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Phosphonoacetate as a Ligand for Constructing Layered and Framework Alkali Metal Uranyl Compounds

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The hydrothermal reactions of KCl, RbCl, CsOH, and CsCl with phosphonoacetic acid and uranium trioxide at 180 °C for three to five days results in the formation of five different crystalline uranyl carboxyphosphonates, $K[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)]\cdot H_2O$, $Rb[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)]\cdot H_2O$, $Cs[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)]\cdot H_2O$, $Cs[(UO_2)(PO_3CH_2CO_2)]$, and $Cs_3[(UO_2)_4(PO_3CH_2O_2)_2(PO_3CH_2CO_2H_{0.5})_2]\cdot nH_2O$, respectively. In all compounds, the UO_2^{2+} moieties are bound by phosphonate and carboxylate forming pentagonal bipyramidal environments around the uranium centers. At low pH, some of the carboxylate portions of the phosphonoacetate are protonated. The addition of hydroxide removes these protons, and a different structure is adopted. In contrast to all other uranyl carboxyphosphonates, $Cs_3[(UO_2)_4(PO_3CH_2O_2)_2(PO_3CH_2CO_2H_{0.5})_2]\cdot nH_2O$ adopts a three-dimensional network structure with large channels along the *c* axis that house the Cs^+ cations.

Introduction

Metal phosphonates have been the subject of substantial investigations that have resulted in a vast expansion of our knowledge of the fundamental structural chemistry of these compounds, as well as their potential applications in ion exchange, catalysis, sorption, and intercalation chemistry.[1] Uranyl phosphonates are among the structurally richest systems studied.[2] These compounds are typically low-dimensional.[2] This feature should be partially attributed to the presence of the UO_2^{2+} cation, whose "yl" oxo atoms are generally not found to bridge between metal centers, effectively removing one dimension of connectivity in most cases.[3] However, polar three-dimensional networks have been found in $UO_2[CH_2(PO_3H)_2](H_2O)$,[4] and pillared structures can be intentionally prepared by judicious selection of the phosphonate.[5] More importantly, there are some unusual aspects of the bonding between phosphonates and U(VI) that can result in room-temperature phase transitions[2a−e] as found in the uranyl phenylphosphonate system.[2b,c] When these one-dimensional compounds are exposed to Na^+ or Ca^{2+} cations in an aqueous environment, they transform into a hollow nanotubular form.[2a] The apparent lability of the uranyl phosphonate U−O bond is surprising in light of the strength of this interaction.[6]

The primary benefit of using phosphonates instead of other oxoanions is the ability to fine-tune chemical and physical properties through modification of the organic residues. A myriad of multifunctional phosphonates have now been developed.[1] One modification of a phosphonate is to add a carboxylate moiety that would allow for the potential binding of this latter group to a second metal center. This idea has been simultaneously explored by our group and that of C. L. Cahill to yield homometallic[7] and heterobimetallic[8] compounds using phosphonoacetate and

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(1) (a) Clearfield, A. *Prog. Inorg. Chem.* **1998**, *47*, 371. (b) Clearfield, A. *Curr. Opin. Solid State Mater. Sci.* **2003**, *6*, 495. (c) Mao, J.-G. *Coord. Chem. Rev.* **2007**, *251*, 1493.

(2) (a) Grohol, D.; Clearfield, A. *J. Am. Chem. Soc.* **1997**, *119*, 9301. (b) Grohol, D.; Clearfield, A. *J. Am. Chem. Soc.* **1997**, *119*, 4662. (c) Grohol, D.; Subramanian, M. A.; Poojary, D. M.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 5264. (d) Aranda, M. A. G.; Cabeza, A.; Bruque, S.; Poojary, D. M.; Clearfield, A. *Inorg. Chem.* **1998**, *37*, 1827. (e) Poojary, D. M.; Cabeza, A.; Aranda, M. A. G.; Bruque, S.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 1468. (f) Poojary, D. M.; Cabeza, A.; Aranda, M. A. G.; Bruque, S.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 5603. (g) Poojary, D. M.; Grohol, D.; Clearfield, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1508. (h) Poojary, D. M.; Grohol, D.; Clearfield, A. *J. Phys. Chem. Solids* **1995**, *56*, 1383. (i) Britel, A.; Wozniak, M.; Boivin, J. C.; Nowogrocki, G.; Thomas, D. *Acta Crystallogr.* **1986**, *C42*, 1502. (j) Grohol, D.; Clearfield, A. *Inorg. Chem.* **1999**, *38*, 751. (k) Cabeza, A.; Aranda, M. A. G.; Cantero, F. M.; Lozano, D.; Martínez-Lara, Bruque, S. *J. Solid State Chem.* **1996**, *121*, 181. (l) Doran, M. B.; Norquist, A. J.; O'Hare, D. *Chem. Mater.* **2003**, *15*, 1449.

