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Periodic Trends in Actinide Phosphonates: Divergence and Convergence between Thorium, Uranium, Neptunium, and Plutonium Systems

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The hydrothermal reactions of both PuO_2^{2+} and PuO_2 with phosphonates results in the formation of Pu(IV) phosphonates. $Pu(CH_3PO_3)_2$, $Pu[CH_2(PO_3)_2](H_2O)$, and $UO_2Pu(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ have been isolated from these reactions and structurally characterized. $Pu(CH_3PO_3)_2$ contains six-coordinate Pu(IV) and adopts a structure closely related to that of α-$Zr(HPO_4)_2$. $Pu[CH_2(PO_3)_2](H_2O)$ forms a novel three-dimensional network with seven-coordinate Pu(IV) and chelating/bridging $[CH_2(PO_3)_2]^{4-}$ anions. The heterobimetallic U(VI)/Pu(IV) diphosphonate, $UO_2Pu(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$, also forms a three-dimensional network. To complete the $An[CH_2(PO_3)_2](H_2O)_n$ (An = Th, U, Np, Pu; n = 1, 2) and $UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ series, $Th[CH_2(PO_3)_2](H_2O)_2$ and $UO_2Th(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ have also been prepared. These compounds are isostructural with their Np(IV) analogues.

Introduction

Phosphonates have played an essential role in actinide partitioning in advanced nuclear fuel cycles.[1] Despite their critical nature and the necessity for understanding bonding in actinide phosphonates, little is known about the solid-state structures of these compounds with all actinides except

U(VI).[2] Quite recently we have undertaken the task of elucidating structural tendencies in transuranium phosphonates with the goal of developing periodic trends and structure−property relationships. To this end, an in situ redox method has been developed for preparing crystalline neptunium(IV) compounds.[3−6] These studies reveal that neptunium phosphonates have their own unique crystal chemistry that is not mimicked by early transition metals, lanthanides, or uranium.[4−6] An explicit aim of this work is to illuminate the differences in bonding between transuranium elements, especially neptunium and plutonium, and elements that have been used as their surrogates, for example, Zr^{4+}, Ce^{4+}, and Th^{4+}.[7]

The solution chemistry of plutonium is remarkably complex, and under some conditions it is possible for Pu(VI), Pu(V), Pu(IV), and Pu(III) to coexist in the same solution.[8] Under hydrothermal conditions, which are generally reducing toward actinides, plutonium should generally be driven to

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the least soluble oxidation state, Pu(IV).[8] Therefore, it should be possible to use similar in situ redox chemistry that we developed with neptunium to prepare Pu(IV) phosphonates. Herein we provide data that supports this hypothesis, and disclose details on the syntheses, structures, and spectroscopic features of two Pu(IV) phosphonates, heterobimetallic mixed-actinide U(VI)/Pu(IV) and U(VI)/Th(IV) phosphonates, and a putative Th(IV) analogue of the transuranium phosphonates.

Experimental Section

Syntheses. UO$_3$ (98%, Strem), methylenediphosphonic acid, CH$_2$(PO$_3$H$_2$)$_2$ (98%, Alfa Aesar), and CH$_3$PO$_3$H$_2$ (98%, Alfa Aesar) were used as received. X-ray powder diffraction studies reveal that the UO$_3$ is actually a mixture of UO$_3$ and UO$_3$·H$_2$O. A 0.037 M stock solution of ^{242}Pu (VI) nitrate was prepare by first digesting PuO$_2$ in 8 M HNO$_3$ for 3 days at 200 °C (in an autoclave). The solution was reduced to a moist residue and redissolved in water. This solution was then ozonated for approximately 5 h to ensure complete oxidation of the plutonium to +6. UV−vis−NIR spectroscopy indicates that only Pu(VI) is present. Reactions were run in PTFE-lined Parr 4749 autoclaves with a 23 mL internal volume for thorium, and with 10 mL internal volume autoclaves for plutonium. Distilled and Millipore filtered water was used in all reactions. Standard precautions were performed for handling radioactive materials during work with thorium and uranium. **Caution!** ^{242}Pu ($t_{1/2}$ = 3.76 × 10^5 y) represents a serious health risk owing to its α and γ emission. All studies with neptunium and plutonium were conducted in a laboratory dedicated to studies on transuranium elements. This laboratory is located in a nuclear science facility and is equipped with a HEPA filtered hoods and negative pressure gloveboxes that are ported directly into the hoods. A series of counters continually monitor radiation levels in the laboratory. The laboratory is licensed by the state of Alabama (a NRC compliant state) and Auburn University's Radiation Safety Office. All experiments were carried out with approved safety operating procedures. All free-flowing solids are worked with in gloveboxes, and products are only examined when coated with either water or Krytox oil and water. There are significant limitations in accurately determining yield with plutonium compounds because this requires drying, isolating, and weighing a solid, which poses certain risks, as well as manipulation difficulties given the small quantities employed in the reactions.

