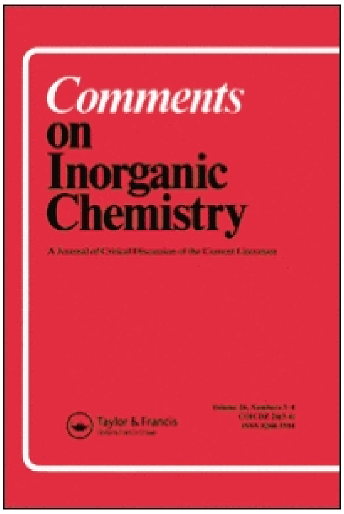

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# USING PHOSPHONATES TO PROBE STRUCTURAL DIFFERENCES BETWEEN TRANSURANIUM ELEMENTS AND THEIR PROPOSED SURROGATES

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# USING PHOSPHONATES TO PROBE STRUCTURAL DIFFERENCES BETWEEN TRANSURANIUM ELEMENTS AND THEIR PROPOSED SURROGATES

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A variety of transuranium phosphonates have now been prepared and structurally characterized allowing for comparisons to be made with other metal ions that have been proposed to be surrogates for transuranics (e.g., $Zr^{4+}$, $Ce^{4+}$, $Th^{4+}$, and $U^{4+}$). The phosphonates that will be discussed in this work include $Np(CH_3PO_3)(CH_3PO_3H)(NO_3)(H_2O) \cdot H_2O$, $Pu(CH_3PO_3)_2$, $M[CH_2(PO_3)_2](H_2O)_n$ (M=Ce, Th, U, Np, Pu; $n = 0 - 2$), and $UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (An = Th, Np, Pu). Through the examination of these structures, rare coordination geometries for actinides have been uncovered. Simple periodic trends based solely on ionic radii are absent. However, there are examples where surrogate elements adopt the same composition and structure as transuranics, such as $Pu(CH_3PO_3)_2$ versus $Zr(CH_3PO_3)_2$.

***Keywords***: actinide phosphonates, cerium phosphonates, mixed-actinide phosphonates, surrogates

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## INTRODUCTION

Transuranium elements, especially plutonium, play a special role in science and politics. With worldwide electrical energy production being approximately 20% nuclear in origin, a nuclear arsenal capable of wiping out the human race, and tens of thousands of metric tons of high-level nuclear waste on hand, it is difficult to ignore the importance of transuranics in our society. The nuclear industry is poised on the brink of a global revival, and advanced nuclear fuel cycles that require complex chemical knowledge are either in place or being seriously considered by many technologically advanced countries. At the heart of this quandary is the profound need for a thorough understanding of the chemistry of the elements most deeply involved in all of these efforts, the actinides.[1–8]

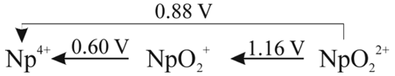
It is sad to write, but liability (not safety) has an immense impact on actinide chemistry. Owing to the radioactivity and toxicity of actinides there are severe restrictions regarding their storage, use, and disposal.[9] These restrictions are so severe that actinide chemistry is conducted at only a handful of universities, and even the once dedicated national laboratories have greatly curtailed their research programs in this area. One of the outcomes of this is the use of less toxic and less or non-radioactive surrogates for transuranium elements. These include early transition metals, especially $Zr^{4+}$, lanthanides (e.g., $Ce^{4+}$ and $Eu^{3+}$), and the early actinides, thorium and uranium.[9] The most central question is: do these surrogates actually mimic the chemistry of transuranics?

In this present work we will probe the structural chemistry of actinide phosphonates to address this aforementioned question. In doing so, new chemistry has been discovered that demonstrates the uniqueness of each transuranium element. In this discussion, we will only investigate the two lightest transuranics, namely neptunium and plutonium. Heavier actinides tend to be trivalent and are outside the scope of this discussion.

## 1. NEPTUNIUM AND PLUTONIUM PHOSPHONATES

The first neptunium phosphonate isolated was $Np(CH_3PO_3)(CH_3PO_3H)$-$(NO_3)(H_2O) \cdot H_2O$.[10] This rather complex formula reflects the incorporation of all of the components of the reaction mixture that contained $NpO_2(NO_3)_2 \cdot nH_2O$, $CH_3PO_3H_2$, and water. Hydrothermal treatment of this reaction mixture results in reduction of the Np(VI) to Np(IV). What is the reducing agent in this reaction? Ligand decomposition was not detected, but can not be ruled out. Nitrate generally serves as an oxidizing agent, leaving water as a possible culprit.

Is Np(VI) capable of oxidizing water? The formal potentials for Np redox reactions are given below.