(3) (a) Sullens, T. A.; Jensen, R. A.; Shvareva, T. Y.; Albrecht-Schmitt, T. E. *J. Am. Chem. Soc.* **2004**, *126*, 2676. (b) Kubatko, K. A.; Burns, P. C. *Inorg. Chem.* **2006**, *45*, 10277. (c) Alekseev, E. V.; Krivovichev, S. V.; Depmeier, W.; Siidra, O. I.; Knorr, K.; Suleimanov, E. V.; Chuprunov, E. V. *Angew. Chem., Int. Ed.* **2006**, *45*, 7233.

(4) Nelson, A.-G. D.; Bray, T. H.; Zhan, W.; Haire, R. G.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2008**, *47*, 4945.

(5) Adelani, P. O.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2009**, *48*, 2732.

(6) (a) Nash, K. L. *J. Alloy and Cmpd.* **1997**, *249*, 33. (b) Jensen, M. P.; Beitz, J. V.; Rogers, R. D.; Nash, K. L. *J. Chem. Soc., Dalton Trans.* **2000**, *18*, 3058. (c) Chiarizia, R.; Horwitz, E. P.; Alexandratos, S. D.; Gula, M. J. *Sep. Sci. Technol.* **1997**, *32*, 1.

(7) (a) Knope, K. E.; Cahill, C. L. *Inorg. Chem.* **2008**, *47*, 7660. (b) Knope, K. E.; Cahill, C. L. *Inorg. Chem.* **2009**, *48*, 6845.

(8) Alsobrook, A. N.; Zhan, W.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2008**, *47*, 5177.

2-phosphonopropionate as the linkage between the metal centers. Homometallic uranyl compounds are currently represented by $UO_2(O_3PCH_2CO_2H)$, $(UO_2)_4(HO_3PCH_2CO_2)(O_3PCH_2CO_2)_2(H_2O)_4\cdot 3H_2O$, $(UO_2)(O_3PCH_2CO_2)\cdot NH_4\cdot H_2O$, and $(UO_2)_3(O_3PCH(CH_3)CO_2)_2(O_3PCH(CH_3)CO_2H)\cdot 2NH_4\cdot H_2O$.[7a] In addition, three organically templated compounds were recently reported that include $[C_{10}H_{10}N_2][(UO_2)_3(O_3PCH_2CO_2)_2\ (O_3PCH_2CO_2H)(H_2O)]\cdot 3H_2O$, $[C_{12}H_{12}N_2][(UO_2)_3(O_3PCH_2CO_2)_2(O_3PCH_2CO_2H)(H_2O)]\cdot 2H_2O$, and $[C_{12}H_{14}N_2][(UO_2)_3(O_3PCH_2CO_2)_2(O_3PCH_2CO_2H)(H_2O)]\cdot 3H_2O$.[7b] All of these aforementioned compounds are layered. Heterobimetallic compounds are thus far only reported for Cu(II). These compounds include $UO_2Cu(PO_3CH_2CO_2)(OH)(H_2O)_2$, $(UO_2)_2Cu(PO_3CH_2CO_2)_2(H_2O)_3$, and $[H_3O](UO_2)_2Cu_2(PO_3CH_2CO_2)_3(H_2O)_2$.[8] The structures of these compounds range from ribbons to three-dimensional networks. However, it should be noted that in the three-dimensional structure of $[H_3O](UO_2)_2Cu_2(PO_3CH_2CO_2)_3(H_2O)_2$ the uranyl phosphonoacetate layers are linked by Cu(II). What has been learned from both the homometallic and heterobimetallic compounds is that the phosphonate portion of the ligand primarily coordinates the U(VI) centers, whereas the carboxylate moiety preferentially but not exclusively binds to the softer metal ions. In $UO_2(O_3PCH_2CO_2H)$, $[C_{10}H_{10}N_2][(UO_2)_3(O_3PCH_2CO_2)_2(O_3PCH_2CO_2H)(H_2O)]\cdot 3H_2O$, $[C_{12}H_{12}N_2][(UO_2)_3(O_3PCH_2CO_2)_2(O_3PCH_2CO_2H)(H_2O)]\cdot 2H_2O$, and $[C_{12}H_{14}N_2][(UO_2)_3(O_3PCH_2CO_2)_2(O_3PCH_2CO_2H)(H_2O)]\cdot 3H_2O$, some of the carboxylate moieties are protonated and dangle between the layers.[7]

