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Uranyl Clusters

Cation-Directed Isomerization of the U_{28} Uranyl-Peroxide ClusterAnna F. Oliveri,^{*,[a]} Christopher A. Colla,^[b] Joseph R. Callahan,^[c] Gwendolyn Bogard,^[a] Jie Qiu,^[d] Mateusz Dembowski,^[e] Peter C. Burns,^[d,e] and William H. Casey^[b,c]

Abstract: The conformational dynamics of nanometer-sized actinide ions are exceptionally sensitive to the choice of counterions. A new means of following these dynamics in solution is presented that follows 1H NMR signals. The direct bond between hydrogen and phosphorus atoms in the bridging phosphonic groups of the $[(UO_2)_{28}(O_2)_{20}(PHO_3)_{24}(H_2O)_{12}]^{32-}$ (U_{28}) cluster allows unparalleled recording of the orientations of these bridges in situ. The μ_3 - PHO_3 bridges are organized into two supersets of conformers (facing inward vs. outward from the cluster), but each of these supersets additionally have four

subsets that can be identified based upon orientations of the lone pairs of electrons in the associated oxygen atoms. The ensemble of these subsets changes over days or weeks depending upon bulk solution chemistry, temperature, and pressure. They also reflect cations trapped within the molecule. The 1H NMR spectra at room temperature indicate that the molecular orientation of this enormous ion tunes itself in response to solution composition, which suggests a strategy for selecting host-guest combinations.

Introduction

The mineral *studtite* is a minor product of uranium-ore weathering and, along with the closely related structure *metastudtite*, are the only known peroxo-bridged minerals.^[1,2] These structures form because radioactive decay dissociates water into hydrogen peroxide and other more ephemeral, reactive products.^[3,4] This chemistry is relevant to societal needs because large amounts of liquid radioactive waste were created during nuclear-weapon development.^[5] The accumulated waste is stored in tanks at the Hanford and the Savannah River Reservations, and one expects the tanks to have steady concentrations of hydrogen peroxide because of the high radiation fields.^[5,6] Exploration of the uranyl peroxide system in the laboratory led to discovery of a large new class of polyoxometalate ions.^[7] The family of clusters now encompasses over 180 structures and extends over virtually the complete range of common solution pH conditions.^[1,8] Some of these ions have fullerene topologies,

including U_{60} that is topologically identical to buckminsterfullerene,^[9] but many bridged derivatives have also been discovered, some of which are persistent in aqueous solutions for weeks or months.^[10,11]

As expected, these large clusters change conformation in response to chemical conditions, but methods of following such dynamic responses in solution have been limited.^[12,13] In order to detect such subtle changes, we exploited the covalent character of the hydrogen-phosphorus bond in the phosphonic bridges (μ_3 - PHO_3) of one variety of these cage clusters. In this way, we could use complementary 1H and ^{31}P NMR analyses.^[12,14] The $[(UO_2)_{28}(O_2)_{20}(PHO_3)_{24}(H_2O)_{12}]^{32-}$, U_{28} (Figure 1), cluster was examined in both the solid state and in solution, where two sets of structural conformational isomers, with hydrogen atoms facing both inward and outward, were identified for each μ_3 - PHO_3 bridge via single crystal X-ray diffraction, ^{31}P , and 1H NMR spectroscopy.^[12,14] These two isomers are identified with red (inward-facing) and blue (outward-facing) in the top of Figure 1 and cannot interconvert.

