CRYSTAL GROWTH & DESIGN

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From Layered Structures to Cubic Frameworks: Expanding the Structural Diversity of Uranyl Carboxyphosphonates via the Incorporation of Cobalt

Andrea N. Alsobrook,[†] Brad G. Hauser,[‡] Joseph T. Hupp,[‡] Evgeny V. Alekseev,[§] Wulf Depmeier,[§] and Thomas E. Albrecht-Schmitt[†,*]

[†]Department of Civil Engineering and Geological Sciences and Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States

[‡]Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

[§]Department of Crystallography, University of Kiel, Kiel, 24118 Germany.

S *Supporting Information*

ABSTRACT: Five heterobimetallic U(VI)/Co(II) carboxyphosphonates have been synthesized under mild hydrothermal conditions by reacting UO_3, $Co(CH_3CO_2)_2 \cdot 4H_2O$, and triethyl phosphonoacetate. These compounds, $Co(H_2O)_4[(UO_2)_2(PO_3CH_2CO_2)_2(H_2O)_2]$ (**CoUPAA-1**), $[Co(H_2O)_6][UO_2(PO_3CH_2CO_2)]_2 \cdot 8H_2O$ (CoUPAA-2), $Co(H_2O)_4[UO_2(PO_3CH_2CO_2)]_2 \cdot 4H_2O$ (**CoUPAA-3**), $Co(H_2O)_4[(UO_2)_6(PO_3CH_2CO_2)_2O_2(OH)_3(H_2O)_3]_2 \cdot 3H_2O$ (**CoUPAA-4**), and $Co_2[(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2] \cdot 16H_2O$ (**CoUPAA-5**), range from two- to three-dimensional structures. **CoUPAA-1** to **CoUPAA-3** all possess uranyl carboxyphosphonate layers that are separated by the Co(II) cation with varying degrees of hydration. **CoUPAA-4** contains both UO_7 pentagonal bipyramids and UO_8 hexagonal bipyramids within the uranyl carboxyphosphonate plane. Unlike the first four low-symmetry compounds, **CoUPAA-5** is a cubic, three-dimensional network with large cavities approximately 16 Å in diameter that are filled with cocrystallized water molecules. Differential gas absorption measurements performed on **CoUPAA-5** displayed a surface area uptake for CO_2 of 40 $m^2\ g^{-1}$ at 273 K, and no uptake for N_2 at 77 K.

INTRODUCTION

The structural chemistry of U(VI) is remarkably rich owing to the flexibility of its coordination geometry that varies from UO_6 tetragonal bipyramids, to UO_7 pentagonal bipyramids, to UO_8 hexagonal bipyramids, all of which contain the well-known uranyl, UO_2^{2+}, core.[1] The majority of uranyl compounds with oxoanions adopt layered structures because the uranyl oxo atoms seldom bridge to other metal centers, effectively eliminating one dimension in which a structure might extend.[1,2] In an effort to deviate from the propensity of uranyl compounds to form 2D architectures, additional metal centers with different coordination preferences have been incorporated into uranyl materials leading to a statistical increase in the occurrence of three-dimensional networks.[3−8] When the networks incorporate both paramagnetic transition metals and cations to counterbalance the anionic charge of the frameworks, multifunctional materials become possible, as exemplified by $A_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$ (A = K, Rb), which is capable of both Cs^+-selective cation exchange and magnetic ordering.[8]

One of the challenges in preparing heterobimetallic uranyl compounds with a single oxoanion is that the reactions often yield mixtures of monometallic products instead heterobimetallic compounds. A solution to this problem is to utilize a multifunctional ligand with two different ligating groups each of which shows a preference for binding different metals. Carboxyphosphonates are one such group of ligands that are capable of simultaneously bonding to both uranyl cations and transition metals.[9−17] Examples of compounds where the transition metals serve as linkers between lower dimensional uranyl-containing substructures include $[H_3O][(UO_2)_2Cu_2(PO_3CH_2CO_2)_3(H_2O)_2$[9] and $Zn(H_2O)_4(UO_2)_2(H_2O)_2(PO_3CH_2CO_2)_2$.[12] In the case of the former compound, Cu(II) joins uranyl phosphonates layers into a three-dimensional structure, whereas in the latter, the Zn(II) cations link one-dimensional uranyl phosphonate chains into sheets. The bonding in $UO_2Cu(PO_3CH_2CO_2)(OH)(H_2O)_2$,[9] where a μ_3-oxo bridge exists between U(VI) and Cu(II) points to the possibility of magnetic coupling between 5f and 3d elements if the U(VI) could be replaced by Np(VI) or Pu(VI).

We recently disclosed the structures and properties of an unusual group of carboxyphosphonates with the formula $[M_2(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2] \cdot 16H_2O$ (M = Mn(II), Co(II), Cd(II)).[15] These compounds adopt a cubic open-framework structure with large cavities filled with water molecules. In addition to forming one of the most complex U(VI) reported to date, bonding exists in these compounds that has not been found in other uranyl carboxyphosphonates. In all other examples the phosphonate exclusively bounds to U(VI) as expected based on the Pearson hardness of phosphonate versus carboxylate. Further exploration of the Co(II) system has shown that it yields more

Received: December 15, 2010
Revised: January 18, 2011
Published: February 08, 2011

dx.doi.org/10.1021/cg101668f | *Cryst. Growth Des.* 2011, 11, 1385–1393

Table 1. Crystallographic Data for $Co(H_2O)_4[(UO_2)_2(PO_3CH_2CO_2)_2(H_2O)_2]$ (CoUPAA-1), $[Co(H_2O)_6][UO_2(PO_3CH_2CO_2)]_2 \cdot 8H_2O$ (CoUPAA-2), $Co(H_2O)_4[UO_2(PO_3CH_2CO_2)]_2 \cdot 4H_2O$ (CoUPAA-3), $Co(H_2O)_4[(UO_2)_6(PO_3CH_2CO_2)_2O_2(OH)_3(H_2O)_3]_2 \cdot 3H_2O$ (CoUPAA-4), and $Co_2[(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2] \cdot 16H_2O$ (CoUPAA-5)

