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Directed Synthesis of Crystalline Plutonium(III) and (IV) Oxalates: Accessing Redox-Controlled Separations in Acidic Solutions

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Abstract

Both binary and ternary solid complexes of Pu(III) and Pu(IV) oxalates have been reported in the literature. However, uncertainties regarding the coordination chemistry and the extent of hydration of some compounds remain due to the absence of any crystallographic characterization. We synthesized single crystals of hydrated oxalates of Pu(III), $Pu_2(C_2O_4)_3(H_2O)_6 \cdot 3H_2O$ (**I**), and Pu(IV), $KPu(C_2O_4)_2(OH) \cdot 2.5H_2O$ (**II**), under moderate hydrothermal conditions and characterized them spectroscopically and by using single crystal X-ray diffraction. Compounds **I** and **II** are the first plutonium III or IV oxalate compounds to be structurally characterized, and **II** contains the first overall reported mixed-ligand actinide(IV) oxalate. Crystallographic data for **I**: monoclinic, space group $P2_{1/c}$, $a = 11.246(3)$ Å, $b = 9.610(3)$ Å, $c = 10.315(3)$ Å, $Z = 4$ and **II**: monoclinic, space group $C_{2/c}$, $a = 23.234(14)$ Å, $b = 7.502(4)$ Å, $c = 13.029(7)$ Å, $Z = 8$.

Introduction

The oxalate anion has long been recognized as an excellent precipitating agent for lanthanide and transuranium separations owing to the remarkably low solubility of f-element oxalates in acidic solution.[1,2] Since the early days of plutonium chemistry, oxalate has been used to control redox behavior and to precipitate plutonium in its lower oxidation states, +III and +IV. In fact, oxalate precipitation has become a major step in the large-scale separation and purification processes of plutonium for the last 50 years.[1,2] Owing to the importance of plutonium oxalate compounds in chemical processing, significant attention has been paid to their solubilities and stabilities in aqueous systems and thermal stabilities for conversion to oxide.[3] Surprisingly, the composition and

structure of plutonium oxalates, and also those of the other transplutonium oxalates, are still under debate. While thermodynamic parameters have been reported for a significant number of transuraniium oxalate compounds, structural analysis has been limited to powder X-ray diffraction.[3] Few, if any, compounds have been studied crystallographically to determine their bonding and coordination geometries.

Due to their significant technological and academic importance, a number of oxalate compounds of the chemically analogous lanthanides are known that can guide our understanding of trivalent actinide oxalate solid state chemistry. The majority of those materials consist of two-dimensional structures comprised of hexagonal or rectangular 4- or 6-membered rings of the general formulas, $[Ln_l(H_2O)_m(C_2O_4)_n]_{4,6}$,[4-8] or $Ln_2(C_2O_4)_3$.[9-12] Cations and/or water molecules can be arranged interstitially between these layers. Interesting complexes of mixed ligands or mixed metals, such as $[Ce(H_2O)]_2[(C_2O_4)_2(CO_3)]\cdot2.5H_2O$[13] or $MM'(C_2O_4)_3(H_2O)_3\cdot nH_2O$,[14] are also derived from layers of 6-membered rings. Recently, there has been an increased effort to direct the synthesis of lanthanide oxalates towards three-dimensional architectures with potential ion-exchange abilities. Several three-dimensional lanthanide oxalates have been reported in which the lanthanide(III) oxalate layers are connected to form open frameworks, as well as several mixed ligand complexes which utilize a combination of both oxalate and other ligands to form their three-dimensional framework.[13,15-20] Trombe et al. synthesized $La(C_2O_4)_2\cdot NH_4$,[8] $(CN_3H_6)_2[Nd(H_2O)]_2(C_2O_4)_4\cdot3H_2O$ and $[N(CH_3)_4][Nd_2(H_2O)_3](C_2O_4)_{3.5}\cdot4H_2O$,[21] in which oxalate ligands connect the Ln(III) layers that are built up from $[Ln_x(H_2O)_y(C_2O_4)_z]_n$ units. Furthermore, Trombe was able to synthesize a 3-dimensional structure of $[N(CH_3)_4][Yb(C_2O_4)_2]$ with channels in all directions instead of connected layers.[21] Mixed Ln(III)/U(IV) oxalate structures have also shown characteristic honeycomb layers connected by oxalate ligands.[22] Oxalates of tetravalent metal centers with the general formula $K_4M(C_2O_4)_4\cdot nH_2O$, where M = Zr, Hf, U and Th, have also been synthesized.[23,24] Akhtar showed that in the latter compound ten-coordinate thorium is bound to five oxalate groups forming chains that are cross-linked by extended hydrogen bonding.

