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

Wolfgang Runde,*,† Lia F. Brodnax,‡ George Goff,† Amanda C. Bean,‡ and Brian L. Scott§

†*Chemistry Division,* ‡*Plutonium Manufacturing and Technology Division,* §*Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

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Both binary and ternary solid complexes of Pu(III) and Pu(IV) oxalates have been previously reported in the literature. However, uncertainties regarding the coordination chemistry and the extent of hydration of some compounds remain mainly because of the absence of any crystallographic characterization. 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**), were synthesized under moderate hydrothermal conditions and characterized by single crystal X-ray diffraction studies. Compounds **I** and **II** are the first plutonium(III) or (IV) oxalate compounds to be structurally characterized via single crystal X-ray diffraction studies. 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 $C2/c$, $a = 23.234(14)$ 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. Since the early days of plutonium chemistry, oxalate has been used to control redox behavior and the precipitation of 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 transuranic oxalates, are still under debate. While the thermodynamic parameters have been reported for a number of transuranic oxalate compounds, structural analysis has been limited to powder X-ray diffraction.[3] Few, if any, compounds have been studied crystallographically to determine their structure.

Because of their significant technological and academic importance a number of oxalate compounds of chemically analogous lanthanide elements are known that can guide our understanding of trivalent actinide oxalate solid state chemistry. The majority of those materials consist of two-dimensional (2D) structures composed 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 the layers. Interesting complexes of mixed ligands or mixed metals, such as $[Ce(H_2O)]_2[(C_2O_4)_2(CO_3)]\cdot 2.5H_2O$[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 toward three-dimensional (3D) architectures with potential ion-exchange abilities. Several 3D lanthanide oxalates have been reported, in which the lanthanide(III) oxalate layers are connected to

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*To whom correspondence should be addressed. E-mail: runde@lanl.gov.

(1) *Plutonium Handbook: A Guide to the Technology*; ed. Wick, O. J., Ed.; American Nuclear Society: LaGrange Park, IL, 1980; Vols. 1 and 2, p 966.

(2) Cleveland, J. M. Solution Chemistry of Plutonium. In *The Plutonium Handbook - A Guide to the Technology*; Wick, O. J., Ed.; American Nuclear Society: LaGrange Park, IL, 1980.

(3) Hummel, W.; Anderegg, G.; Rao, L.; Puigdomenech, I.; Tochiyama, O. Chemical thermodynamics of compounds and complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with selected organic ligands. In *Chemical Thermodynamics*; Mompean, F., Illemassène, M., Perrone, J., Eds.; Elsevier: New York, 2005; Vol. 9.

(4) Chapelet-Arab, B.; Duvieubourg, L.; Nowogrocki, G.; Abraham, F.; Grandjean, S. *J. Solid State Chem.* **2006**, *179*(12), 4029–4036.

(5) Fourcade-Cavillou, F.; Trombe, J. *Solid State Sci.* **2002**, *4*, 1199–1208.

(6) Ollendorff, W.; Weigel, F. *Inorg. Nucl. Chem. Lett.* **1969**, *5*(4), 263–70.

(7) Trombe, J. C.; Jaud, J. *J. Chem. Crystallogr.* **2003**, *33*(1), 19–26.

(8) Trombe, J. C.; Thomas, P.; Brouca-Cabarrecq, C. *Solid State Sci.* **2001**, *3*(3), 309–319.

(9) Hansson, E. *Acta Chem. Scand.* **1970**, *24*(8), 2969.

(10) Huang, S. H.; Zhou, G. D.; Mak, T. C. W. *J. Crystallogr. Spectrosc. Res.* **1991**, *21*(2), 127–131.

(11) Palkina, K. K.; Kuz'mina, N. E.; Kova'chukova, O. V.; Strashnova, S. B.; Zaitsev, B. E. *Russ. J. Inorg. Chem.* **2001**, *46*(9), 1348–1351.

(12) Hansson, E.; Albertsson, J. *Acta Chem. Scand.* **1968**, *22*(5), 1682–1683.

