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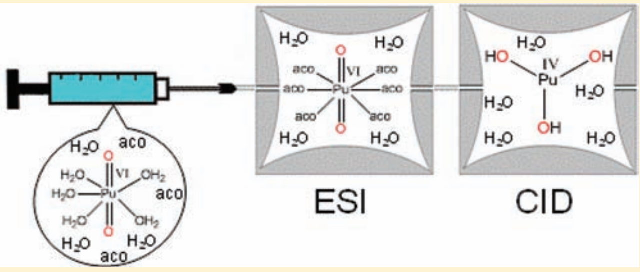
Gas-Phase Coordination Complexes of Dipositive Plutonyl, PuO_2^{2+}: Chemical Diversity Across the Actinyl Series

Daniel Rios,[†] Philip X Rutkowski,[†] Michael J. Van Stipdonk,[‡] and John K. Gibson*[,†]

[†]Chemical Sciences Division, The Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

[‡]Department of Chemistry, Wichita State University, Wichita, Kansas 67260-0051, United States

S Supporting Information



ABSTRACT: We report the first transmission of solvent-coordinated dipositive plutonyl ion, $Pu^{VI}O_2^{2+}$, from solution to the gas phase by electrospray ionization (ESI) of plutonyl solutions in water/acetone and water/acetonitrile. ESI of plutonyl and uranyl solutions produced the isolable gas-phase complexes, $[An^{VI}O_2(CH_3COCH_3)_{4,5,6}]^{2+}$, $[An^{VI}O_2(CH_3COCH_3)_3(H_2O)]^{2+}$, and $[An^{VI}O_2(CH_3CN)_4]^{2+}$; additional complex compositions were observed for uranyl. In accord with relative actinyl stabilities, $U^{VI}O_2^{2+} > Pu^{VI}O_2^{2+} > Np^{VI}O_2^{2+}$, the yields of plutonyl complexes were about an order of magnitude less than those of uranyl, and dipositive neptunyl complexes were not observed. Collision-induced dissociation (CID) of the dipositive coordination complexes in a quadrupole ion trap produced doubly- and singly-charged fragment ions; the fragmentation products reveal differences in underlying chemistries of plutonyl and uranyl, including the lower stability of Pu(VI) as compared with U(VI). Particularly notable was the distinctive CID fragment ion, $[Pu^{IV}(OH)_3]^+$ from $[Pu^{VI}O_2(CH_3COCH_3)_6]^{2+}$, where the plutonyl structure has been disrupted and the tetravalent plutonium hydroxide produced; this process was not observed for uranyl.

INTRODUCTION

The chemistry of the early actinides, thorium through americium, is particularly significant, both technologically and scientifically.[1] The distinctive linear hexavalent actinyl ions, $\{O{=}An^{VI}{=}O\}^{2+}$, are important in the solution chemistry of U,[2a] Np,[2b] and Pu;[2c] americyl, $Am^{VI}O_2^{2+}$, is a stable species but is not predominant under most conditions.[2d] The uranyl ion is particularly prevalent and has been extensively studied by both experiment and theory.[3] A particular area of interest is the coordination of actinyl ions in solution; NMR[4] and XAFS[5] have shown that the aqueous actinyl ions are coordinated by five inner-sphere waters in the equatorial plane.

The first reported transfer of uranyl ions from solution to the gas phase using electrospray ionization mass spectrometry (ESI/MS) was as monopositive pentavalent $U^{V}O_2^{+}$, reported in 1992.[6] Thereafter, advances in fundamental understanding of uranyl coordination chemistry have been achieved by using this experimental technique, whereby complexes of pentavalent and hexavalent uranyl ions, monopositive and dipositive, have been transferred from solution to the gas phase.[7] Of particular relevance to the present work, ESI of solutions of uranyl in water/acetone and water/acetonitrile have revealed the affinity of gas-phase uranyl for the more basic organic ligands and pentacoordination as in $[U^{VI}O_2(CH_3COCH_3)_5]^{2+}$ and $[U^{VI}O_2(CH_3CN)_5]^{2+}$.[7e,8] The stability of the dipositive actinyl ions in solution decreases as follows:[9] $U^{VI}O_2^{2+} \gg Pu^{VI}O_2^{2+} > Np^{VI}O_2^{2+} > Am^{VI}O_2^{2+}$. Although $U^{VI}O_2^{2+}$ ligated by basic electron-donating ligands has been sufficiently stabilized to enable its transfer from solution to the gas phase, it does not necessarily follow that the less stable dipositive actinyl ions can be similarly transferred from solution to gas. The standard reduction potentials for $An^{VI}O_2^{2+} \rightarrow An^{V}O_2^{+}$ are 0.09 V for $U^{VI}O_2^{2+}$, 0.95 V for $Pu^{VI}O_2^{2+}$, 1.16 V for $Np^{VI}O_2^{2+}$, and 1.60 V for $Am^{VI}O_2^{2+}$.[10] It is evident that relative to $U^{VI}O_2^{2+}$ the other three $An^{VI}O_2^{2+}$ should be prone to reduction during ESI and that after $U^{VI}O_2^{2+}$ the $Pu^{VI}O_2^{2+}$ ion presents the best prospect for transfer from solution to gas.

Early plutonium ESI/MS work focused on the speciation of Pu(IV) in the gas phase.[11] The first report appeared in 2003, where ESI/MS was used to identify the molecular structure of radiolytic products of irradiated TRPO−kerosene systems.[11a] More recently, Walther et al. employed ESI/MS to characterize tetravalent plutonium polymer growth.[12] To the best of our knowledge, there are no reports of ESI/MS studies of $Pu^{VI}O_2^{2+}$ solutions.

The prevalent oxidation state of plutonium in aqueous solutions is Pu(IV), but hexavalent plutonyl, $Pu^{VI}O_2^{2+}$, is stable and can be a significant solution species.[13] A central object of actinide chemistry is to identify variations in chemistry across the series, particularly for the early actinides, U, Np, and Pu, which exhibit a variety of oxidation states under moderate conditions, from

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An(III) to An(VI).[14] Higher oxidation states are well established,[14] and of particular interest are the existence of Pu(VII) and even Pu(VIII) in highly alkaline solutions.[1,15] In the present work, solvent-coordinated $Pu^{VI}O_2^{2+}$ ions were transferred from solution to the gas phase by ESI of plutonyl in acetone/water and acetonitrile/water. Ion complexes were isolated in an ion trap for mass analysis and collision-induced dissociation (CID) by excitation of a specific ion complex composition and subsequent fragmentation upon collisions with helium. Parallel studies of uranyl revealed inherent differences between the coordination and the redox chemistries of Pu and U in the gas phase. New formally hypercoordinated gas-phase uranyl complexes were identified. Initial attempts to transfer $Np^{VI}O_2^{2+}$ from solution to the gas phase were unsuccessful.

■ EXPERIMENTAL SECTION

Plutonyl solutions in acetone/water and acetonitrile/water were prepared at a concentration of 80 μM in an organic solvent/water ratio of 90/10 from a $[Pu^{VI}O_2(ClO_4)_2]$ stock solution in water; a 180 μM solution in water/acetone was also prepared to establish that there were negligible concentration effects in this range. The 180 μM uranyl solutions were prepared using aqueous $[U^{VI}O_2(ClO_4)_2]$ to give solutions with compositions of 90% acetone/10% water and 90% acetonitrile/10% water. Solutions of 160 μM $[Np^{VI}O_2(ClO_4)_2]$ in 90% acetone/10% water and 90% acetonitrile/10% water were similarly prepared. The actinide isotopes (>99%) were U-238 (α-decay half-life = 4×10^9 years), Pu-242 (α-decay half-life = 4×10^5 years), and Np-237 (α-decay half-life = 2×10^6 years). All handling of these hazardous radionuclides was in a containment glovebox in a radiological laboratory. The ESI/MS and CID experiments were performed with an Agilent 6340 Quadrupole Ion Trap (QIT) mass spectrometer with MS^n collision-induced dissociation (CID) capabilities. The source region of the QIT/MS is inside of a radiological-containment glovebox. In high-resolution mode, the instrument has a detection range of m/z 50−2200 and a resolution of $m/z \approx 0.25$. Mass spectra were recorded in the positive-ion accumulation and detection mode. Typical instrumental parameters for obtaining the dipositive ion mass spectra, as determined by optimizing on the ion peak of interest, were as follows: if different, the corresponding "harsh" parameters used for monopositive ions, AnO_2^+ and AnO_2OH^+, are given in parentheses: nebulizer gas pressure, 12 (15) psi; capillary voltage and current, −4500 V, 1.221 (14.648) nA; end plate voltage offset and current, −500 V, 22.5 (37.5) nA; dry gas flow rate, 5 L/min; dry gas temperature, 100 (325) °C; capillary exit, 75 (141.7) V; skimmer, 29.2 (26.3) V; octopole 1 and 2 DC, 11.46 (13.75) and 7.40 (2.13) V; octopole RF amplitude, 50.0 (58.3) Vpp; lens 1 and 2, −2.3 (−4.8) and −77.5 (−65.5) V; trap drive, 49.9 (216.8). The parameters were somewhat different for selected spectra, where the conditions were optimized to enhance a particular low-intensity dipositive species. Solutions were injected into the electrospray capillary via a syringe pump at a rate of 60 μL min^{-1}. Nitrogen gas for nebulization and drying in the ion transfer capillary was supplied from the boil-off of a liquid nitrogen dewar. CID experiments were performed using the He trapping gas at a pressure of $\sim 10^{-4}$ Torr; tickling voltages ranged between 0.1 and 1.0 V applied for 40 ms. The background water pressure in the ion trap was $\sim 10^{-6}$ Torr. A gas inlet into the trap allowed for addition of an excess of D_2O to elucidate hydrolysis processes.