	CoUPAA-1	CoUPAA-2	CoUPAA-3	CoUPAA-4	CoUPAA-5
formula mass	969.00	1097.00	983.95	539.95	2085.62
color and habit	pale orange, tablet	orange, tablet	orange, tablet	orange, tablet	red, block
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$Im\bar{3}$ (No. 204)
a (Å)	6.9383(2)	20.5730(13)	9.3568(9)	11.1148(5)	26.3861(3)
b (Å)	3.3245(3)	9.4979(6)	9.5026(10)	15.6485(7)	26.3861(3)
c (Å)	15.8920(6)	13.3841(9)	12.1282(12)	18.8376(8)	26.3861(3)
α (de)	97.130(1)	90	90	90	90
β (deg)	96.340(1)	105.219(1)	103.912(1)	92.647(1)	90
γ (deg)	91.740(1)	90	90	90	90
V (Å)	904.32(5)	2523.5(3)	1046.73(18)	3272.9(2)	18370.7(4)
Z	2	4	2	2	16
T (K)	100	100	100	100	100
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	3.559	2.887	3.176	4.348	3.579
μ (Mo Kα) (cm^{-1})	190.48	136.93	164.69	30.044	220.66
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.0191	0.0281	0.0194	0.0445	0.0176
$RB_{wB}(FB_{oPB}{}^{2P})^b$	0.0481	0.0808	0.0528	0.1028	0.0429

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

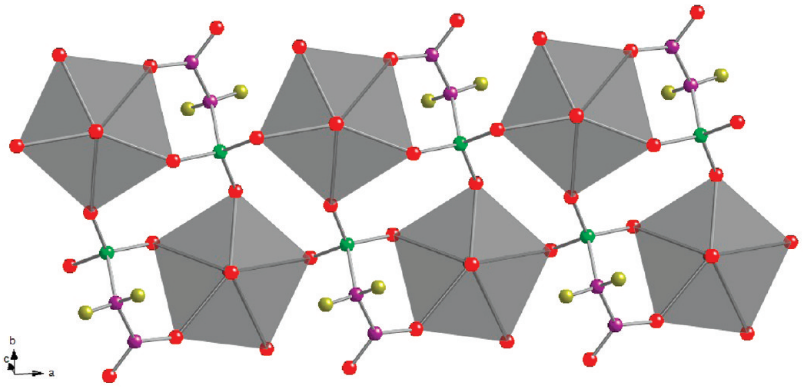

Figure 1. View of the uranyl phosphonate plane found in $Co(H_2O)_4[(UO_2)_2(PO_3CH_2CO_2)_2(H_2O)_2]$ (**CoUPAA-1**) along the *c*-axis. UO_7 pentagonal bipyramids = gray, phosphorus = green, oxygen = red, carbon = purple, and hydrogen = yellow.

compounds than any other transition metal/U(VI) carboxyphosphonate system reported to date with the successful isolation and characterization of $Co(H_2O)_4[(UO_2)_2(PO_3CH_2CO_2)_2(H_2O)_2]$ (**CoUPAA-1**), $[Co(H_2O)_6][UO_2(PO_3CH_2CO_2)]_2 \cdot 8H_2O$ (**CoUPAA-2**), $Co(H_2O)_4[UO_2(PO_3CH_2CO_2)]_2 \cdot 4H_2O$ (**CoUPAA-3**), $Co(H_2O)_4[(UO_2)_6(PO_3CH_2CO_2)_2O_2(OH)_3(H_2O)_3]_2 \cdot 3H_2O$ (**CoUPAA-4**), and $Co_2[(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2] \cdot 16H_2O$ (**CoUPAA-5**).

EXPERIMENTAL SECTION

Syntheses. Uranium trioxide (98%, Strem), triethyl phosphonoacetate (98%, Alfa Aesar), cobalt(II) acetate tetrahydrate (98%, Alfa Aesar), boric acid (99.9%, Alfa Aesar), and acetic acid (99.5%, ACROS Organics) 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 during work with UO_3 and the products of the reactions. The products were thoroughly washed with water and then rinsed with methanol and allowed to dry.

*$Co(H_2O)_4[(UO_2)_2(PO_3CH_2CO_2)_2(H_2O)_2]$ (**CoUPAA-1**).* UO_3 (286.3 mg, 0.126 mmol), triethyl phosphonoacetic acid (0.120 mL, 0.602 mmol), $Co(CO_2CH_3)_2 \cdot 4H_2O$ (249 mg, 0.512 mmol), 1 mL of acetic acid, and 5 mL of water were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 180 °C in a box furnace for 5 days. The autoclave was then cooled at an average rate of 9 °C/h to 35 °C. Initial pH 4.37. Final pH 2.40. **CoUPAA-1** forms pale orange tablets.

*$[Co(H_2O)_6][UO_2(PO_3CH_2CO_2)]_2 \cdot 8H_2O$ (**CoUPAA-2**) and $Co(H_2O)_4[UO_2(PO_3CH_2CO_2)]_2 \cdot 4H_2O$ (**CoUPAA-3**).* UO_3 (286.3 mg, 0.877 mmol), triethyl phosphonoacetic acid (0.120 mL, 0.602 mmol), $Co(CO_2CH_3)_2 \cdot 4H_2O$ (249 mg, 0.653 mmol), and 5 mL of water were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 200 °C in a box furnace for 3 d. The autoclave was then cooled at an average rate of 3 °C/h to 35 °C. **CoUPAA-2** and **CoUPAA-3** both form orange tablets.

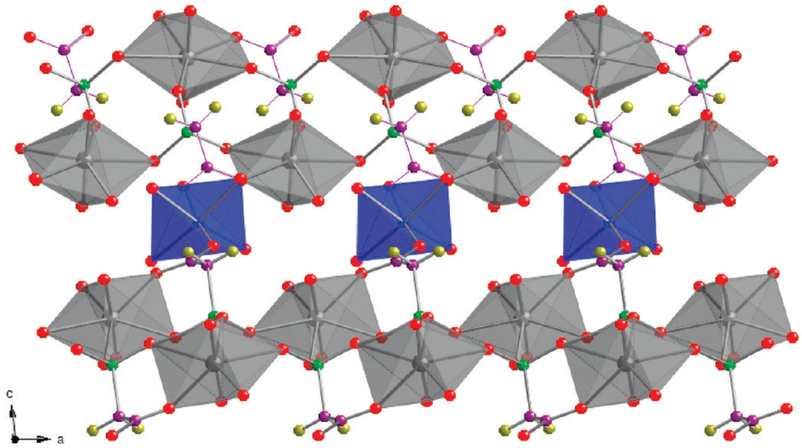

Figure 2. Depiction of stacking of the layers in **$Co(H_2O)_4[(UO_2)_2(PO_3CH_2CO_2)_2(H_2O)_2]$ (CoUPAA-1)** showing the dangling carboxylic acid moiety and Co^{2+} along the *b*-axis. UO_7 pentagonal bipyramids = gray, cobalt = blue, phosphorus = green, oxygen = red, carbon = purple, and hydrogen = yellow.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Co(H_2O)_4[(UO_2)_2(PO_3CH_2CO_2)_2(H_2O)_2]$ (CoUPAA-1)

