High-Yield Synthesis and Single-Crystal X-ray Structure of a Plutonium(III) Aquo Complex: $[Pu(H_2O)_9][CF_3SO_3]_3$

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Detailed structural studies of plutonium complexes are rare. Thus, the coordination chemistry basics, such as ligand affinities, preferred coordination numbers, and geometries of plutonium complexes, are inferred from d- and f-block ions that are thought to be similar or related. To improve chemical separations processes and enhance ion-specific ligand design, direct determination of actinide molecular structures and bond distances is needed. Because of their simplicity and prevalence in nuclear materials processing and environmental chemistry, aqueous complexes are particularly important to fully characterize.

The hydration numbers for the actinide ions have been investigated using a number of methods, including luminescence, extended X-ray absorption fine structure (EXAFS), and nuclear magnetic resonance (NMR).[1] Studies using luminescence lifetimes have estimated 9.2 ± 0.5 bound waters for curium(III).[2] For americium(III), Carnall concluded a hydration number of 9 based on similarities in optical spectra of $AmCl_3$, Am(III) doped in $LaCl_3$, and Am(III) aqueous solutions.[3] From EXAFS studies, a value of 8−10 has been estimated for aqueous plutonium(III).[1b,e] Detailed relativistic density functional calculations suggest 8 or possibly 9 ligating water molecules.[4]

Like the lanthanides, actinide metals are very easily oxidized; however, unlike the lanthanides, the resulting actinide ions can easily vary in oxidation states from III to VI and even, with some difficulty, VII. Classically, most plutonium chemistry starts with dissolution of the metal in hydrochloric, perchloric, or nitric acid. This produces a stock solution of plutonium(III) from which other oxidation states and compounds can be made. Dissolution of plutonium metal in triflouromethanesulfonic (triflic) acid also produces a plutonium(III) solution. Triflic acid has advantages over the commonly used acids because the triflate anion is much more weakly coordinating than chloride and nitrate and does not have the potential hazards of perchlorate. Additionally, triflate often forms a strong hydrogen bond, which provides the basis for an extended H-bonding network and well-ordered solids.

Isostructural triflates have been prepared and crystallized for nearly all the lanthanide ions.[5] This allows for direct structural comparison within the lanthanide series. Preparation of the analogous actinide compounds would allow for comparison within the actinide series and between 4f and 5f ions.

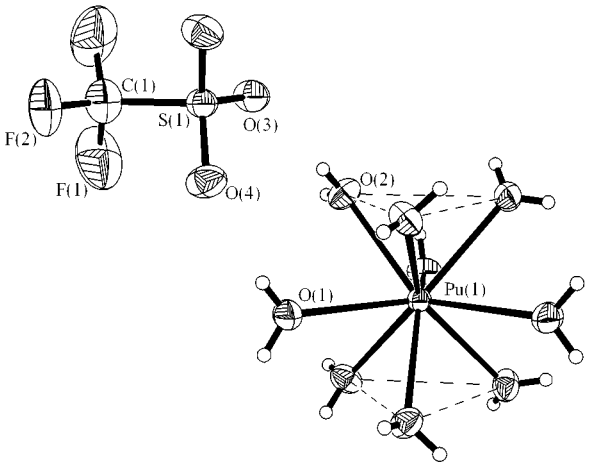

Figure 1. Thermal ellipsoid plot (40%) of $[Pu(H_2O)_9][CF_3SO_3]_3$.

The plutonium triflate molecule reported here was prepared by simple dissolution of plutonium metal in triflic acid followed by concentrating the resultant solution.[6] The crystals are isotypic to the lanthanide triflates, crystallizing in the hexagonal space group $P6_3/m$ with $a = 13.9283(6)$ Å and $b = 7.3816(4)$ Å.[7] The plutonium(III) is coordinated by 9 water molecules arranged in an ideal tricapped, trigonal-prismatic (TCTP) geometry (Figure 1). The two unique plutonium aquo bond distances are to O(1), 2.574(3) Å (capping), and O(2), 2.476(2) Å (prismatic). The weighted average of the plutonium to water distances of 2.51 Å compares very well to those reported in two separate EXAFS studies of plutonium(III) in dilute chloride solutions of 2.51 and 2.49 Å.[1b,e] The plutonium to water distance is, as expected, longer than those within a plutonium(IV) complex. The recently reported 9-coordinate distorted TCTP Pu(IV) complex, $[Al(H_2O)_6][Pu(DFE)(H_2O)_3]_2[CF_3SO_3]_5$, contains Pu(IV) bound to prismatic waters at 2.461(12), 2.472(11), and 2.456(12) Å.[11] Theoretical calculations have closely predicted the plutonium to water

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(6) Preparation of $[Pu(H_2O)_9][CF_3SO_3]_3$: 0.050 g (2.09×10^{-4} mol) of ^{239}Pu strips was added to 2 mL of 1.0 M CF_3SO_3H, giving a blue solution. The solution was concentrated to saturation (0.20 mL, 1.1 M Pu(III)) and placed into a refrigerator at 7 °C overnight. Large blue crystals were isolated and washed with cold ethanol, 0.170 g, 96% yield.

