Uranyl Clusters

Dynamic Phosphonic Bridges in Aqueous Uranyl Clusters

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Abstract: The uranyl cage clusters $(UO_2)_{22}(O_2)_{15}(PHO_3)_{20}(H_2O)_{10}^{26-}$ (**U22**) and $(UO_2)_{28}(O_2)_{20}(PHO_3)_{24}(H_2O)_{12}^{32-}$ (**U28**) can be probed in aqueous solutions by using a combination of ^{1}H Diffusion-Ordered Spectroscopy (DOSY) and ^{1}H-^{31}P Heteronuclear-Single Quantum Coherence (HSQC) spectroscopy. This class of clusters is ideal for ^{1}H NMR analysis in D_2O because of the covalent character of the H–P bond in the phosphonic bridges. ^{1}H DOSY indicates that the clusters are stable in solu-

tion and provides hydrodynamic radii of 9.8 ± 0.4 Å for the **U22** and 12.3 ± 0.5 Å for the **U28** clusters. Furthermore, ^{1}H-^{31}P HSQC delivers unequivocal signal assignment for both nuclei, which enables solution dynamics to be monitored by variable-temperature experiments, and reveals the presence of phosphonic-bridge conformers. The results provide some of the first dynamic information about steady conformational changes in these enormous actinide macroions.

Introduction

Environmental scientists and geochemists are intensely interested in the speciation of actinide elements in solution because of existing extensive subsurface contamination and the potential for leakage during the mining and storage of radioactive materials. In oxidizing environments, uranium typically exists as the uranyl ion (UO_2^{2+}) and has an affinity for radiolytic peroxide, such as is represented in the mineral studtite.[1] An entirely new class of uranyl-peroxide compounds was discovered in the past decade, and these cluster ions can extend to ca. 4 nm in size.[2] Varieties are stable and soluble across the entire pH range of natural waters.[3] These clusters are particularly relevant to environmental chemistry because H_2O_2 forms during the dissociation of water by radiolysis in repositories for radioactive waste.[4,5] Here we use the PHO_3^{2-} bridges in one unique set of such clusters to establish both the stabilities and dynamics in solution via Nuclear Magnetic Resonance (NMR) spectroscopy.

Results and Discussion

Uranyl-peroxide cage clusters with phosphonic bridges, $K_{14}Na_{12}(UO_2)_{22}(O_2)_{15}(PHO_3)_{20}(H_2O)_{10}$ (**U22**) and $K_{32}(UO_2)_{28}(O_2)_{20}(PHO_3)_{24}(H_2O)_{12}$ (**U28**),[6] were synthesized for this study because the hydrogen atoms of phosphonate are not labile on the NMR

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timescale (Figure 1). NMR spectroscopy allows access to detailed solution stability and structural information by probing individual nuclei instead of entire molecules, although information about the dynamics of these large actinide clusters is exceedingly rare.[7] Herein ^{1}H Diffusion-Ordered Spectroscopy (DOSY), ^{1}H-^{31}P Heteronuclear Single Quantum Coherence (HSQC), and variable temperature ^{1}H and ^{31}P NMR spectroscopy
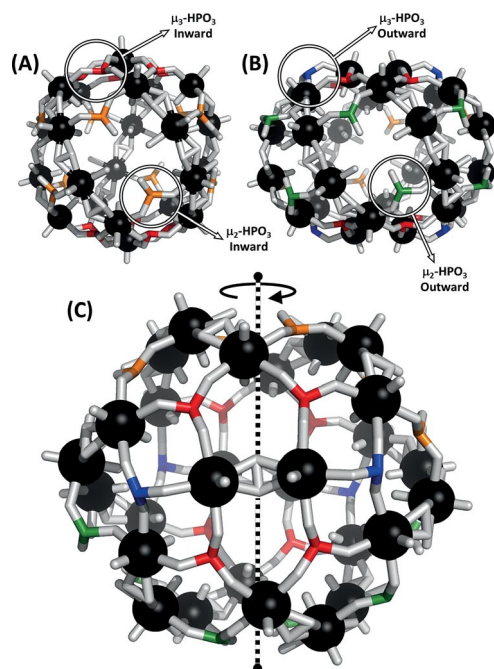

