Inorganic Chemistry

Unexpected Roles of Alkali-Metal Cations in the Assembly of Low-Valent Uranium Sulfate Molecular Complexes

Zenghui Yue, Xiaofeng Guo, Mei-Ling Feng, Yue-Jian Lin, Yu Ju, Xiao Lin, Zhi-Hui Zhang, Xiaojing Guo, Jian Lin,* Yu-Ying Huang, and Jian-Qiang Wang



counterions in metal-ligand interactions remains ambiguous and requires further investigation. In this work, we describe the targeted isolation, through the choice of alkali-metal ions, of a family of tetravalent uranium sulfates, showing the influence of the overall topology and, unexpectedly, the U^{IV} nuclearity upon the inclusion of such countercations. Analyses of



the structures of uranium(IV) oxo/hydroxosulfate oligomeric species isolated from consistent synthetic conditions reveal that the incorporation of Na⁺ and Rb⁺ promotes the crystallization of 0D discrete clusters with a hexanuclear $[U_6O_4(OH)_4(H_2O)_4]^{12+}$ core, whereas the larger Cs^+ ion allows for the isolation of a 2D-layered oligomer with a less condensed trinuclear $[U_3(O)]^{10+}$ center. This finding expands the prevalent view that counterions play an innocent role in molecular complex synthesis, affecting only the overall packing but not the local oligomerization. Interestingly, trends in nuclearity appear to correlate with the hydration enthalpies of alkali-metal cations, such that the alkali-metal cations with larger hydration enthalpies correspond to more hydrated complexes and cluster cores. These findings afford new insights into the mechanism of nucleation of U^{IV}, and they also open a new path for the rational design and synthesis of targeted molecular complexes.

INTRODUCTION

The mechanisms of the formation of metal-ligand (ML) molecular complexes have been extensively studied, which, however, were mostly limited to the interactions between the metal ions and coordinating ligands.¹ The contributions of other species between ML complexes, such as counterions and solutes, have been practically overlooked owing to their relatively little influence on the local coordination of molecular ions and thermodynamics that drives the reactions.² Counterions have been generally used as charge-balancing species to control the ionic strength,³ metal-complex solubility,⁴ and overall packing of molecular ions.⁵⁻¹⁰ Nevertheless, our recent study demonstrates the correlation between the hydration enthalpies of countercations $(A^+ = Li^+, Na^+, K^+, Rb^+, Cs^+,$ NH_4^+ , or NR_4^+) and the formation of thorium nitrato molecular complexes from aqueous solution, wherein a transition from the more hydrated $[Th(NO_3)_5(H_2O)_2]^-$ to less hydrated $[Th(NO_3)_6]^{2-}$ ML complex occurs with decreasing hydration enthalpies of counterions.¹¹ Moreover, the electrochemical properties and chemical reactivity within a series of alkali-metal cerium(III) 1,1'-binolate complexes can be fine-tuned by the choice of alkali metals.¹² Jin and coworkers suggest that hydrophobic tetra-n-alkylammonium (TAA⁺) cations tend to stabilize higher oxidation states of neptunium dioxo cations in aqueous solution, while the hydrated Li⁺ cation does not have such an effect.¹³ All of these results suggest that, in addition to their function as innocent

charge-balancing species, the counterions also influence the thermodynamics and electrochemical properties, that eventually affect the compositions of the ML molecular complexes.

As one of the most commonly used families of counterions, alkali-metal ions are inherent to the advanced nuclear fuel cycles.^{14,15} Through the heating of fuels with salts of alkali metals, uranium and plutonium are converted to solid-state ternary oxides, uranates and plutonates, respectively, while volatile fission products can be removed during the reactions.¹⁶ These uranates are one of the main constituents of yellowcake and essential to the reprocessing of spent nuclear fuel.¹⁷ Therefore, besides the influences of pH value, temperature, and relative concentration, exploring the effect of alkali metal on the formation of uranium molecular complexes is of great necessity.

The importance of the coordination chemistry of uranium sulfate is highlighted by the widespread nature of uranium sulfate minerals and the extensive use of sulfuric acid in nuclear fuel cycles.^{18,19} Sulfate can adopt rich binding modes including monodentate and bidentate, as well as a variety of bridging modes in both solution and solid states, endowing a rich but

Received: October 30, 2019



unpredictable effect on the structure and speciation.^{3,20-23} Despite the fact that numerous uranium sulfate complexes have been reported, the majority are based on the uranyl ions and only a few of them incorporate the lower-oxidation-state uranium ions (III and IV).^{24–29} Furthermore, U^{IV} ions are inclined to hydrolyze and condense to form polynuclear species owing to the high Lewis acidity of U^{IV}, which makes predicting their behavior difficult in both solid and solution states.³⁰⁻³⁶ The formation of these polyoxo/hydroxo complexes and the resulting discrepancies of their solubility from that of monomeric ions underpin several critical processes including the spent fuel cycle and the fate of uranium in the environment.^{33,37} The chemistry of low-valent uranium clusters still remains underdeveloped. Hence, expansion of the alkali-metal uranium molecular complexes and an in-depth understanding of the formation mechanisms are highly desirable.

Herein we report a series of alkali-metal-containing uranium(IV) sulfates that are hydrothermally synthesized by utilizing zinc amalgam as in situ reductants. We also explore how variation of the alkali metals and systematic changes in the acidity affect the formation of these uranium molecular complexes by combined techniques, including X-ray crystallography, X-ray absorption, electronic, and vibrational spectroscopies. We provide evidence that counterions such as alkalimetal ions can assume a vital role in mediating the nuclearity of the uranium(IV) polyoxo/hydroxo clusters and controlling the overall solid-state packing molecular complexes.

EXPERIMENTAL SECTION

Synthesis. Caution! The uranium precursor containing depleted uranium was used in this synthesis, and 238 U is an α -emitting radioisotope. All handling of radioactive materials requires proper procedures. All operations should be performed in a laboratory specially designed for actinide element studies.

Materials. UO₂(CH₃COO)₂·2H₂O (99.9%, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences), H₂SO₄ (98%, Alfa-Aesar), Na₂CO₃ (99.99%, Aladdin), K₂CO₃ (99.99%, Aladdin), Rb₂CO₃ (99.99%, Aladdin), Cs₂CO₃ (99.99%, Aladdin), Zn (99.99%, Aladdin), and Hg (99.9%, Aladdin) were used as received. Millipore filtered water with a resistance of 18.2 MΩ·cm was used, and all of the reactions were performed in poly(tetrafluoroethylene)-lined Parr 4749 autoclaves with a 23 mL internal volume.

Mixtures of UO₂(CH₃COO)₂·2H₂O (0.2 mmol, 0.0848 g), A₂CO₃ (A = Na, K, Rb, or Cs; 0.6–1.2 mmol), and 98% H₂SO₄ (2–6.44 mmol, 0.11–0.35 mL) with molar ratios of $[U]/[A]/[H_2SO_4]$ ranging from 1:6:10 to 1:3:35 were loaded into a Teflon liner (Table S1). Additional water (1.89–1.65 mL) was added to the mixture to keep the total volume of solutions equal to 2 mL (Table S1). Zn amalgam was prepared according to the method by Cross et al., and the amalgam was placed at the bottom of the liner.²⁵ The autoclave was sealed, placed in a box furnace, heated to 150 °C for 2 h, and then slowly cooled to room temperature at a cooling rate of 5 °C/h. The reaction products were rinsed with deionized water, followed by rinsing with ethanol. Green crystals of seven A⁺–U^{IV}– sulfates and gold crystals of four ternary A⁺–U^{III}–sulfates were isolated as pure or mixed phases, as shown in Figure 1.

