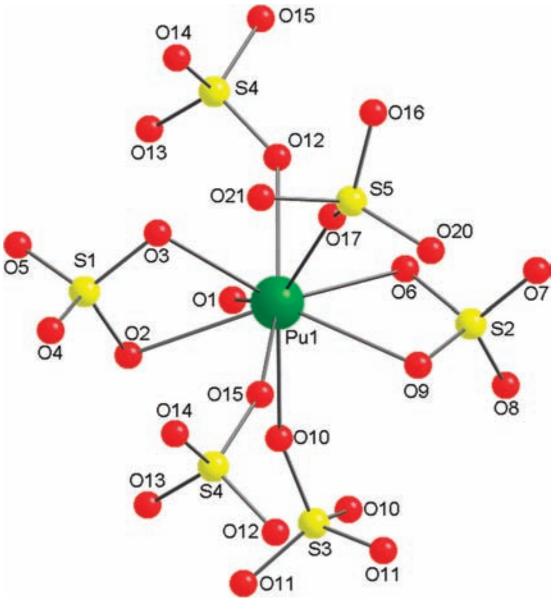

Figure 3. Local coordination environment of the Pu cation in $Na_{10}Pu_2(SO_4)_9(H_2O)_4$.

coordination number is similar to that seen for the homoleptic Th aqua ion.[12] The α-phase of plutonium bis(sulfate) tetrahydrate is isostructural with the previously described $Zr(SO_4)_4(H_2O)_4$ and α-$Ce(SO_4)_2(H_2O)_4$.[13,14] To date, only Ce and Pu are known to crystallize in both of these orthorhombic space groups, *Pnma* and *Fddd*. Homoleptic, aqua-ion coordination has not been reported for these harder cations in the solid state.

$Na_{10}Pu_2(SO_4)_9(H_2O)_4$ crystallizes in the orthorhombic space group *Pbcn*, with a = 27.162(2) Å, b = 6.892(1) Å, and c = 17.646(1) Å. Additional crystallographic parameters are available in Tables 1 and 2. The Pu(IV) cation in this compound is nine coordinate. The immediate coordination sphere of the plutonium is occupied by four monodentate sulfate anions, two bidentate sulfate anions and a water molecule, as shown in Figures 2 and 3. The bond distance for the $Pu-OH_2$ interaction is 2.450(5) Å, typical of $An(IV)-OH_2$ distances.[12] The bond distances for the monodentate Pu(IV)-OSO_3 interactions span the range of 2.247(5) Å to 2.428(5) Å with an average Pu(IV)-OSO_3 distance of 2.32(8) Å. The remaining bonds belonging to the bidentate $Pu-O_2SO_2$ interaction span the range of 2.379(5) Å to 2.481(5) Å, with an average distance of 2.43(5) Å. The plutonium polyhedra form double chains linked through edge sharing sulfate tetrahedra that propagate down the b-axis in this crystal. The double chains are isolated from the neighboring double chains by the charge balancing sodium cations and the water of hydration in the crystal interstitial space, Figure 2. This compound is isostructural with the previously reported double sulfate of Np(IV), $Na_{10}Np_2(SO_4)_9(H_2O)_4$.[15] To date similar structures have not been reported for Th or U(IV).

