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Heptavalent Actinide Tetroxides NpO_4^- and PuO_4^-: Oxidation of Pu(V) to Pu(VII) by Adding an Electron to PuO_4

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Abstract

The highest known actinide oxidation states are Np(VII) and Pu(VII), both of which have been identified in solution and solid compounds. Recently a molecular Np(VII) complex, $NpO_3(NO_3)_2^-$, was prepared and characterized in the gas-phase. In accord with the lower stability of heptavalent Pu, no Pu(VII) molecular species has been identified. Reported here are the gas-phase synthesis and characterization of NpO_4^- and PuO_4^-. Reactivity studies and density functional theory computations indicate the heptavalent metal oxidation state in both. This is the first instance of Pu(VII) in the absence of stabilizing effects due to condensed phase solvation or crystal fields. The results indicate that addition of an electron to neutral PuO_4, which has a computed electron affinity of 2.56 eV, counterintuitively results in oxidation of Pu(V) to Pu(VII), concomitant with superoxide reduction.

Introduction

The actinide (An) series of elements is characterized by filling of the 5f orbitals.[1] For the early actinides, through Am, the 5f orbital energies are sufficiently high and their radial distributions are sufficiently diffuse that they can become substantially engaged in chemical bonding, with varying degrees of ionic and covalent character.[2-7] A result of this characteristic of the early actinides is that a wide range of oxidation states, up to Np(VII) and Pu(VII), have been identified in solid or solution.[8-18] For the heavier actinides, beginning with Cm, the 5f orbitals are lower in energy and more spatially compact, with the result that oxidation states above An(IV) are difficult to achieve.[1]

An attribute of gas-phase chemistry is the ability to characterize the intrinsic stabilities of oxidation states, both high and low, absent stabilizing or destabilizing effects that may be introduced in condensed phases by interactions, and potentially chemical reactions, with secondary species such as counter ions and solvent molecules. Recent examples of the ability to identify the intrinsic stabilities of metal oxidation states in elementary gas-phase species include the discovery of the nonavalent oxidation state in $Ir(IX)O_4^+$,[19] and the first pentavalent lanthanides in $Pr(V)O_2^+$ and NPrO.[20,21] Neither of the extreme IX oxidation state in the periodic table, nor the V oxidation state in the lanthanide series have yet been achieved in condensed phase.

It was previously reported that the oxidation states in gas-phase $NpO_3(NO_3)_2^-$ and $PuO_3(NO_3)_2^-$ which are essentially AnO_3^+ cores coordinated by two NO_3^- ligands, are Np(VII) and Pu(VI), respectively. These results reveals the intrinsically higher stability of Np(VII) versus Pu(VII) as expected from the An(VII/VI) reduction potentials.[1] Gas-phase displacement reaction (1) for An = U has been identified as a route to UO_4^-.[22]

$$AnO_2(C_2O_4)^- + O_2 \rightarrow AnO_4^- + 2(CO_2) \qquad (1)$$

The oxidation state in UO_4^- was reported as U(VI), which is the highest accessible chemical oxidation state of uranium. For transuranium elements such as Np and Pu, because oxidation states above An(VI) are accessible the AnO_4^- species are candidates for achieving the An(VII) oxidation state. In the present work, NpO_4^- and PuO_4^- were synthesized via reaction (1) with An = Np and Pu. Gas-phase reactivity experiments and density functional theory (DFT) computations indicate that the oxidation states are Np(VII) and Pu(VII) in these anionic tetroxide molecules. In the case of plutonium this is the first identified heptavalent species identified in the gas phase.

Experimental Details

Caution! The Np-237 and Pu-242 isotopes employed in this work are radioactive and must be handled only with proper precautions and controls.[23]

The general experimental approach has been described previously,[24] and the experimental methods were similar to those employed for analogous studies with the actinides Pa and U.[22]