Routes to synthesize single-crystal quality materials of transuranium oxalates are difficult and thus limits our understanding of the structure of those compounds. Only

powder X-ray diffraction data are available for the binary An(III) oxalates, $An_2(C_2O_4)_3 \cdot 10H_2O$ (An = Pu, Am, Cm).[25-28] While the degree of hydration of An(III) oxalate precipitates remains under discussion, thermogravimetric measurements[27] and the analogy to $Ln_2(C_2O_4)_3 \cdot 10H_2O$[6,10,12] support the suggestion of Pu(III), Am(III), and Cm(III) decahydrates based upon their similar ionic radii. Slightly different levels of hydration, i.e., 9.2 H_2O,[11] 9.5 H_2O,[29] and 10.5 H_2O,[9] are attributed to variations of the disordered water between lattice layers. Furthermore, lower levels of hydration are reported upon thermal decomposition. Five hydrates of Pu(III) oxalates with the general formula $Pu_2(C_2O_4)_3 \cdot nH_2O$ are reported in air or argon, with the hydration number n equal to 10, 9, 2, 1, or 0 (only in Ar) depending on the temperature.[30] Sali *et al.* reports different thermal behavior in air, with the Pu(III) oxalate decahydrate dehydrating to a monohydrate at 100°C and then to the anhydrous form at 150°C.[31] In the range between 25° and 50°C , $Am_2(C_2O_4)_3 \cdot 7H_2O$ dehydrates to form the tetrahydrate continuing to the anhydrous Am(III) oxalate at 240°C via 3 additional hydrates.[32] Plutonium(IV) is reported to complex as $Pu(C_2O_4)_2 \cdot nH_2O$ ($n = 2$,[33] or 6[33,34]). Arab-Chapelet has reported unique mixed An(III)/An(IV) oxalates indicated by powder XRD.[35,36] Single crystal structural characterization of transuranium oxalates is thus far limited to $Np(C_2O_4)_2 \cdot 6H_2O$[37] and $H_2Np_2(C_2O_4)_5 \cdot 9H_2O$.[38] Despite these investigations, the nature of plutonium precipitates from oxalate-containing waste and reprocessing streams remains poorly understood. Understanding the nature of transuranium oxalate compounds formed under process conditions is critical to optimize conditions to remove plutonium from solution via precipitation. In this work, we provide the first single crystal characterization and spectroscopy of Pu(III and IV) oxalate compounds in the solid state.

Experimental

Taking advantage of both the high affinity and the reducing capacity of the oxalate anion towards actinide cations, we developed a redox-supported synthesis route that produced crystalline Pu materials for more efficient separation and structural exploration. Oxalate is a well known reductant in acidic medium, allowing the complete reduction of Pu(IV) to Pu(III).[1,2]

0.2 ml of a Pu(IV) solution (0.1 M Pu) in 1 M HCl was added to 2 ml of 0.5 M oxalic acid and heated to 80°C. Within days, blue Pu(III) crystals of poor quality at room temperature. The same compound was obtained by applying mild hydrothermal conditions (200°C) to a solution of 25 mM Pu(IV), 0.25 M HCl, and 1.3 M oxalic acid for 48 hours. Upon slow cooling (13C/hr), blue rectangular crystals formed (Figure 1-left). Single-crystal X-ray diffraction analysis revealed the crystalline product to be the binary hydrated Pu(III) oxalate, $Pu_2(C_2O_4)_3(H_2O)_6 \cdot 3H_2O$ (**I**).