As is well documented for silicates, the oxygen atoms of the μ_3 - PHO_3 bridges are not static, and orientation is dictated by a combination of electronic and steric effects that vary with counterion.^[15,16] Each of the inward- and outward-facing μ_3 - PHO_3 bridge (super)sets is fixed, but can assume four additional orientation subsets depending on the position of the lone pairs of electrons on adjacent bridging oxygens relative to the hydrogen atom (Figure 1A–D). These conformers were identifiable in solution by careful examination of variable temperature 1H and ^{31}P NMR spectra.^[14]

In subsequent text, the two supersets are distinguished with subscripts, *I* and *O*, that identify whether the particular isomer is oriented to face inward, toward the cluster center, or outward,

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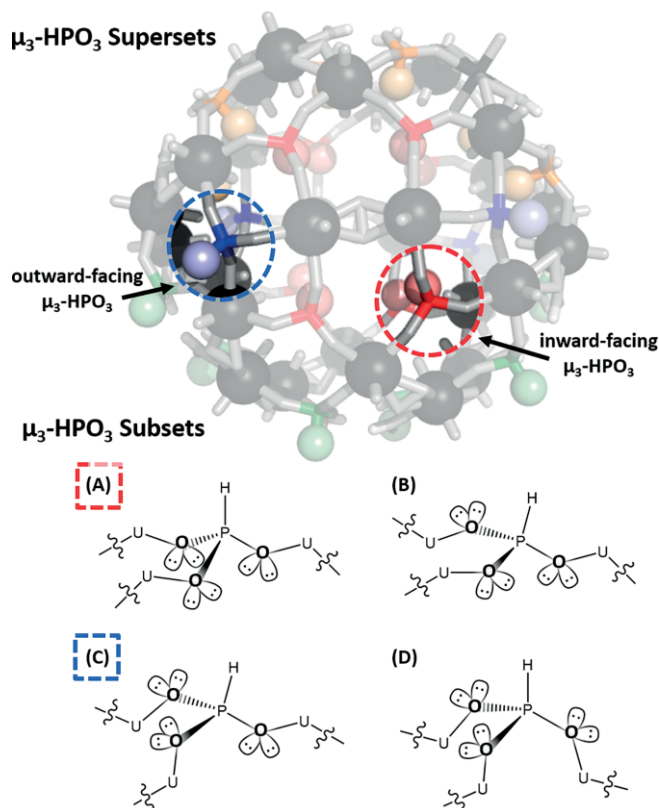


Figure 1. (Top) Two supersets of conformational bridge isomers (inward- and outward-facing μ_3 -PHO₃ bridges) exist within the **U₂₈** cluster. These supersets cannot interconvert. (Bottom) Four subsets (**A–D**) of both inward- and outward-facing conformers, which can dynamically interconvert, can be further identified when considering the orientation of the oxygen atom lone pairs. The coloured boxes around conformer **A** and **C** correlate to the highlighted conformational examples in the top image. In the solid-state structure, the **inward-facing** μ_3 -PHO₃ bridges (red) exist as conformer **A** (**A_I**), while the **outward-facing** μ_3 -PHO₃ bridges (blue) exist as conformer **C** (**C_O**). Uranium atoms are represented by black spheres, oxygen atoms are grey sticks, and the H atoms of the H-P units are emphasized as spheres in this representation.

toward the bulk solution. The subsets are identified by the letters **A–D**. This nomenclature will be used to organize the eight possible μ_3 -PHO₃ bridge conformational isomers for the following discussion (Table 1). Thus, for example, conformer **A** can

Table 1. The eight possible μ_3 -PHO₃ bridge conformers of the **U₂₈** cluster. Each conformer is derived from two supersets separated into four subsets.

Supersets	Subsets			
	A	B	C	D
Inward-facing H	A _I	B _I	C _I	D _I
Outward-facing H	A _O	B _O	C _O	D _O

exist with either an overall inward (**A_I**) or overall outward (**A_O**) orientation. Minute changes in the solution structure of this **U₂₈** cluster can be examined by identifying which μ_3 -PHO₃ bridge conformers (**A_{I/O}**–**D_{I/O}**) relate to each ¹H NMR signal that was previously assigned to the massive cluster using ¹H DOSY NMR at room temperature.^[14] In this manuscript, we propose proton signal assignment and investigate the structural effects caused by the introduction of various potential guest counter-cations.

