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General Route to Three-Dimensional Framework Uranyl Transition Metal Phosphates with Atypical Structural Motifs: The Case Examples of $Cs_2\{(UO_2)_4[Co(H_2O)_2]_2(HPO_4)(PO_4)_4\}$ and $Cs_{3+x}[(UO_2)_3CuH_{4-x}(PO_4)_5]\cdot H_2O$

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The reaction of $UO_2(NO_3)_2\cdot 6H_2O$ with Co or Cu metal, phosphoric acid, and CsCl under mild hydrothermal conditions results in the formation of $Cs_2\{(UO_2)_4[Co(H_2O)_2]_2(HPO_4)(PO_4)_4\}$ (**1**) or $Cs_{3+x}[(UO_2)_3CuH_{4-x}(PO_4)_5]\cdot H_2O$ (**2**). The structure of **1** contains uranium atoms in pentagonal bipyramidal and hexagonal bipyramidal environments. The interaction of the uranyl cations and phosphate anions creates layers in the [*ab*] plane. The uranyl phosphate layers are joined together by octahedral Co centers wherein the Co is bound by phosphate and two cis water molecules. In addition, the Co ions are also ligated by a uranyl oxo atom. The presence of these octahedral building units stitches the structure together into a three-dimensional framework where void spaces are filled by Cs^+ cations. The structure of **2** contains uranium centers in UO_6 tetragonal bipyramidal and UO_7 pentagonal bipyramidal geometries. The uranyl moieties are bridged by phosphate anions into sinusoidal sheets that extend into the [*bc*] plane and are linked into a three-dimensional structure by Cu^{II}. The Cu centers reside in square planar environments. Charge balance is maintained by Cs^+ cations. Both the overall structures and the uranyl phosphate layers in **1** and **2** are novel.

The structural chemistry of U^{VI} is dominated by the formation of layered compounds containing uranyl, UO_2^{2+}, cations wherein the uranyl units are aligned in a roughly parallel fashion.[1] These layered compounds have been shown to display several important and potentially useful properties including fast proton conductivity and ion exchange that is particularly well-known for uranyl phosphates.[2] More recently, attention has been focused on preparing uranyl phases that adopt three-dimensional networks that may find applications in the storage of key radionuclides from spent nuclear fuel and as new selective ion-exchange materials.[3] One of the most appealing features of constructing new solids from uranyl-containing polyhedra is that the uranium centers in these compounds can adopt coordination environments seldom seen in transition metal chemistry such as UO_7 pentagonal bipyramids and UO_8 hexagonal bipyramids.[1]

Our group recently reported the syntheses, structures, and ion-exchange properties of the first uranyl gallium phosphates with open-framework structures.[3] Since that time, we have devoted our research to preparing additional mixed-metal uranyl phosphates where the gallium centers have been replaced by transition metals, which may, in turn, lead to new architectures and properties not found with gallium. This is aptly illustrated by $Cs_2[UO_2(VO_2)_2(PO_4)_2]\cdot 0.59H_2O$, which adopts a three-dimensional polar structure containing distorted VO_5 square pyramids.[4] Herein we communicate a relatively general and quite facile route to preparing first-row transition metal uranyl phosphates with three-dimensional structures with varying degrees of openness. We illustrate this with the examples of the Co^{II} and Cu^{II} compounds, $Cs_2\{(UO_2)_4[Co(H_2O)_2]_2(HPO_4)(PO_4)_4\}$ (**1**) and $Cs_{3+x}[(UO_2)_3CuH_{4-x}(PO_4)_5]\cdot H_2O$ (**2**), both of which display new methods of constructing three-dimensional uranyl phosphate frameworks.[5]

The reaction of $UO_2(NO_3)_2\cdot 6H_2O$ with Co or Cu metal, phosphoric acid, and CsCl under mild hydrothermal condi-

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tions results in the formation of **1** and **2** as single crystals.[6] Crystals of **2** were very large, exceeding several millimeters in length. The direct use of transition metals as reactants has been previously applied to the hydrothermal synthesis of mixed-valent vanadium(III)/vanadium(IV),[7] titanium(III)/titanium(IV),[8] and cobalt(II)[9] phosphates. We demonstrate herein that this methodology is more general and that mixed-metal uranyl transition metal phosphates can also be prepared.

