Inorg. Chem. **2008**, 47, 9050−9054

Inorganic Chemistry
Article

$[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$: An Open-Framework Uranyl Zinc Phosphate Templated by Diprotonated 4,4′-Bipyridyl

Yaqin Yu, Wei Zhan, and Thomas E. Albrecht-Schmitt*

Department of Chemistry and Biochemistry and Center for Actinide Science, Auburn University, Auburn, Alabama 36849

Received June 17, 2008

Under mild hydrothermal conditions, a new organically templated uranyl zinc phosphate, $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$ (**UZnP-2**), has been synthesized. Structural analysis reveals that **UZnP-2** is constructed from UO_7 pentagonal bipyramids that are linked into edge-sharing dimers that are in turn joined together by ZnO_4 and PO_4 tetrahedra to form a three-dimensional network. Intersecting channels occur along the *a*, *b*, and *c* axes. These channels house the diprotonated 4,4′-bipyridyl cations and water molecules. Ion-exchange experiments demonstrate that replacement of the 4,4′-bipyridyl cations by alkali and alkaline-earth metal cations results in a rearrangement of the framework. Further characterization of **UZnP-2** is provided by Raman and fluorescence spectroscopy. The latter method reveals strong emission from the uranyl moieties with characteristic fine structure.

Introduction

Uranium phosphates have been the subject of intense interest for many decades for a variety of reasons, a partial list of which includes their importance in the transport of uranium in the environment,[1] the abundance and diversity of uranium phosphate minerals,[2] the unique structures that these compounds adopt,[2,3] their use as long-term storage waste forms for radioactive materials,[4] their use as ion-exchange materials,[5] and their use as proton conductors.[6] Of late, there has been interest in expanding structural diversity and physicochemical properties of uranyl phosphates through the incorporation of main group elements and transition metals. Examples of these materials include Ga^{3+} in $Cs[UO_2Ga(PO_4)_2]$ and $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$,[5a] Cu^{2+} in $Cs_{3+x}[(UO_2)_3CuH_{4-x}(PO_4)_5]\cdot H_2O$,[7] V^{4+} in $A_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$ (A = K, Rb),[5b] V^{5+} in $Cs_2[(UO_2)(VO_2)_2(PO_4)_2]\cdot 0.59H_2O$,[8] and Co^{2+} in $Cs_2\{(UO_2)_4[Co(H_2O)_2]_2(HPO_4)(PO_4)_4\}$.[7] These uranyl/M/phosphates have displayed a variety of properties including second-harmonic generation,[8] magnetic ordering,[5b] and ion exchange with promising selectivity.[5a,b] Selectivity for Cs^+ has been demonstrated in

---

* Author to whom correspondence should be addressed. E-mail: albreth@auburn.edu.

(1) (a) Sowder, A. G.; Clark, S. B.; Fjeld, R. A. *J. Radioanal. Nucl. Chem.* **2001**, *248*, 517. (b) Murakami, T.; Ohnuki, T.; Isobe, H.; Tsutomu, T. *Am. Mineral.* **1997**, *82*, 888.

(2) For recent additions to this series, see: (a) Locock, A. J.; Burns, P. C. *Can. Mineral.* **2003**, *41*, 489. (b) Locock, A. J.; Burns, P. C. *Can. Mineral.* **2003**, *41*, 91. (c) Locock, A. J.; Burns, P. C. *Am. Mineral.* **2003**, *88*, 240. (d) Locock, A. J.; Burns, P. C. *J. Solid State Chem.* **2002**, *163*, 275. (e) Burns, P. C. *Am. Mineral.* **2000**, *85*, 801.

(3) (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.

(4) (a) Wallez, G.; Clavier, N.; Dacheux, N.; Quarton, M.; van Beek, W. *J. Solid State Chem.* **2006**, *179*, 3007. (b) Chukova, O. V.; Boyko, R. S.; Gaididei, G. I.; Nagornyi, P. G.; Nedilko, S. G.; Nedyelko, I. M.; Radzivanov, V. I.; Sakun, V. P.; Boyko, V. V. *Funct. Mater.* **2004**, *11*, 147. (c) Terra, O.; Clavier, N.; Dacheux, N.; Podor, R. *New J. Chem.* **2003**, *27*, 957. (d) Brandel, V.; Dacheux, N.; Genet, M. *Radiochemistry (Moscow, Russ. Fed.)* **2001**, *43*, 16.