Figure 1. Molecular structures of (A) **U22** and (B and C) **U28** determined by single-crystal X-ray diffraction (Na^+ and K^+ counterions have been omitted for clarity). **U28** (C) has a C_2 axis. Black spheres are U^{VI} sites and the 4 types of phosphonic bridges are labelled and emphasized with color – red: inward-facing μ_3-PHO_3; blue: outward-facing μ_3-PHO_3; orange: inward-facing μ_2-PHO_3; green: outward-facing μ_2-PHO_3.

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Communication

were used to characterize and observe the dynamics of the U_{22} and U_{28} clusters in aqueous solution.

On the basis of symmetry and orientation, there are four general types of binding environments for protons on the phosphonic bridges in these clusters (Figure 1). These protons are on μ_2-PHO_3 and μ_3-PHO_3 bridges that point either into, or out of, the cage cluster (Figure 1). The ^1H and ^{31}P NMR spectra at ambient conditions ($7.2 \leq pD \leq 8.0$) of the U_{22} and U_{28} phosphonic clusters yield broad doublets because of the large $J_{H,P}$ coupling constants (630–707 Hz) associated with a direct H–P bond (Figure 2A–D).[8] The signals associated with the U_{22} and U_{28} clusters can be distinguished from smaller solutes by the diffusion coefficients provided by ^1H DOSY (Figure 2E).[9] ^1H DOSY verifies that the U_{22} and U_{28} clusters are stable in solution as intact clusters. The large clusters diffuse more slowly

than smaller species that might be present from the synthesis or as minor decomposition products.[6] ^1H DOSY indicates that all signals between +5.5 and +10.5 ppm diffuse at rates expected for nanometer-sized clusters (except the sharp doublet centered at +6.8 ppm, which is assigned to free H_3PO_3) and therefore correspond to the phosphonic bridge hydrogen atoms (Figure 2C and E). As expected, U_{28} ($0.90 \times 10^{-10} \pm 0.16 \times 10^{-10}$ m^2 s^{-1}) diffuses more slowly than U_{22} ($1.23 \times 10^{-10} \pm 0.07 \times 10^{-10}$ m^2 s^{-1}), which indicates a slightly larger species. The Einstein–Stokes equation can be used to estimate sizes from the measured diffusion coefficients if viscosities are independently estimated.

