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Structural and Spectroscopic Characterization of Plutonyl(VI) Nitrate under Acidic Conditions

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Supporting Information

ABSTRACT: The plutonyl(VI) dinitrate complex $[PuO_2(NO_3)_2(H_2O)_2]\cdot H_2O$ (**1**) has been structurally characterized by single-crystal X-ray diffraction and spectroscopically characterized by solid-state vis-NIR and Raman spectroscopies. Aqueous solution spectroscopic studies indicate only weak plutonyl(VI) nitrate complexation, with the mononitrate complex dominating and negligible dinitrate formation, even in concentrated nitric acid.

The aqueous chemistry of plutonium (Pu) is extremely complex. Under appropriate conditions, five oxidation states (III–VII) are accessible and often multiple oxidation states are present simultaneously.[1] Pu and uranium (U) complexation by the weakly coordinating nitrate (NO_3^-) anion is of importance because nitric acid is utilized extensively in the dissolution of used nuclear fuel and is therefore present in the subsequent steps of solvent extraction and separation.[2] The structure and speciation of plutonium(IV) nitrate complexes have been studied, stability constants determined, and the limiting species identified as the hexanitrate $[Pu(NO_3)_6]^{2-}$ anion.[3] Uranyl(VI) nitrate complexation has been studied in aqueous and organic media as well as in the solid state.[3b,4] While there is evidence that up to three nitrates may coordinate UO_2^{2+} in aqueous solution, a recommended thermodynamic equilibrium constant of $\log \beta_1^\circ = 0.30 \pm 0.15$ exists only for the $UO_2NO_3^+$ mononitrate.[3b] In contrast, relatively little is known about the speciation, stability, and structures of the plutonyl(VI) dioxo cation (PuO_2^{2+}) with nitrate in aqueous acidic solutions. A recent review states that the only species known to be significant in aqueous solution is the $PuO_2NO_3^+$ mononitrate,[1] but other literature is conflicting and suggests that di- and trinitrate complexes also exist (see the Supporting Information).[5] Addressing these uncertainties has the potential of improving the ability to predict and control Pu(VI) speciation under industrially relevant nuclear fuel processing conditions. Moreover, it is this applied relevance, coupled with a fundamental interest in the chemistry of the actinyl moieties, that has increased recent research on the chemistry of Pu(VI).[6]

Crystals of $[PuO_2(NO_3)_2(H_2O)_2]\cdot H_2O$ (**1**) suitable for X-ray diffraction were grown by evaporation of an aqueous solution of Pu(VI) in nitric acid (see the Supporting Information).[7] Single-crystal structural analysis of **1** reveals two independent molecules in the unit cell (Figure 1, Table 1, and the Supporting Information). Each molecule consists of a plutonyl(VI) dioxo cation coordinated to two trans bidentate nitrate anions and two trans water molecules. Compound **1** also crystallizes with a lattice water molecule. The geometry around the eight-coordinate Pu center is best described as distorted hexagonal-bipyramidal.[8]

The linear dioxo PuO_2^{2+} moiety has an average Pu–O distance of 1.728(7) Å, which falls within the range (1.69–1.77 Å) observed in other structurally characterized plutonyl(VI) dioxo cations.[6] The nitrate anions in **1** are coordinated with an average Pu–O distance of 2.497(11) Å, which is longer than the average Pu–O distance for the bound water molecules [2.432(9) Å] in **1**, reinforcing the fact that nitrate is a very weak chelator to Pu(VI).

Compound **1** is the first structurally characterized aquo adduct of plutonyl(VI) nitrate. The only other examples of plutonyl(VI) nitrates are the recently reported triphenylphosphine oxide (TPPO) complex of formula $[PuO_2(NO_3)_2(TPPO)_2]$[6d] and two N-alkylated 2-pyrrolidone (NRP) complexes of formula $[PuO_2(NO_3)_2(NRP)_2]$,[9] all crystallized from organic solvents (alcohols) rather than aqueous solutions. The TPPO complex has an average Pu–O distance for the coordinated nitrate anions of 2.522(3) Å, which is slightly longer than the corresponding distance in **1** and is probably a reflection of the steric demands of TPPO, which is coordinated closer to the Pu center [Pu–O of 2.353(2) Å] than the water molecules in **1**. The NRP ligands are less sterically encumbered than TPPO, and the Pu–O (nitrate) distances in the Pu^{VI}–NRP complexes are statistically identical with those in **1**.