Distances (Å)			
U(1)−O(11)	1.773(5)	Co(1)−O(19)	2.104(3)
U(1)−O(12)	1.777(3)	Co(1)−O(18)	2.106(3)
U(1)−O(1)	2.322(3)	Co(1)−O(20)	2.148(3)
U(1)−O(3)	2.344(3)	P(1)−O(1)	1.519(3)
U(1)−O(2)	2.368(3)	P(1)−O(2)	1.526(3)
U(1)−O(5)	2.446(3)	P(1)−O(3)	1.533(3)
U(1)−O(15)	2.482(3)	P(1)−C(1)	1.801(4)
U(2)−O(13)	1.765(3)	P(2)−O(6)	1.526(3)
U(2)−O(14)	1.784(3)	P(2)−O(8)	1.528(3)
U(2)−O(8)	2.340(3)	P(2)−O(7)	1.531(3)
U(2)−O(7)	2.351(3)	P(2)−C(3)	1.811(4)
U(2)−O(6)	2.358(3)	C(1)−C(2)	1.516(6)
U(2)−O(9)	2.397(3)	C(2)−O(4)	1.263(5)
U(2)−O(16)	2.544(3)	C(2)−O(5)	1.264(5)
Co(1)−O(10)	2.044(3)	C(3)−C(4)	1.512(6)
Co(1)−O(4)	2.087(3)	C(4)−O(9)	1.264(5)
Co(1)−O(17)	2.093(3)	C(4)−O(10)	1.262(5)
Angles (deg)			
O(11)−U(1)−O(12)	177.73(13)	O(13)−U(2)−O(14)	177.43(13)

*$Co(H_2O)_4[(UO_2)_6(PO_3CH_2CO_2)_2O_2(OH)_3(H_2O)_3]_2\cdot 3H_2O$ (**CoUPAA-4**) and $Co_2[(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2]\cdot 16H_2O$ (**CoUPAA-5**).* UO_3 (286.3 mg, 0.870 mmol), triethyl phosphonoacetic acid (0.120 mL, 0.602 mmol), $Co(CO_2CH_3)_2\cdot 4H_2O$ (249 mg, 1 mmol), and 5 mL of water were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 150 °C in a box furnace for 5 days. The autoclave was then cooled at an average rate of 9 °C/h to 35 °C. **CoUPAA-4** forms orange tablets. **CoUPAA-5** forms large red blocks.

Crystallographic Studies. Crystals of **CoUPAA-1**, **CoUPAA-2**, **CoUPAA-3**, **CoUPAA-4**, and **CoUPAA-5** were mounted on glass fibers, and optically aligned on a Bruker APEXII Quazar X-ray diffractometer using a digital camera. Initial intensity measurements were either 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 with exposure time per frame of 30 to 60 s, depending on the crystal.

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 (SCALE).[18] The program suite SHELXTL (v 6.12) was used for space group determination (XPREP), direct methods structure solution (XS), and least-squares refinement (XL).[19] The final refinements included anisotropic displacement parameters for all atoms. Secondary extinction was not noted. Some crystallographic details are given in Table 1. Additional details can be found in the Supporting Information.

Powder X-ray Diffraction. Powder XRD measurements were used to confirm the bulk purity of **CoUPAA-5**. The structure does not collapse after heating and dehydration at 180 °C. The calculated and measured diffraction data are shown in Figure S1 in the Supporting Information.

Thermogravimetric Analysis. Thermogravimetric analysis of **CoUPAA-5** shows water loss and decomposition when heated from 22 to 867 °C. Figure S2 in the Supporting Information shows three steps of water loss for **CoUPAA-5** with percentages less than 10% for each interval. A weight loss of 6% occurs near 170 °C. This is followed by an approximate loss of 9% around 370 °C. The final weight loss of water was around 480°, where 4% was lost. This gives a total weight loss of about 19−20%. Even though most of the water was removed, **CoUPAA-5** showed no signs of decomposition.

Differential Gas Absorption Isotherm Measurements. Adsorption measurements were performed using an Autosorb 1-MP from Quantachrome Instruments. Research grade CO_2 obtained from Airgas Inc. (Radnor, PA) were used for all adsorption measurements. Samples were soaked in absolute ethanol for 3 days replacing solvent every 24 h. The sample was then filtered and loaded into a sample tube of known weight and activated at room temperature and dynamic vacuum for 12 h then heated to 80 °C to completely remove guest solvents. After activation, the sample and tube reweighed to obtain the precise mass. The CO_2 adsorption isotherm was held at 273 K in an ice−water bath. The void volume of the system was determined by using He gas. Surface area, pore volume, and pore diameter determined using the slit-pore NLDFT model for CO_2 at 273 K on carbon from AS1Win version 2.01 by Quantachrome Instruments.

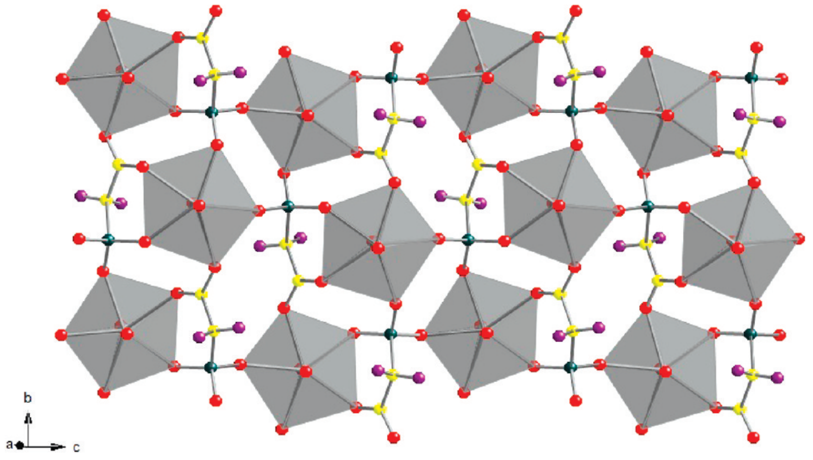

Figure 3. View of the uranyl phosphonate plane in $[Co(H_2O)_6][UO_2(PO_3CH_2CO_2)]_2 \cdot 8H_2O$ (**CoUPAA-2**). UO_7 pentagonal bipyramids = gray, phosphorus = green, oxygen = red, carbon = purple, and hydrogen = yellow.

