# Preparation, Stability, and Structural Characterization of Plutonium(VII) in Alkaline Aqueous Solution

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S *Supporting Information*

ABSTRACT: A freshly prepared solution of Pu(VI) in 2 M NaOH was oxidized to Pu(VII), via ozonolysis, while simultaneously collecting X-ray absorption spectra. Analyses of the XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) data, acquired throughout the in situ experiments, show a dioxo coordination environment for Pu(VI), PuO_2^{2+}, typical for it and the hexavalent actinyl species of U and Np, and its evolution into a tetraoxo-coordination environment for Pu(VII), PuO_4^-, like that known for Np(VII). The EXAFS data provide average Pu–O distances of 1.79(1) and 1.88(1) Å, respectively. The second coordination shells, also fit as O atoms, provide Pu–O distances of 2.29–2.32 Å that are independent of the Pu oxidation state. The coordination numbers for the distant O atoms in sums with those for the nearest O atoms are consistent with 6-O environments for both Pu(VI) and Pu(VII) ions in accordance with their previously proposed speciation as $[Pu^{VI}O_2(OH)_4]^{2-}$ and $[Pu^{VII}O_4(OH)_2]^{3-}$, respectively. This solution speciation accounts precisely for the Pu(VI) and Pu(VII) coordination environments reported in various solid state structures. The Pu(VII) tetraoxo-dihydroxo anion was found to have a half-life of 3.7 h. Its instability is attributed to spontaneous reduction to Pu(VI) and not to a measurable extent of disproportionation. We found no direct evidence for Pu(VIII) in the X-ray data and, furthermore, the stoichiometry of the oxidation of Cr(III) by Pu is consistent with that expected for a valence-pure Pu(VII) preparation by ozonation and, in turn, stoichiometrically equivalent to the established Np(VII)/Cr(III) redox reaction.
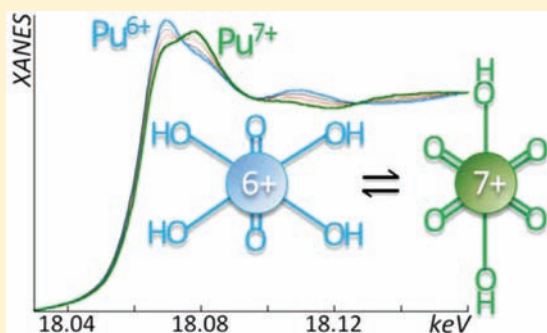
INTRODUCTION

Although the actinide hypothesis clearly placed thorium, uranium, and the transuranic elements within the 5f series in the periodic table, the lighter members of this group demonstrate chemistries that are more consistent with their d element counterparts than with the corresponding lanthanide, 4f series. Such behavior continues to raise questions about the relative importance of the d versus f character to the metal–ligand bonding across the first half of the actinide series.[1−5] Studies focused on analyzing electronic behaviors of high-valent 5f ions indicate that configuration mixing, between 5f and 6d orbitals, may become increasingly important with increasing oxidation state while decreasing in importance with increasing atomic number.[6] Unfortunately, the higher-valent ions tend to be less stable across this same series, with the trivalent states typical of the 4f ions dominating the chemistry of Am and subsequent actinides. For example, the most stable oxidation states in aqueous solution are hexavalent U (as the linear dioxo uranyl UO_2^{2+}), pentavalent Np (as the linear dioxo neptunyl NpO_2^+), tetravalent Pu(IV), and trivalent for Am(III) and heavier ions.[7]

Consistent with this behavior is the increasing paucity of solid-state structural information for the high-valent transuranic compounds traversing the 5f series, with only a small number of structures reported for compounds containing heptavalent Np

or Pu (see Table 1). Focusing on compounds that include only oxygen as the metal's ligating ion, structural preferences are evident. U(VI) exists predominantly as the UO_2^{2+} ion, with a coordination number of four, five, or six from ligands binding in the plane perpendicular to the linear dioxo moiety.[8−15] Np(V) and (VI) structures are also dominated by the dioxo moiety,[16] although cation–cation interactions (in which the oxo-ligand on one Np binds in an equatorial position of a neighboring Np ion) are prevalent in neptunyl(V) chemistry.[17,18] Although much fewer in number, published Pu(V) and Pu(VI) oxidic structures all have the linear dioxo moiety at their core.[19−21]

In contrast to the dioxo ligand coordination exhibited by the pentavalent and hexavalent actinide ions, the limited solid-state structures reported for both Np(VII) and Pu(VII) all share the same tetragonal-bipyramidal unit, a tetraoxo square plane of 4 short oxo groups with two longer hydroxide or water ligands in a linear arrangement perpendicular to the planar tetraoxo unit.[22−30] Although rare, a tetraoxo core geometry has also been reported for U(VI).[31] Calculations implicating d orbital participation in Np(VII)-tetraoxo bonding may explain in part the unusual tetraoxo geometry for the highest-valent actinide species.[32] Similar oxo coordination numbers and distances are

