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Plutonium(IV) Cluster with a Hexanuclear $[Pu_6(OH)_4O_4]^{12+}$ Core

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Supporting Information

ABSTRACT: A mixed hydroxo/oxo plutonium(IV) carboxylate resulting from the hydrolysis and condensation of Pu^{IV} in an acidic aqueous solution has been isolated. The structure of $Li_6[Pu_6(OH)_4O_4(H_2O)_6(HGly)_{12}]Cl_{18}\cdot 10.5H_2O$ (**1**) consists of a cationic $[Pu_6(OH)_4O_4]^{12+}$ core that is decorated by glycine ligands. The synthesis, structure, and characterization of the hexanuclear unit, which represents the first example of a Pu^{IV} polynuclear complex containing both hydroxo- and oxo-bridging ligands, are described herein.

Hydrolysis and condensation reactions play an important role in governing solution thermodynamics and the overall fundamental chemistry of metal cations.[1] This is especially true for metal ions of high charge density and acidity that undergo these reactions to produce hydr(oxo) complexes even under very acidic conditions. Generally exemplified by the tetravalent metal ions, hard ions readily form polynuclear species and ultimately colloidal phases whose chemical and structural speciation is critical to their chemistry. The resulting oligomers have chemistries very different from those of their mononuclear precursors, as is evidenced by their catalytic and electrochemical behavior,[2] surface complexation,[3] and resultant environmental transport.[4] The actinide, An^{IV}, ions provide an opportunity to systematically study trends in hydrolysis chemistry, specifically the compounds that form, their structures, and their reactivity.[1c,4a,b,5]

The An^{IV} ions, Th−Pu, are stable in aqueous solution and form a chemical series wherein a systematic decrease in the ionic radius is accompanied by an increase in the metal ion's charge density and acidity.[6] The importance of these changes and their relative effect on hydrolysis and condensation reactions can be independently probed to understand this complex, often intractable chemistry within the broader context of the periodic table. Known hydroxo/oxo compounds isolated from aqueous solutions of Th^{IV} include dimeric hydroxo and hexameric and octameric hydr(oxo) complexes.[5a,6a] Tetrameric[7] and pentameric[8] oligomers have also been proposed. The speciation of Pu^{IV} is much more complex. The propensity of Pu^{IV} to hydrolyze and form polynuclear phases has been widely studied because of its detrimental impact on metal separations and tendency to form intractable precipitates.[5a,9] Relatively little is known regarding the composition and structure of oligomers that exist in solution and occur somewhere between the mononuclear hydrolysis products and what is known as the Pu polymer.[10] Lower-order Pu^{IV} polynuclear complexes are largely absent from thermodynamic descriptions of aqueous speciation[5a,b,6b,11] Recently, a well-defined Pu^{IV}-oxo cluster containing 38 Pu atoms has been isolated and its structure determined.[3,12] Pu−Pu correlations matching those seen in the solid-state structure have been observed in solutions containing the polymer, which together with their facile separation using a carboxylic acid support the hypothesis that the Pu polymer is comprised of chemically and structurally well-defined clusters. However, with the exception of one Pu^{IV} dimer,[13] there are no other reports characterizing the solid-state structure of plutonium oxo/hydroxo oligomeric species.