Pu(CH$_3$PO$_3$)$_2$. A 333 μL volume of a 0.037 M stock solution of Pu(VI) was placed in an autoclave along with 2.3 mg (0.0246 mmol) of CH$_3$PO$_3$H$_2$. The autoclave was sealed and heated at 180 °C for 3 days followed by slow cooling to room temperature over a 24 h period. The product consisted of blue prisms of Pu(CH$_3$PO$_3$)$_2$.

Pu[CH$_2$(PO$_3$)$_2$](H$_2$O). A 333 μL volume of a 0.037 M stock solution of Pu(VI) was placed in an autoclave along with 4.3 mg (0.0246 mmol) of CH$_2$(PO$_3$H$_2$)$_2$. The autoclave was sealed and heated at 180 °C for 3 days followed by slow cooling to room temperature over a 24 h period. The product consisted of an amorphous red precipitate and blue tablets of Pu[CH$_2$(PO$_3$)$_2$](H$_2$O).

UO$_2$Pu(H$_2$O)$_2$[CH$_2$(PO$_3$)(PO$_3$H)]$_2$. Five milligrams of PuO$_2$ (0.018 mmol) was reacted with 5.1 mg (0.018 mmol) of UO$_3$ and 6.3 mg (0.036 mmol) of methylenediphosphonic acid in 333 μL of water at 180 °C for 3 days in a PTFE-lined autoclave, followed by slow cooling to room temperature over 24 h. The product mixture consisted of an amorphous red precipitate, blue plates of Pu[CH$_2$(PO$_3$)$_2$]-(H$_2$O), yellow acicular crystals of UO$_2$[CH$_2$(PO$_3$H)$_2$](H$_2$O), and a low yield of orange-pink prisms of the desired product.

UO$_2$Th(H$_2$O)$_2$[CH$_2$(PO$_3$)(PO$_3$H)]$_2$. Th(NO$_3$)$_4$·xH$_2$O (249.9 mg, 0.5206 mmol) and UO$_2$(NO$_3$)$_2$·6H$_2$O (258.3 mg, 0.5145 mmol) were reacted with methylenediphosphonic acid (91.6 mg, 0.5204 mmol) in 2 mL of water at 200 °C for 3 days in a PTFE-lined autoclave, followed by slow cooling to room temperature over 24 h. Pale yellow prisms of the mixed actinide compound were isolated as the sole product.

Th[CH$_2$(PO$_3$)$_2$](H$_2$O)$_2$. ThO$_2$ (269.3 mg, 1.02 mmol) was reacted with methylenediphosphonic acid (179.3 mg, 1.02 mmol) in 2 mL of water at 200 °C for 3 days in a PTFE-lined autoclave, followed by slow cooling to room temperature over 24 h. Colorless prisms of Th[CH$_2$(PO$_3$)$_2$](H$_2$O)$_2$ were isolated as the sole product.

Crystallographic Studies. Single crystals of Pu(CH$_3$PO$_3$)$_2$, Pu[CH$_2$(PO$_3$)$_2$](H$_2$O), and UO$_2$Pu(H$_2$O)$_2$[CH$_2$(PO$_3$)(PO$_3$H)]$_2$ were glued into Cryoloops with epoxy. Crystals of UO$_2$Th-(H$_2$O)$_2$[CH$_2$(PO$_3$)(PO$_3$H)]$_2$ and Th[CH$_2$(PO$_3$)$_2$](H$_2$O)$_2$ were mounted as normal on glass fibers. The crystals were optically aligned on a Bruker APEX CCD X-ray diffractometer using a digital camera. Initial intensity measurements were performed using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation from a sealed tube and monocapillary collimator. SMART (v 5.624) was used for preliminary determination of the cell constants and data collection control. The intensities of reflections of a sphere were collected by a combination of 3 sets of exposures (frames). Each set had a different ϕ angle for the crystal and each exposure covered a range of 0.3° in ω. A total of 1800 frames were collected with an exposure time per frame of 30 to 60 s, depending on the crystal. Crystals of Pu[CH$_2$(PO$_3$)$_2$](H$_2$O) were marginal at best and invariably twinned, and required the use of the GEMINI program to separate individual components of the twin.[9]