Repeating the above hydrothermal reaction for 24 hours at 180°C, but with the addition of KOH to ~pH 3, inhibited the reduction of Pu(IV) to Pu(III) and a mixture of light and dark green Pu(IV) needles were obtained (Figure 1-right). Single-crystal X-ray diffraction analysis revealed the dark green compound to be the three-dimensional Pu(IV) oxalate, $KPu(C_2O_4)_2(OH) \cdot 2.5H_2O$ (**II**).
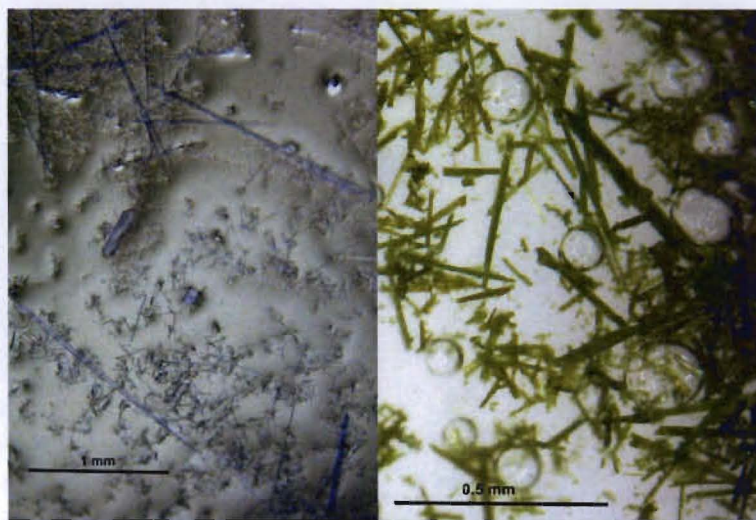
Figure 1: Blue crystals of **I** (left) and green crystals of **II** (right)

Crystallographic Studies

In order to mitigate the health hazards of plutonium, the crystals were contained in epoxy and sealed in a quartz capillary coated in acrylic. Data were collected on a Bruker Platform diffractometer with 1k CCD, and cooled to 141 K using a Bruker Kryoflex cryostat. The instrument was equipped with a sealed, graphite monochromatized MoKα X-ray source ($\lambda = 0.71073$ Å). A hemisphere of data was

collected using φ scans, with 30 second frame exposures and 0.3° frame widths. Data collection, initial indexing, and cell refinement were handled using SMART software.[39] Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT software,[40] and the data were corrected for absorption using the SADABS program.[41] Decay of reflection intensity was monitored *via* analysis of redundant frames. The structure was solved using Direct methods and difference Fourier techniques. Hydrogen atoms were not refined. For **I**, the final refinement included anisotropic temperature factors on all atoms. For **II**, the final refinement included anisotropic temperature factors on Pu and K atoms only (light atoms were refined isotropically due to absorption problems). Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[42] Table 1 shows the important crystallographic parameters for both **I** and **II**.

Table 1: Crystallographic data for $Pu_2(C_2O_4)_3(H_2O)_6 \cdot 3H_2O$ (**I**) and $KPu(C_2O_4)_2(OH) \cdot 2.5H_2O$ (**II**).

	$Pu_2(C_2O_4)_3(H_2O)_6 \cdot 3H_2O$ (**I**)	$KPu(C_2O_4)_2(OH) \cdot 2.5H_2O$ (**II**)
FW (g/mol)	446.03	505.14
a (Å)	11.246(3)	23.234(14)
b (Å)	9.610(3)	7.502(4)
c (Å)	10.315(3)	13.029(7)
α (deg)	90.00	90.00
β (deg)	114.477(4)	99.980(10)
γ (deg)	90.00	90.00
volume (Å^3)	1014.6(5)	2237(2)
Z	4	8
R-factor %	3.94	9.17
Space Group	P 2$_1$/c	C 2/c
System	monoclinic	monoclinic