It is important to note that these E° values are given at 25°C and 1 atm. The mild hydrothermal reactions described here occurred at 180–200°C and approximately 17 atm (if $H_2O$ exhibits the vapor pressure of pure water), and therefore these formal potentials can only be used for guidance.[11] The reduction potentials for $NpO_2^{2+}$ are known up to 300°C, and they are essentially invariant with increasing temperature. In contrast, the oxidation of water changes from approximately 1.23 V at 25°C to 1.092 V at 200°C.[12] Therefore, water is more easily oxidized at higher temperatures. Our calculations show that the oxidation of water by Np(VI) is favorable at 200°C. This, however, only converts Np(VI) to Np(V). How is Np(V) converted to Np(IV)? Reactions 1–3 provide two possible routes to Np(IV). The first is via a second reduction by water step. There is evidence for this type of reaction in the literature. It was found that when Np(V) perchlorate was heated at 200°C in neutral aqueous media that $NpO_2$ precipitates. Water was proposed to be the reductant in this reaction (Rxn 2). However, Np(IV) could also be generated by the disproportation of the Np(V) to Np(VI) and Np(IV) (Rxn 3). If the Np(IV) were removed from solution the reaction mixture by precipitation, it would be eventually driven entirely to Np(IV) via the combination of Rxn 1 and 3.[13]

$$4NpO_2^{2+} + 2H_2O \xrightarrow[H_2O]{180\,^{\circ}C,3d} 4NpO_2^{+} + 4H^{+} + O_2 \qquad \text{Rxn (1)}$$

$$4NpO_2^{+} + 12H^{+} \xrightarrow[\text{phosphonate}]{180^{\circ}C,3d} Np^{4+}(\text{phosphonate})_{(s)} + 6H_2O + O_2 \qquad \text{Rxn (2)}$$

$$2NpO_2^{+} + 4H^{+} \xrightarrow[\text{phosphonate}]{180^{\circ}C,3d} Np^{4+}(\text{phosphonate})_{(s)} + NpO_2^{2+} + 2H_2O \qquad \text{Rxn (3)}$$

Isotopic labeling studies are underway to test for the production of $^{18}O_2$ from O-18 enriched water. Until these studies are complete, it will remain unclear what the reducing agent is.

Regardless of the reducing agent, Np(IV) is in fact produced, providing a facile route to new Np(IV) compounds. Thus far, these have been restricted to iodates, fluorophosphates, and phosphonates.[10,11,13,14] The oxidation state of the Np has been confirmed by bond-valence sum calculations, UV-vis-NIR diffuse reflectance spectroscopy, and magnetic susceptibility measurements.

The formation of $Np(CH_3PO_3)(CH_3PO_3H)(NO_3)(H_2O) \cdot H_2O$ was quite surprising because one would have predicted that $Np(CH_3PO_3)_2$ would be the likely product of this reaction if the Np(IV) were to

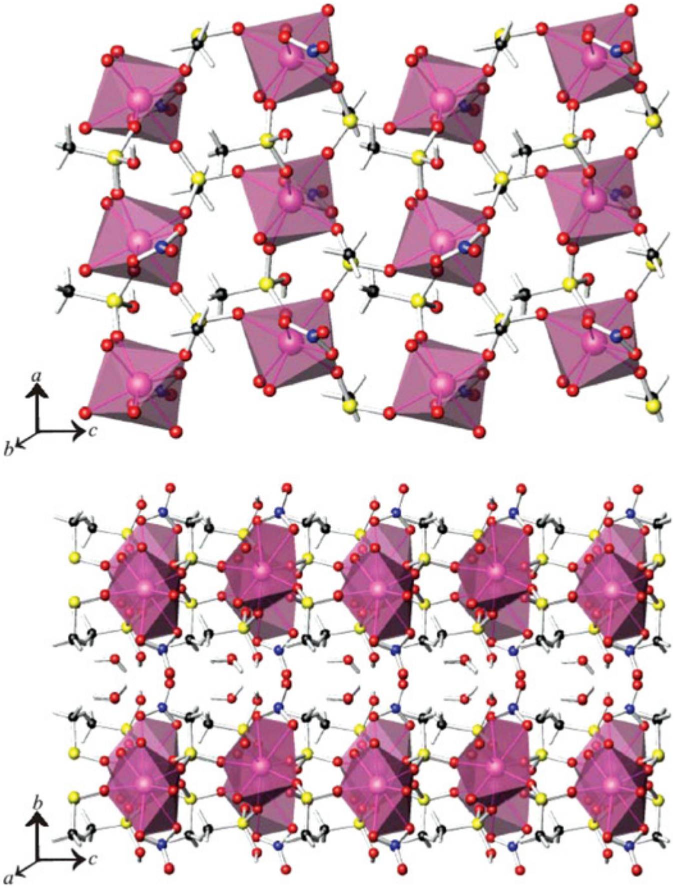


**Figure 1.** Two views of the polar, lamellar structure of $Np(CH_3PO_3)(CH_3PO_3H)(NO_3)(H_2O) \cdot H_2O$. $NpO_8$ = pink, P = yellow, O = red, N = blue, H = white.

