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Comparisons of Pu(IV) and Ce(IV) Diphosphonates

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The hydrothermal reaction of PuO_2 with $CH_2(PO_3H_2)_2$ results in the formation of α-Pu[$CH_2(PO_3)_2$](H_2O), β-Pu[$CH_2(PO_3)_2$](H_2O) (**1**), γ-Pu[$CH_2(PO_3)_2$](H_2O) (**2**), and Pu[$CH_2(PO_3)_2$](H_2O)·H_2O (**3**) as crystalline compounds with blue, green, red, and very pale peach coloration, respectively. In all cases single crystal X-ray diffraction studies reveals Pu^{4+} coordinated by $[CH_2(PO_3)_2]^{4-}$ and water to yield PuO_7 units. The methylenediphosphonate anions bridge between these units to yield three-dimensional networks. Bond-valence parameters of $R_o = 2.068$ and $b = 0.385$ have been derived for Pu^{4+} using a combination of the data reported in this work with that available in crystallographic databases. UV—vis—NIR spectroscopic measurements demonstrate that despite the dramatic color differences all of the compounds contain Pu^{4+}, and that subtle changes in the visible region of the spectra account for different colors.

Introduction

Structural data on plutonium compounds are sorely lacking by comparison with earlier actinides, or other metals in general. This data is important because it provides necessary information for developing periodic trends in the actinide series, and helps to establish parameters for verifying oxidation states, which can be ambiguous with plutonium owing to its ability to easily change its oxidation state both in solution and in high-temperature solid-state reactions.[1,2] For example, $M_2O(PO_4)_2$ phases can be prepared when M = Zr, Th, U, and Np. However, attempts prepare a similar compound with Pu(IV) results in spontaneous reduction to Pu(III), and monazite-like phases with the composition MPO_4 result.[2] There are also more applied reasons for understanding the crystal chemistry of plutonium. In particular, the development of advanced waste forms for storing plutonium will require detailed knowledge of its structural chemistry.[3−6]

Restrictions for working with radioactive elements have forced many researchers to switch to less- or non-radioactive surrogates, for example, UO_2^{2+} for PuO_2^{2+}, Ce^{4+} for Pu^{4+}, and Eu^{3+} for Am^{3+} and Cm^{3+}. The question is: Do these less- or non-radiative surrogates actually mimic the chemistry of transuranium elements? If we neglect the effects of radiolysis, which can play a substantial role with shorter-lived isotopes (e.g., ^{238}Pu, ^{239}Pu, ^{241}Pu, and ^{241}Am), we are still left with the task of proving that the chemical behavior of one element is ostensibly the same as another. Plutonium is particularly problematic in this regard because it is capable of adopting oxidation states that are not possible for cerium, and the redox potentials for these reactions are quite different from that of the Ce^{3+}/Ce^{4+} couple. A plethora of studies now exist that demonstrate that in a number of basic systems surrogates do not properly mimic the behavior of transuranics both in solution[7] and in the solid-state.[8−10] This has important implications for how we model actinides in the environment. For example, the primary hydrolysis product for UO_2^{2+} is a trimer, whereas for PuO_2^{2+}, it is a dimer.[7] Recent studies by Raymond and co-workers have demonstrated that with both complex octadentate ligands and simple chelators that Pu^{4+} and Ce^{4+} complexes can be different, even if the same coordination number is achieved at the metal center.[10]

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Uranyl and plutonyl iodates adopt substantially different crystal structures even when synthesized under the same conditions.[8] Finally, Brandel and Dacheux have carefully reviewed the structural chemistry of tetravalent metal phosphates,[11,12] and significant differences can be observed even in a seemingly straightforward system like $M(PO_3)_4$ (M = Ce, Th, U, Pa, Np, Pu).[11]