(13) Romero, S.; Mosset, A.; Trombe, J. C. *J. Solid State Chem.* **1996**, *127* (2), 256–266.

(14) Gavilan, E.; Audebrand, N.; Jeanneau, E. *Solid State Sci.* **2007**, *9* (11), 985–999.

form open frameworks, as well as several mixed ligand complexes, which utilize a combination of both oxalate and other ligands to form their 3D framework.[13,15−20] Trombe et al. synthesized $La(C_2O_4)_2 \cdot NH_4$,[8] $(CN_3H_6)_2[Nd(H_2O)]_2(C_2O_4)_4 \cdot 3H_2O$, and $[N(CH_3)_4][Nd_2(H_2O)_3](C_2O_4)_{3.5} \cdot 4H_2O$,[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 et al. were able to synthesize a 3D 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] Tetravalent U and Th oxalates of the form $An(C_2O_4)_2 \cdot nH_2O$ (An = U or Th), as well as mixed U−Th oxalates of the same structure, have been synthesized.[23,24] 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 reported.[25,26] Akhtar showed that in the latter compound ten-coordinate thorium is coordinated by five oxalate groups forming chains that are cross-linked by extended hydrogen bonding.

Synthesis routes for single-crystal quality materials of transuranium oxalates are extremely rare. 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).[27−30] While the degree of hydration of An(III) precipitates remain under discussion, thermogravimetric measurements[29] and the analogy to $Ln_2(C_2O_4)_3 \cdot 10H_2O$[6,10,12] support declaration of Pu(III), Am(III), and Cm(III) decahydrates based upon their similar ionic radii. Slightly different levels of hydration, that is, $9.2H_2O$,[11] $9.5H_2O$,[31] and $10.5H_2O$,[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.[32] 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.[33] 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.[34] Pu(IV) is reported to complex as $Pu(C_2O_4)_2 \cdot nH_2O$ (n = 2,[35] or 6[35−37]) and $PuO(C_2O_4) \cdot 3H_2O$.[28] Arab-Chapelet et al. has reported unique mixed An(III)/An(IV) oxalates indicated by powder XRD.[38,39] Single crystal structural characterization of transuranic oxalates is thus far limited to $Np(C_2O_4)_2 \cdot 6H_2O$[40] and $H_2Np_2(C_2O_4)_5 \cdot 9H_2O$.[41] Despite these investigations, the nature of Pu precipitates from waste and reprocessing streams remains poorly understood. Understanding the nature of transuranium oxalate compounds formed under process conditions is critical to optimizing 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 Section

Taking advantage of both the high affinity and the reducing capacity of the oxalate anion toward 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]

A 0.2 mL aliquot of a Pu(IV) solution (0.1 M ^{239}Pu, $t_{1/2} = 2.4 \times 10^4$ yr) 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 were formed 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 h. Upon slow cooling (13 °C/h), blue rectangular crystals formed (Figure 1-left), with nearly quantitative recovery of Pu. 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 h 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), also resulting in nearly quantitative recovery of Pu. Single-crystal X-ray diffraction analysis revealed the dark green compound to be the 3D Pu(IV) oxalate, $KPu(C_2O_4)_2(OH) \cdot 2.5H_2O$ (**II**).

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(15) Baker, P.; Smith, A. J. *Cryst. Struct. Commun., Section C* **1990**, *C46*, 984.

(16) Thomas, P.; Trombe, J. C. *J. Chem. Crystallogr.* **2000**, *30*(10), 633–639.

(17) Trombe, J. C.; Jaud, J.; Galy, J. *J. Solid State Chem.* **2005**, *178*(4), 1094–103.

(18) Trombe, J. C.; Romero, S. *Solid State Sci.* **2000**, *2*(2), 279–283.

(19) Trombe, J.-C.; Galy, J.; Enjalbert, R. *Acta Crystallogr., Section C: Cryst. Struct. Commun.* **2002**, *58*(10), M517–M520.

(20) Yuan, Y. P.; Song, J. L.; Mao, J. G. *Inorg. Chem. Commun.* **2004**, *7* (1), 24–26.