The viscosities of the solutions used for DOSY experiments were calculated by using the internal standard tetraethylammonium (TEA) hydroxide, which was primarily chosen because all cluster solutions already have small amounts remaining from the synthesis (Figure 2A, C, and E).[6] Separately, a calibration curve was created by using various concentrations of aqueous TEA solutions that related the measured diffusion coefficients to the measured viscosities (see Experimental Section). The diffusion coefficients of the TEA ion in U_{22} and U_{28} solutions were then used to calculate directly the viscosities of the experimental solutions. By using the calculated viscosities and the measured diffusion coefficient of each cluster, the hydrodynamic radii were calculated and complement the previous single crystal X-ray diffraction (XRD) and small angle X-ray scattering (SAXS) size analyses of the cluster's core dimensions (Table 1).[6,10]
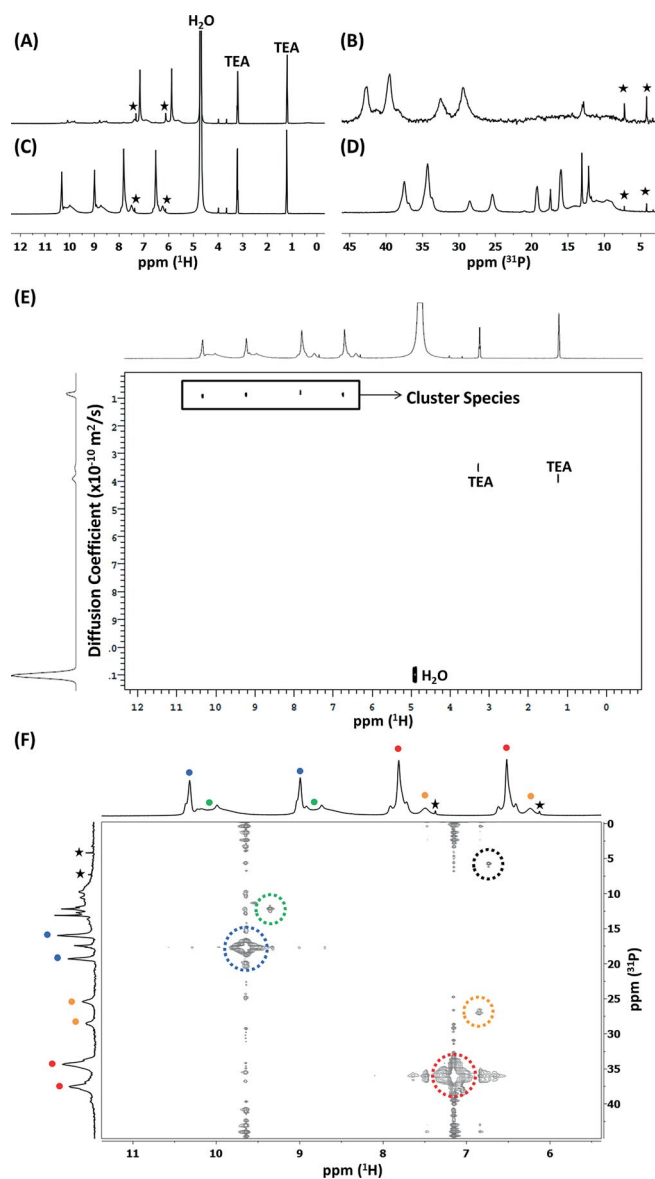

Table 1. Various size measurements of the U_{22} and U_{28} cage clusters.[6]

Technique	Radius type	U_{22} radius [Å]	U_{28} radius [Å]
DOSY	Hydrodynamic	9.8 ± 0.4	12.3 ± 0.5
SAXS	Inner/Outer Cage	5.5/9.1	5.7/10.2
XRD	Inner/Outer Cage	5.5/9.1	5.8/10.8

On the basis of the crystal structures of these two clusters, every hydrogen atom of the phosphonic bridges in U_{22} points into the cage and away from the bulk solution. In contrast, U_{28} has 14 inward-pointing and 10 outward-pointing phosphonic bridges.[6] The strong doublet signals in the ^1H NMR spectrum of U_{22} appear in the range +5.5 to +8.0 ppm, while U_{28} has signals from +5.5 to +10.5 ppm, which indicates that the nuclei inside the cage are more shielded than those on the outside (Figure 2A and C). The inward facing and outward facing regions in the ^{31}P NMR spectra can be determined in the same fashion. The two sets of ^{31}P signals in the spectrum of U_{22} appear downfield in the +25 to +45 ppm range, while U_{28} has ^{31}P signals from +15 to +45 ppm (Figure 2B and D). ^1H-^{31}P HSQC confirms that the inward-facing phosphonic-bridge signals of the 1D ^1H and ^{31}P spectra correlate (Figure 2F). With phosphonic bridges pointing out of the cage, we see an opposite trend. HSQC reveals that the ^1H NMR signals between +8.5 and +10.5 ppm correlate to the ^{31}P signals between +15 and +22 ppm (Figure 2F).