Crystallographic Studies. Single-crystal X-ray diffraction (SCXRD) data for all U^{IV} molecular complexes were collected on a Bruker D8-Venture single-crystal X-ray diffractometer equipped with a Turbo X-ray source (Mo K α radiation, $\lambda = 0.71073$ Å), adopting the direct-drive rotating-anode technique and a CMOS detector at 173 or 296 K. The data frames were collected using the program *APEX2* and processed using the program *SAINT* routine in *APEX2*.³⁸ The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the *SHELXTL-2014* program.³⁹ All non-H

atoms were refined with anisotropic displacement parameters. Selected crystallographic information is listed in Table S2. Atomic coordinates and additional structural information are provided in the CIFs. Numerous crystals of $RbU^{IV}SO_{4}$ -1 were examined and are all severely twinned, and the final refinement of the structural model is less than satisfactory. As a result, only the unit cell parameters are provided and some general bonding aspects are discussed. $RbU^{IV}SO_{4}$ -2 contains one SO_{4}^{2-} tetrahedron disordered over two sites, as shown in Figure S1.

Powder X-ray Diffraction (PXRD). PXRD patterns were collected from 5 to 50°, with a step of 0.02°, using a Bruker D8 Advance X-ray diffractometer with Cu K α radiation (λ = 1.54056 Å) equipped with a Lynxeye 1D detector, and selected PXRD results are provided in Figure S2.

Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy. EXAFS analysis of samples that were prepared by adding ground powder of NaU^{IV}SO₄, KU^{IV}SO₄-2, and RbU^{IV}SO₄-1 was conducted. U L3-edge X-ray absorption spectra were collected at the beamline 14W1 at Shanghai Synchrotron Radiation Facility.⁴⁰ The electron beam energy of the storage ring was 3.5 GeV, and the maximum stored current was approximately 210 mA. Data were recorded with a Si(111) double-crystal monochromator in fluorescence mode. The U L3-edge EXAFS data were analyzed in terms of the standard procedures in Demeter.⁴¹ Normalized absorption coefficients and EXAFS theoretical fittings were obtained using Athena and Artemis software, respectively. Theoretical phase and amplitude functions were calculated from the program FEFF 9.0.42 fitting procedure was performed on the k^3 -weighted Fourier transform (FT)-EXAFS from 3 to 11.5 Å⁻¹, and an R window of 1.4-5 Å was used for the fitting in tetravalent uranium sulfate compounds.

UV–Vis–Near-IR Spectroscopy. UV–vis–NIR data were acquired from single crystals using a Craic Technologies microspectrophotometer. Crystals were placed on quartz slides under Krytox oil, and the data were collected from 200 to 800 nm. The exposure time was autooptimized by the Craic software.

Fourier Transform Infrared (FTIR) Spectroscopy. The IR spectra in the range of 400-4000 cm⁻¹ were recorded on ground powder using a Thermo Nicolet 6700 FTIR spectrometer equipped with a diamond attenuated-total-reflectance accessory. The presence of coordinating or hydrating H₂O molecules as well as OH groups in NaU^{IV}SO₄, KU^{IV}SO₄-1, KU^{IV}SO₄-2, RbU^{IV}SO₄-2, CsU^{IV}SO₄-1, and $CsU^{IV}SO_4$ -2 can be confirmed by the O-H stretching and the H-O-H bending bands at 3600-2800 and ~1600 cm⁻¹, respectively (Figure S3).⁴³ RbU^{IV}SO₄-1, however, does not display any vibration bands from H₂O molecules or bridging –OH groups. Free tetrahedral SO_4^{2-} (T_d symmetry) have four typical vibration modes, A_1 (ν_1 symmetric stretch at 983 cm⁻¹), doubly degenerate E (ν_2 bending at 450 cm⁻¹), and two triply degenerate T_2 modes (ν_3 asymmetric stretching at 1105 cm⁻¹ and ν_4 bending at 611 cm⁻¹).⁴³ Owing to the crystal-field effects and correlation field splittings of sulfates within solid-state compounds, splitting and shifts of those bands occur, which result in multiple stretching (ν_1 and ν_3) and bending (ν_2 and ν_4) bands at the ranges of 800–1300 and 400–700 cm⁻¹, respectively.⁴³

Inductively Coupled Plasma Optical Emission Spectrometry/Mass Spectrometry (ICP-OES/MS) Analysis. To determine the formulas of NaU^{IV}SO₄ and RbU^{IV}SO₄-2, the molar ratios of Na/ U in NaU^{IV}SO₄ and Rb/U in RbU^{IV}SO₄-2 were measured by dissolving 1 mg of samples in 1 mL of 20% HNO₃. The concentrations of Na/U and Rb/U in aqueous solutions were determined by ICP-OES and ICP-MS, respectively, showing that NaU^{IV}SO₄ has a Na/U molar ratio of 2.08 (calcd 2) and RbU^{IV}SO₄-2 has a Rb/U molar ratio of 1.86(4) (calcd 1.83).

RESULTS AND DISCUSSION

Synthesis. The assembly of uranium molecular complexes is systematically controlled by introducing alkali-metal cations with a periodic trend of the ionic radius $(Na^+ < K^+ < Rb^+ < Cs^+)$ and by fine-tuning of the $[CO_3^{2-}]/[H_2SO_4]$ ratio.

Hydrothermal reactions between $UO_2(CH_3COO)_2$, A_2CO_3 , and H_2SO_4 with the presence of zinc amalgam result in the crystallization of seven alkali-metal-containing uranium(IV) sulfates and four previously reported uranium(III) sulfates as pure or mixed phases (Figure 1a and Table S1).²⁵ The



Figure 1. (a) Crystal images of trivalent and tetravalent uranium sulfates. (b) Products that form as a function of $[CO_3^{2-}]/[H_2SO_4]$ in the A–U–SO₄ system (A = Na, K, Rb, and Cs). The acidity is controlled by varying the molar ratio of A₂CO₃ and H₂SO₄.

resulting products were characterized for phase purity using PXRD analysis (Figure S2), and the evolutions of the respective phases are illustrated in a composition diagram as a function of $[CO_3^{2-}]/[H_2SO_4]$ (Figures 1b and S4). For the $Na^+-U-SO_4^{2-}$ system, olive prisms of $NaU(SO_4)_2(H_2O)$ $(NaU^{III}SO_4)$ can be obtained at low $[CO_3^{2-}]/[H_2SO_4]$ (0.09-0.30), while green prisms of $Na_{12}[U_6O_4(OH)_4(H_2O)_4]$ - $(SO_4)_{12} \cdot (H_2O)_2$ (NaU^{IV}SO₄) are the dominant phase when $0.30 \leq [CO_3^{2-}]/[H_2SO_4] \leq 0.60$ (Figure 1b). Coprecipitation of $NaU^{III}SO_4$ and $NaU^{IV}SO_4$ occurs in the intermediate 0.22 < $[CO_3^{2-}]/[H_2SO_4] < 0.30$ range. For the K/Rb/Cs⁺-U-SO₄²⁻ reactions, one trivalent uranium sulfate and two distinct tetravalent uranium phases have been isolated in each system. Mixtures of gold crystals of trivalent uranium(III) sulfate $[K_5U_2(SO_4)_6(H_2O) (KU^{III}SO_4), RbU(SO_4)_2 (RbU^{III}SO_4), or$ $CsU(SO_4)_2$ (CsU^{III}SO₄)] and dark-green crystals of uranium-(IV) sulfate $[K_4U_2(SO_4)_6(H_2O)_2 (KU^{IV}SO_4-1), RbU^{IV}SO_4-1]$ or $Cs_4U_3(SO_4)_8(H_2O)_3 \cdot 2H_2O$ (CsU^{IV}SO₄-1)] cocrystallize when $0.09 < [CO_3^{2-}]/[H_2SO_4] < 0.3$ for K, 0.09 <

