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Syntheses, Structures, and Ion-Exchange Properties of the Three-Dimensional Framework Uranyl Gallium Phosphates, $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ and $Cs[UO_2Ga(PO_4)_2]$

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The reaction of $UO_2(NO_3)_2\cdot 6H_2O$ with Cs_2CO_3 or CsCl, H_3PO_4, and Ga_2O_3 under mild hydrothermal conditions results in the formation of $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ (**UGaP-1**) or $Cs[UO_2Ga(PO_4)_2]$ (**UGaP-2**). The structure of **UGaP-1** was solved from a twinned crystal revealing a three-dimensional framework structure consisting of one-dimensional ${}^{1}_{\infty}[Ga(OH)(PO_4)_2]^{4-}$ chains composed of corner-sharing GaO_6 octahedra and bridging PO_4 tetrahedra that extend along the c axis. The phosphate anions bind the UO_2^{2+} cations to form UO_7 pentagonal bipyramids. The UO_7 moieties edge-share to create dimers that link the gallium phosphate substructure into a three-dimensional ${}^{3}_{\infty}[(UO_2)_2(GaOH)_2(PO_4)_4]^{4-}$ anionic lattice that has intersecting channels running down the b and c axes. Cs^+ cations and water molecules occupy these channels. The structure of **UGaP-2** is also three-dimensional and contains one-dimensional ${}^{1}_{\infty}[Ga(PO_4)_2]^{3-}$ gallium phosphate chains that extend down the a axis. These chains are formed from fused eight-membered rings of corner-sharing GaO_4 and PO_4 tetrahedra. The chains are in turn linked together into a three-dimensional ${}^{3}_{\infty}[UO_2Ga(PO_4)_2]^{1-}$ framework by edge-sharing UO_7 dimers as occurs in **UGaP-1**. There are channels that run down the a and b axes through the framework. These channels contain the Cs^+ cations. Ion-exchange studies indicate that the Cs^+ cations in **UGaP-1** and **UGaP-2** can be exchanged for Ca^{2+} and Ba^{2+}. Crystallographic data: **UGaP-1**, monoclinic, space group $P2_1/c$, $a = 18.872(1)$, $b = 9.5105(7)$, $c = 14.007(1)$ Å, $\beta = 109.65(3)°$, $Z = 4$ ($T = 295$ K); **UGaP-2**, triclinic, space group $P\bar{1}$, $a = 7.7765(6)$, $b = 8.5043(7)$, $c = 8.9115(7)$ Å, $\alpha = 66.642(1)°$, $\beta = 70.563(1)°$, $\gamma = 84.003(2)°$, $Z = 2$ ($T = 193$ K).

Introduction

The syntheses, structures, and physicochemical properties of gallium phosphates have been the subjects of intense interest for two decades because of their enormously rich structural chemistry that is particularly well noted for the forming microporous open-framework topologies that in some cases are similar to the $AlPO_4$ family of compounds.[1−4] The diversity in this class of compounds finds its origins in the fundamental coordination chemistry of Ga(III), which occurs as GaO_4 tetrahedra (e.g., in $[H_3N(CH_2)_3NH_3][GaH(PO_4)_2]$[5] and $[Ga(HPO_4)(PO_4)(OH)]\cdot[(C_2H_7N)_3N]\cdot H_2O$[6]), GaO_5 trigonal bipyramids (e.g., in $[NH_4][Ga(OH)(PO_4)]$[7] and $Ga_3(PO_4)_3\cdot C_3H_9N\cdot H_2O$[8]), and GaO_6 octahedra (e.g., in $[NH_4]_3[Ga_2(PO_4)_3]$[7] and $Rb(GaPO_4)_2(OH)(H_2O)\cdot H_2O$[9]). In fact, there are examples of compounds where Ga exhibits multiple geometries in the same compound as has been found for $Na[Ga_2(OH)(PO_4)_2]$[10] and $Na_3Ga_5(PO_4)_4O_2(OH)_2\cdot 2H_2O$,[11] which contain GaO_5 trigonal bipyramids and GaO_6 octahedra. These fundamental building units can combine with phosphate tetrahedra in a vast number of permutations to create zero-dimensional structures in $[Ga(HPO_4)(PO_4)(OH)]\cdot[(C_2H_7N)_3N]\cdot$