$K_8Pu_2(SO_4)_8(H_2O)_5$ and $Rb_8Pu_2(SO_4)_8(H_2O)_4$. The sulfate complexes of plutonium with potassium and rubidium form similar complexes with respect to the immediate coordination of Pu(IV) in the complexes. Both structures form molecular, dimeric structures of Pu linked by sulfate anions as shown in Figure 4. The crystals of these complexes are a deep emerald green color. Both structures crystallize in the monoclinic space group $P2_1/c$, with similar lattice parameters, a = 12.364(1) Å, 12.490(3) Å, b = 11.109(1) Å, 11.360(2) Å, c = 13.450(1) Å, 13.480(3) Å, β = 111.68(1)°, 109.36(3)°, and V = 1717.0(1) Å^3, 1804.5(6) Å^3, for the potassium and rubidium analogues, respectively. The difference between these two structures is the hydration state in the crystal and will be discussed below. The plutonium coordination number in both complexes is nine. The coordination sphere of the plutonium is completely occupied by sulfate anions with all water molecules residing outside the primary coordination sphere of the plutonium cation. Except for the sulfate anion bridging two plutonium atoms, the sulfate coordination is exclusively bidentate in these complexes. The monodentate sulfate oxygen in the potassium containing structure has a bond distance to the plutonium cation of 2.324(3) Å, versus a marginally shorter 2.300(4) Å in the rubidium containing structure. The range of bond distances in the bidentate sulfate coordination mode spans 2.359(2) Å to 2.437(2) Å with an average $Pu-O_2SO_2$ distance of 2.39(4) Å for the potassium containing compound. In the rubidium containing phase, the range of bond distances arising from the bidentate sulfate coordination spans 2.363(4) Å to 2.443(4) Å, with an average bond distance of 2.39(3) (Å), statistically the same as for the potassium containing material. The main structural difference between these two compounds is the hydration state of the crystal. During the structural refinement, residual electron density located ~2.87 Å from the potassium cation in $K_8Pu_2(SO_4)_8(H_2O)_5$ was identified and modeled as a partially occupied water molecule, imparting a higher hydration state to the potassium

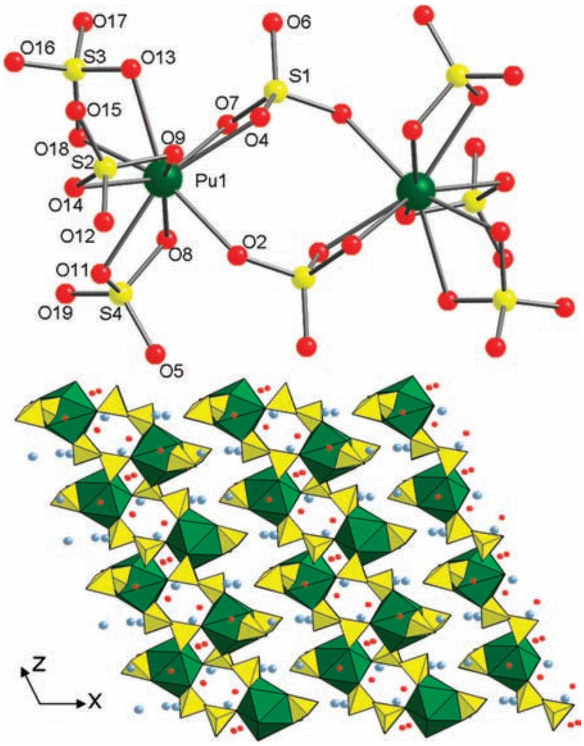

Figure 4. a. Local structure of Pu in $K_8Pu_2(SO_4)_8 \cdot 5H_2O$. This molecular unit contains nine-coordinate plutonium(IV) with an inner-coordination sphere occupied solely by sulfate anions. All of the sulfate anions coordinate in a bidentate geometry except for the bridging sulfate tetrahedron forming the dimer in the solid-state. Aside from the differing hydration state of the crystal interstices, this compound is isostructural with $Rb_8Pu_2(SO_4)_8 \cdot 4H_2O$. b. Packing diagram of the $MPu_2(SO_4)_8 \cdot nH_2O$ (M = K+, Rb+, n = 5, 4).

