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# Comparison of Thorium(IV) and Uranium(VI) Carboxyphosphonates

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The hydrothermal reactions of thorium nitrate and uranyl acetate with carboxyphenylphosphonic acid and HF result in the formation of $ThF_2(PO_3C_6H_4CO_2H)$ and $UO_2(PO_3HC_6H_4CO_2H)_2 \cdot 2H_2O$, respectively. $ThF_2(PO_3C_6H_4CO_2H)$ adopts a pillared structure constructed from thorium oxyfluoride layers built from $[ThO_4F_4]$ units that are bridged by carboxyphenylphosphonate to yield a three-dimensional network. $UO_2(PO_3HC_6H_4CO_2H)_2 \cdot 2H_2O$ forms one-dimensional chains of $UO_6$ tetragonal bipyramids that are bridged by the phosphonate moiety of the ligand. The carboxylate portion of the structure links the chains together into layers via a hydrogen-bonding network. The higher effective charge and more isotropic coordination of the Th(IV) centers versus the uranium centers contained within uranyl cations allow for coordination by the protonated carboxylate portions of the ligands to the thorium cations, which does not occur with uranium in carboxyphosphonates. $UO_2(PO_3HC_6H_4CO_2H)_2 \cdot 2H_2O$ displays vibronically coupled fluorescence and the potential for energy transfer from the ligand to the charge-transfer bands of the uranyl cations. The main fluorescence by the ligand is quenched in $ThF_2(PO_3C_6H_4CO_2H)$.

## Introduction

Our understanding of the solid-state chemistry of actinides has rapidly expanded over the past decade owing to the development of new synthetic methods and analytical techniques. Uranyl oxoanion chemistry is particularly demonstrative of this expansion, with the number of unique structure types of purely inorganic uranyl compounds more than doubling between 1997 and 2005.[1] Despite the sheer number of new uranyl topologies, novel structures continue to appear at a rapid rate owing to three factors. First, new synthetic methods are being applied.[2] Second, new oxoanions are being used to ligate uranium. Third, the coordination chemistry of uranium is highly flexible, which is exemplified by U(VI) occurring as tetragonal, pentagonal, and hexagonal bipyramids in almost limitless combinations.[3] While new uranyl compounds can probably be made ad nauseum, we are finally reaching the point where topological relationships can be developed,[4] and of equal importance, the rudiments of materials design are finally taking place, yielding solids with selective ion-exchange,[5] mixed valency,[6] ionic conductivity,[7] enhanced fluorescence,[8] magnetic ordering,[5f,9] and nonlinear optical properties.[2b,5g,10]

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Actinide carboxyphosphonates are a rapidly expanding family of compounds that are exclusively known where the actinide is uranium in the form of uranyl, $UO_2^{2+}$. There are about 20 of these compounds that have been reported in the past few years.[11-15] The best represented carboxyphosphonate in this family is phosphonoacetate, although a smaller subset of compounds with 2-phosphonopropionate have been prepared and characterized.[12] The compounds are typically layered with anionic uranyl carboxyphosphonate networks separated by either alkali metal or organoammonium cations. The addition of transition metals allows for the lower dimensional features to be connected into higher dimensional frameworks. $(UO_2)_2(PPA)_2(HPPA)Zn_2(H_2O)_2 \cdot 3H_2O$[15] and $[H_3O](UO_2)_2Cu_2(PPA)_3(H_2O)_2$ (PPA = phosphonoacetate)[11] are both examples of structures where the transition metals connect low-dimensional uranyl phosphonoacetate networks into three-dimensional frameworks, although it was shown in $Cs_3[(UO_2)_4(PO_3CH_2CO_2)_2(PO_3CH_2CO_2H_{0.5})_2] \cdot nH_2O$ that canting of the uranyl polyhedra can lead to the formation of a 3D framework without the addition of transition metals.[14]