(21) Trombe, J. C.; Mohanu, A. *Solid State Sci.* **2004**, *6*, 1403–1419.

(22) Chapelet-Arab, B.; Nowogrocki, G.; Abraham, F.; Grandjean, S. *J. Solid State Chem.* **2005**, *178*(10), 3046–3054.

(23) Duvieubourg-Garela, L.; Vigier, N.; Abraham, F.; Grandjean, S. *J. Solid State Chem.* **2008**, *181*(8), 1899–1908.

(24) Hingant, N.; Clavier, N.; Dacheux, N.; Barre, N.; Hubert, S.; Obbade, S.; Taborda, F.; Abraham, F. *J. Nucl. Mater.* **2009**, *385*(2), 400–406.

(25) Akhtar, M. N.; Smith, A. J. *Section B: Struct. Sci.* **1975**, *B31*, 1361.

(26) Johnson, F. A.; Larsen, E. M. *Inorg. Chem.* **1962**, *1*(1), 159.

(27) Chackraburtty, D. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1963**, *16*(8), 834.

(28) Jenkins, I. L.; Moore, F. H.; Waterman, M. J. *J. Inorg. Nucl. Chem.* **1965**, *27*(1), 77–80.

(29) Scherer, V.; Fochler, M. *J. Inorg. Nucl. Chem.* **1968**, *30*(6), 1433.

(30) Weigel, F.; ter Meer, N. *Inorg. Nucl. Chem. Lett.* **1967**, *3*(10), 403–408.

(31) Michaelides, A.; Skoulika, S.; Aubry, A. *Mater. Res. Bull.* **1988**, *23* (4), 579–85.

(32) Rao, G. S.; Subramanian, M. S.; Welch, G. A. *J. Inorg. Nucl. Chem.* **1963**, *25*(10), 1293–1295.

(33) Sali, S. K.; Noronha, D. M.; Mhatre, H. R.; Mahajan, M. A.; Chander, K.; Aggarwal, S. K.; Venugopal, V. *Nucl. Technol.* **2005**, *151*(3), 289–96.

(34) Markin, T. L. *J. Inorg. Nucl. Chem.* **1958**, *7*(3), 290–291.

(35) Jenkins, I. L.; Moore, F. H.; Waterman, M. J. *J. Inorg. Nucl. Chem.* **1965**, *27*(1), 81–87.

(36) Rao, V. K.; Pius, I. C.; Subbarao, M.; Chinnusamy, A.; Natarajan, P. R. *J. Radioanal. Nucl. Chem.* **1986**, *100*(1), 129–134.

(37) Vigier, N.; Grandjean, S.; Arab-Chapelet, B.; Abraham, F. *J. Alloys Compd.* **2007**, No. 444, 594–597.

(38) Arab-Chapelet, B.; Grandjean, S.; Nowogrocki, G.; Abraham, F. *J. Alloys Compd.* **2007**, No. 444, 387–390.

(39) Arab-Chapelet, B.; Grandjean, S.; Nowogrocki, G.; Abraham, F. *J. Nucl. Mater.* **2008**, *373*(1−3), 259–268.

(40) Grigor'ev, M. S.; Charushnikova, I. A.; Krot, N. N.; Yanovskii, A. I.; Struchkov, Y. T. *Radiochemistry* **1997**, *39*(5), 420–423.

(41) Charushnikova, I. A.; Krot, N. N.; Katser, S. B. *Radiochemistry* **1998**, *40*(6), 558–564.

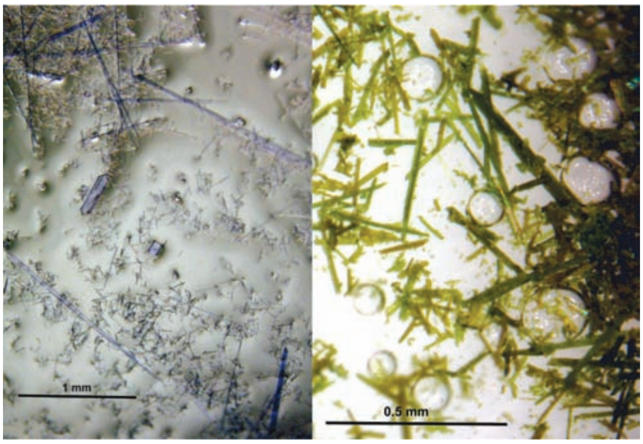

Figure 1. Blue crystals of I (left) and green crystals of II (right).