Results and Discussion

The two-dimensional structure of **I** consists of [PuO₉] polyhedra that are linked through the carboxylate groups in the [C₂O₄] ligands to form staggered layers in the crystallographic *ac* plane with an extended network of water molecules between the

layers. Six oxygen atoms from three chelating oxalate anions and three additional oxygens from coordinated water molecules complete a distorted tricapped trigonal-prismatic geometry around the plutonium atom. Figure 2 shows a thermal ellipsoid plot of a coordination polyhedra of **I**. Table 2 lists selected bond lengths and angles.
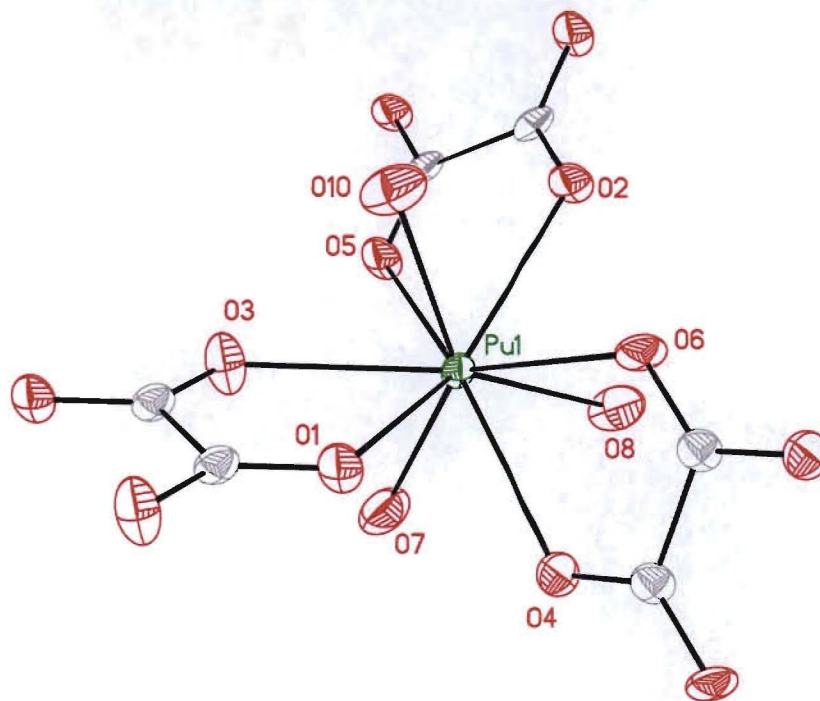

Figure 2: Thermal ellipsoid (50% probability) plot of the plutonium coordination and atomic numbering scheme in $Pu_2(C_2O_4)_3(H_2O)_6 \cdot 3H_2O$ (**I**).

Table 2: Selected bond distances (Å) and angles (degree) for $Pu_2(C_2O_4)_3(H_2O)_6 \cdot 3H_2O$ (**I**)

$Pu_2(C_2O_4)_3(H_2O)_6 \cdot 3H_2O$ (**I**)	
Pu1—O1	2.528(6)
Pu1—O2	2.521(6)
Pu1—O3	2.562(8)
Pu1—O4	2.525(7)
Pu1—O5	2.480(6)
Pu1—O6	2.482(7)
Pu1—O7	2.513(8)
Pu1—O8	2.552(7)
Pu1—O10	2.503(7)
C1—C1	1.566(17)

C2—C2	1.523(18)
C3—C3	1.59(2)

O1—Pu1—O3	62.9(2)
O2—Pu1—O5	64.9(2)
O4—Pu1—O6	64.9(2)
O7—Pu1—O8	71.9(3)
O7—Pu1—O10	143.8(3)
O8—Pu1—O10	136.4(2)