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H_2O[6] and $[C_6H_5NH]_2[H_8Ga_4P_4O_{21}]$,[12] one-dimensional chains as found in the organically templated gallium phosphates $[NH_3(CH_2)_4NH_3][Ga(PO_4)(PO_3OH)]$,[13] $[(1R,2R)\text{-}C_6H_{10}(NH_3)_2][Ga(OH)(HPO_4)_2]\cdot H_2O$,[14] and $[NH_3(CH_2)_2(NH_3)][Ga(H_2PO_4)(P_2O_7)]$,[15] two-dimensional sheets in $[C_5H_6N][Ga(HPO_4)_2(H_2O)_2]$[16] and $[NH_4]Ga(OH)(PO_4)]$,[7] and three-dimensional networks in $NaGa_2(OH)(PO_4)_2$,[10] $Na_3Ga_5(PO_4)_4O_2(OH)_2\cdot 2H_2O$,[11] and $[NH_3(CH_2)_3(NH_3)][Ga_3(PO_4)_3(H_2O)]$.[17]

The structural complexity and properties of gallium phosphates can be expanded through the inclusion of transition metals into the anionic lattice. The incorporation of transition metals into gallium phosphates can take place in several ways. First, partial substitution at Ga sites can take place to yield disordered compounds, which is illustrated by $[C_5H_5NH][CoGa_2P_3O_{12}]$, where CoO_4/GaO_4 disorder exists.[18] Anomalous X-ray scattering is a powerful tool in this regard and has been used to establish the distribution of Zn^{2+} and Ga^{3+} in a series of zinc-substituted gallium phosphates.[19] Second, the transition metal centers can force the adoptions of new structure types to accommodate additional building units as occurs in $Rb[(VO)(H_2O)Ga(PO_4)_2]$[20] and $Mn_3(H_2O)_6Ga_4(PO_4)_6$,[21] the latter of which forms gallium phosphate channels to house $Mn_3(H_2O)_6O_8$ clusters. This compound also exhibits superexchange interactions between Mn(II) centers, illustrating the one of many properties that can be added to gallium phosphates by incorporating transition metals.[21]

We have recently initiated a program for preparing uranyl compounds with three-dimensional open-framework structures, with a particular focus on the use of octahedral anions, such as periodate, IO_6^{5-}, as building units.[22,23] The formation of three-dimensional network structures incorporating the approximately linear uranyl, UO_2^{2+}, cation is not common because uranyl-containing polyhedra typically condense with uranyl units parallel to one another, and, because the uranyl oxo atoms are typically terminal, layered structures most often result.[24] Despite this structural propensity, a number of different uranyl systems have been shown to adopt three-dimensional framework structures including phosphates such as $[C_4H_{12}N_2](UO_2)[(UO_2)(PO_4)]_4\cdot 2H_2O$[25] and $[(UO_2)_3(PO_4)O(OH)(H_2O)_2](H_2O)$,[26] the fluorophosphate $[C_6H_{14}N_2]_2[(UO_2)_6(H_2O)_2F_2(PO_4)_2(HPO_4)_4]\cdot 4H_2O$,[27] arsenates, for example, $[NH(C_2H_5)_3][(UO_2)_2(AsO_4)(AsO_3OH)]$,[25] vanadates, for example, $A(UO_2)_4(VO_4)_3$ (A = Li, Na),[28] and oxides, for example, $(NH_4)_3(H_2O)_2\{[(UO_2)_{10}O_{10}(OH)][(UO_4)(H_2O)_2]\}$.[29] Herein, we report the preparation and characterization of the first examples of actinide-containing gallium phosphates, $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ (**UGaP-1**) and $Cs[UO_2Ga(PO_4)_2]$ (**UGaP-2**), both of which possess three-dimensional framework structures.

Experimental Section

Syntheses. $UO_2(NO_3)_2\cdot 6H_2O$ (98%, Alfa-Aesar), Ga_2O_3 (99.99%, Alfa-Aesar), Cs_2CO_3 (99.99%, Alfa-Aesar), H_3PO_4 (98%, Aldrich), KCl (99%, Aldrich), NaCl (99%, Aldrich), CsCl (99.9%, Cerac), $CaCl_2$ (99%, Aldrich), and $BaCl_2$ (99%, Aldrich) were used as received. Reactions were performed in the PTFE-lined Parr 4749 autoclaves. Distilled and Millipore filtered water with a resistance of 18.2 M$\Omega\cdot$cm was used in all reactions. Standard precautions were performed for handling radioactive materials during work with $UO_2(NO_3)_2\cdot 6H_2O$ and the products of the reactions. Semiquantitative SEM/EDX analyses were performed using a JEOL 840/Link Isis instrument. Cs, U, Ga, and P percentages were calibrated against standards.

$Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ (UGaP-1). $UO_2(NO_3)_2\cdot 6H_2O$ (0.238 g, 0.47 mmol), Ga_2O_3 (0.112 g, 0.94 mmol), H_3PO_4 (0.186 g, 1.88 mmol), Cs_2CO_3 (0.464 g, 1.41 mmol), and 1 mL of water were loaded into a 23 mL autoclave. The autoclave was then heated to 180 °C in a box furnace for 12 d and slow cooled at 3 °C/h to room temperature. The product mixture consisted of a colorless solution and a bright yellow precipitate. The solid was washed with water and methanol and allowed to dry. Rectangular shape tablets of **UGaP-1** were then separated, with a yield of 130 mg (55% yield based on the U), from the mixture for further study. The Cs:U:Ga:P ratio determined from EDX analysis was approximately 2:1:1:2.

$Cs[UO_2Ga(PO_4)_2]$ (UGaP-2). $UO_2(NO_3)_2\cdot 6H_2O$ (0.307 g, 0.61 mmol), Ga_2O_3 (0.144 g, 1.22 mmol), H_3PO_4 (0.239 g, 2.44 mmol), and CsCl (0.309 g, 1.83 mmol) were loaded into the 23 mL autoclave followed by the addition of 2 mL of water. The autoclave was heated for 4 d at 180 °C in a box furnace and then cooled to room temperature at 9 °C/h. The solid product consisted of a mixture of white and green-yellow crystals. After the mother liquor was decanted, the product was washed with water and methanol and allowed to dry. Rectangular shape yellow green tablets of **UGaP-2** were then separated from the white precipitate. The isolated yield was 46 mg (15% yield based on the U). EDX analysis provided a Cs:U:Ga:P ratio of 1:1:1:2.

Crystallographic Studies. Crystals of $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ (**UGaP-1**) and $Cs[UO_2Ga(PO_4)_2]$ (**UGaP-2**) were mounted on glass fibers and aligned on a Bruker SMART APEX CCD X-ray diffractometer. Intensity measurements were performed using graphite monochromated Mo Kα 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

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Table 1. Crystallographic Data for $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ (**UGaP-1**) and $Cs[UO_2Ga(PO_4)_2]$ (**UGaP-2**)

formula	$Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$	$Cs[UO_2Ga(PO_4)_2]$
formula mass	1641.04	662.60
color and habit	yellow tablet	yellow-green tablet
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	18.872(1)	7.7765(6)
b (Å)	9.5105(7)	8.5043(7)
c (Å)	14.007(1)	8.9115(7)
α (deg)	90	66.642(1)
β (deg)	109.65(3)	70.563(1)
γ (deg)	90	84.003(2)
V (Å^3)	2367.5(3)	509.96(7)
Z	4	2
T (K)	295	193
λ (Å)	0.71073	0.71073
maximum 2θ (deg)	56.64	56.60
ρ_{calcd} (g cm^{-3})	4.598	4.315
μ(Mo Kα) (cm^{-1})	223.20	223.65
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.0424	0.0283
$R_w(F_o^2)^b$	0.0973	0.0626

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

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 for **UGaP-1** and 120 s for **UGaP-2**.

Crystals of **UGaP-1** suffered from two problems. First, the crystal cracked when cooled to 193 K, and the data were therefore collected at 295 K. Second, all of the crystals examined proved to be twinned. GEMINI was used to separate the individuals components of the twin, and the structure was solved as follows.

For **UGaP-1** and **UGaP-2**, 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 face-indexed analytical absorption correction was initially applied using XPREP, where individual shells of unmerged data were corrected analytically.[30] These files were subsequently treated with a semiempirical absorption correction by SADABS.[31] The program suite SHELXTL (v 6.12) was used for space group determination (XPREP), direct methods structure solution (XS), and least-squares refinement (XL).[30] The final refinements included anisotropic displacement parameters for all atoms. Secondary extinction was not noted for either crystal. Some crystallographic details are given in Table 1. Additional details can be found in the Supporting Information.