behave like Zr(IV).[10] However, Np(IV) tends to adopt eight- and nine-coordinate environments both in solution and in the solid state. This is accomplished, in part, by retaining nitrate in the inner coordination sphere. The second odd feature of this compound is the protonated methylphosphonate anions. A close look at Figure 1 shows that these anions are aligned along the *c* axis, rendering the structure polar. $Np(CH_3PO_3)(CH_3PO_3H)(NO_3)(H_2O) \cdot H_2O$ forms thick layers that stack along *b* that are interconnected by hydrogen bonding networks involving the interlayer water molecules[10]

Do transuranium phosphonate structures differ from transition metal and lanthanide phosphonates? Definitely, yes. There are no light actinide, lanthanide, or early transition metal counterparts to this Np(IV) compound.

In contrast with the preparation of $Np(CH_3PO_3)(CH_3PO_3H)(NO_3)(H_2O) \cdot H_2O$, the reaction of Pu(VI) with methylphosphonic acid yields blue crystals of $Pu(CH_3PO_3)_2$, the structure of which is shown in Figure 2. This compound has a structure that is very similar to $\alpha$-$Zr(HPO_4)_2$, and contains octahedral $PuO_6$ units.[15] This result is surprising because, like the other actinides, Pu(IV) prefers higher coordination numbers. Nevertheless, this is a clear example where Pu(IV) behaves like Zr(IV).

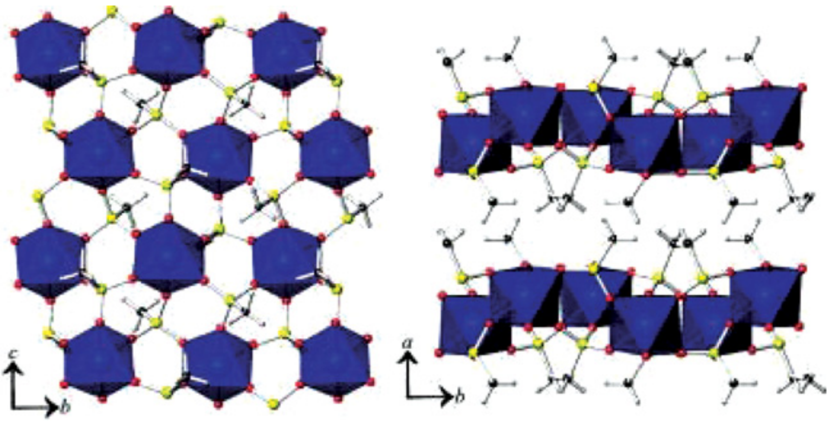


**Figure 2.** Two views of the lamellar structure of $Pu(CH_3PO_3)_2$. $PuO_6$ = blue, P = yellow, O = red, C = black.

## 2. LANTHANIDE AND ACTINIDE DIPHOSPHONATES, $M[CH_2(PO_3)_2](H_2O)_N$ (M=CE, TH, U, NP, PU; N = 0 – 2)

The structural chemistry of f-block methylenediphosphonates has proven to be remarkably rich. These compounds are formulated as $M[CH_2(PO_3)_2](H_2O)_2$ (M = Ce, Th, U, Np), $M[CH_2(PO_3)_2](H_2O)$ (M = Ce, U, Pu), and $Ce[CH_2(PO_3)_2]$.[13,16] In all cases, the metal ions are in the tetravalent oxidation state. In some cases the synthetic chemistry is not as consistent between elements as would be desired. Only a few crystals of $U[CH_2(PO_3)_2](H_2O)$ are isolated from a given reaction, and this compound often does not form at all. This argues that this U(IV) compound may result from some impurity in the autoclaves acting as a reducing agent, which has been observed many times before in other works. While the synthesis of $Pu[CH_2(PO_3)_2](H_2O)$ is reproducible, it results in a product mixture containing several Pu(IV) methylenediphosphonate compounds; crystals of $Pu[CH_2(PO_3)_2](H_2O)$ are marginally suitable for X-ray diffraction studies. In contrast, $M[CH_2(PO_3)_2](H_2O)_2$ (M = U, Ce, Th, Np) can all be isolated in high yield. It is important to note that $U[CH_2(PO_3)_2](H_2O)_2$ and $Np[CH_2(PO_3)_2](H_2O)_2$ result from the previously discussed hydrothermal reduction of U(VI) and Np(VI),