Recent advances in X-ray diffraction technology, specifically the availability of microfocused sources coupled with CCD detectors, have enable investigators to obtain remarkable diffraction data from microcrystals without having to travel to synchrotrons. This new technology has enabled us to deeply probe a rather simple Ce^{4+}/Pu^{4+} diphosphonate system, $M[CH_2(PO_3)_2](H_2O)$. We now report on the structures and electronic spectroscopy of β-$Pu[CH_2(PO_3)_2](H_2O)$ (**1**), γ-$Pu[CH_2(PO_3)_2](H_2O)$ (**2**), and $Pu[CH_2(PO_3)_2](H_2O)\cdot H_2O$ (**3**). Two of these compounds have cerium analogues that we have very recently characterized.[13] The structures of the first two compounds have the lowest R-factors reported for plutonium compounds, and represent significant improvements on the information acquired from α-$Pu[CH_2(PO_3)_2](H_2O)$, for which only twinned crystals of poorly quality could be obtained.[14] As mentioned, very little structural information is available on plutonium compounds. There are only fourteen Pu(IV) structures in the ICSD database, and seven in CSD, although others exist that have not been archived. In addition to providing new fundamental data on the crystal chemistry of plutonium compounds, this information allows for the potential discernment of differences in the bonding metrics for Ce^{4+} and Pu^{4+}, for which the ionic radius has been calculated to be the approximately the same.[15] Finally, we now have enough structural data on plutonium compounds to provide bond-valence parameters for Pu(IV).[16] This will aid future researchers in the assignment of plutonium oxidation states, which is not always straightforward for the reasons mentioned above.

Experimental Section

Syntheses. $^{242}PuO_2$ (99.98% isotopic purity, Oak Ridge National Laboratory) was used as received. While the plutonium is of very high isotopic purity, there are trace amounts of ^{238}Pu, ^{240}Pu, ^{241}Pu, ^{244}Pu, and ^{241}Am. The majority of the radioactivity comes from the ^{241}Pu even though it represents only 0.008% of the plutonium. ***Caution!*** *^{242}Pu ($t_{1/2} = 3.76 \times 10^5$ y) still represents a serious health risk owing to its α and γ emission* (*weak*). This isotope was selected because of its long half-life, which increased the longevity of the crystals. Specialized facilities and procedures are needed for this work. All free-flowing solids are worked with in negative-pressure gloveboxes, whereby the air atmosphere of the box is continuously pulled on through a HEPA-filtered hood, and products are only examined when coated with either water or Krytox oil and water. There are some limitations in accurately determining yield with plutonium compounds because this requires weighing a dry solid, which poses certain risks as well as manipulation difficulties given the small quantities that we work with. Methylenediphosphonic acid, $CH_2(PO_3H_2)_2$ (98%, Alfa Aesar) was used as received.

Table 1. Crystallographic Data for β-$Pu[CH_2(PO_3)_2](H_2O)$ (**1**), γ-$Pu[CH_2(PO_3)_2](H_2O)$ (**2**), $Pu[CH_2(PO_3)_2](H_2O)\cdot(H_2O)$ (**3**)

compound	**1**	**2**	**3**
formula mass	431.98	431.98	450.00
color and habit	green, tablet	red, block	very pale peach, needle
space group	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)	$P2_1/n$ (No. 14)
a (Å)	8.6692(5)	8.5990(11)	5.2504(2)
b (Å)	8.7012(5)	11.2761(15)	8.2896(3)
c (Å)	9.5318(6)	13.7865(18)	16.4629(7)
α (deg)	71.403(4)	90	90
β (deg)	72.248(3)	90	93.912(1)
γ (deg)	82.859(4)	90	90
V (Å^3)	648.72(7)	1336.8(2)	714.86(5)
Z	2	8	4
T (K)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
maximum 2θ (deg.)	28.63	27.09	28.87
ρ_{calcd} (g cm^{-3})	4.423	4.293	4.181
μ(Mo $K\alpha$) (cm^{-1})	106.43	103.30	96.78
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$[a]	0.0141	0.0319	0.0161
$R_w(F_o^2)$[b]	0.0335	0.0716	0.0336

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

PuO_2 (4.6 mg, 0.0168 mmol) was combined with $CH_2(PO_3H_2)_2$ (12.4 mg, 0.0704 mmol) in a 10 mL PTFE autoclave linear. A 500 μL portion of distilled and Millipore filtered water was added to the solids. The closed linear was sealed inside a stainless steel autoclave, and then heated to 180 °C for 3 days in a furnace. The furnace was turned off, and the autoclave was allowed to cool to room temperature before opening. The product consisted of a mixture of crystals of different colors. Relatively large green crystals of β-$Pu[CH_2(PO_3)_2](H_2O)$ (**1**) were easily isolated. γ-$Pu[CH_2(PO_3)_2](H_2O)$ (**2**) forms red polycrystalline masses that must be cleaved for the isolation of twinned crystals. $Pu[CH_2(PO_3)_2](H_2O)\cdot H_2O$ (**3**) forms clusters of nearly colorless acicular crystals. A very pale peach coloration is observed if one looks down the length of the crystals. Blue tablets of α-$Pu[CH_2(PO_3)_2](H_2O)$ have already been described.[14]