It has been previously shown that rigid diphosphonates with phenyl spacers allow for the construction of uranyl compounds with pillared structures.[16] Carboxyphosphonates represents a variation on this where one of the phosphonate moieties has been replaced by a carboxylate group. It has been demonstrated in the carboxyphosphonates that the $PO_3$ moiety has a much stronger propensity for binding the U(VI) centers than does the carboxylate portion.[11-15] This would be consistent with comparative studies of phosphonates and carboxylates in solution.[17] Using this ligand we have examined how the carboxylate portion differs from bonding between Th(IV) and U(VI). These actinides vary substantially in their effective charges with Th(IV), displaying an effective charge that matches its formal oxidation state, whereas U(VI), contained within $UO_2^{2+}$, behaves as a cation with an effective charge of 3.3.[18] Furthermore, they also diverge in their preferred coordination environments with Th(IV), favoring eight- and nine-coordinate dodecahedral and tricapped trigonal prismatic environments lacking central actinyl units, while U(VI) is found as the various bipyramids previously discussed. Herein we report the synthesis, structures, and fluorescence properties of $ThF_2(PO_3C_6H_4CO_2H)$ and $UO_2(PO_3HC_6H_4CO_2H)_2 \cdot 2H_2O$.

## Experimental Section

**Synthesis.** $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$ (98%, Alfa-Aesar), $Th(NO_3)_4 \cdot xH_2O$ (99%, Aldrich), HF (48 wt %, Aldrich), and 4-carboxyphenylphosphonic acid (97%, Epsilon Chimie) were used as received. Reactions were run in PTFE-lined Parr 4749 autoclaves with a 23 mL internal volume. Distilled and Millipore-filtered water with a resistance of 18.2 MΩ·cm was used in all reactions. Standard precautions were performed for handling radioactive materials. Experimental and calculated powder X-ray diffraction patterns can be found in the Supporting Information. These data demonstrate that high-purity samples can be obtained for both compounds.

**Table 1.** Crystallographic Data for $ThF_2(PO_3C_6H_4CO_2H)$ (Thcpp) and $UO_2(PO_3HC_6H_4CO_2H)_2 \cdot 2H_2O$ (Ucpp)

| | Thcpp | Ucpp |
|---|---|---|
| formula mass | 469.11 | 706.22 |
| color and habit | white, tablet | yellow, tablet |
| space group | $P2_1/c$ (No. 14) | $P\bar{1}$ (No. 2) |
| $a$ (Å) | 7.5507(2) | 5.5126(13) |
| $b$ (Å) | 5.6983(2) | 6.7658(15) |
| $c$ (Å) | 23.3644(7) | 13.762(3) |
| α (deg) | 90 | 90.981(2) |
| $\beta$ (deg) | 99.0066(3) | 95.009(2) |
| $\gamma$ (deg) | 90 | 106.399(2) |
| $V$ (Å) | 992.88(5) | 490.05(19) |
| $Z$ | 4 | 1 |
| $T$ (K) | 100 | 100 |
| $\lambda$ (Å) | 0.71073 | 0.71073 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 3.138 | 2.393 |
| $\mu$(Mo Kα) (mm$^{-1}$) | 15.21 | 8.518 |
| $R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$ | 0.014 | 0.019 |
| $R_w(F_o^2)^b$ | 0.034 | 0.044 |

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

**$ThF_2(PO_3C_6H_4CO_2H)$ (Thcpp).** $Th(NO_3)_4 \cdot xH_2O$ (96.2 mg, 0.200 mmol) and 4-carboxyphenylphosphonic acid (40.5 mg, 0.200 mmol) were loaded into a 23 mL PTFE-lined autoclave. Water (0.5 mL) was added to the solids, followed by addition of two drops of HF. The autoclave was sealed and heated to 190 °C in a box furnace, and the temperature was held constant for 72 h. The autoclave was then cooled at an average rate of 5 °C/h until it reached room temperature. Initial pH = 0.77. The resulting product was washed with distilled water and methanol and allowed to air-dry at room temperature. Colorless tablets of Thcpp were isolated. Yield: 70 mg (74% based on thorium).

**$UO_2(PO_3HC_6H_4CO_2H)_2 \cdot 2H_2O$ (Ucpp).** $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$ (53.4 mg, 0.126 mmol), 4-carboxyphenylphosphonic acid (50.4 mg, 0.250 mmol), 0.5 mL of water, and two drops of HF were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 180 °C in a box furnace for 3 days. The autoclave was then cooled at an average rate of 5 °C/h to 25 °C. Initial pH = 2.55. The resulting yellow product was washed with distilled water and methanol and allowed to air-dry at room temperature. Yellow tablets of Ucpp suitable for X-ray diffraction studies were formed. Yield: 58.8 mg (66% based on uranium).