Results and Discussion

Structure in the Solid State

The choice of counter-cation in the synthesis determines the initial array of conformational bridge subsets that are found in the solid state.^[12] When crystallized in the presence of only K⁺ counter-cations, the set of inward-facing μ_3 -PHO₃ bridges (identified with red in Figure 1) is dominated by the conformer with all the lone pairs of electrons on the oxygen atoms pointing in the opposite direction (outward) from the proton (**A_I**) (Figure 1). In contrast, the μ_3 -PHO₃ bridges with outward-facing hydrogen atoms (identified in blue in Figure 1) prefer the subset conformation with one set of the electron lone pairs pointing inward, while the other two sets point in the same direction as the hydrogen atom (**C_O**) (Figure 1). The K⁺ counter-cation is always necessary for the synthesis of the **U₂₈** cluster; therefore, **A_I** and **C_O** are henceforth treated as the initial structure (i.e., the control) for all further discussion of conformer changes in the solid and solution.

Upon examination of the locations of potassium cations in the crystal structure of **U₂₈**^[12] sample, it appears that the conformers **A_I** and **C_O** are preferred because of guest cations inside the cage, which stabilize the orientation of the lone pairs of electrons within these bridges. Without an internal K⁺ ion, the lone pairs prefer to point outward, into bulk solvent. This preference was resolved using a closely related cluster, the [(UO₂)₂₂(O₂)₁₅(PHO₃)₂₀·(H₂O)₁₀]²⁶⁻ (**U₂₂**), which utilizes potassium salts in the synthesis, but crystallizes with no K⁺ cations inside the cage (Figure 2D).^[12] All protons on the μ_3 -PHO₃ bridges of the **U₂₂** point into the cluster, and the lone pairs point outwards, toward the bulk solvent.^[14] Only conformer **A_I** exists in freshly crystallized **U₂₂**. Correspondingly, if no cations were inside of the **U₂₈** cage, one would expect the outward-facing μ_3 -PHO₃ bridges to exhibit the structure of conformer **D_O**, where all the lone pairs of electrons point outward along with the hydrogen atom. The **U₂₈** cluster, however, cannot be crystallized without internal counterions, and the K⁺ ions cause one set of lone pairs to rotate inward. This rotation forms conformer **C_O** and alleviates strain in the bond angles associated with a sterically unfavorable orientation like **D_O** (Figure 1C–D).

Of the possible eight bridge conformers, only two (**A_I** and **C_O**) are observed in the **U₂₈** crystal structure (identified with dashed circles and boxes in Figure 1), and some potassium ions sit inside the cluster as guests (Figure 2A). These caged cations