Crystallographic Studies. Crystals of all three compounds were mounted on glass fibers with epoxy and optically aligned on a Bruker APEXII Quazar X-ray diffractometer using a digital camera. Care must be taken to ensure that the epoxy has hardened before the crystals are moved. We have now moved away from using glass fibers to Mitegen mounts, which offer much more surface area to which to stick the crystals. Initial intensity measurements were performed using a IμS X-ray source, a 30 W microfocused sealed tube (MoKα, λ = 0.71073 Å) with high-brilliance and high-performance focusing Quazar multilayer optics. Standard APEXII software was used for determination of the unit cells and data collection control. The intensities of reflections of a sphere were collected by a combination of four sets of exposures (frames). Each set had a different φ angle for the crystal and each exposure covered a range of 0.5° in ω. A total of 1464 frames were collected with an exposure time per frame of 10 to 50 s, depending on the crystal. SAINT software was used for data integration, included Lorentz polarization corrections. Semiempirical absorption corrections were applied using the program SADABS for **1** and **3**.[17] Selected crystallographic information are listed in Table 1. Atomic coordinates and additional structural information are

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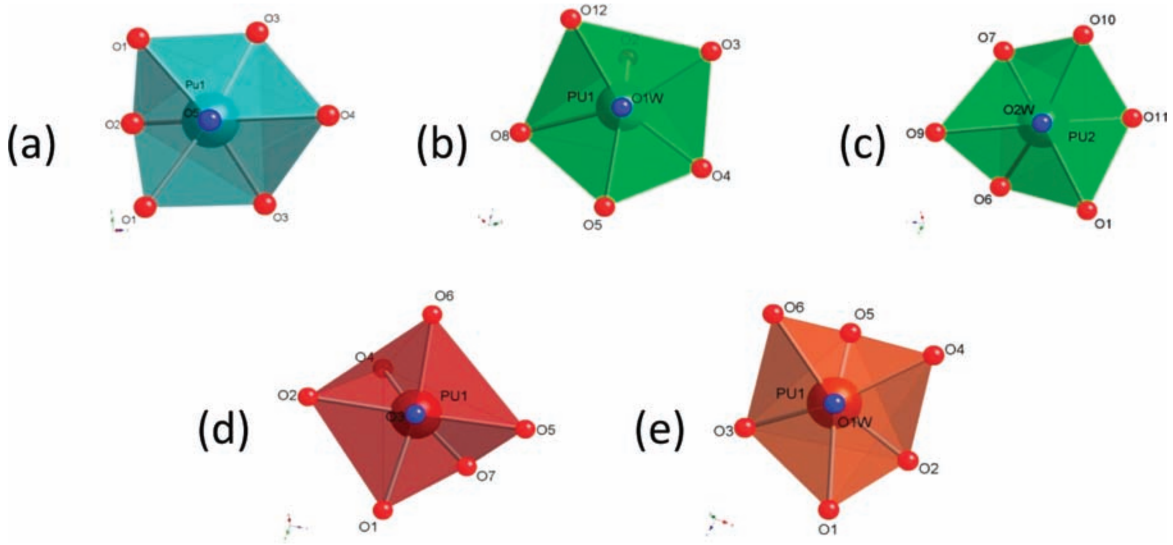

Figure 1. PuO_7 coordination environments found in α-$Pu[CH_2(PO_3)_2](H_2O)$ (a), *β*-$Pu[CH_2(PO_3)_2](H_2O)$ (**1**) (b,c), *γ*-$Pu[CH_2(PO_3)_2](H_2O)$ (**2**) (d), and $Pu[CH_2(PO_3)_2](H_2O)\cdot H_2O$ (**3**) (e). The description of these units varies from capped octahedra to dodecahedra with a missing vertex.

provided in the Supporting Information (CIFs). In the case of the *γ*-$Pu[CH_2(PO_3)_2](H_2O)$, a fragment was cleaved off of a polycrystalline mass. This fragment proved to be a two component twin. The use of Cell_Now and Twinabs allowed for proper treatment of the twinning, and a suitable refinement of the structure was obtained.

UV−vis−NIR Spectroscopy. UV−vis−NIR data were acquired from either single crystals or oriented single crystals using a Craic Technologies microspectrophotometer. Crystals were placed on quartz slides under oil, and the data was collected from 200 to 1700 nm. While the crystals of $Pu[CH_2(PO_3)_2](H_2O)\cdot H_2O$ are dichroic, they are too small to collect in different orientations.