The Pu–O bond lengths for the three bound waters of 2.50, 2.51, and 2.55 Å, for O(10, 7, and 8) respectively, are slightly shorter than the reported bond length for a capping water in the Pu(III) aquo complex, $[Pu(H_2O)_9][CF_3SO_3]_3$, of 2.574(3) Å.[43] The Pu–O_{ox} bond distances range from 2.480 to 2.562 Å and are close to those found in other trivalent lanthanide oxalate compounds. The *bis*-chelating oxalate ligands assume the common planar geometry with bond distances and angles consistent with those reported in the literature. The basic building unit in the layer consists of a six-membered ring $[Pu(C_2O_4)]_6$ using $C(1)_2O_4$ and $C(3)_2O_4$ ligands, exhibiting an aperture of about 8.2 x 9.3 Å (Figure 3). The Pu--Pu distances range from 6.18 to 6.58 Å and the Pu-Pu-Pu angles are 104.59, 119.39 and 129.99°.
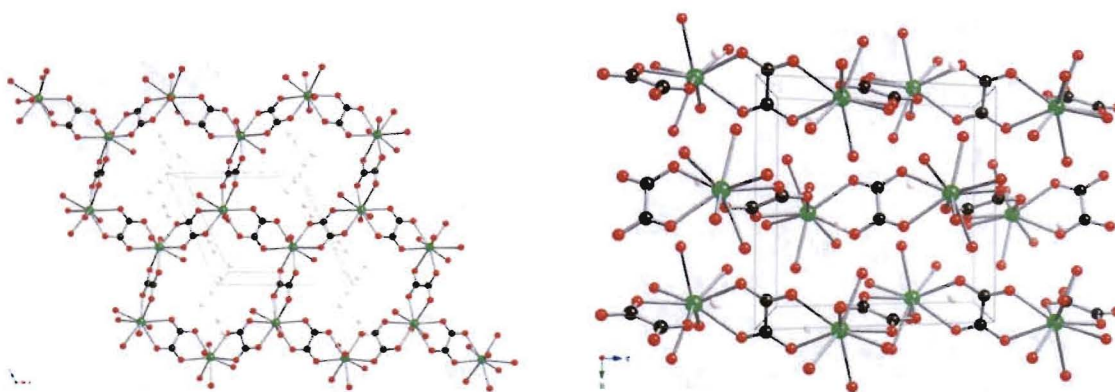
Figure 3: Packing in $Pu_2(C_2O_4)_3(H_2O)_6 \cdot 3H_2O$ (**I**): (left) honeycomb structure along the *b* axis and (right) layers in the *ab* plane.

In contrast to **I**, compound **II** is a 3D-network of $[PuO_9]$ polyhedra that are linked in all directions by $[C_2O_4]$ groups. The nine-coordinate plutonium atom is bound to eight oxygen atoms from four *bis*-chelating oxalate ligands and one oxygen atom from a

coordinated water molecule to complete a distorted tricapped prismatic geometry. Figure 4 shows a thermal ellipsoid plot of the coordination polyhedra in **II**, while Table 3 lists selected bond lengths and angles. The $Pu-O_{ox}$ bond distances range between 2.454 and 2.507 Å which are in close agreement with those found in **I**, ranging from 2.480 to 2.562 Å. The four oxalate groups are arranged circularly around the Pu atom while the hydroxide ligand lies above that base. This arrangement is very similar to that found in the molecular structure of $[C(NH_2)_3]_5[Nd(CO_3)_4(H_2O)] \cdot 2H_2O$ where four bidentate carbonate ligands form the corner of a pseudo-square pyramid with a coordinated water molecule at the top.[44]
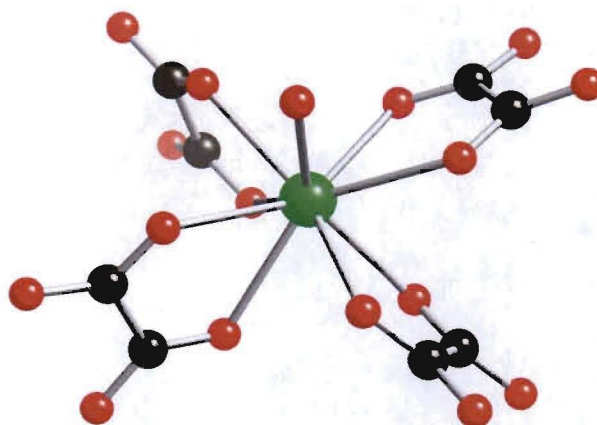

Figure 4: Thermal ellipsoid (50% probability) plot of the plutonium coordination and atomic numbering scheme in $KPu(C_2O_4)_2(OH) \cdot 2.5H_2O$ (**II**).