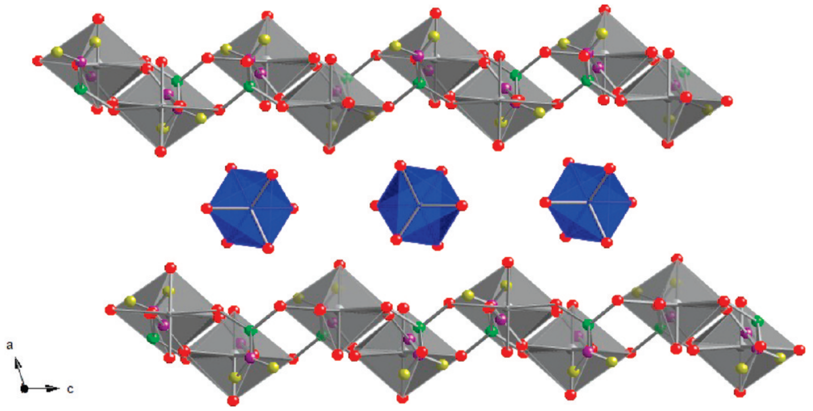

Figure 4. Image of $[Co(H_2O)_6][UO_2(PO_3CH_2CO_2)]_2 \cdot 8H_2O$ (**CoUPAA-2**) along the *b*-axis showing the Co^{2+} cation along the interlayer space. UO_7 pentagonal bipyramids = gray, cobalt = blue, phosphorus = green, oxygen = red, carbon = purple, and hydrogen = yellow.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Co(H_2O)_6][UO_2(PO_3CH_2CO_2)]_2 \cdot 8H_2O$ (CoUPAA-2).

	Distances (Å)		
U(1)−O(6)	1.775(4)	Co(1)−O(9)	2.086(4)
U(1)−O(7)	1.788(4)	Co(1)−O(10)	2.126(4)
U(1)−O(1)	2.329(4)	Co(1)−O(10)	2.126(4)
U(1)−O(3)	2.329(4)	P(1)−O(1)	1.522(4)
U(1)−O(2)	2.347(4)	P(1)−O(3)	1.525(4)
U(1)−O(5)	2.416(4)	P(1)−O(2)	1.529(4)
U(1)−O(4)	2.420(3)	P(1)−C(1)	1.806(5)
Co(1)−O(8)	2.070(4)	C(2)−O(4)	1.279(6)
Co(1)−O(8)	2.070(4)	C(2)−O(5)	1.249(6)
Co(1)−O(9)	2.086(4)	C(1)−C(2)	1.514(7)
	Angles (deg)		
O(6)−U(1)−O(7)	179.08(16)		

RESULTS AND DISCUSSION

Synthesis. The syntheses of **CoUPAA-1**, **CoUPAA-2**, **CoUPAA-3**, **CoUPAA-4**, and **CoUPAA-5** are relatively straightforward, and involve typical mild hydrothermal treatment of the appropriate starting materials with the slow hydrolysis of triethyl phosphonoacetic acid yielding phosphonoacetate. This slow hydrolysis step is the key to achieving the formation of crystals.[10,12] Direct addition of phosphonoacetic acid leads to the formation of powders. **CoUPAA-5** is the most complex structure in this set of compounds. By changing the molar ratio of the cobalt reagent, adding boric acid to lower crystallization temperatures,[20] or adjusting the pH with acetic acid, the additional four Co(II) compounds were isolated. Only **CoUPAA-5** can be isolated as a pure compound. All other are found in product mixtures.

Structure of $Co(H_2O)_4[(UO_2)_2(PO_3CH_2CO_2)_2(H_2O)_2]$ (CoUPAA-1). The structure of **CoUPAA-1** consists of one-dimensional uranyl phosphonate ribbons that are linked together by partially hydrated Co(II) cations. There are in fact two crystallographically unique uranium centers contained within these ribbons, but both are found as the common UO_7 pentagonal bipyramid. These ribbons are recognized from uranyl chromates and sulfates and have the Demesmaekerite topology.[1,2] U(1) has an average uranyl, U═O, bond distance of 1.775(3) Å. The equatorial U−O bonds to the phosphonate oxygen atoms vary slightly from 2.322(3) to 2.368(3) Å; whereas the U−O bonds to the carboxylate moiety and the coordinating water molecule are much longer at 2.446(3) and 2.482(3) Å, respectively. U(2) follows a similar pattern with an average uranyl, U═O, bond distance of 1.774(3) Å, and

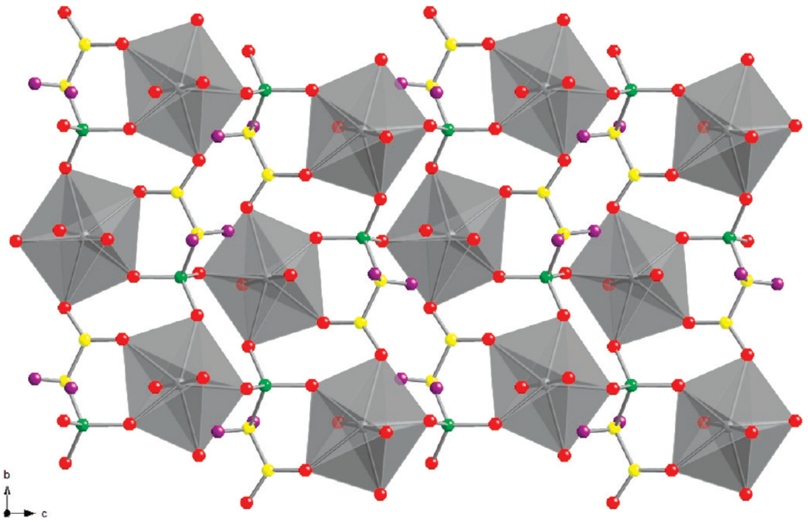

Figure 5. View of the uranyl phosphonate layers along the *c*-axis showing the 6-coordinate Co(II) in **$Co(H_2O)_4[UO_2(PO_3CH_2CO_2)]_2 \cdot 4H_2O$ (CoUPAA-3)**. UO_7 pentagonal bipyramids = gray, phosphorus = green, oxygen = red, carbon = purple, and hydrogen = yellow.