Results and Discussion

Synthesis. The hydrothermal reaction of PuO_2 with methylenediphosphonic acid, $CH_2(PO_3H_2)_2$, results in the formation of four different crystalline products. The colors of the crystals are blue,[14] green, red, and very pale peach. The formula of these compounds are α-$Pu[CH_2(PO_3)_2](H_2O)$,[14] *β*-$Pu[CH_2(PO_3)_2](H_2O)$ (**1**), *γ*-$Pu[CH_2(PO_3)_2](H_2O)$ (**2**), and $Pu[CH_2(PO_3)_2](H_2O)\cdot H_2O$ (**3**), respectively.

General Structural Characteristics. The structures of **1**−**3** are composed of Pu^{4+} centers bound by methylenediphosphonate and water to yield seven-coordinate plutonium in the form of PuO_7 units. While this coordination number is not nearly as common as eight- or nine-coordinate systems, it also occurs in $U[CH_2(PO_3)_2](H_2O)$,[14] as well as several related or isostructural Ce^{4+} phases,[13] and is known more generally from the monoclinic form of zirconia.[18] $[CH_2(PO_3)_2]^{4-}$ can chelate and/or bridge between tetravalent actinides.[14,19] When it chelates, it uses two oxygen atoms to do this. Each oxo donor is from one of the PO_3 moieties. This same bonding mode occurs in $UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (An = Th, Np, Pu) where eight-coordinate An^{4+} ions are found.[14] In the process of chelating the plutonium ions with $[CH_2(PO_3)_2]^{4-}$, four of the oxygen atoms are directed away from the first plutonium center, and these serve to bridge between the Pu^{4+} ions to create extended structures. A seventh site is occupied by water. The PuO_7 coordination environments are shown in Figure 1. Views of the extended structures of **1**, **2**, and **3** are shown in Figures 2, 3, and 4. From these figures it appears in some cases that single PO_3 groups are using two oxygen atoms to chelate plutonium centers. This is an illusion caused by the superposition of the polyhedra. The framework adopted by **3** is more open than that found for the other compounds, and accounts for the occluded water molecule in

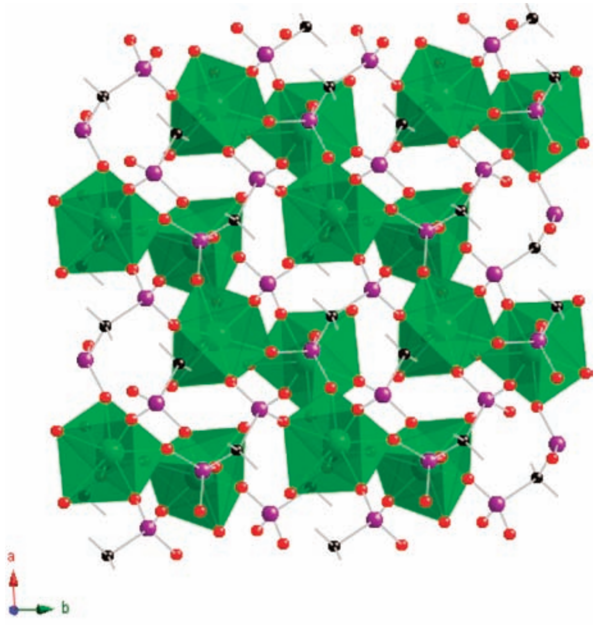

Figure 2. Depiction of the three-dimensional framework structure of *β*-$Pu[CH_2(PO_3)_2](H_2O)$ (**1**) along the *c* axis. This structure is constructed from two seven-coordinate PuO_7 units that are bridged by the methylenediphosphonate as shown in green.