The interpretation of the NMR spectra relies on inferences about the dynamics of the bridge orientation within the cage clusters. In the ^1H NMR spectra, μ_3-PHO_3 bridges are assumed to produce relatively sharp signals because of the rigid binding conformation. The μ_2-PHO_3 bridges are assumed to have more

Figure 2. The ^1H and ^{31}P NMR spectra of U_{22} (A,B, respectively) and U_{28} (C,D, respectively) in D_2O. The ^1H DOSY (E) and ^1H-^{31}P HSQC (F) of U_{28}. (*) H_3PO_3 signals. The 2D NMR spectroscopic data for U_{22} is provided in the Supporting Information.

freedom and therefore produce broader signals. HSQC differentiates between the μ_2-PHO$_3$ and μ_3-PHO$_3$ bridges in the ^{31}P NMR spectra where differentiation is more difficult at ambient conditions. Complete signal assignments are provided in Figure 3 and in the Supporting Information. It should be noted that there are small signals in the spectra of **U$_{22}$** in the region assigned to outward-facing bridges (Figure 2A), which indicates that a small number convert to this orientation, which is dynamically interesting and will be explored in more detail in a subsequent paper. It is also virtually impossible to see signals for μ_2-PHO$_3$ that face toward the bulk solution in the ^{31}P NMR spectra at room temperature. However, the signals are clearly evident in the +10 to +20 ppm region in the HSQC spectra and become evident in the 1D ^{31}P spectra at decreased temperatures.

Our interpretations of the **U$_{22}$** and **U$_{28}$** NMR spectra are supported by variable-temperature (VT) NMR experiments conducted over the temperature range 5–55 °C (Figure 3 and Supporting Information). Upon heating the **U$_{28}$** cluster, four μ_3-PHO$_3$ signals appear in the regions of the ^{31}P NMR spectra assigned to both inward-facing and outward-facing bridges (Figure 3E), which make up the set of conformers (Figure 4A–D). The difference between conformers is the orientation of the lone pairs on the oxygens atoms of the PHO$_3$ moieties. Elevated temperatures cause the cluster to tumble faster through solution, sharpening these ^{31}P signals. We speculate that the μ_3-PHO$_3$ conformer signals are undetectable in the ^{1}H NMR spectra unless the sample is cooled, because of broadening caused by movement (Figure 3C). Although both types of phosphonic bridges can flex, or convert between conformers, the μ_3-PHO$_3$
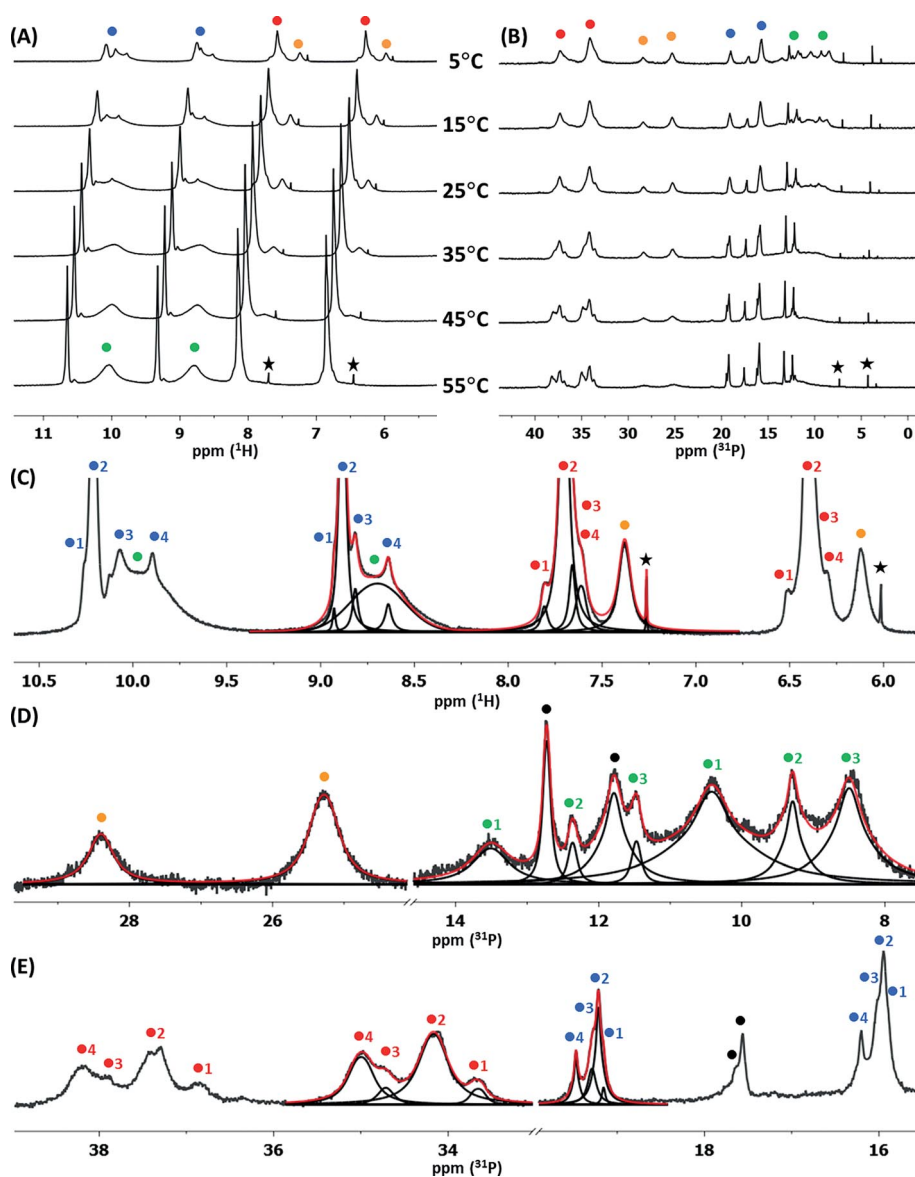