Published structural work on metal oligomers provides direction for further study. A number of carboxylate donor ligands have been used to isolate $[An_6(OH)_4O_4]^{12+}$ cluster cores,[14] and the aqueous and/or solid-state structures of related glycine-complexed clusters have been described for Th^{IV},[15] Np^{IV},[16] and Zr^{IV}.[17] Glycine is the simplest of the amino acids, and the pK_a values for the carboxyl and amino groups are 2.34 and 9.6, respectively. Under acidic conditions, the free ligand exists predominately in its fully protonated state ($^+H_3NCH_2CO_2H$). At pH values ranging from 4 to 8, it exists primarily as the neutral zwitterion ($^+H_3NCH_2CO_2^-$), and under more basic conditions, deprotonation of the amino group results in the anionic species ($H_2NCH_2CO_2^-$). Glycine has been used to isolate $[Zr_6(OH)_8]^{16+}$[17b] and $[Zr_6(OH)_4O_4]^{12+}$[17a] cluster cores, and both the anionic and neutral ligands have been shown to exist in one Zr^{IV} (hydr)oxo structure.[17a] It is thus capable of accommodating various charges on the cluster core and provides a suitable ligand for isolating An^{IV} clusters, whose protonation state may depend on the solution conditions and/or the overall acidity of the complex. In an effort to complement previous structural studies and to extend our understanding of hydrolysis/condensation chemistry across the An^{IV} series, we report a mixed OH/O-bridged Pu^{IV} hexanuclear cluster complexed by glycine ligands.

Caution! *Experiments were performed with* ^{242}Pu, *an* α*-emitting isotope, in a radiological facility using strict controls that allowed for the safe handling and manipulation of the material.* Single crystals of $Li_6[Pu_6(OH)_4O_4(H_2O)_6(HGly)_{12}]Cl_{18}\cdot 10.5H_2O$ (**1**) were prepared by evaporation of an aqueous solution made by the addition of a $^{242}Pu^{IV}$/HCl solution (100 μL of a 56 mM solution; 0.006 mmol of ^{242}Pu), 1 M glycine (0.006 mmol), and 1 M LiOH (50 μL, 0.05 mmol). Orange platelike crystals of **1** were isolated after more than 1 week. Prior to the formation of **1**, reddish-orange blocks of **2** were formed. The structures of **1** and **2** were determined using single-crystal X-ray diffraction. Because of difficulties associated with the refinement of **2**, we herein report

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the details of the refinement and structure of only **1**.[18] Cell parameters for **2** and a comment on the structure are provided.[19]

The structure of **1** consists of a mixed hydroxo/oxo $[Pu_6O_4(OH)_4]^{12+}$ core built from six Pu^{IV} cations bridged by four μ_3-O and four μ_3-OH groups (Figure 1). Overall, each Pu^{IV} is nine-coordinated, bound to four O atoms from the μ_3-OH/O groups (O1 and O2), one bound water molecule (O3), and four O atoms (O4–O7) from four bridging glycine ligands. Glycine zwitterions link adjacent Pu^{IV}, resulting in a net cationic molecular complex, $[Pu_6(OH)_4O_4(H_2O)_6(HGly)_{12}]^{12+}$. Noncoordinating Cl^- ions balance the excess positive charge of the cluster as well as the Li^+ cations present in the structure.

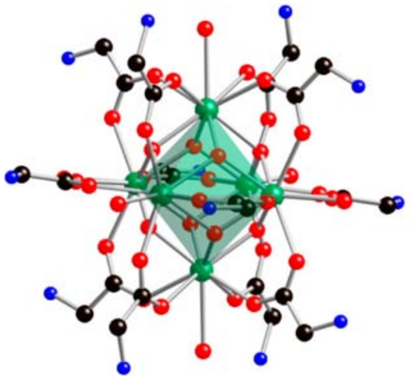

Figure 1. Illustration of the glycine-decorated $[Pu_6(OH)_4O_4(H_2O)_6]^{12+}$ core observed in **1**.

The H atoms of the μ_3-OH groups were not located during refinement; however, the Pu–O bond distances (Table 1) for O1 and O2 are longer than expected for a Pu–O bond but shorter than expected for a Pu–OH bond. Elongated thermal ellipsoids for O1 and O2 are consistent with disordering of the μ_3-OH and μ_3-O atoms on the faces of the cluster. A relatively longer Pu–O3 distance is consistent with that of bound water. The Pu cation was found to have a bond-valence-summation value consistent with that of Pu^{IV}.