**Crystallographic Studies.** Single crystals of Thcpp and Ucpp were mounted on glass fibers and optically aligned on a Bruker APEXII CCD X-ray diffractometer using a digital camera. Initial intensity measurements were performed using a standard sealed tube (Mo) with a monocapillary collimator. 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 $\varphi$ angle for the crystal, and each exposure covered a range of 0.5° in $\omega$. A total of 1464 frames were collected with an exposure time per frame of 30 or 40 s, depending on the crystal. SAINT software was used for data integration including Lorentz and polarization corrections. Semiempirical absorption corrections were applied using the program SADABS.[19] The program suite SHELXTL was used for space group determination (XPREP), direct methods structure

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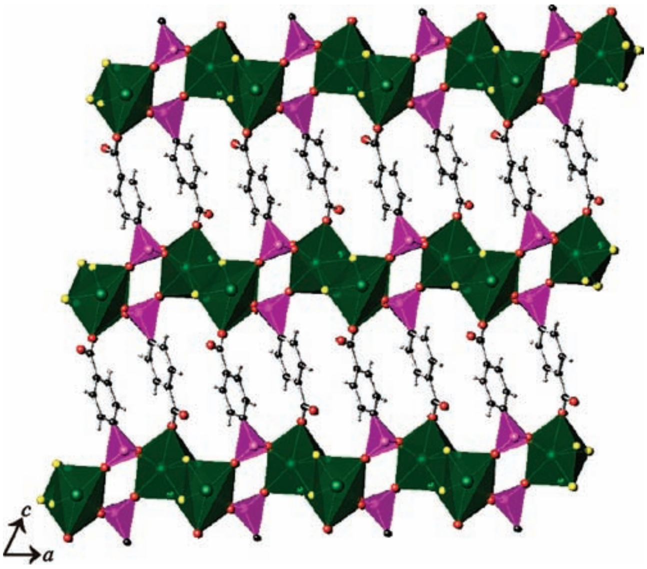

**Figure 1.** Polyhedral representation of the structure of $ThF_2(PO_3C_6H_4CO_2H)$ viewed along the *b* axis. The structure contains dodecahedral $[ThO_4F_4]$ units (deep green), oxygen = red, phosphorus = magenta, fluoride = yellow, carbon = black, hydrogen = white.

solution (XS), and least-squares refinement (XL).[20] The final refinements included anisotropic displacement parameters for all atoms. Selected crystallographic information is listed in Table 1. Atomic coordinates, bond distances, and additional structural information are provided in the Supporting Information (CIF).

**Fluorescence Spectroscopy.** Absorption and fluorescence data were acquired from the ligand and both compounds from single crystals using a Craic Technologies UV−vis−NIR microspectrophotometer with a fluorescence attachment. Excitation was achieved using 365 nm light from a mercury lamp for the fluorescence spectroscopy. The absorption spectra are provided in the Supporting Information.

**Powder X-ray Diffraction.** Powder X-ray diffraction patterns of the products of both reactions were collected on a Scintag theta−theta diffractometer equipped with a diffracted-beamed monochromatic set for Cu Kα ($\lambda$ = 1.5418 Å) radiation at room temperature in the angular range from 10° to 80° ($2\theta$) with a scanning step width of 0.05° and a fixed counting time of 1 s/step. The collected patterns were compared with those calculated from single-crystal data using ATOMS and Mercury (see Supporting Information).

**Infrared Spectroscopy.** Infrared spectra were obtained from single crystals of both compounds using a SensIR Technology IlluminatIR FT-IR microspectrometer. A single crystal of each compound was placed on a glass slide, and the spectrum was collected with a diamond ATR objective. The spectra can be found in the Supporting Information.

## Results and Discussion

**Synthesis.** $ThF_2(PO_3C_6H_4CO_2H)$ and $UO_2(PO_3HC_6H_4CO_2H)_2 \cdot 2H_2O$ can be prepared under mild hydrothermal conditions in reasonable yield. The addition of HF to the reactions is essential, and it serves as both a mineralizing agent and ligand in the preparation of Thcpp and only as a mineralizing agent in the synthesis of Uccp. The reaction temperature and the amount of water present in the reactions have to be carefully controlled to obtain Thcpp and Ucpp.