Anionic actinyl oxalate complexes, $AnO_2(C_2O_4)^-$ for An = Np and Pu, were produced by ESI of ethanol solutions containing 100 µM AnO_2^{2+} (diluted from 28 mM $NpO_2(ClO_4)_2$ at pH = 1, and 8 mM $PuO_2(ClO_4)_2$ at pH = 1) and 10 mM NaC_2O_4. The experiments were performed using an Agilent 6340 quadrupole ion trap mass spectrometer with MS^n collision induced dissociation (CID) capability; the CID energy is an instrumental parameter that provides an indication of relative ion excitation. Ions in the trap alternatively can undergo ion-molecule reactions at ~300 K [25] by applying a reaction time of up to 10 s. Anion mass spectra were acquired using the following parameters: solution flow rate, 60 µL/h; nebulizer gas pressure, 12 psi; capillary voltage offset and current, -4000 V and 208 nA; end plate voltage offset and current, -500 V and 3025 nA ; dry gas flow rate, 3 L/min; dry gas temperature, 325 °C; capillary exit, -50 V; skimmer, -36 V; octopole 1 and 2 DC, -10.9 V and -3.0 V; octopole RF amplitude, 190 V_{pp}; lens 1 and 2, 10.0 V and 91.0 V; trap drive, 50. Nitrogen gas for nebulization and drying was supplied from the boil-off of a liquid nitrogen Dewar. The background water pressure in the ion trap is estimated as ~10^{-6} Torr;[23] reproducibility of hydration rates of $UO_2(OH)^+$ [26] established that the water pressure was constant to within <10%. The helium buffer gas pressure in the trap is constant at ~10^{-4} Torr. The ion trap has been modified to allow for the introduction of reagent gases through a gas manifold and leak valve. Although the isotopic purity of the $^{18}O_2$ was unknown, the relative pressure of $^{18}O_2$ and $^{16}O_2$ was determined by monitoring the previously reported reaction of $UO_2(CH_3CO_2)_2^-$ with O_2 to yield $UO_2(O_2)(CH_3CO_2)_2^-$.[27]

Computational Approach

The computational approach follows that of earlier work on protactinium and uranium.[22] All the calculations in the manuscript were performed at the density functional theory (DFT) level using the development version of the open-source NWChem software suite.[28] This work used the Stuttgart small-core effective core-potential, associated spin-orbit potentials and basis sets for the actinide atoms,[29] and the all-electron DFT optimized valence triple-ζ polarized (TZVP) basis sets[30] for the light atoms in the molecular complexes studied (C, O, H). An unrestricted wave function was used for all open-shell DFT calculations. For each open-shell complex multiple spin-states were explored. The geometries of the complexes were optimized, followed by frequency calculations to ensure the calculated structure had no imaginary frequencies and was in a minimum energy configuration. For each experimentally observed species all possible bonding and coordination patterns were tested. Oxidation states were assigned based on Mulliken atomic spin populations. Atomic spin populations have been shown to provide a reliable picture of the actinide oxidation state by Maurice et al.[31]

Results and Discussion

Observed Reactions

The anion complexes $NpO_2(C_2O_4)^-$ and $PuO_2(C_2O_4)^-$ were produced by ESI of solutions of neptunyl(V) or plutonyl(V) with sodium oxalate in ethanol. CID of mass-selected ions indicated a contribution at 357 m/z from $Na_4H(C_2O_4)_3^-$, which is isobaric with $NpO_2(C_2O_4)^-$; no such isobaric contaminant was apparent for $PuO_2(C_2O_4)^-$ at 362 m/z (Supporting Information Fig, S1).

Isolation of $NpO_2(C_2O_4)^-$ and $PuO_2(C_2O_4)^-$ resulted in spontaneous exothermic replacement of C_2O_4 by O_2, reaction (1), a phenomenon that was previously observed for $UO_2(C_2O_4)^-$.[22] As is apparent from the results shown in Figure 1, both $UO_2(C_2O_4)^-$ and UO_4^- efficiently add H_2O, which is present as a background gas in the ion trap, whereas the corresponding Np and Pu species are much less reactive with H_2O. Reaction (1) was confirmed as the source of NpO_4^- and PuO_4^-, where the four oxygen atoms are naturally abundant (99.8%) ^{16}O, by admitting isotopically enriched $^{18}O_2$ into the trap and observing the appearance of $Np^{16}O_2{}^{18}O_2^-$ and $Pu^{16}O_2{}^{18}O_2^-$ (Supporting Information Fig. S2).