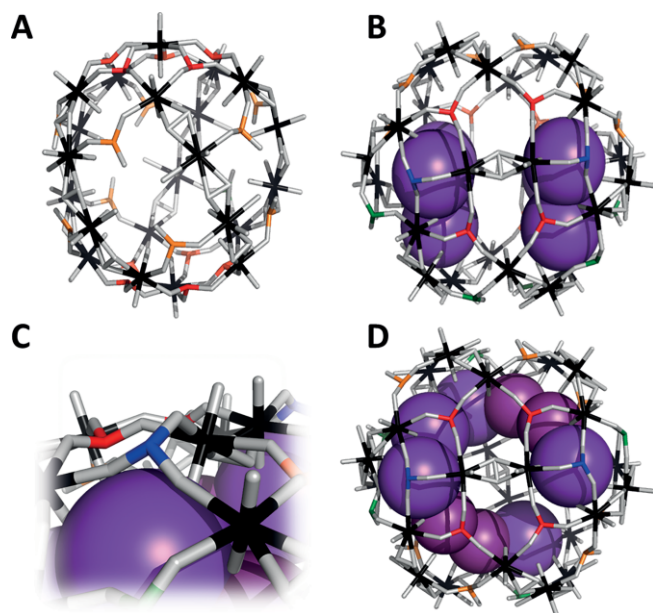


Figure 2. Structures determined via single-crystal X-ray diffraction of A) U_{28} with caged K^+ cations, B) U_{28} with caged K^+ and Na^+ cations, C) conformer B_0 interacting with a caged K^+ ion, and D) U_{22} with no caged K^+ cations. Inward- and outward-facing phosphite bridges are emphasized with color (red: inward-facing μ_3 - PHO_3 , and blue: outward-facing μ_3 - PHO_3 bridges, additionally, orange: inward-facing μ_2 - PHO_3 , green: outward-facing μ_2 - PHO_3). Hydrogen atoms have been eliminated for clarity, uranium atoms are black, oxygen atoms are light grey, and cations are purple spheres.

appear to interact with oxygen atom lone pairs on the interior of the cage, stabilizing specific conformer subsets. To further investigate the guests' role in determining the cage structure, additional cations were added to the synthesis, and the effects were studied in the solid state using X-ray diffraction of crystals.^[12]

The U_{28} cluster was also previously crystallized from aqueous solutions that contained Rb^+ , Cs^+ , or Na^+ (in addition to K^+).^[12] For solutions that contained Rb^+ and Cs^+ , this crystallization yields mixed (K^+ and Rb^+/Cs^+) cations inside the cage structure. With Rb^+/Cs^+ acting as guests, the μ_3 - PHO_3 bridge conformers present (A_1 and C_0) were identical to the control case where K^+ was the only counter-cation used in crystallization. When U_{28} crystallizes with added Na^+ , three interesting things happen (Figure 2B): 1) more cations appear to enter the cage, 2) the set of conformational isomers (initially A_1 and C_0) present become more diverse as B_0 appears, and 3) a new constitutional isomer forms, leading to a new U_{28} structure (See the Supporting Information, CCDC 1575381). The constitutional change to the U_{28} structure is most evident by examining the setting of the peroxo bridges that are in the center of the structures, where a rotation from *eclipsed* to *staggered* is observed (Figure 2A–B). These two constitutional isomers of the U_{28} augment the proposed eight conformational isomers of the phosphonic bridges (e.g., A_1 , C_0) discussed above because the B_0 isomer is observed in the solid state for the first time in this structure (Figure 2C).

Structure in Solution

The signals for the 1H NMR spectrum of U_{28} can be related to the eight conformational bridge isomers at room temperature because the electronic environment of the proton changes as the oxygen atoms rotate to invert geometry (Figure 3). Note that by rotating geometry, we do not mean a superset conversion of the inward-facing hydrogen atom shown in red in Figure 3 to the outward-facing position shown in blue, but simply conversion between subsets A–D. We previously assigned the upfield doublets ($J_{H,P}$) to the protons inside of the cage and the downfield doublets to protons on the outside of the cage.^[14] The electronic environment could change drastically causing a proton far inside the cluster cage (D_1) to have a very different chemical shift than a proton far outside of the cage (D_0) (Figure 3). This change would make the signal with the lowest chemical shift, upfield, conformer D_1 . In our control (K^+ solid sample), the only inward-facing conformer is A_1 ; again referring to Figure 3, this would be the third signal from the right. This A_1 orientation is the dominant inward-facing conformer present. The protons in conformer B_1 and B_0 are closest to the inner- or outer-surfaces of the cage cluster, meaning that in this conformation, the proton on the inward- and outward-facing bridges would have the most similar electronic environments. This 1H NMR signal assignment is also supported by the predominant, outward-facing, conformer in solution being C_0 , which also matches the control. Therefore, the 1H -NMR signals for the μ_3 - PHO_3 bridge conformers from lowest to highest ppm are assigned: $D_1 < C_1 < A_1 < B_1 < B_0 < A_0 < C_0 < D_0$.