■ RESULTS

Gas-Phase Complexes Produced by ESI/MS. The compositions of all of the ESI plutonyl and uranyl ion complexes, some of which were of low intensity, were definitively confirmed by CID fragmentation. ESI/MS of 180 μM $^{242}Pu^{VI}O_2^{2+}$ and $^{238}U^{VI}O_2^{2+}$ in 90/10 acetone/water (Figure 1) exhibit peaks with the following compositions: $[An^{VI}O_2(aco)_6]^{2+}$, $[An^{VI}O_2(aco)_5]^{2+}$, $[An^{VI}O_2(aco)_4]^{2+}$, and $[An^{VI}O_2(aco)_3(H_2O)]^{2+}$, where aco = CH_3COCH_3 and An = Pu or U. It is apparent from the spectra that the abundances of the uranyl complexes were much greater than those of the plutonyl complexes, typically by about an order of magnitude. A result of the inefficient formation of plutonyl complexes was a great enhancement of the relative intensities of impurity peaks in the plutonyl spectra (Figure 1a). The compositions of all of the assigned peaks were confirmed by isolation and CID to fragments definitively assigned as containing U or Pu, as discussed below; this was particularly crucial for the plutonyl complexes, which were in relatively low abundance. Throughout, "aco" represents acetone (CH_3COCH_3), "aco-H" represents the deprotonated acetone enolate ($CH_3CO{=}CH_2$), and "acn" represents acetonitrile (CH_3CN). The transformation of aco to aco-H in gas-phase uranyl complexes has been reported before,[8] and it has been shown that ketones with alpha protons are bound to metals with an equilibrium between the ketone and the enol tautomers.[16] ESI of $Np^{VI}O_2^{2+}$ solutions under comparable conditions did not yield any detectable dipositive gas-phase neptunyl complexes.

The peak at m/z 233 appeared in both plutonyl and uranyl ESI/MS; CID confirmed a contribution to this peak from $[Pu^{VI}O_2(CH_3COCH_3)_3(H_2O)]^{2+}$ in the plutonyl spectrum but also a major contribution from $[Na(CH_3COCH_3)_3(H_2O)_2]^{+}$. The plutonyl spectrum has other relatively intense peaks which are due to Na^+ clusters as verified by CID: $[Na(aco)(H_2O)]^+$ was a characteristic fragment ion from these clusters. Several of the most intense sodium cluster peaks are identified by blue asterisks in Figure 1a. The compositions of these peaks are as follows: $[Na(aco)(H_2O)_{10}]^+$ (m/z 261), $[Na(aco)(H_2O)_{11}]^+$ (m/z 279), $[Na(aco)_5]^+$ (m/z 313), $[Na(aco)_2(H_2O)_{10}]^+$ (m/z 319), $[Na(aco)(acn)_2(H_2O)_9]^+$ (m/z 325), $[Na(aco)_4(H_2O)_4]^+$ (m/z 327), $[Na(aco)_3(H_2O)_8]^+$ (m/z 341), and $[Na(aco)(acn)_2(H_2O)_{10}]^+$ (m/z 343). Sodium contamination is ubiquitous; the presence of acetonitrile in some of the sodium peaks indicates residual solvent contamination in the flow system. The relatively large intensities of sodium clusters in the plutonyl spectra largely reflect the very low intensities of the plutonyl peaks.

In view of the large contribution of isobaric $[Na(CH_3COCH_3)_3(H_2O)_2]^+$ to the purported $[Pu^{VI}O_2(CH_3COCH_3)_3(H_2O)]^{2+}$ complex at m/z 233, this latter complex was confirmed by ESI from a CD_3COCD_3/D_2O solution: the $[Pu^{VI}O_2(CD_3COCD_3)_3(H_2O)]^{2+}$ ion appeared at m/z 242 without interference from a sodium−acetone complex, as confirmed by CID. The corresponding uranyl complex from ESI of CD_3COCD_3/D_2O was $[U^{VI}O_2(CD_3COCD_3)_3(H_2O)]^{2+}$. The appearance of H_2O rather than D_2O in these complexes indicates that the $[An^{VI}O_2(CD_3COCD_3)_3]^{2+}$ complexes were produced by ESI from solution but then rapidly hydrated in the gas phase to $[An^{VI}O_2(CD_3COCD_3)_3(H_2O)]^{2+}$ prior to ion accumulation and acquisition of mass spectra. The abundance of $[Pu^{VI}O_2(CD_3COCD_3)_3(H_2O)]^{2+}$ relative to $[Pu^{VI}O_2(CD_3COCD_3)_4]^{2+}$, ∼20%, was similar to that of $[U^{VI}O_2(CH_3COCH_3)_3(H_2O)]^{2+}$ relative to $[U^{VI}O_2(CH_3COCH_3)_4]^{2+}$ (Figure 1b). Under these experimental conditions, the relative ESI ion abundances were $[An^{VI}O_2(aco)_4]^{2+} \approx [An^{VI}O_2(aco)_5]^{2+} > [An^{VI}O_2(aco)_6]^{2+} > [An^{VI}O_2(aco)_3(H_2O)]^{2+}$ for both An = U and Pu. The peak at m/z 242 in the uranyl ESI spectrum (Figure 1b) corresponds to $[UO_2(aco)_4(-H_2O)]^{2+}$, the nature of which is indeterminate, as discussed below.

ESI peaks at higher m/z corresponding to monopositive ions were also observed, such as $[Pu^{V}O_2(aco)_3]^+$ (m/z 448) and