Another bonding property to analyze is the effect of the actinide contraction upon bond distances in actinyl(VI) nitrate complexes. $[UO_2(NO_3)_2(H_2O)_2]\cdot H_2O$ is isostructural with **1**;[10] the nitrate anions are coordinated with an average U–O distance of 2.497(14) Å, and the water molecules are coordinated with an average U–O distance of 2.447(9) Å, which are statistically identical with those in **1**. However, it is worth pointing out that the unit cell volume is 11.3 $Å^3$ smaller for Pu(VI) compared to the U(VI) analog, which may be a reflection of the actinide contraction. No analogous Np(VI) or Am(VI) nitrate structures are reported for comparison with **1**.

The structural characterization of the plutonyl(VI) dinitrate complex **1** afforded the possibility of acquiring definitive spectroscopic signatures on the pure solid compound for a direct comparison to solution spectra. This would allow the determination of whether or not "$Pu^{VI}O_2(NO_3)_2$" exists in nitric acid solutions. The visible–near-IR (vis–NIR) spectrum of Pu(VI) in 1 and 3.2 M HNO_3 is indistinguishable from that of

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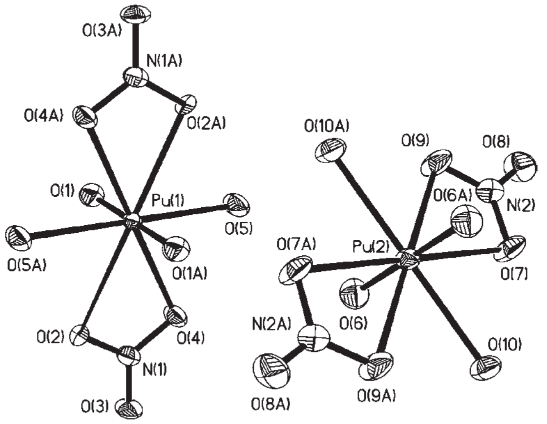

Figure 1. Thermal ellipsoid plot (50% probability level) of the structure of **1** showing the two independent molecules in each unit cell. The two outer-sphere water molecules have been omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1

Pu(1)−O(1)	1.727(5)	Pu(2)−O(6)	1.728(5)
Pu(1)−O(2)	2.519(5)	Pu(2)−O(7)	2.503(7)
Pu(1)−O(4)	2.472(5)	Pu(2)−O(9)	2.492(5)
Pu(1)−O(5)	2.425(7)	Pu(2)−O(10)	2.438(5)
O(1)−Pu(1)−O(1A)	180.0(0)	O(6)−Pu(2)−O(6A)	180.0(0)
O(2)−Pu(1)−O(4)	50.97(15)	O(7)−Pu(2)−O(9)	51.1(2)
O(2)−Pu(1)−O(5A)	64.9(2)	O(7)−Pu(2)−O(10)	65.22(19)
O(4)−Pu(1)−O(5)	64.15(19)	O(9)−Pu(2)−O(10A)	63.94(18)

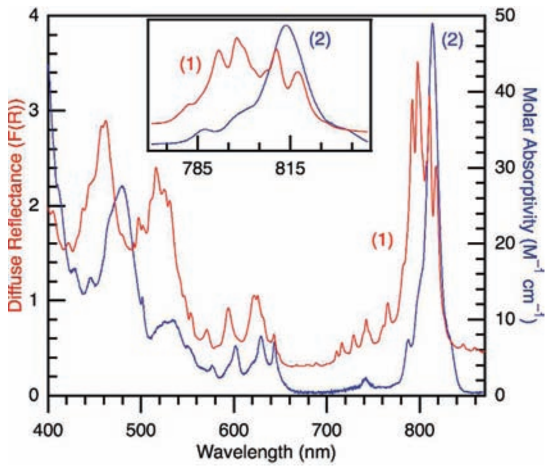

Figure 2. Vis-NIR diffuse-reflectance spectrum of crystalline plutonyl(VI) dinitrate **1** [spectrum (1), left axis]. The solution electronic absorption spectrum of 3.50 mM Pu(VI) in 15.2 M HNO_3 is shown for comparison [spectrum (2), right axis]. The inset shows an expansion of the 775−825 nm region.

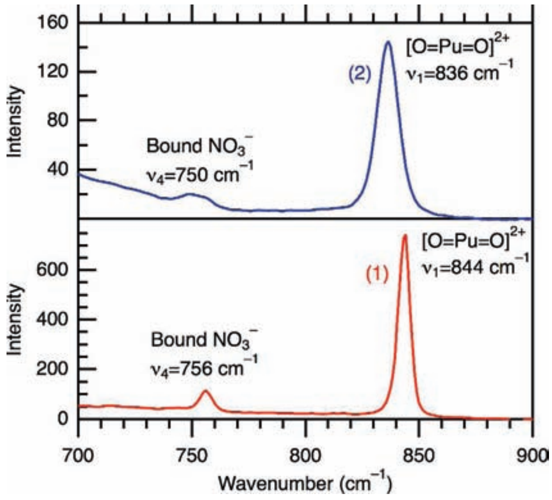

Figure 3. Raman spectra of (1) solid plutonyl(VI) dinitrate **1** and (2) 0.39 M Pu(VI) in a 15.2 M HNO_3 solution.

the PuO_2^{2+} aquo ion in 1 M $HClO_4$, indicative of negligible nitrate complexation.