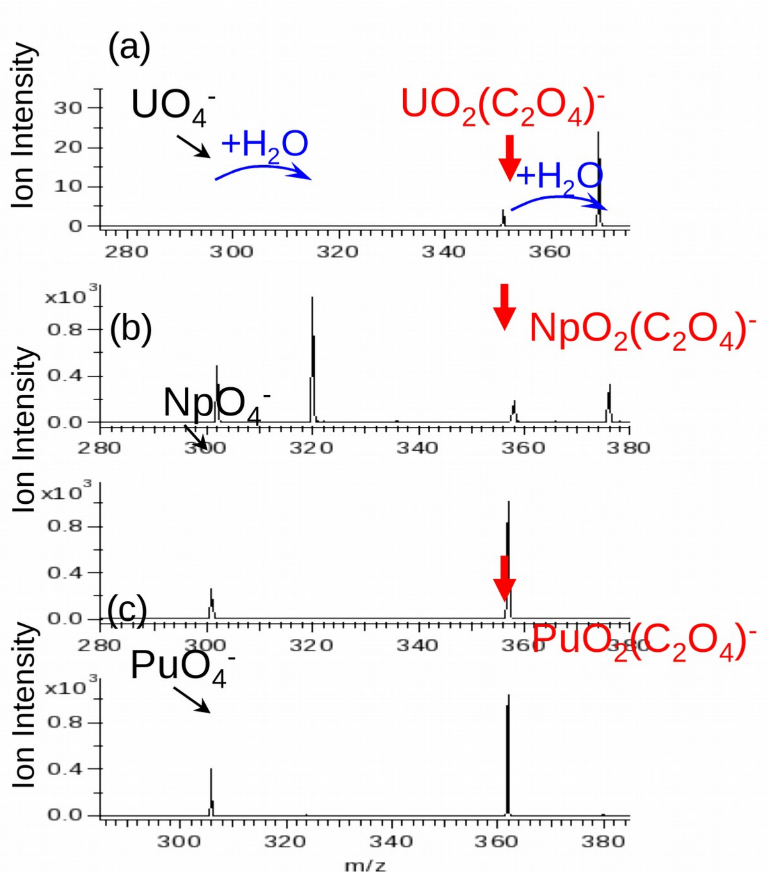

Figure 1. Mass spectrum acquired after isolation for 500 ms of (a) $UO_2(C_2O_4)^-$, (b) $NpO_2(C_2O_4)^-$ and (b) $PuO_2(C_2O_4)^-$ in the ion trap under the same conditions. The identified AnO_4^- are products of reactions with background O_2. The results for $UO_2(C_2O_4)^-$ reported previously[22] and are included here for direct comparison.

The apparently lower reactivity of NpO_4^- and PuO_4^-, as compared with UO_4^-, towards H_2O suggests a higher stability of these two transuranic tetroxide anions. The reactions with H_2O according to reaction (2) were quantified by isolating the three AnO_4^- for variable reaction times and then acquiring mass spectra.

$$AnO_4^- + H_2O \rightarrow AnO_5H_2^- \qquad (2)$$

Representative spectra are shown in Fig. 2 for reactions of NpO_4^- and PuO_4^- for 4 s. Whereas less than half of these tetroxides reacted with water under these condition, UO_4^- contrastingly converted to >90% $UO_5H_2^-$ within less than 1 s under the same reaction conditions. Pseudo-first order rates obtained for the three AnO_4^- under the same reaction conditions indicate that the rate of reaction (2) for An = U is approximately 40 times faster than for An = Np or Pu, with the rates for the latter two AnO_4^- being roughly comparable to within a factor of two. These results confirm that UO_4^- is substantially more susceptible to water addition than are NpO_4^- and PuO_4^-.