(5) (a) Shvareva, T. Y.; Sullens, T. A.; Shehee, T. C.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2005**, *44*, 300. (b) Shvareva, T. Y.; Skanthakumar, S.; Soderholm, L.; Clearfield, A.; Albrecht-Schmitt, T. E. *Chem. Mater.* **2007**, *19*, 132. (c) Ok, K. M.; Doran, M. B.; O'Hare, D. *Dalton Trans.* **2007**, *30*, 3325. (d) Howe, A. T. *Inorg. Ion Exch. Mater.* **1982**, 133. (e) Pozas-Tormo, R.; Moreno-Real, L.; Martinez-Lara, M.; Rodriguez-Castellon, E. *Can. J. Chem.* **1986**, *64*, 35. (f) Paterson-Beedle, M.; Macaskie, L. E.; Lee, C. H.; Hriljac, J. A.; Jee, K. Y.; Kim, W. H. *Hydrometallurgy* **2006**, *83*, 141.

(6) (a) Childs, P. E.; Halstead, T. K.; Howe, A. T.; Shilton, M. G. *Mater. Res. Bull.* **1978**, *13*, 609. (b) Gordon, R. E.; Strange, J. H.; Halstead, T. K. *Solid State Commun.* **1979**, *31*, 995. (c) Howe, A. T.; Shilton, M. G. *J. Solid State Chem.* **1980**, *34*, 149. (d) Childs, P. E.; Howe, A. T.; Shilton, M. G. *J. Solid State Chem.* **1980**, *34*, 341. (e) Lundsgaard, J. S.; Malling, J.; Birchall, M. L. S. *Solid State Ion.* **1982**, *7*, 53. (f) Colomban, P.; Pham Thi, M. *Rev. Chim. Mineral.* **1985**, *22*, 143.

(7) Shvareva, T. Y.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2006**, *45*, 1900.

(8) Shvareva, T. Y.; Beitz, J. V.; Duin, E. C.; Albrecht-Schmitt, T. E. *Chem. Mater.* **2005**, *17*, 6219.

10.1021/ic801125w CCC: $40.75

$A_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$ (A = K, Rb), making this material potentially useful for the sequestration of ^{137}Cs from nuclear waste.[5b]

At the heart of uranyl phosphate chemistry is the phenomenal richness of the observed crystal chemistry that can be attributed in part to the structural versatility of U(VI), which generally occurs as tetragonal, pentagonal, and hexagonal bipyramids.[2,3] Less obvious influencers of structure include the cations that are used to maintain charge balance with the anionic lattices that are adopted by uranyl compounds. Organoammonium cations have played an important role in directing the structures of novel anionic uranyl phosphate topologies. A number of open-framework uranyl phosphates have been prepared using cyclic amines (e.g., piperazine and 1,4-diazabicyclo[2.2.2]octane) as structure-directing agents in hydrothermal syntheses.[9] The goal of the present work is to utilize both transition metal polyhedra as structural building units and an organic amine as a template to form an open-framework uranyl/transition metal/phosphate that can be tested in a variety of applications including ion exchange and luminescence. This strategy has proven to be successful, and herein we report the synthesis, structure, ion exchange, and Raman and fluorescence spectroscopy of $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$ (**UZnP-2**).