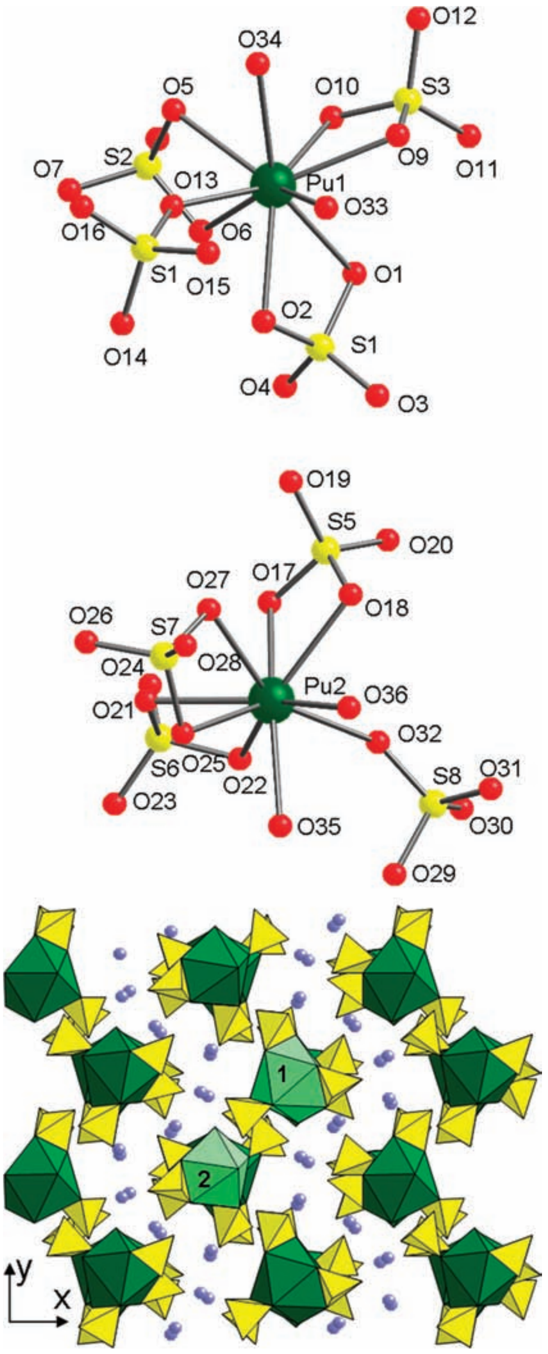

Figure 5. (a) Local coordination environment of the plutonium atoms in $Cs_4Pu(SO_4)_4(H_2O)_2$. (b) Polyhedral representation and packing of the molecular $Cs_4Pu(SO_4)_4(H_2O)_2$ units in the crystal, Pu(1) and Pu(2) labeled and rendered lighter.

compound. The refinement of the Rb structure did not require the inclusion of this extra water of hydration to complete the model.

$Cs_4Pu(SO_4)_4(H_2O)_2$ crystallizes in the monoclinic space group, $P2_1/n$, $a = 18.642(3)$ Å, $b = 10.488(1)$ Å, $c = 20.445(3)$ Å, $\beta = 91.61(1)°$. The resulting thin rose-pink plates consist of molecular anionic sulfate complexes of Pu(IV) charged balanced by cesium cations. There are two crystallographically unique plutonium sites in this complex. As shown in Figure 5, the total coordination number about each plutonium atom is nine. The coordination sphere of each plutonium atom consists of one oxygen atom belonging to a monodentate sulfate anion, six oxygen atoms coming from three sulfate anions in bidentate coordination, and the remaining two coordination sites being occupied by water molecules. The bond distances for the bidentate sulfate oxygen−plutonium interaction span 2.340(6) Å to 2.440(6) Å for Pu(1) averaging 2.40(4) Å, and 2.333(6) Å to 2.439(6) Å for Pu(2) with a mean of 2.40(4) Å. The monodentate sulfate oxygen bond distances are 2.270(6) Å and 2.301(6) Å for Pu(1) and Pu(2), respectively. The $Pu-OH_2$ bond distances for Pu(1) are 2.362(6) Å and 2.395(5) (Å), and 2.347(6) Å and 2.413(6) Å for Pu(2). The molecular units are separated by the charge compensating Cs cations in the crystal. Unlike the Rb or K containing compounds, the primary coordination sphere in this complex is shared between water and sulfate oxygen atoms, with all of the water molecules in the inner-coordination sphere of the plutonium cation.