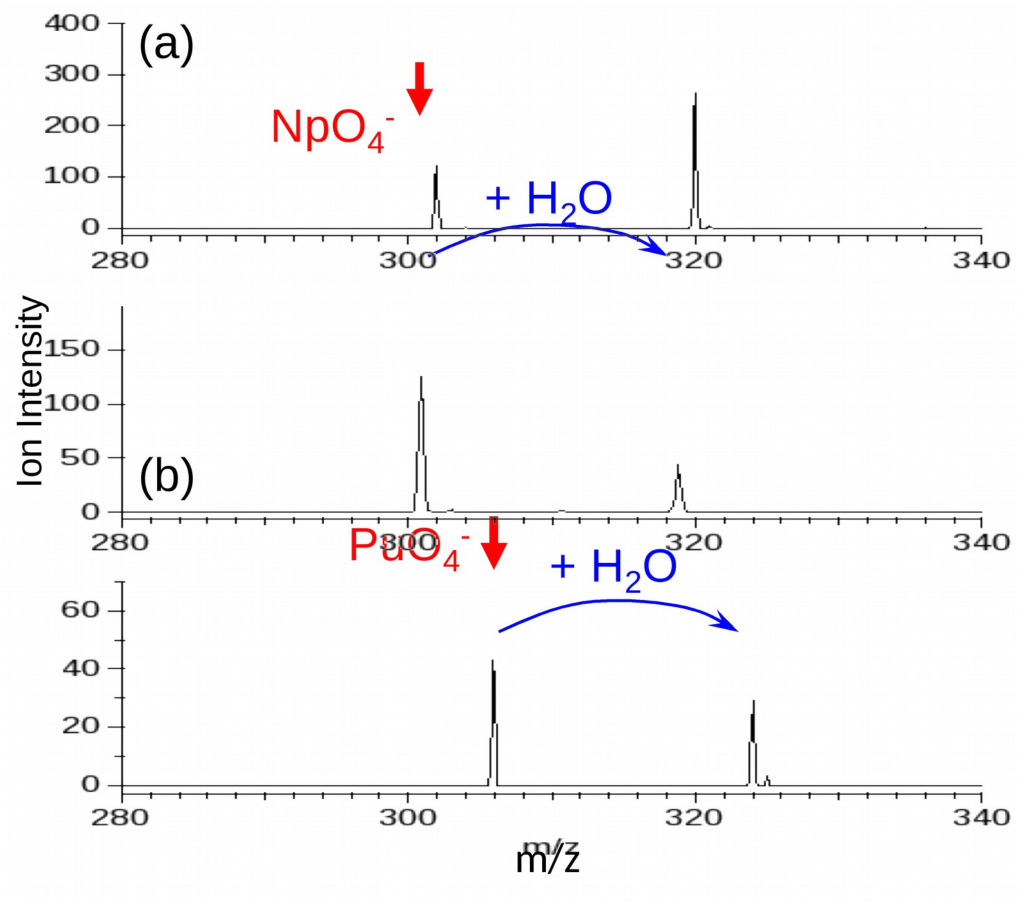

Figure 2. Mass spectrum acquired after isolation for 4 s of (a) NpO_4^- and (b) PuO_4^- in the ion trap under the same conditions. The two water-addition processes occur at similar rates to within a factor of two, and at a rate ~30 times slower than the corresponding reaction of UO_4^- as is evident in Fig. 1.[22]

The experimental results suggest that the nature of NpO_4^- and PuO_4^- may be similar to one another and different than that of UO_4^-. The latter was previously computed as a U(VI) superoxide complex with two U=O double bonds and two U-O bonds each having a bond order of ~1.5. The hypothesis based on the observations is that NpO_4^- and PuO_4^- are tetroxides with four An=O double bonds and oxidation states Np(VII) and Pu(VII). As discussed below, computational results that substantiate this hypothesis are in accord with the experimental observations.

Computed Structures and Reaction Energies

The computed lowest-energy structures of $NpO_2(C_2O_4)^-$ and $PuO_2(C_2O_4)^-$ have actinyl(V) moieties with a bidentate-coordinated $C_2O_4^{2-}$ ligand, as was reported for $UO_2(C_2O_4)^-$.[22] The spin-states are triplet for the Np complex and quartet for the Pu complex, with both exhibiting pentavalent actinide oxidation states. All computed structures and energies are included in Supporting Information. Computed reaction energies are given in Table 1, while the charges, spin-population and assigned oxidation states are shown in Table 2. Addition of H_2O to both $NpO_2(C_2O_4)^-$ and $PuO_2(C_2O_4)^-$ is computed to be exothermic by approximately -70 kJ/mol via physisorption hydration, with chemisorptive hydrolysis significantly less exothermic. This contrasts with $UO_2(C_2O_4)^-$, which was computed to add water via chemisorption hydrolysis with a substantial higher exothermicity of -171 kJ/mol. In accord with these disparate computed energies, and different natures of water-addition, this process was observed for $UO_2(C_2O_4)^-$ but not for $NpO_2(C_2O_4)^-$ or $PuO_2(C_2O_4)^-$ (Fig. 1). Hydrolysis of $AnO_2(C_2O_4)^-$, which involves no change in oxidation state, results in disruption of the O=An=O actinyl moiety to yield a $O{=}An(OH)_2$ bis hydroxide. The present results indicate that neptunyl and plutonyl are less susceptible towards this disruption as compared with uranyl, a result in correspondence to previous findings that oxo-exchange of actinyls with water becomes decreasingly favorable from uranyl to plutonyl due to increasing An=O bond covalency.[32,33]

Table 1. Computed reaction energies (kJ/mol). The values in parenthesis are the reaction energies with the spin-orbit correction included.

	Np	**Pu**
$AnO_2(C_2O_4)^- + H_2O \rightarrow AnO_2(C_2O_4)(H_2O)^-$	-71	-67
$AnO_2(C_2O_4)^- + H_2O \rightarrow AnO(C_2O_4)(OH)_2^-$	-55	-26
$AnO_2(C_2O_4)^- + O_2 \rightarrow AnO_2(C_2O_4)(O_2)^-$	-127 (-80)	-45 (-74)
$AnO_2(C_2O_4)(O_2)^- \rightarrow AnO_4^- + 2(CO_2)$	-47 (-170)	-40 (-64)
$AnO_2(C_2O_4)^- + O_2 \rightarrow AnO_4^- + 2(CO_2)$	-174 (-250)	-85 (-138)
$AnO_4^- + H_2O \rightarrow AnO_4(H_2O)^-$	-53	-53
$AnO_4^- + H_2O \rightarrow AnO_3(OH)_2^-$	-75	-72

Table 2. Spin States, Mulliken Atomic Charges (q), Atomic Spin Populations (μ) of Actinyl Oxygens, and Assigned Oxidation States for $NpO_2(C_2O_4)^-$, $PuO_2(C_2O_4)^-$, $NpO_2(C_2O_4)(O_2)^-$, $PuO_2(C_2O_4)(O_2)^-$, NpO_4^-, and PuO_4^-.