Experimental Section

Synthesis. $UO_2(C_2H_3O_2)_2\cdot 2H_2O$ (98%, Baker), 4,4′-bipyridyl (98%, Alfa-Aesar), $Zn(CN)_2$ (98%, Alfa-Aesar), and H_3PO_4 (98%, Aldrich) were used as received. Reactions were run in polytetrafluoroethylene-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 the reactions. Standard precautions were performed for handling radioactive materials during work with $UO_2(C_2H_3O_2)_2\cdot 2H_2O$ and the products of the reactions. Semiquantitative energy dispersive X-ray analysis was performed using a JEOL 7000F. **Warning!** *This reaction might generate HCN.*

$[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$ (UZnP-2). $UO_2(C_2H_3O_2)_2\cdot 2H_2O$ (0.2269 g, 0.535 mmol), 4,4′-bipyridyl (0.0417 g, 0.267 mmol), $Zn(CN)_2$ (0.0314 g, 0.267 mmol), and H_3PO_4 (2 mL, pH = 1.3) were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 180 °C in a box furnace for three days. The autoclave was then cooled at an average rate of 9 °C/h to 35 °C. Yellow tablets were recovered and thoroughly washed with water, then rinsed with methanol and allowed to dry. Powder X-ray diffraction data were collected and compared to a simulated diffraction pattern indicating a relatively homogeneous phase with a minor impurity. Yield: 133.8 mg (53.7% based on uranium).

Crystallographic Studies. A single crystal of **UZnP-2** was mounted on a thin glass fiber 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 ($\lambda = 0.71073$ 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 three 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 s.

Table 1. Crystallographic Data for $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$ (**UZnP-2**)

compound	**UZnP-1**
formula mass	2848
color and habit	yellow, tablet
space group	$P\bar{1}$ (No. 2)
a (Å)	10.980(2)
b (Å)	13.029(3)
c (Å)	13.599(3)
α (deg)	62.312(3)
β (deg)	70.921(3)
γ (deg)	72.954(3)
V (Å^3)	1604.7(5)
Z	1
T (K)	193
λ (Å)	0.71073
maximum 2θ (deg.)	28.30
ρ_{calcd} (g cm^{-3})	2.938
μ(Mo $K\alpha$) (cm^{-1})	161.14
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.0581
$R_w(F_o^2)$ ^{b}	0.1738

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

For **UZnP-2**, the determination of integrated intensities and global refinement were performed with the Bruker SAINT (v. 6.02) software package using a narrow-frame integration algorithm. The data were treated with a semiempirical absorption correction by SADABS.[10] The program suite SHELXTL (v. 6.12) was used for space group determination (XPREP), direct methods structure solution (XS), and least-squares refinement (XL).[11] The final refinement included anisotropic displacement parameters for all atoms. Some crystallographic details are given in Table 1, and selected bond distances and angles are given in Table 2. Additional details can be found in the Supporting Information.

Fluorescence Spectroscopy. The fluorescence emission spectrum of **UZnP-2** was acquired using a PI Acton spectrometer (SpectraPro SP 2356, Acton, NJ) that is connected to the side port of an epifluorescence microscope (Nikon TE-2000U, Japan). The emission signal was recorded by a back-illuminated digital CCD camera (PI Acton PIXIS:400B, Acton, NJ) operated by a PC. The excitation was generated by a mercury lamp (X-Cite 120, EXFO, Ontario, Canada) filtered by a band-pass filter at 450−490 nm. The emission signal was filtered by a long-pass filter with a cutoff wavelength of 515 nm.

Raman Spectroscopy. The Raman spectrum of **UZnP-2** was acquired from a single crystal using a Renishaw inVia Confocal Raman microscope with a 514 nm Ar^+ laser.

Ion Exchange. A total of 15 mg of finely ground **UZnP-2** was placed in small vials along with 5 mL of a 5 M solution of NaCl, KCl, $CaCl_2$, $SrCl_2$, or $BaCl_2$. The solutions were mixed with a mechanical shaker for seven days. The mixtures were filtered and the solids were dried for subsequent powder X-ray diffraction measurements.

---

(9) (a) Locock, A. J.; Burns, P. C. *J. Solid State Chem.* **2004**, *177*, 2675. (b) Doran, M. B.; Stuart, C. L.; Norquist, A. J.; O'Hare, D. *Chem. Mater.* **2004**, *16*, 565. (c) Danis, A. J.; Runde, W. H.; Scott, B.; Fettinger, J.; Eichhorn, B. *Chem. Comm.* **2001**, *22*, 2378. (d) Burns, P. C.; Alexopoulos, C. M.; Hotchkiss, P. J.; Locock, A. J. *Inorg. Chem.* **2004**, *43*, 1816. (e) Locock, A. J.; Burns, P. C. *J. Solid State Chem.* **2002**, *167*, 226.