Table 1. Summary of the Pu–O and Pu–Pu Distances in 1

	N	distance (Å)
$Pu-O(H_2)$	1	2.688
$Pu-\mu_3$-O/OH	4	2.29(2)
$Pu-O(CO_2^-)$	4	2.42(6)
$Pu\cdots Pu_{adjacent}$	4	3.770(2)
$Pu\cdots Pu_{terminal}$	1	5.331

The hexanuclear core described herein exhibits structural similarities with the Pu_{38} nanoclusters[12] and bulk PuO_2, suggesting that it may be related to the larger aggregates as well as the parent oxide. The average Pu–O distance in the cluster core of **1** is 2.29(2) Å, in good agreement with the Pu–O distances observed in the Pu_{38} cluster and bulk PuO_2, which average 2.30 and 2.33 Å, respectively. The Pu–O distances compare particularly well with those of the Pu^{IV} cations within the Pu_{38} cluster that are near the center and corners of the core, which have distances of 2.32–2.35 and 2.30–2.37 Å, respectively. The $Pu-O(H_2)$ distance of 2.688(3) Å for the bound water molecule in **1** is longer than those in the Pu_{38} cluster, which range from 2.46 to 2.53 Å. The distances in **1** are consistent with the Th hexamers, which have relatively long $Th-O(H_2)$ bond distances and for which density functional theory calculations found that the water molecules of solvation had little effect on the geometry/electronic structure of the cluster core.[20] Such similarities between the Pu_6 and Pu_{38} clusters as well as the oxide point to an opportunity to understand the magnetic and electronic effects in oxidic Pu phases as a function of the cluster size.

Compound **1** was further characterized by Raman spectroscopy (Figure 2). For comparison, the spectrum of a pH 6 glycine solution, where the zwitterion is the prevalent solution species, was also collected. The spectrum of **1** is dominated by stretches characteristic of the glycine ligand, but shifts attributable to metal-ion complexation are observed. For example, the C–C stretching mode at 916 cm^{-1} in complex **1** is observed at 899 cm^{-1} for the free ligand. The broad peak at 449 cm^{-1} in the spectrum of **1** is noticeably absent from the glycine spectrum and is likely attributed to a Pu–O stretch.

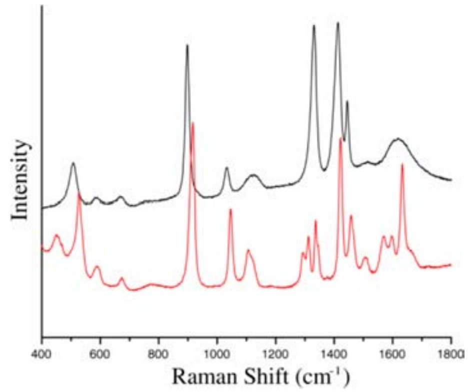

Figure 2. Raman spectrum of **1** (red) compared with that of a pH 6 glycine solution (black) over 400–1800 cm^{-1}.

The solution and solid-state structures of mixed OH/O Th^{IV} [14,15] and U^{IV} [21] hexanuclear cores, similar to that in **1**, have been reported. Moreover, extended X-ray absorption fine structure (EXAFS) data suggest the presence of a Np^{IV} hexanuclear cluster in solution.[16] Interestingly, all of the An^{IV} hexamers isolated from aqueous solution and reported to date are mixed OH/O complexes with equal combinations of oxo and hydroxo ligands. Similar clusters have also been observed for Zr^{IV},[17a] Ce^{IV},[22] and Bi^{III}.[23] Related structures differing in the number of hydroxo ligands and also by an additional μ_6-oxo group at their centers are fairly prevalent in Ln^{III} chemistry.[24] Isolation of the hexanuclear unit across the M^{IV} series and within other metal-ion systems suggests some similarity in their condensation behavior or at least that the hexamer is a common building unit that exists in the aqueous chemistry of many metal ions. For Pu, it was recently shown using EXAFS that hydrolyzed Pu^{IV} clusters show similarities with bulk PuO_2 and freshly prepared plutonium colloids show oligomers with 5–6 Pu atoms per cluster.[25] Such units are consistent with the hexanuclear core observed in this work.