For these compounds, determination of integrated intensities and global refinement were performed with the Bruker SAINT (v 6.02) software package using a narrow-frame integration algorithm. The data were treated with a semiempirical absorption correction by SADABS.[10] The program suite SHELXTL (v 6.12) was used for space group determination (XPREP), direct methods structure

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Table 1. Crystallographic Data for $Pu(CH_3PO_3)_2$ (**Pu-1**), $Pu[CH_2(PO_3)_2](H_2O)$ (**Pu-2**), $UO_2Pu(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (**U/Pu-1**), $UO_2Th(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (**U/Th-1**), and $Th[CH_2(PO_3)_2](H_2O)_2$ (**Th-1**)

compound	Pu-1	Pu-2	U/Pu-1	U/Th-1	Th-1
mass	430.01	431.99	894.01	884.05	440.03
color and habit	blue, prism	blue, tablet	orange-pink, prism	yellow, prism	colorless, prism
space group	$P2_1/c$	$P2_1/m$	$P2_1/m$	$P2_1/m$	$Pna2_1$
a (Å)	8.0895(12)	6.513(3)	5.4763(7)	5.5558(4)	8.9658(4)
b (Å)	10.7001(10)	5.753(2)	20.078(3)	20.5994(15)	9.7748(5)
c (Å)	9.4541(14)	9.023(4)	6.8762(9)	6.9482(5)	8.8042(4)
α (deg)	90	90	90	90	90
β (deg)	92.331(3)	106.344(7)	98.485(2)	99.1140(10)	90
γ (deg)	90	90	90	90	90
V (Å^3)	817.7(2)	324.4(2)	747.79(17)	785.16(10)	771.59(6)
Z	4	2	2	2	4
T (K)	193	193	193	298	193
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
maximum 2θ (deg.)	28.31	28.34	28.43	28.29	28.32
ρ_{calcd} (g cm^{-3})	3.493	4.381	3.966	3.714	3.788
μ(Mo $K\alpha$)	84.35	106.40	156.97	202.47	197.49
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.0197	0.0603	0.0401	0.0253	0.0193
$R_w(F_o^2)^b$	0.0458	0.1487	0.1045	0.0661	0.0748

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

solution (XS), and least-squares refinement (XL).[11] The final refinements included anisotropic displacement parameters and a correction for secondary extinction when necessary. Minor symmetry induced disorder of the methylene carbon atom in $Pu[CH_2(PO_3)_2](H_2O)$ was noted, and has been refined appropriately. Key crystallographic details are given in Table 1. Additional details can be found in the Supporting Information.

Fluorescence Spectroscopy. The fluorescence emission spectrum of $UO_2Th(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ was acquired using a PI Acton spectrometer (SpectraPro SP 2356, Acton, NJ) that is connected to the side port of an epi-fluorescence microscope (Nikon TE-2000U, Japan). The emission signal was recorded by a back-illuminated digital CCD camera (PI Acton PIXIS:400B, Acton, NJ) operated by a PC. For this compound, the excitation was generated by a mercury lamp (X-Cite 120, EXFO, Ontario, Canada) filtered by a band-pass filter at 450−490 nm. The emission signal was filtered by a long-pass filter with a cutoff wavelength of 515 nm.

Raman Spectroscopy. The Raman spectra of $UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (An = Th, Np, Pu) were acquired from single crystals enclosed in quartz capillaries using a Renishaw inVia Confocal Raman microscope with a 514 nm Ar$^+$ laser.

Results and Discussion

Synthesis. Our basic conjecture is that even though Pu(VI) is not as strong of an oxidizing agent as Np(VI) ($E° = 1.159$ V for Np(VI); $E° = 0.936$ V for Pu(VI)),[12] it will still be reduced from Pu(VI) to the least soluble oxidation state, Pu(IV), under hydrothermal conditions where water is acting as the reductant. These are not homogeneous reactions but rather are driven in part by the free energy of the formation of the highly insoluble Pu(IV) phosphonates. This hypothesis was tested by starting with a stock solution of PuO_2^{2+} (as the nitrate) to which either methylphosphonic acid or methylenediphosphonic acid were added. The addition of the

phosphonic acid does not result in color change or any detectable reduction. However, upon heating the PuO_2^{2+} is reduced to Pu^{4+} and is isolated in the form of either $Pu(CH_3PO_3)_2$ or $Pu[CH_2(PO_3)_2](H_2O)$.