(10) (a) Sheldrick, G. M. *Acta Crystallogr.* **1995**, *A51*, 33. (b) Program for absorption correction using SMART CCD based on the method of Blessing: Blessing, R. H. *SADABS*; Bruker AXS: Madison, WI, 2001.

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$ (**UZnP-2**)[a]

Distances (Å)			
U(1)−O(18)	1.750(8)	P(1)−O(1)	1.583(10)
U(1)−O(17)	1.757(7)	P(1)−O(2)	1.503(8)
U(1)−O(7)	2.297(8)	P(1)−O(3)	1.528(8)
U(1)−O(12)#3	2.304(7)	P(1)−O(4)	1.538(8)
U(1)−O(3)#4	2.396(8)	P(2)−O(5)	1.556(7)
U(1)−O(4)	2.453(7)	P(2)−O(6)	1.537(7)
U(1)−O(3)	2.541(8)	P(2)−O(7)	1.507(8)
U(2)−O(20)	1.772(8)	P(2)−O(8)	1.502(8)
U(2)−O(19)	1.788(8)	P(3)−O(9)	1.568(7)
U(2)−O(16)#5	2.292(7)	P(3)−O(10)	1.534(7)
U(2)−O(11)#5	2.319(7)	P(3)−O(11)	1.528(8)
U(2)−O(5)#6	2.384(7)	P(3)−O(12)	1.503(8)
U(2)−O(6)	2.409(7)	P(4)−O(13)	1.548(8)
U(2)−O(5)	2.508(8)	P(4) −O(14)	1.540(7)
U(3)−O(21)	1.770(8)	P(4)−O(15)	1.526(8)
U(3)−O(22)	1.786(8)	P(4)−O(16)	1.527(8)
U(3)−O(14)#1	2.282(7)	Zn(1)−O(15)#1	1.908(7)
U(3)−O(8)	2.291(7)	Zn(1)−O(13)	1.944(8)
U(3)−O(10)#3	2.400(7)	Zn(1)−O(2)#2	1.947(8)
U(3)−O(9)	2.466(7)	Zn(1)−O(9)	1.974(7)
U(3)−O(10)	2.561(7)		

Angles (deg)			
O(15)#1−Zn(1)−O(13)	114.7(3)	O(15)#1−Zn(1)−O(2)#2	112.9(3)
O(13)−Zn(1)−O(2)#2	104.2(3)	O(15)#1−Zn(1)−O(9)	104.8(3)
O(13)−Zn(1)−O(9)	112.5(3)	O(2)#2−Zn(1)−O(9)	107.8(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y, -z + 1$; #2 $-x + 1, -y + 1, -z$.

Results and Discussion

Synthesis. Uranyl transition metal phosphates can be prepared from a variety of sources. Two divergent routes uncovered by us rely on the use of transition metals either in elemental form or as cyanide salts; $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$ (**UZnP-2**) was synthesized by the latter method.[12] What differentiates **UZnP-2** from other three-dimensional framework uranyl transition metal phosphates prepared thus far is the presence of organic ammonium cations in the reaction mixture. In this case, 4,4′-bipyridyl, which becomes diprotonated by the phosphoric acid, was employed to direct the formation of the anionic lattice. While the yield was low for **UZnP-2**, the product is surprisingly pure according to powder X-ray diffraction measurements.

Structure of $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$ (UZnP-2). UZnP-2 possesses an open-framework structure consisting of UO_7 pentagonal bipyramids that are linked into edge-sharing dimers that are joined together by ZnO_4 and PO_4 tetrahedra. Intersecting channels occur along the *a*, *b*, and *c* axes. These channels house the diprotonated 4,4′-bipyridyl cations and water molecules and are approximately 5.6 × 8.7 Å. Various views of this structure are shown in Figure 1. The basic building units are shown in Figure 2. The view down the *a* axis shows something peculiar about the channels that extend in this direction in that they appear to be void spaces. We suspect that disordered water resides in these channels, but these are not resolved in the structure. The Checkcif program notes that there are very large void spaces in the structure, which was investigated further using PLATON.[13] This calculation reveals 20% void space in the structure.