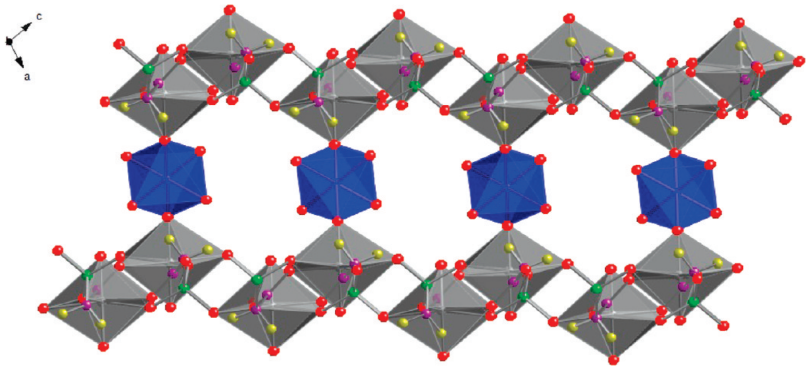

Figure 6. Depiction of the anionic layer found in **$Co(H_2O)_4[UO_2(PO_3CH_2CO_2)]_2 \cdot 4H_2O$ (CoUPAA-3)** along the *a*-axis. UO_7 pentagonal bipyramids = gray, cobalt = blue, phosphorus = green, oxygen = red, carbon = purple, and hydrogen = yellow.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $Co(H_2O)_4[UO_2(PO_3CH_2CO_2)]_2 \cdot 4H_2O$ (CoUPAA-3).

	Distances (Å)		
U(1)−O(6)	1.775(3)	Co(1)−O(9)	2.057(3)
U(1)−O(7)	1.807(3)	Co(1)−O(7)	2.133(3)
U(1)−O(3)	2.313(3)	Co(1)−O(7)	2.133(3)
U(1)−O(2)	2.326(3)	P(1)−O(1)	1.513(3)
U(1)−O(1)	2.340(3)	P(1)−O(2)	1.529(3)
U(1)−O(5)	2.407(3)	P(1)−O(3)	1.531(3)
U(1)−O(4)	2.431(3)	P(1)−C(1)	1.812(4)
Co(1)−O(8)	2.049(3)	C(2)−O(4)	1.273(5)
Co(1)−O(8)	2.049(3)	C(2)−O(5)	1.260(5)
Co(1)−O(9)	2.049(3)	C(1)−C(2)	1.510(5)
	Angles (deg)		
O(6)−U(1)−O(7)	177.92(11)		

equatorial bonds to the phosphonate oxygen atoms ranging from 2.340(3) to 2.358(3) Å. Again, longer bonds to the carboxylate moiety and water molecule are found at 2.397(3) and 2.544(3) Å, respectively. The bond-valence sums for U(1) and U(2) are 6.01 and 5.99, both of which are consistent with U(VI).[21] The Co−O bond distances range from 2.044(3) to 2.148(3) Å, and the bond-valence sum is 2.01, which is consistent with Co(II).[22] A depiction of the uranyl phosphonate chains is shown in Figure 1, and the layers in Figure 2. Selected bond distances are given in Table 2.

Structure of $[Co(H_2O)_6][UO_2(PO_3CH_2CO_2)]_2 \cdot 8H_2O$ (CoUPAA-2). CoUPAA-2 adopts a layered structure in which the Co(II) cations do not form covalent contacts with the uranyl carboxyphosphonate layers. Here the anionic layers are separated from one another by $[Co(H_2O)_6]^{2+}$ cations. The uranium center is found in the form of a UO_7 pentagonal bipyramid, and it is bound by both the phosphonate and carboxylate portions of the ligand. The average U═O bond distance is 1.781(4) Å. The three shorter U−O bonds are to the coordinated phosphonate group and range from 2.329(4) to 2.347(4) Å, whereas the bonds to the carboxylate moiety are 2.416(4) and 2.420(4) Å. The bond-valence sum for uranium is 6.10.[21] A view of the uranyl carboxyphosphonate layers is shown in Figure 3, and the separation of these layers by the $[Co(H_2O)_6]^{2+}$ cations in Figure 4. Selected bond distances are given in Table 3.

Structure of $Co(H_2O)_4[UO_2(PO_3CH_2CO_2)]_2 \cdot 4H_2O$ (CoUPAA-3). The structure of **CoUPAA-3** is quite similar to that of **CoUPAA-2** in that the Co(II) cations are not bound by the ligand, and the Co(II) cations are found between uranyl carboxyphosphonate layers. Again the uranium centers are found

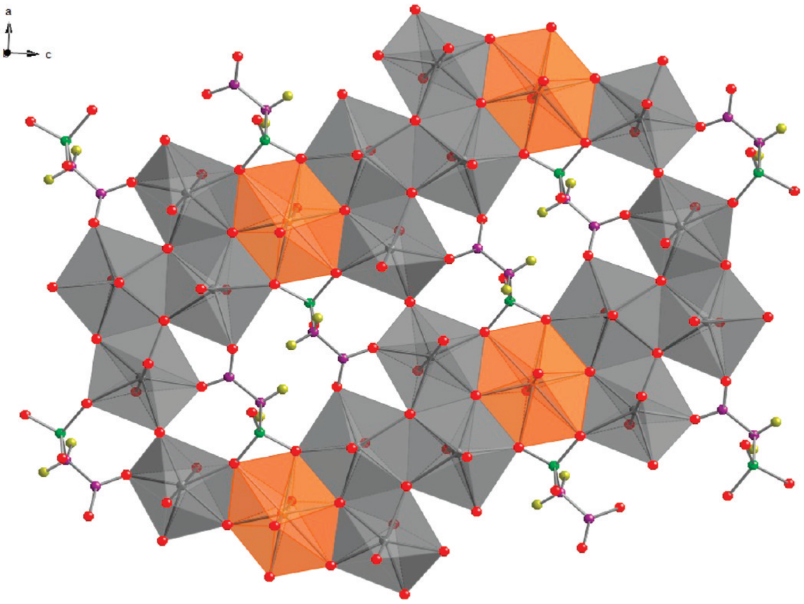

Figure 7. Illustration of the edge-sharing tetramers of uranyl pentagonal bipyramids and the hexagonal bipyramids in **$Co(H_2O)_4[(UO_2)_6(PO_3CH_2CO_2)_2O_2(OH)_3(H_2O)_3]_2 \cdot 3H_2O$ (CoUPAA-4)** along the *b*-axis. UO_8 hexagonal bipyramids = orange, UO_7 pentagonal bipyramids = gray, phosphorus = green, oxygen = red, carbon = purple, and hydrogen = yellow.