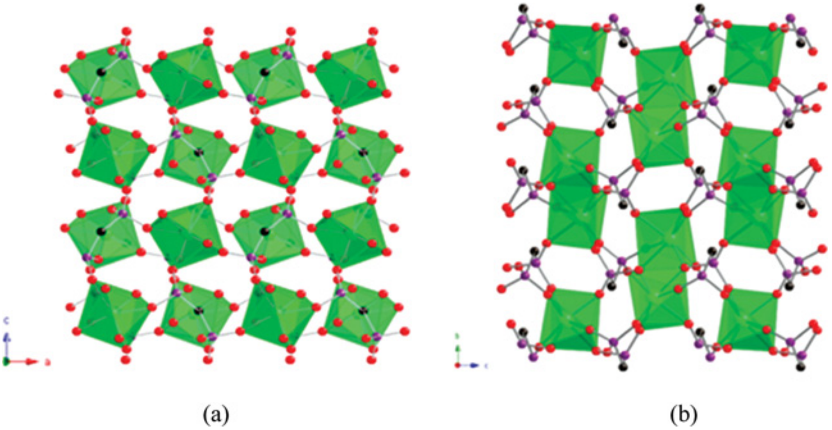


**Figure 3.** (a) A view of part of the structure of $Ce[CH_2(PO_3)_2](H_2O)_2$ showing polar three-dimensional framework with Ce(IV) metal centers bound by **C1P2** and isolated water molecules to form a $CeO_8$ distorted dodecahedra. $Ce[CH_2(PO_3)_2](H_2O)_2$ compound is isostructural with $M[CH_2(PO_3)_2](H_2O)_2$ (M=U, Th, Np). (b) A view of part of the structure of $Ce[CH_2(PO_3)_2]$ down the a axis. $CeO_{7(8)}$ = green, P = yellow, O = red, C = black.

**Table 1.** Crystallographic data for $Ce[CH_2(PO_3)_2]$ **(CeC1P2–1)**, $\alpha$-$Ce[CH_2(PO_3)_2](H_2O)$ ($\alpha$-CeC1P2), $\beta$-$Ce^{IV}[CH_2(PO_3)_2](H_2O)$ **(β-CeC1P2)**, $Ce[CH_2(PO_3)_2](H_2O)_2$ **(CeC1P2-2)** and $U[CH_2(PO_3)_2](H_2O)_2$ **(UC1P2-2)**

| Compound | CeC1P2–1 | $\alpha$-CeC1P2 | $\beta$-CeC1P2 | CeC1P2-2 | UC1P2-2 |
|---|---|---|---|---|---|
| Mass | 312.9 | 328.09 | 328.09 | 344.09 | 442.00 |
| Color and habit | Colorless, needle | Colorless, needle | Colorless, needle | Colorless, needle | Green, square prism |
| Space group | $P2_1/c$ | $P\overline{1}$ | *Pbca* | $Pna2_1$ | $Pna2_1$ |
| $A$ (Å) | 7.4760(7) | 8.698(1) | 8.6082(4) | 8.840(2) | 8.8728(5) |
| $B$ (Å) | 8.5256(8) | 8.730(1) | 11.3256(5) | 9.687(2) | 9.7201(6) |
| $c$ (Å) | 9.3727(8) | 9.545(1) | 13.8384(6) | 8.680(2) | 8.7295(5) |
| $\alpha$ (deg) | 90 | 71.359(1) | 90 | 90 | 90 |
| $\beta$ (deg) | 101.429(1) | 72.227(1) | 90 | 90 | 90 |
| $\gamma$ (deg) | 90 | 82.787(1) | 90 | 90 | 90 |
| $V$ (Å3) | 585.55(9) | 653.7(1) | 1349.1(1) | 743.3(2) | 752.87(8) |
| $Z$ | 4 | 2 | 8 | 4 | 4 |
| $T$ (K) | 296(2) | 296(2) | 100(2) | 296(2) | 296(2) |
| $\lambda$ (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Maximum $2\theta$ (deg.) | 28.72 | 28.79 | 28.72 | 28.72 | 28.61 |
| $\rho$calcd (g cm-3) | 3.540 | 3.334 | 3.230 | 3.075 | 3.899 |
| $\mu$(Mo $K\alpha$) | 82.85 | 74.41 | 72.11 | 65.61 | 219.92 |
| $R(F)$ for $F_o^2 > 2\sigma\ )F_o^{2a}$ | 0.0163 | 0.0289 | 0.0307 | 0.0260 | 0.0156 |
| $Rw(F_o^2\ )^b$ | 0.0379 | 0.0680 | 0.0695 | 0.0568 | 0.0370 |

[a] $R(F) = \sum \| F_0 | - | F_c \| / \sum |F_0|$.