Ion-Exchange Studies. An Accumet Basic AB 15 pH meter was used for potentiometric measurements. The ion-exchange properties of **UGaP-1** and **UGaP-2** were evaluated to determine the uptake values of Na^+, K^+, Ca^{2+}, and Ba^{2+} ions from NaCl, KCl, $CaCl_2$, and $BaCl_2$ solutions, respectively, in the range of the concentrations from 0.0001 to 0.1 M. The release values of Cs^+ ions were also measured. The concentrations of the solutions before and after uptake and release were determined using ion-selective electrodes.[32] The volume-to-mass ratio was 200:1 (2 mL of the solution for 0.01 g of sample).

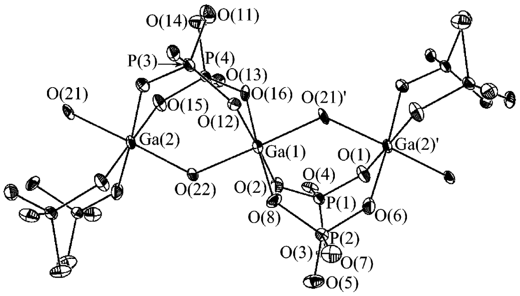

Figure 1. A view of the one-dimensional $^1_\infty[Ga(OH)(PO_4)_2]^{4-}$ chains composed of corner-sharing GaO_6 octahedra and bridging PO_4 tetrahedra that extend along the c axis in $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ (**UGaP-1**). 50% probability ellipsoids are depicted.

Results and Discussion

Synthesis. While the syntheses of $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ (**UGaP-1**) and $Cs[UO_2Ga(PO_4)_2]$ (**UGaP-2**) appear superficially similar, the reaction stoichiometries, durations, and perhaps most importantly pH are dramatically different. For the preparation of both compounds, we noted a reduction in pH between the starting reaction mixtures and that of the final mother liquor. The pH decreased from 9.1 to 7.1 during the crystallization of **UGaP-1** and from 2.4 to 1.9 during the formation of **UGaP-2**. The substitution of Cs_2CO_3 by CsCl in the preparation of **UGaP-2** plays a significant role in controlling the pH of these reactions. The synthesis of **UGaP-1** and **UGaP-2** also proved to be highly sensitive to temperature, and changes by as little as 10 °C had dramatic effects on yield, product crystallinity, and crystal size.

Structure of $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ (UGaP-1). The structure of **UGaP-1** was solved to reveal a three-dimensional framework of interconnected one-dimensional gallium phosphate and uranyl phosphate chains that run approximately perpendicular to one another. The gallium phosphate chain is composed of corner-sharing GaO_6 octahedra and bridging PO_4 tetrahedra that extend along the c axis, can be formulated as $^1_\infty[Ga(OH)(PO_4)_2]^{4-}$, and are depicted in Figure 1. We propose on the basis of charge balance considerations and bond-valence sums that the Ga−O−Ga backbone that runs down the gallium phosphate chains is protonated. The bond-valence sums for the O(21) and O(22) atoms in this chain are 1.12 and 1.16, which are values expected for hydroxyl sites.[33,34] Not surprisingly, given the presence of cesium and uranium in this structure, the hydrogen atoms could not be reliably located. This type of chain is similar to that found in the aluminophosphate mineral Tancoite, $LiNa_2H[Al(PO_4)_2(OH)]$,[35,36] and has been recognized in a large number of aluminum, gallium, and transition metal phosphates.[14,37−43] The Ga−O bond distances range from 1.940(7) to 2.036(7) Å. The P−O bond distances show

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]$ (**UGaP-1**)