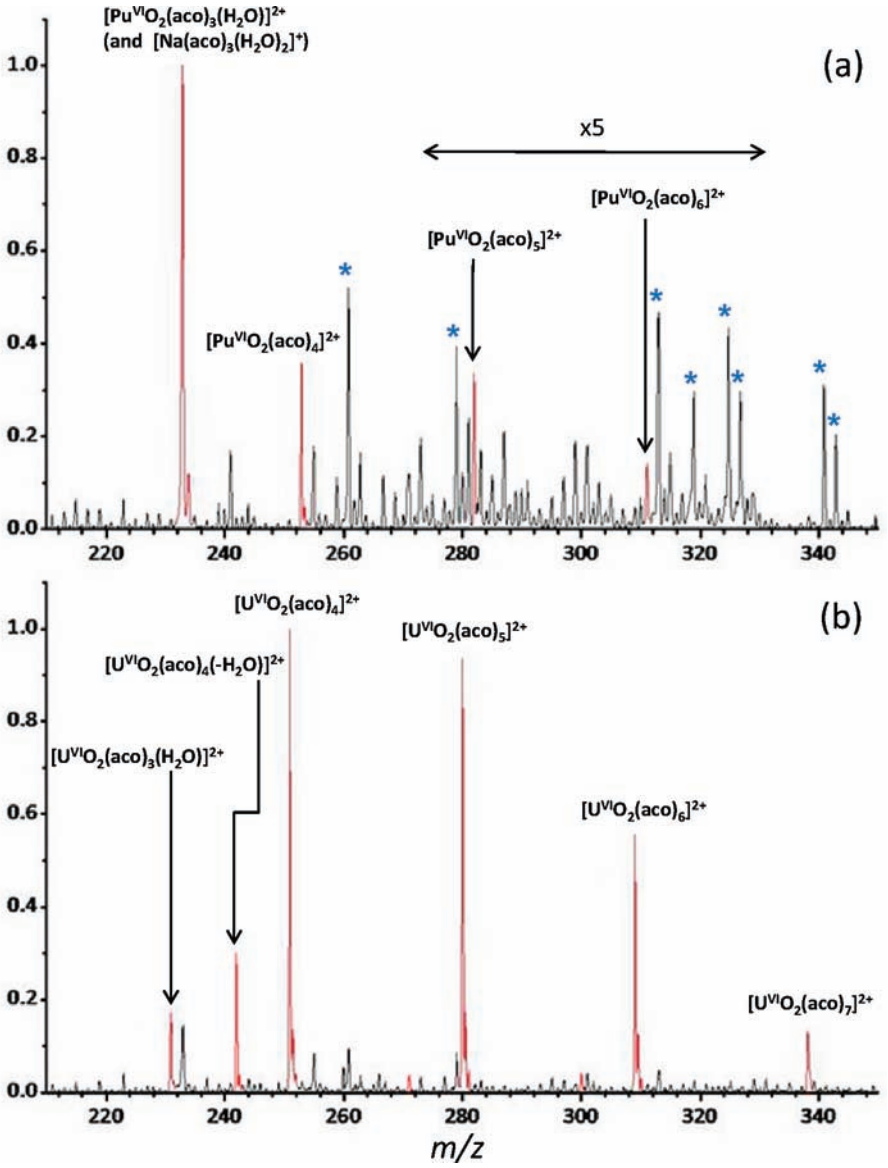


Figure 1. ESI/MS of water/acetone solutions of (a) $Pu^{VI}O_2(ClO_4)_3$ and (b) $U^{VI}O_2{}^{VI}(ClO_4)_3$. The compositions of relatively intense Na^+ cluster peaks identified by blue asterisks are specified in the text.

$[U^{VI}O_2(aco\text{-}H)(aco)_3]^+$ (*m*/*z* 501), the latter of which incorporates a deprotonated acetone ligand, $CH_3CO{=}CH_2$ (enolate). The monopositive ion complexes produced by ESI were not a focus of this work.

For plutonyl/acetonitrile, the only plutonium complex which could be confidently and reproducibly identified in the ESI mass spectrum was $[Pu^{VI}O_2(acn)_4]^{2+}$ (Figure S1, Supporting Information); this species was definitively assigned based on its distinctive CID pattern, as discussed below. The plutonyl/acetonitrile spectrum is dominated by sodium acetonitrile cluster ions. For uranyl/acetonitrile, the several previously reported[7e] dipositive complexes, in addition to $[U^{VI}O_2(acn)_4]^{2+}$, were also identified in this work. The results for acetone and even more so those for acetonitrile clearly demonstrate that transmission of dipositive plutonyl from solution to the gas phase is much less efficient than for dipositive uranyl and that the (slightly) more basic acetone ligands enhance the stabilization of $Pu^{VI}O_2{}^{2+}$ from solution to gas.

Collision-Induced Dissociation of Gas-Phase Complexes. Most of the reported CID results were obtained at roughly comparable excitation energies. As there was generally no evident energy threshold for the appearance of the different CID fragment ions, it was not possible to obtain reproducible energy-dependent fragmentation information for these complexes under these experimental conditions. The CID fragmentation patterns did not change appreciably upon varying the energy within the range employed, with substantial fragmentation occurring at relatively low energies near the fragmentation onset threshold.

The $[An^{VI}O_2(aco)_{4,5,6}]^{2+}$, $[An^{VI}O_2(aco)_3(H_2O)]^{2+}$, and $[An^{VI}O_2(acn)_4]^{2+}$ ions were apparent in the parent ESI spectra for both An = U and Pu in abundances adequate for isolation and CID. Representative CID spectra are shown in Figures 2−5 and S2, Supporting Information; the CID results are compiled in Table 1. The CID products correspond to four general routes, which are color coded in green, blue, red, and purple in Table 1. Using the same color coding as in Table 1, these generic processes

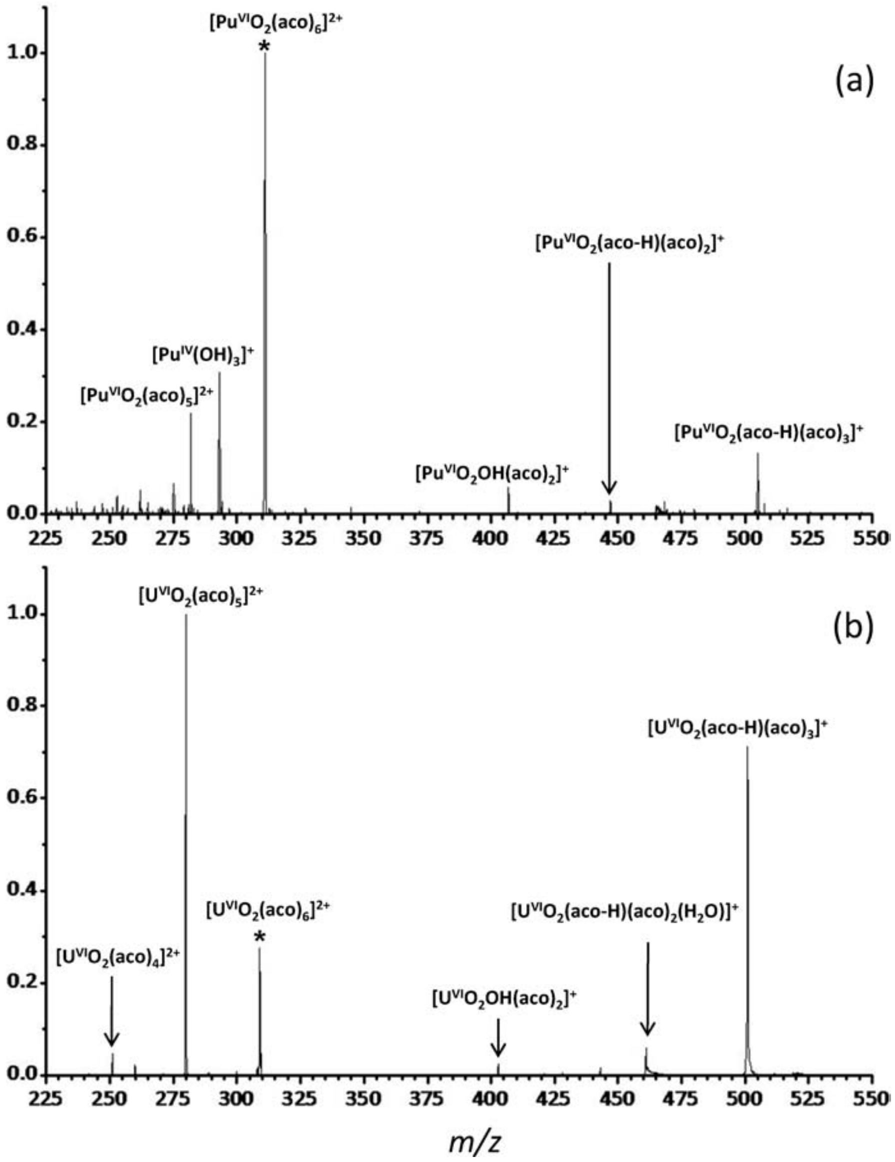


Figure 2. CID of (a) $[\mathrm{Pu^{VI}O_2(aco)_6}]^{2+}$ and (b) $[\mathrm{U^{VI}O_2(aco)_6}]^{2+}$.

are formally represented by eqs 1−5, where $(\mathrm{L})_n = (\mathrm{aco})_{4-6}$, $(\mathrm{aco})_3(\mathrm{H_2O})$, or $(\mathrm{acn})_4$.