Table 3: Selected bond distances (Å) and angles (degree) for $KPu(C_2O_4)_2(OH) \cdot 2.5H_2O$ (**II**).

$KPu(C_2O_4)_2(OH) \cdot 2.5H_2O$ (**II**)	
Pu1—O1	2.54(2)
Pu1—O2	2.547(19)
Pu1—O3	2.463(15)
Pu1—O4	2.491(18)
Pu1—O5	2.50(2)
Pu1—O6	2.508(18)
Pu1—O7	2.50(2)
Pu1—O8	2.500(16)
Pu1—O9	2.46(2)
C1—C1	1.66(4)
C2—C2	1.58(5)
C3—C3	1.58(5)

O1—Pu1—O2	62.5(7)
O3—Pu1—O8	67.3(5)
O4—Pu1—O7	65.8(6)
O5—Pu1—O6	65.1(6)

Within the crystallographic *ab* plane six [PuO$_9$] polyhedra and six oxalate ligands form a honeycomb structure with approximately 8.3 x 12.3 Å apertures, which are filled with K atoms and water molecules (Figure 5). Channels with approximate dimensions of 5.5 Å x 4.5 Å run down the *b* axis and are lined by four [PuO$_9$] polyhedra and four oxalate ligands.
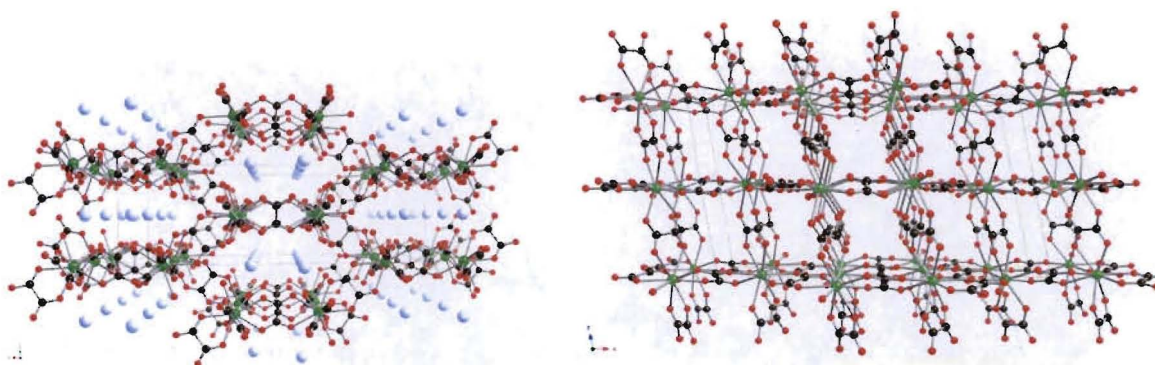

Figure 5: Packing in KPu(C$_2$O$_4$)$_2$(OH)•2.5H$_2$O (**II**): (left) honeycomb structure along the *c* axis and (right) view down the *b* axis showing the three-dimensional channel structure. Interstitial water and K atoms are omitted for clarity.