 $[{\rm CO_3}^{2-}]/[{\rm H_2SO_4}] < 0.27$ for Rb, and $0.09 < [{\rm CO_3}^{2-}]/[{\rm H_2SO_4}]$ is increased, transitions from the first phase of uranium(IV) sulfate to the second U^{IV} phase, KU^{IV}SO_4-2, Rb₁₁[U₆O₄-(OH)₄(H₂O)₄](SO₄)₁₂·(H₃O) (RbU^{IV}SO_4-2), and Cs₄[U₃O-(SO₄)₇]·2.2H₂O (CsU^{IV}SO_4-2) occur at 0.3 < [CO₃²⁻]/[H₂SO₄] < 0.4 for K, 0.4 < [CO₃²⁻]/[H₂SO₄] < 0.45 for Rb, and 0.12 < [CO₃²⁻]/[H₂SO₄] < 0.16 for Cs, respectively. Furthermore, the products continue to evolve with increasing [CO₃²⁻]/[H₂SO₄] to progress forward to a pure phase of KU^{IV}SO₄-2, RbU^{IV}SO₄-2, or CsU^{IV}SO₄-2. An excess of Na₂CO₃, Rb₂CO₃, or Cs₂CO₃ leads to the formation of a black UO₂ powder in each system.

Structures and Topological Descriptions. Single-crystal X-ray analysis revealed that $NaU^{IV}SO_4$ and $RbU^{IV}SO_4$ -2 crystallize in monoclinic space group C2/m and tetragonal space group P_4/mnc , respectively (Table S2). Both of their structures are composed of discrete molecular clusters built from the assembly of $[U_6O_4(OH)_4(H_2O)_4]^{12+}$ hexanuclear cores and sulfates, charge-balanced by Na⁺/Rb⁺ cations, and solvent species (Figure 2a,b). The $[U_6O_4(OH)_4(H_2O)_4]^{12+}$ octahedral core consists of six U^{IV} cations bridged by four μ_3 -O and four μ_2 -OH groups with U···U distances of 3.8277(4)-3.9120(5) Å, as well as four capping H₂O molecules located on the vertexes of the equatorial plane (Figure 2c and Table S3). While $[U_6O_4(OH)_4(H_2O)_6]^{12+}$ cores with one capping H_2O molecule on each vertex are well documented for a wide variety of tetravalent metal oxohydroxo clusters, [U₆O₄(OH)₄- $(H_2O)_4]^{12+}$ hexamers with two capping H_2O molecules missing are unprecedented.^{31,35,44-46} It is noteworthy that a thorium hydroxoselenate, $Th_3O_2(OH)_2(SeO_4)_3$, contains a similar hexanuclear core, $[Th_6O_4(OH)_4]^{12+}$, without decoration of the H_2O molecules.⁴⁷ The O or OH groups appear to be distributed over the six μ_3 nodes of the octahedron, as confirmed by the bond valence sum of O atoms of the nodes (Table S3). Furthermore, the average U–O bond distances range from 2.286(10) to 2.454(5) Å, corresponding to values between U-OH (2.40-2.50 Å) and U-O (2.20-2.27 Å) bonds based on the published U^{IV} hexanuclear clusters with lower symmetry (Table S3).³⁷ Two crystallographically independent U^{IV} centers can be identified in the hexanuclear core, the polar U(1) and equatorial U(2), with squareantiprismatic and monocapped square-antiprismatic geometries, respectively (Figure 2d). The U–O bond distances range from 2.286(10) to 2.367(6) Å for U–O/OH, from 2.389(5) to 2.454(5) Å for U–O(SO₄^{2–}), and 2.649(5) Å for U–O(H₂) (Table S3). The $[U_6O_4(OH)_4(H_2O)_4]^{12+}$ unit is further decorated by 12 bridging μ_2 -SO₄²⁻ (Figure 2e) rather than μ_3 -SO₄²⁻ anions found in the 3D framework U₆O₄(OH)₄-(SO₄)₆ and other thorium oxohydroxosulfate open frameworks, e.g., $Th_3[Th_6(OH)_4O_4(H_2O)_6](SO_4)_{12}(H_2O)_{13}$.^{36,46} It is noteworthy that μ_2 ligands are inclined to terminate the clusters and result in the formation of discrete molecular moieties, while μ_3 or μ_4 ligands are capable of providing additional bridging bonds to form 3D frameworks.⁴⁸

 $KU^{IV}SO_4$ -1 crystallizes in an infinite 3D framework with a chiral space group C2, and it is isotypic to the previously reported cerium analogue $K_2Ce(SO_4)_3(H_2O)$.⁵¹ As shown in Figure 3a, $KU^{IV}SO_4$ -1 is composed of two crystallographically independent U^{IV} centers, five K⁺ cations, six SO_4^{2-} anions, and two coordinating H_2O molecules without inclusion of any bridging oxo and hydroxo groups. As a result, monomeric U^{IV} units are the exclusive phase of uranium in $KU^{IV}SO_4$ -1. Both



Figure 2. (a) Polyhedral representations of (a) $NaU^{IV}SO_4$ and (b) $RbU^{IV}SO_4$ -2. (c) Ball-and-stick representation of the $[U_6O_4(OH)_4(H_2O)_4]^{12+}$ hexanuclear core. (d) Coordination geometries of U(1) and U(2) in $NaU^{IV}SO_4$ and $RbU^{IV}SO_4$ -2. (e) Representation of the μ_2 -SO₄²⁻ anions bridging the U^{IV} ions in the hexamer. U^{IV} atoms are shown in green, Na in light blue, Rb in orange, S in gray, O in red, and H₂O molecules in dark blue.



Figure 3. (a) Polyhedral representation of $KU^{IV}SO_4$ -1. (b) Selected coordination environments of U(1) and U(2). U^{IV} atoms are shown in green, K in purple, S in gray, and O in red.

U(1) and U(2) adopt a nine-coordinate distorted monocapped square-antiprismatic geometry, within which eight O atoms are donated from six SO_4^{2-} and one O atom is from H₂O molecules (Figure 3b). The average U–O(SO_4^{2-}) and U–O(H₂) bond distances are 2.416 and 2.461 Å, respectively (Table S4). Interestingly, sulfates in KU^{IV}SO₄-1 exhibit extraordinarily rich binding modes, including μ_3 -bridging (monodentate, ×1; bidentate, ×1) for S(1), S(3), and S(5), μ_3 -bridging (monodentate, ×3) for S(4), μ_2 -bridging for S(6), and η_2 -terminal bidentate mode for S(2).

 $CsU^{IV}SO_4$ -1 adopts a 2D anionic lamellar architecture (Figure 4a) with orthorhombic space group *Pnma*. The structure of $CsU^{IV}SO_4$ -1 is composed of $[U_3(SO_4)_8(H_2O)_3]^{4-}$ layers extending along the *b* and *c* axes, with Cs⁺ and hydrating H₂O molecules residing within the interlamellar spacing (Figure 4a). The $[U_3(SO_4)_8(H_2O)_3]^{4-}$ layer consists of two crystallographically unique U^{IV} centers, four SO_4^{2-} anions, and three coordinating H₂O molecules (Figure 4b). The U(1) polyhedron edge-shares with another U(1) center generated from the $\overline{1}$ symmetry operation,

resulting in the formation of a $U^{\ensuremath{\text{IV}}}$ dimer via the bridging of four SO_4^{2-} anions. This contrasts sharply with thorium(IV) and plutonium(IV) hydroxonitrato species isolated from the nitric acid solutions, which contain the hydroxo-bridged $[Th_2(\mu_2\text{-}OH)_2]^{6+}$ and $[Pu_2(\mu_2\text{-}OH)_2]^{6+}$ dimeric moieties, respectively.^{52,53} Compared to the terminal bidentate mode of NO₃⁻, monodentate bridging ligation of SO₄²⁻ allows additional bridging between the metal centers and ligands, promoting oligomerization and formation of condensed molecular complexes. Sulfate groups also join the U^{IV} dimers and monomers, and their assembly forms the fundamental building unit of the $[U_3(SO_4)_8(H_2O)_3]^{4-}$ layers, as shown in Figure 4c. Two different coordination environments of U^{IV} are observed in $CsU^{IV}SO_4$ -1. The coordination geometry of U(2) in the dimer is a capped square antiprism with six O atoms donated from SO₄²⁻ anions and three O atoms from H₂O molecules, while that of the U(1) monomer is an irregular muffin with nine O atoms provided by SO₄²⁻ anions. The U- $O(SO_4^{2-})$ bond lengths range from 2.297(5) to 2.541(5) Å, and the $U-O(H_2)$ bond distances vary from 2.431(8) and 2.483(7) Å (Table S5).