■ DISCUSSION

The "Actinide Concept" was born out of observations from a multitude of chemical and physical studies of the actinide elements, including the crystal structures of the binary halides and oxides.[3] The actinide oxides AnO_2 and CeO_2 all crystallize in the cubic space group $Fm\bar{3}m$, the fluorite structure under ambient pressure, with a systematic contraction in the An−O bond distance and ionic radii of the An(IV) ions. Conversely, the Group(IV) metals form monoclinic and tetragonal phases under ambient conditions, demonstrating the different chemistries involved between the d- and f-elements in the solid-state.[16,17] Within other simple An(IV) systems, particularly complexes crystallized from solution such as the anionic $An(IV)Cl_6^{2-}$ complexes, they are observed to be isostructural across the actinide series and with Ce(IV); the Group(IV) metals crystallizing instead in the cubic $Fm\bar{3}m$ space group. As noted in the sulfate system studied here, the crystal chemistry changes as a function of the countercation in the $An(IV)Cl_6^{2-}$, changing from monoclinic for the lighter alkali metal cations to trigonal and hexagonal for the heavier cations Rb and Cs, yet isomorphic across the series for a given alkali metal cation. Within other oxoanion systems such as phosphate, periodic correlations across the actinide series are beginning to emerge despite some gaps in the data available. The crystal chemistry of the An(IV) and particularly the Pu(IV) sulfate system is revealed to be more complex.

At this time a search of the literature for inorganic An(IV) structures where SO_4^{2-} is the only anion reveals five Th(IV) sulfate complexes, zero Pa(IV) sulfate complexes, two U(IV) sulfate complexes, four Np(IV) sulfate complexes, and two Pu(IV) sulfate complexes.[6,9,10,15,18−23] In comparison to the lanthanide and transition metal literature the number of reports is relatively small and sporadic. This is in part because of the difficulty in maintaining tetravalent U in its reduced state in aqueous solution and the lack of access to suitable infrastructure and isotopes for investigating the transuranium elements. A summary of the previously reported structures is provided in Table 3.

To date, reported $An(IV)(SO_4)_2(H_2O)_4$, (An: U to Pu) materials have been isostructural with $Ce(SO_4)_2(H_2O)_4$, crystallizing in the orthorhombic space group *Pnma*.[9,10,14] No such structural report exists for Th(IV) despite the reports of many hydrates of the bis(sulfato) complex prepared and characterized by quantitative analytical techniques.[24] Instead, there are two

Table 3. Summary of Currently Known An(IV) Sulfate Complexes

	formula	CN	N(bi), N(mono), N(H_2O)	(avg)An−O (Å)	ref
Th	$Th(SO_4)_2(H_2O)_8$	10	4, 0, 6	2.52(4)	40
	$Th_3(SO_4)_6(H_2O)_6 \cdot H_2O$	9	0, 7, 2	2.43(9)	20
	$Na_2Th(SO_4)_3(H_2O)_3 \cdot 3H_2O$	9	0, 6, 3	2.45(10)	19
	$K_4Th(SO_4)_4(H_2O)_2$	9	2, 4, 3	2.42(18)	25
	$Cs_2Th(SO_4)_3(H_2O)_2$	10	6, 2, 2	2.51(8)	18
U	$U(SO_4)_2(H_2O)_4$	8	0, 4, 4	2.40(2)	10
	$Na_{1.5}(NH_4)_{4.5}U(SO_4)_5(H_2O) \cdot H_2O$	9	6, 2, 1	2.42(7)	6
Np	$Np(SO_4)_2(H_2O)_4$	8	0, 4, 4	2.33(3)	23
	$Na_{10}Np_2(SO_4)_9(H_2O)_4$	9	4, 4, 1	2.40(8)	15
	$K_{5.5}(H_5O_2)_{0.5}Np(SO_4)_5 \cdot H_2O$	10	10, 0, 0	2.45(8)	21
	$Cs_2Np(SO_4)_3(H_2O)_2$	9	6, 2, 1	2.40(6)	22
Pu	α-$Pu(SO_4)_2(H_2O)_4$	8	0, 4, 4	2.32(3)	
	β-$Pu(SO_4)_2(H_2O)_4$	8	0, 4, 4	2.33(3)	9
	$Na_{10}Pu_2(SO_4)_9(H_2O)_4$	9	4, 4, 1	2.38(8)	
	$K_8Pu_2(SO_4)_8(H_2O)_5$	9	8, 1, 0	2.39(4)	
	$Rb_8Pu_2(SO_4)_8(H_2O)_4$	9	8, 1, 0	2.38(4)	
	$Cs_2Pu(SO_4)_4(H_2O)_2$	9	6, 1, 2	2.38(4)	