A single alkali metal uranyl phosphonate has been reported, $Na[UO_2(PO_3CH_2CO_2)]\cdot 2H_2O$, and this compound along with the previously mentioned ammonium compounds demonstrate the potential that small cations might play a structure-directing role in determining the topology of the anionic layers.[7,8] Herein, we expand on our first report with the successful preparation and structure determination of five alkali metal uranyl phosphonoacetate compounds, $K[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)]\cdot H_2O$ (**KUPAA**), $Rb[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)]\cdot H_2O$ (**RbUPAA**), $Cs[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)]\cdot H_2O$ (**CsUPAA**), $Cs[(UO_2)(PO_3CH_2CO_2)]$ (**CsUPAA-2**), and $Cs_3[(UO_2)_4(PO_3CH_2CO_2)_2(PO_3CH_2CO_2H_{0.5})_2]\cdot nH_2O$ (**CsUPAA-3**). In this work, we explore how countercation size and pH play roles in determining the formation of layered compounds as well as the first three-dimensional network uranyl carboxyphosphonate.

Experimental Section

Syntheses. Uranium trioxide (98%, Strem), phosphonoacetic acid (98%, Alfa Aesar), potassium chloride (99.997%, Alfa Aesar), cesium hydroxide hydrate (99.9%, Alfa Aesar), cesium chloride (99%, Alfa Aesar), and rubidium chloride (99.8%, Alfa Aesar) 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 were 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, then rinsed with methanol, and allowed to dry. All reactions yielded yellow crystals. The first four compounds form tablets. Crystals of the final compound grow as prisms.

$K[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)]\cdot H_2O$ (KUPAA). UO_3 (105 mg, 0.367 mmol), phosphonoacetic acid (140 mg, 1.000 mmol), KCl (150 mg, 1 mmol), and 3 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 d. The autoclave was then cooled at an average rate of 9 °C/h to 35 °C. Initial pH 1.18. Final pH 1.37. Yield 102.3 mg (62.7% based on uranium).

$Rb[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)]\cdot H_2O$ (RbUPAA). UO_3 (120.6 mg, 0.421 mmol), phosphonoacetic acid (120 mg, 0.857 mmol), RbCl (120 mg, 1 mmol), and 3 mL of water were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 180 °C in a box furnace for 3 d. The autoclave was then cooled at an average rate of 9 °C/h to 35 °C. Initial pH 1.01. Final pH 0.84. Yield 147.4 mg (74.9% based on uranium).

$Cs[(UO_2)(PO_3CH_2CO_2)]$ (CsUPAA-2). UO_3 (286 mg, 1 mmol), phosphonoacetic acid (140 mg, 1 mmol), and 2 mL of water were loaded into a 23 mL autoclave. There was an addition of 0.8 mL of 1 M CsOH to the above starting reaction mixture, and this resulted in the isolation of **CsUPAA-2**. The autoclave was sealed and heated to 180 °C in a box furnace for 3 d. The autoclave was then cooled at an average rate of 9 °C/h to 35 °C. Initial pH 1.91. Final pH 1.99. Yield 349.5 mg (64.7% based on uranium).

$Cs[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)](H_2O)\cdot H_2O$ (CsUPAA) and $Cs_3[(UO_2)_4(PO_3CH_2O_2)_2(PO_3CH_2CO_2H_{0.5})_2]\cdot nH_2O$ (CsUPAA-3). UO_3 (108 mg, 0.384 mmol), phosphonoacetic acid (0.108 mg, 0.773 mmol), CsCl (168 mg, 1 mmol), and 1.5 mL of water were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 180 °C in a box furnace for 3 d. The autoclave was then cooled at an average rate of 9 °C/h to 35 °C. Initial pH 1.16. Final pH 0.77. Yield 131.4 mg (65.9% based on uranium).

Crystallographic Studies. Crystals of **KUPAA**, **RbUPAA**, **CsUPAA**, **CsUPAA-2**, and **CsUPAA-3** were mounted on glass fibers and 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 30−60 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. A numerical, face-indexed absorption correction was applied using XPREP.[9] 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 solution (XS), and least-squares refinement (XL).[9] The final refinements included anisotropic displacement parameters for all non-hydrogen atoms. Secondary extinction was not noted. Some crystallographic details are given in Table 1. Additional details can be found in the Supporting Information.

Fluorescence Spectroscopy. Fluorescence data were acquired on all four 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.

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(9) Sheldrick, G. M. *SHELXTL PC, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*, version 6.12; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 2001.

(10) Sheldrick, G. M. *SADABS 2001*, Program for absorption correction using SMART CCD based on the method of Blessing. *Acta Crystallogr.* **1995**, *A51*, 33.