From control studies we were surprised to learn that ThO_2 dissolves under mild hydrothermal conditions in the presence of methylenediphosphonic acid, and this allows for the isolation of $Th[CH_2(PO_3)_2](H_2O)_2$. This implies that we might not need to use PuO_2^{2+} as our source of plutonium, but rather we can simply use brute force methods and digest PuO_2 under acidic conditions in the presence of phosphonates. The reaction of PuO_2 with methylenediphosphonic acid in water at 180 °C under autogenously generated pressure results in the formation of crystals of $Pu[CH_2(PO_3)_2](H_2O)$ as we found when PuO_2^{2+} was used as the source of plutonium.

Since our discovery of a heterobimetallic mixed-actinide phosphonate, currently represented only by $UO_2Np(H_2O)_2$-$[CH_2(PO_3)(PO_3H)]_2$,[6] we have sought to prepare U(VI)/Pu(IV) compounds of this type. Again we started with the in situ hydrothermal reduction of PuO_2^{2+} to Pu^{4+} to provide our source of tetravalent plutonium. However, we invariably found that when UO_3 and PuO_2^{2+} are reacted simultaneously with methylenediphosphonic acid that the heterobimetallic compound does not form, but only $Pu[CH_2(PO_3)_2](H_2O)$ and $UO_2[CH_2(PO_3H)_2](H_2O)$ are isolated. However, with our new knowledge concerning the solubility of PuO_2 in the presence of methylenediphosphonic acid, we resorted to the direct reaction of the appropriate oxides, UO_3 and PuO_2, with methylenediphosphonic acid. This reaction afforded crystals of the desired compound, $UO_2Pu(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$, albeit in low yield. Similar reactions were performed by replacing the PuO_2 with ThO_2. These result in the formation of $UO_2Th(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ in high yield.

Crystal Chemistry of $Pu(CH_3PO_3)_2$. The structure of $Pu(CH_3PO_3)_2$ is surprising simple and is formed from Pu(IV) centers that are bridged by $CH_3PO_3^{2-}$ anions (Table 2). The binding of the plutonium centers by the methylphosphonate creates an octahedral environment with Pu−O bond distances ranging from 2.188(3) to 2.235(3) Å. P−O bonds in the phosphonate are essentially invariant and average 1.523(3)
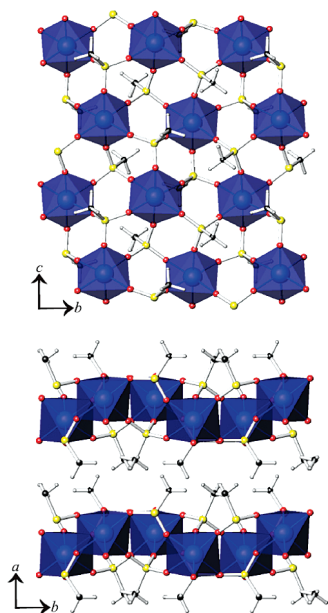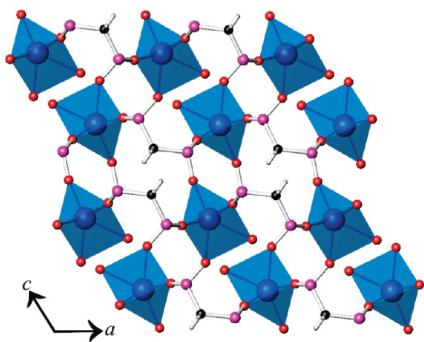
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Table 2. Selected Bond Distances (Å) for $Pu(CH_3PO_3)_2$ (**Pu-1**)

Distances (Å)			
Pu(1)−O(4)	2.188(3)	P(1)−O(6)	1.525(3)
Pu(1)−O(1)	2.196(3)	P(1)−C(1)	1.779(4)
Pu(1)−O(3)	2.204(3)	P(2)−O(1)	1.526(3)
Pu(1)−O(2)	2.210(3)	P(2)−O(2)	1.528(3)
Pu(1)−O(6)	2.228(3)	P(2)−O(5)	1.529(3)
Pu(1)−O(5)	2.235(3)	P(2)−C(2)	1.778(4)
P(1)−O(4)	1.523(3)		
P(1)−O(3)	1.524(3)		