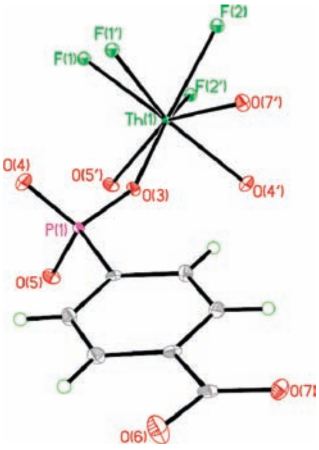

**Figure 2.** Local coordination environment in $ThF_2(PO_3C_6H_4CO_2H)$. Ellipsoids are shown at the 50% probability level.

**General Structural Characteristics.** $ThF_2(PO_3C_6H_4CO_2H)$ (Thcpp) crystallizes in the centrosymmetric, monoclinic space group $P2_1/c$ and possesses thorium oxyfluoride layers that extend in the [*ab*] plane that are linked by the carboxyphenylphosphonate ligand into what could be described as a pillared structure, as shown in Figure 1. The thorium polyhedra consist of eight-coordinate $[ThO_4F_4]$ dodecahedra as depicted in Figure 2. The thorium units edge-share via bridging fluoride ions to create one-dimensional chains that extend along the *b* axis. These chains are in turn linked by bridging $PO_3$ moieties to yield layers. The resulting sheets are cross-linked together by the carboxyphosphonate ligands into a neutral three-dimensional network.

The Th−F bond distances, which range from 2.329(2) to 2.460(2) Å, are on average longer than the Th−O bonds to the phosphonate group, with the latter bond distances occurring from 2.273(2) to 2.312(2) Å. The single Th−O bond to the carboxylate moiety is substantially longer than all of the other interactions, at 2.552(2) Å. The C−O bonds within the carboxylate moiety are 1.234(3) and 1.313(3) Å. The shorter C−O bond length represents the oxygen atom participating with an interaction with the Th(IV) center. The oxygen atom involved in the considerably longer C−O bond does not interact with a metal center. This is indicative of a protonated group, C−OH, and this is also required for charge balance considerations. The various bridging ligands yield a typical spacing between the thorium atoms of approximately 4 Å. Similar distances have been reported in actinide-organic open-framework structures.[21] The P−O bond distances are normal and range between 1.515(2) and 1.525(2) Å.[16] Using the Th−F and Th−O bond distances, a bond-valence sum of 4.21 was calculated, which is consistent with Th(IV).[22]

**Structure of $UO_2(PO_3HC_6H_4CO_2H)_2 \cdot 2H_2O$ (Ucpp).** Ucpp crystallizes in the centrosymmetric, triclinic space group $P\bar{1}$, and forms one-dimensional chains in which the uranium atoms are found as $UO_6$ tetragonal bipyramids,

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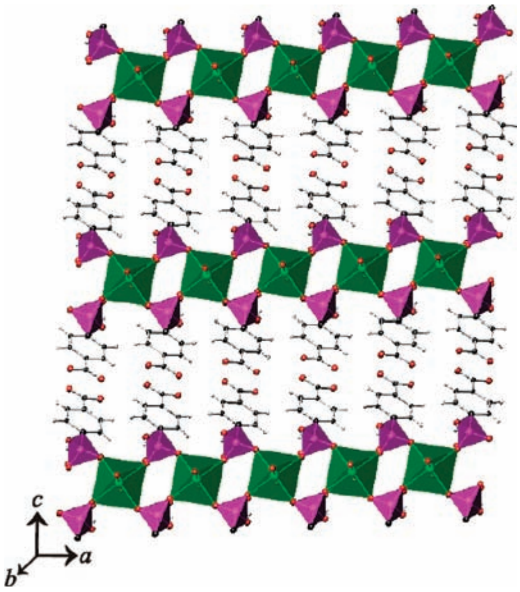

**Figure 3.** Polyhedral view along the *b* axis of $UO_2(PO_3HC_6H_4CO_2H)_2\cdot 2H_2O$. The structure is constructed from $UO_6$ tetragonal bipyramids (green), oxygen = red, phosphorus = magenta, carbon = black, hydrogen = white.