Table 1. Representative M−O Distances for U(VI), Np(VI)/Np(VII), and Pu(VI)/Pu(VII) Oxygen Ligation in 6-Fold Coordination Obtained from X-ray Single-Crystal Structural Refinements

compound	site	short M−O		long M−O		ref
		r (Å)	CN	r (Å)	CN	
U(VI) (6-coordinate)						
average UO_2 + 4 O in equatorial plane (based on 54 structures)		1.816(50)	2	2.264(60)	4	8
Li_4UO_5	U	1.99	4	2.23	2	85
Na_4UO_5	U	1.99	4	2.32	2	85
$Ba_4[(UO_2)_7(UO_4)(AsO_4)_2O_7]$	U5	2.021(8)	4	2.257(8)	2	31
$Cd_2(H_2O)_2U(OH)(CH_3COO)(UO_2)_5(OH)_2O_8]\cdot0.5H_2O$	U1	1.987(7)	4	2.323(8)	2	31
Np(VI) (6-coordinate)						
average NpO_2 + 4 O in equatorial plane (based on 4 structures)	Np	1.752(16)	2	2.286(11)	4	16
Np(VII)						
$LiCo(NH_3)_6Np_2O_8(OH)_2\cdot2H_2O$	Np1	1.850	2	2.38	1	22
		1.961	2	2.39	1	
	Np2	1.891	4	2.355	2	
$K_3NpO_4(OH)\cdot2H_2O$	Np	1.888(5)	4	2.340(2)	2	28
$Na_4[NpO_4(OH)_2]OH\cdot2H_2O$	Np	1.880−1.917	4	2.315(2)	2	30
				2.362(2)		
$Na_3NpO_4(OH)_2$	Np	1.89(3)	2	2.26(4)	2	23
		1.90(2)	2			
$Na_3NpO_4(OH)\cdot2H_2O$	Np	1.89(1)	2	2.33(2)	2	24
		1.91(2)	2			
$Na_3NpO_4(OH)_2\cdot4H_2O$	Np	1.9006(7)	2	2.3414(7)	2	30
		1.9007(7)	2			
Pu(VI)						
$SrPuO_4$	Pu	1.900	2	2.347	6	86
$K_{11}(K_3(PuO_2)_3(GeW_9O_{34})$	Pu1	1.701	2	2.381 (ave)	5	21
Pu(VII)						
$Na_3PuO_4(OH)_2\cdot2H_2O$	Pu	1.8876(15)	2	2.3325(16)	2	30
		1.8771(16)	2			
$K_3PuO_4(OH)_2\cdot2H_2O$	Pu	1.889(2)	4	2.340(2)	2	28
$Cs_3[PuO_4(OH)_2]\cdot3H_2O$	Pu	1.8889(14)	2	2.3726(15)	2	30
		1.8685(15)	2			
$Na_4[PuO_4(OH)_2]OH\cdot2H_2O$	Pu	1.8805−1.9109(15)	4	2.2952(19)	2	30
				2.339(2)		

seen for many high-valent transition metals, although they coordinate with tetrahedral geometry.

The aqueous solution speciation of Np(VII) is similar to that seen in the solid state, with four short oxo ligands forming a tetraoxo moiety.[32−35] The situation is less clear for Pu(VII), at least in part because its propensity to oxidize water has made it difficult to study.[36,37] Chemical evidence suggests that it follows behavior similar to Np(VII), forming the $[Pu^{VII}O_4(OH)_2]^{3−}$ moiety.[38] In contrast, XANES (X-ray absorption near-edge structure) data obtained from a solution in which Pu(VI) was oxidized electrochemically in concentrated NaOH, are consistent with a dioxo complex, exhibiting very slightly reduced Pu−O bond lengths (0.01−0.02 Å) when compared with those from the initial solution.[39,40] Such a reversion to the dioxo ligation for Pu(VII) would have interesting implications for the underlying role of d orbitals in the electronic stabilization of these structural variations. Further complicating speciation data is the evolution of optical absorption spectra at extreme (10−17 M) hydroxide concentration, which suggests the presence of $[Pu^{VII}O_5(OH)]^{4−}$ and $[Pu^{VII}O_6]^{5−}$ in addition to the $[Pu^{VII}O_4(OH)_2]^{3−}$ anion.[38]

Adding to the interest surrounding the speciation of Pu(VII) in aqueous solution has been the suggestion that it may be further oxidized to Pu(VIII). Recognizing the added stability conferred by a closed shell configuration, evidence for Pu(VIII)

$(5f^0)$ was first sought using strong oxidization agents on Pu(VII) in highly alkaline solutions.[41] Although initially thought unsuccessful, several further studies argue the presence of Pu(VIII),[42−45] including volatility studies consistent with the presence of PuO_4, mimicking the behavior of RuO_4 and OsO_4.[46] The concentration of Pu(VIII), generated in solution by ozonolysis, has been evaluated to be about 15%.[43,44,47]

Herein we report results from the characterization of Pu ozonolysis in alkaline, aqueous solutions. In situ X-ray absorption fine structure (XAFS) spectrochemical studies at the Advanced Photon Source (APS) are used to provide the chemical speciation of both the starting Pu(VI) and its oxidized product, which is characterized as Pu(VII). The kinetics of the autoreduction of Pu(VII) under an oxygen atmosphere is obtained from the time-correlated, in situ XANES spectra. A principal component analysis (PCA) of the EXAFS data together with complementary laboratory optical studies were used to confirm the purity of the Pu(VII) phase.

■ EXPERIMENTAL METHODS

Caution! [242]Pu is an α-emitting radioisotope and as such is considered a health risk. Its use requires appropriate infrastructure and personnel trained in the handling of radioactive materials.