Species	**An**	q_{An}	μ_{An}	q_O	μ_O	$q_{O\text{-}O2}$	$\mu_{O\text{-}O2}$	**oxidation/ spin state**
$AnO_2(C_2O_4)^-$	Np	1.55	2.25	-0.64	-0.11			V / $5f^2$ triplet
	Pu	1.48	3.39	-0.58	-0.18			V / $5f^3$ quartet
$AnO_2(C_2O_4)(O_2)^-$	Np	1.67	1.16	-0.55	-0.06	-0.20	0.50	VI / $5f^1$ triplet
	Pu	1.63	2.33	-0.49	-0.15	-0.22	0.50	VI / $5f^2$ quartet
AnO_4^-	Np	1.61	0.00	-0.65	0.00			VII / $5f^0$ singlet
	Pu	1.42	1.40	-0.61	-0.10			VII / $5f^1$ doublet

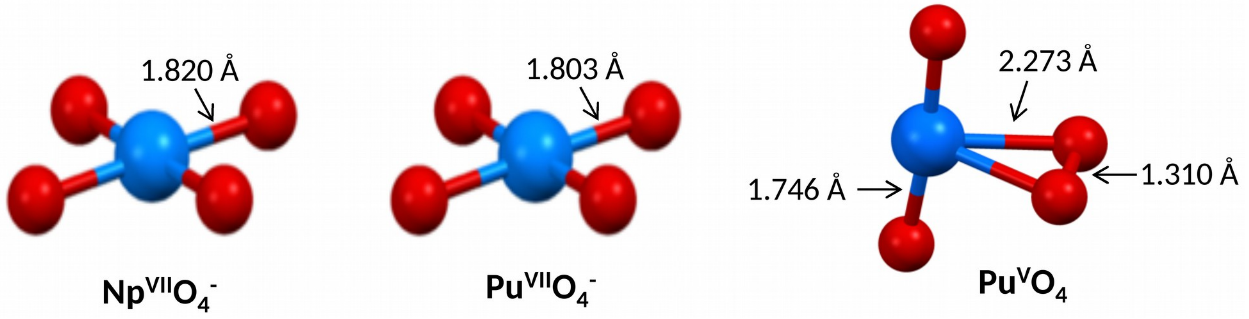

Figure 3. Computed structures of anions NpO_4^-, PuO_4^- and neutral PuO_4. The two anions are square planar with O-An-O bond angles of 90°. Neutral PuO_4 is plutonyl(V) coordinated by a superoxide ligand; the O_{yl}-Pu-O_{yl} bond angle is 176.6°.

The computed structures of ground-state singlet NpO_4^- and doublet PuO_4^- are shown in Figure 3. Both are square planar with bond lengths only slightly greater than for the corresponding actinyls, indicative of slightly elongated An=O double bonds. The structures and spin-states indicate that these species comprise heptavalent Np(VII) and Pu(VII). Earlier work also found the square planar NpO_4^- as the ground-state isomer.[34,35] Bolvin and coworkers[34] attributed the preference of a planar versus a tetrahedral structure to neptunium accepting more electrons from the oxygens via covalent bonding of the 5f-orbitals. The D_{4h} square planar PuO_4^- is similar to the neutral PuO_4 structure proposed by Straka et al.[36] that was later found to be meta-stable by Huang et al.[35] which was later determined to be a meta-stabl As indicated in Table 1, reaction (1) is computed to be exothermic by -174 kJ/mol and -85 kJ/mol for An = Np and Pu, respectively. The net reaction (1) is considered to proceed via addition of O_2 to $An(V)O_2(C_2O_4)^-$ to yield superoxides $An(VI)O_2(C_2O_4)(O_2)^-$, reaction (3), where the nature of the product is based on the spin states and structures, including the O-O distances that are characteristic of superoxide ligands (Supporting Information).

$$AnO_2(C_2O_4)^- + O_2 \rightarrow AnO_2(C_2O_4)(O_2)^- (3)$$

The computed energies for reaction (3) for An = Np and Pu are -127 kJ/mol and -45 kJ/mol, respectively, which would be anticipated to be much more similar based on the condensed-phase oxidation potentials for Np(V) (-1.16 V) and Pu(V) (-0.94 V), both of which are substantially lower than that of U(V) (-0.09 V).[1] When spin-orbit coupling is included the computed energies for reaction (3) become very similar (-80 kJ/mol and -74 kJ/mol for Np and Pu respectively), in accord with the experimental observation. Spin-orbit coupling does not change the thermodynamics for reaction (1). It was previously reported that reaction (3) is exothermic by -218 kJ/mol for An = U. Elimination of carbon dioxide from the products of reaction (3) according to reaction (4) results in net reaction (1) = (3) + (4), and the observed AnO_4^- products.