Figure 3. Variable-temperature ^{1}H NMR (A) and ^{31}P NMR (B) spectra for a saturated solution of **U$_{28}$** in D$_2$O. Peak fitting of the **U$_{28}$** signals is shown for the ^{1}H NMR spectrum at 15 °C (C), the μ_2-PHO$_3$ ^{31}P signals at 5 °C (D), and the μ_3-PHO$_3$ ^{31}P signals at 55 °C (E). Specific phosphonic bridges are indicated by color – red ball: μ_3-PHO$_3$ inward-facing; blue ball: μ_3-PHO$_3$ outward-facing; orange ball: μ_2-PHO$_3$ inward-facing; green ball: μ_2-PHO$_3$ outward-facing. Additional signals are free H$_3$PO$_3$ (*) and unassigned phosphorus-containing contaminants (black ball).

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bridges are rigid in comparison to the μ_2-PHO$_3$ bridges. The μ_2-PHO$_3$ bridges also have motional flexibility that is not available to the μ_3-PHO$_3$ bridges, which means that the conformers (Figure 4E–G) are only visible in the ^{31}P NMR spectra at low temperatures (Figure 3D) where rotational motions are slowed.
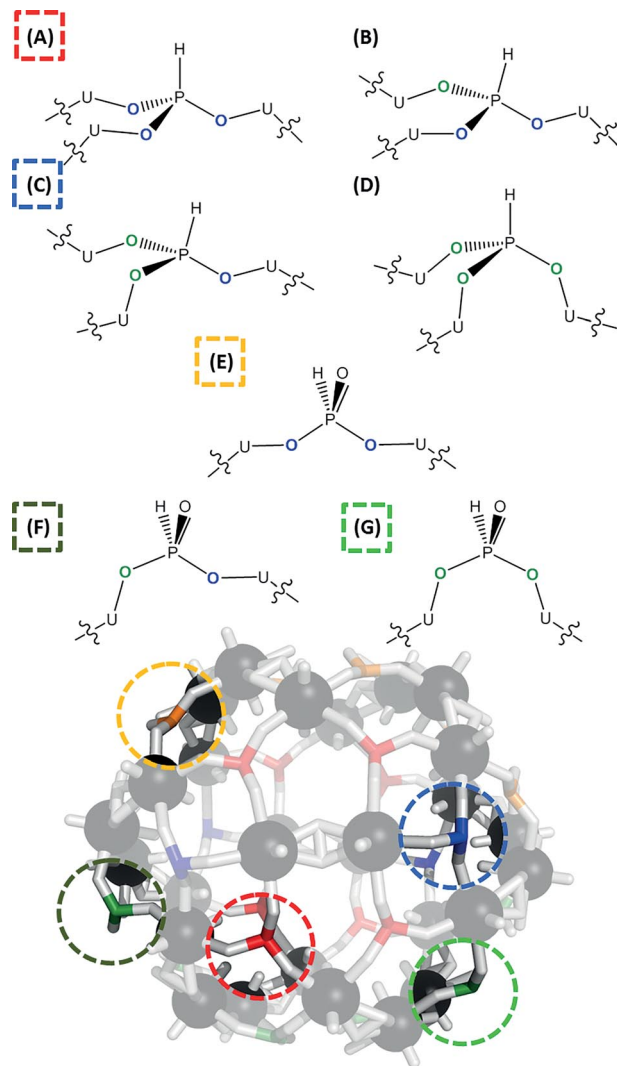