As the U_{28} crystals (with only K^+ counter-cations) are dissolved into aqueous solution, the ensemble of isomers varies with time, temperature, pressure, and solution composition, in a similar way as silicates.^[17,18] The evolution does not affect the relative proportion of inward- and outward-facing μ_3 - PHO_3 isomers, since these moieties do not interconvert, but does cause major changes in the subsets (A–D).

Not only does the ensemble of conformational isomers evolve with time (Figure 4), but so does the specific location of a proton with respect to the surface of the U_{28} cage. We can track these changes with 1H NMR via the assigned signals in unprecedented detail. The rates of conformer changes are affected by temperature and pressure, but the final proportion of conformers does not differ from the naturally aged solutions, which are shown in Figure 4. When only K^+ counterions are present, the initial structure is dominated by the A_1 conformer, as expected, but μ_3 - PHO_3 bridge conformers B_1 – D_1 evolve to each become $\approx 15\%$ of the total, leaving only $\approx 55\%$ of the bridges in this original A_1 conformation (Figure 4A). The outward-facing μ_3 - PHO_3 bridge conformers also evolve in relative concentration, but much more slowly, which is in itself interesting (Figure 4B).

The addition of cations other than potassium to the U_{28} solution affects the initial population of conformers, the rate of evolution of conformer change, and the ultimate ratio of bridge conformers at equilibrium. However, ionic strengths also increase as these counterions are changed because these cations are superadded to the potassium that is released by dissolution of the U_{28} potassium salts to make the stock solution. When