$$[\mathrm{An^{VI}O_2(L)_n}]^{2+} \rightarrow [\mathrm{An^{VI}O_2(L)_{n\text{-}x}}]^{2+} + \mathrm{xL} \qquad (1)$$

$$[\mathrm{An^{VI}O_2(L)_n}]^{2+} + \mathrm{H_2O} \rightarrow [\mathrm{An^{VI}O_2(OH)(L)_{n\text{-}x}}]^{+} + \mathrm{HL}^{+} + (\mathrm{x\text{-}1})(\mathrm{L}) \qquad (2a)$$

$$[\mathrm{An^{VI}O_2(aco)_n}]^{2+} \rightarrow [\mathrm{An^{VI}O_2(aco\text{-}H)(aco)_{n\text{-}x}}]^{+} + \mathrm{Haco}^{+} + (\mathrm{x\text{-}2})(\mathrm{aco}) \qquad (2b)$$

$$[\mathrm{An^{VI}O_2(aco)_5}]^{2+} \rightarrow [\mathrm{An^{VI}O_2(aco)_4(\text{-}H_2O)}]^{2+} + \mathrm{aco} \qquad (3a)$$

$$[\mathrm{An^{VI}O_2(aco)_5}]^{2+} \rightarrow [\mathrm{An^{V}O_2(aco)_2(\text{-}H_2O)}]^{+} + \mathrm{aco}^{+} + 2(\mathrm{aco}) \qquad (3b)$$

$$[\mathrm{An^{VI}O_2(aco)_4}]^{2+} \rightarrow [\mathrm{An^{VI}O_2(aco)_4(\text{-}H_2O)}]^{2+} \qquad (3c)$$

$$[\mathrm{An^{VI}O_2(L)_n}]^{2+} \rightarrow [\mathrm{An^{V}O_2(L)_{n\text{-}x}}]^{+} + \mathrm{L}^{+} + (\mathrm{x\text{-}1})(\mathrm{L}) \qquad (4)$$

$$[Pu^{VI}O_2(aco)_6]^{2+} + H_2O \rightarrow [Pu^{IV}(OH)_3]^{+} + Haco^{+} + 2(aco\text{-}H) + 3(aco) \qquad (5)$$

Equation 1 is the loss of one or more neutral ligands with no change in the charge or oxidation state; gas-phase hydration was also observed for some of these CID products. Equation 2a is hydrolysis by reaction with indigenous water, concomitant with charge reduction by elimination of a proton, presumably as a protonated acetone or acetonitrile (protonated acetone was identified as a product during CID). The proposed gas-phase hydrolysis, eq 2a, was further substantiated by addition of $\mathrm{D_2O}$ into the ion trap: CID hydrolysis species such as $[\mathrm{U^{VI}O_2(OD)(aco)_{1,2}}]^{+}$ appeared, confirming the participation of gaseous water in the trap. The hydroxide monohydrates, $[\mathrm{U^{VI}O_2(OH)(aco)_2(H_2O)}]^{+}$ and $[\mathrm{U^{VI}O_2(OH)(acn)_2(H_2O)}]^{+}$, were also produced, indicating rapid hydration by indigenous water in the trap. Equation 2b produces hexavalent monopositive enolates; the $[\mathrm{U^{VI}O_2(aco\text{-}H)(aco)_2(H_2O)}]^{+}$ hydrate was also produced. The nature of the $[\mathrm{An^{VI}O_2(aco)_4(-H_2O)}]^{2+}$ and $[\mathrm{An^{V}O_2(aco)_2(-H_2O)}]^{+}$ products in eqs 3a−3c, in which water has been eliminated from the acetone CID complexes, is discussed below (the indicated compositions are formal). Equation 4 is charge and oxidation state reduction, presumably by elimination of an ionized acetone or acetonitrile molecule. Equation 5 is specific to plutonyl but was a reproducibly dominant CID

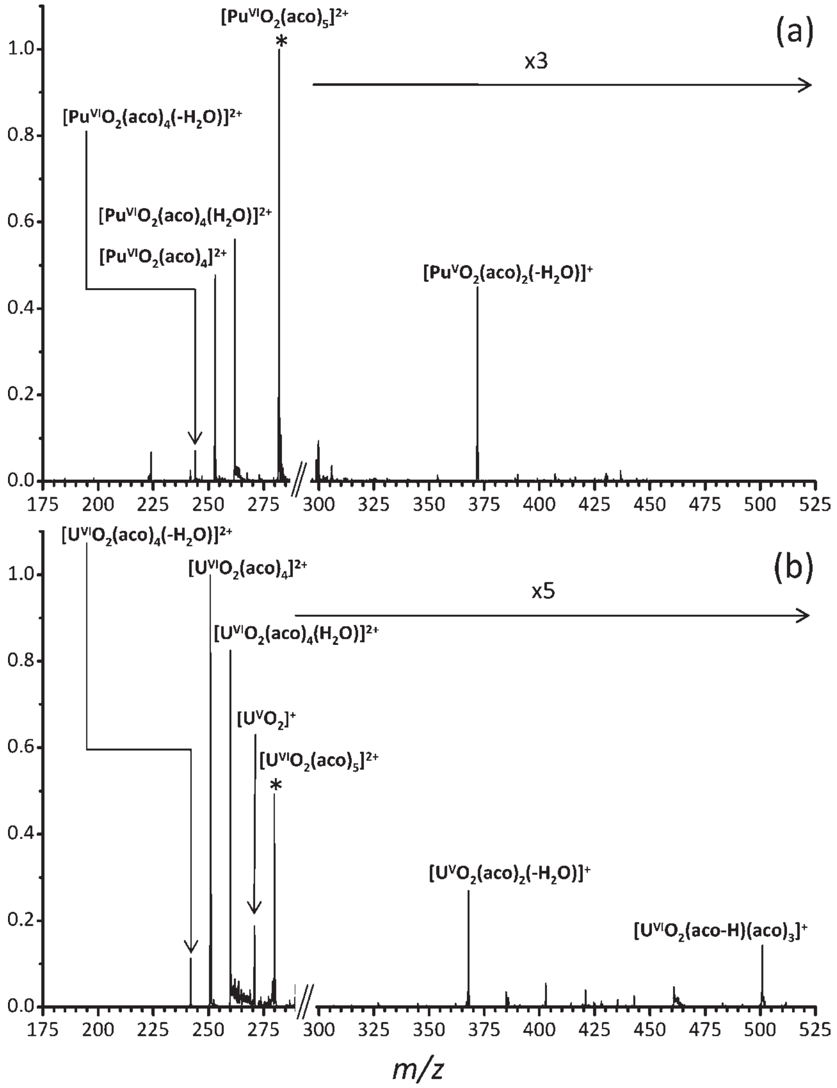


Figure 3. CID of (a) $[Pu^{VI}O_2(aco)_5]^{2+}$ and (b) $[U^{VI}O_2(aco)_5]^{2+}$.

channel (Figure 2a); a possible reduction pathway is discussed below.

■ DISCUSSION

Transfer of $Pu^{VI}O_2^{2+}$ from solution to gas. The ESI results represent the first report of transfer of dipositive hexavalent plutonyl complexes from solution to the gas phase using acetone or acetonitrile (or water) as stabilizing ligands. Bare $Pu^{VI}O_2^{2+}$ has been produced before in the gas phase by oxidation of Pu^{2+}.[17] As the electron affinity of $Pu^{VI}O_2^{2+}$ (15.1 ± 0.4 eV)[18] is more than 2 eV above the ionization energies (IEs) of water (12.6 eV), acetone (9.7 eV), and acetonitrile (12.2 eV),[19] stabilization of dipositive plutonyl against electron transfer from these neutrals requires charge donation by coordinating ligands. Coordination of the actinyl by electron-donating ligands reduces the effective electron affinity of the complexed dipositive actinyl such that charge exchange is not energetically favorable. The results suggest that four basic ligands are needed to stabilize dipositive actinyl ions in the gas phase and that nucleophilic acetone and acetonitrile are more effective than water at stabilizing dipositive ions in the gas phase. The electron-donating capacity of a ligand can be correlated with its gas-phase basicity, which are 660, 748 and 782 kJ/mol, for water, acetonitrile, and acetone, respectively.[19] Water ligands are evidently not adequately basic to stabilize dipositive actinyls from solution to gas; no dipositive actinyl ions were produced from aqueous solutions. Bühl et al.[20] alternatively consider the ligand dipole moment (D) and polarizabilty (σ) as the parameters which determine the efficacy of coordination, as the D and σ values are much greater for both acetone and acetonitrile than for water, the same favored coordination is predicted. The more basic acetone ligand is more effective at stabilization than acetonitrile, as indicated by the greater yields of dipositive complexes from acetone solutions, particularly for plutonyl. Furthermore, the observation of $[An^{VI}O_2(CD_3COCD_3)_3(H_2O)]^{2+}$ from CD_3COCD_3/D_2O solutions provides evidence that $[An^{VI}O_2(CD_3COCD_3)_3]^{2+}$, with only three acetone ligands, was produced by ESI and subsequently hydrated in the gas phase.