Table 3. Selected Bond Distances (Å) for $Pu[CH_2(PO_3)_2](H_2O)$ (**Pu-2**)

Distances (Å)			
Pu(1)−O(2)	2.18(2)	P(1)−O(1)	1.478(17)
Pu(1)−O(1)	2.190(15)	P(1)−O(1)′	1.478(17)
Pu(1)−O(1)′	2.190(16)	P(1)−O(2)	1.53(2)
Pu(1)−O(3)	2.225(17)	P(1)−C(1)	1.83(2)
Pu(1)−O(3)′	2.225(17)	P(2)−O(3)	1.462(17)
Pu(1)−O(4)	2.295(17)	P(2)−O(3)′	1.462(17)
Pu(1)−O(5)	2.49(2)	P(2)−O(4)	1.508(17)
		P(2)−C(1)	1.78(2)

Å. The layered topology that is created is closely related to that of the well-known structure of α-Zr(HPO$_4$)$_2$, which forms the basis for many zirconium phosphonate materials.[13] Plutonium is not generally found with coordination numbers this low, and this structure clearly represents a case where a non-radioactive surrogate like Zr(IV) provides a good mimic of Pu(IV) and vice versa. Different views of the structure are shown in Figure 1.
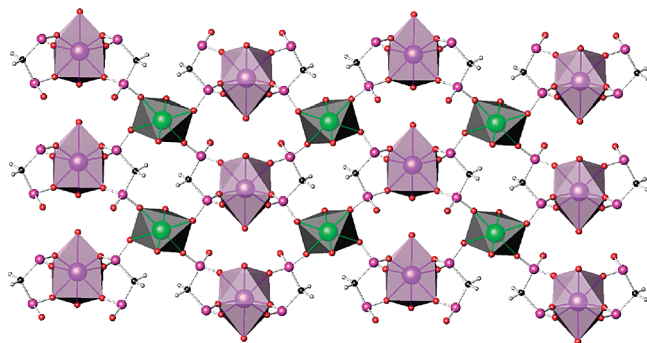
Crystal Chemistry of $Pu[CH_2(PO_3)_2](H_2O)$. Owing to twinning and disorder, the structure of $Pu[CH_2(PO_3)_2](H_2O)$ does not have as low residuals as the others reported in this work (Table 3). Nevertheless, given the paucity of structural data on plutonium compounds, its details are important. The monohydrate of Pu(IV) methylenediphosphonate has the same stoichiometry as that of its U(IV) analogue.[5] Further-

more, it contains similar An(IV)O$_7$ (An = U, Pu) polyhedra as $U[CH_2(PO_3)_2](H_2O)$. These building units are exceedingly rare in actinide crystal chemistry. The Pu−O bond distances range from 2.18(2) to 2.49(2) Å, with the longest bond being with the terminal water molecule. Both compounds adopt three-dimensional framework structures where the [CH$_2$-(PO$_3$)$_2$]$^{4-}$ anions chelating Pu(IV) and also bridge between Pu(IV) cations. The compounds are not isotypic, however. $U[CH_2(PO_3)_2](H_2O)$ is actually of higher symmetry and crystallizes in the orthorhombic space group *Pbca*.[5] In contrast, $Pu[CH_2(PO_3)_2](H_2O)$ is monoclinic and crystallizes in *P2$_1$/m*. A depiction of the structure of $Pu[CH_2(PO_3)_2](H_2O)$ is shown in Figure 2.

Crystal Chemistry of $UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (An = Th, Np, Pu). Given the complex nature of the formula of these compounds, it might be considered surprising that $UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (An = Th, Np, Pu) form compounds with identical composition that are also isotypic (Tables 4, 5). This is especially true since the compounds are arrived at by different routes. This suggests that this composition and structure might represent an energetic well. The structure of $UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ consists of UO$_6$ tetragonal bipyramids containing an uranyl, UO$_2^{2+}$,

Figure 1. Two views of the lamellar structure of $Pu(CH_3PO_3)_2$. PuO$_6$ octahedra are shown in blue.

Figure 2. Depiction of the structure of $Pu[CH_2(PO_3)_2](H_2O)$. The PuO$_7$ units are shown in blue.