At HNO_3 concentrations of 5.8 M and above, there are observable changes in the Pu(VI) vis−NIR spectrum (Figure S1 in the Supporting Information). Noticeably, the characteristic PuO_2^{2+} aquo ion 830 nm absorbance ($^3H_{4g} \rightarrow {}^3\Pi_{2g}$ transition)[11] decreases in intensity, and a new band at 815 nm grows in. We attribute this change in the electronic absorption spectrum to an increasing concentration of the first plutonyl(VI) nitrate complex, $PuO_2NO_3^+$. Above HNO_3 concentrations of 11.9 M, the 815 nm band still dominates but begins to drop in intensity, while a shoulder at 800 nm grows in (Figure S1 in the Supporting Information), which could be indicative of the onset of a second species at very high nitrate concentrations. Previous studies have demonstrated that if the same Pu(VI) species is present in both the solid state and solution, then the electronic absorption spectra show good correlation.[6a,b] The diffuse-reflectance spectrum of pure plutonyl(VI) dinitrate compound **1** was collected and is markedly different from the solution vis−NIR spectra of Pu(VI) in nitrate media (Figure 2). The 775−825 nm region is complex, with four prominent bands exhibited (λ_{max} at 792.0, 797.6, 810.4, and 817.6 nm). While complex to interpret why this pure species displays multiple peaks in the $^3H_{4g} \rightarrow {}^3\Pi_{2g}$ transition region of the spectrum, the spectra bear strong similarity to the signature of plutonyl(VI) carbonates in both the solution and solid state. For instance, while PuO_2CO_3 displays one intense band near 813 nm in both the solution and solid state,[7,12] $PuO_2(CO_3)_3^{4-}$ displays multiple less intense peaks centered at a lower wavelength.[13,14] Therefore, given the difference between the solution and solid-state spectra, the vis−NIR data suggest that the dinitrate *does not* form to an appreciable extent, even in concentrated 15.2 M HNO_3.

Turning to Raman spectroscopy, Pu(VI) in 1 M $HClO_4$ displays a symmetrical O═Pu═O stretching vibration, ν_1, at 836 cm^{-1} (Figure S2 in the Supporting Information), in agreement with previously reported values.[15] In 15.2 M HNO_3, the PuO_2^{2+} ν_1 vibration was unchanged at 836 cm^{-1}, but a new band at 750 cm^{-1}, attributed to the ν_4 vibration of coordinated NO_3^-, was observed (Figure 3) and can likely be attributed to the mononitrate complex $PuO_2(NO_3)^+$. In analogous uranyl nitrate solution Raman studies, similar behavior has been observed. In this case, the absence of change in the ν_1 symmetrical O═U═O stretch energy in high-nitrate media has been attributed to the weak nature of actinyl nitrate complexation.[16] The Raman spectrum of solid plutonyl dinitrate **1** (Figure 3) exhibits bands at 844 and 756 cm^{-1}, which are assigned to the ν_1 stretch vibration of plutonyl and the ν_4 vibration of bound NO_3^-, respectively. There is some experimental evidence with solid uranyl nitrates that ν_1 increases with the number of bound nitrates.[17] Here, the absence of the 844 cm^{-1} band in the solution spectra strengthens the conclusions from the vis−NIR data that the dinitrate complex is not present to an appreciable extent, even in a concentrated nitric acid solution.

In summary, we have structurally characterized the first aqueous plutonyl(VI) nitrate complex (**1**), probed its spectroscopic electronic and vibrational signatures, and concluded that these signatures are not significantly present in nitric acid solutions. This casts doubt on previous postulations that the dinitrate species is a significant component of solution speciation. We hope that additional studies will lead to the determination of thermodynamic parameters and that specialized spectroscopic tools, such as extended X-ray absorption fine structure, can be utilized to further confirm solution speciation.

■ ASSOCIATED CONTENT

Supporting Information. A CIF file for **1**, vis−NIR and Raman spectra of plutonium(VI) in HNO_3, and a plutonyl(VI) nitrate solution chemistry literature study. This material is available free of charge via the Internet at http://pubs.acs.org.

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