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	$P2_1/c$	$C2/c$
system	monoclinic	monoclinic

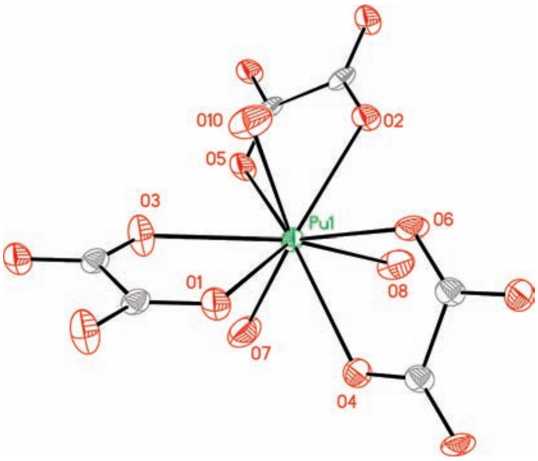

Figure 2. Thermal ellipsoid (50% probability) plot of the plutonium coordination and atomic numbering scheme in $Pu_2(C_2O_4)_3(H_2O)_6 \cdot 3H_2O$ (**I**).

Table 2. Selected Bond Distances (Å) and Angles (deg) 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)

Crystallographic Studies

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 Mo Kα X-ray source (λ = 0.71073 Å). A hemisphere of data was collected using φ scans, with 30 s frame exposures and 0.3° frame widths. Data collection, initial indexing, and cell refinement were handled using the SMART software.[42] Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using the SAINT software,[43] and the data were corrected for absorption using the SADABS program.[44] Decay of reflection intensity was monitored via analysis of redundant frames, and no significant decay was measured. The structure was solved using direct methods and difference Fourier techniques. Hydrogen atom positions were not included in the refinement model because of the difficulty in finding hydrogen atom positions on lattice water molecules, particularly in the presence of a heavy atom like plutonium. 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 because of absorption problems). Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[45] Table 1 shows the important crystallographic parameters for both **I** and **II**. Additional solid phase characterization (diffuse reflectance) as well as solution characterization of the dissolved crystals was performed using a Cary 5 UV−vis-NIR spectrophotometer with a diffuse reflectance attachment.

Results and Discussion

The 2D structure of **I** consists of $[PuO_9]$ polyhedra that are linked through the carboxylate groups in the $[C_2O_4]$ 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 single polyhedra of **I**, while Table 2 lists selected bond lengths and angles.

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 that reported for a capping water in the Pu(III) aquo complex, $[Pu(H_2O)_9][CF_3SO_3]_3$, of

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[42] *SMART-NT 4*; Bruker, AXS. Inc: Madison, WI, 1996.
[43] *SAINT-NT 5.050*; Bruker AXS. Inc: Madison, WI, 1998.
[44] Sheldrick, G. *SADABS*, first release; University of Gottingen: Gottingen, Germany.
[45] *SHELXTL*, Version 6.10; Bruker AXS, Inc.: Madison, WI, 2001.

