

Rapid Self-Assembly of Uranyl Polyhedra into Crown Clusters

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Supporting Information

Synthesis

Caution: Although depleted uranium was used in these experiments, it is radioactive and should only be handled by qualified personnel in appropriate facilities.

Clusters self-assembled in aqueous solution, and in each case crystals formed within 15 minutes. Crystallization continued for ~3.5 h, at which time they were replaced by a fine-grained amorphous yellow precipitate over the course of 2 h. At that time the solution over the precipitate had become colorless. Although LiOH is included in two of the synthesis procedures given below because these produced the crystals that were characterized by X-ray diffraction, other experiments verified that LiOH is not needed to produce these clusters.

U32_{R-1}: 0.250 mL of 0.5 M aqueous uranyl nitrate hexahydrate was combined with 0.300 mL of 30 % peroxide and 0.150 mL of 4 M aqueous ammonium hydroxide in a 4 mL glass vial.

U32_{R-2}: 0.100 mL of 0.5 aqueous (UO₂)(NO₃)₂ · 6 H₂O, 0.200 mL of 30 % peroxide, 0.05 mL of 4 M aqueous NH₄OH, and 0.050 mL of 4 M aqueous LiOH were combined in a 4 mL glass vial.

U32_{R-3}: 0.100 mL of 0.5 M aqueous (UO₂)(NO₃)₂ · 6 H₂O, 0.200 mL of 30 % peroxide, 0.05 mL of 4 M aqueous NH₄OH, and 0.100 mL of 4 M aqueous LiOH were combined.

Single-Crystal X-ray Diffraction

X-ray diffraction data were collected for each compound at 110 K using a Bruker Platform goniometer, an APEX II CCD detector, and MoK α radiation. Semi-empirical corrections for absorption were applied to the full sphere of data collected in each case. Data were integrated using the Bruker APEX II software and the SHELXTL system of programs was used for the solution and refinement of each structure.

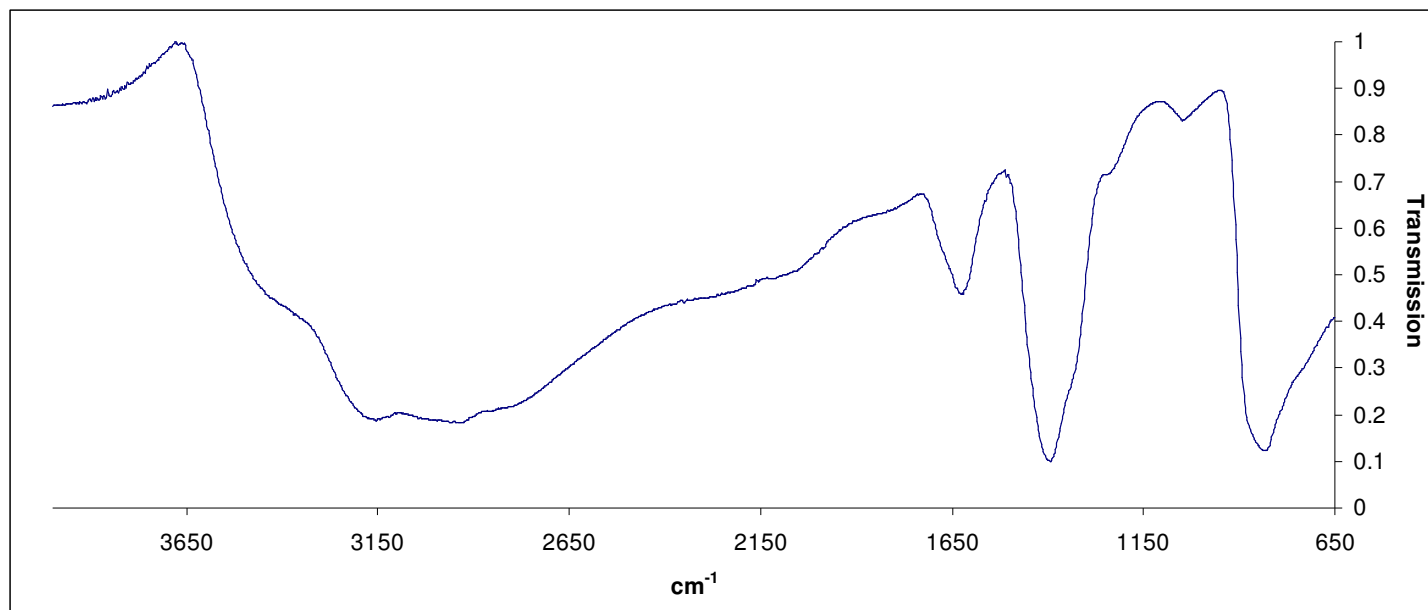
Structure refinements for crystals containing nano-scale clusters of uranyl polyhedra are difficult due to several factors: (1) the strong scattering contrast between the U atoms and lighter atoms makes it difficult to precisely determine the positions of the lighter atoms, (2) the presence of significant void spaces within the clusters reduces diffraction intensity, and (3) disorder of counterions and H₂O groups that occur between and within the clusters is common. Useful data for such a crystal is typically only attainable to 2 θ ~ 45° for Mo radiation. The refined bond lengths have errors of ~ 0.02 Å or more, the data generally does not support refinement of anisotropic displacement parameters for O atoms, and it is not possible to locate H atoms. Despite these various shortcomings, X-ray diffraction provides essential and reliable information concerning the polyhedral connectivity and compositions of clusters of uranyl polyhedra.

The SQUEEZE routine, as implemented in PLATON¹, performs corrections for solvent-accessible void spaces. Data corrected using this routine provided superior structure refinements for crystals containing U_{32R-1} , U_{32R-2} , and U_{32R-3} as judged by significant improvements of the agreement indices. SQUEEZE indicated that crystals of U_{32R-1} contain 8026 Å³ of solvent-accessible void space containing 6917 electrons. For crystals of U_{32R-2} , the routine indicated the presence of 7909 Å³ of solvent-accessible void space containing 4591 electrons. In the case of crystals of U_{32R-3} , SQUEEZE indicated the presence of 7909 Å³ of solvent-accessible void space containing 6974 electrons. Note that the NH_4^+ counter ions are located in the void spaces and were not located in the structure determination.

Crystallographic details are provided in a separate file containing tables for each compound. CIF files are available online.

Infrared Spectra

Infrared spectra were obtained for single crystals of each compound using a SensIR technology IlluminatIR FT-IR microspectrometer. A single crystal of each compound was placed on a glass slide, and the spectrum was collected with a diamond attenuated total reflectance (ATR) objective. Each spectrum was taken from 650 to 4000 cm⁻¹ with a beam aperture of 100 µm. The three spectra were indistinguishable, and only one is shown here. Peaks at 1633 cm⁻¹ and the band from 2770-3470 cm⁻¹ are due to water and hydroxide vibrations. Ammonium vibrations occur at 1403, 1251, and 1055 cm⁻¹ and the mode at 839 cm⁻¹ is attributed to the uranyl ion.



X-ray powder diffraction data was collected for the fine-grained precipitate using a Bruker Davinci system at Cu radiation. The data indicate that the powder is essentially amorphous. Y axis: Intensity (counts), X axis: 2-theta (Cu radiation).