Figure 3. Illustration of the structure of $UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (An = Th, Np, Pu) consisting of UO$_6$ tetragonal bipyramids (gray/green) containing an uranyl, UO$_2^{2+}$, core, and AnO$_8$ distorted dodecahedra (purple) containing an An(IV) center that are bridged by partially protonated methylenediphosphonate.

Table 4. Selected Bond Distances (Å) for $UO_2Pu(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (**U/Pu-1**)

Distances (Å)			
Pu(1)−O(4)	2.213(7)	P(1)−O(2)	1.483(8)
Pu(1)−O(4)	2.213(7)	P(1)−O(3)	1.496(8)
Pu(1)−O(6)	2.262(7)	P(1)−O(1)	1.551(9)
Pu(1)−O(6)	2.262(7)	P(1)−C(1)	1.746(10)
Pu(1)−O(2)	2.277(7)	P(2)−C(1)	1.796(10)
Pu(1)−O(2)	2.277(7)	P(2)−O(4)	1.498(7)
Pu(1)−O(7)	2.465(10)	P(2)−O(5)	1.540(6)
Pu(1)−O(8)	2.475(4)	P(2)−O(6)	1.495(7)
U(1)−O(9) (×2)	1.753(7)		
U(1)−O(3) (×2)	2.262(7)		
U(1)−O(5) (×2)	2.293(6)		

Table 5. Selected Bond Distances (Å) for UO$_2$Th(H$_2$O)$_2$[CH$_2$(PO$_3$)-(PO$_3$H)]$_2$ (**U/Th-1**)

	Distances (Å)		
Th(1)−O(1)	2.348(4)	P(1)−O(2)	1.543(4)
Th(1)−O(1)	2.348(4)	P(1)−O(3)	1.511(4)
Th(1)−O(3)	2.322(4)	P(1)−O(1)	1.512(4)
Th(1)−O(3)	2.322(4)	P(1)−C(1)	1.793(5)
Th(1)−O(4)	2.405(4)	P(2)−C(1)	1.789(5)
Th(1)−O(4)	2.405(4)	P(2)−O(4)	1.500(4)
Th(1)−O(8)	2.558(6)	P(2)−O(5)	1.571(4)
Th(1)−O(9)	2.523(6)	P(2)−O(6)	1.505(4)
U(1)−O(7) (×2)	1.766(4)		
U(1)−O(2) (×2)	2.312(4)		
U(1)−O(6) (×2)	2.281(4)		

core, and AnO$_8$ distorted dodecahedra containing an An(IV) center that are bridged by partially protonated methylenediphosphonate, as shown in Figure 3. We can differentiate between the hexavalent uranium and the tetravalent actinide on the basis of coordination geometry instead of X-ray scattering alone, which would be very similar for the two elements. Reaffirmation of the presence of An(IV) and U(VI) is also provided by Raman and visible diffuse reflectance spectroscopic data.[6]

In the case of UO$_2$Pu(H$_2$O)$_2$[CH$_2$(PO$_3$)(PO$_3$H)]$_2$, the uranium atom resides on an inversion center providing one unique U≡O bond of 1.753(7) Å, and two unique equatorial bonds of 2.262(7) and 2.293(6) Å. These compare very well with the Np analogue.[6] The Pu−O bonds occur from 2.213(7) to 2.475(4) Å. There are in fact six short bonds that range from 2.213(7) to 2.277(7) Å, and two long bonds to the coordinating water molecules of 2.465(10) and 2.475(4) Å. Here the Pu−O bonds are slightly shorter than the Np−O bonds as expected from the actinide contraction. The expected difference should be on the order of 0.02 Å.[14] As implied from its larger ionic radius, the Th−O bonds are the longest in this series (see Table 5).

Crystal Chemistry of Th[CH$_2$(PO$_3$)$_2$](H$_2$O)$_2$. Thorium(IV) methylenediphosphonate dihydrate was prepared to determine if its structure would be similar with that of the other members of this series (Table 6). The Th(IV) centers are found as ThO$_8$ distorted dodecahedra with Th−O bond distances ranging from 2.288(4) to 2.695(5) Å. The bond distances can really be divided into two groups: those formed in conjunction with the methylenediphosphonate, which range from 2.288(4) to 2.429(5) Å, and much longer Th−O bonds of 2.649(4) and 2.695(5) Å to the two coordinating water molecules. A view of the structure is shown in Figure 4. This compound is isotypic with Np[CH$_2$(PO$_3$)$_2$](H$_2$O)$_2$, and this allows for comparison between the bond distances. In the case of the Np(IV) analogue, the Np−O bonds average 2.283(3) Å for the neptunium phosphonate bonds and 2.622(3) Å for those to the two water molecules. The Th−O bonds are notably longer and average 2.342(5) and 2.672(6) Å for the same sets of bonds. This is an example of the actinide contraction associated with the decreased ionic radius of Np(IV) (0.98 Å) relative to that of Th(IV) (1.05 Å).[14] Here is a case where periodic trends hold true.