[b] $R(F_0^2) = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.

whereas redox chemistry is not taking place in the preparation of $M[CH_2(PO_3)_2](H_2O)_2$ (M = Ce, Th).[13,16]

The central point of this particular discussion is that the crystals of $M[CH_2(PO_3)_2](H_2O)_n$ (M = Ce, Th, U, Np, Pu; $n = 0 - 2$) are probably not forming under identical conditions. This would be unimportant if we were dealing with thermodynamic products. However, hydrothermal reactions are well known to produce so-called kinetically stabilized phases. Therefore the differences observed in the compositions and structures of these compounds may not be a reflection of fundamental bonding differences between these elements, but rather different crystals growth conditions that lead to different products whose stabilities may not be very different. However, it should be considered that many important processes involving actinides, such as biphasic extractions, revolve around very small differences in energies.[17] Therefore, if we are going to look for differences between transuranics and surrogates, we must choose systems where subtle differences in energies are reflected in large overall changes. The methylenediphosphonate unit is of particular relevance because this unit is the functional group used in the commercially available Diphonix resins that can used to remove actinides from solution.[18] With these thoughts in mind, we can discuss the structure of these compounds, which have yielded a number of surprises.

Views of the structures of $M[CH_2(PO_3)_2](H_2O)_n$ (M = Ce, Th, U, Np, Pu; $n = 0 - 2$) are shown in Figure 3. Selected crystallographic details and bond distances for new compounds reported in this work can be found in Tables 1–6. In each case the compounds are found to adopt three-dimensional network structures. $M[CH_2(PO_3)_2](H_2O)_2$ (M = Ce, U, Th, Np) contain metal ions in eight-coordinate environments

**Table 2.** Selected bond distance (Å) for $U[CH_2(PO_3)_2](H_2O)_2$

| Distance (Å) | | | |
|---|---|---|---|
| U(1)-O(1) | 2.344(4) | P(1)-O(1) | 1.523(4) |
| U(1)-O(2) | 2.262(3) | P(1)-O(2) | 1.509(3) |
| U(1)-O(3) | 2.272(3) | P(1)-O(3) | 1.525(4) |
| U(1)-O(4) | 2.397(3) | P(2)-O(4) | 1.521(4) |
| U(1)-O(5) | 2.228(3) | P(2)-O(5) | 1.520(5) |
| U(1)-O(6) | 2.279(4) | P(2)-O(6) | 1.518(4) |
| U(1)-O(7) | 2.711(4) | P(1)-C(1) | 1.783(6) |
| U(1)-O(8) | 2.631(3) | P(2)-C(1) | 1.823(7) |

**Table 3.** Selected bond distance (Å) for $Ce[CH_2(PO_3)_2](H_2O)_2$

| Distance (Å) | | | |
|---|---|---|---|
| Ce(1)-O(1) | 2.202(4) | P(1)-O(1) | 1.533(4) |
| Ce(1)-O(2) | 2.234(5) | P(1)-O(2) | 1.533(5) |
| Ce(1)-O(3) | 2.404(4) | P(1)-O(3) | 1.524(5) |
| Ce(1)-O(4) | 2.321(5) | P(2)-O(4) | 1.531(5) |
| Ce(1)-O(5) | 2.256(5) | P(2)-O(5) | 1.524(5) |
| Ce(1)-O(6) | 2.237(4) | P(2)-O(6) | 1.524(4) |
| Ce(1)-O(7 W) | 2.681(5) | P(2)-C(1) | 1.792(9) |
| Ce(1)-O(8 W) | 2.623(4) | P(1)-C(1) | 1.814(11) |