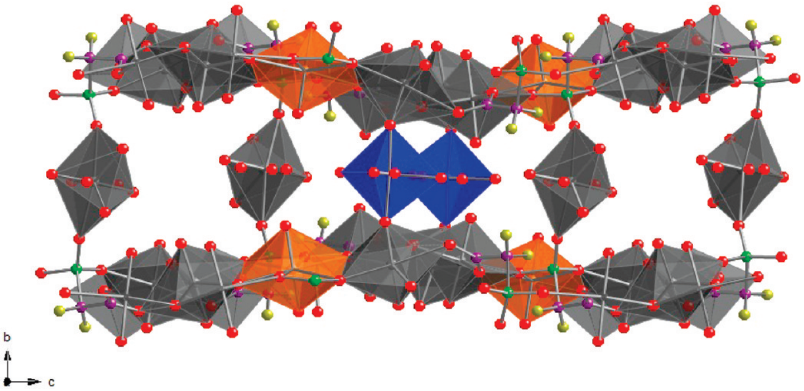

Figure 8. Depiction of the layered uranyl phosphonate with UO_7 and CO_6 in between the planes in **$Co(H_2O)_4[(UO_2)_6(PO_3CH_2CO_2)_2O_2(OH)_3(H_2O)_3]_2 \cdot 3H_2O$ (CoUPAA-4)** along the *a*-axis. UO_8 hexagonal bipyramids = orange, UO_7 pentagonal bipyramids = gray, cobalt = blue, phosphorus = green, oxygen = red, carbon = purple, and hydrogen = yellow.

as isolated UO_7 pentagonal bipyramids that are bridged by the phosphonoacetate ligands. There is only a single crystallographically unique UO_2^{2+} group with uranyl bond lengths of 1.775(3) and 1.807(3) Å. Herein lies the key difference between the structures. The uranyl oxo atoms are engaged in coordinating the Co(II) cations and have replaced two trans waters molecules. Therefore the $[Co(H_2O)_4]^{2+}$ cations actually join the layers together in this compound. The coordination of the uranyl oxo atom to Co(II) results in a slight lengthening of the U=O bond distance. The bond-valence sum for uranium is 6.05, which is consistent with U(VI).[21] Each phosphonoacetate ligand binds to four uranyl moieties as in **CoUPAA-2**. The U−O equatorial bonds range from 2.313(3) to 2.431(3) Å, with the three shorter bonds belonging to U−O−P linkages, and the longer two bonds to the carboxylic portion. Figure 5 shows the uranyl phosphonoacetate layer along the *a* axis.

The cobalt cation has six bond lengths ranging from 2.049(3) to 2.133(3) Å forming an octahedron. The bond-valence of the cation is 2.11, which is consistent with this compound containing Co(II).[22] The longest two Co−O bonds (2.133(3) Å) corresponds to the coordination by the uranyl cation. The four remaining Co−O bonds are to terminal water molecules. Figure 6 illustrates the uranyl phosphonate layers being joined by the Co(II) cations. Selected bond distances are given in Table 4.

Structure of $Co(H_2O)_4[(UO_2)_6(PO_3CH_2CO_2)_2O_2(OH)_3(H_2O)_3]_2 \cdot 3H_2O$ (CoUPAA-4). The structure of **CoUPAA-4** is very complex in that it contains layers formed from five crystallographically unique U(VI) cations and phosphonoacetate. The uranium centers occur as both the common UO_7 pentagonal bipyramid and the somewhat rare UO_8 hexagonal bipyramid. The occurrence of the UO_8 hexagonal bipyramid in this compound is intriguing because normally this coordination geometry is only found in the presence of small chelating ligands like nitrate, carbonate, and borate.[23] In fact, opposite edges of the hexagonal bipyramid are occupied by chelating phosphonate moieties. The remaining opposite vertices are oxo groups from the hydrolysis of

Table 5. Selected Bond Distances (Å) and Angles (deg) for $Co(H_2O)_4[(UO_2)_6(PO_3CH_2CO_2)_2O_2(OH)_3(H_2O)_3]_2\cdot 3H_2O$ (CoUPAA-4).

Distance (Å)

U(1)−O(11)	1.758(12)	U(5)−O(27)	2.312(9)
U(1)−O(12)	1.784(11)	U(5)−O(2)	2.374(9)
U(1)−O(23)	2.259(12)	U(5)−O(26)	2.453(9)
U(1)−O(24)	2.276(10)	U(5)−O(9)	2.455(10)
U(1)−O(3)	2.485(9)	U(6)−O(21)	1.779(12)
U(1)−O(8)	2.496(9)	U(6)−O(22)	1.781(13)
U(1)−O(2)	2.688(9)	U(6)−O(6)	2.297(11)
U(1)−O(7)	2.721(9)	U(6)−O(1)	2.301(10)
U(2)−O(13)	1.754(12)	U(6)−O(29)	2.434(13)
U(2)−O(14)	1.758(11)	U(6)−O(28)	2.447(11)
U(2)−O(24)	2.278(10)	U(6)−O(30)	2.481(11)
U(2)−O(25)	2.366(9)	Co(1)−O(20)	1.931(13)
U(2)−O(8)	2.369(9)	Co(1)−O(16)	1.934(12)
U(2)−O(4)	2.405(9)	Co(1)−O(32)	2.11(2)
U(2)−O(26)	2.433(9)	Co(1)−O(31)	2.13(2)
U(3)−O(15)	1.751(12)	Co(1)−O(33)	2.17(2)
U(3)−O(16)	1.806(12)	Co(1)−O(34)	2.27(2)
U(3)−O(23)	2.286(12)	P(1)−O(1)	1.495(11)
U(3)−O(27)	2.340(9)	P(1)−O(2)	1.524(9)
U(3)−O(7)	2.356(9)	P(1)−O(3)	1.541(9)
U(3)−O(25)	2.405(9)	P(1)−C(1)	1.816(14)
U(3)−O(5)	2.452(10)	P(2)−O(6)	1.497(11)
U(4)−O(17)	1.751(11)	P(2)−O(7)	1.529(9)
U(4)−O(18)	1.770(12)	P(2)−O(8)	1.543(10)
U(4)−O(23)	2.272(12)	P(2)−C(3)	1.826(13)
U(4)−O(26)	2.382(9)	C(1)−C(2)	1.535(17)
U(4)−O(3)	2.384(8)	C(2)−O(5)	1.244(16)
U(4)−O(10)	2.386(10)	C(2)−O(4)	1.247(15)
U(4)−O(25)	2.398(9)	C(3)−C(4)	1.519(16)
U(5)−O(19)	1.755(13)	C(4)−O(10)	1.232(16)
U(5)−O(20)	1.794(12)	C(4)−O(9)	1.253(16)
U(5)−O(24)	2.289(10)		