Distances (Å)			
U(1)−O(3)	2.364(7)	Ga(2)−O(6)	1.984(7)
U(1)−O(3)′	2.503(7)	Ga(2)−O(10)	2.036(7)
U(1)−O(4)	2.400(7)	Ga(2)−O(15)	1.982(7)
U(1)−O(5)	2.255(8)	Ga(2)−O(21)	1.930(7)
U(1)−O(7)	2.307(7)	Ga(2)−O(22)	1.924(7)
U(1)−O(17)	1.805(7)	P(1)−O(1)	1.526(7)
U(1)−O(18)	1.794(7)	P(1)−O(2)	1.516(8)
U(2)−O(9)	2.306(7)	P(1)−O(3)	1.574(7)
U(2)−O(11)	2.223(7)	P(1)−O(4)	1.544(8)
U(2)−O(13)	2.390(7)	P(2)−O(5)	1.523(8)
U(2)−O(14)	2.376(7)	P(2)−O(6)	1.515(7)
U(2)−O(14)	2.606(7)	P(2)−O(7)	1.542(7)
U(2)−O(19)	1.795(7)	P(2)−O(8)	1.529(7)
U(2)−O(20)	1.786(7)	P(3)−O(9)	1.546(8)
Ga(1)−O(2)	1.971(7)	P(3)−O(10)	1.531(7)
Ga(1)−O(8)	1.948(7)	P(3)−O(11)	1.546(8)
Ga(1)−O(12)	1.971(7)	P(3)−O(12)	1.545(7)
Ga(1)−O(16)	1.988(7)	P(4)−O(13)	1.547(7)
Ga(1)−O(21)	1.962(7)	P(4)−O(14)	1.571(8)
Ga(1)−O(22)	1.940(7)	P(4)−O(15)	1.532(7)
Ga(2)−O(1)	1.973(7)	P(4)−O(16)	1.521(7)
Angles (deg)			
O(18)−U(1)−O(17)	178.3(3)	O(20)−U(2)−O(19)	178.1(3)

little variation and occur from 1.515(7) to 1.574(7) Å. Selected bond distances and angles are given in Table 2.

There are two crystallographically unique uranium centers in **UGaP-1.** Both of these U atoms are found as part of uranyl, UO_2^{2+}, cations with short U═O bond distances of 1.794(7) and 1.805(7) Å to U(1), and 1.786(7) and 1.795(7) Å to U(2). In both cases, the uranyl cations are nearly linear with O(18)−U(1)−O(17) and O(20)−U(2)−O(19) bond angles of 178.3(3)° and 178.1(3)°, respectively. The phosphate anions bind the UO_2^{2+} cations to form UO_7 pentagonal bipyramids with U(1)−O and U(2)−O distances being found from 2.255(8) to 2.503(7) Å and 2.223(7) to 2.606(7) Å, respectively. These bond distances can be used to calculate bond-valence sums for the U(1) and U(2) centers of 5.94 and 5.96, which are consistent with hexavalent uranium.[33,34,44] The bond angles in the pentagonal plane show substantial variation because the phosphate anions are found in both chelating and bridging modes. Therefore, there is an acute angle of 58.9(3)° in the equatorial plane ascribed to the chelation of the uranyl cation containing U(1) by a phosphate anion. The remaining angles in this plane range from 63.1(3)° to 81.7(3)°. The same situation occurs for U(2) with an acute angle of 57.6(2)° and the other angles ranging from 61.9(3)° to 84.8(3)°. The UO_7 moieties edge-share to create dimers that are bridged by phosphate anions to create one-dimensional chains that can be formulated as ${}^1_\infty[UO_2(PO_4)_2]^{4-}$. There are two different uranyl phosphate chains: one chain exclusively contains U(1) and the other contains U(2). These chains are illustrated in Figure 2. The one-dimensional topology of these chains is similar to that found in $Sr[UO_2(SeO_3)_2]{\cdot}2H_2O$, where one of the P−O bonds on each phosphate anion has been replaced by a stereochemically active lone-pair on Se(IV).[45] These chains are distinct from those found in the one-dimensional uranyl phosphate, parsonite, $Pb_2[UO_2(PO_4)_2]$.[46]

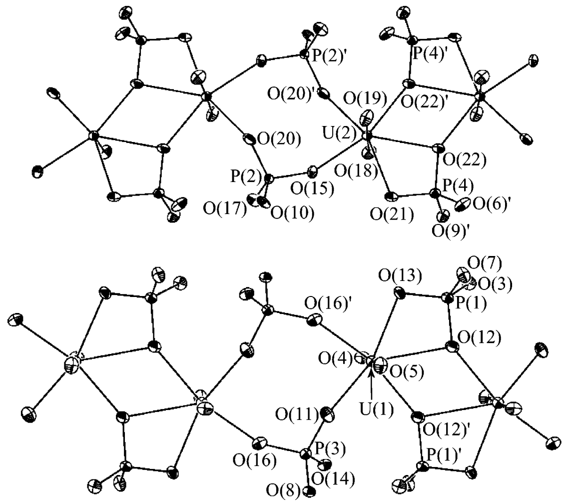

Figure 2. A depiction of the one-dimensional ${}^1_\infty[UO_2(PO_4)_2]^{4-}$ chains in $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]{\cdot}H_2O$ (**UGaP-1**). 50% probability ellipsoids are depicted.