(7) Single-crystal X-ray analysis on the title compound was performed on a Bruker P4/CCD/PC system. A hemisphere of data was collected using a combination of ϕ and ω scans, with 0.3° frame widths. The data were corrected for absorption using an analytical technique.[8] Crystal data: hexagonal, space group $P6_3/m$, $a = 13.9283(6)$ Å, $b = 7.3816(4)$ Å, $Z = 2$, $V = 1240.16$ Å^3, $T = 218$ K, ρ(calc) = 2.280 g/cm^3, $\mu = 3.046$ mm^{-1}, $\lambda = 0.71073$ Å, $2\theta_{max} = 56.92°$, total data = 6672, unique data = 1068 ($R_{int} = 0.0322$), R1/wR2 [$I > 2\sigma(I)$] = 0.0243/0.0452. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were clearly located in a difference Fourier map and refined isotropically. SHELXTL version 5.1 was used for structure solution, refinement based on F^2, graphics and publication materials.[9,10]

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Table 1. Selected Interatomic Distances in $[Pu(H_2O)_9][CF_3SO_3]_3$

metal complex	M−O(1) (cap)	M−O(2) (prism)	O(1)···O(3)	O(2)···O(3)	O(2)···O(4)	ref
La	2.611(2)	2.513(2)	2.932(2)	2.843(3)	2.753(2)	4b
Nd (X-ray)	2.571(2)	2.451(2)	2.945(2)	2.841(2)	2.754(2)	4b
(neutron)	2.572(2)	2.469(2)	2.945(2)	2.816(2)	2.752(2)	4b
Sm	2.548(2)	2.418(2)	2.953(2)	2.831(3)	2.755(2)	4b
Lu	2.519(5)	2.287(4)	3.012(4)	2.797(6)	2.739(5)	4b
Pu	2.574(3)	2.476(2)	2.927(3)	2.833(3)	2.759(3)	this work

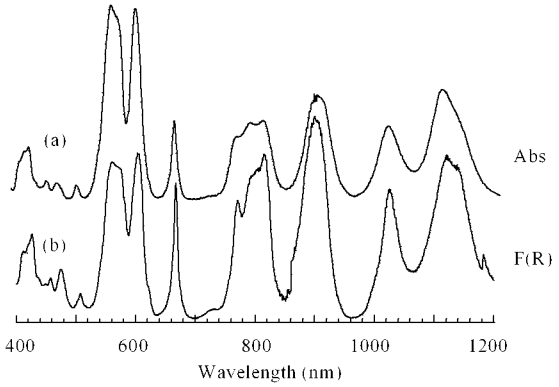

Figure 2. UV/vis/near-IR spectra for $[Pu(H_2O)_9][CF_3SO_3]_3$: (a) in 1 M triflic acid solution; (b) diffuse reflectance of neat ground single crystals.

distances of 2.585 and 2.491 Å for the prismatic and capping waters, respectively.[4]

The study of the lanthanide triflate salts has shown that the difference in distances between the capping waters and the prismatic waters increases from 0.1 to 0.2 Å across the series, suggesting that with the lanthanide contraction, nonacoordination becomes less stable.[12] This was attributed to the differential contraction of the lanthanide to water bonds as a consequence of an electronic influence of the metal center.[5b,c] The capping waters which are bound in a trigonal fashion (in contrast to the tetrahedrally oriented prismatic waters) have a repulsive contribution because across the series the polarization of the electron density at the metal center increases more rapidly in the direction of the capping waters. The analogous difference in the title compound is 0.098 Å, which compares well with the beginning of the lanthanide series. Neodymium and europium(III) are often used as surrogates for the trivalent light actinides (U−Cm) because of comparable ionic radii. Our data show that the metal to water bond distances for the plutonium compound (vide supra) do compare most favorably with those in the neodymium compound, which has bond distances of 2.572(2) Å (capping) and 2.451(2) Å (prism) from X-ray studies and 2.572(2) and 2.469(2) Å from neutron diffraction studies.[5b]

All of the bound waters hydrogen bond to triflate anions: O(1) with O(3) and O(2) with O(4) and O(3) of another triflate. Table 1 is a summary of the bond distances for the plutonium complex and three of the lanthanide complexes. In the lanthanide series, the hydrogen bond to the capping water lengthens (weakens) across the series, while the prismatic water hydrogen bonding somewhat shortens (strengthens). The Pu(III) and Nd(III) complexes have the same (within error) M−O(1) bond distances; however, the M−O(2) distance is ca. 0.02 Å longer in the Pu(III) structure. This suggests that on a relative basis, Nd has stronger interactions with the tetrahedrally configured waters than Pu does. These differences are also reflected in a shorter hydrogen bond in the plutonium structure between O(1) and O(3). The prismatic water (O(2)) in the Pu(III) structure has a hydrogen bond interaction comparable to that in the Nd(III) structure, consistent with the similar metal to O(1) distance.

This single-crystal X-ray structure verifies the nonacoordinate plutonium(III) ion in the solid state. To infer the hydration number of plutonium(III) in solution we measured the solid-state diffuse reflectance spectrum of ground single crystals and compared it with the solution UV/vis/near-IR spectrum of plutonium(III) in triflic acid (Figure 2).

The spectra suggest similar chromophores in solution and the solid state, supporting the conclusion that plutonium(III) in aqueous acidic solutions is predominantly 9-coordinate.

This compound is important not only because it is the first single-crystal X-ray discrete molecular structure containing plutonium(III), but also because it is an easily prepared starting material. The crystals are prepared in quantitative yield. And in contrast with most actinide salts isolated from acid solutions, the triflate salt is acid free. Thus, this compound provides a preferred entry into plutonium chemistry, particularly for extractions, synthesis, and solution thermodynamic studies.

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Supporting Information Available: A packing diagram viewed down the *a*-axis and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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