The most critical aspect of the structural analysis of **II** is the terminal Pu–O$_{OH}$ bond since it affects the nominal oxidation state calculated from the charges of the coordinated ligands. A neutral water molecule would result in a +III charged Pu ion, while a coordinated hydroxo group would indicate a Pu(IV) center. Clearly, the Pu–O bond length of 2.504 Å is significantly longer than the O=Pu=O distances of 1.812 Å in the Pu(V) complex, [Co(NH$_3$)$_6$][PuO$_2$(C$_2$O$_4$)$_2$]•3H$_2$O,[45] and also longer than the plutonyl-oxygen bond lengths of 1.75 and 1.81 Å found in the Pu(VI) solution species, PuO$_2$^{2+} and PuO$_2$(OH)$_4$^{2-}, respectively.[46] This clearly rules out the existence of the V and VI oxidation states of the Pu atom in compound **II**. While the the Pu–O bond length found in **II** is unusually long for a terminal Pu-OH bond, it is comparable to the Pu-OH$_2$ distances observed in **I** (2.503-2.552) Å or in the Pu(H$_2$O)$_9$^{3+} ion (2.476-2.574) Å.[43] However,

complexation of hard anions such as oxalate and carbonate are known to significantly affect neighboring bond distances. As in **II**, the coordination of strong σ-donor ligands at the base of the square pyramidal $[Nd(CO_3)_4(H_2O)]^{5-}$ anion results in a lengthening of the axial Nd–O_w bond to 2.649(4) Å.[44] Because the Ln–O_w bond distances vary significantly in hydrated lanthanide(III) oxalates (i.e. 2.379(4) in $Gd(C_2O_4)_2(H_2O)\cdot NH_4$,[8] or an average 2.52(1) Å in $[Nd(H_2O)_2]_2(C_2O_4)_3$,[7] the confirmation of the nature of the terminal Pu-O bond (OH or H_2O) solely based upon comparing bond lengths is difficult.

The different colors of **I** and **II**, blue and green, respectively, are great indicators of different Pu oxidation states. There are many examples of blue Pu(III) compounds, foremost the characteristic blue color of the Pu^{3+}(aq) ion in aqueous acidic solution.[47] The most common examples for Pu(IV) compounds are the different shades of green Pu(IV) hydroxides and oxides. It is well established that the different absorbance features exhibited by the Pu ion in its various oxidation states can be used to spectroscopically probe the oxidation state of Pu. Therefore, conventional UV-vis-NIR diffuse reflectance spectroscopy was used to verify the oxidation states of plutonium in the solids **I** and **II**, which can be seen in Figure 6.
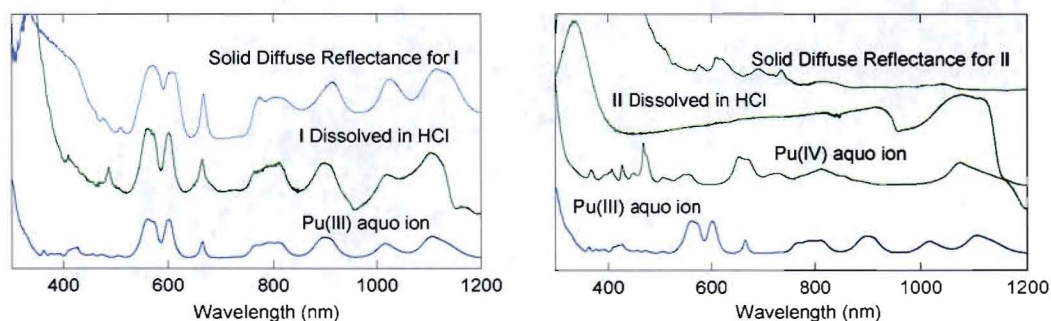
Figure 6: UV/vis absorbance and reflectance spectra for **I** (left) and **II** (right).

The diffuse reflectance spectra of **I** and **II** solids are shown in Figure 6 compared with the absorbances of Pu(III) and Pu(IV) ions in acidic solutions. The electronic absorbance spectrum of Pu^{3+}(aq) in acidic solution is characterized by the peaks at 562, 601 and 666 nm. This characteristic fingerprint between 500 and 700 nm is also observed in the diffuse reflectance spectrum in **I** and in the absorbance spectrum of **I** dissolved in 0.1 M HCl, confirming the presence of trivalent plutonium. The

coordination of Pu(III) in **I** with oxalate causes a moderate shift and broadening of its peaks to higher wavelengths, namely 571, 608 and 668 nm.