Working in the Actinide Facility's hot laboratories, 1.25 mL of deaerated, carbonate-free 10 M NaOH was added to an aliquot (3.1

mL) of a deaerated, 24 mM solution of chemically purified, valence-pure ^{242}Pu(VI) in 1 M HClO$_4$.[48] After mixing, 2 mL of the resulting clear green solution of 17 mM ^{242}Pu in approximately 2 M NaOH was injected into a methacrylate UV fluorometer cuvette (Perfector Scientific, no. 9014, 1 × 1 × 4.5 cm^3) that was mounted within our actinide containment system of previous design.[49−51] The cuvette was sealed with the matching liquid-tight polyethylene cap (Perfector Scientific, no. 9020), through which two 20-gauge Teflon syringe needles with Luer lock hubs (Hamilton no. 90620) were press fitted for service as gas feed and gas exhaust. The solution was saturated with and sealed under O$_2$, whereupon the system was transported to the APS where it was anchored within the 12-BM-B hutch in a prealigned position. A gaseous oxygen (AGA Research grade, 99.999%) sparge (20 sccm) of the alkaline solution began 65 min after its preparation and continued throughout the acquisition of X-ray absorption data (2 scans) for the initial Pu(VI) species. Because the electrolytic oxidation of Pu(VI) competes with that of the aqueous OH$^−$ electrolyte itself, we were able to produce and maintain the Pu(VII) species more efficiently through in situ chemical oxidation with gaseous ozone, which has a standard electrode potential (+1.247 V) for the O$_3$↑/O$_2$↑,OH$^−$ couple.[52] The high standard electrode potential (+0.95 V)[52] for the Pu(VI) → Pu(VII) oxidation indicates that the Pu(VII) species is unstable with respect to its reduction by water at all concentrations of hydroxide,[34,37,53−55] which is oxidized at a standard electrode potential of +0.4011 V for the O$_2$↑/OH$^−$ couple. The electrode potential reported for the ozone/ozonide, O$_3$(aq)/O$_3$$^−$(aq), couple of +1.02−1.03 V[56,57] is +0.07 V greater than that for the Pu(VII)/Pu(VI) couple of +0.95 V. This small, positive difference indicates that the cell reaction, i.e., the one-electron reduction of ozone and the one-electron oxidation of Pu(VI), is a spontaneous redox process. A Labozone generator (Ozonology Inc., L-25) provided a 6% concentration of O$_3$ in the O$_2$ feed (20 sccm) to produce an opaque green solution that was maintained at steady-state conditions throughout the acquisition of XAFS data (9 scans) for the initial Pu(VII) species. Once the ozone generator was shut down, we followed the decay of Pu(VII) under a continuous O$_2$ sparge over the course of approximately 24 h. The resulting solution was without precipitate and had the same appearance of the initial solution of Pu(VI). XAFS data (6 scans) were acquired for the O$_2$-sparged solution as a check on chemical reversibility. The O$_3$ generator was re-energized and the Pu(VI) solution was reoxidized to the opaque, green solution of Pu(VII) for which XAFS data (5 scans) were acquired, once again, for comparison with the response for the solution obtained upon the initial oxidation of Pu(VI). The same cell and conditions were employed for in situ optical experiments with a Cary-14 Olis-conversion spectrophotometer. The optical spectra for the alkaline Pu(VI) and Pu(VII) species, provided as Supporting Information, are in agreement with the numerous spectra found in the literature.[36,38,42,47,53,58−60]

Optical stopped-flow studies were performed to probe the Pu(VII) oxidation of Cr(III) to Cr(VI) with an Olis RSM 1000 rapid-scanning spectrophotometer in combination with an Olis USA ambient temperature stopped-flow cell. All methods and manipulations were performed in the same manner and under the same conditions as described previously for the Np(VII) oxidation of Cr(III) using Cr(ClO$_4$)$_3$·6H$_2$O (Sigma-Aldrich cat. no., 401447) and H$_2$O.[61,62]
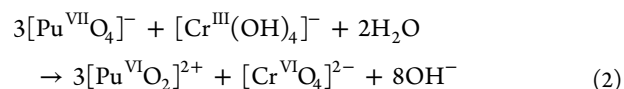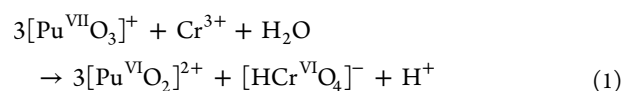
Plutonium L$_3$-edge X-ray absorption data were acquired in the conventional 45/45° configuration with a 13-element fluorescence detector (without slits and filters) on bending magnet station 12-BM-B with a Rh focusing mirror and Si⟨111⟩ monochromator.[63] The incident X-ray energy was calibrated using Zr foil by setting the inflection point in the first differential XANES to 17.998 eV. The data in the XANES region were acquired at 0.8 eV/pt, between 18.027 and 18.102 keV, for the purpose of linear regression analysis and XANES-fitting. The EXAFS data were sampled at steps of 0.04 Å^{-1} and analyzed by use of EXAFSPAK and WinXAS[64] with single-scattering Pu−O phase and oxygen backscattering amplitude from FEFF8.00.[65] In view of the high-k (Å^{-1}) data available here (k_{max} = 16.5 Å^{-1}, Δk ≈ 14 Å^{-1}) and the sizable number of independent parameters (N_{idp} ≈ 19),[66] we were able to refine seven parameters in the curve fitting of

Pu−O backscattering. Three parameters (interatomic distance, r; O coordination number, N_O; Debye−Waller factor, σ^2) were refined for each Pu−O term in the two-shell model. One energy shift parameter (ΔE_0) and one scalar, S_0^2 = 1, were common to both shells.