**Table 4.** Selected bond distance (Å) for α-$Ce[CH_2(PO_3)_2](H_2O)$

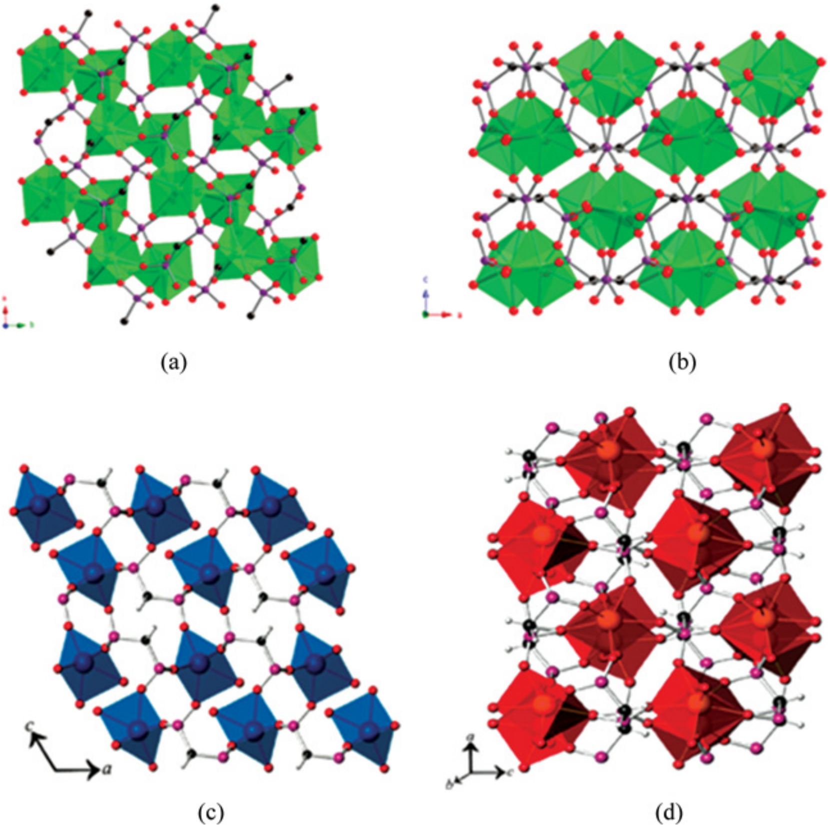
| Distance (Å) | | | |
|---|---|---|---|
| Ce(1)-O(1) | 2.212(4) | P(1)-O(1) | 1.521(4) |
| Ce(1)-O(4) | 2.288(4) | P(1)-O(2) | 1.529(4) |
| Ce(1)-O(6) | 2.263(4) | P(1)-O(3) | 1.521(4) |
| Ce(1)-O(9) | 2.257(4) | P(2)-O(4) | 1.543(4) |
| Ce(1)-O(10) | 2.249(4) | P(2)-O(5) | 1.524(4) |
| Ce(1)-O(12) | 2.194(4) | P(2)-O(6) | 1.524(4) |
| Ce(1)-O(1 W) | 2.528(4) | P(3)-O(7) | 1.529(4) |
| Ce(2)-O(2) | 2.261(3) | P(3)-O(8) | 1.527(4) |
| Ce(2)-O(3) | 2.226(3) | P(3)-O(9) | 1.530(4) |
| Ce(2)-O(5) | 2.261(4) | P(4)-O(10) | 1.521(4) |
| Ce(2)-O(7) | 2.231(4) | P(4)-O(11) | 1.508(4) |
| Ce(2)-O(8) | 2.318(4) | P(4)-O(12) | 1.521(4) |
| Ce(2)-O(11) | 2.243(4) | | |
| Ce(2)-O(2 W) | 2.472(4) | | |

**Table 5.** Selected bond distance (Å) for β-$Ce[CH_2(PO_3)_2](H_2O)$

| Distance (Å) | | | |
|---|---|---|---|
| Ce(1)-O(1) | 2.220(4) | P(1)-O(1) | 1.522(5) |
| Ce(1)-O(2) | 2.354(4) | P(1)-O(2) | 1.533(4) |
| Ce(1)-O(3) | 2.304(4) | P(1)-O(5) | 1.526(5) |
| Ce(1)-O(4) | 2.240(4) | P(1)-C(1) | 1.788(6) |
| Ce(1)-O(5) | 2.260(4) | P(2)-O(3) | 1.528(5) |
| Ce(1)-O(6 W) | 2.457(5) | P(2)-O(4) | 1.542(5) |
| Ce(1)-O(7) | 2.256(5) | P(2)-O(7) | 1.523(5) |
| | | P(2)-C(1) | 1.812(6) |

**Table 6.** Selected bond distance (Å) for Ce[$CH_2(PO_3)_2$]

| Distance (Å) | | | |
|---|---|---|---|
| Ce(1)-O(1) | 2.213(2) | P(1)-O(3) | 1.518(2) |
| Ce(1)-O(2) | 2.197(2) | P(1)-O(5) | 1.517(2) |
| Ce(1)-O(3) | 2.297(2) | P(1)-O(6) | 1.559(2) |
| Ce(1)-O(4) | 2.232(2) | P(1)-C(1) | 1.798(3) |
| Ce(1)-O(5) | 2.306(2) | P(2)-C(1) | 1.798(3) |
| Ce(1)-O(6) | 2.421(2) | P(2)-O(1) | 1.525(2) |
| Ce(1)-O(6) | 2.442(2) | P(2)-O(2) | 1.534(2) |
| | | P(2)-O(4) | 1.517(2) |



(a) (b) (c) (d)

**Figure 4.** Depictions of the structures of M[$CH_2(PO_3)_2$]($H_2O$) where M=Ce, U, Pu. $CeO_7$ = green, P = yellow, O = red, C = black. (a) α-Ce[$CH_2(PO_3)_2$]($H_2O$); (b) β-Ce[$CH_2(PO_3)_2$]($H_2O$); (c) Pu[$CH_2(PO_3)_2$]($H_2O$)[16]; (d) U[$CH_2(PO_3)_2$]($H_2O$)[13].