Table 1. Crystallographic Data for K[$(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)$]·$H_2O$ (**KUPAA**), Rb[$(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2COOH)(H_2O)$]·$H_2O$ (**RbUPAA**), Cs[$(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)$]·$H_2O$ (**CsUPAA**), Cs[$(UO_2)(PO_3CH_2CO_2)$] (**CsUPAA-2**), and $Cs_3[(UO_2)_4(PO_3CH_2CO_2)_2(PO_3CH_2CO_2H_{0.5})_2]\cdot nH_2O$ (**CsUPAA-3**)

compound	KUPAA	RbUPAA	CsUPAA	CsUPAA-2	CsUPAA-3
formula mass	890.15	936.52	983.95	539.95	2085.62
color and habit	yellow, tablet	yellow, tablet	yellow, tablet	yellow, tablet	yellow, tablet
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
a (Å)	7.9819(5)	8.0934(18)	8.4688(4)	8.0242(6)	27.4474(15)
b (Å)	8.3498(5)	8.3792(19)	9.0850(5)	9.5019(7)	8.7901(4)
c (Å)	12.1983(7)	12.321(3)	11.4791(6)	10.5219(8)	15.9852(8)
α (deg)	80.143(1)	79.791(4)	83.5870(10)	90	90
β (deg)	83.068(1)	81.808(4)	77.4380(10)	92.993(1)	110.706(2)
γ (deg)	85.789(1)	85.365(4)	84.6840(10)	90	90
V (Å)	793.97(8)	812.6(3)	854.52(8)	801.15(10)	3607.6(3)
Z	2	2	2	4	4
T (K)	193	193	296	193	193
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	3.707	3.811	3.809	4.477	3.827
μ (Mo Kα) (cm^{-1})	209.17	231.57	212.91	249.35	211.66
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.0342	0.0454	0.0203	0.0283	0.0287
$R_w(F_o^2)^b$	0.1272	0.1550	0.0471	0.0869	0.0816

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

Results and Discussion

Synthesis. The syntheses of **KUPAA**, **RbUPAA**, **CsUPAA**, **CsUPAA-2**, and **CsUPAA-3** are relatively straightforward and involve typical mild hydrothermal treatment of the appropriate starting materials. The reaction ratios are important and have to be carefully controlled to achieve the formation of relatively pure phases. Powder X-ray diffraction experiments reveal that **KUPAA**, **RbUPAA**, and **CsUPAA-2** can be isolated with low impurity levels. However, **CsUPAA** and **CsUPAA-3** form in the same reactions, and we could not find conditions under which only one formed.

Structure of A[$(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)$]·$H_2O$ (A = K, Rb, Cs). KUPAA, RbUPAA, and **CsUPAA** are isotypic, and only **KUPAA** will be discussed. Important bond distances and angles are available for **KUPAA**, **RbUPAA**, and **CsUPAA** in the Supporting Information. The structure of **KUPAA** consists of two crystallographically unique uranium centers both of which are found in the form of uranyl, UO_2^{2+}, cations with an average U=O bond distance of 1.775(7) Å. The equatorial U−O bonds vary considerably. For U(1) there are four short U−O bonds to phosphonate oxygen atoms that range from 2.274(7) to 2.302(7) Å. There are also two substantially longer U−O bonds of 2.501(7) and 2.598(7) Å to the carboxylate moieties of one of the two phosphonoacetate ligands. The shorter of these two distances is to a μ_2-O atom and the second longer one to a μ_3-O atom. The second uranium center, U(2), which shares a corner with UO_7 pentagonal bipyramid containing U(1), displays a similarly large range of equatorial U−O bonds with three short distances to the PO_3 moiety, ranging from 2.296(7) to 2.322(7) Å, and two long distances of 2.501(7) and 2.510(6) Å. The first of these long distances is to a coordinating water molecule. The second is to the μ_3-O atom of the carboxylate portion of one of the phosphonoacetates. The bond−valence sums for U(1) and U(2) are 6.12 and 6.08, respectively, both of which are consistent with U(VI).[11] All of these linkages form the basis of the sheets that are shown in Figure 1.

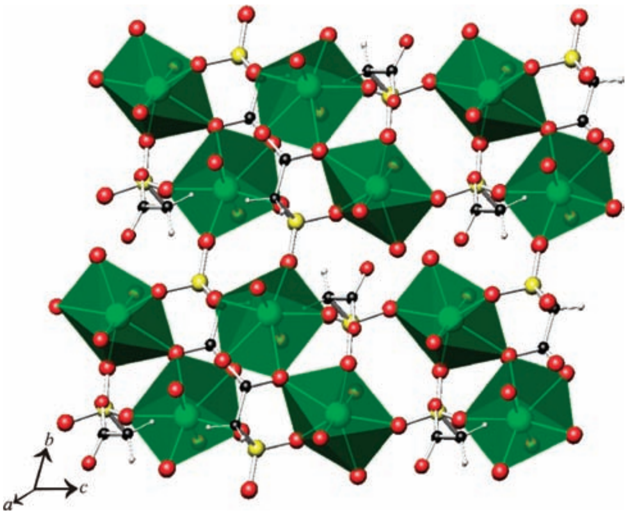

Figure 1. View of the layers found in A[$(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)$]·$H_2O$ (A = K, Rb, Cs). UO_7 pentagonal bipyramids = green, oxygen = red, phosphorus = yellow, carbon = black, and hydrogen = white.