$$AnO_2(C_2O_4)(O_2)^- \rightarrow AnO_4^- + 2(CO_2) \qquad (4)$$

In contrast to reaction (3), the computed energy for reaction (4) is similar for An = Np (-47 kJ/mol) and An = Pu (-40 kJ/mol) when spin-free DFT results are considered. Although accurate An(VII/VI) oxidation potentials are not known, it is well established that Np(VII) is a significantly more stable oxidation state than Pu(VII).[1,37] Given that reaction (4) corresponds to oxidation from An(VI) to An(VII) one would expect that it should be more energetically favorable for Np than Pu. Here again, when spin-orbit effects are accounted for (see Table 1) the exothermic computed reaction energy for Np becomes significantly more favorable than that of Pu. As is apparent in Figure 1, the rates for reaction (4) are roughly comparable, suggesting that neither reaction exhibits substantial barriers; this interpretation is in accord with the proposed nature of the reaction as association of an intact O_2 molecule followed by elimination of a C_2O_4 ligand that is presumed to promptly dissociate to two CO_2 molecules due to very weak binding in neutral O_2C-CO_2. No barrier due to cleavage of a strong bond is associated with displacement reactions such as these. Reaction (4) was previously computed to be endothermic by +78 kJ/mol for An = U. The faster rate of net reaction (1) for An = U may be related to the higher exothermicity for association reaction (3).

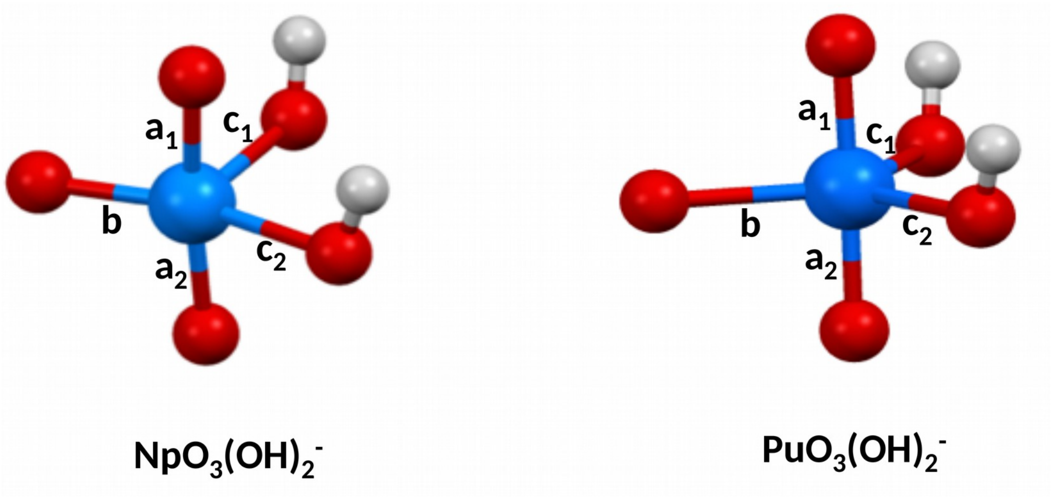

Figure 4. Computed structures of $NpO_5H_2^-$ and $PuO_5H_2^-$. The indicated bond distances are as follows (in Å). $NpO_5H_2^-$: $a_1 = 1.77$; $a_2 = 1.70$; $b = 1.84$; $c_1 = 2.19$; $c_2 = 2.16$. $PuO_5H_2^-$: $a_1 = 1.76$; $a_2 = 1.75$; $b = 2.13$; $c_1 = c_2 = 2.19$.

Both NpO_4^- and PuO_4^- spontaneously and exothermically add H_2O, with the computed lowest-energy product structures being the chemisorption hydroxides shown in Figure 4. The ground state for $NpO_5H_2^-$ is a Np(VII) $5f^0$ singlet that lies only 15 kJ/mol lower in energy than the Np(VI) $5f^1$ open-shell (OS) singlet in which the $5f^1$ electron is spin-paired with the electron on the radical O atom. In contrast, for $PuO_5H_2^-$ has three different electronic states that are found to be close in energy at the DFT level of theory. The Pu(VI) $5f^2$ OS doublet structure is found to be the ground state, 19 kJ/mol lower energy than the Pu(VII) $5f^1$ doublet and 8 kJ/mol lower than the Pu(VI) $5f^2$ quartet. These energy differences for both Np and Pu are relatively small, suggesting that both spin-orbit coupling and multi-reference techniques will be required to make definitive statements about the group state of the AnO_4^- species. The essential difference between these species is revealed by the short $Np{=}O_{eq}$ bond distance (b = 1.84 Å) as compared with the longer single $Pu\text{-}O_{eq}$ bond distance (b = 2.13 Å) as shown in Fig. 4. Reaction (5), which is reaction (2) but with the hydroxide product structures specified, occurs for both An = Np and Pu, with the products having the different oxidation states, Np(VII) and Pu(VI).

$$An(VII)O_4^- + H_2O \rightarrow AnO_3(OH)_2^- \quad (5)$$

This result demonstrates the slightly greater intrinsic stability of Np(VII) versus Pu(VII), with the difference here computed as 34 kJ/mol = 0.35 eV. Notably, this rather small disparity is similar to the estimated difference between the Np(VII/VI) and Pu(VII/VI) reduction potentials.[1]