best described as distorted dodecahedra. Two of the sites in $M[CH_2(PO_3)_2](H_2O)_2$ (M = Ce, U, Th, Np) are from bound water molecules. These compounds are isotypic. The oddest compounds in this series are $M[CH_2(PO_3)_2](H_2O)$ (M = α-Ce, β-Ce, U, Pu) shown in Figure 4. These compounds are not all isostructural despite having the same composition. $U[CH_2(PO_3)_2](H_2O)$ and $M[CH_2(PO_3)_2](H_2O)$ (M=Ce, Pu) both contain $MO_7$ units that resemble square antiprisms with a missing vertex. $MO_7$ units with actinides in the +4 oxidation state are exceedingly rare. These authors are only aware of one other compound with them, $U(UO_2)(PO_4)_2$, although in this compound the U(IV) sites are found as pentagonal bipyramids. In summary, $Ce^{4+}$, $Th^{4+}$, $U^{4+}$, $Np^{4+}$, and $Pu^{4+}$ when combined with methylenediphosphonate yield two different compositions and four different structure types. The utility of surrogates for neptunium and plutonium in this system is questionable.

## 3. HETEROBIMETALLIC MIXED-ACTINIDE PHOSPHONATES

The previously discussed structures of $M[CH_2(PO_3)_2](H_2O)_n$ (M = Ce, Th, U, Np, Pu; n = 0 – 2) yielded one consistent bonding feature shown in Figure 5, that of the methylenediphosphonate bonding to the $M^{4+}$

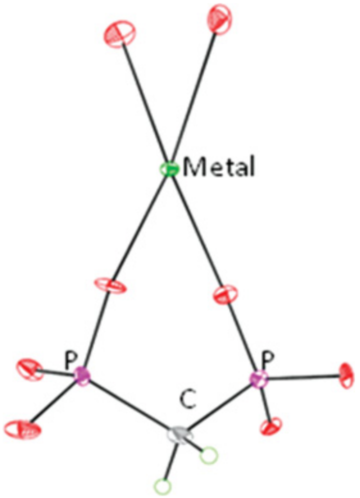


**Figure 5.** Depiction of the bonding mode of the methylenediphosphonic acid ligand, showing chelation to some tetravalent actinides.

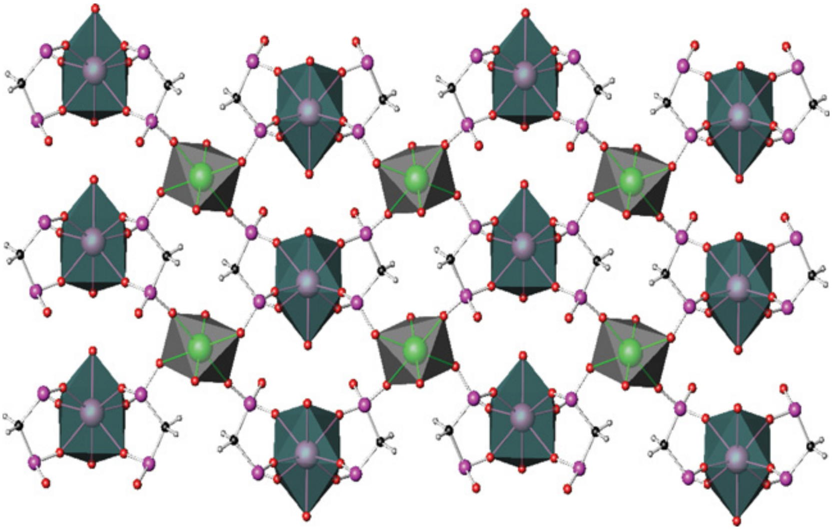


**Figure 6.** An illustration of the structure $UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$(An = Th, Np, Pu) consisting of $UO_6$ units (grey/green) containing $UO_2^{2+}$ core, and $AnO_8$ distorted dodecahedra (blue) with an An(IV) center that are bridged by partially protonated methylenediphosphonate.

centers. This bonding mode leaves two oxygen atoms on both of the $PO_3$ moieties to bond to additional metal atoms. Given this preorganization, we wondered if these oxygen atoms could bond to a different metal center? What about a second, but different, actinide? Complexation studies on the log $\beta_{11}$ for $UO_2^{2+}$ and $Th^{4+}$ interacting with methylenediphoshonate show that they are remarkably similar.[19] If two neighboring $An^{4+}$ centers are introduced (e.g., $Np^{4+}$ and $Pu^{4+}$) a disordered structure will almost certainly result. The two sites can undoubtedly not be distinguished based on X-ray scattering. However, if the oxidation state of one of the actinides is raised to + 5 or + 6 then an actinyl, $AnO_2^{n+}$ (n = 1, 2) core should exist, yielding completely different coordination geometries based on tetragonal, pentagonal, or hexagonal bipyramids, which are generally very different from those found with +4 actinides, which again are typically found as various distortions of a dodecahedron (eight-coordinate) or a tricapped trigonal bipyramid (nine coordinate)[14]