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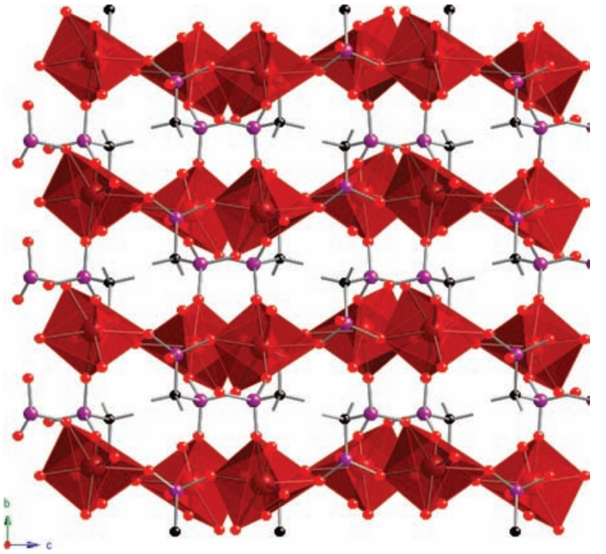

Figure 3. View of the three-dimensional framework structure of γ-Pu[CH$_2$(PO$_3$)$_2$](H$_2$O) (**2**) along the *a* axis. This structure is constructed from seven-coordinate PuO$_7$ units that are both bridged and chelated by the methylenediphosphonate.

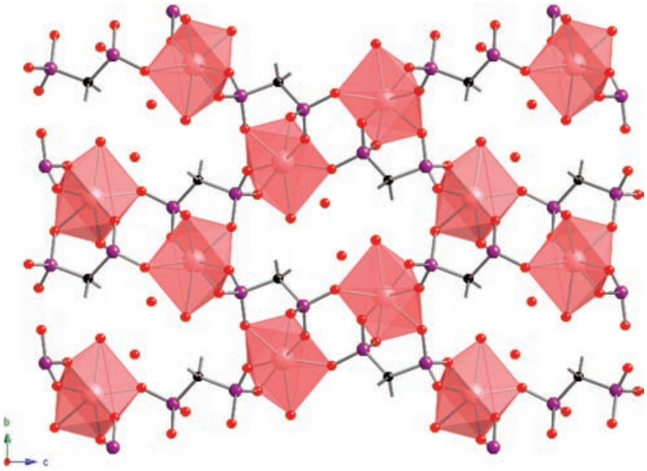

Figure 4. View along the *a* axis of the structure of Pu[CH$_2$(PO$_3$)$_2$](H$_2$O)·H$_2$O (**3**). This structure consists of a three-dimensional network constructed from PuO$_7$ units that are chelated and bridged by methylenediphosphonate. An additional occluded water molecule fills the voids in the structure.

the structure. Selected bond distances are given in Tables 2, 3, and 4.

The PuO$_7$ units found in these compounds do not conform to idealized shapes that are easily described, and vary from units best described as dodecahedra with a missing vertex to capped octahedra. Of the two PuO$_7$ units found in β-Pu[CH$_2$(PO$_3$)$_2$](H$_2$O), the polyhedron containing Pu(2) can be described as a capped octahedron where the capping group is along one of the C_3 axes. The same description applies to the PuO$_7$ units in Pu[CH$_2$(PO$_3$)$_2$](H$_2$O)·H$_2$O. The PuO$_7$ polyhedra in α-Pu[CH$_2$(PO$_3$)$_2$](H$_2$O) and γ-Pu[CH$_2$(PO$_3$)$_2$](H$_2$O), as well as the Pu(1) unit in β-Pu[CH$_2$(PO$_3$)$_2$](H$_2$O), are better described as dodecahedra with a missing vertex. Much like distorted trigonal bipyramids versus square pyramids in transition metal chemistry, there are probably very small differences in energies between these different geometries.

Table 2. Selected Bond Distances (Å) for β-Pu[CH$_2$(PO$_3$)$_2$](H$_2$O) (**1**)

Bond Distances (Å)			
Pu(1)−O(2)	2.253(2)	P(1)−O(1)	1.526(3)
Pu(1)−O(3)	2.221(2)	P(1)−O(2)	1.530(3)
Pu(1)−O(4)	2.234(2)	P(1)−O(3)	1.517(3)
Pu(1)−O(5)	2.329(2)	P(1)−C(1)	1.810(3)
Pu(1)−O(8)	2.255(2)	P(2)−O(4)	1.527(3)
Pu(1)−O(12)	2.231(2)	P(2)−O(5)	1.526(2)
Pu(1)-O(1W)	2.429(3)	P(2)−O(6)	1.530(2)
Pu(2)−O(1)	2.214(2)	P(2)−C(2)	1.800(3)
Pu(2)−O(6)	2.258(2)	P(3)−O(7)	1.525(3)
Pu(2)−O(7)	2.253(2)	P(3)−O(8)	1.528(2)
Pu(2)−O(9)	2.289(2)	P(3)−O(9)	1.543(3)
Pu(2)−O(10)	2.250(2)	P(3)−C(1)	1.797(3)
Pu(2)−O(11)	2.195(2)	P(4)−O(10)	1.528(3)
Pu(2)-O(2W)	2.493(3)	P(4)−O(11)	1.523(3)
		P(4)−O(12)	1.521(3)
		P(4)−C(2)	1.794(3)