Principal component analysis (PCA) was carried out on isolated EXAFS spectra[67] spanning the k-range of 2.5 ≤ k ≤ 10 Å^{-1} using the procedure outlined by Malinowski.[68] The data matrix was formed by column-wise stacking of the individual EXAFS spectra, and PCA was conducted on the covariance matrix about the origin. The separation of primary components from secondary error components was determined using the IND function,[69] and the confidence level for the inclusion of specific components was calculated using the Malinowski F-test.[70,71]

■ RESULTS

Optical Studies. Immediately upon acidification of a 1 M NaOH solution of Pu(VII) with 3 equiv of 1 M HClO$_4$, a broad optical response with an absorbance maximum of ∼300 nm and a first-order decay, $t_{1/2}$ = 14 s, was observed. This behavior is attributed to the rapid oxidation of H$_2$O by Pu(VII). The corresponding response for Np(VII) in 1 M HClO$_4$ obtained in previous experiments[61] revealed two broad bands with absorbance maxima at ∼360 and 420 nm whose disappearance was orders of magnitude slower, exhibiting first- and second-order behavior with respect to Np(VII). As exemplified by the optical spectrum included in the Supporting Information, the spectrophotometric analyses of the Pu(VI) produced in the redox reaction between Pu(VII) and Cr(III) in acid *and* base are consistent with the expected 3:1 molar ratio of eqs 1 and 2, respectively.

$$3[\text{Pu}^{\text{VII}}\text{O}_3]^+ + \text{Cr}^{3+} + \text{H}_2\text{O}$$
$$\rightarrow 3[\text{Pu}^{\text{VI}}\text{O}_2]^{2+} + [\text{HCr}^{\text{VI}}\text{O}_4]^- + \text{H}^+ \qquad (1)$$

$$3[\text{Pu}^{\text{VII}}\text{O}_4]^- + [\text{Cr}^{\text{III}}(\text{OH})_4]^- + 2\text{H}_2\text{O}$$
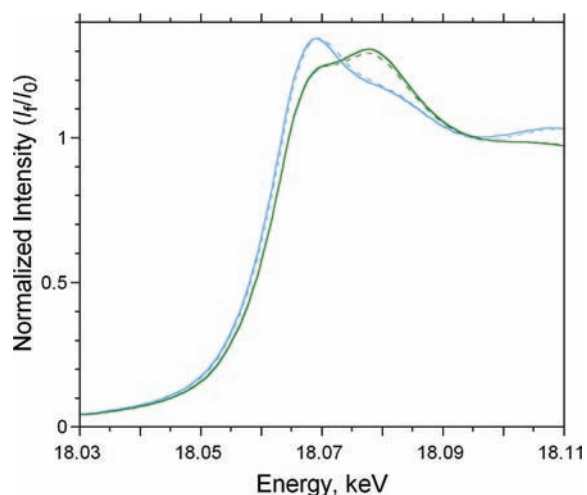$$\rightarrow 3[\text{Pu}^{\text{VI}}\text{O}_2]^{2+} + [\text{Cr}^{\text{VI}}\text{O}_4]^{2-} + 8\text{OH}^- \qquad (2)$$

The detailed half reactions are supplied as Supporting Information. With the standard reduction potentials for the Pu(VII)/Pu(VI) and Cr(VI)/Cr(III) half-reactions in acid solutions, +2.4 (est) and +1.37 V, respectively,[52] the complete cell reaction of eq 1 has a positive potential of approximately 1 V, meaning the reaction is spontaneous under standard conditions.[72] Similarly, the standard reduction potentials for the Pu(VII)/Pu(VI) and Cr(VI)/Cr(III) half-reactions in base solutions, +0.95 and −0.14 V, respectively,[52] demonstrate that the overall reaction of eq 2 has a positive cell potential of 1.09 V. Moreover, within the limits of experimental uncertainties for the molar extinction coefficients (±10%), we estimate that the extent of the Pu(VI) to Pu(VII) oxidation in our small-volume experimental configuration is between 90 and 100%.

XANES. The L$_3$-edge XANES data for the single Pu solution are shown in Figure 1. Spectra were collected for the initial, freshly prepared solution of Pu(VI) immediately upon arrival at the APS and after achieving the following three steady-state conditions, in order: initial oxidation of the fresh Pu(VI) solution with ozone; the subsequent autoreduction of Pu(VII) under oxygen; and final reoxidation of Pu(VI) with ozone.

The initial Pu(VI) solution provides a response, Figure 1—blue solid line, that is typical of a plutonyl(VI) moiety, [PuO$_2$]$^{2+}$, with the postedge shoulder feature at 18.082 keV that is similar to the spectra of uranyl(VI), neptunyl(VI), and plutonyl(VI) in aqueous acidic solutions[40] as well as uranyl(VI)
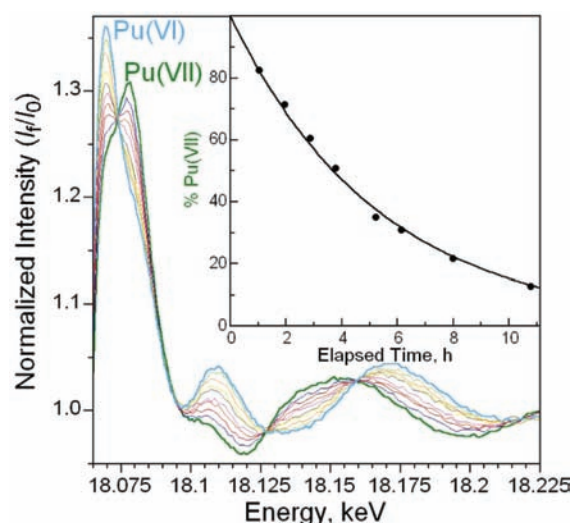
Figure 1. Pu L$_3$-edge XANES for solution of freshly prepared Pu(VI) and after initial oxidation Pu(VII) are shown as solid lines, blue and green, respectively. The dashed lines show the XANES response obtained upon reduction of Pu(VII) to Pu(VI) and following subsequent reoxidation to Pu(VII).