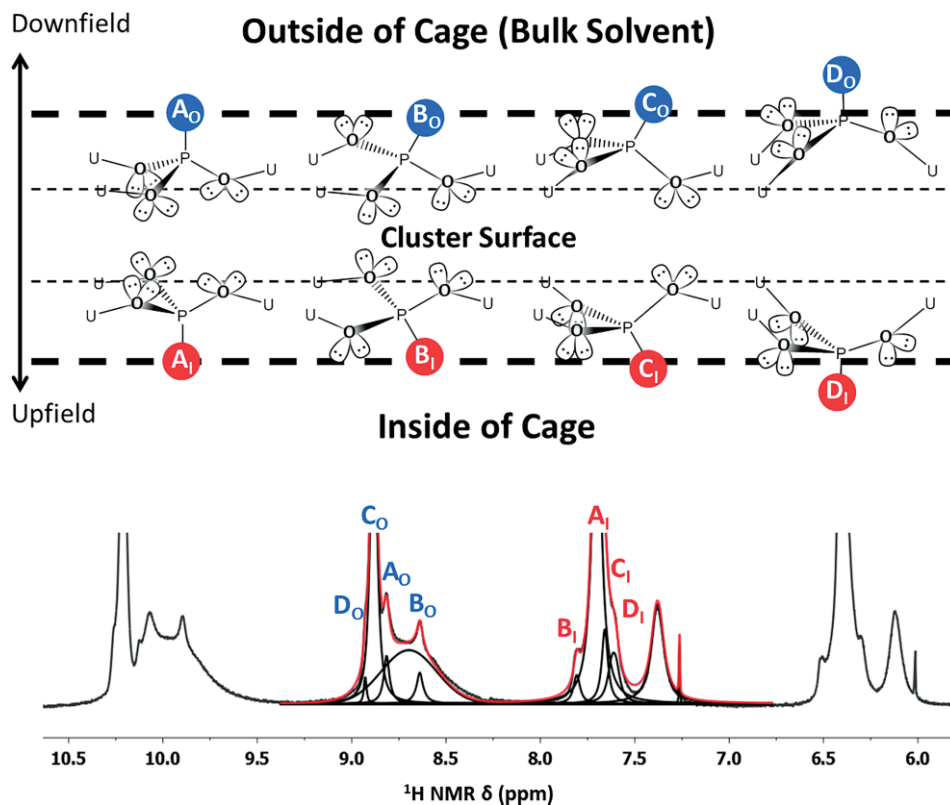


Figure 3. (Top) Two supersets of conformers are organized depending upon whether the μ_3 - PHO_3 bridges face outward (subscript "O", blue) or inward (subscript "I", red) to the cluster. The four additional conformer subsets can be distinguished, not only by structure, but also by the distance between the positions of the proton with respect to the surface of the U_{28} cage cluster. (Bottom) The ^1H -NMR signals for the inward-facing μ_3 - PHO_3 bridges are upfield of the outward-facing bridges,^[14] indicating that the proton environment inside of the U_{28} cage is more shielded than those outside of the cage. Signals for the μ_3 - PHO_3 bridge conformers from lowest to highest ppm are assigned: $\text{D}_1 < \text{C}_1 < \text{A}_1 < \text{B}_1 < \text{B}_0 < \text{A}_0 < \text{C}_0 < \text{D}_0$.

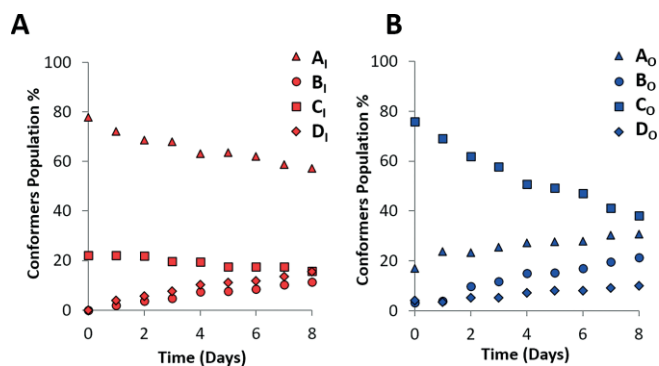


Figure 4. Evolution of the bridge conformation populations within the U_{28} cluster in solution. The percentage of each conformer in solution is plotted over time for both the A) inward-facing (red) and B) outward-facing bridges (blue). This data was acquired by integrating the area under the ^1H NMR signals.

di/trivalent cations (Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , and La^{3+}) were added to solutions of the dissolved potassium salt of U_{28} , immediate precipitation was observed. The results of these additions will therefore not be discussed further.

Addition of monovalent cations (Li^+ , Na^+ , Rb^+ , Cs^+ , and NH_4^+) did not cause precipitation, but in the presence of most of these monovalent cations (Li^+ , Rb^+ , Cs^+), the ensemble of conformers of U_{28} in solutions evolve in an identical fashion as solutions that have only K^+ counterions present. The most interesting results were observed in the solutions containing Na^+ and NH_4^+ counter-cations, because unique conformer configurations were observed (Figure 5 and the Supporting Information), but the second constitutional isomer, with bridges staggered relative to one another, from Figure 2B was not observed.

The addition of Na^+ changes the conformer populations almost immediately (Figure 5). In contrast to the case where K^+ is the only counter-cation, there are visible changes in the ^1H -NMR signals as increasing equivalents of Na^+ are added to solutions of the U_{28} cluster. The inward-facing μ_3 - PHO_3 bridges change from an A_1 subset dominating the population (Figure 5A) to an ensemble that is clearly dominated by conformer C_1 (Figure 5B). Inward-facing conformers B_1 and D_1 remain less than 20% of the total. This high population of conformer C_1 means that two sets of lone pairs of electrons rotate inward, and are stabilized by, the additional Na^+ cations inside the cage structure (Figure 5C). Addition of NH_4^+ to the U_{28} solution has a similar, yet smaller effect as Na^+ .