Table 3. Selected Bond Distances (Å) for γ-Pu[CH$_2$(PO$_3$)$_2$](H$_2$O) (**2**)

Bond Distances (Å)			
Pu(1)−O(1)	2.347(7)	P(1)−O(1)	1.524(6)
Pu(1)−O(2)	2.220(6)	P(1)−O(2)	1.504(7)
Pu(1)−O(3)	2.234(7)	P(1)−O(3)	1.538(7)
Pu(1)−O(4)	2.224(6)	P(1)−C(1)	1.796(10)
Pu(1)−O(5)	2.293(6)	C(1)−P(2)	1.819(10)
Pu(1)−O(6)	2.238(8)	P(2)−O(4)	1.539(7)
Pu(1)−O(7)	2.419(7)	P(2)−O(5)	1.515(7)
		P(2)−O(6)	1.523(8)

Table 4. Selected Bond Distances (Å) for Pu[CH$_2$(PO$_3$)$_2$](H$_2$O)·(H$_2$O) (**3**)

Bond Distances (Å)			
Pu(1)−O(1)	2.299(3)	P(1)−O(1)	1.527(3)
Pu(1)−O(2)	2.292(3)	P(1)−O(2)	1.523(3)
Pu(1)−O(3)	2.217(3)	P(1)−O(3)	1.536(3)
Pu(1)−O(4)	2.219(3)	P(1)−C(1)	1.793(4)
Pu(1)−O(5)	2.264(3)	P(2)−O(4)	1.531(3)
Pu(1)−O(6)	2.263(3)	P(2)−O(5)	1.528(3)
Pu(1)-O(1W)	2.526(3)	P(2)−O(6)	1.522(3)
		P(2)−C(1)	1.798(4)

Comparisons of Pu(IV) and Ce(IV) Structures. The structure of **1** provides an unusual opportunity to compare Pu−O bond distances not just with Ce−O bond distances from an isostructural compound but also within the same structure because there are two crystallographically unique plutonium centers in **1**. The internal comparison yields an average Pu−O bond distance of 2.248(3) Å for both Pu^{4+} centers. This average compares well with the average Ce−O bond distance of 2.250(4) Å. In fact, if 3σ on the errors is used, then the differences between the distances are not statistically significant. The variations in the Pu−O(H$_2$O) and Ce−O(H$_2$O) bond distances are also potentially informative as they might provide different results than found with the Pu−O bonds from the PO$_3$ moieties. These distances are 2.429(3) and 2.493(3) Å for **1**, and 2.528(4) and 2.472(4) Å for cerium. The averages of 2.461(3) and 2.500(4) Å appear to be different by 0.039(4) Å, but if one looks at the internal variations between the two different sites (0.064(3) and 0.056(4) Å), the difference is larger between sites than it is between compounds. In short, the errors within the models for the structures of **1** and its cerium counterpart are such that the bond distances appear to be essentially the same.

γ-Pu[$CH_2(PO_3)_2$](H_2O) (**2**) is isotypic with β-Ce[$CH_2(PO_3)_2$](H_2O), which provides us an additional opportunity to discern differences in bond distances between Pu^{4+} and Ce^{4+}. The average M−O bond distances to the oxygen atoms from the PO_3 groups are 2.260(8) Å and 2.272(5) Å for plutonium and cerium, respectively. The Pu−O(H_2O) and Ce−O(H_2O) bond distances are 2.419(7) Å and 2.457(5) Å. The average Pu−O bond distances for all seven oxygen donors in **1** and **2** are 2.248(3) Å and 2.260(8) Å, giving a difference of 0.012(8) Å (i.e., they are not statically different), while the difference between **2** and β-Ce[$CH_2(PO_3)_2$](H_2O) is also 0.012(8) Å. We conclude that there are no measurable differences between Pu−O bonds and Ce−O bonds in this system.