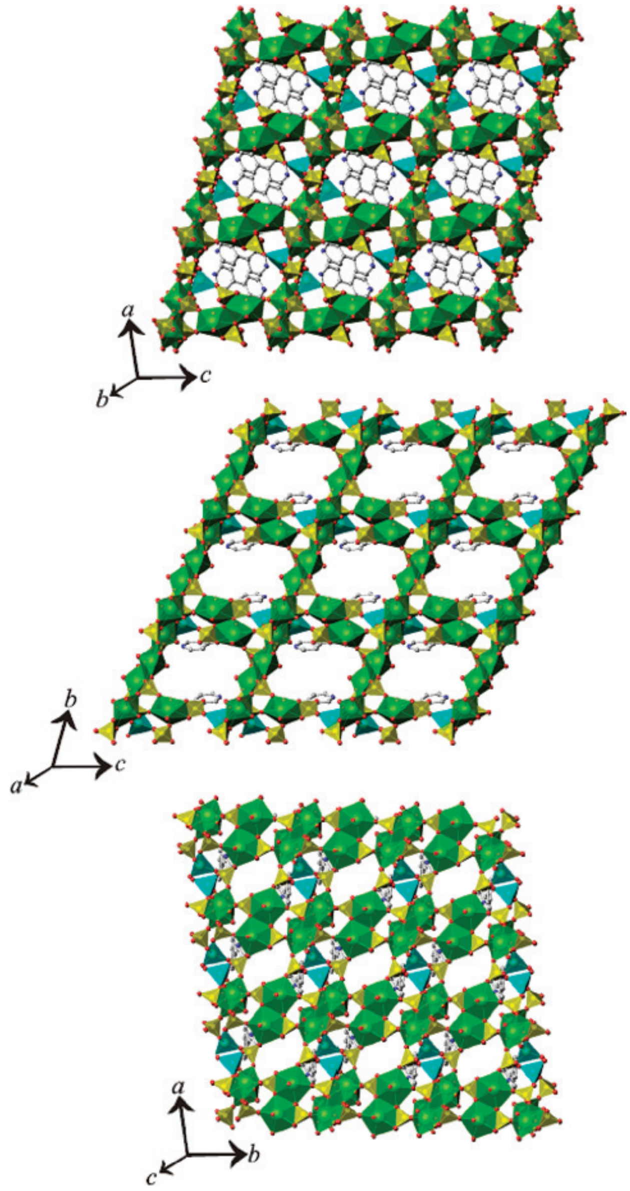

Figure 1. Three views of the open-framework structure of $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$ (**UZnP-2**). UO_7 = green, ZnO_4 = light blue, PO_4 = yellow.

There are three crystallographically unique uranium centers in the structure of **UZnP-2**. Each of these units contains a nearly linear uranyl, UO_2^{2+}, core. The U≡O distances within the uranyl cations average 1.771(8) Å, whereas those in the equatorial plane are considerably longer and average 2.394(8) Å. These bond distances are typical for uranyl polyhedra[14] and can be used to calculate bond-valence sums of 6.08, 5.97, and 5.91 for U(1), U(2), and U(3), respectively, which is consistent with the expected oxidation state of U(VI) in UO_2^{2+}.[14,15] The single zinc center is found as a ZnO_4 distorted tetrahedron with Zn−O bond distances ranging from 1.908(7) to 1.974(7) Å, yielding a reasonable value

---

(12) Yu, Y.; Zhan, W.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2007**, *46*, 10214.