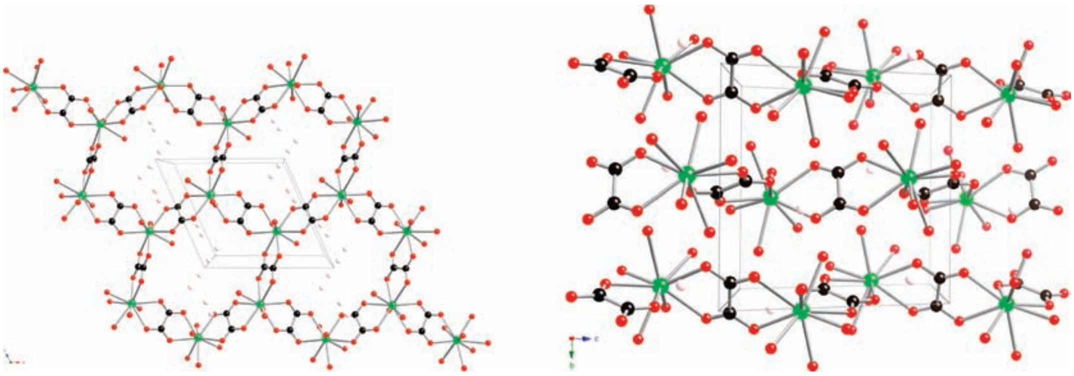

Figure 3. Packing in $Pu_2(C_2O_4)_3(H_2O)_6 \cdot 3H_2O$ (**I**): (left) honeycomb structure along the *b* axis and (right) layers in the *ab* plane.

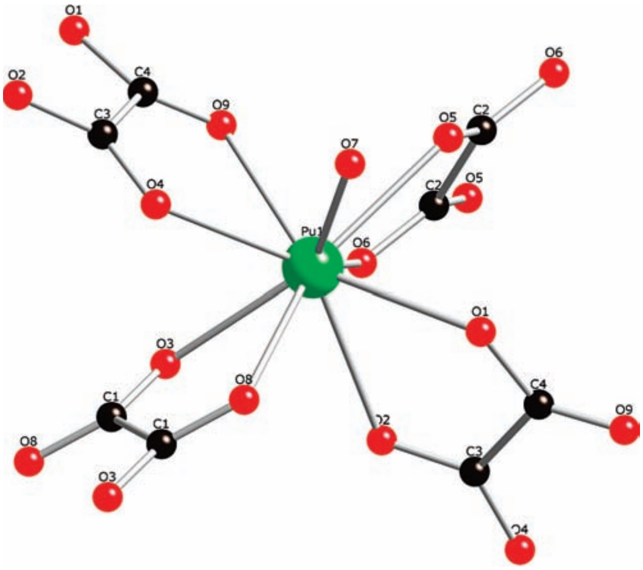

Figure 4. Schematic illustrating the plutonium coordination and atomic numbering scheme in $KPu(C_2O_4)_2(OH) \cdot 2.5H_2O$ (II).

2.574(3) Å.[46] 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 × 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°.

Table 3. Selected Bond Distances (Å) and Angles (deg) 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)

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 Pu atom is bound to eight oxygen atoms from four bis-chelating oxalate ligands and one oxygen atom (O7) from a coordinated hydroxide ion to complete a distorted tricapped prismatic geometry. Figure 4 shows the coordination of the anionic unit of **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 pseudosquare pyramid with a coordinated water molecule at the top.[47]

Within the crystallographic *ab* plane six $[PuO_9]$ polyhedra and six oxalate ligands form a honeycomb structure with approximately 8.3 × 12.3 Å apertures, which are filled with K atoms and water molecules (Figure 5). Channels with approximate dimensions of 5.5 Å × 4.5 Å run down the *b* axis and are lined by four $[PuO_9]$ polyhedra and four oxalate ligands.

The most interesting aspect of the structure of **II** is the terminal Pu$-$O$_{OH}$ bond since it affects the nominal Pu 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 result in a Pu(IV) center. Clearly, the Pu$-$O bond length of 2.50(2) Å is significantly longer than the Pu=O distances of 1.812 Å in the Pu(V) complex, $[Co(NH_3)_6][PuO_2(C_2O_4)_2] \cdot 3H_2O$,[48] and longer than the 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.[49] This clearly rules

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(46) Matonic, J. H.; Scott, B. L.; Neu, M. P. *Inorg. Chem.* **2001**, *40*(12), 2638–2639.

(47) Runde, W.; Neu, M. P.; Van Pelt, C.; Scott, B. L. *Inorg. Chem.* **2000**, *39*(6), 1050.

(48) Grigor'ev, M. S.; Krot, N. N.; Bessonov, A. A.; Antipin, M. Y. *Radiochemistry* **2005**, *47*(5), 460–463.