Because CsU^{IV}SO₄-2 has been reported in our previous study, a brief description of its structure is given for structural comparisons.³⁵ CsU^{IV}SO₄-2 crystallizes in the space group $P\overline{3}$, and it features infinite sheets with open channels extending along the c axis (Figure 4d). The anionic $[U_3O(SO_4)_7]^{4-1}$ honeycomb lattice consists of $[U^{IV}_{3}(\mu_{3}-O)]^{10+}$ trinuclear oxocentered U^{IV} cores chelated by 13 SO_4^{2-} anions, including one $S(1)O_4^{2-}$, six $S(2)O_4^{2-}$, and six $S(3)O_4^{2-}$ anions (Figure 4e). Both the μ_3 -O atom and S(1)O₄²⁻ coordinate with three U^{IV} ions generated from the $\overline{3}$ symmetry operation, and those μ_3 bridging ligands assist the assembly of the trimeric species. $S(2)O_4^{2-}$ and $S(3)O_4^{2-}$ function as intertrimer linkers through μ_3 -bridging between different trimers. The U^{IV} center coordinates with one μ_3 -O and eight O atoms donated from SO_4^{2-} anions, forming a 9-fold coordination geometry with a monocapped square antiprism around the U^{IV} atoms (Figure 4f).



Figure 4. (a) Polyhedral representation of $CsU^{IV}SO_4$ -1. (b) Monomeric and dimeric units in $CsU^{IV}SO_4$ -1. (c) Selected coordination environments of U(1) and U(2) in $CsU^{IV}SO_4$ -1. (d) Polyhedral representations of $Cs_4[U_3O(SO_4)_7]$ -2.2H₂O ($CsU^{IV}SO_4$ -2). (e) Polyhedral representation of the $[U^{IV}_3(\mu_3$ -O)]^{10+} trinuclear core decorated by sulfate groups. (f) Selected coordination environments of U(1) in $CsU^{IV}SO_4$ -1. The U^{IV} atoms are shown in green, Cs in pink, K in purple, S in gray, O in red, and H₂O molecules in dark blue.

During the structural refinement of RbU^{IV}SO₄-1, all examined crystals of RbU^{IV}SO₄-1 were severely twinned and final refinement was less than satisfactory. As a result, only the unit cell parameters are provided, and some general bonding aspects are discussed (Table S2). Two crystallographically independent U atoms, four Rb atoms, and six unique S atoms can be localized unambiguously in the difference Fourier map (Figure S5a). The U(1)-U(2) interatomic distance is 5.370(6) Å and is in good agreement with those refined in KU^{IV}SO₄-1, suggesting the dominance of U^{IV} monomers in RbU^{IV}SO₄-1 (Figure S5b). KU^{IV}SO₄-2 crystallizes as clusters of microcrystals, making SCXRD data difficult to obtain. As a result, EXAFS spectroscopy was used to determine the local coordination environment of U^{IV} in $KU^{IV}SO_4$ -2. As shown in Figure 5a,b, the U L_3 -edge spectra of KU^{IV}SO₄-2 and NaU^{IV}SO₄ are quite similar, showing U-O/OH, U-S, and U-U paths at the first, second, and third coordination shells, respectively. Peaks at 1.8 Å in the FTIR spectra for all complexes can be attributed to the backscattering of O atoms (O/OH) in the coordination spheres. The coordination number and U-U interatomic distance of KU^{IV}SO₄-2 from theoretical fitting are highly consistent with those of $NaU^{IV}SO_4$ -2, suggesting the presence of hexanuclear U^{IV} moieties in $KU^{IV}SO_4$ -2 (Table S6). Furthermore, the EXAFS spectrum of RbU^{IV}SO₄-1 was collected, and its FT data show two main peaks located at 1.8 and 2.7 Å, contrasting sharply with those of hexameric NaU^{IV}SO₄ and KU^{IV}SO₄-2. Theoretical fittings show that the first and second shells can be attributed to the U-O(SO₄) and U-S_(bidentate) paths, respectively, both of which are in good agreement with the bonding distances of monomeric KU^{IV}SO₄-1 from the SCXRD result (Table S4).

Structure-Directing Effect of Alkali-Metal Cations. The series of alkali-metal uranium(IV) sulfates presented herein affords the opportunity to investigate the effect of alkalimetal cations on the formation of ML molecular complexes. Structural comparisons between the alkali-metal-containing uranium(IV) sulfates with other structurally characterized uranium(IV) oxohydroxosulfates suggest that alkali metal plays



Figure 5. (a) U L_3 -edge k^3 -weighted EXAFS spectra and (b) corresponding FTs of NaU^{IV}SO₄, KU^{IV}SO₄-2, and RbU^{IV}SO₄-1. Solid lines: experimental data. Dotted lines: theoretical fitting. Phase shifts (Δ) are not corrected on the FTs.

a significant role in determining the overall packing of the ML molecular complexes.^{26,36,54} At low acidic (high $[CO_3^{2-}]/[H_2SO_4]$ ratio) conditions, the presence of Na⁺ and Rb⁺ in NaU^{IV}SO₄ and RbU^{IV}SO₄-2 promotes crystallization of 0D discrete $[U_6O_4(OH)_4(H_2O)_4](SO_4)_{12}^{12-}$ molecular moieties. In addition, larger Cs⁺ in CsU^{IV}SO₄-2 promotes crystallization of a 2D-layered $[U_3O(SO_4)_7]^{4-}$ structure with an interlayer separation of 9.859(1) Å. These results indicate that the incorporation of counterions into ML molecular complexes appears to result in a dimensional reduction of its overall

topology. This idea was first proposed by Tulsky and Long, who demonstrated that the incorporation of an ionic agent into the covalent framework results in decreasing dimensionality of the covalent structural unit.⁵⁵ Furthermore, Krivovichev et al. suggest that even more innocent H₂O molecules can act as dimensionality reduction agents as well.⁵⁶ At high acidic (low $[CO_3^{2^-}]/[H_2SO_4]$ ratio) conditions, the larger ionic radii of Cs⁺ enables higher coordination number with O atoms and longer Cs–O bond distances, which promotes crystallization of a 2D U₃(SO₄)₈(H₂O)₃^{4–} lamellar structure with an interlayer separation of 9.486(1) Å. In contrast, the structure of KU^{IV}SO₄-1, being isolated from a similar condition with the presence of smaller K⁺ cations, features a higher 3D dimension than that of CsU^{IV}SO₄-1.