Using the same conditions as for uranyl and plutonyl, it has not yet been possible to transfer $Np^{VI}O_2^{2+}$ from solution to the gas phase and identify it by ESI/MS. This is indicative of the greater propensity for neptunyl (VI) to reduce to neptunyl (V), as discussed above, and reveals an intrinsic aspect of actinyl

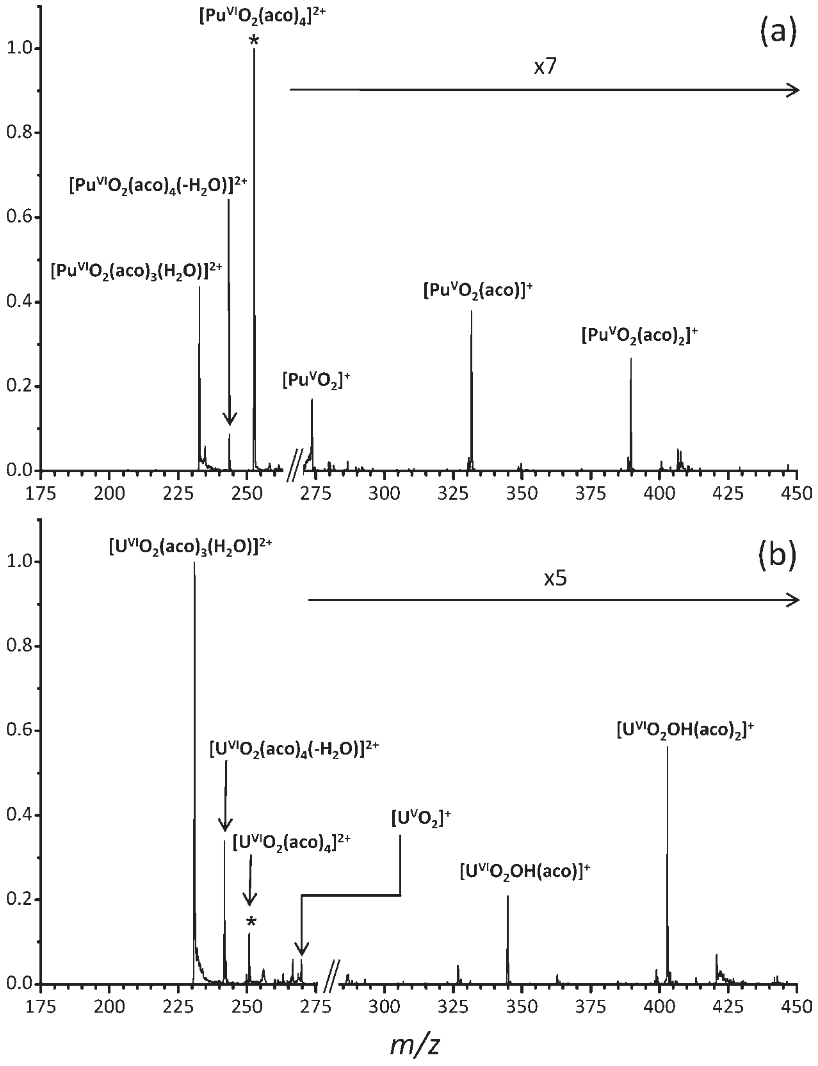


Figure 4. CID of (a) $[Pu^{VI}O_2(aco)_4]^{2+}$ and (b) $[U^{VI}O_2(aco)_4]^{2+}$.

chemistry. In separate experiments, the ESI and instrumental conditions were adjusted to favor production of bare monopositive actinyl ions. The ESI conditions for monopositives correspond to the "harsh" instrumental parameters given in the Experimental Section, where the greatest difference is the much lower trap drive employed to favor the dipositive complexes. The higher trap drive evidently results in higher kinetic energy ions which experience degrading hyperthermal collisions in the trap. The key role of the trap drive in obtaining dipositive complexes was confirmed by observing its effect without varying any other parameters: dipositive ion abundances decreased drastically upon increasing the trap drive from 50 to 80, while monopositive abundances concomitantly increased. Upon ESI from water using the "harsh" monopositive ion conditions, all three pentavalent $An^{V}O_2^{+}$ are produced (An = U, Np, Pu); substantial hexavalent $U^{VI}O_2(OH)^{+}$ and minor $Pu^{VI}O_2(OH)^{+}$ also appear, but no $Np^{VI}O_2(OH)^{+}$ is observed. The collection of ESI results, for the monopositive and dipositive actinyls, clearly shows that Np(VI) is less stable than both U(VI) and Pu(VI) and readily reduces to Np(V), in direct relationship to known actinyl chemistry in the condensed phase.[9,10]

Change in Coordination from Solution to Gas. In acetone/water solutions of uranyl, neptunyl, and presumably plutonyl, inner-shell cation coordination is by five water molecules, with no acetones.[4,21] Madic and co-workers[4] performed an NMR study of $U^{VI}O_2^{2+}$, $Np^{VI}O_2^{2+}$, and $Pu^{VI}O_2^{2+}$ solution to determine the cation hydration numbers; these experiments were performed with an excess of acetone to achieve adequately low temperatures for high resolution: they reported five inner-sphere waters and no inner-sphere acetones. It is not necessarily obvious why coordination in solution should be by the much weaker base, water, whereas in the gas-phase coordination it is by the stronger base, acetone. A recent DFT study of uranyl in water/acetonitrile by Bühl et al.[20] clarifies this phenomenon, which they characterize as "cooperative polarization effects in water". Whereas inner-shell coordination in the gas phase is by the intrinsically better ligand, acetonitrile, that in solution is by water surrounded by second-shell acetonitrile molecules. The uranyl–water interaction is enhanced by hydrogen bonding of the inner-shell waters to nitrogen, $(UO_2)OH_2\cdots N{\equiv}CCH_3$, which polarizes the coordinating water such that the charge on the oxygen atom of the water is increased. Although Bühl et al. evaluate this effect in the context of the enhanced dipole moment of water, it can also be presumed that the increased charge on the oxygen atom in the polarized water due to the strong $H\cdots N$ hydrogen bonds

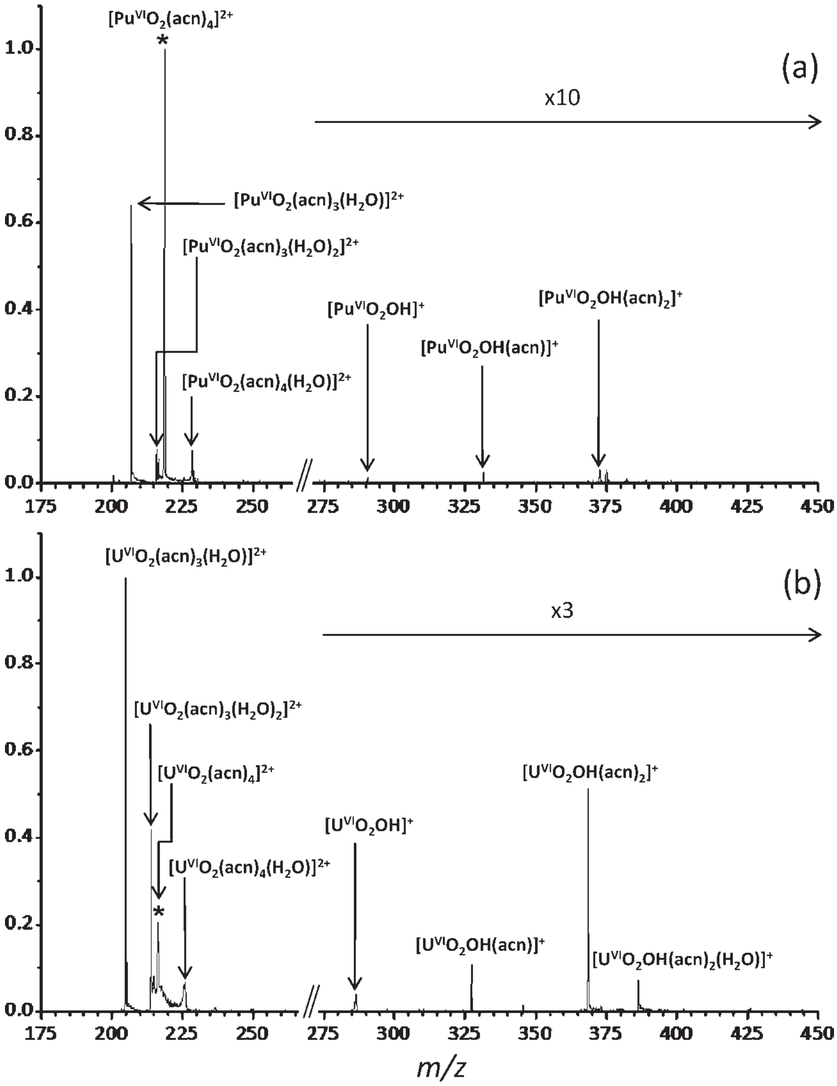


Figure 5. CID of (a) $[Pu^{VI}O_2(acn)_4]^{2+}$ and (b) (a) $[U^{VI}O_2(acn)_4]^{2+}$.