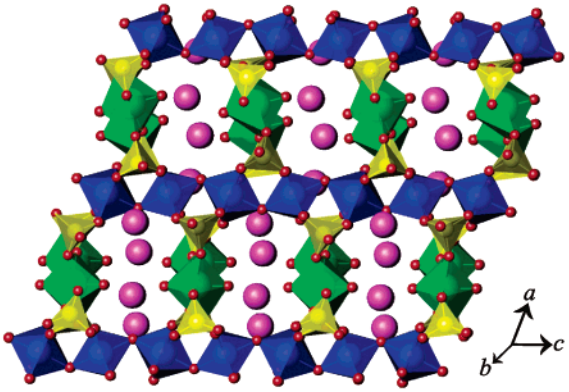

Figure 3. An illustration of the three-dimensional ${}^3_\infty[(UO_2)_2(GaOH)_2(PO_4)_4]^{4-}$ anionic lattice of $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]{\cdot}H_2O$ (**UGaP-1**) that has intersecting channels running down the *b* and *c* axes. These channels house Cs^+ cations and water molecules. Cs is shown in magenta, UO_7 pentagonal bipyramids are shown in green, GaO_6 octahedra are in blue, and PO_4 tetrahedra are in yellow.

The interconnection of the ${}^1_\infty[Ga(OH)(PO_4)_2]^{4-}$ and ${}^1_\infty[UO_2(PO_4)_2]^{4-}$ substructures creates a three-dimensional ${}^3_\infty[(UO_2)_2(GaOH)_2(PO_4)_4]^{4-}$ anionic lattice that has intersecting channels running down the *b* and *c* axes. Small tunnels also extend down [111]. A view showing the largest channels, which measure approximately 3.5 × 7.3 Å, extending along *b* is shown in Figure 3. There are four crystallographically unique Cs^+ cations and a water molecule in **UGaP-1** that occupy these channels. The Cs^+ cations form

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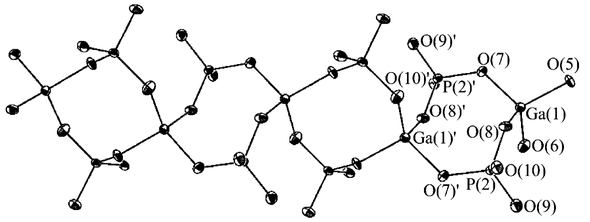

Figure 4. A view of the one-dimensional $^{1}_{\infty}[Ga(PO_4)_2]^{3-}$ gallium phosphate chains in $Cs[UO_2Ga(PO_4)_2]$ (**UGaP-2**) formed from fused eight-membered rings of alternating corner-shared GaO_4 and PO_4 tetrahedra. 50% probability ellipsoids are depicted.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Cs[UO_2Ga(PO_4)_2]$ (**UGaP-2**)

Distances (Å)			
U(1)−O(1)	1.774(5)	P(1)−O(3)	1.512(5)
U(1)−O(2)	1.779(5)	P(1)−O(4)	1.538(5)
U(1)−O(3)	2.482(5)	P(1)−O(5)	1.534(5)
U(1)−O(4)	2.385(5)	P(1)−O(6)	1.546(5)
U(1)−O(4)′	2.501(5)	P(2)−O(7)	1.552(5)
U(1)−O(9)	2.283(5)	P(2)−O(8)	1.552(5)
U(1)−O(10)	2.295(5)	P(2)−O(9)	1.505(5)
Ga(1)−O(5)	1.807(5)	P(2)−O(10)	1.519(5)
Ga(1)−O(6)	1.824(5)		
Ga(1)−O(7)	1.801(5)		
Ga(1)−O(8)	1.822(5)		
Angles (deg)			
O(1)−U(1)−O(2)	177.2(2)		

between 8 and 10 long contacts with oxygen atoms in the structure with average distances of 3.254(8), 3.374(8), 3.171(8), and 3.243(8) Å to Cs(1), Cs(2), Cs(3), and Cs(4), respectively. There is a short interaction of 2.869(13) Å between the water molecule and Cs(3). In addition, the water molecule forms hydrogen-bonding interactions of 2.740(8) and 2.821(8) Å with phosphate oxygen atoms in the gallium phosphate chain.