More strikingly, a closer structural examination suggests that counterions have a structure-directing effect on the nuclearity of U^{IV} ions. The formation of $[U_6(OH)_4O_4]^{12+}$ hexanuclear clusters with the presence of Na, Rb, and K counterions is not surprising because of the prevalence of such oligomers in both solid and solution states for a variety of tetravalent metal ions, including Zr, Ce, Th, U, Np, and Pu.^{31,45,48,49,57} Numerous reactions with various pH conditions and different temperatures were attempted to prepare a hexanuclear species templated by Cs⁺ cations but were unsuccessful. CsU^{IV}SO₄-2, a much less common uranium(IV) hydro/oxo species with trinuclear $[U_3(O)]^{10+}$ cores embedded, dominates at the high $[CO_3^{2-}]/[H_2SO_4]$ range. This type of trinuclear moiety with a μ_3 -oxo bridge has only been observed in two thorium(IV)/ uranium(IV) trimesate coordination polymers, where the trimeric organization is stabilized by a ligand with C_3 symmetry.^{58,59} Unlike thorium(IV)/uranium(IV) trimesate, trinuclear formation in CsU^{IV}SO₄-2 appears to be promoted by the Cs⁺ cation. How does the counterion influence the nuclearity of U^{IV} ions from aqueous solution? To uncover the mechanism, the coordination environments of the alkali metals in the oligomers have been examined and are shown in Figure 6. H₂O molecules can be identified at the first coordination spheres of Na(1)⁺, Rb(1)⁺, and Rb(2)⁺ for the NaU^{IV}SO₄ and



Figure 6. Selected coordination environments of alkali-metal cations: (a) Na(1) in the structure of NaU^{IV}SO₄; (b) Rb(1) in the structure of RbU^{IV}SO₄-2; (c) Rb(2) in the structure of RbU^{IV}SO₄-2; (d) Cs(1) in the structure of CsU^{IV}SO₄-2. U^{IV} atoms are shown in green, Na in light blue, Rb in orange, Cs in pink, S in gray, O in red, and H₂O molecules in dark blue.

RbU^{IV}SO₄-2, whereas all coordinated O atoms of Cs⁺ cations are donated from sulfate groups for the Cs compound. This correlation between the number of coordinating H₂O molecules and the ionic sizes of the counterions can be attributed to variation in their affinity to H₂O, termed the hydration energy $(\Delta H_{\rm hydr})$ in the following order: Na⁺ (-415 kJ/mol > K⁺ (-330 kJ/mol > Rb⁺ (-305 kJ/mol > Cs⁺ (-280 kJ/mol).⁶⁰ The incorporation of more hydrophilic counterions leads to the crystallization of molecular clusters with more hydrated hexameric $[U_6O_4(OH)_4(H_2O)_4]^{12+}$ cores. Particularly, O(W1) in RbU^{IV}SO₄-2 serves as a bridging unit for the $[U_6O_4(OH)_4(H_2O)_4]^{12+}$ hexamer and $Rb(2)^+$ cation, suggesting the dominance of ion-hydration-association interactions between these species.^{61,62} In contrast, the more hydrophobic Cs⁺ cation appears to dictate different reaction outcomes, where ion-association interactions are favored and a less hydrated trinuclear $[U_3(O)]^{10+}$ core is isolated in the resulting coordination polymer.

Effect of the pH on Oligomerization. The pH of the solution was fine-tuned by changing the $[CO_3^{2-}]/[H_2SO_4]$ ratio, and introduction of such a variation provides opportunities to delineate the roles of the pH on the formation of ML molecular complexes. Nucleation reductions with increasing acidity of the solution can be observed in this $A^+ - U^{IV} - SO_4^{2-}$ system. Specifically, a higher $[CO_3^{2-}]/$ [H₂SO₄] (higher pH) ratio gives rise to the formation of a hexanuclear $[U_6O_4(OH)_4(H_2O)_4]^{12+}$ core in the Na, K, and Rb systems or a trinuclear $[U_3O]^{10+}$ core in the Cs system, both of which contain oxo/hydro bridges. At the region of lower $[CO_3^{2-}]/[H_2SO_4]$ ratio, molecular complexes $(KU^{IV}SO_4-1, RbU^{IV}SO_4-1)$ and $(CsU^{IV}SO_4-1)$ with low nuclearity are formed, and they are composed of purely isolated mononuclear UO₈ or UO₉ centers. A U dimeric unit can be identified in CsU^{IV}SO₄-1 as well, but the U ions in this unit are exclusively bridged by SO₄²⁻ anions rather than OH groups found in thorium and plutonium hydroxonitrato species.^{52,53} These results indicate that increasing the pH can promote hydrolysis owing to increasing hydroxyl concentration, species essential to the olation/oxolation mechanisms for aggregation of the tetravalent actinide ions. A similar nucleation reduction with increasing acidity has been observed in a thorium sulfate system, showing that the elevation of the pH to 2.4 promotes the formation of Th hexamers in $Th_3[Th_6(OH)_4O_4(H_2O)_6](SO_4)_{12}(H_2O)_{13}$, whereas lower pH leads to the crystallization of monomeric thorium sulfate hydrate $Th(SO_4)_2(H_2O)_7 \cdot (H_2O)_2$.

Effects of the Nuclearity on Electronic Transitions. The solid-state UV-vis spectra of uranium(IV) sulfate complexes acquired from single crystals are shown in Figure 7. The tetravalent nature of U ions in uranium(IV) sulfate complexes can be verified by the typical f-f transition bands of U^{IV} (5f²) at wavelengths longer than 400 nm, which can be assigned to the transitions from ground state $({}^{3}H_{4})$ to excited states $({}^{3}P_{2}, {}^{1}I_{6}, {}^{3}P_{1}, {}^{3}P_{0}, {}^{1}G_{4}$, and ${}^{1}D_{2}).^{63}$ Differences in the nuclearity give rise to considerable variances in the spectra of those complexes. First, the molecular complexes with low nuclearity (monomer or dimer in KU^{IV}SO₄-1, RbU^{IV}SO₄-1, and CsU^{IV}SO₄-1) exhibit negligible ligand-to-metal chargetransfer (LMCT) absorbance ranging from 300 to 400 nm, while NaU^{IV}SO₄, KU^{IV}SO₄-2, RbU^{IV}SO₄-2, and CsU^{IV}SO₄-2 featuring hexanuclear or trinuclear cores show strong absorbance in this region. A similar evolution of the LMCT bands from monomeric to hexameric species in the solution-



Figure 7. UV–vis absorption spectra of uranium(IV) sulfates with lower nuclearity ($KU^{IV}SO_4$ -1, $RbU^{IV}SO_4$ -1, and $CsU^{IV}SO_4$ -1) and higher nuclearity ($NaU^{IV}SO_4$, $KU^{IV}SO_4$ -2, $RbU^{IV}SO_4$ -2, and $CsU^{IV}SO_4$ -2). The arrow symbols highlight the blue shifts of the ${}^{1}I_{6}$, ${}^{3}P_{1}$, and ${}^{3}P_{0}$ peaks of $RbU^{IV}SO_4$ -1.

state uranium(IV) glycine system has been reported.⁶⁴ Second, an emerging peak at 673 nm for NaU^{IV}SO₄, KU^{IV}SO₄-2, $RbU^{IV}SO_4-2$, and $CsU^{IV}SO_4-2$ reveals that the electronic transitions of U^{IV} in the oligomers with high nuclearity are redshifted to the longer wavelength. Such variations of the LMCT and f-f transition bands are indicative and thus excellent probes to determine not only the valence but also the nuclearity of $U^{\rm IV}$ in both solid and solution states. 31,50,64,65 In addition, noticeable blue shifts of the ${}^{1}I_{6}$, ${}^{3}P_{1}$, and ${}^{3}P_{0}$ peaks as well as merging of the ${}^{3}P_{2}$ and ${}^{1}I_{6}$ bands in the absorption spectrum of RbU^{IV}SO₄-1 can be observed, which accounts for the atypical optical properties of RbU^{IV}SO₄-1 compared to other uranium(IV) sulfates. Specifically, NaU^{IV}SO₄, KU^{IV}SO₄-1, KU^{IV}SO₄-2, RbU^{IV}SO₄-2, CsU^{IV}SO₄-1, and CsU^{IV}SO₄-2 exhibit brown color under standard fluorescence lighting but are green when illuminated by natural or light-emitting-diode lighting (termed the Alexandrite effect), as shown in Figure 8, while RbU^{IV}SO₄-1 does not feature this type of dichroism and its color remains unchanged under variable lighting conditions.