Angles (Å)

O(11)−U(1)−O(12)	178.7(5)	O(17)−U(4)−O(18)	177.4(5)
O(13)−U(2)−O(14)	177.8(5)	O(19)−U(5)−O(20)	178.8(5)
O(15)−U(3)−O(16)	178.7(5)	O(21)−U(6)−O(22)	176.9(6)

water. Hydroxo groups are also found as bridges between the UO_7 units in the layers. Although such hydrolysis products are exceedingly common in uranium oxoanion chemistry,[24] they have proven to be a rarity in uranyl phosphonates perhaps because of the low pH under which these compounds are synthesized. There is actually a sixth crystallographically unique uranyl cation that bridges between the layers with its uranyl axis oriented approximately perpendicular to the axis of the uranyl cations within the layer. As found in **CoUPAA-4** some of the uranyl cation coordinate $[Co(H_2O)_4]^{2+}$ cations. A view of the layers and the joining of the layers can be found in Figures 7 and 8, respectively. Selected bond distances are given in Table 5.

Structure of $Co_2[(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2]\cdot 16H_2O$ (CoUPAA-5). **CoUPAA-5** crystallizes in the high-symmetry cubic space group $Im\bar{3}$. Previous uranyl carboxyphosphonates have not crystallized in crystal systems with symmetries higher than orthorhombic. The structure is also different from other uranyl carboxyphosphonates except **CoUPAA-4** in that it incorporates both UO_7 pentagonal bipyramids and UO_8 hexagonal bipyramids. These units assemble to form a nearly planar cluster containing eight uranyl polyhedra shown in the central portion of Figure 9. These clusters are found extended into chains in compounds and minerals with the Phosphuranylite topology.[1,2] Four such clusters are linked by additional intermediate uranyl groups that are bound by phosphonates. These groups are linkers not only for the clusters within one cell, but also connect cage-to-cage. As required by the cubic symmetry, the top and bottom of the cavities are capped again by the clusters of UO_7 and UO_8 polyhedra. The subunits are assembled together by a disordered triad of Co(II) cations that are bound by variety of interactions that include bonds with the uranyl apical oxygen atoms. When assembled together, the subunits form a large cavity approximately 16 Å in diameter that is filled with cocrystallized water molecules. In addition there are channels between the cavities that are filled with the Co(II) cations and water molecules.

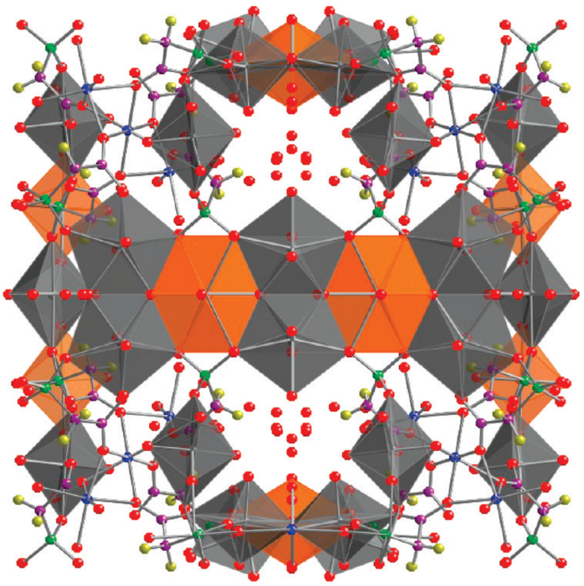

Figure 9. Illustration of the three-dimensional network of $Co_2[(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2]\cdot 16H_2O$ (**CoUPAA-5**) along the [*ab*] plane. This gives a view of the disordered water molecules and cobalt cations. UO_8 hexagonal bipyramids = orange, UO_7 pentagonal bipyramids = gray, cobalt = blue, phosphorus = green, oxygen = red, carbon = purple, and hydrogen = yellow.

85% of uranyl compounds contain uranium in the form of a pentagonal bipyramid, and it is not surprising therefore that the family of uranyl carboxyphosphonates have thus far been found to exclusively contain this unit. This may be one of the reasons for the propensity for low-symmetry in this family. **CoUPAA-5** is unusual in this regard in that it contains the much rarer, although certainly well-precedented,[1] UO_8 hexagonal bipyramid, as does **CoUPAA-4**. UO_6 tetragonal bipyramids are still absent from the uranyl carboxyphosphonate family. These units create the previously described cluster that repeats itself to create part of the walls of the cavities. These clusters are recognized as portions of the infinite chains found within the sheets of the minerals with the $[(UO_2)_3(SeO_3)_2O_2]^{2-}$ sheet topology.[1] The structure is surprising rich in comparison to many of the

Table 6. Selected Bond Distances (Å) and Angles (°) for $Co_2[(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2]\cdot 16H_2O$ (CoUPAA-5)