Structure of $Cs[UO_2Ga(PO_4)_2]$ (UGaP-2). The structure of **UGaP-2** is three-dimensional, being constructed from one-dimensional $^{1}_{\infty}[Ga(PO_4)_2]^{3-}$ gallium phosphate chains and one-dimensional uranyl phosphate chains, the former of which extend down the *a* axis. These gallium phosphate chains are formed from fused eight-membered rings of alternating corner-shared GaO_4 and PO_4 tetrahedra as shown in Figure 4. These types of rings are important building units in gallium phosphate chemistry and have been observed before in compounds such as $[Ga(HPO_4)(PO_4)(OH)]\cdot[(C_2H_7N)_3N]\cdot H_2O$[6] and $[NH_3(CH_2)_4NH_3][Ga(PO_4)(HPO_4)]$.[47] The Ga atoms are the sites of ring fusion for these chains. The Ga and P sites are easily distinguished from one another in these rings with average Ga−O and P−O bond distances of 1.814(5) and 1.532(5) Å, respectively. The two crystallographically unique PO_4^{3-} anions each use two oxygen atoms to bridge between Ga centers. The oxygen atoms that are not used in this fashion instead bind the uranium centers in the structure. Selected bond distances and angles for **UGaP-2** can be found in Table 3.

Unlike **UGaP-1**, there is only one crystallographically unique U center in **UGaP-2** that is found in the form of a UO_7 pentagonal bipyramid. There are two short U═O bonds of 1.774(5) and 1.779(5) Å that make up the approximately linear uranyl cation with an O−U−O angle of 177.2(2)°. The equatorial U−O distances range from 2.283(5) to 2.501(5) Å and are within normal limits. Bond-valence sum calculations on U yield a value of 5.97, which is consistent with U(VI).[33,34,44] The UO_7 units edge-share to create dimers with a central inversion center. These dimers are bridged by phosphate anions to create one-dimensional chains, whose formula can be described as $^{1}_{\infty}[UO_2(PO_4)_2]^{4-}$, and are illustrated in Figure 5. As can be seen from this figure, these chains are essentially the same as those found in **UGaP-1**.

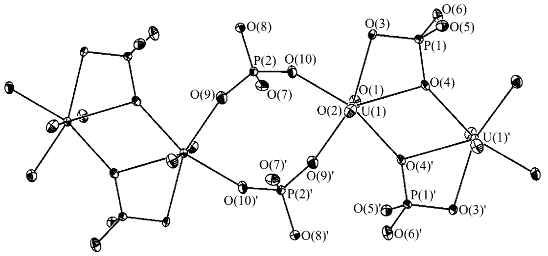

Figure 5. An illustration of the one-dimensional $^{1}_{\infty}[UO_2(PO_4)_2]^{4-}$ chains in $Cs[UO_2Ga(PO_4)_2]$ (**UGaP-2**). 50% probability ellipsoids are depicted.

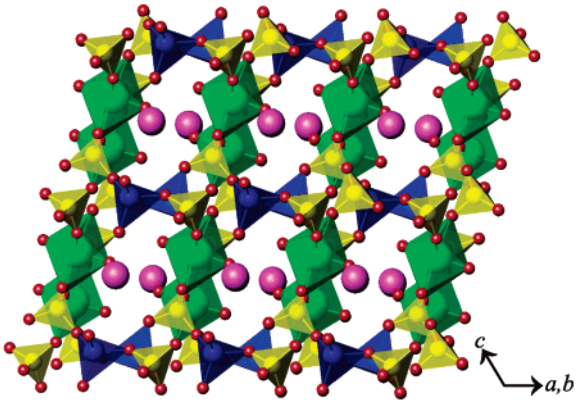

Figure 6. A depiction of the three-dimensional $^{3}_{\infty}[UO_2Ga(PO_4)_2]^{1-}$ framework in $Cs[UO_2Ga(PO_4)_2]$ (**UGaP-2**) with intersecting channels running down the *a* and *b* axes. Cs is shown in magenta, UO_7 pentagonal bipyramids are shown in green, GaO_4 tetrahedra are in blue, and PO_4 tetrahedra are in yellow.