The synthesis can be accomplished by two different methods. In the first method $NpO_2^{2+}$ and $UO_3$ are introduced simultaneously with methylenediphosphonic acid. The Np(VI) is hydrothermally reduced to Np(IV).

The U(VI) remains unchanged.[14] Alternatively, methylenediphosphonic acid can be directly reacted with $AnO_2$ (An = Th, Pu) and $UO_3$.[16] Both methods result in the formation of the heterobimetallic mixed-actinide compounds, $UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (An = Th, Np, Pu). These compounds are isotypic, and since they are arrived at by different routes at different pH's, they probably represent an energetic sink.

$UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (An = Th, Np, Pu) adopts a three-dimensional framework structure containing $AnO_8$ distorted dodecahedra and $UO_6$ tetragonal bipyramids. Therefore, even though these actinides can not be distinguished on the basis of X-ray scattering, they can be differentiated by their coordination environments, as shown in Figure 4. In addition, visible diffuse reflectance spectroscopic data clearly shows the absorption features of $UO_2^{2+}$ and $Np^{4+}$ for $UO_2Np(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$.

One of the physical consequences of the presence of two different actinides in the same compound is energy transfer between the $UO_2^{2+}$ units, which typically fluoresce, and the $Np^{4+}$ and $Pu^{4+}$. Examination of the absorption features of $Np^{4+}$ and $Pu^{4+}$ and the emission features of $UO_2^{2+}$ show that they overlap. Therefore, no emission is observed from the uranyl units in $UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (An = Np, Pu).

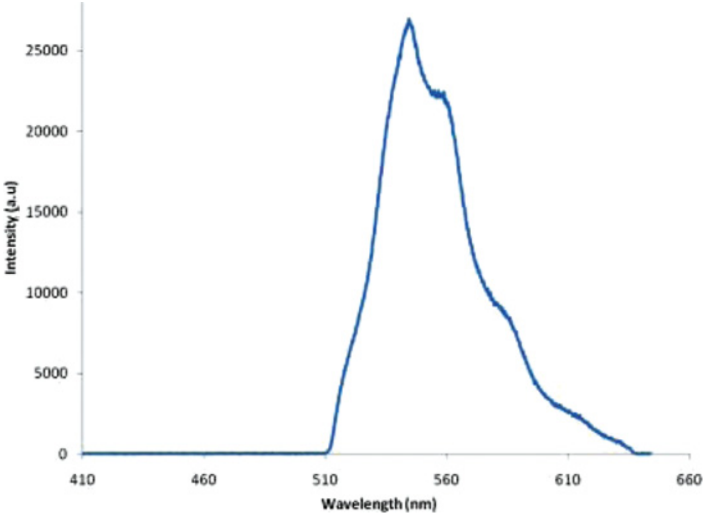


**Figure 7.** The fluorescence spectrum of $UO_2Th(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ showing the emission from the uranyl units with vibronic structure.

However, in $UO_2Th(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$, the $Th^{4+}$ centers lack 5f electrons and charge transfer bands are absent in the visible region of the spectrum. Here fluorescence from the uranyl units with characteristic fine-structure is clearly observed, as shown in Figure 7.[17]

## 4. CONCLUSIONS

While this work is still in its infancy, we are already seeing significant differences between the structures found with transuranium elements and those found with surrogates. There are certainly examples where isostructural series exist, but there are also neptunium and plutonium compounds that do not have lighter counterparts. There are two facets that need to be explored with this. On the one hand, we can exploit subtle differences between transuranics and other elements to design important chemical processes, such as improved spent nuclear fuel reprocessing methods, or the development of highly specific advanced waste forms. On the other hand, we can not turn our back on the utility of surrogates. The fact is that the ionic radius of $Ce^{4+}$ and $Pu^{4+}$ are remarkably similar. We can use $Ce^{4+}$ in very large quantities, run hundreds of reactions under different conditions, and perform measurements on these compounds that will simply be impossible with neptunium and plutonium. A few key reactions with transuranics will allow us to know if there are chemical differences with surrogates after we have gathered massive amounts of data on less or non-radioactive counterparts. However, we must never lose sight of the absolute necessity of working with the transuranics themselves if we are going to make accurate predictions about their chemistry.

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