Many of the reported hexanuclear clusters are decorated by monocarboxylate ligands. In addition to our report herein, glycine-complexed hexamers have been structurally characterized for Th^{IV},[15] Np^{IV},[16] and Zr^{IV}.[17] Like the core observed in **1**, the Th–glycine hexamer is built from a mixed OH/O core, $[Th(OH)_4O_4(H_2O)_6]^{12+}$, with a net cationic charge. The cluster is decorated by 12 glycine ligands; however, 6 of the glycine ligands are neutral, while the other 6 are anionic.[15] A similar example is found in a Zr–glycine complex.[17a] By contrast, the

$[Pu_6(OH)_4O_4(H_2O)_6]^{12+}$ core is ligated by 12 neutral glycine ligands, and the charge on the core is balanced entirely by Cl^- ions. Changes in the protonation state of glycine in the Zr, Th, and Pu complexes could result from differences in the solution conditions or alternatively may point to changes in the acidity of the metal ions or their complexes and the stability fields over which these units form for each of the metal ions.

The $[An(OH)_4O_4(H_2O)_6]^{12+}$ cluster appears to be a prevalent unit in An^{IV} solution and solid-state chemistry, yet details of the relative conditions over which these units form and are stable are unclear. The presence of complexing ligands and counterions in solution confound our understanding of the underlying fundamental chemistry. That is, there are two competing reactions in these systems—hydrolysis/condensation and complexation—and the degree to which one affects the other is unclear given the limited structural data available for both solution and the solid state. In common ligand systems other than glycine, such similarities are not observed within the An^{IV} series. For example, from chloride media, hydroxo bridged dimers have been isolated for thorium.[26] This is in contrast to the oxo-bridged Pu_{38} nanocluster that has been isolated for Pu.[12] For Pu, only one -OH bridged complex has been described.[13] Consistent with their known separation chemistry, such differences in size and composition point to the increased propensity of Pu^{IV} to hydrolyze compared to Th^{IV}. Admittedly, there still remains a relative paucity of data available to fully discern similarities and differences observed in An^{IV} oxo/hydroxo complexes and how they relate to the condensation behavior of the An^{IV} ions. The work reported here fills one gap in our understanding.

■ ASSOCIATED CONTENT

Supporting Information

Details of Pu^{IV}/HCl solution preparation, data collection and refinement of **1**, and X-ray crystallographic data for **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(18) Crystal data of **1**: M_r = 3461.88 g·mol^{-1}, crystal size = 0.19 × 0.09 × 0.06 mm, trigonal, $R\bar{3}$, a = 22.497(2) Å, b = 22.497(2) Å, c = 15.124(2) Å, α = 90°, β = 90°, γ = 120°, V = 6628.6(11) Å^3, Z = 3, ρ_{calcd} = 2.602 g·cm^{-3}, μ = 5.049 mm^{-1}, Mo Kα (0.71073 Å), T = 100 K, $2\theta_{max}$ = 52.8, measured reflections 25140, independent reflections 3038, R_{int} = 0.0480, R1 = 0.0220 [$I > 2\sigma(I)$], wR2 = 0.0454 (all data). Crystallographic data have been deposited with the CCDC and may be obtained at http://www.ccdc.cam.ac.uk/ by referencing CCDC 927720.

(19) Crystal data of **2**: tetragonal, $I4/mmm$, a = 12.5644(8) Å, b = 12.5644(8) Å, c = 25.3595(15) Å, α = 90°, β = 90°, γ = 90°, V = 4003.4(4), Mo Kα (0.71073 Å), T = 100 K. The structure is built from a hexanuclear $Pu_6(OH)_xO_{8-x}$ core that is decorated by 8 glycine ligands.

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