	Distances (Å)		
U(1)−O(6)	1.783(4)	Co(1)−OW(2)	2.053(5)
U(1)−O(7)	1.798(4)	Co(1)−O(9)	2.128(3)
U(1)−O(12)	2.266(2)	Co(1)−O(9)	2.128(3)
U(1)−O(12)	2.266(3)	Co(1)−OW(1A)	2.140(8)
U(1)−O(3)	2.378(2)	Co(1)−OW(1A)	2.140(8)
U(1)−O(3)	2.378(2)	Co(2)−OW(4)	2.077(4)
U(1)−O(13)	2.429(4)	Co(2)−OW(4)	2.077(4)
U(2)−O(8)	1.808(3)	Co(2)−OW(4)	2.077(4)
U(2)−O(9)	1.826(3)	Co(2)−O(5)	2.082(3)
U(2)−O(12)	2.186(3)	Co(2)−O(5)	2.082(3)
U(2)−O(14)	2.192(4)	Co(2)−O(5)	2.082(3)
U(2)−O(2)	2.630(3)	Co(3)−O(5)	2.105(3)
U(2)−O(2)	2.630(3)	Co(3)−O(5)	2.105(3)
U(2)−O(3)	2.631(3)	Co(3)−O(5)	2.105(3)
U(2)−O(3)	2.631(3)	Co(3)−O(5)	2.105(3)
U(3)−O(10)	1.790(5)	Co(3)−O(5)	2.105(3)
U(3)−O(11)	1.791(5)	Co(3)−O(5)	2.105(3)
U(3)−O(14)	2.269(3)	P(1)−O(1)	1.499(3)
U(3)−O(14)	2.269(3)	P(1)−O(2)	1.526(3)
U(3)−O(2)	2.383(3)	P(1)−O(3)	1.533(2)
U(3)−O(2)	2.383(3)	P(1)−C(1)	1.808(4)
U(3)−O(15)	2.436(5)	C(2)−O(4)	1.251(4)
Co(1)−OW(1)	2.041(7)	C(2)−O(5)	1.261(4)
Co(1)−OW(1)	2.041(7)	C(1)−C(2)	1.517(5)
Co(1)−OW(2)	2.053(5)		
	Angles (deg)		
O(6)−U(1)−O(7)	174.11(17)	O(10)−U(3)−(11)	177.31(13)
O(8)−U(2)−O(9)	179.37(15)		

[a] Co−O bond lengths include disordered oxygen atoms.

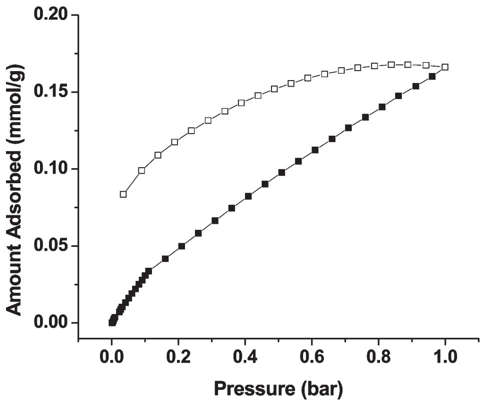

Figure 10. Carbon dioxide isotherm of $Co_2[(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2]\cdot 16H_2O$ (**CoUPAA-5**) at 273 K. Nitrogen isotherms performed at 77 K showed no uptake of gas. The CO_2 isotherm exhibits hysteresis, suggesting constricted pores.

actinide carboxyphosphonates.[9−15] Selected bond distances are given in Table 6. The bond-valence sums are consistent with U(VI) and Co(II).[22]

One of the few examples of an actinide material with a porous structure that is capable of significant gas absorption is TOF-2, a Th(IV) metal−organic framework, which exhibits differential gas sorption with a surface area for CO_2 uptake of 293 m^2/g at 77 K.[25] In **CoUPAA-5**, the observation of a large cavity filled with water led to speculation that these might be compounds capable of gas sorption. After performing TGA thermograms, the water molecules were easily removed upon heating as evidenced by the loss of the cage water molecules up to 230 °C, followed by loss of coordinating water molecules and decomposition. Despite facile water loss, attempted assessments of nitrogen sorption demonstrated that the compound does not behave as a porous material, at least under cryogenic conditions (77 K). However, like TOF-2, this material does sorb CO_2, yielding an NLDFT surface area of 40 m^2/g (142 m^2/cm^3 of framework) at 273 K. The CO_2 isotherm additionally yields a micropore volume of (122 cm^3/g) and apparent average pore diameter of 4.8 Å. Figure 10 shows the CO_2 isotherm.

CONCLUSIONS

The structural chemistry of the U(VI)/Co(II) phosphonoactetates is remarkably rich yielding five different compounds with both layered and three-dimensional topologies. Two different coordination geometries are found for U(VI) in these structures; both the UO_7 pentagonal bipyramid and the UO_8 hexagonal bipyramid. High symmetry structures are adopted and hydrolysis products form. These are rarities in uranyl carboxyphosphonates. The incorporation of transition metals into uranyl carboxyphosphonate clearly substantially increases the structural diversity of not just the total system but also the uranyl oxoanion substructures.

ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic files in CIF format for $Co(H_2O)_4[(UO_2)_2(PO_3CH_2CO_2)_2(H_2O)_2]$ (**CoUPAA-1**), $[Co(H_2O)_6][UO_2(PO_3CH_2CO_2)]_2\cdot 8H_2O$ (**CoUPAA-2**), $Co(H_2O)_4[UO_2(PO_3CH_2CO_2)]_2\cdot 4H_2O$ (**CoUPAA-3**), $Co(H_2O)_4[(UO_2)_6(PO_3CH_2CO_2)_2O_2(OH)_3(H_2O)_3]_2\cdot 3H_2O$ (**CoUPAA-4**), and $Co_2[(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2]\cdot 16H_2O$ (**CoUPAA-5**). Powder X-ray diffraction, thermogravimetric analysis, and differential gas absorption isotherm measurements for $Co_2[(UO_2)_6(PO_3CH_2CO_2)_3O_3(OH)(H_2O)_2]\cdot 16H_2O$ (**CoUPAA-5**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org/.

AUTHOR INFORMATION

Corresponding Author

*E-mail: talbrec1@nd.edu.

ACKNOWLEDGMENT

We are grateful for support provided by the Heavy Elements Program, U.S. Department of Energy under Grants DE-FG02-01ER16026 and DE-SC0002215, as well as DOE's Separations Program (Grant DE-FG02-0815967), and by Deutsche Forschungsgemeinschaft within the DE 412/43-1 research project. Thifs material is based upon work supported as part of the Materials Science of Actinides, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award DE-SC0001089.

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