and neptunyl(VI) in alkaline solutions.[32,35,73−76] In contrast, the spectrum of the solution after initial oxidation, Figure 1— green solid line, shows a pre-edge shoulder at 18.071 keV as well as positive shifts of the edge rise and edge peak. Similar spectral changes were seen upon the oxidation of Np(VI) to the tetraoxo Np(VII) moiety under similar conditions,[32,35] indicating an increase in the Pu valence to VII and a coordination environment that is different from the linear, *trans*-dioxo Pu(VI) configuration. Details about the XANES spectra of Figure 1 as obtained by curve fitting with Gaussian and arctangent peak functions are provided in the Supporting Information.

The subsequent in situ reduction of Pu(VII) under oxygen provides a solution for which the XANES response, Figure 1— blue dashed line, is essentially the same as the starting Pu(VI) solution. The following reoxidation of Pu^{6+} via ozonolysis provides a solution for which the XANES response, Figure 1— green dashed line, is identical with that for the initially oxidized species. Taken together, these data are considered direct evidence to the chemical reversibility of the Pu(VI)/Pu(VII) redox couple. Additionally, indirect evidence for the reversible interconversion of *two* Pu species is provided by the observation of five isosbestic points in X-ray absorption data of Figure 2 obtained throughout the course of the Pu(VII) → Pu(VI) reduction.

Information about the kinetics of the autoreduction of Pu(VII) under an oxygen atmosphere was also obtained from the time-correlated, in situ XANES spectra depicted in Figure 2. The relative Pu(VII) and Pu(VI) concentrations were extracted by linear regression analyses of the XANES for the intermediate admixtures using the spectra for the two end member solutions. A similar approach was applied to extract quantitative kinetic parameters from in situ EXAFS data of solution reactions.[77] The data (circles) and the single-exponential fit (line, R^2 = 0.9957) are shown as the inset to Figure 2. The fitted exponential term, 5.2(1) × 10^{-5} s^{-1}, provides a value of 1.3(1) × 10^4 s (3.7 h) for the half-life ($t_{1/2}$) of the reduction of Pu(VII) to Pu(VI) at 25 °C in 2 M NaOH. This value is consistent with previous estimates of ca. 3−8 h[58,78] and with
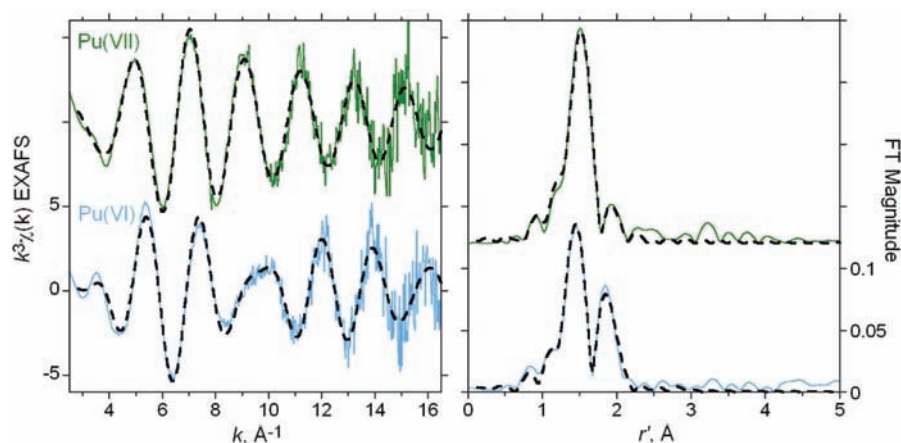

Figure 2. (inset) Autoreduction of Pu(VII) as a function of time. The relative concentrations of Pu(VII) were obtained from linear regression analyses of the XAFS data shown here, including the edge peaks and postedge features. The fit (solid line, R^2 = 0.9957) with an exponential function, $f(t) = 100e^{-\lambda t}$ provides a first-order decay constant, λ, of 5.2(1) × 10^{-5} s^{-1}, from which is extracted $t_{1/2}$ = 3.7 h (1.3 × 10^4 s).

the most recent value of 1.32 × 10^4 s[79] reported for the autoreduction of Pu(VII) in 1 M NaOH at 25 °C.

EXAFS. The Pu $k^3\chi(k)$ EXAFS and the corresponding Fourier transform (FT) data for the pristine solution of Pu(VI) and after initial oxidation to Pu(VII) are shown in Figure 3. The data obtained upon subsequent reduction and reoxidation are identical and omitted for clarity.