The structure of **1**[10] contains three crystallographically unique uranium atoms, two of which are in pentagonal bipyramidal environments and one of which is in a hexagonal bipyramidal geometry. In each case, there is a central uranyl core designated by two short U═O distances. The uranyl bond distances are within expected limits and range from 1.767(5) to 1.794(5) Å. The uranyl units form longer interactions with the oxygen atoms from the phosphate anions. These distances range from 2.263(5) to 2.507(6) Å. The interaction of the uranyl cations and phosphate anions creates layers in the [*ab*] plane that are depicted in Figure 1 (note that there is a disordered phosphate within the layers). This layer is a new topology for a uranium oxide.[1] Other than the disordered phosphate anion, the phosphate units are approximately tetrahedral with normal P−O bond distances. The uranyl phosphate layers are joined together by octahedral Co centers wherein the Co is bound by phosphate and two cis water molecules. In addition, the Co ions are also ligated by a uranyl oxo atom from the U(3) uranyl unit. This Co−O bond distance is 2.105(5) Å, and it fits well within the other Co−O bond distances, which range from 2.031(5) to 2.159(6) Å. This kind of interaction is rare[11] but is known from compounds such as $[Cu(H_2O)_4](UO_2HGeO_4)_2 \cdot 2H_2O$.[11f] The Co centers form dimers via two μ_3-oxo atoms from two phosphate anions. The presence of these octahedral building units stitches the structure together into a three-dimensional framework where void spaces are filled by Cs^+ cations. There are channels in this structure that extend down the *b* axis, as is shown in Figure 2. The method of construction of this mixed-metal phosphate differs from that of $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4] \cdot H_2O$,[3] $Cs[UO_2Ga(PO_4)_2]$,[3] and $Cs_2[(UO_2(VO_2)_2(PO_4)_2] \cdot 0.59H_2O$,[4] all of which contain interconnected one-dimensional substructures.

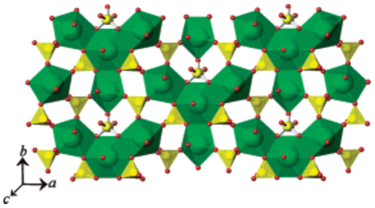

Figure 1. View down the *c* axis of the uranyl phosphate layers in **1**. One of the phosphate anions is disordered and is shown in ball-and-stick format. Uranium polyhedra are in green and phosphate in yellow.

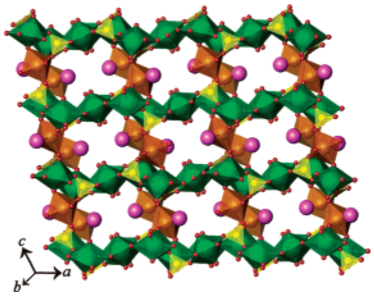

Figure 2. Illustration of the three-dimensional structure of **1** as viewed down the *b* axis. Uranium polyhedra are in green, phosphate in yellow, and cobalt in orange.

Bond-valence sum calculations provide values of 6.08, 6.24, and 6.07 for U(1), U(2), and U(3), respectively, confirming the expected oxidation state of 6+.[12] More importantly, the sum for the Co center is 1.98, consistent with that of Co^{II}.[13,14] Spectroscopic verification of the oxidation state for Co was provided by UV−vis−NIR diffuse reflectance spectroscopy. The spectrum yields three main bands at 525, 770, and 1030 nm corresponding to the $^4T_{2g}$---$^4T_{1g}$, $^4A_{2g}$---$^4T_{1g}$, and $^4T_{1g}(P)$---$^4T_{1g}$ transitions, respectively, that are expected for octahedral Co^{II}.[15] In addition to these bands is an absorption feature centered near 440 nm with considerable fine structure. These features are assigned to absorption by the uranyl cation.[16] Totalling the charges of the metal centers and phosphate anions reveals that there must be one