CONCLUSIONS

Seven tetravalent uranium sulfates and four trivalent uranium sulfates templated by alkali-metal ions (Na⁺, K⁺, Rb⁺, and Cs⁺) have been synthesized and characterized. The synthesis performed highlighted the success of using Zn amalgam as an in situ reductant for isolating low-valent uranium molecular



Figure 8. Photographs of alkali-metal-containing uranium(IV) sulfates showing the Alexandrite effect.

complexes. The trivalent uranium sulfates have been reported, but the novelty of the tetravalent uranium sulfates in terms of their composition and structure allows a systematic investigation to reveal the underlying role of alkali-metal cations in the formation of ML molecular complexes.²⁵ Compared to $U_6O_4(OH)_4(SO_4)_{67}$ a 3D uranium oxo/hydroxosulfato complex composed of octahedral U₆ oligomers, the hexameric cores are well retained in the Na⁺⁻ and Rb⁺-incorporated molecular complexes (NaU^{IV}SO₄ and RbU^{IV}SO₄-2), but dimensional reductions of the overall topologies from a dense 3D framework to 0D discrete clusters have been observed.³⁶ The incorporation of Cs⁺ ions into the framework under similar synthesis conditions allows for a dimensional reduction from a 3D framework to a 2D-layered structure of CsU^{IV}SO₄-2. More significantly, a trinuclear $[U^{IV}_{3}(\mu_{3}-O)]^{10+}$ core rather than the commonly observed $[U_6O_4(OH)_4]^{12+}$ hexamer is embedded in CsU^{IV}SO₄-2. These results indicate that the incorporation of counterions into ML molecular complexes not only influences the overall solid-state packing of uranium molecular complexes but also affects the oligomerization of U^{IV} ions. To the best of our knowledge, the reactions of hydrolysis and nucleation are governed by various conditions including the pH, temperature, relative concentration, and ligand species, but the effect of counterions has barely been investigated. These results expand the general perspective of the pH and ligand as the dominant influence of the nuclearity and shed further light on a new strategy for the design and synthesis of targeted oligomers.

Moreover, nucleation reduction from oxo/hydroxo-bridged hexameric or trimeric U^{IV} cores found in $KU^{IV}SO_4$ -2, $RbU^{IV}SO_4$ -2, and $CsU^{IV}SO_4$ -2 to monomeric and dimeric U^{IV} centers in $KU^{IV}SO_4$ -1, $RbU^{IV}SO_4$ -1, and $CsU^{IV}SO_4$ -1 with increasing acidity represents a nice illustration that hydrolysis and nucleation occur for U^{IV} ions at low-acidity conditions in an aqueous medium. Such nucleation reduction can be associated with variation of the LMCT bands and f–f electronic transitions, as illustrated by the UV–vis spectra of those complexes. This correlation offers an alternative way to determine the relative size and nuclearity of U^{IV} oligomeric species and design new materials with some type of optical eccentricity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03182.

PXRD patterns, possible structure of **RbUSO**₄-1, structure of U₆O₄(OH)₄(SO₄)₆, coordination geometry of S(2)O₄²⁻ in **RbU^{IV}SO**₄-2, optical micrographs, FTIR spectra, SEM images, EDS spectra, synthesis details, crystallographic data, EXAFS analysis, and selected bond distances (PDF)

Accession Codes

CCDC 1959585–1959588 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Jian Lin – Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China; orcid.org/0000-0002-3536-220X; Email: linjian@sinap.ac.cn

Authors

- Zenghui Yue Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China; University of Chinese Academy of Sciences, Beijing 100049, China; Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China
- Xiaofeng Guo Department of Chemistry, Washington State University, Pullman, Washington 99164-4630, United States; orcid.org/0000-0003-3129-493X
- Mei-Ling Feng State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China; orcid.org/0000-0003-2524-0994
- Yue-Jian Lin Department of Chemistry, Fudan University, Shanghai 200433, China
- Yu Ju Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, China

Xiao Lin – Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

Zhi-Hui Zhang – Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, China; orcid.org/0000-0002-8744-7897

Xiaojing Guo – The Education Ministry Key Laboratory of Resource Chemistry and Shanghai Key Laboratory of Rare Earth Functional Materials, Department of Chemistry and Chemical Engineering, Shanghai Normal University, Shanghai 200234, China; Orcid.org/0000-0001-6489-0717

Yu-Ying Huang – Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China

Jian-Qiang Wang – Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China; Orcid.org/ 0000-0003-4123-7592 https://pubs.acs.org/10.1021/acs.inorgchem.9b03182

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by grants from the National Natural Science Foundation of China (Grants 21701184, 21876182, and 21676291) and the Shanghai Pujiang Program (Grant 17PJ1410600)

REFERENCES

(1) Richens, D. T. Ligand Substitution Reactions at Inorganic Centers. *Chem. Rev.* 2005, 105, 1961.

(2) Misra, A.; Kozma, K.; Streb, C.; Nyman, M. Beyond Charge Balance: Counter-Cations in Polyoxometalate Chemistry. *Angew. Chem., Int. Ed.* **2020**, *59*, 596.

(3) Hu, Y.-J.; Knope, K. E.; Skanthakumar, S.; Kanatzidis, M. G.; Mitchell, J. F.; Soderholm, L. Understanding the Role of Aqueous Solution Speciation and Its Application to the Directed Syntheses of Complex Oxidic Zr Chlorides and Sulfates. J. Am. Chem. Soc. 2013, 135, 14240–14248.

(4) Hickam, S.; Aksenov, S. M.; Dembowski, M.; Perry, S. N.; Traustason, H.; Russell, M.; Burns, P. C. Complexity of Uranyl Peroxide Cluster Speciation from Alkali-Directed Oxidative Dissolution of Uranium Dioxide. *Inorg. Chem.* **2018**, *57*, 9296–9305.

(5) Danis, J. A.; Lin, M. R.; Scott, B. L.; Eichhorn, B. W.; Runde, W. H. Coordination Trends in Alkali Metal Crown Ether Uranyl Halide Complexes: The Series $[A(Crown)]2[UO2 \times 4]$ Where A = Li, Na, K and X = Cl, Br. *Inorg. Chem.* **2001**, *40*, 3389–3394.

(6) Bang, S.-e.; Ok, K. M. Structure-Directing Effect of Alkali Metal Cations in New Molybdenum Selenites, Na2Mo2O5(SeO3)2, K2Mo2O5(SeO3)2, and Rb2Mo3O7(SeO3)3. *Inorg. Chem.* 2015, 54, 8832–8839.

(7) Kim, Y.; Lee, D. W.; Ok, K. M. Rich Structural Chemistry in New Alkali Metal Yttrium Tellurites: Three-Dimensional Frameworks of NaYTe₄O₁₀, KY(TeO₃)₂, RbY(TeO₃)₂, and a Novel Variant of Hexagonal Tungsten Bronze, CsYTe₃O₈. *Inorg. Chem.* **2015**, *54*, 389–395.

(8) Bang, S.-e.; Lee, D. W.; Ok, K. M. Variable Framework Structures and Centricities in Alkali Metal Yttrium Selenites, AY(SeO3)2 (A = Na, K, Rb, and Cs). *Inorg. Chem.* **2014**, *53*, 4756–4762.

(9) Shlyapnikov, I. M.; Goreshnik, E. A.; Mazej, Z. Increasing Structural Dimensionality of Alkali Metal Fluoridotitanates(IV). *Inorg. Chem.* **2018**, *57*, 1976–1987.