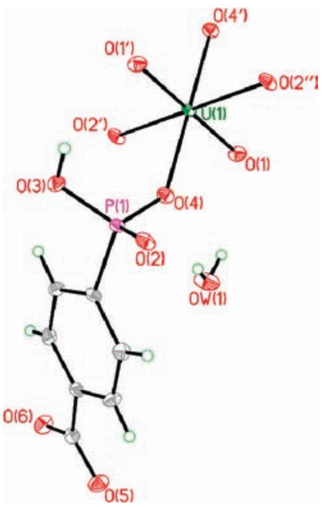

**Figure 4.** ORTEP diagram of the compound $UO_2(PO_3HC_6H_4CO_2H)_2\cdot 2H_2O$. The ellipsoids are shown at the 50% probability level.

a less common coordination environment for uranium.[3] The $UO_6$ units contain a central uranyl cation, $UO_2^{2+}$, that is bridged by the phosphonate moieties parallel to the *b* axis (Figure 3). These chains are similar to those found in uranyl phenylphosphonates.[23] These uranyl phosphonate chains are cross-linked by hydrogen bonds between the carboxylate groups of neighboring chains to yield layers. There are further hydrogen bonds with the cocrystallized water molecules that link the layers into a three-dimensional network.

The uranium is bound by two oxygen atoms along the axial positions, creating a characteristic uranyl cation, $UO_2^{2+}$, with bond distances of 1.784(2) Å (×2). The additional four oxygen atoms from the phosphonate moieties (O(2′), O(2″), O(4), and O(4′)) are bound to the uranyl cation in the equatorial plane with an average bond distance of 2.295(2) Å (Figure 4). These distances can be used to calculate a bond-valence sum for the uranium center of 6.12, which agrees well with the formal oxidation state of +6.[3] Three P−O bond distances of 1.506(2), 1.529(2), and 1.556(2) Å reveal the presence of a P−OH group, which also corresponds to the only oxygen atom from the phosphonate group that is not coordinating a uranium center. The carboxylate C−O bond distances of 1.267(4) and 1.271(4) Å are essentially equal and demonstrate that the proton is equally distributed over both oxygen atoms, as shown in Figure 3. The hydrogen-bonding contacts between the pairs of oxygen atoms are 2.602(4) Å, which is quite reasonable for this type of hydrogen-bonding network.

From these two structures some interesting comparisons can be made. First, these low-pH syntheses yield structures in which the carboxylate moieties are protonated. Second, in previously described uranyl carboxyphosphates, protonated carboxylate moieties have not been found to interact with the uranium atoms and are invariably directed into the interlayer space. Uranyl and Th(IV) coordination environments are substantially different, as are their effective charges.[18] These two factors are likely to be responsible for the bonding differences between U(VI) and Th(IV) to the carboxylic acid portions of the ligand. This makes extended structures that are created by metal−ligand bonds instead of structures where higher dimensionality is created by hydrogen-bonding networks. It should be noted that the interaction between the carbonyl group and the Th(IV) center is quite long and probably represents a weak interaction similar to coordinating water molecules, which have similar Th−O distances.

**Fluorescence Spectroscopy.** The emission of green light centered near 520 nm by uranyl compounds has been known for centuries, and in fact it was this property from which the term "fluorescence" was first coined in France in the late 1700s. The emission is strong enough from some compounds that the long-wavelength UV light in sunlight is enough to induce a green glow that can be clearly observed by the naked eye. The charge-transfer-based emission is in fact vibronically coupled to both bending and stretching modes of the uranyl cation, and while most investigators describe a five-peak spectrum, far more lines can be observed, particularly at low temperatures.[24] Furthermore, the resolution of individual vibronic transitions can also be coupled to the crystallinity of the sample, and disorder within the equatorial plane of the uranyl group, as occurs in glasses, significantly decreases the resolution of individual transitions.[24] The emission is, in fact, exceedingly complex and has been examined in detail from solid samples (e.g., from salts of $[UO_2Cl_4]^{2-}$) by Denning and co-workers.[25] Not all uranyl compounds fluorescence, however, and the mechanisms