The EXAFS obtained from the Pu(VI) solutions has a distinguishing modulation between 9−10.5 Å^{-1} that is characteristic of actinyl(VI) species, $[AnO_2]^{2+}$, with equatorial O coordination, e.g., H_2O, OH^-, $^-O_2CHCH_3$, etc.[12] The FT response with two peaks at 1.45 and 1.85 Å (before phase shift correction) is diagnostic of the *trans*-axial O^{2-} and equatorial OH$^-$ backscattering, respectively. In contrast, the EXAFS for the solution of Pu(VII) has the appearance of a damped sinusoid and the FT data reveal an intense peak at 1.51 Å followed by a weak one at 1.93 Å (before phase shift correction). These features bear strong resemblance to the Np EXAFS and FTs of alkaline solutions of the $[Np^{VII}O_4]^-$ species with *trans*-axial OH$^-$ coordination.[32,35] Quantitative information about the coordination environments of Pu(VI) and of Pu(VII) are provided by means of curve fitting analyses of the $k^3\chi(k)$ EXAFS. The metrical information is provided in Table 2, and the best fits are shown as dashed lines in Figure 3.

The coordination environment of Pu(VI) is consistent with plutonyl speciation, having two close O atoms at 1.79(1) Å. There are four distant O atoms at 2.29−2.31 Å to complete the local coordinative saturation of Pu(VI) in what is likely to be an axially compressed square bipyramid. Such coordination geometry is consistent with experiments and theory reported for U(VI) and Np(VI) speciation in the solid state and in solutions under both acidic and basic conditions.[8,11,15,32,35,73−75] This information serves to resolve the ambiguity about the probable form of Pu(VI) in alkaline solutions.[34] In view of the two likely entities, $[PuO_2(OH)_4]^{2-}$ and $[PuO_4(H_2O)_2]^{2-}$, the EXAFS-determined coordination

Figure 3. (left) k^3-Weighted EXAFS of Pu(VII): (top) offset for clarity and Pu(VI), (bottom) from experiment (solid lines) compared with the fit (dashed lines). (right) FT data, which are uncorrected for phase shift (r') as shown, of the EXAFS, both experiment and fit, shown at left.

Table 2. Results of Two-Shell (Oxygen) Curve Fitting to the $k^3\chi(k)$ EXAFS of Figure 3 for Pu(VI) and Pu(VII)[a]

			Reaction Sequence				
parameter	Pu(VI)	→	Pu(VII)	→	Pu(VI)	→	Pu(VII)
ΔE_0, eV	8.9		6.8		9.1		6.2
1st O shell							
r, Å[b]	1.79		1.88		1.79		1.88
N_O[c]	2.2		4.0		2.1		3.6
σ^2, Å^2 [d]	0.0020(4)		0.0026(5)		0.0015(3)		0.0026(6)
2nd O shell							
r, Å[e]	2.31		2.31		2.29		2.32
N_O[f]	4.1		3.0		3.9		2.5
σ^2, Å^2 [d]	0.007(1)		0.009(2)		0.005(1)		0.007(1)

[a]One value of the threshold energy shift, ΔE_0, was linked to and refined with both O shells. Its estimated standard deviation is ±0.5 eV. [b]Estimated standard deviation is ±0.01 Å. [c]Estimated standard deviation is ±0.5. [d]Estimated standard deviations are shown in parentheses. [e]Estimated standard deviation is ±0.02 Å. [f]Estimated standard deviation is ±1.

environment is consistent with the presence of the former dianionic species.

In contrast, the coordination environment of Pu(VII) determined from EXAFS data analyses is inconsistent with simple, dioxo, plutonyl species. Rather, the immediate coordination sphere of Pu(VII) includes four O atoms at 1.88(1) Å with an additional two distant O atoms at 2.31−2.32 Å. These metrical details are consistent with those obtained from both experimental and theoretical studies of the speciation of Np(VII)[32,35] in alkaline solutions as well as with the average Pu−O and Pu−OH interatomic distances of 1.879−1.889 and 2.317−2.373 Å observed in solid salts of $[PuO_4(OH)_2]^{3-}$.[28−30,80] It should be noted that the axial O coordination number included in Table 2 reports a range that is greater than two. Although a higher coordination cannot be ruled out and may indicate the possibility for some combination of O_3^-, OH^-, and H_2O ligation to form seven-coordinate molecular anions, as observed for Mn(III) porphyrinato complexes,[81] this result likely involves issues with the specific choice of EXAFS fitting procedure. The second O shell Debye−Waller factors, σ^2, and their corresponding uncertainties are significantly larger (2.7−3.6×) than the corresponding values for the first O shell; see Table 2. We had a similar issue arise in our fitting of Np(VII) EXAFS data,[32] which was not substantiated in subsequent work.[35] The direct and well-known correlation between the σ^2 values and the coordination numbers, N_O, figures intricately

into the fits described herein. For example, in fits to the Pu(VII) EXAFS with a single σ^2 to account for both Pu−O and Pu−OH interactions, the second shell O−CN decreases to 1.3−1.5. Despite this realistic scenario, the data do not allow the elimination of a Pu(VII) ozonide/peroxo complex as a potentially stable solution species. It should be noted that although Pu(VII) is commonly formed by oxidizing Pu(VI) in aqueous solution using an ozone sparge, as was done here, it has also been made by alternative routes.[53]

PCA. The principal component analysis resulted in the identification of two abstract mathematical components in the k^3-weighted EXAFS data at the >99.9% confidence level. They are made available in the Supporting Information. A third component contributes to the measured spectra at a confidence level of <41%, suggesting that the third component belongs to the set of secondary error components. Malinowski's recommended criteria for accepting a component as primary is if it reaches the 90−95% confidence level.[71] Two components are also detected through the use of the empirical Malinowski IND function.[69] Therefore, this statistical approach to the EXAFS data analysis shows that it is likely there are two solution components that contribute to the spectral response. This is in agreement with the results of the linear regression analysis (Figure 2) using the Pu(VI) and Pu(VII) end member spectra to model the response of the mixtures of the two species.