(13) (a) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34. (b) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

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

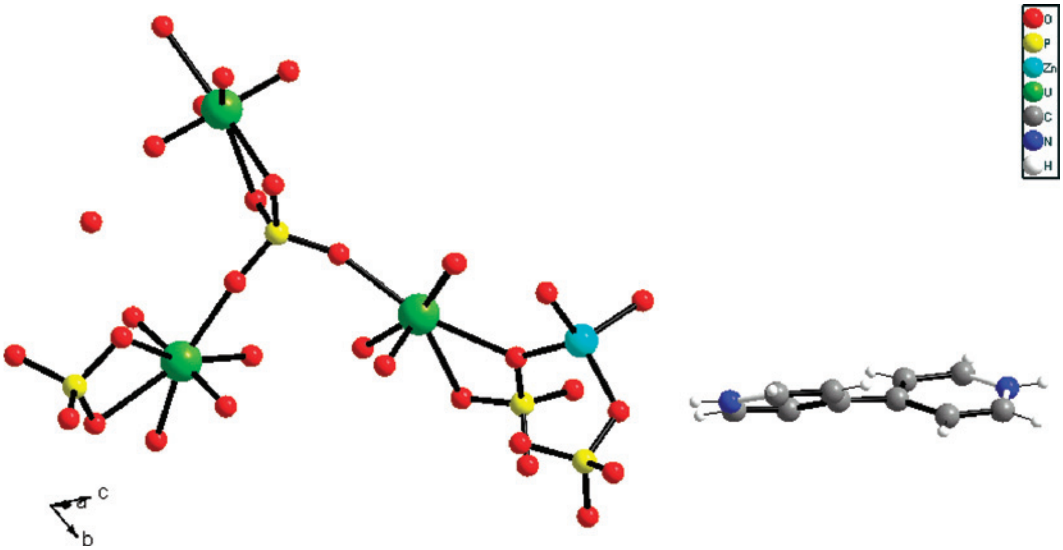

Figure 2. A depiction of the basic building units in $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$ (**UZnP-2**).

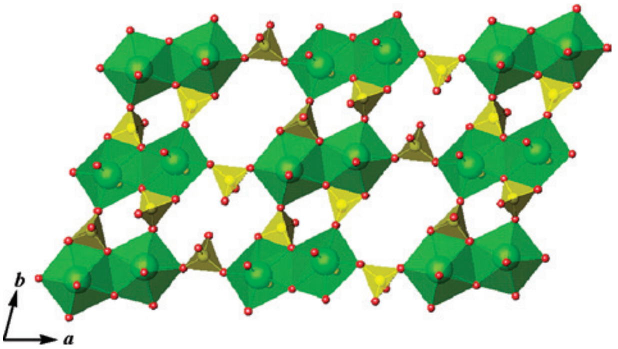

Figure 3. A view of the [*ab*] plane showing the two-dimensional substructure constructed by uranyl phosphate dimers in $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$ (**UZnP-2**).

for Zn(II) of 2.10.[15] The P−O bond distances average 1.533(10) Å. However, this average encompasses both short and long P−O bonds. For example, the P(1)−O(2) bond is 1.503(8) Å, and the oxygen atom is terminal. This linked and can be described as P=O. This contrasts sharply with the long P(1)−O(1) of 1.583(10) Å, which is also terminal, and most likely represents a P−OH bond.

The structure of **UZnP-2** shares some common structural building features with previous members of the UO_2^{2+}/M/PO_4series. The most obvious similarity is found in the edge-sharing dimers of UO_7 pentagonal bipyramids that are linked by phosphate anions. This unit is also found in $Cs[UO_2Ga(PO_4)_2]$ and $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$.[5a] **UZnP-2** differs from these aforementioned compounds in two respects. First, the dimers form sheets (shown in Figure 3) instead of chains that are linked by a second set of dimers that are composed of the third crystallographically unique uranium center. What makes **UZnP-2** especially different from $Cs[UO_2Ga(PO_4)_2]$ and $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ is the absence of metal-containing one-dimensional chains. Rather, here, there are small clusters containing two Zn centers and seven phosphate anions. Finally, there is an expansion of the intersecting channels needed to accommodate the larger $[H_2bipy]^{2+}$ cations versus those where alkali metals are employed.[5,7,8] We will demonstrate shortly that these larger channels do not equate with improved properties, a common myth perpetuated in the literature on open-framework compounds.