(49) Conradson, S. D.; Abney, K. D.; Begg, B. D.; Brady, E. D.; Clark, D. L.; den Auwer, C.; Ding, M.; Dorhout, P. K.; Espinosa-Faller, F. J.; Gordon, P. L.; Haire, R. G.; Hess, N. J.; Hess, R. F.; Keogh, D. W.; Lander, G. H.; Lupinetti, A. J.; Morales, L. A.; Neu, M. P.; Palmer, P. D.; Paviet-Hartmann, P.; Reilly, S. D.; Runde, W. H.; Tait, C. D.; Veirs, D. K.; Wastin, F. *Inorg. Chem.* **2004**, *43*(1), 116–131.

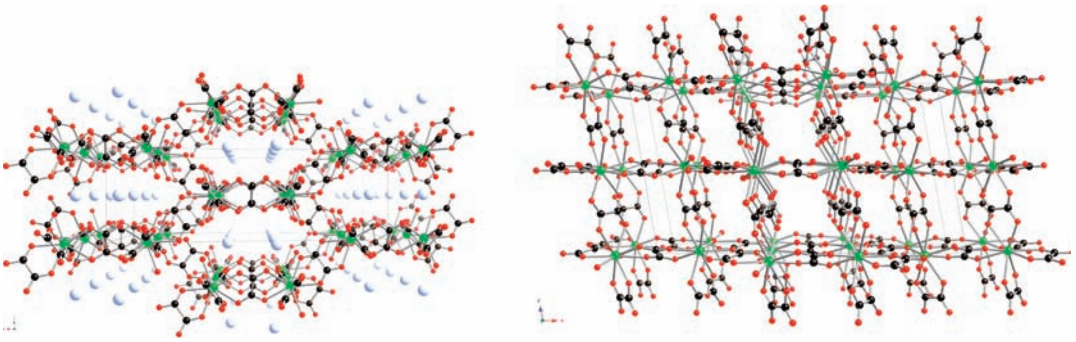

Figure 5. Packing in $KPu(C_2O_4)_2(OH)\cdot 2.5H_2O$ (**II**): (left) honeycomb structure along the *c* axis and (right) view down the *b* axis showing the 3D channel structure.

out the V and VI oxidation states for **II**. While 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 $Pu(H_2O)_9{}^{3+}$ ion (2.476−2.574) Å.[46] However, complexation of hard anions such as oxalate and carbonate are known to significantly affect neighboring bond distances.[50] 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,[45] when compared to the Nd−O_w bond of 2.469(2)-2.572(2) Å in the aquo ion $[Nd(H_2O)_9]^{3+}$.[51] 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 averaged 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) by comparing only bond lengths is difficult.

The different colors of **I** and **II**, blue and green, respectively, are also 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.[52] Multiple compounds of Pu(IV) with various functional groups have been reported, the most common examples being the different shades of green Pu(IV) hydroxides and oxides.[52] 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.

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 486, 562, 601, and 666 nm. This characteristic fingerprint is 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 only a minor shift and broadening of its peaks to higher wavelengths, namely, 509, 571, 608, and 668 nm. 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 peak positions and absorption strengths, although there is a substantial shift in peak wavelengths. Unfortunately, because of the extreme insolubility of **II** even in highly acidic solutions (i.e., 6 M HCl) the low concentration of dissolved Pu prohibited a comparison of the absorbance bands of **II** when dissolved in acid. 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**. Specifically, the double peaks around 570 and 600 nm which are characteristic of Pu(III) and can be seen in both the aquo ion and when coordinated with an oxo-ligand as in **I**, are absent in **II** which supports the assignment of Pu(IV). Together, the resulting