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(6) **1** was prepared by loading $UO_2(NO_3)_2 \cdot 6H_2O$ (0.285 g, 0.57 mmol), Co powder (0.067 g, 1.14 mmol), H_3PO_4 (0.167 g, 1.72 mmol), CsCl (0.479 g, 2.85 mmol), and 1.5 mL of Millipore-filtered water into a 23-mL autoclave. The reaction was run at 195 °C in a box furnace for 5 days and then cooled at a rate of 9 °C/h to room temperature. The product mixture contained bright-orange crystals of **1** and water-soluble blue crystals of cesium tetrachlorocobalt(II). The desired product was isolated by washing the mixture with water and methanol. Yield: 78 mg (27% based on U). **2** was prepared by loading $UO_2(NO_3)_2 \cdot 6H_2O$ (0.285 g, 0.57 mmol), Cu powder (0.072 g, 1.14 mmol), H_3PO_4 (0.167 g, 1.72 mmol), CsCl (0.477 g, 2.85 mmol), and 1.5 mL of Millipore-filtered water into a 23-mL autoclave. The reaction was run at 195 °C in a box furnace for 5 days and then cooled at a rate of 9 °C/h to room temperature. Large clusters of green crystals of **2** were isolated, washed with methanol, and allowed to dry. Yield: 169 mg (49% based on U).

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(10) Crystallographic Data. **1**: monoclinic, *C*2/*c*, $Z = 4$, $a = 18.0551(8)$ Å, $b = 10.7478(5)$ Å, $c = 15.3504(7)$ Å, $\beta = 99.242(1)°$, $V = 2940.1(2)$ Å^3 ($T = 193$ K), $\mu = 258.86$ cm^{-1}, R1 = 0.0281, wR2 = 0.0677. **2**: orthorhombic, *Pbcm*, $Z = 4$, $a = 7.5867(4)$ Å, $b = 19.957(1)$ Å, $c = 17.9726(9)$ Å, $V = 2721.2(2)$ Å^3 ($T = 193$ K), $\mu = 231.04$ cm^{-1}, R1 = 0.0354, wR2 = 0.0835. Bruker APEX CCD diffractometer: Mo Kα, $\lambda = 0.71073$ Å, 0.3° ω scans. The data were corrected for Lorentz and polarization effects and for absorption (numerical for **1** and SADABS for **2**); the structure was solved by direct methods, followed by a refinement of F^2 by full-matrix least squares.[17]

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proton within the structure. This proton most likely resides on the terminal oxygen atom of the phosphate anion containing P(1). Unfortunately, the disorder of this anion does not allow for conclusive bond distance comparisons.

Similar to the structure of **1**, **2**[10] contains two-dimensional uranyl phosphate layers that are linked into a three-dimensional structure by a transition metal center. Beyond this general similarity, the structures of **1** and **2** are dramatically different for a number of reasons. One of these is that there are two crystallographically unique uranium centers in **2** that are found as UO_6 tetragonal bipyramids and UO_7 pentagonal bipyramids. The uranyl U═O bond distances for these two polyhedra range from 1.770(6) to 1.803(8) Å. The equatorial U−O distances range from 2.236(5) to 2.514(5) Å. Taking into account the differences in coordination number, these distances were used to calculate bond-valence sums of 5.96 and 6.08 for U(1) and U(2), respectively.[12] The uranyl moieties are bridged by phosphate anions into sinusoidal sheets that extend into the [*bc*] plane. These sheets are shown in Figure 3. Again, this is apparently a new layered topology for a uranium oxide compound.[1]

The uranyl phosphate layers in **2** are interconnected by Cu centers that reside in square planar environments, being bound by four phosphate anions with two Cu−O distances of 1.962(6) and 1.964(6) Å. The bond-valence sum for the Cu site is 1.85 and is consistent with that of Cu^{II}.[13,14] The UV−vis−NIR diffuse-reflectance spectrum of **2** shows a fine-structured absorption feature centered near 440 nm that can be assigned to the uranyl cation as in **1**.[16] In addition, there is a broad band with a maximum at 550 nm corresponding to the d−d z^2 to $x^2 - y^2$ transition expected for square planar Cu^{II}.[15] The overall structure is three-dimensional, as can be seen in Figure 4. However, the structure is much less open than that of **1** or other mixed-metal uranyl transition metal phosphates prepared thus far.