◼ DISCUSSION

The formation of Pu(VII) in alkaline solution is examined by in situ XAFS data taken during ozonolysis and subsequent O_2 sparge of a single highly alkaline aqueous solution initially containing Pu(VI). Metrical analyses of the EXAFS data, presented in Table 2, reveal Pu(VI) in solution as the plutonyl moiety, with two oxo ligands at 1.79(1) Å and four equatorial oxygens at a distance of 2.30(1) Å. The determination of dioxo ligation is generally consistent with previous reports for hexavalent Np speciation in alkaline solution.[32,35,74] Previously published distances of 1.76 and 2.30 Å have been reported for EXAFS results from Pu(VI) in alkaline solution[40] although no spectra or fitting details are provided in the report. The absence of an experimentally determined coordination number prohibits a direct comparison with the results presented here. There are very few Pu(VI) solid state structures reported with which to compare these solution distances. The single crystal structural determination of hexavalent Pu in homoleptic aqua coordination has been reported for $[PuO_2(H_2O)_5](ClO_4)_2$, with two O at about 1.73 Å and five equatorial waters at 2.3994−2.4173 Å.[82] The Pu1 site in $K_{11}(K_3(PuO_2)_3(GeW_9O_{34})$ is reported to be Pu(VI) with two O at 1.701 Å and 5 O at an average of 2.381 Å.[21] These values are markedly different from those seen here for hexavalent Pu in alkaline solution, perhaps at least in part because of the additional coordinating O in the equatorial plane in the solid-state structure. A more extensive structural database for higher-valent Pu compounds would have been very helpful in this regard.

Metrical results from the Pu(VII) fits point to a coordination environment different from that seen for the hexavalent ion, with four short oxo ligand distances at 1.88(1) Å and two more distant O ligands at 2.31(2) Å. Although the coordinating distances are similar for the two components of the first coordination shells in Pu(VI) and Pu(VII), in the former case there are two short dioxo moieties and four longer O distances whereas the reverse is true for the Pu(VII). This comparative result was also observed for the solution coordinations of Np(VI)/Np(VII).[32,35] As seen from Table 1, this coordination environment compares very favorably with that seen in the four Pu(VII) solid-state structural studies reported to date. It is also noted that these results compare precisely with published DFT calculations, which obtain a Pu(VII) tetraoxo coordination at 1.876(1) Å.[83]

It is of note that the EXAFS results are not able to address the planarity of the tetraoxo ligands. In order to address this issue directly, the data from Figure 3 have been modeled with multiple-scattering pathways. In the case of an extremely rigid $PuO_4(OH)_2$ moiety in solution, multiple-scattering effects are expected similar to those commonly seen in PuO_2^{2+} and UO_2^{2+}. Upon inspection of the Pu(VII) spectrum, there appears to be a small peak at ~3.2 Å (r'). This peak was fit to a symmetric model derived from a PuO_4 unit in perfect square-planar geometry with OH groups above and below the tetraoxo plane. All O−Pu−O bond angles were constrained to 90 degrees, and all bond lengths were constrained to single scattering paths derived from the single scattering path EXAFS fitting. As expected, the goodness-of-fit improves upon addition of the MS path to the EXAFS model. However, the two models only differ from each other at the 63% confidence level, showing that our EXAFS data are not of sufficient quality to support the inclusion of this multiple-scattering path in our fit. Therefore, although suggested by our data and the corresponding solid-state crystal structures,[28,30] we cannot confirm the planarity of the Pu(VII) tetra-oxo moiety in solution.

The Pu(VII) coordination determined here, namely the tetraoxo form $[PuO_4]^-$, is inconsistent with the previously reported dioxo coordination for Pu(VII) in alkaline solution.[39,40] A comparison of our XANES data, shown in Figure 1, with those in the aforementioned citations confirms that the solutions are indeed different. It may be that there are two (or more) forms of Pu(VII).[45] Our rapid, approx. 1 h, access to the beamline with a fresh sample under oxygen saturation in combination with the in situ methodology employed for Pu redox control minimizes concerns about sample integrity that may otherwise take on paramount significance during more extended shipping and handling times. Although artifacts of unanticipated sample alteration may have contributed to the earlier studies, the generation of different Pu(VII) under slightly different conditions cannot be ruled out.

Whereas dioxo complexes dominate pentavalent and hexavalent solid-state actinide chemistry, the situation is markedly different for corresponding high-valent, transition-metal ions. For example, the structures of oxidic complexes of high-valent transition-metal elements in periods 6−8 (the Cr, Mn, and Fe groups) are dominated by tetrahedral coordination.[84] Initially speculated to be the result of solid-state lattice-stabilization energetics, DFT calculations showed the involvement of d character in the bonding of the $[NpO_4]^-$ unit.[32] Such d character participation is not observed in the corresponding DFT calculations of the Pu(VII) analog,[83] nor is the nonplanarity observed in any of the crystal structures reported to date (see Table 1).