Fluorescence Measurements on UO$_2$An(H$_2$O)$_2$[CH$_2$(PO$_3$)(PO$_3$H)]$_2$ (An = Th, Np, Pu). The emission of green light that occurs from uranyl compounds when they are excited by long wavelength UV light has proven to be a
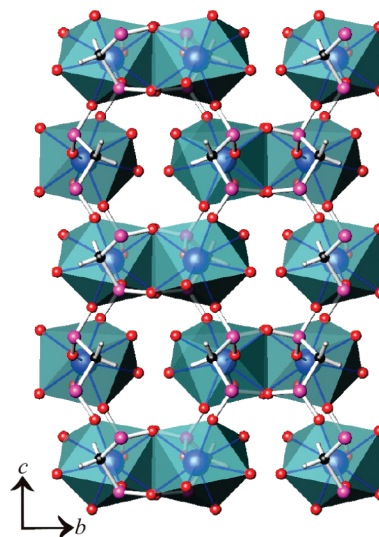
Figure 4. Depiction of the structure of Th[CH$_2$(PO$_3$)$_2$](H$_2$O)$_2$. ThO$_8$ distorted dodecahedra are shown in blue. The coordinating water molecules are found in small channels that extend along the *a* axis.

Table 6. Selected Bond Distances (Å) for Th[CH$_2$(PO$_3$)$_2$](H$_2$O)$_2$ (**Th-1**)

	Distances (Å)		
Th(1)−O(5)	2.294(5)	P(1)−O(1)	1.534(6)
Th(1)−O(2)	2.306(5)	P(1)−O(3)	1.527(6)
Th(1)−O(6)	2.317(5)	P(1)−O(2)	1.538(5)
Th(1)−O(3)	2.320(5)	P(1)−C(1)	1.764(8)
Th(1)−O(1)	2.381(6)	P(2)−O(4)	1.527(6)
Th(1)−O(4)	2.430(5)	P(2)−O(6)	1.523(5)
Th(1)−O(1w)	2.651(5)	P(2)−O(5)	1.524(5)
Th(1)−O(2w)	2.693(5)	P(2)−C(1)	1.828(9)

useful diagnostic tool for a variety of purposes including energy transfer and detection.[15] One of the characteristic features of this emission is vibronic fine-structure, whose features have been assigned.[16] Fluorescence spectra for UO$_2$An(H$_2$O)$_2$[CH$_2$(PO$_3$)(PO$_3$H)]$_2$ (An = Th, Np, Pu) were recorded from single crystals in quartz capillaries. The spectrum of UO$_2$Th(H$_2$O)$_2$[CH$_2$(PO$_3$)(PO$_3$H)]$_2$ is shown in Figure 5. Emission from UO$_2$Np(H$_2$O)$_2$[CH$_2$(PO$_3$)(PO$_3$H)]$_2$ and UO$_2$Pu(H$_2$O)$_2$[CH$_2$(PO$_3$)(PO$_3$H)]$_2$ was not detected. UO$_2$Th(H$_2$O)$_2$[CH$_2$(PO$_3$)(PO$_3$H)]$_2$ is the only one of these compounds that shows vibronic fine-structure typical for uranyl-containing compounds.[15,16] An examination of the absorption spectra of typical Np(IV) and Pu(IV) compounds shows that the emission from uranyl units overlaps with the f-f absorption features of these transuranium ions. Energy transfer is therefore expected, and this is why uranyl emission from these compounds is not observed. In contrast, Th(IV) compounds are typically colorless and lack f-f transitions, allowing for the observation of uranyl-based emission from this compound.