Figure 4. Representations of the possible rigid μ_3-PHO$_3$ bridge conformers (A–D) and the μ_2-PHO$_3$ bridge conformers (E–G). The two possible orientations of the oxygen atoms are shown in blue and green. Five of these conformers are visible in the crystal structure of the **U$_{28}$** cluster.

The differences between the population of phosphonate-bridge conformers in the solid-state structure of these clusters and in solution imply fascinating dynamics upon dissolution. Out of the 14 possible bridge conformers, five are present in the crystal structure of **U$_{28}$** (Figure 4), and **U$_{22}$** only has two (Figure 4A and E). Over the temperature range in this study, 12 conformers are visible for both the **U$_{28}$** and **U$_{22}$** clusters in solution.

Conclusion

The phosphonic bridges in the **U$_{22}$** and **U$_{28}$** uranyl cage clusters allow insight into the dynamics of large actinide cluster species.

The NMR experiments clearly show that the clusters are stable in aqueous solutions and have hydrodynamic radii that complement core sizes obtained from X-ray methods. HSQC assist in the assignment of NMR signals to specific nuclei in the cluster structure, which allows identification of different conformations of the phosphonic bridges. This work is particularly significant because the sets of such actinide clusters now extend to beyond >60 distinct molecules,[1,3] yet the dynamics of these ions in solution are poorly understood. Preliminary high-pressure NMR data indicates systematic changes in the population of phosphonic-bridge conformers, which will certainly also be affected by the choice of solution composition and counterions. This work is underway.

Experimental Section

Chemicals were purchased from Sigma–Aldrich and were used as received without further purification. The $(UO_2)_{28}(O_2)_{20}(PHO_3)_{24}$-$(H_2O)_{12}{}^{32-}$ and $(UO_2)_{22}(O_2)_{15}(PHO_3)_{20}(H_2O)_{10}{}^{26-}$ clusters were synthesized according to literature procedures.[6] All ^{1}H and ^{31}P NMR experiments were performed on Varian 600 MHz and Bruker 500 MHz spectrometers. 1D data was processed using MestReNova. All spectra were acquired at 298 K in 5 mm tubes. The ^{1}H DOSY experiments were performed on the Varian 600 MHz spectrometer using the Gradient Stimulated Echo with Spin-Lock and Convection Compensation (DgsteSL_cc) pulse sequence. All Varian Software standard default settings were kept for DOSY unless otherwise stated. The diffusion delay was increased to 200 ms, the diffusion gradient length was set to 2 ms, the number of increments was increased to 40, the lowest-gradient value was set to 1000, and the highest-gradient value was lowered to 25000. The alternate gradient sign on odd scans and lock gating during gradients options were also selected. Using an Ostwald viscometer, the viscosity of TEA/D$_2$O solutions was measured (5, 8, 11, and 14 %) and then plotted against the measured diffusion coefficient to produce a standard calibration curve. The TEA contaminant signals in the cluster solutions were then used to calculate the viscosity for each DOSY experiment. The gradient strengths of the Varian 600 MHz were calibrated by using β-cyclodextrin.[9] The ^{1}H-^{31}P HSQC experiments were performed using a modified ^{1}H-^{13}C phase cycled pulse sequence on the Bruker 500 MHz spectrometer.

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