Converting Pu(V)O_4 to Pu(VII)O_4^-

The neutral PuO_4 molecule was previously reported as a Pu(V) species with a plutonyl superoxide structure.[35] Computations performed for this species in the present work yielded essentially the same result, with the computed structure of PuO_4 included in Fig. 3. The bond distances, as well as the charges on the O atoms, are in accord with the assignment as Pu(V) with an O_2^- ligand. Neutral NpO_4 is less pertinent than PuO_4 in the context of high actinide oxidation states, particularly the octavalent state, because Np has only seven valence electrons outside of the [Rn] core such that oxidation states above Np(VII) are not viable.

The results for PuO_4 and PuO_4^- indicate reaction (6), in which addition of an electron to neutral PuO_4 counterintuitively results in oxidation of Pu(V) to Pu(VII).

$$\mathrm{Pu(V)O_4} + e^- \rightarrow \mathrm{Pu(VII)O_4^-} \qquad (6)$$

Reaction (6) is exothermic by 247 kJ/mol = 2.56 eV, which is thus the predicted computed electron affinity of PuO_4. Addition of an electron to a metal-containing complex typically results in reduction of the metal center, such as addition of an electron to $U(VI)F_6$ to yield $U(V)F_6^-$ where the added electron resides on the uranium metal center.[38] The idiosyncratic oxidation of PuO_4 upon addition of an electron is enabled by the superoxide ligand, which gets reduced to two oxygen dianion ligands.

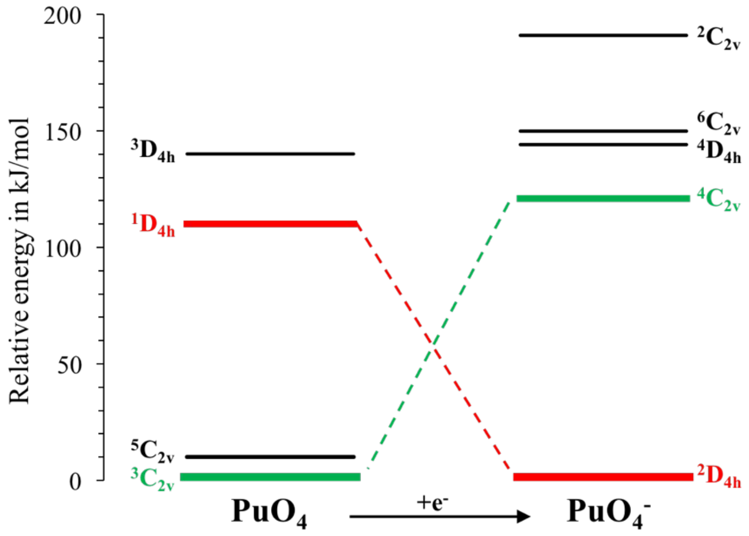

Figure 5. Relative energies (in kJ/mol) of different isomers. Superoxide structures are designated by C_{2v}, the square planar structures have the label D_{4h}, and the superscript defines the spin-state.

The relative energies for the superoxide and square planar structures for both the PuO_4 and PuO_4^- are shown in Figure 5. A similar picture can be drawn for neptunium. The ground-state of the neutral PuO_4 can be formally represented as $Pu^{5+}(O^{2-})_2(O_{2-})$, or alternatively and equivalently as the plutonyl(V) superoxide complex $(PuO_2^+)(O_2^-)$.[35] In contrast, there are no O-O bonds in square planar PuO_4^- but rather four Pu=O double bonds, which can formally be represented in the extreme ionic model as $[Pu^{7+}(O^{2-})_4]^-$. The square planar isomer for the neutral species is 110 kJ/mol less stable than the superoxide isomer. However, when an electron is added the square planar isomer becomes more stable than the superoxide by 120 kJ/mol. Analysis of the electronic structure shows that the extra electron does not reduce the plutonium, but instead reduces the superoxide to a chemically meta-stable peroxide. In essence, addition of an electron to PuO_4 results in reduction of the superoxide moiety, $O_2^- + 3e^- \rightarrow 2(O^{2-})$, concomitant with two-electron oxidation from Pu(V) to Pu(VII). The phenomenon is essentially a manifestation of the low stability of the Pu(VIII) oxidation state in the structure of PuO_4 in which all of the valence electrons have been removed to yield a closed-shell $5f^0$ configuration; instead O-O bonding and a Pu(V) oxidation state are favored. Rather than forming four Pu=O double bonds in neutral PuO_4 the more energetically favorable situation is to form two Pu=O (plutonyl) bonds and two Pu-O bonds each with a formal bond order of 0.5 and a Pu configuration of essentially $5f^3$. The Pu(VII) oxidation state is sufficiently stable that addition of an electron to PuO_4 results in oxidation of Pu(V) with destruction of the O-O superoxide bonding.