(10) Sykora, R. E.; Ok, K. M.; Halasyamani, P. S.; Albrecht-Schmitt, T. E. Structural modulation of molybdenyl iodate architectures by alkali metal cations in $AMoO_3(IO_3)$ (A = K, Rb, Cs): A facile route to new polar materials with large SHG responses. *J. Am. Chem. Soc.* **2002**, *124*, 1951–1957.

(11) Jin, G. B.; Lin, J.; Estes, S. L.; Skanthakumar, S.; Soderholm, L. Influence of Countercation Hydration Enthalpies on the Formation of Molecular Complexes: A Thorium–Nitrate Example. *J. Am. Chem. Soc.* **2017**, *139*, 18003–18008.

(12) Robinson, J. R.; Carroll, P. J.; Walsh, P. J.; Schelter, E. J. The Impact of Ligand Reorganization on Cerium(III) Oxidation Chemistry. *Angew. Chem., Int. Ed.* **2012**, *51*, 10159–10163.

(13) Estes, S. L.; Qiao, B.; Jin, G. B. Ion association with tetra-nalkylammonium cations stabilizes higher-oxidation-state neptunium dioxocations. *Nat. Commun.* **2019**, *10*, 59.

(14) Sakamura, Y. Effect of alkali and alkaline-earth chloride addition on electrolytic reduction of UO_2 in LiCl salt bath. *J. Nucl. Mater.* **2011**, *412*, 177–183.

(15) Lindemer, T. B.; Besmann, T. M.; Johnson, C. E. Thermodynamic review and calculations—alkali-metal oxide systems with nuclear fuels, fission products, and structural materials. *J. Nucl. Mater.* **1981**, *100*, 178–226.

Complete contact information is available at:

(16) Griffiths, T. R.; Volkovich, V. A.; Yakimov, S. M.; May, I.; Sharrad, C. A.; Charnock, J. M. Reprocessing spent nuclear fuel using molten carbonates and subsequent precipitation of rare earth fission products using phosphate. *J. Alloys Compd.* **2006**, *418*, 116–121.

(17) Hausen, D. M. Characterizing and classifying uranium yellow cakes: A background. *JOM* **1998**, *50*, 45–47.

(18) Gurzhiy, V. V.; Plasil, J. Structural complexity of natural uranyl sulfates. *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.* **2019**, 75, 39–48.

(19) Kaushik, C. P.; Mishra, R. K.; Sengupta, P.; Kumar, A.; Das, D.; Kale, G. B.; Raj, K. Barium borosilicate glass – a potential matrix for immobilization of sulfate bearing high-level radioactive liquid waste. *J. Nucl. Mater.* **2006**, *358*, 129–138.

(20) Wilson, R. E. Structural Periodicity in Plutonium(IV) Sulfates. Inorg. Chem. 2011, 50, 5663-5670.

(21) Wilson, R. E.; Skanthakumar, S.; Knope, K. E.; Cahill, C. L.; Soderholm, L. An Open-Framework Thorium Sulfate Hydrate with 11.5 Å Voids. *Inorg. Chem.* **2008**, *47*, 9321–9326.

(22) Knope, K. E.; Wilson, R. E.; Skanthakumar, S.; Soderholm, L. Synthesis and Characterization of Thorium(IV) Sulfates. *Inorg. Chem.* **2011**, *50*, 8621–8629.

(23) Kalaji, A.; Skanthakumar, S.; Kanatzidis, M. G.; Mitchell, J. F.; Soderholm, L. Changing Hafnium Speciation in Aqueous Sulfate Solutions: A High-Energy X-ray Scattering Study. *Inorg. Chem.* **2014**, *53*, 6321–6328.

(24) Knope, K. E.; Soderholm, L. Solution and Solid-State Structural Chemistry of Actinide Hydrates and Their Hydrolysis and Condensation Products. *Chem. Rev.* **2013**, *113*, 944–994.

(25) Cross, J. N.; Villa, E. M.; Darling, V. R.; Polinski, M. J.; Lin, J.; Tan, X.; Kikugawa, N.; Shatruk, M.; Baumbach, R.; Albrecht-Schmitt, T. E. Straightforward Reductive Routes to Air-Stable Uranium(III) and Neptunium(III) Materials. *Inorg. Chem.* **2014**, *53*, 7455–7466.

(26) Schnaars, D. D.; Wilson, R. E. Uranium(IV) Sulfates: Investigating Structural Periodicity in the Tetravalent Actinides. *Inorg. Chem.* **2012**, *51*, 9481–9490.

(27) Chemey, A. T.; Celis-Barros, C.; Huang, K.; Sperling, J. M.; Windorff, C. J.; Baumbach, R. E.; Graf, D. E.; Páez-Hernández, D.; Ruf, M.; Hobart, D. E.; Albrecht-Schmitt, T. E. Electronic, Magnetic, and Theoretical Characterization of $(NH_4)_4UF_8$, a Simple Molecular Uranium(IV) Fluoride. *Inorg. Chem.* **2019**, *58*, 637–647.

(28) Wacker, J. N.; Han, S. Y.; Murray, A. V.; Vanagas, N. A.; Bertke, J. A.; Sperling, J. M.; Surbella, R. G.; Knope, K. E. From Thorium to Plutonium: Trends in Actinide(IV) Chloride Structural Chemistry. *Inorg. Chem.* **2019**, *58*, 10578–10591.

(29) Gui, D.; Dai, X.; Zheng, T.; Wang, X.; Silver, M. A.; Chen, L.; Zhang, C.; Diwu, J.; Zhou, R.; Chai, Z.; Wang, S. An Ultrastable Heterobimetallic Uranium(IV)/Vanadium(III) Solid Compound Protected by a Redox-Active Phosphite Ligand: Crystal Structure, Oxidative Dissolution, and First-Principles Simulation. *Inorg. Chem.* **2018**, *57*, 903–907.

(30) Falaise, C.; Kozma, K.; Nyman, M. Thorium Oxo-Clusters as Building Blocks for Open Frameworks. *Chem. - Eur. J.* **2018**, *24*, 14226–14232.

(31) Tamain, C.; Dumas, T.; Hennig, C.; Guilbaud, P. Coordination of Tetravalent Actinides (An = Th^{IV} , U^{IV} , Np^{IV} , Pu^{IV}) with DOTA: From Dimers to Hexamers. *Chem. - Eur. J.* **2017**, *23*, 6864–6875.

(32) Falaise, C.; Volkringer, C.; Hennig, C.; Loiseau, T. Ex-Situ Kinetic Investigations of the Formation of the Poly-Oxo Cluster U_{38} . *Chem. - Eur. J.* **2015**, *21*, 16654–16664.

(33) Martin, N. P.; Volkringer, C.; Henry, N.; Trivelli, X.; Stoclet, G.; Ikeda-Ohno, A.; Loiseau, T. Formation of a new type of uranium(iv) poly-oxo cluster $\{U_{38}\}$ based on a controlled release of water via esterification reaction. *Chem. Sci.* **2018**, *9*, 5021–5032.

(34) Martin, N. P.; Volkringer, C.; Roussel, P.; März, J.; Hennig, C.; Loiseau, T.; Ikeda-Ohno, A. {Np38} clusters: the missing link in the largest poly-oxo cluster series of tetravalent actinides. *Chem. Commun.* **2018**, *54*, 10060–10063.

(35) Lin, J.; Yue, Z.; Silver, M. A.; Qie, M.; Wang, X.; Liu, W.; Lin, X.; Bao, H.-L.; Zhang, L.-J.; Wang, S.; Wang, J.-Q. In Situ Reduction

from Uranyl Ion into a Tetravalent Uranium Trimer and Hexamer Featuring Ion-Exchange Properties and the Alexandrite Effect. *Inorg. Chem.* **2018**, *57*, 6753–6761.