It is widely recognized that heptavalent transuranic ions are short-lived, unstable species even in strongly basic solutions where their domain of stability is favored.[36,37,53,54,58,59,79] We have confirmed that the spontaneous reduction of freshly prepared Pu(VII) is rapid, $t_{1/2} = 3.7$ h (1.3×10^4 s) at 25 °C, in the absence of O_3 under continuous O_2 saturation in the single solution examined here. This half-life is in exact agreement with an independent report.[79] The Pu(VI) coordination observed following reduction of Pu(VII) is the same as the initially prepared Pu(VI) species. Moreover, subsequent reoxidation of Pu(VI) generates the Pu(VII) as found in the initially oxidized solution, thereby demonstrating chemical reversibility.

The results reported here bear upon the ancillary issue of the possible existence of Pu(VIII) in alkaline solutions subjected to ozonation.[42−45] Our optical, stop-flow experiments, which find 90−100% oxidation of Pu(VI) to Pu(VII), coupled with optical spectra of the oxidized solution that show no evidence of Pu(VI) in fully ozonized solutions, and thus, the concurrent, quantitative oxidation of Cr(III) to Cr(VI) is consistent with the sole presence of Pu(VII). Furthermore, XANES data, obtained as the fully oxidized Pu decays to Pu(VI), exhibits five isosbestic points, a result indicative of only two species contributing to the observed transformation. PCA of the EXAFS further support this data interpretation; there is no statistical basis upon which to include a third component in the data fitting. It is possible that the XAFS spectrum, both the XANES and EXAFS components, from a Pu(VIII) moiety is indistinguishable from that obtained from the heptavalent species. Coupled with the expected low yield of the octavalent Pu species,[42] and their calculated transitory stabilities,[79] the presence of a minor Pu(VIII) component cannot be totally ruled out.

Our results are consistent with the original, quantitative observations about the kinetics of Pu(VII) autoreduction[60,79] and failure to stabilize Pu(VIII) in either a solid material or in solution.[41] Although the Pu(VII) lifetime is hours under alkaline solution conditions, even then, the reduction of Pu(VII) by H_2O is spontaneous according to the reaction of eq 3 with a positive cell potential, +0.55 V, calculated from the standard reduction potentials for the half-reactions.[52]

$$2[Pu^{VII}O_4]^- + 3H_2O \rightarrow 2[Pu^{VI}O_2]^{2+} + 6OH^- + \frac{1}{2}O_2 \tag{3}$$
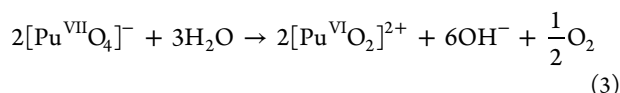
Based upon estimated electrode potentials for the Pu(VII)/Pu(VIII) couple,[79,83] which are well outside of the range of the thermodynamic stability of water, the absence of X-ray evidence for its existence in 2 M NaOH is not surprising.

It is interesting to note that when PCA is conducted using unweighted EXAFS data, the results indicate the presence of three components with all three components contributing to the measured spectra at a confidence level of >99.8%. Inspection of the third abstract component shows features that are predominantly in the low-k range. The change from three components to two components, upon k^3-weighting the EXAFS data, is directly related to the way the measurements were conducted. Since individual EXAFS data points were measured for longer periods of time at high k-values than at low k-values, the distribution of statistical noise is expected to have a k-dependence. Malinowski's IND function[69] works best for data sets that have relatively uniform noise. It is therefore warranted for us to run PCA on k^3-weighted data—in essence, renormalizing the error—in the absence of any further knowledge of the k-dependence of the noise in our measurement. Furthermore, it is possible that the EXAFS technique is not sufficiently sensitive to resolve a third chemical species in the mixture, if its EXAFS signature is similar to a linear combination of the previous two components.

In view of the even more extreme reactivity of Pu(VIII) in aqueous media, it will take particularly innovative chemistry to prepare, isolate, and obtain a complete crystallographic characterization of an octavalent Pu species. Until that time, this work provides the first glimpse into the tetraoxo coordination environment of Pu(VII) in alkaline solution.

CONCLUSIONS

We have utilized purpose-built equipment and facilities infrastructure for in situ synchrotron radiation studies (XANES and EXAFS) of the Pu(VI)/Pu(VII) speciation in an aqueous alkaline solution of 2 M NaOH. The results are consistent with a tetraoxo monoanionic form of Pu(VII) as $[PuO_4]^-$ with additional (approx. 2) distant O coordination, which explains the existence of the $[PuO_4(OH)_2]^{3-}$ anion in the crystalline solid state salts, and a conventional dioxo dianionic form of Pu(VI) as $[PuO_2(OH)_4]^{2-}$. The Pu(VII) ion is unstable with respect to autoreduction to Pu(VI) with a half-life of 3.7 h in a first-order process. In view of the high electrode potentials estimated for the Pu(VII)/Pu(VIII) redox couple, which are ≥0.13 V more positive than that for the $O_3(aq)/O_3^-(aq)$ couple and, moreover, outside the domain of thermodynamic stability of H_2O, the absence of evidence for Pu(VIII) in the aqueous media studied here is consistent with the solution chemistry, including the stoichiometry of the Pu(VII)/Cr(III) reaction that indicated preparation of valence-pure Pu(VII).

ASSOCIATED CONTENT

Ⓢ Supporting Information

Plutonium(VI)/(VII) optical spectra, XANES spectra, and fitting results as well as details from the PCA of the $k^3\chi(k)$ EXAFS. This material is available free of charge via the Internet at http://pubs.acs.org

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