In contrast, the diffuse reflectance and absorbance spectra of Pu(IV) compounds with oxygen-donor ligands generally lack the presence of a characteristic pattern that could be used to definitively identify Pu(IV). The electronic absorption spectrum of Pu^{4+}(aq) shows several different Laporte-forbidden *f-f* transition bands in the visible region 400-800 nm, with predominant absorbance bands at 577, 609, 620, 691 and 737 nm. Above 500 nm, the diffuse reflectance spectrum of **II** shows strong similarities to the spectra of Pu^{4+}(aq) with regard to relative peaks positions and intensity ratios, although there are substantial shifts in peak wavelengths. Unfortunately, compound **II** is highly insoluble even in concentrated acids (i.e. 6 M HCl), therefore the low concentration of dissolved Pu resulted in very weak absorbances and prohibited a comparison and definite assignment of the Pu oxidation state. Comparing the diffuse reflectance of **II** to the aquo ions of Pu(III, V, and VI) shows little resemblance in absorption features, further supporting the designation of Pu(IV) in **II**. Together, the data obtained from structurally characterizing single crystals of **I** and **II**, the distinct chemical behavior of plutonium during synthesis and solubility in acid, and the characteristic colorimetric and spectroscopic fingerprints of **I** and **II** allow the identification of Pu(III) in **I** and Pu(IV) in **II**.

Conclusions

After more than fifty years of technological application we were able to produce the first crystalline plutonium(III) and (IV) oxalate compounds, which exhibit intriguing structural properties. Historically, the solid plutonium(III) and (IV) oxalate systems were thought to be dominated by the two hydrates, $Pu_2(C_2O_4)_3 \cdot 10H_2O$ and $Pu(C_2O_4)_2 \cdot 6H_2O$. For these compounds, only powder X-ray diffraction data have been reported and no distinction between coordinated and lattice water could be made.[25,26,33,34] A number of different hydrates are also suggested to exist at different temperatures without strong experimental evidence for the binding mechanism of hydration waters. In this work, compound **I** reveals three water molecules bound to the Pu(III) atoms to accommodate a

common Pu(III) structural geometry, a distorted tricapped trigonal-prism, which is also preferred in many other trivalent actinide and lanthanide compounds.

The most interesting structural aspect of compound **II** is that it comprises the structural charateristics of both two- and three-dimensional lanthanide oxalates. The arrangement of tetranuclear units of oxalate-bridged [PuO_9] polyhedra along the crystallographic b axis are very similar to the three-dimensional lanthanide oxalates. However, six oxalate-bridged [PuO_9] polyhedra form distorted hexagonal frameworks along the c axis similar to the honeycomb-structures of reported two-dimensional lanthanide oxalates. For the first time, structural analysis of **I** and **II** has provided direct insight into the coordination chemistry of Pu(III) and Pu(IV) oxalato complexes in aqueous solution. Interestingly, the coordination chemistry of Pu(IV) in **II** compares well with that found for the limiting complex of Nd(III) in carbonate solution, $Nd(CO_3)_4(H_2O)^{5-}$, rather than that of the chemical analogues Zr(IV) and Th(IV). It is very likely that $Pu(C_2O_4)_4(H_2O)^{5-}$ is the limiting Pu(IV) solution complex at high oxalate concentrations with a coordination geometry as illustrated in Figure 4.

The two new structures described herein provide fundamental insight into the chemical sensitivity of highly important separation processes. The formation of Pu(III) and Pu(IV) oxalates appears to be very sensitive to reaction conditions. In addition to those complexes discussed here, preliminary experiments indicate that increased ionic strength will also affect the redox behavior of Pu and increase the stability of Pu(IV). Therefore, relatively minor changes in pH and ionic strength not only change the solubility limiting species, but also affect the redox equlibrium between Pu(III) and Pu(IV). These simple solution parameters could be used to tune Pu oxidation state for more effective separations.

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