Fluorescence Spectroscopy. It has been known for centuries that green emission can be observed from some uranyl compounds when excited by long-wavelength UV light. Fluorescence from uranyl compounds can be identified from the vibronic fine-structure characteristic of the UO_2^{2+} moiety.[16] Emission from uranyl-containing networks is complex and easily influenced by subtle changes in bonding, as indicated by Grohol and Clearfield's report on 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 changes in the phosphonate anions.[17] The organic ligand can exhibit the antenna effect, yielding enhanced emission by the uranyl cations.[18] The fluorescence spectra of $[Ag(4,4'\text{-bipy})]_2[(UO_2)_2H_3(PO_4)_3]$, $Ag(2,2'\text{-bipy})(UO_2)(HPO_4)(PO_4)$, and $[Zn(2,2'\text{-bipy})]_2[UO_2(HPO_4)_3]$ compounds exhibited substantial differences in their emission properties.[12] As shown in Figure 4, **UZnP-2** shows fine structure in its emission with peaks at 535, 555, and 582 nm assigned to vibronic coupling typical for the UO_2^{2+} moiety.

Raman Spectroscopy. The key feature in the Raman spectrum of **UZnP-2** is the band at 833 cm^{-1}, which is attributed to the υ_1 symmetric stretching mode for the UO_2^{2+} units. The UO_2^{2+} bending mode is found at a much lower

---

(15) (a) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192. (b) Brown, I. D. *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*; Oxford University Press: New York, 2002. (c) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

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

(17) Grohol, D.; Clearfield, A. *J. Am. Chem. Soc.* **1997**, *119*, 4662.

(18) (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. (c) Cahill, C. L.; de Lill, D. T.; Frisch, M. *CrystEngComm* **2007**, *9*, 15.

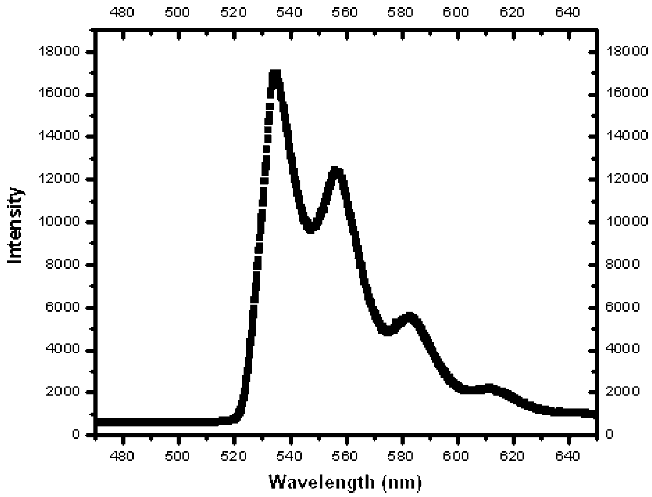

Figure 4. The fluorescence spectrum of $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$ (**UZnP-2**) showing fine structure in its emission with peaks at 535, 555, and 582 nm assigned to vibronic coupling for the UO_2^{2+} moiety.

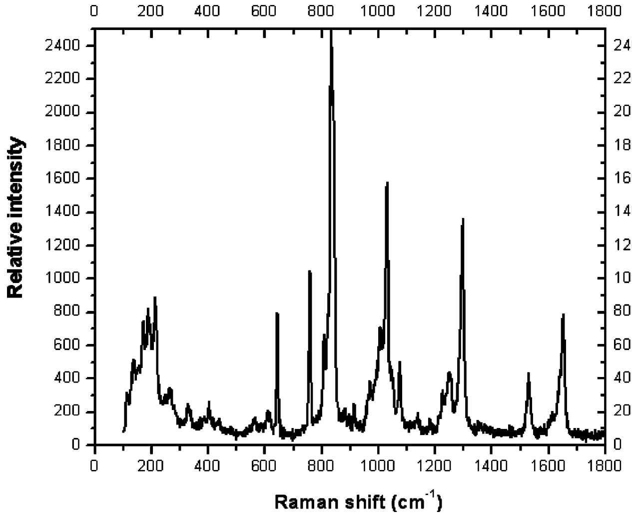

Figure 5. The Raman spectrum of $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$ (**UZnP-2**).

frequency, in this case, at 213 cm^{-1}. The presence of P—O stretching modes from the phosphate anions is also readily observed by Raman spectroscopy with a feature at 1030 cm^{-1}, which is assigned to an antisymmetric stretching mode. A weak band at 402 cm^{-1} is attributed to PO_4^{3-} bending vibrations. The Raman spectrum of **UZnP-2** is shown in Figure 5.