structures of a thorium sulfate distinct from the other structures of the An(IV) sulfate complexes known. The first of these was reported by Habash and Smith and is a ten-coordinate structure of the formula $Th(SO_4)_3(H_2O)_6 \cdot 2H_2O$, and the second reported previously by Wilson et al., $Th_3(SO_4)_6(H_2O)_6 \cdot H_2O$.[18,20] Reported here is the single crystal structure of α-$Pu(SO_4)_2(H_2O)_4$, given the α-designation by Jayadevan et al., which crystallizes in the orthorhombic *Fddd* space group.[9] The stoichiometry of the two complexes is identical, only the local coordination environment about the Pu being different with respect to the arrangement of the sulfate tetrahedra and water molecules about the plutonium. As mentioned earlier, this complex is isostructural with the zirconium bis(sulfate) tetrahydrate complex first reported by Singer and Cromer.[13] Both Zr and Hf crystallize in the *Fddd* space group, both heavy Group IV metals, with both phases reported for Ce(IV).[14] The observation that the crystal chemistry of the plutonium complexes are tracking Ce(IV) is not in and of itself novel and has been observed before. However, that there does not, despite the work already done in this field, appear to be a self-consistent and complete set of these complexes across the An(IV) series raises questions as to the underlying chemical origin of these deviations and underscores the necessity of investigating this chemistry.

The alkali metal containing An(IV)-sulfates provide a wide variety of structural and stoichiometric diversity across the actinide series. The sodium salts of the tetravalent actinide sulfates include the nine-coordinate complexes $Na_2Th(SO_4)_3(H_2O)_3$, $Na_{10}Np_2(SO_4)_9(H_2O)_4$, and $Na_{10}Pu_2(SO_4)_9(H_2O)_4$.[15,18] Unlike the $Ce(SO_4)_2(H_2O)_4$ and $Zr(SO_4)_2(H_2O)_4$ structure types where the coordination of the sulfate anions to the An(IV) cations is strictly monodentate across the series, the coordination mode in the alkali metal containing materials shares both monodentate and bidentate coordinating sulfate anions as shown in Table 3. The structure of $Na_{10}Pu_2(SO_4)_9(H_2O)_4$ is the only example of the alkali metal containing actinide sulfates to be found that is isostructural with any other alkali metal containing actinide complex. There are no corresponding structures of Ce, Th, or U available for this complex in the literature.