As found in the structure of $UO_2(O_3PCH_2CO_2H)$,[7] there is a dangling carboxylic acid moiety that is directed between the layers of **KUPAA** as shown in Figure 2. The protonation of this group is indicated by the slight asymmetry of the C−O bonds, which are 1.265(12) and 1.299(12) Å. These and other oxygen atoms from the layers form a total of nine long contacts with the interlayer K^+ cations with distances ranging from 2.732(8) to 3.282(8) Å. There is a single cocrystallized water molecule that also interacts with the K^+ cations.

Structure of Cs[$(UO_2)(PO_3CH_2CO_2)$] (CsUPAA-2). This compound is the least complex of the four uranyl carboxyphosphonates detailed in this report. Unlike the other three, there is only a single crystallographically unique uranium site. The uranium is bound by two oxo atoms with an average U=O distance of 1.790(7) Å, thus, forming the well-known uranyl cation, UO_2^{2+}. Further

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(11) Burns, P. C.; Ewing, R. C.; Hawthorne, F. C. *Can. Mineral.* **1997**, *35*, 1551.

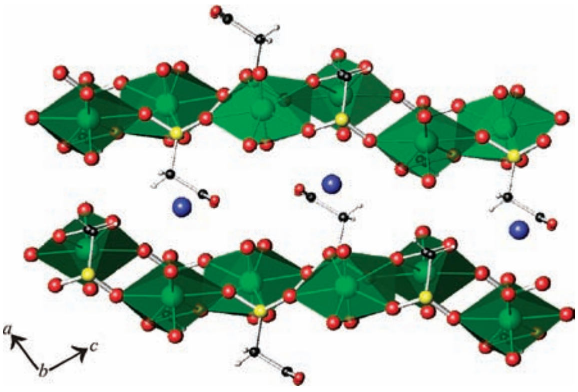

Figure 2. A depiction of the stacking of the layers in $A[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)]\cdot H_2O$ (A = K, Rb, Cs) showing the dangling carboxylic acid moiety. UO_7 pentagonal bipyramids = green, potassium (rubidium, cesium) = blue, oxygen = red, phosphorus = yellow, carbon = black, and hydrogen = white.

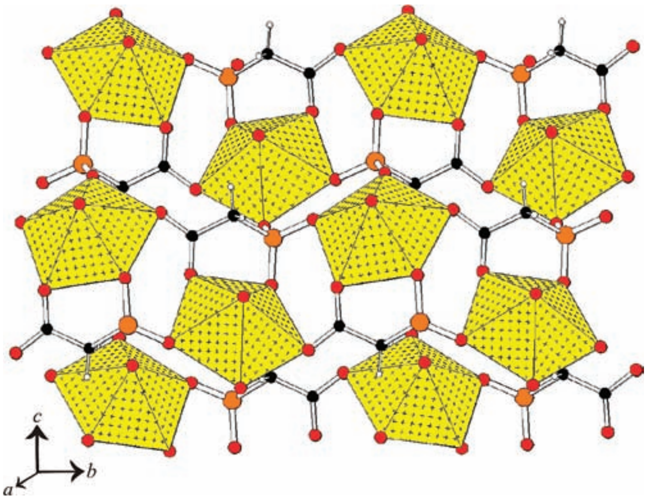

Figure 3. Illustration of the layers in $Cs[(UO_2)(PO_3CH_2CO_2)]$. UO_7 pentagonal bipyramids = yellow, oxygen = red, phosphorus = yellow, carbon = black, and hydrogen = white.

ligation of the uranium center perpendicular to the uranyl axis by five oxygen atoms from the phosphonoacetate anion creates a pentagonal bipyramidal environment, which is by far the most common environment for U(VI).[12] The equatorial U−O bonds range from 2.320(6) to 2.457(7) Å. The three shortest U−O bond lengths are from the phosphonate portion of the ligand at 2.320(7), 2.324(7), and 2.333(7) Å. The two longer U−O bonds are to the carboxylate moiety at 2.436(7) and 2.457(7) Å. The bond−valence sum for the uranium atom is 6.00, which is consistent with U(VI).[11]