Bond-Valence Parameters for Plutonium(IV). While Pu(IV) structures are sparse, the addition of these three structures provides enough data when combined with that available in crystallographic databases to determine the bond-valence parameters for Pu(IV).[20−23] Using the following equations,[24,25] we derived the bond-valence parameters for Pu(IV) using the structures available in ICSD combined with the data presented in this paper.

$$S = \exp((R_o - R)/b) \qquad (1)$$

$$R_s = R_o - b \ln(S) \qquad (2)$$

R_s is the measured bond distance, which is calculated as the average Pu−O bond distance of each compound, and S is the bond-valence that corresponds to this distance. S is calculated using V/N; where V is the ionic charge, which is treated as the same as the formal oxidation state, and N is the coordination number. Although there are fourteen Pu^{4+} crystals in the ICSD, as shown in Table 5,[26] only a few of these are of sufficient quality to be used for bond-valence calculations (those with *). On the basis of these data, a plot of R_s versus ln(S) was generated, as shown in Figure 6. This straight line has a slope of −0.385 and intercept 2.068 ($R^2 = 0.9909$), yielding $b = 0.385$ and $R_o = 2.068$. The results of the bond-valence sums using eq 1 for each compound are also shown in Table 5, and indicate that these parameters fit for most of the compounds. Using these parameters the bond-valence sum for plutonium in $Na_6[Pu(CO_3)_5]\cdot Na_2CO_3\cdot 33H_2O$ was calculated to be 4.06, which is in agreement with the structure and spectroscopic data.[27]

Table 5. Results from the Calculation of Bond-Valence Parameters for Pu(IV)[a]

name	CN	R	S	ICSD
$Pu(SO_4)_2(H_2O)_4$	8	2.283	4.69	31290[26a]
PuO_2*	8	2.337	3.97	31726,[26b] 55456,[26c] 647325[26d]
$Ba(PuO_3)$	6	2.195	4.31	43768[26e]
$BaPuO_3$*	6	2.228	3.96	65033[26f]
$(NH_4)_2(Pu(NO_3)_6)$*	12	2.484	4.07	71550[26g]
$Pu(Te_2O_6)$	8	2.348	4.00	90383[26h]
$K_4Pu(SO_4)_4(H_2O)_2$*	9	2.386	3.96	91480[26i]
$Na_4Pu(MoO_4)_4$	8	2.348	3.86	154652[26g]
$Pu(IO_3)_4$*	8	2.334	4.01	249470[26k]
$Pu(SeO_3)_2$*	8	2.334	4.08	418050[26l]
$Pu_{0.5}Pa_{0.5}O_2$	8	2.357	3.77	61312[26m]
PuO_2*	8	2.336	3.98	647331[26p]
$Pu(CH_3PO_3)_2$*	6	2.210	4.15	260294[26n]
α-Pu[$CH_2(PO_3)_2$](H_2O)	7	2.264	4.45	260295[26o]
β-Pu[$CH_2(PO_3)_2$](H_2O)*	7	2.279	4.11	this work
β-Pu[$CH_2(PO_3)_2$](H_2O)*	7	2.279	4.15	this work
γ-Pu[$CH_2(PO_3)_2$](H_2O)*	7	2.285	4.07	this work
Pu[$CH_2(PO_3)_2$](H_2O)·(H_2O)*	7	2.297	3.97	this work

[a] CN = coordination number; R = bond distance average; S = bond-valence sum; ICSD = Inorganic Crystal Structural Database.

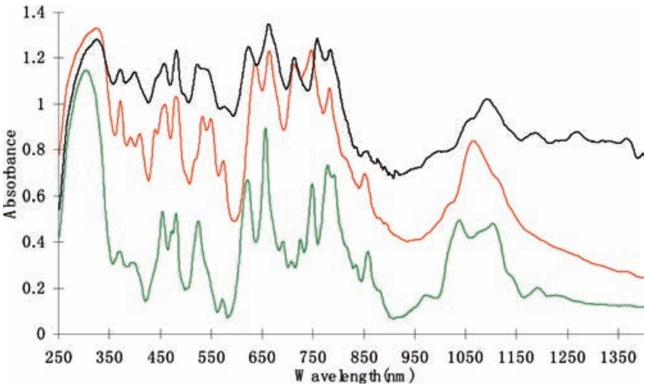

Figure 5. UV−vis−NIR spectra of green crystals of β-Pu[$CH_2(PO_3)_2$](H_2O) (**1**) (green), red crystals of γ-Pu[$CH_2(PO_3)_2$](H_2O) (**2**) (red), and very pale peach crystals of Pu[$CH_2(PO_3)_2$](H_2O)·H_2O (**3**) (black).

