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Uranyl Diphosphonates with Pillared Structures

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A series of five uranyl diphosphonates with pillared and canted pillared structures have been prepared and characterized. These compounds are constructed from UO_6 tetragonal bipyramids and UO_7 pentagonal bipyramids that are bridged by the diphosphonate anions. All of these compounds fluoresce at room temperature.

Uranyl phosphonates have displayed remarkably rich structural chemistry,[1] phase transitions,[1a−e] and luminescence.[1b] Phase transitions in the uranyl phenylphosphonate system are perhaps the most intriguing, where it was documented that a transformation from a cis (α-UPP) to a trans (β-UPP) conformation occurs at room temperature.[1b,c] Upon exposure to Na^+ or Ca^{2+} cations in an aqueous environment, both of these phases transform from one-dimensional structures into a hollow nanotubular form, γ-UPP.[1a] The structural complexity of uranyl methyl- and phenylphosphonates has been enhanced through the incorporation of organoammonium cations.[2] Traditionally, protonated aliphatic amines have been used to direct the structures of uranyl compounds. We have demonstrated that aromatic amines such as bipyridyl can also serve as structure-directing agents and also as ligands for uranyl cations.[3] Herein, we describe preliminary results on the syntheses, structures, and Raman and fluorescence spectroscopy of uranyl diphosphonates that adopt complex pillared structures. These compounds contrast with previously reported templated uranyl phosphonates that were all two-dimensional.[2]

Hydrothermal reactions (180 °C, autogenously generated pressure, 24 h) of uranyl nitrate or uranyl acetate with 1,4-benzenediphosphonic acid in the presence of a variety of organic templates (1,10-phenanthroline, 2,2′-bipyridyl, piperazine, and 1,4-diazabicyclo[2.2.2]octane) and very small quantities of hydrofluoric acid result in the formation of crystals of five new uranyl diphosphonates with organic structure-directing agents $[C_{10}H_{10}N_2]_2\{(UO_2)_3[C_6H_4(PO_3)_2]_2\}_2\cdot 2H_2O$ (UBBISP1), $[C_4H_{12}N_2]\{(UO_2)_2[C_6H_4(PO_3H)_2]_3\}\cdot 2H_2O$ (UBBISP2), $[C_{10}H_9N_2]_2\{(UO_2)_2[C_6H_4(PO_3H)_2]_3\}\cdot 2H_2O$ (UBBISP3), $[C_6H_{12}N_2]\{(UO_2)_2[C_6H_4(PO_3H)_2]_3\}\cdot 2H_2O$ (UBBISP4), and $[C_{12}H_{10}N_2]\{(UO_2)_3[C_6H_4(PO_3)_2]_2\}\cdot H_2O$ (UBBISP5). There are subtle features associated with these reactions. For example, when all other conditions are held constant, the replacement of uranyl nitrate by uranyl acetate can result in the formation of different structures, as was found with UBBISP1 and UBBISP3. This is most likely a subtle pH effect.

Single-crystal X-ray diffraction studies on each of these compounds reveal a three-dimensional structure constructed from UO_7 pentagonal bipyramids or combinations of UO_7 units and UO_6 tetragonal bipyramids that are bridged by PO_3 moieties of the diphosphonate anions. The UO_6 and UO_7 units contain a central uranyl, UO_2^{2+}, core with typical U=O bond distances averaging 1.778(8) Å. The structures could be considered to be pillared in the sense that there are uranyl layers that are bridged by the diphosphonate anions. However, in UBBISP2, UBBISP4 (UBBISP2 and UBBISP4 possess the same basic framework), and UBBISP5, the uranyl phosphonate layers are corrugated. A consequence of this is that the pillars are canted in these compounds. There is no correlation between the presence of only UO_7 building units versus those compounds with a combination of UO_7 and UO_6 building units and the overall framework that is formed. For example, both UBBISP1 and UBBISP5 possess both kinds of building units, but UBBISP5 has highly puckered uranyl layers and canted phosphonates, whereas UBBISP1 has relatively flat layers and the phosphonates are approximately perpendicular to these layers. There is also no correlation between the partial protonation of the phosphonates found in UBBISP2, UBBISP3, and UBBISP4 and the overall

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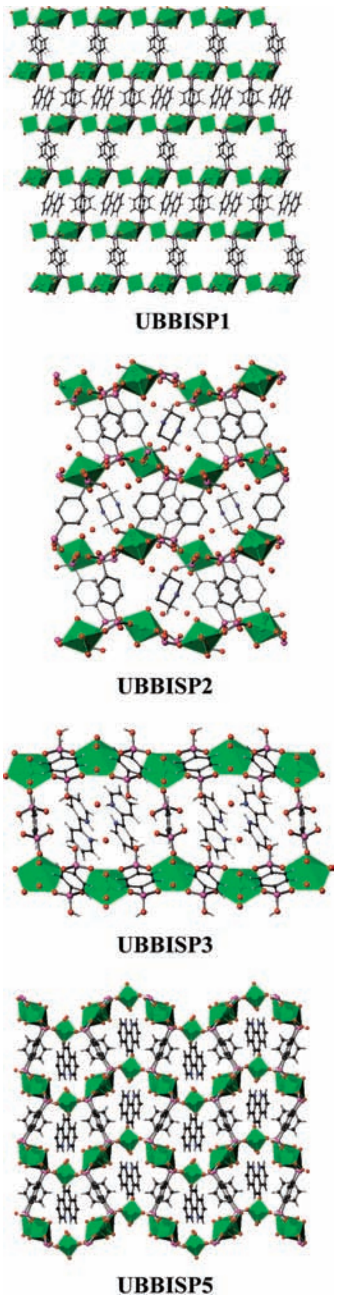