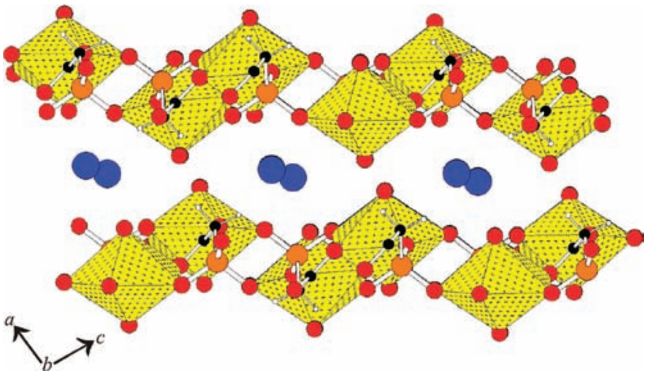

Figure 4. View of the stacking of the layers in $Cs[(UO_2)(PO_3CH_2CO_2)]$. UO_7 pentagonal bipyramids = green, oxygen = red, cesium = blue, phosphorus = yellow, carbon = black, and hydrogen = white.

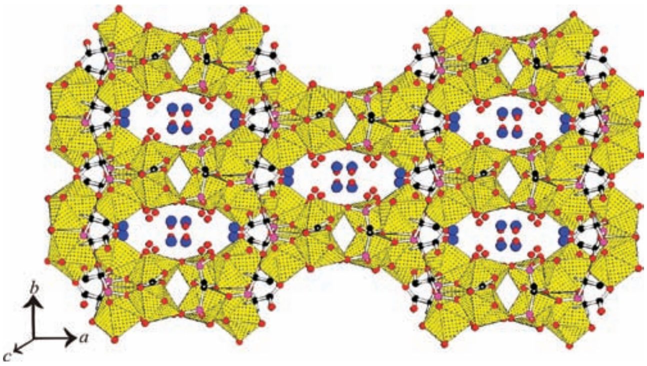

Figure 5. Drawing of the three-dimensional framework structure of $Cs_3[(UO_2)_4(PO_3CH_2CO_2)_2(PO_3CH_2CO_2H_{0.5})_2]\cdot nH_2O$ with channels along the *c* axis that house the Cs^+ cations. UO_7 pentagonal bipyramids are shown in yellow. Cs^+ cations are shown in blue.

Each phosphonoacetate ligand binds to four uranyl moieties and acts as a chelating and bridging ligand. The bridging of the uranyl cations by the phosphonoacetate anion creates a lamellar structure with Cs^+ cations residing between the layers. A view of part of one of the layers is shown in Figure 3. The stacking of the layers is shown in Figure 4. The cesium cation forms 11 long contacts with surrounding oxygen atoms from the layers with distances ranging from 3.072(7) to 3.804(6) Å. The uranyl phosphonoacetate layers are essentially the same as those found in $Na[UO_2(PO_3CH_2CO_2)]\cdot 2H_2O$.[8] Given that the ionic radii of Na^+ and Cs^+ cations differ by approximately 0.6 Å, it is found that these cations are apparently only playing space-filling and charge-balancing roles and do not direct the formation of specific aspects of the structure.

Structure of $Cs_3[(UO_2)_4(PO_3CH_2CO_2)_2(PO_3CH_2CO_2H_{0.5})_2]\cdot nH_2O$ (CsUPAA-3). The structure of **CsUPAA-3** is strikingly different from the other four compounds discussed in this paper. Rather than being layered, the structure adopts a complex three-dimensional framework with channels along the *c* axis as shown in Figure 5. These large channels contain disordered water molecules and Cs^+ cations and are approximately 9.3 × 14.0 Å. This framework forms via the canting of uranyl pentagonal bipyramids, which dramatically differs from the layered compounds where these groups have a tendency to be parallel to one another. Again, there are two crystallographically unique uranium centers, both of which are found in the form of uranyl cations with an average U═O bond distance of 1.780(4) Å. The uranyl centers are additionally ligated by five oxygen atoms from both the phosphonate and carboxylate portions of the phosphonoacetate anions, of which there are two unique molecules. For U(1) and U(2), three of the equatorial atoms are from phosphonate, and the remaining two atoms are

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(12) (a) Burns, P. C.; Miller, M. L.; Ewing, R. C. *Can. Mineral.* **1996**, *34*, 845. (b) Burns, P. C. In *Uranium: Mineralogy, Geochemistry and the Environment*; Burns, P. C.; Finch, R., Eds.; Mineralogical Society of America: Washington, DC, 1999; Chapter *1*. (c) Burns, P. C. *Mater. Res. Soc. Symp. Proc.* **2004**, *802*, 89. (d) Burns, P. C. *Can. Mineral.* **2005**, *43*, 1839.