(36) Lundgren, G. The Crystal Structure of $U_6O_4(OH)_4(SO_4)_6$. Ark. Kemi **1953**, 5, 349–363.

(37) Falaise, C.; Volkringer, C.; Vigier, J.-F.; Henry, N.; Beaurain, A.; Loiseau, T. Three-Dimensional MOF-Type Architectures with Tetravalent Uranium Hexanuclear Motifs (U_6O_8). *Chem. - Eur. J.* **2013**, *19*, 5324–5331.

(38) APEX2 v2011.4-1: Bruker APEX2 Software Suite; Bruker AXS: Madison, WI, 2011.

(39) Sheldrick, G. A short history of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112–122.

(40) Yu, H. S.; Wei, X. J.; Li, J.; Gu, S. Q.; Zhang, S.; Wang, L. H.; Ma, J. Y.; Li, L. N.; Gao, Q.; Si, R.; Sun, F. F.; Wang, Y.; Song, F.; Xu, H. J.; Yu, X. H.; Zou, Y.; Wang, J. Q.; Jiang, Z.; Huang, Y. Y.. The XAFS beamline of SSRF. *Nucl. Sci. Technol.* **2015**, *26*.

(41) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 2005, 12, 537–541.

(42) Rehr, J. J.; Kas, J. J.; Vila, F. D.; Prange, M. P.; Jorissen, K. Parameter-free calculations of X-ray spectra with FEFF9. *Phys. Chem. Chem. Phys.* **2010**, *12*, 5503–5513.

(43) Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, Theory and Applications in Inorganic Chemistry; Wiley, 1997.

(44) Sun, Q.; Liu, C.; Zhang, G.; Zhang, J.; Tung, C.-H.; Wang, Y. Aqueous Isolation of 17-Nuclear Zr-/Hf- Oxide Clusters during the Hydrothermal Synthesis of ZrO_2/HfO_2 . *Chem. - Eur. J.* **2018**, 24, 14701–14706.

(45) Estes, S. L.; Antonio, M. R.; Soderholm, L. Tetravalent Ce in the Nitrate-Decorated Hexanuclear Cluster $[Ce_6(\mu_3-O)_4(\mu_3-OH)_4]^{12+}$: A Structural End Point for Ceria Nanoparticles. J. Phys. Chem. C **2016**, 120, 5810–5818.

(46) Lin, J.; Jin, G. B.; Soderholm, L. $Th_3[Th_6(OH)_4O_4(H_2O)_6]-(SO_4)_{12}(H_2O)_{13}$: A Self-Assembled Microporous Open-Framework Thorium Sulfate. *Inorg. Chem.* **2016**, *55*, 10098–10101.

(47) Xiao, B.; Langer, E.; Dellen, J.; Schlenz, H.; Bosbach, D.; Suleimanov, E. V.; Alekseev, E. V. Chemical and Structural Evolution in the Th-SeO₃²⁻/SeO₄²⁻ System: from Simple Selenites to Cluster-Based Selenate Compounds. *Inorg. Chem.* **2015**, *54*, 3022–3030.

(48) Knope, K. E.; Soderholm, L. Plutonium(IV) Cluster with a Hexanuclear $[Pu_6(OH)_4O_4]^{12+}$ Core. *Inorg. Chem.* **2013**, *52*, 6770–6772.

(49) Knope, K. E.; Wilson, R. E.; Vasiliu, M.; Dixon, D. A.; Soderholm, L. Thorium(IV) Molecular Clusters with a Hexanuclear Th Core. *Inorg. Chem.* **2011**, *50*, 9696–9704.

(50) Vanagas, N. A.; Wacker, J. N.; Rom, C. L.; Glass, E. N.; Colliard, I.; Qiao, Y.; Bertke, J. A.; Van Keuren, E.; Schelter, E. J.; Nyman, M.; Knope, K. E. Solution and Solid State Structural Chemistry of Th(IV) and U(IV) 4-Hydroxybenzoates. *Inorg. Chem.* **2018**, 57, 7259–7269.

(51) Iskhakova, L. D. G.; Yu, M.; Bondar, S. A.; Klejnman, I. A.; Novik, V. K.; Trunov, V. K. Kristallaufbau von $K_2Ce(SO_4)_3$ ·H₂O. *Neorg. Mater.* **1988**, 24, 998–1003.

(52) Wilson, R. E.; Skanthakumar, S.; Sigmon, G.; Burns, P. C.; Soderholm, L. Structures of Dimeric Hydrolysis Products of Thorium. *Inorg. Chem.* **2007**, *46*, 2368–2372.

(53) Knope, K. E.; Skanthakumar, S.; Soderholm, L. Two Dihydroxo-Bridged Plutonium(IV) Nitrate Dimers and Their Relevance to Trends in Tetravalent Ion Hydrolysis and Condensation. *Inorg. Chem.* **2015**, *54*, 10192–10196.

(54) Lundgren, G. THE CRYSTAL STRUCTURE OF U-(OH)₂SO₄. Ark. Kemi **1952**, 4, 421–428.

(55) Tulsky, E. G.; Long, J. R. Dimensional Reduction: A Practical Formalism for Manipulating Solid Structures. *Chem. Mater.* **2001**, *13*, 1149–1166.

(56) Kovrugin, V. M.; Gurzhiy, V. V.; Krivovichev, S. V. Structural topology and dimensional reduction in uranyl oxysalts: eight novel

phases in the methylamine– $(UO_2)(NO_3)_2$ – H_2SeO_4 – H_2O system. Struct. Chem. 2012, 23, 2003–2017.

(57) Hu, Y.-J.; Knope, K. E.; Skanthakumar, S.; Soderholm, L. Understanding the Ligand-Directed Assembly of a Hexanuclear Th^{IV} Molecular Cluster in Aqueous Solution. *Eur. J. Inorg. Chem.* **2013**, 2013, 4159–4163.

(58) Volkringer, C.; Mihalcea, I.; Vigier, J.-F.; Beaurain, A.; Visseaux, M.; Loiseau, T. Metal–Organic-Framework-Type 1D-Channel Open Network of a Tetravalent Uranium Trimesate. *Inorg. Chem.* **2011**, *50*, 11865–11867.

(59) Martin, N. P.; Volkringer, C.; Falaise, C.; Henry, N.; Loiseau, T. Synthesis and Crystal Structure Characterization of Thorium Trimesate Coordination Polymers. *Cryst. Growth Des.* **2016**, *16*, 1667–1678.

(60) Marcus, Y. A simple empirical model describing the thermodynamics of hydration of ions of widely varying charges, sizes, and shapes. *Biophys. Chem.* **1994**, *51*, 111–127.

(61) Ohtaki, H.; Radnai, T. Structure and dynamics of hydrated ions. *Chem. Rev.* **1993**, *93*, 1157–1204.

(62) Marcus, Y.; Hefter, G. Ion Pairing. Chem. Rev. 2006, 106, 4585-4621.

(63) Carnall, W. T.; Liu, G. K.; Williams, C. W.; Reid, M. F. Analysis of the crystal-field spectra of the actinide tetrafluorides 0.1. UF_4 , NpF₄, and PuF₄. *J. Chem. Phys.* **1991**, *95*, 7194–7203.

(64) Falaise, C.; Neal, H. A.; Nyman, M. U(IV) Aqueous Speciation from the Monomer to UO_2 Nanoparticles: Two Levels of Control from Zwitterionic Glycine Ligands. *Inorg. Chem.* **2017**, *56*, 6591–6598.

(65) Wacker, J. N.; Vasiliu, M.; Huang, K.; Baumbach, R. E.; Bertke, J. A.; Dixon, D. A.; Knope, K. E. Uranium(IV) Chloride Complexes: UCl_6^{2-} and an Unprecedented $U(H_2O)_4Cl_4$ Structural Unit. *Inorg. Chem.* **2017**, *56*, 9772–9780.