Figure 1. Views of the pillared and canted pillared networks of the uranyl diphosphonate series UBBISP1−5. Disordered cations have been omitted for clarity from UBBISP1, resulting in the open channels viewed here.

topology of the framework; i.e., the protonation is not the exclusive cause of the puckering of the layers. These compounds do share in common two-dimensional features that are most likely induced by the terminal nature of the uranyl oxo atoms.

The presence of the protonated organic amines and water molecules creates channels in the structures. These channels measure approximately 6.3 × 8.3, 8.0 × 8.3, and 8.2 × 8.2 Å in UBBISP1, UBBISP2, and UBBISP5, respectively. The question always arises as to whether the organoammonium cations are space-filling, structure-directing, or true templates?[4] In this group of compounds, UBBISP2 and

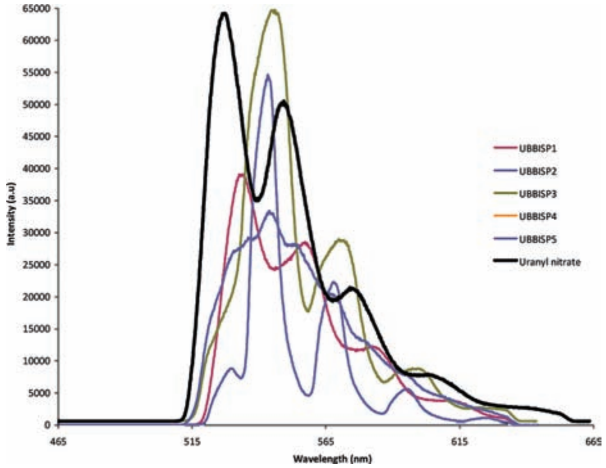

Figure 2. Fluorescence spectra of UBBISP1−5 showing fine structure from emission of the uranyl moieties.

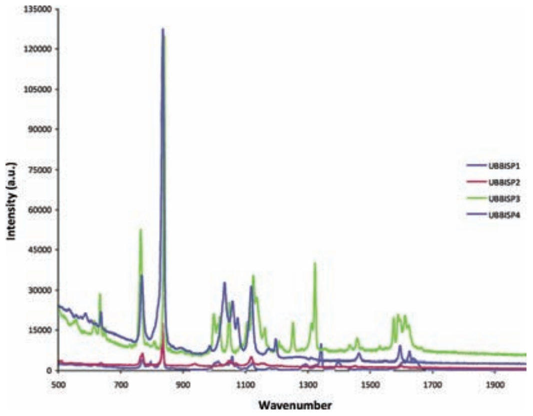

Figure 3. Raman spectra of UBBISP1−4.

UBBISP4 possess the same basic anionic framework, suggesting that these cations may merely be space-filling. However, four different structure types are represented between UBBISP1 and UBBISP5, suggesting that the cations do play a structure-directing role.

The presence of uranyl cations in these diphosphonates creates the potential that these compounds might act as luminescent materials. The emission of green light with fine vibronic structure has been known from uranyl compounds for many decades.[5] However, it has been noted in other uranyl phosphonates that emission is not always observed at room temperature.[1] The fluorescence emission spectra of single crystals of UBBISP1−5 were acquired using an epifluorescence microscope. The excitation was generated by a mercury lamp filtered by a band-pass filter at 450−490 nm. The emission signal was filtered by a long-pass filter with a cutoff wavelength of 515 nm. In each case, fluorescence with fine structure is observed at room temperature. Five peaks are clearly resolved for these compounds, as was found for the benchmark compound, uranyl nitrate hexahydrate, in this region of the spectrum.

The Raman spectra of these compounds were also collected from single crystals using a Raman confocal micro-

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scope. All of these compounds exhibit a symmetric ν_1 uranyl stretching mode at 834 cm^{-1}. It is interesting to note that two modes are not observed for those compounds with two different environments for the uranyl units. In addition, a large number of P−O stretches are found in the 1100 cm^{-1} region.

This work has provided data that support the use of diphosphonates for constructing luminescent pillared uranyl materials. However, the central question that will be addressed by ongoing studies is whether or not the templates can be exchanged with other cations and what effect this will have on the framework structure.

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Supporting Information Available: X-ray crystallographic files for UBBISP1−3 and UBBISP5 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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