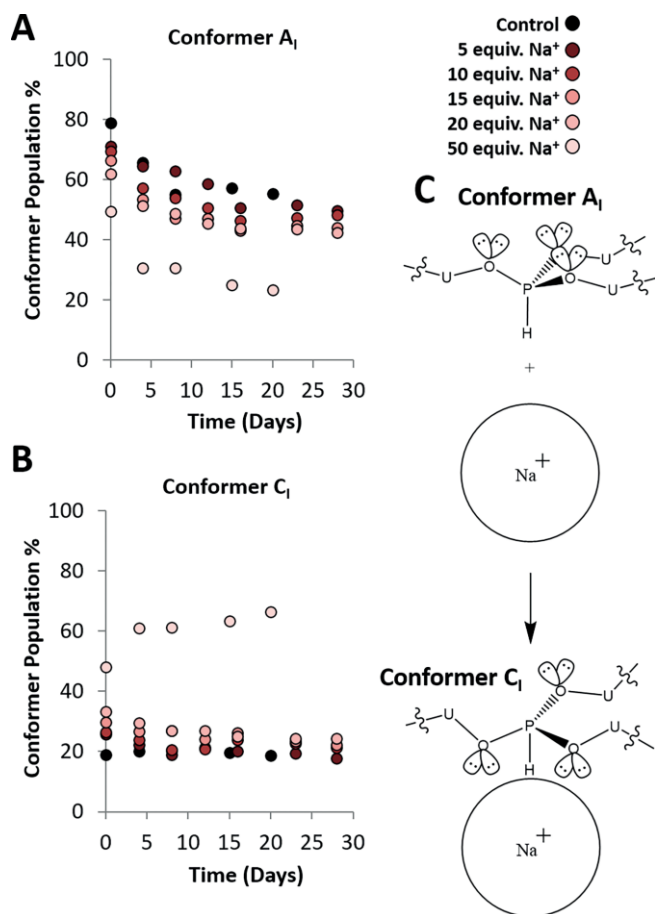


Figure 5. Changes in the isomer population (as percentages) of the inward-facing conformers as a function of time. As more Na⁺ is introduced to the system, A) conformer A₁ becomes less abundant, and B) conformer C₁ becomes preferred, C) indicating that the bridge inverts, much like an umbrella in a strong wind.

Conclusions

Changes in the isomer populations of nanometer-sized uranyl peroxide clusters in solution have long been suspected but have been difficult to document because the molecules include few NMR-sensitive nuclei. Here we utilize the unreactive nature of the hydrogen atom on the phosphonic bridges to follow subtle changes in isomer populations with solutions composition. The importance of counterions is unsurprising, given that these highly charged anions are separated from one another by only a few water molecules in solution.

The response of the surface of the molecules to changes in counterion concentrations suggests a means of adapting these molecules for host–guest chemistry. Supramolecular assemblies rely on noncovalent interactions, such as hydrogen bonding, π – π stacking, and Lewis Acid–Base chemistry, to maintain nested structures. The flexibility of the cage structure that we demonstrate, the reversible nature of the ligand–metal–bond, and the

high number of oxygen atoms creates the flexible host environment for manipulation.

Experimental Section

Chemicals were purchased and were used as received without further purification. The (UO₂)₂₈(O₂)₂₀(HPO₃)₂₄(H₂O)₁₂³²⁻ and (UO₂)₂₂(O₂)₁₅-(HPO₃)₂₀(H₂O)₁₀²⁶⁻ cluster was synthesized at University of Notre Dame according to previously published literature procedures.^[12] All ¹H NMR experiments were performed on a Bruker 800 MHz spectrometer. All spectra were acquired at 298 K in 5 mm tubes. NMR spectroscopic data were processed using MestReNova. Structural images of the cluster were produced in PyMol from a cif file. Cartoon images of μ_3 -PHO₃ bridge conformers were produced in ChemDraw and are not meant to represent real bond length and angles. CCDC 1575381 (for U₂₈) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: Actinide chemistry · NMR spectroscopy · Cluster compounds · Reaction kinetics · Isomerization

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