Channels for the Cs^+ cations and water molecules that are observed in other mixed-metal uranyl phosphate structures are not as distinct in **2**, although there may be channels extending down the *c* axis. Of interest, however, is that there are two Cs^+ sites within the structure. One of these sites is fully occupied. The second site is occupied by 0.57. This has important consequences for the degree of protonation for **2**. There are two phosphate anions with terminal oxo atoms in **2**. For the phosphate anion containing P(1), there are two terminal oxo atoms with P−O bond distances of 1.560(9) Å, as compared to the bridging P−O bond distances of 1.501(6) Å. We propose that both of these aforementioned sites are protonated. A second phosphate anion containing P(2) has three bridging P−O bond distances of 1.509(7) Å and one terminal distance of 1.548(7) Å. This latter site is likely to be protonated also. However, if all three of these terminal sites are fully protonated, then there is an excess positive charge of 0.14. A closer look at the terminal oxygen atom around P(2) reveals an elongated thermal ellipsoid for this atom. We speculate that this elongation represents an average of protonated and deprotonated oxygen positions. Therefore, a potentially correct formula for **2** can be written as $Cs_{3.14}[(UO_2)_3Cu(H_2PO_4)(H_{1.93}PO_4)_2(PO_4)_2]\cdot H_2O$.

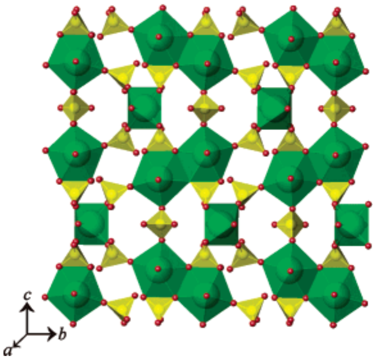

Figure 3. Depiction of uranyl phosphate layers in **2**. Uranium polyhedra are in green and phosphate in yellow.

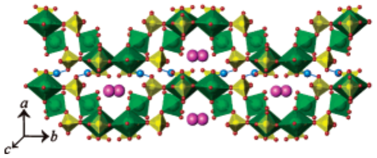

Figure 4. View of the three-dimensional structure of **2** wherein the Cu^{II} centers link uranyl phosphate layers together. Uranium polyhedra are in green, phosphate in yellow, and copper in blue. Some of the Cs^+ sites have been omitted for clarity.

The combination of the work reported herein along with our previous disclosures on $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$,[3] $Cs[UO_2Ga(PO_4)_2]$,[3] and $Cs_2[(UO_2(VO_2)_2(PO_4)_2]\cdot 0.59H_2O$[4] demonstrates that the construction of mixed-metal uranyl phosphates with three-dimensional-framework structures can be accomplished by both the interconnection of one-dimensional uranyl phosphate and main group or transition metal phosphate substructures and the linking of uranyl phosphate layers by transition metal centers. The metal centers contained in these structures span from tetrahedral environments in $Cs[UO_2Ga(PO_4)_2]$[3] to square planar geometries in **2**, to square pyramidal coordination in $Cs_2[(UO_2(VO_2)_2(PO_4)_2]\cdot 0.59H_2O$,[4] to octahedral $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$[3] and **1**. Likewise, the UO_6 tetragonal bipyramid, the UO_7 pentagonal bipyramid, and the UO_8 hexagonal bipyramid all occur in this small group of compounds, illustrating the remarkable structural diversity of U^{VI}. It is now clear that the incorporation of additional metal centers into uranyl phosphates provides for substantial enhancement in potential physicochemical properties. Some of the properties explored thus far include selective ion exchange, nonlinear optics, and magnetism. Measurements of some of these properties for **1** and **2** are underway.

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Supporting Information Available: X-ray crystallographic files for **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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