from the carboxylate moieties. The two different UO_7 units share a single corner as found in $A[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)]\cdot H_2O$ (A = K, Rb, Cs). This differs from $Cs[(UO_2)(PO_3CH_2CO_2)]$, where the UO_7 pentagonal bipyramids are isolated. There are notable U−O bond distance differences between the U−O bonds to phosphonate and the U−O bonds to carboxylate. The average U−O bond to phosphonate is 2.316(4) Å, whereas the U−O bond to carboxylate is 2.484(4) Å. The bond−valence sums for U(1) and U(2) are 6.04 and 6.06, respectively, both of which are consistent with the formal oxidation state of +6.[11] There are two different cesium sites, one of which is ordered and the other is disordered over two sites. The cesium ions form 12 long interactions with the surrounding oxygen atoms from the framework as well as with the water molecules.

Thus far we have intentionally neglected to discuss the P−O and C−O bond distances in great detail for these compounds because they are generally unremarkable. There is substantial asymmetry in the C−O bond lengths that is induced by several factors. The first of these is whether or not the oxygen atom is involved in metal coordination. As expected the C−O bond lengthens upon metal binding. It lengthens even more when it bridges between two uranium centers. The second factor is protonation. When the oxygen atom is protonated, it generally does not bond with a uranium center, and the bond length is intermediate between the μ_2-O and μ_3-O C−O bond distances.

Comments on the Synthesis of Uranyl Carboxyphosphonates. One of the overriding goals of our research efforts is to utilize the known differences in the strengths of carboxylate actinide interactions versus phosphonate actinide interactions, where the latter are known to be much stronger[13] in the construction of novel actinide materials. In the Cu(II)/U(VI) phosphonoacetate compounds, there was a clear preference for the carboxylate to bind the Cu(II) and the phosphonate to bind the U(VI).[8] By replacing the transition metal with alkali metal cations, the carboxylate is found bound to the U(VI) as well in all cases. However, the carboxylate U(VI) bonds are considerably longer and presumably weaker than the phosphonate U(VI) bonds. By examining the Na^+ and Cs^+ structures, it is found that the cations only play space-filling and charge-balancing roles.[8] What appears to play a more significant role is protonation of carboxylate sites, which effectively eliminates their involvement in metal binding.

The use of CsOH to raise the pH of the reactions versus those where the Cs^+ source is CsCl yields very different compounds. When the pH is low, **CsUPAA** and **CsUPAA-3** form where partial protonation of the carboxyphosphonate persists. When the pH is raised, protonation is eliminated and $Cs[(UO_2)(PO_3CH_2CO_2)]$ is isolated. The difference in the starting pH values of these reactions is substantial. We propose that pH plays a far more important role than cation size in these hydrothermal crystallizations.

Fluorescence Spectroscopy. The emission of green light from uranyl compounds upon irradiation with long wavelength UV light has been known for centuries. The emission is, in fact, quite complex and has been examined in detail from solid samples by Denning and co-workers.[14] Uranyl fluorescence typically has a characteristic five peak spectrum ascribed to coupling between charge-transfer transitions and uranyl stretching and bending modes. All five compounds described in this report show spectra characteristic for compounds containing UO_2^{2+}. The emission spectrum of $Cs_3[(UO_2)_4(PO_3CH_2CO_2)_2(PO_3CH_2CO_2H_{0.5})_2]\cdot nH_2O$ is shown in Figure 6. As shown in Figure 6, the vibronic transitions are clearly resolved at room temperature. Enhancement of uranyl fluorescence has been achieved in organically templated uranyl compounds where energy transfer from the templates to the uranyl units is thought to take place.[15] These compounds do not contain such chromophores, but the fluorescence is nevertheless intense enough to be visible to the naked eye.

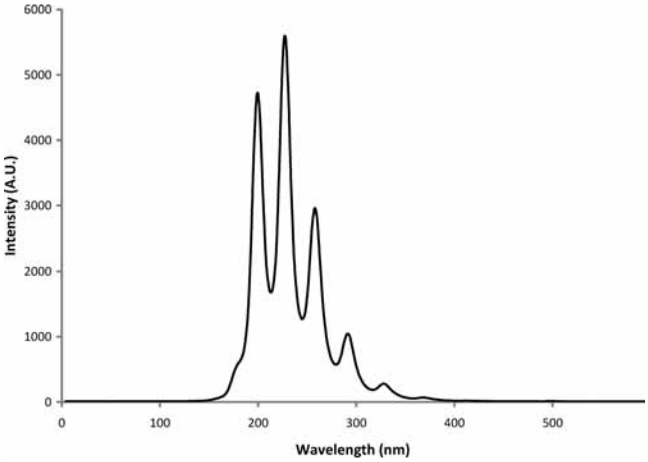

Figure 6. Fluorescence spectrum of $Cs_3[(UO_2)_4(PO_3CH_2CO_2)_2(PO_3CH_2CO_2H_{0.5})_2]\cdot nH_2O$ showing the emission of green light with well-defined charge-transfer vibronic transitions.