The known compounds containing potassium in this group share few similarities in crystal chemistry, structure or stoichiometry. Among the potassium containing ternary actinide sulfates are $K_{5.5}(H_{2.5}O)Np(SO_4)_5(H_2O)$, a ten-coordinate structure, the nine-coordinate $K_4Th(SO_4)_4(H_2O)_2$, and the plutonium compound reported here and previously, $K_8Pu_2(SO_4)_8(H_2O)_5$.[21,25,26] The reported neptunium(IV) complex contains sulfate anions, which coordinate to the neptunium cation in an exclusively bidentate coordination mode. The neptunium complex crystallizes in discrete mononuclear molecular units unlike the thorium and plutonium analogues, which form discrete dimeric units. Among the plutonium and thorium compounds, the plutonium dimers are linked through both corner and edge-sharing sulfate tetrahedra, while the thorium complex is linked only though edge sharing tetrahedra. Unlike the plutonium coordination sphere, which is entirely populated by sulfate anions, the thorium coordination sphere contains two water molecules. There are three Ce(IV) sulfate structures containing potassium, a tris(sulfate) complex $K_2Ce(SO_4)_3(H_2O)$, a bis(bisulfate)-tetrakis(sulfate) $K_6Ce(HSO_4)_2(SO_4)_4(H_2O)$, and the complex isostructural with the plutonium complex $K_8Ce_2(SO_4)_8(H_2O)_n$ (n = 5, 4), as well as a complex containing ammonium cations that is isostructural with the plutonium compound reported here.[27−33] The tris(sulfate) complex of Ce(IV) forms a framework structure of two crystallographically unique Ce atoms. The coordination sphere of the cerium atoms is nine-coordinate with 4 bidentate sulfate oxygen linkages, and four monodentate sulfate linkages and a water molecule, the two being different isomers of each other. The complex $K_6Ce(HSO_4)_2(SO_4)_4(H_2O)$ forms discrete molecular units of Ce(IV)-SO_4/HSO_4 polyhedra. The coordination number in this Ce(IV) complex is nine divided among 8 bidentate sulfate oxygen atoms and one monodentate sulfate oxygen atom from a protonated bisulfate ligand.

There are no other An(IV) sulfate complexes containing Rb^+ as a countercation. This compound is nearly isostructural with the K^+ containing complex, excepting its hydration state, and possesses the same dark emerald green color. Among Ce, Zr, and Hf, there is one structure of a seven coordinate $Rb_4Hf(SO_4)_4H_2O$ complex, with a coordination sphere of four bidentate sulfate oxygen atoms and three monodentate sulfate oxygen atoms.[34]

For An(IV) sulfates containing Cs, there are two other structures reported in the literature, $Cs_2Th(SO_4)_3(H_2O)_2$ and $Cs_2Np(SO_4)_3(H_2O)_2$.[18,22] While the stoichiometry of these complexes is identical, the structures have subtle differences. For the nine-coordinate thorium complex, the coordination sphere about the thorium is occupied by two monodentate sulfate anions and one bidentate sulfate anion. These join to the neighboring thorium atoms to form infinite two-dimensional sheets separated by the cesium cations. In the neptunium structure, also nine-coordinate, the coordination sphere is occupied by predominantly bidentate sulfate tetrahedra that edge share with the next nearest neptunium neighbor to form a more complex network of double chains, which further link into sheets. Unlike the thorium structure, there is only one water molecule in the inner-coordination sphere of the thorium cation. Both of these structures are different in stoichiometry from the plutonium structure reported here. The plutonium complex forms discrete mononuclear molecular units. The plutonium, like the thorium and neptunium complexes is nine coordinate. In $Cs_4Pu(SO_4)_4(H_2O)_2$, the coordination environment of the plutonium is occupied by three bidentate sulfate ligands and one monodentate sulfate ligand. The two water molecules in this structure reside in the coordination sphere of the plutonium.

As demonstrated in Table 3, the crystal chemistry of these complexes is quite diverse. There seems to be no systematic trend to the sulfate coordination mode in the solid-state crystal chemistry moving across the actinide series or within tetravalent cations in general. While the mean bond distance decreases from thorium to plutonium, this is to be expected based on the effects of the actinide contraction and the filling of the 5f electronic shell. Regarding any systematics to the structure, stoichiometry, or coordination geometry of the reported complexes, cues from the synthetic preparation are not straightforward. Within the thorium sulfate system, the degree of hydration of the complexes and to a lesser degree the coordination mode of the sulfate tracked with the temperature of crystallization and to a lesser extent the metal to ligand ratio.[24] Within the compounds of formula $An(SO_4)_2(H_2O)_4$, many of the actinides are isostructural belonging either to the $Ce(SO_4)_2(H_2O)_4$ structure type *Pnma*, or the $Zr(SO_4)_2(H_2O)_4$ structure type, *Fddd*, apparently determined by the temperature of crystallization.[9,14] The observations of significant temperature effects on the structure and stoichiometry of the resulting complexes may suggest a significant entropic effect in the solution speciation preceding crystallization, the magnitude of which has been estimated recently for the Pu(IV)-SO_4^{2-} system,[35] as well as the lattice energetics involved in the crystallization process.