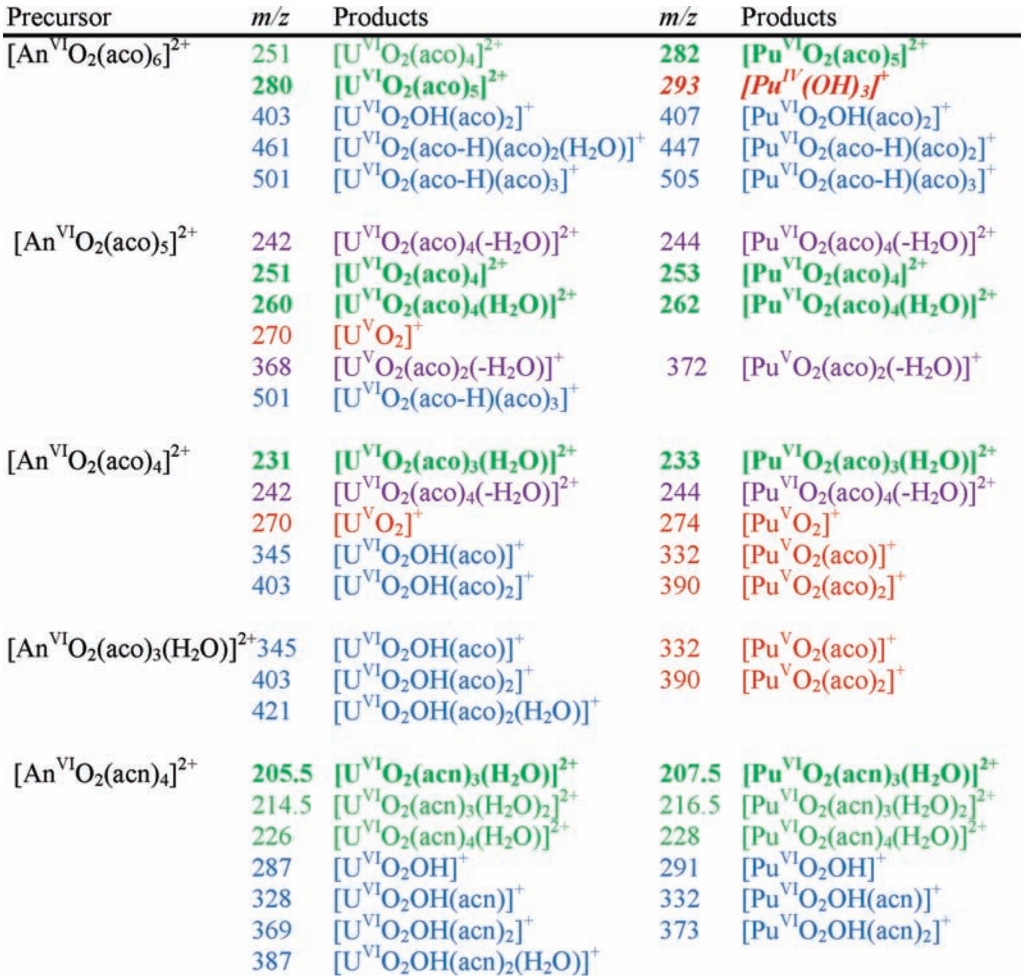
effectively increases the basicity of the coordinated water molecules. A similar "cooperative polarization effect" should hold for other strong Lewis bases, such as acetone, in water solutions. Such a cooperative effect is not present in small gas-phase actinyl complexes with only strongly bound inner-shell ligands. The work of Bühl et al. has effectively resolved the conundrum as to why actinyl ions should be coordinated by the intrinsically weaker base, water, in solution but by the stronger base, acetonitrile or acetone, in the gas phase.

Observed Differences between Uranium and Plutonium Chemistry. The much greater ESI yields of $U^{VI}O_2^{2+}$ complexes as compared with $Pu^{VI}O_2^{2+}$ complexes (Figures 1 and S1, Supporting Information) reflect the propensity of hexavalent plutonyl to reduce to the pentavalent (and even the tetravalent) oxidation state. The absence of gas-phase complexes of the even less stable $Np^{VI}O_2^{2+}$ ion substantiates this interpretation.

Although the speciation of plutonyl and uranyl are rather similar in the water/acetone ESI mass spectra (Figure.1), the plutonyl and uranyl complexes exhibit substantial and revealing differences upon CID, as is evident from Table 1. The nature of the CID products formally comprising acetone ligands with elimination of a water molecule, i.e., those in purple in Table 1 and in eqs 3a, 3b, and 3c, are indeterminate. Two viable assignments are monoxide bis-enolates and mesityl oxide (mo) complexes, i.e., $[An^{VI}O_2(aco)_4(-H_2O)]^{2+}$ would correspond to $[An^{VI}O(aco\text{-}H)_2(aco)_2]^{2+}$ or $[An^{VI}O_2(mo)(aco)_2]^{2+}$, where (aco-H) is the enolate, $CH_3C(O){=}CH_2$, and (mo) is the dehydrated acetone dimer, $CH_3C(O)CH{=}C(CH_3)_2$. A key point for the purposes of the present discussion is that plausible compositions retain the oxidation state of the precursor complex, either An(V) or An(VI). Future experiment and theory efforts will aim to reveal the nature of these new types of species.

CID of $[An^{VI}O_2(aco)_6]^{2+}$ was generally similar for An = U and Pu, with the glaring exception of the appearance of $[Pu^{IV}(OH)_3]^+$ as a major product, as discussed below. All other CID products of these ions retained the hexavalent oxidation state, either as ligated dipositive ions or as monopositive ions with a hydroxide or an enolate ligand. CID of the two $[An^{VI}O_2(aco)_5]^{2+}$ was also essentially similar, with the dominant products being $[An^{VI}O_2(aco)_4]^{2+}$ and their hydrates, $[An^{VI}O_2(aco)_4(H_2O)]^{2+}$. The retention primarily of the hexavalent oxidation state upon CID of $[An^{VI}O_2(aco)_{5,6}]^{2+}$ can be attributed to stabilization of metal center charge and oxidation state by electron donation from the numerous basic ligands. The appearance of some

Table 1. CID Products of $[AnO_2(aco)_n]^{2+}$, $[AnO_2(aco)_3(H_2O)]^{2+}$, and $[AnO_2(acn)_n]^{2+\,a}$