UV−vis−NIR Spectroscopy. The UV−vis−NIR spectrum of Pu(IV) is well-known, and has been described in several works.[27−30] The spectrum consist of a series of weak, Laporte-forbidden f-f transitions. Normally when these data are acquired from solutions or powders at room temperature, these transitions are relatively broad for f-f transitions. Data acquired at 4 K, yields much sharper features.[31] Here the use of single crystals of **1** and

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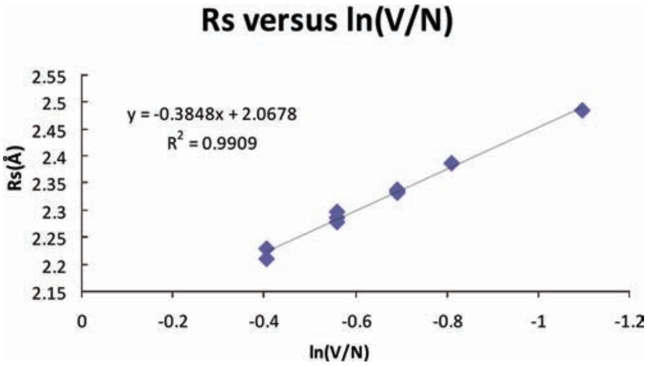

Figure 6. Plot of R_s, the average Pu−O bond distance of each compound, versus ln(*V*/*N*), yielding bond-valence parameters of $b = 0.385$ and $R_o = 2.068$.

2, and a few intergrown crystals for **3**, produces much sharper features than normally obtained at room temperature, and more transitions are clearly resolved. Despite the dramatic color differences, the measurements demonstrate that β-Pu[$CH_2(PO_3)_2$](H_2O) (**1**), γ-Pu[$CH_2(PO_3)_2$](H_2O) (**2**), and Pu[$CH_2(PO_3)_2$](H_2O)·H_2O (**3**) are all Pu^{4+} compounds as shown in Figure 5. This indicates that the visual color of transuranium compounds is often not a good indication of oxidation state.[6] The four plutonium compounds can be divided into two groups by similar coloration. The red (**3**) and peach (**2**) compounds have Pu^{4+} chelated by the diphosphonate, and the in blue (α) and green (**1**) compounds the diphosphonate only bridges. The primary effect on the UV−vis−NIR spectra is that in **1** the peak near 547 nm (green region) is substantially diminished with respect to the intensity of this peak in **2** and **3**. This transition is in a region where multiple *J* values contribute, and transitions in this region have not been definitely assigned.[31] The human eye is very sensitive in this region of the visible spectrum, and this subtle change amidst a series of numerous f-f transitions causes the dramatic changes in the observed color even though the differences appear minor in the spectrum.

Conclusions

In conclusion, four Pu^{4+} and four Ce^{4+} compounds with the same ligands have been prepared. Two of the plutonium compounds do not have cerium analogues, and two of the cerium compounds are unique to cerium. Two of the plutonium compounds are isotypic with cerium phases. We started by asking the very simple question: Is Ce^{4+} a good surrogate for Pu^{4+}? The answer appears to be probably not in this system. It is important to note that all of the plutonium compounds can be arrived at in one reaction; whereas no more than two form at a time with cerium.[13] The synthesis of the additional two cerium compounds required dramatic changes in reaction conditions.[13] At the most fundamental level Pu^{4+} and Ce^{4+} are different in that they form different compounds under the same conditions. However, these differences can not be discerned by solely looking at the M−O bond distances.

We are still left with two baffling questions: (1) What is special about the ionic radius of Ce^{4+} and Pu^{4+} that results in a high degree of structural flexibility that is diminished in neighboring, larger ions? Only one or two compounds form when U^{4+} or Np^{4+} are combined with methylenediphosphonate.[14] (2) If Pu^{4+} and Ce^{4+} are nearly identical in bonding metrics, why do they form different compounds? The MO_7 polyhedra are not identical in these eight phases, and vary from units best described as dodecahedra with a missing vertex to capped octahedra. One explanation is that the answer lies in the subtle involvement of 5f/6d orbitals in bonding with Pu^{4+}, which would be greatly diminished by comparison with the 4f/5d orbitals potentially used in Ce^{4+} compounds.

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Supporting Information Available: X-ray crystallographic files for β-Pu[$CH_2(PO_3)_2$](H_2O) (**1**), γ-Pu[$CH_2(PO_3)_2$](H_2O) (**2**), and Pu[$CH_2(PO_3)_2$](H_2O)·H_2O (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.