The gallium phosphate and uranyl phosphate chains run approximately perpendicular to one another to create a three-dimensional $^{3}_{\infty}[UO_2Ga(PO_4)_2]^{1-}$ framework with intersecting channels running down the *a* and *b* axes, one view of which is shown in Figure 6. These channels at their largest are 3.1 × 6.7 Å and are of the size expected to house Cs^+ cations in the absence of occluded water molecules. The Cs^+ cations form long ionic contacts with the surrounding anionic lattice with eight contacts ranging from 3.115(5) to 3.440(5) Å.

Ion-Exchange Studies on $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ (UGaP-1) and $Cs[UO_2Ga(PO_4)_2]$ (UGaP-2). The exchange and mobility of interlayer cations in two-dimensional uranyl compounds have been studied in great detail, particularly for layered uranyl phosphates.[48] Both layered[49] and open-framework uranyl vanadates, such as $A(UO_2)_4(VO_4)_3$ (A = Li, Na),[28] have been shown to exhibit high cationic conductivities. We have also shown that the

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layered uranyl iodate, K[$UO_2(IO_3)_3$], shows selective ion-exchange of K^+ for Cs^+.[50] Given the three-dimensional framework structures of **UGaP-1** and **UGaP-2**, we were interested in evaluating the potential exchange of Cs^+ with H^+, Na^+, K^+, Ca^{2+}, and Ba^{2+} ions. Ion-exchange values were determined by potentiometric measurements using ion-selective electrodes.[32,50] This technique allows for the determination of both uptake and release of different ions by using different ion-selective electrodes.

Direct measurement of cation uptake often over- or underestimates actual ion-exchange values because of the typically large concentration of the exchanging ion in solution relative to the ion initially present in the material, as well as simple sorption by the material. Therefore, more realistic values can be obtained by measuring the concomitant release of Cs^+ cations into solution. For **UGaP-1** and **UGaP-2**, no exchange of Cs^+ was noted with H^+, Na^+, or K^+. However, the Cs^+ cations in **UGaP-1** and **UGaP-2** can be exchanged for both Ca^{2+} and Ba^{2+} cations. For **UGaP-1**, a Ca^{2+} uptake of 0.43(1) mequiv/g was found. Measurement of Cs^+ cation release for this process yielded a similar value of 0.57(1) mequiv/g. When Cs^+ cations are exchanged for Ba^{2+} cations, a release value of 0.36(1) mequiv/g was found. The smaller channel size of **UGaP-2** apparently better accommodates Ca^{2+} than does **UGaP-1**, and a large uptake value of 1.79(1) mequiv/g was found; the Cs^+ release was 1.06(1) mequiv/g. **UGaP-1** and **UGaP-2** show a similar ability to exchange Cs^+ for Ba^{2+}, and a release of 0.31 mequiv/g was measured for **UGaP-2**.

Conclusions

In this work, we have demonstrated that uranyl gallium phosphates can be prepared under mild hydrothermal conditions. Our original goal was to prepare three-dimensional framework compounds by incorporating octahedral GaO_6 building units. The crystal structure of $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ (**UGaP-1**) indicates that this strategy was successful. However, the structure of $Cs[UO_2Ga(PO_4)_2]$ (**UGaP-2**), which contains tetrahedral GaO_4 units, demonstrates that octahedral gallium is not necessary for the construction of open-framework uranyl gallium phosphates. Ion-exchange experiments show that the Cs^+ cations in **UGaP-1** and **UGaP-2** can be exchanged with Ca^{2+} and Ba^{2+} cations, but that appreciable exchange does not take place with alkali metal cations. We are currently investigating methods for preparing uranyl gallium phosphates with larger channels than those found in **UGaP-1** or **UGaP-2**.

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Supporting Information Available: X-ray crystallographic files for $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ (**UGaP-1**) and $Cs[UO_2Ga(PO_4)_2]$ (**UGaP-2**) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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