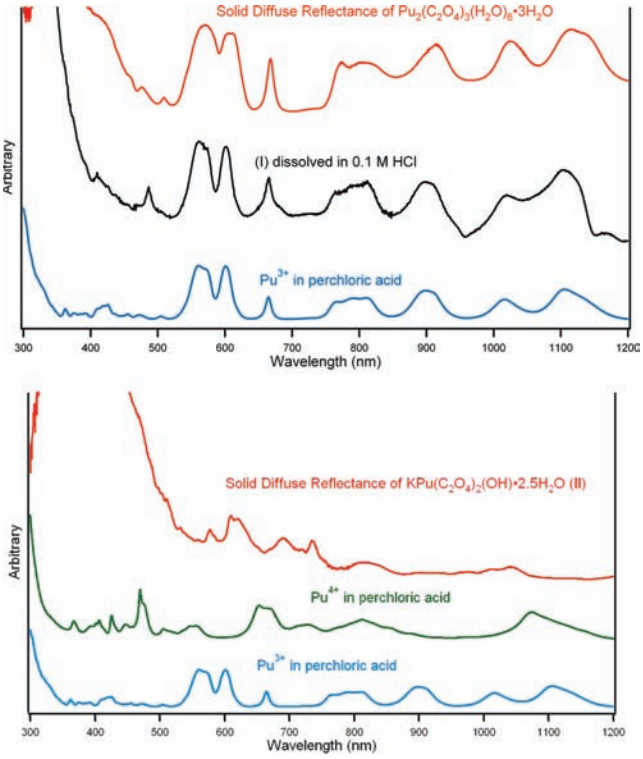

Figure 6. Spectroscopic comparison of the solution UV−vis and solid state diffuse reflectance spectra of Pu(III) with **I** (top) and Pu(IV) with **II** (bottom).

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(50) Burns, C. J.; Neu, M. P.; Boukhalfa, H.; Gutowski, K. E.; Bridges, N. J.; Rogers, R. D. *The Actinides. Compr. Coord. Chem. II* **2004**, *3*, 189–345.

(51) Chatterjee, A.; Maslen, E. N.; Watson, K. J. *Acta Crystallogr., Sect. B* **1988**, *44*(4), 381–386.

(52) Clark, D. L.; Hecker, S. S.; Jarvinen, G. D.; Neu, M. P. Plutonium. In *The Chemistry of the Actinide and Transactinide Elements*; Morss, N.M.E. L. R., Fuger, J., Katz, J. J., Eds.; Springer: Dordrecht, The Netherlands, 2006; pp 813−1264.

data from structurally characterizing single crystals of **I** and **II**, the distinct general chemistry behavior of plutonium during synthesis and dissolution, and the characteristic colorimetric and spectroscopic fingerprints of **I** and **II** allow the determination of Pu(III) in **I** and Pu(IV) in **II**.

Conclusions

After more than 50 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 which only powder X-ray diffraction data have been reported.[27,28,35,36] A number of different hydrates are also suggested to exist at different temperatures without strong experimental evidence for the binding mechanism of the hydration waters. Compound **I** reveals that three water molecules are bound to the Pu(III) atom to accommodate a common Pu(III) structural geometry, 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 benchmarks of both 2D and 3D lanthanide oxalates. Tetranuclear units of oxalate-bridged $[PuO_9]$ polyhedra are arranged along the crystallographic *b* axis, very similar to the 3D lanthanide oxalates. However, six oxalate-bridged $[PuO_9]$ polyhedra form distorted hexagonal frameworks along the *c* axis similar to the honeycomb-structures of 2D lanthanide oxalates. Structural analysis of **II** has for the first time provided direct insight into the coordination chemistry of Pu(IV) oxalato complexes in aqueous solution. Unexpectedly, the coordination chemistry of **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 assuming 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 redox behavior and subsequent formation of Pu(III) or Pu(IV) oxalates appears to be more sensitive to reaction conditions than the analogous lanthanide, thorium, or uranium systems. In addition to those complexes discussed here, preliminary experiments indicate that increased ionic strength will also inhibit the redox behavior of Pu. Therefore, relatively minor changes in pH and ionic strength not only change the solubility limiting species, but also affect the reduction of Pu(IV) to Pu(III). These simple solution parameters could be used to easily tune Pu separations.

Supporting Information Available: Crystallographic data in CIF file format. This material is available free of charge via the Internet at http://pubs.acs.org.