Conclusions

As previously discussed, the majority of naturally occurring and synthetic uranyl compounds are layered because of the terminal nature of the "yl" oxygen atoms of the uranyl units.[12] Three-dimensional uranyl-containing networks are rare, but the number of these has increased dramatically over the past 10 years primarily because additional building units have been added that circumvent the limitations of the bonding requirements of the uranyl cation. This is aptly illustrated by uranyl transition metal phosphates and uranyl gallium phosphates such as $Cs_2\{(UO_2)_4[Co(H_2O)_2]_2(HPO_4)(PO_4)_4\}$, $Cs_{3+x}[(UO_2)_3CuH_{4-x}(PO_4)_5]\cdot H_2O$, $Cs_2[UO_2(VO_2)_2(PO_4)_2]\cdot 0.59H_2O$, $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$, and $Cs[UO_2Ga(PO_4)_2]$, where the presence of an additional metal center gives rise three-dimensional networks.[16]

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(13) Nash, K. L. *J. Alloy and Cmpd.* **1997**, *249*, 33.

(14) Denning, R. G.; Norris, J. O. W.; Short, I. G.; Snellgrove, T. R.; Woodwark, D. R. *Lanthanide and Actinide Chemistry and Spectroscopy* , ACS Symp. Ser. No. 131; Edelstein, N. M. Ed; American Chemical Society: Washington, DC, 1980; Chapter *15*.

(15) (a) Almond, P. M.; Talley, C. E.; Bean, A. C.; Peper, S. M.; Albrecht-Schmitt, T. E. *J. Solid State Chem.* **2000**, *154*, 635. (b) Frisch, M.; Cahill, C. L. *Dalton Trans.* **2006**, *39*, 4679.

(16) (a) Shvareva, T. Y.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2006**, *45*, 1900. (b) Shvareva, T. Y.; Beitz, J. V.; Duin, E. C.; Albrecht-Schmitt, T. E. *Chem. Mater.* **2005**, *17*, 6219. (c) Shvareva, T. Y.; Sullens, T. A.; Shehee, T. C.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2005**, *44*, 300.

However, the isolation of uranyl compounds with three-dimensional networks has also been achieved by controlling pH. This was observed in organically templated uranyl fluorides, for example.[17] Here we provide a new family of uranyl compounds, where at first glance they appear to follow the general rules of uranyl structural chemistry with layered structures dominating. However, again we find that by controlling pH different bonding motifs can be isolated. As opposed to fluorides, the transformative feature in the compounds reported in this work is clear—protonation of the carboxylate groups. The uranyl carboxyphosphonate family is rapidly expanding in size but again primarily displays layered motifs. The exception to this is $[H_3O](UO_2)_2Cu_2(PO_3CH_2CO_2)_3(H_2O)_2$.[8] Again, the presence of the addition metal center is what renders the structure three-dimensional. $Cs_3[(UO_2)_4(PO_3CH_2CO_2)_2(PO_3CH_2CO_2H_{0.5})_2]\cdot nH_2O$ is the most unusual member of this family. It is three-dimensional by virtue of two features, canting of the uranyl units and protonation of some of carboxylate groups. The fact that this compound and $Cs[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)]\cdot H_2O$ are isolated together suggests that there may be very small energetic difference between the layered and three-dimensional structures.

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Supporting Information Available: X-ray crystallographic files in CIF format for $K[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)]\cdot H_2O$ (**KUPAA**), $Rb[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)]\cdot H_2O$ (**RbUPAA**), $Cs[(UO_2)_2(PO_3CH_2CO_2)(PO_3CH_2CO_2H)(H_2O)]\cdot H_2O$ (**CsUPAA**), $Cs[(UO_2)(PO_3CH_2CO_2)]$ (**CsUPAA-2**), and $Cs_3[(UO_2)_4(PO_3CH_2CO_2)_2(PO_3CH_2CO_2H_{0.5})_2]\cdot nH_2O$ (**CsUPAA-3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) (a) Halasyamani, P. S.; Walker, S. M.; O'Hare, D. *J. Am. Chem. Soc.* **1999**, *121*, 7415–7416. (b) Walker, S. M.; Halasyamani, P. S.; Allen, S.; O'Hare, D. *J. Am. Chem. Soc.* **1999**, *121*, 10513–10521.