Precursor	*m/z*	Products	*m/z*	Products
$[An^{VI}O_2(aco)_6]^{2+}$	251	$[U^{VI}O_2(aco)_4]^{2+}$	**282**	**$[Pu^{VI}O_2(aco)_5]^{2+}$**
	280	**$[U^{VI}O_2(aco)_5]^{2+}$**	***293***	***$[Pu^{IV}(OH)_3]^{+}$***
	403	$[U^{VI}O_2OH(aco)_2]^{+}$	407	$[Pu^{VI}O_2OH(aco)_2]^{+}$
	461	$[U^{VI}O_2(aco\text{-}H)(aco)_2(H_2O)]^{+}$	447	$[Pu^{VI}O_2(aco\text{-}H)(aco)_2]^{+}$
	501	$[U^{VI}O_2(aco\text{-}H)(aco)_3]^{+}$	505	$[Pu^{VI}O_2(aco\text{-}H)(aco)_3]^{+}$
$[An^{VI}O_2(aco)_5]^{2+}$	242	$[U^{VI}O_2(aco)_4(\text{-}H_2O)]^{2+}$	244	$[Pu^{VI}O_2(aco)_4(\text{-}H_2O)]^{2+}$
	251	**$[U^{VI}O_2(aco)_4]^{2+}$**	**253**	**$[Pu^{VI}O_2(aco)_4]^{2+}$**
	260	**$[U^{VI}O_2(aco)_4(H_2O)]^{2+}$**	**262**	**$[Pu^{VI}O_2(aco)_4(H_2O)]^{2+}$**
	270	$[U^{V}O_2]^{+}$		
	368	$[U^{V}O_2(aco)_2(\text{-}H_2O)]^{+}$	372	$[Pu^{V}O_2(aco)_2(\text{-}H_2O)]^{+}$
	501	$[U^{VI}O_2(aco\text{-}H)(aco)_3]^{+}$		
$[An^{VI}O_2(aco)_4]^{2+}$	**231**	**$[U^{VI}O_2(aco)_3(H_2O)]^{2+}$**	**233**	**$[Pu^{VI}O_2(aco)_3(H_2O)]^{2+}$**
	242	$[U^{VI}O_2(aco)_4(\text{-}H_2O)]^{2+}$	244	$[Pu^{VI}O_2(aco)_4(\text{-}H_2O)]^{2+}$
	270	$[U^{V}O_2]^{+}$	274	$[Pu^{V}O_2]^{+}$
	345	$[U^{VI}O_2OH(aco)]^{+}$	332	$[Pu^{V}O_2(aco)]^{+}$
	403	$[U^{VI}O_2OH(aco)_2]^{+}$	390	$[Pu^{V}O_2(aco)_2]^{+}$
$[An^{VI}O_2(aco)_3(H_2O)]^{2+}$	345	$[U^{VI}O_2OH(aco)]^{+}$	332	$[Pu^{V}O_2(aco)]^{+}$
	403	$[U^{VI}O_2OH(aco)_2]^{+}$	390	$[Pu^{V}O_2(aco)_2]^{+}$
	421	$[U^{VI}O_2OH(aco)_2(H_2O)]^{+}$		
$[An^{VI}O_2(acn)_4]^{2+}$	**205.5**	**$[U^{VI}O_2(acn)_3(H_2O)]^{2+}$**	**207.5**	**$[Pu^{VI}O_2(acn)_3(H_2O)]^{2+}$**
	214.5	$[U^{VI}O_2(acn)_3(H_2O)_2]^{2+}$	216.5	$[Pu^{VI}O_2(acn)_3(H_2O)_2]^{2+}$
	226	$[U^{VI}O_2(acn)_4(H_2O)]^{2+}$	228	$[Pu^{VI}O_2(acn)_4(H_2O)]^{2+}$
	287	$[U^{VI}O_2OH]^{+}$	291	$[Pu^{VI}O_2OH]^{+}$
	328	$[U^{VI}O_2OH(acn)]^{+}$	332	$[Pu^{VI}O_2OH(acn)]^{+}$
	369	$[U^{VI}O_2OH(acn)_2]^{+}$	373	$[Pu^{VI}O_2OH(acn)_2]^{+}$
	387	$[U^{VI}O_2OH(acn)_2(H_2O)]^{+}$		

[a] The color coding of the products is as described in the text. CID products which were consistently dominant are indicated in bold.

pentavalent products from $[An^{VI}O_2(aco)_5]^{2+}$ indicates a decrease in this stabilization.

The dominant CID product for both of the $[An^{VI}O_2(aco)_4]^{2+}$ was $[An^{VI}O_2(aco)_3(H_2O)]^{2+}$, but significant differences in the chemistry of uranyl and plutonyl appeared in the less abundant products: whereas the hexavalent $[U^{VI}O_2(OH)(aco)_{1,2}]^{+}$ were produced (eq 2a), charge reduction by electron transfer resulted in reduction to pentavalent $[Pu^{V}O_2(aco)_{1,2}]^{+}$ (eq 4). Hydrolysis of uranyl to retain the U(VI) oxidation state presents a distinct contrast to plutonyl, where no such hydrolysis occurs and loss of aco^{+} results in Pu(V), directly reflecting the comparative U(VI/V) and Pu(VI/V) reduction potentials discussed above. For the two $[An^{VI}O_2(aco)_3(H_2O)]^{2+}$, all CID products are monopositive; elimination of a ligand from these species, which have the weak base water as one of the four donor ligands, evidently favors charge reduction by elimination of aco^{+}. The difference between uranyl and plutonyl is striking: in all products the U(VI) oxidation state is retained by hydrolysis, whereas from the plutonyl complex only Pu(V) is produced, by charge reduction absent hydrolysis.

It was not possible to obtain an adequate $[Pu^{VI}O_2(acn)_5]^{2+}$ ion intensity to acquire reliable CID results (Figure S1, Supporting Information). For both of the $[An^{VI}O_2(acn)_4]^{2+}$, the dominant CID product was $[An^{VI}O_2(acn)_3(H_2O)]^{2+}$, in parallel with CID of $[An^{VI}O_2(aco)_4]^{2+}$. The singly charged products from $[An^{VI}O_2(acn)_4]^{2+}$ reveal a significant difference between the acn and the aco ligands. For $[U^{VI}O_2(aco)_4]^{2+}$, CID charge reduction was accompanied by hydrolysis such that the U(VI) oxidation state was retained; for $[Pu^{VI}O_2(aco)_4]^{2+}$, the monopositive products were not hydrolyzed and they comprised Pu(V). In contrast, for both of the $[An^{VI}O_2(acn)_4]^{2+}$ ions (An = U, Pu), charge reduction was accompanied by hydrolysis and the An(VI) oxidation state was retained. These alternate processes, charge reduction with and without oxidative hydrolysis, are examples of eqs 2a and 4, as shown in eq 6 (An = U, Pu and L = acn; An = U and L = aco) and eq 7.

$$[An^{VI}O_2(L)_4]^{2+} + H_2O \rightarrow [An^{VI}O_2(OH)(L)_2]^{+} + HL^{+} + L \qquad (6)$$

$$[Pu^{VI}O_2(aco)_4]^{2+} \rightarrow [Pu^{V}O_2(aco)_2]^{+} + aco^{+} + aco \qquad (7)$$

For $[U^{VI}O_2(L)_4]^{2+}$, eq 6 was observed for both L = aco and can such that the stable U(VI) oxidation state was retained. For $[Pu^{VI}O_2(L)_4]^{2+}$, eq 6 was observed for L = acn whereas reduction to Pu(V) according to eq 7 was observed for L = aco. This disparity between the two ligands may reflect their comparative IEs, 9.7 eV for aco and 12.2 eV for acn, and proton affinities (PAs), 812 kJ mol^{-1} (8.42 eV) for aco and 779 kJ mol^{-1}

(8.07 eV) for acn.[19] Whereas the PAs of aco and acn differ by only 0.35 eV, IE[aco] is 2.5 eV lower than IE[acn]. The lower IE[aco] would facilitate the electron-transfer reduction eq 7, which appears for An = Pu; in the case of uranyl, the stability of U(VI) evidently results in eq 6 for both aco and acn. Retention of the U(VI) oxidation state for both acn and aco ligands during charge reduction, versus formation of Pu(VI) only with acn, is another example of intrinsic differences in actinyl chemistry revealed in the gas phase.

Reduction of Pu(VI) to Pu(IV). Upon CID of $[\mathrm{Pu^{VI}O_2(CH_3COCH_3)_6}]^{2+}$, a reproducibly intense peak appears at *m*/*z* 293, which corresponds to the $[\mathrm{Pu^{IV}(OH)_3}]^{+}$ ion (Figure 2a), which is a common species in aqueous Pu(IV) solutions.[13] It should be emphasized that this CID process appeared at the same relatively low energies as the additional fragmentation products for this and other complexes: this was not a high-energy phenomenon. The observed CID process corresponds to conversion of $\mathrm{Pu^{VI}O_2}^{2+}$ to $\mathrm{Pu^{IV}(OH)_3}^{+}$, which reduction process involves disrupting the robust "-yl" oxygen bonds. As it seems improbable that multiple water molecules would be involved in the reduction reaction at a water pressure of only $\sim 10^{-6}$ Torr, we propose that the mechanism for this remarkable process directly involves acetone ligands. The key role of the acetone ligands is substantiated by the observation that this reduction process is not observed when fewer than six acetones are present; this process was observed only for the (formally) hypercoordinated $[\mathrm{PuO_2(aco)_6}]^{2+}$ ion complex.