Deviations in structure and stoichiometry begin to occur upon introduction of other cations of crystallization in these complexes. At this time, we have only prepared one compound that is isostructural and stoichiometric with another alkali containing An(IV) sulfate, $Na_{10}Pu_2(SO_4)_9(H_2O)_4$. This leaves open for consideration the role that both the actinide ion plays in the coordination chemistry and the role of the alkali metal cation. Previous preparations of the alkali metal containing plutonium sulfate complexes have demonstrated marked differences in the optical spectra of these complexes, as observed here with color changes between green, pink, and red depending on the complex, suggesting a strong interaction between the actinide ion and coordinated ligands.[36,37] These changes are most noticeable when the coordination sphere of the Pu is hydrated. Previous investigations into the optical properties of these complexes noted changes in the optical spectra correlating with hydration of the plutonium sulfate complexes in both the solution and the solid states. The ability to form a variety of hydrates within the An(IV)-SO_4^{2-} system suggests a potentially rich opportunity to probe the electronic structure of the tetravalent actinides by minimal but deliberate perturbation of the coordination sphere of the metal.

The most agreement and similarity between the complexes synthesized and characterized here with Pu(IV) are with those of Ce(IV). Both Ce and Pu crystallize in the α and β phases of $M(SO_4)_2(H_2O)_4$, as well as the complexes of $K_8M(SO_4)_8(H_2O)_5$ are isostructural. Further investigation is required across the early actinides within this system to determine if in fact this is a chemical effect or if it is simply the result of an incomplete set of data. It is worth noting that despite the lack of data within the An(IV) systems, the structural and chemical diversity within this seemingly simple chemical system is profound.

While there is no clear trend as of yet developed within the solid state complexes of the An(IV)-SO_4^{2-} system, there is an emergence of a trend within the solution state coordination chemistry. In their extensive work on the structural chemistry of the An(IV) sulfates in solution, Hennig and co-workers noted that the coordination mode of the sulfate anion trends toward a preponderance of bidentate coordination at the heavier actinides for samples with a pH near 1 and where the ligand is in excess to the actinide.[5−7] This trend may suggest that the more polarizing actinide ions Np and Pu are more effective in stabilizing sulfate anion versus the predicted bisulfate anion at this pH resulting in the bidentate coordination. This is not however reproduced in the solid state structures. Structural rearrangements between solution and solid-state within the U(IV) system were previously demonstrated by Hennig et al.[6] As well, the relative contributions of these changes in coordination are not clear from the measured solution formation constants within the An(IV)-SO_4^{2-} system.

■ CONCLUSION

Five new compounds within the plutonium sulfuric acid system have been reported here. Among these compounds only one is isostructural with any other An(IV) sulfate compound prepared to date. The diversity among the structure types and stoichiometries within this system underscores the importance of investigating the structural chemistry of actinide coordination complexes particularly if we wish to gain a predictive understanding of this chemistry through modeling and simulations. The results of this work and previous studies have advanced our understanding of this chemical system but additional work is still needed. Continuation of a systematic study into the structures of An(IV) complexes in the solid state should reveal whether or not there is an isostructural series of complexes and under what conditions they may be formed. Studies into the spectroscopic and electronic properties of these complexes should provide insight into the role the actinide ion takes in directing the chemistry in these systems, noting the significant color changes observed in the Pu system. Theoretical calculations into the energetics of these complexes across the actinide series would provide additional insight into the complex chemistry within this system and perhaps unlock the role of both the actinide ion and the counterions within these systems. Furthermore, solution structural studies using either XAS[5−7] or HEXS (high-energy X-ray scattering)[38,39] are necessary to probe the correlation between the solid state coordination, the solution state coordination, and to complete the emergence of the Periodic trend noted by Hennig and co-workers in the solution state. Toward this end, both studies are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work is supported by the U.S. DOE, OBES, Chemical Sciences under contract DE-AC02-06CH11357.

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