Summary

The two new molecular oxide anions NpO_4^- and PuO_4^- were synthesized by an unusual spontaneous exothermic gas-phase displacement reaction: the oxalate dianion ligand in $NpO_2(C_2O_4)^-$ and $PuO_2(C_2O_4)^-$ is replaced by dissociated O_2, with elimination of neutralized oxalate as two CO_2 molecules. The observed similar rates of addition of water to these two tetroxide anions, which are much slower than the rate of addition to $U(VI)O_4^-$, suggested that they have similar structures, and possibly the heptavalent oxidation state that would differentiate them from the uranium congener.

Computed reaction energies are in accord with experimental observations, providing confidence in the validity of the computational results. The computations confirm the hypothesis that the new tetroxide anions are the heptavalent species, $Np(VII)O_4^-$ and $Pu(VII)O_4^-$. This is the first report of Pu(VII) in a bare gas-phase Pu(VII) molecule, and the first report of both Np(VII) and Pu(VII) as elementary molecular oxides, this demonstrating the intrinsic stabilities of these heptavalent oxidation states absent stabilizing effects in condensed phase environments.

Both $Np(VII)O_4^-$ and $Pu(VII)O_4^-$ spontaneously add H_2O to yield AnO_5H_2, which are computed to be chemisorption hydroxides, $AnO_3(OH)_2^-$, rather than physisorption hydrates, $AnO_4(H_2O)^-$. $NpO_3(OH)_2^-$ is computed as a Np(VII) species, essentially neptunyl(VI), NpO_2^{2+}, coordinated by one O^{2-} ligand (i.e. an $Np=O_{eq}$ double bond) and two OH^- hydroxides. In contrast, $PuO_3(OH)_2^-$ is computed as Pu(VI) with an O^- ligand (i.e. a $Pu-O_{eq}$ single bond). Hydrolysis of NpO_4^- according to reaction (5) results in retention of the Np(VII) oxidation state whereas for PuO_4^- reduction to Pu(VI) occurs. This result reveals the (slightly) lower intrinsic stability of Pu(VII) versus Np(VII).

An intriguing result of this work is the structure and oxidation state of anionic PuO_4^- in comparison with that previously reported, and confirmed here, for neutral PuO_4. The oxidation state is Pu(V) in PuO_4, with a plutonyl moiety coordinated by a superoxide ligand, O_2^-. Addition of an electron to PuO_4 yields PuO_4^- in which the oxidation state is Pu(VII) with Pu forming four Pu=O double bonds in a square planar structure. Conversion of PuO_4 to PuO_4^- occurs by oxidation of Pu(V) ($5f^3$) to Pu(VII) ($5f^1$) concomitant with reduction of O_2^- to $2(O^{2-})$. The unusual phenomenon of metal oxidation by addition of an electron is enabled by the redox active dioxygen ligand that exhibits the ability of the two O atoms to form strong bonds with one another, and thereby form M-O bonds with formal bond orders ranging from 0.5 in superoxides, (O_2^-) to 1 in peroxides (O_2^{2-}), to 2 in conventional oxides (O^{2-}).

Supporting Information

CID spectra of $NpO_2(C_2O_4)^-$ and $PuO_2(C_2O_4)^-$; mass spectra for reactions of $NpO_2(C_2O_4)^-$ and $PuO_2(C_2O_4)^-$ with a $^{16}O_2/^{18}O_2$ mixture; mass spectra for reactions of $Np^{16}O_4^-$ and $Pu^{16}O_4$ with $H_2{}^{18}O$; computed structures of $AnO_2(C_2O_4)^-$ and $AnO_2(C_2O_4)(O_2)^-$ for An = Np, Pu; computational results for all considered Np and Pu species.

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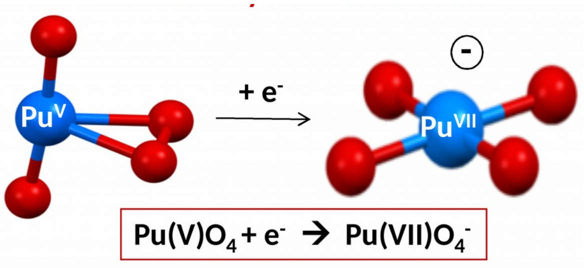
TOC



A heptavalent plutonium oxide molecule was prepared by spontaneous gas-phase replacement of the oxalate ligand in $Pu^{V}O_2(C_2O_4)^{-}$ by O_2 to yield $Pu^{VII}O_4^{-}$ and two CO_2 molecules. Whereas the oxidation state in the neutral PuO_4 molecule has been reported as Pu^{V}, addition of an electron results in counterintuitive oxidation to Pu^{VII}.

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