Whereas the six aco ligands evidently stabilize Pu(VI) against reduction to Pu(V), they enable a distinctive pathway for reduction to Pu(IV). The formal proposed reaction is shown in eq 8, where the postulated neutral products are acetone and the acetone enolate dimer.

$$[\mathrm{Pu^{VI}O_2(aco)_6}]^{2+} + \mathrm{H_2O} \rightarrow [\mathrm{Pu^{IV}(OH)_3}]^{+} + \mathrm{Haco}^{+} + 3\mathrm{aco} + (\mathrm{aco\text{-}H})_2 \tag{8}$$

In eq 8 it is proposed that two of the H atoms in the tris-hydroxide product derive from two acetones in the congested coordination sphere, resulting in elimination of a dehydrogenated acetone dimer, possibly hexane-2,5-dione, $\mathrm{CH_3COCH_2CH_2COCH_3}$, which is more stable than two enolate radicals by ~ 360 kJ mol^{-1}.[22] The charge reduction corresponds to hydrolysis by water in the trap. Equation 8 can alternatively be presented as the processes given by eqs 8a and 8b, reduction/dimerization and hydrolysis/ligand elimination, which are presumed to occur in a concerted mechanism.

$$[\mathrm{Pu^{VI}O_2(aco)_6}]^{2+} \rightarrow [\mathrm{Pu^{IV}(OH)_2(aco)_4}]^{2+} + (\mathrm{aco\text{-}H})_2 \tag{8a}$$

$$[\mathrm{Pu^{IV}(OH)_2(aco)_4}]^{2+} + \mathrm{H_2O} \rightarrow [\mathrm{Pu^{IV}(OH)_3}]^{+} + \mathrm{Haco}^{+} + 3(\mathrm{aco}) \tag{8b}$$

Experiments were performed to test this hypothetical route to $[\mathrm{Pu^{IV}(OH)_3}]^{+}$. Equation 8 should not occur upon substitution of hexafluoroacetone for acetone. However, ESI of plutonyl from hexafluoroacetone/water did not produce any dipositive complexes, presumably due to the low gas-phase basicity of $\mathrm{CF_3COCF_3}$, which at 640 kJ mol^{-1} is much lower than that of acetone and even less than that of water.[19] CID of the perdeuterated acetone complex, $[\mathrm{Pu^{VI}O_2(acod_6)_6}]^{2+}$, should produce $[\mathrm{Pu^{IV}(OH)(OD)_2}]^{+}$ according to eq 8; however, it was not practical to generate adequate $[\mathrm{Pu^{VI}O_2(acod_6)_6}]^{2+}$ from acod$_6$/water solutions for effective isolation and CID. A final experiment in which gaseous $\mathrm{D_2O}$ was added to the ion trap and CID of $[\mathrm{Pu^{VI}O_2(aco)_6}]^{2+}$ was performed, which did provide some evidence for the expected $[\mathrm{Pu^{IV}(OD)(OH)_2}]^{+}$ product; these results support, but do not confirm, the postulated eq 8. The very low dipositive plutonyl complex intensities render such isotopic-labeling experiments generally nondefinitive.

The remarkably efficient Pu(VI)/Pu(IV) reduction/hydrolysis process is distinctive to plutonyl: the $[\mathrm{U^{IV}(OH)_3}]^{+}$ complex is not produced. Generation of $[\mathrm{Pu^{IV}(OH)_3}]^{+}$ from plutonyl is indicative of the greater ease in disrupting the weaker plutonyl bonds as well as the greater propensity for plutonyl to reduce to the tetravalent oxidation state. Further examination of this gas-phase process, both experimentally and theoretically, promises to illuminate the mechanism by which plutonyl is reduced to Pu(IV) in the condensed phase.

Hypercoordinated Uranyl Complexes. Formation of apparently hypercoordinated uranyl complexes, $[\mathrm{U^{VI}O_2(CH_3COCH_3)_{7,8}}]^{2+}$, in the gas phase is an observation not reported before.[8] Density functional theory calculations on $[\mathrm{U^{VI}O_2(CH_3COCH_3)}_n]^{2+}$ ($n = 1-6$) complexes[23] indicate that $[\mathrm{U^{VI}O_2(CH_3COCH_3)_6}]^{2+}$ should be a marginally stable gas-phase species with six equatorial acetone ligands bound to the uranium metal center. The computed binding energy of the sixth acetone, at merely 11 kJ mol^{-1}, is substantially less than that computed for the fifth acetone, 53 kJ mol^{-1}, and much lower than that computed for each of the first four acetones, ≥ 130 kJ mol^{-1}. The $[\mathrm{U^{VI}O_2(aco)}_n]^{2+}$ complexes with $n = 1-5$ have been reported previously.[8] Our ESI results have produced both $[\mathrm{U^{VI}O_2(aco)_6}]^{2+}$ and $[\mathrm{Pu^{VI}O_2(aco)_6}]^{2+}$, which might be taken to suggest that the predicted hexacoordinate uranyl complex as well as its plutonyl counterpart are indeed stable gas-phase species. However, a complicating result is the observation of species corresponding to $[\mathrm{U^{VI}O_2(aco)_7}]^{2+}$ and $[\mathrm{U^{VI}O_2(aco)_8}]^{2+}$, both of which were confirmed by isolation and CID to produce $[\mathrm{U^{VI}O_2(aco)}_{n-x}]^{2+}$ ($n = 7, 8$; $x = 1, 2$; see Figure S3, Supporting Information). Uranyl coordinated by seven or eight inner-sphere acetone molecules is seemingly implausible. Accordingly, the observation of $[\mathrm{U^{VI}O_2(aco)_6}]^{2+}$ and $[\mathrm{Pu^{VI}O_2(aco)_6}]^{2+}$ cannot necessarily be taken as evidence of hexacoordination of actinyls by acetones. The nature of these new apparently hypercoordinated actinyl ions, $[\mathrm{An^{VI}O_2(aco)_{6,7,8}}]^{2+}$, will be examined by both experiment and theory.

■ CONCLUDING REMARKS

ESI of the dipositive hexavalent plutonyl ion from acetone/water and acetonitrile/water solution produced gas-phase complexes in which the plutonyl ion is coordinated to at least four electron-donating ligands: $[\mathrm{Pu^{VI}O_2(L)_{4,5}}]^{2+}(\mathrm{g})$, where L = acetone or acetonitrile. The yields of the hexavalent plutonyl complexes were much lower than that of the corresponding uranyl complexes, and no hexavalent neptunyl complexes could be identified using these electron-donor ligands; these results are in accord with the relative stabilities across the actinyl series: $\mathrm{U^{VI}O_2}^{2+} > \mathrm{Pu^{VI}O_2}^{2+} > \mathrm{Np^{VI}O_2}^{2+}$. Upon CID of the hexavalent uranyl and plutonyl complexes, a greater propensity of Pu(VI) to reduce to Pu(V) was revealed, in parallel with the known redox chemistry of these actinyls. CID of $[\mathrm{Pu^{VI}O_2(aco)_6}]^{2+}$ in the presence of $\sim 10^{-6}$ Torr $\mathrm{H_2O}$ distinctively resulted in $[\mathrm{Pu^{IV}(OH)_3}]^{+}$ as a major product: this observation reflects the propensity for reduction to the stable Pu(IV) oxidation state and may provide insights into the mechanism of the reduction of plutonyl to Pu(IV), which requires disruption of the robust plutonyl oxo bonds; no U(IV) species were observed. The chemical nature of the acetone ligand, specifically the enol tautomer which can deprotonate to provide an enolate ligand, results in a richer CID chemistry for acetone complexes as compared with acetonitrile complexes. The appearance of apparently hypercoordinated actinyl/acetone complexes is intriguing and merits further experimental and theoretical investigation; this work is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ESI/MS of water/acetonitrile solutions of $PuO_2^{VI}(ClO_4)_3$ and $UO_2^{VI}(ClO_4)_3$; CID spectra for $[An^{VI}O_2(aco)_3(H_2O)]^{2+}$; CID spectrum for $[U^{VI}O_2(aco)_8]^{2+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: JKGibson@lbl.gov.

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