Ion-Exchange Studies. The ion-exchange properties of **UZnP-2** were evaluated to determine whether the $[H_2bipy]^{2+}$ cations can be exchanged for Na^+, K^+, Ca^{2+}, Sr^{2+}, and Ba^{2+} cations. X-ray powder diffraction patterns after ion exchange has taken place show that replacement of the 4,4′-bipyridyl cations by alkali and alkaline-earth metal cations results in a rearrangement of the framework, as shown in Figure 6. This is especially pronounced with K^+. This type of structural rearrangement has been previously noted in uranyl phosphates.[5c] These results sharply contrast with ion-exchange studies on $Cs[UO_2Ga(PO_4)_2]$,[5a] $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$,[5a] and $A_{3.48}[(UO_2)(VO)_4H_{1.52}(PO_4)_5]$ (A = K, Rb),[5b] where the basic framework remains intact after ion exchange. It may well be that uranyl phosphate frameworks with large pores are not stable when the organic cations are exchanged.

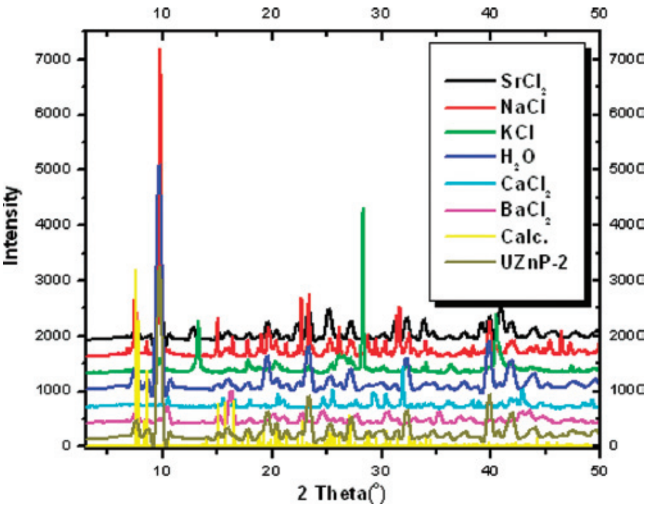

Figure 6. X-ray powder diffraction patterns after ion exchange has taken place. These patterns show that replacement of the 4,4′-bipyridyl cations by alkali and alkaline-earth metal cations results in the rearrangement of the framework in $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$ (**UZnP-2**).

Conclusions

A new member of the $UO_2^{2+}/M/PO_4$ series, $[H_2bipy]_2[(UO_2)_6Zn_2(PO_3OH)_4(PO_4)_4]\cdot H_2O$ (**UZnP-2**), has been synthesized, and structure−property correlations have been developed. This is the first uranyl transition metal phosphate where an organic amine, in this case, protonated 4,4′-bipyridyl, has been used to direct the formation of the anionic lattice. Previous applications of the bipyridyl unit in similar systems have resulted in coordination of the transition metal by the bipyridyl ligands as has been found in $[Ag(4,4'\text{-bipy})]_2[(UO_2)_2H_3(PO_4)_3]$, $Ag(2,2'\text{-bipy})(UO_2)(HPO_4)(PO_4)$, and $[Zn(2,2'\text{-bipy})]_2[UO_2(HPO_4)_3]$.[12] The use of an organic structure-directing agent creates larger pores than have been observed in previous members of this family of compounds, where the largest cation employed before was Cs^+. The larger channels found in **UZnP-2** do not result in improved ion-exchange properties but, rather, reduce the stability of the framework with respect to ion-exchange reactions.

Acknowledgment. This work was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, Heavy Elements Program, U.S. Department of Energy under Grant DE-FG02-01ER15187.

Supporting Information Available: X-ray crystallographic files in CIF format for **UZnP-2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC801125W