Conclusions

Structural data on compounds containing transuranium elements is sorely lacking, making predictive aspects of the coordination chemistry of these elements challenging.[7f,h] The few studies that have been performed outside of simple binaries (e.g., AnO$_2$ or AnX$_3$; An = actinide, X = halide) have not

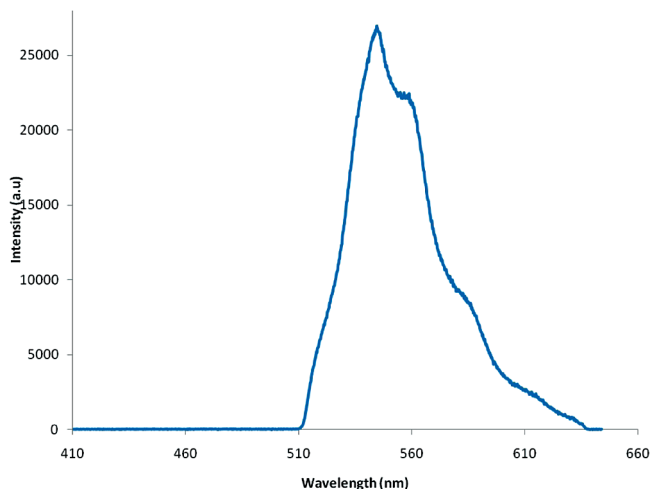(14) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

Figure 5. Fluorescence spectrum of $UO_2Th(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ showing the emission from the uranyl units with partial resolution of the vibronic structure.

yielded simple periodic trends.[7] In the $An[CH_2(PO_3)_2](H_2O)_n$ (An = Th, U, Np, Pu; n = 1, 2) series we find that thorium and neptunium adopt the same composition (i.e., $An[CH_2(PO_3)_2](H_2O)_2$) and are isotypic. Whereas uranium and plutonium crystallize as compounds with the same formula (i.e., $An[CH_2(PO_3)_2](H_2O)$), but are not isotypic. Therefore, sequential changes or periodic trends that might occur as a function of the actinide ion, such as ionic radius, are not clearly identified in this system. We postulate that if such a trend were to occur, the most likely scenario would be a reduction in the coordination number of the actinide as one moves to heavier members of the actinide series owing to the actinide contraction. Instead, it is observed that Th and Np are eight-coordinate, and U and Pu are in a rare seven-coordinate environment. While many suggestions can be put forward to explain these differences, the most likely scenario is that the compounds that are isolated are a reflection of not only the traits of the actinide ion but also the conditions under which the crystals are growing. Mild hydrothermal reaction conditions are known to yield kinetic products in many cases. The exact product that is isolated is often highly sensitive to the particular reaction conditions. Since we are likely not to be comparing a series of thermodynamic products, it is difficult to pinpoint what factors are responsible for the formation of a specific compound. While we have held as many conditions constant as possible in comparing reactions, we do not know the point in the reactions where crystal nucleation occurs. The degree of hydration of the actinide ion would be substantially affected by the dielectric constant of water, which changes substantially between 25 and 180 °C. This factor alone could be responsible for $An[CH_2(PO_3)_2](H_2O)_2$ forming versus $An[CH_2(PO_3)_2](H_2O)$. It is important to note that even when thermodynamic products obtained from high-temperature solid-state reactions are compared that differences in structure and composition between neighboring actinides have been noted.[7i−p]

One of the important discoveries made in the course of this work is that isotypic U(VI)/An(IV) (An = Th, Np, Pu) phosphonates can be prepared and isolated as single crystals. This is surprising because the structure of $UO_2An(H_2O)_2$-$[CH_2(PO_3)(PO_3H)]_2$ (An = Th, Np, Pu) is very complex, and since the methylenediphosphonate ligand is partially protonated, the formation of this compound is probably highly pH sensitive. Nevertheless, this is what occurs, and the first U(VI)/Pu(IV) and U(VI)/Th(IV) phosphonates has been isolated and characterized. The challenge that remains is to isolate a heterobimetallic An(VI)/An(IV) compound where both actinides are transuranium elements possessing 5f electrons (U(VI) is $5f^0$). If certain bonding requirements can be met, magnetic coupling between two different actinides with differing numbers of 5f electrons could be investigated. This is the direction our program is heading in.

Supporting Information Available: X-ray crystallographic files in CIF format for $Pu(CH_3PO_3)_2$, $Pu[CH_2(PO_3)_2](H_2O)$, $UO_2Pu(H_2O)_2$-$[CH_2(PO_3)(PO_3H)]_2$, $UO_2Th(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$, and $Th[CH_2(PO_3)_2](H_2O)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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