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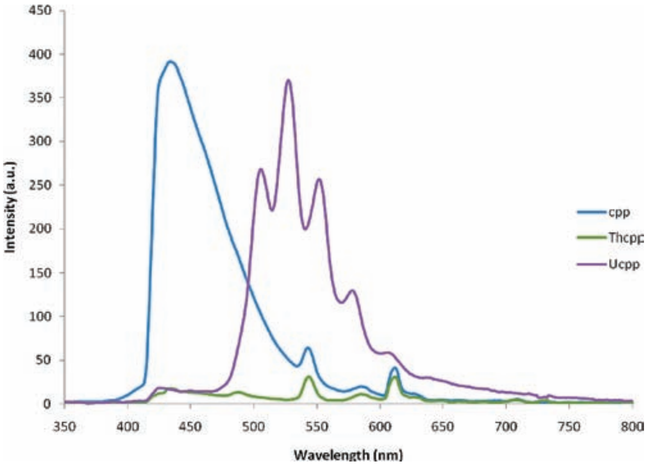

**Figure 5.** Fluorescence spectrum of ($H_2PO_3C_6H_4CO_2H$) (ligand), $ThF_2(PO_3C_6H_4CO_2H)$, and $UO_2(PO_3HC_6H_4CO_2H)_2 \cdot 2H_2O$.

for quenching are not well understood. For example, Grohol and Clearfield reported significant variances in the luminescent properties of two closely related uranyl phosphonates, $[UO_2(HO_3PC_6H_5)_2(H_2O)]_2 \cdot 8H_2O$ and $UO_2(HO_3PC_6H_5)_2(H_2O) \cdot 2H_2O$, whose structural differences are based largely on conformational differences in the phosphonates.[26]

$ThF_2(PO_3C_6H_4CO_2H)$ and $UO_2(PO_3HC_6H_4CO_2H)_2 \cdot 2H_2O$ are very distinctive in their fluorescent properties, as shown in Figure 5. One of the primary differences between carboxyphenylphosphonate and previously studied carboxyphosphonates is the presence of the aromatic linker. We and others have shown that fluorescence can be enhanced by having aromatic groups in close proximity to the uranyl cations.[8] The ligand itself fluoresces in the same region that the uranyl cation absorbs (see Supporting Information), and intense emission with vibronic coupling is clearly observed from $UO_2(PO_3HC_6H_4CO_2H)_2 \cdot 2H_2O$. It is possible that the primary emission from the ligand is completely absorbed by the uranyl cation. In contrast, in $ThF_2(PO_3C_6H_4CO_2H)$ the primary emission from the ligand is quenched; however, the reemission is nonradiative. The quenching of the fluorescence in this compound is not via energy transfer or paramagnetic quenching because thorium does not have absorption bands in this region and is a $5f^0$ system. A second possibility is that the uranium center in $UO_2(PO_3HC_6H_4CO_2H)_2 \cdot 2H_2O$ also quenches the emission from the ligand and that the emission from the uranyl unit is not enhanced by energy transfer from the ligand. Unfortunately, the ligand's absorption coincides with U−O charge-transfer bands at 300 nm (see Supporting Information). Therefore, the ligand cannot be independently excited by changing the excitation wavelength.

## Conclusions

The purpose of this work was to compare and contrast the structural chemistry and luminescent properties of thorium and uranium compounds that both contain the carboxyphenylphosphonate ligand. There are two important features that differentiate the systems from each other. First, we have shown that the higher effective charge[18] and more isotropic coordination environment of Th(IV) allow for interactions with a carboxylic acid group (−COOH), which has not been observed in uranyl carboxyphosphonates. However, upon deprotonation, it regularly bonds to U(VI) in this family of compounds. This allows one to utilize carboxylic acid groups in the construction of extended frameworks that contain thorium. Second, we have shown that both metal centers dramatically affect the luminescence from the ligand. With uranium there is overlap between the emission of the ligand and the absorption by the uranyl cation, potentially leading to energy transfer, which would enhance the fluorescence observed from the uranyl units.[8] In the thorium compound, the fluorescence from the ligand is quenched, and the primary emission from the ligand is not observed. This latter observation would not have been predicted on the basis of the absorption properties of thorium. In short, more than just the structures of actinide carboxyphosphonates can be altered by changing the spacer between the phosphonate and carboxylate portions of the ligand. Furthermore, the use of a rigid phenyl spacer allows for the synthesis of a pillar compound more similar to those found with 1,4-phenyldiphosphonate.[16]

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**Supporting Information Available:** X-ray crystallographic files in CIF format for $ThF_2(PO_3C_6H_4CO_2H)$ (Thcpp) and $UO_2(PO_3HC_6H_4CO_2H)_2 \cdot 2H_2O$ (Ucpp). Powder X-ray diffraction patterns, IR spectra, and absorption spectra are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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