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Mixed-Valent Uranium(IV,VI) Diphosphonate: Synthesis, Structure, and Spectroscopy

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Supporting Information

ABSTRACT: A mixed-valent uranium(IV,VI) diphosphonate, $(H_3O)_2(UO_2)_3U(H_2O)_2[CH_2(PO_3)_2]_3 \cdot 6H_2O$ (**UC1P2S**), has been synthesized under hydrothermal conditions. S-2-butanol was used to reduce uranium VI to IV. The tetravalent uranium centers adopt eight-coordinate geometries, while hexavalent uranyl units are all tetragonal bipyramids. The UV−vis−NIR spectrum of **UC1P2S** shows absorption features for both U(VI) and U(IV).

Mixed-valent uranium compounds are becoming increasingly represented in the literature owing to recent explorations of the instability of the +5 oxidation state for uranium as well as the coprecipitation of solutions that contain both U(IV) and U(VI).[1] Uranium compounds containing two or more oxidation states have been known for many decades and are even naturally occurring in minerals like ianthithite, $[U_2(UO_2)_4O_6(OH)_4(H_2O)_4] \cdot 5H_2O$,[2] and U_3O_8, which exists in pitchblende. These compounds contain uranium in both the +4 and +6 oxidation states. Lii and co-workers have reported a family of mixed-valent uranium silicates and germanates synthesized in supercritical water.[3] Cahill et al. have prepared compounds in this class by adding reductants such as zinc metal and hydrazine to mild hydrothermal reactions.[4] Mixed-valent uranium(IV,VI) oxyfluorides, orthophosphates, and carboxylates have also been reported.[5−7] These compounds normally conform to Robin-Day class I mixed-valent compounds because U(IV) and U(VI) adopt completely different coordination geometries. In the former, coordination numbers vary from six to nine, but the environment around uranium is usually isotropic.[8],[9] In contrast, U(VI) is typically found within a linear dioxo uranyl unit, UO_2^{2+}. The remaining donor atoms, which can vary from four to six, lie perpendicular to the uranyl unit forming tetragonal, pentagonal, or hexagonal bipyramids.[9] Uranium compounds that simultaneously contain +5 and +6 often fall into class II or class III mixed-valent compounds,[11] because both form the uranyl unit, which makes it possible for the two ions to reside on the same site.

However, it is noteworthy that these mixed U(IV/VI) compounds were synthesized using uranium dioxide as the starting material, with the exception of Lii et al.'s compounds that were prepared in supercritical water.[6,7] The in situ reduction of U(VI) under hydrothermal conditions can result in U(V/VI) solids.[5] Even if the reducing agents can reduce uranium from VI to IV, it is challenging to trap both states in one compound owing to their large solubility differences;[13] i.e., one normally obtains a mixture of U(IV) and U(VI) compounds.

We have demonstrated over the past few years that diphosphonates can coordinate actinides in all common oxidation states with essentially every known geometry.[12] More importantly, such ligands are able to bond to two different actinide elements with different oxidation states at the same time in one structure forming heterobimetallic compounds. For example, $UO_2M^{IV}(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (M = Ce, Th, Np, Pu)[12] are ordered compounds in which U(VI) and M(IV) ions adopt distinct crystallography sites. In contrast, we have shown that plutonium(VI) and uranium(VI) can occupy the same crystallographic site to form disordered heterobimetallic compounds.[12d] These studies indicate that it is possible for diphosphonates to stabilize both uranium +4 and +6. Attempts to prepare mixed-valent U(IV/VI) compounds with a variety of reducing agents has typically yielded a mixture of U(IV) and U(VI) compounds,[12b,d] and mixed-valent uranium phosphonate compounds have been unknown until now. Herein, we report the first mixed tetra- and hexavalent diphosphonate compound of uranium, $(H_3O)_2(UO_2)_3U(H_2O)_2[CH_2(PO_3)_2]_3 \cdot 6H_2O$ (**UC1P2S**).[14,15] This compound was synthesized by partial reduction of U(VI) to U(IV) using (S)-2-butanol as the reducing agent. The ligand used here is the simplest diphosphonate, $[CH_2(PO_3)_2]^{4-}$, methylenediphosphonate (**C1P2**).

The crystal structure of **UC1P2S** is a three-dimensional framework with small cavities. The structure features four unique uranium centers: three are hexavalent, and one is tetravalent, as shown in Figure 1. The tetravalent uranium centers adopt an eight-coordinate environment. Shape8 calculations[16] indicate that the distortion of the dodecahedron is close to both D_{4d} and C_{2v}. These UO_8 polyhedra are part of dimers shown in Figure 2. The uranium(IV) polyhedron is shown in Figure 2 (top) and, if described as a square antiprism, has four oxygen atoms in one plane from two C1P2 units, which chelate the uranium center. Of the four oxygen atoms in the opposite plane, two are occupied by water molecules and two are from the C1P2 ligand that bridges to a symmetry-related U(IV) site, thus forming the dimer (Figure 2, bottom). The bond distances within these units are within the range expected for eight-coordinate U(IV), with the longest bonds to the coordinating water molecules at 2.556(8) and 2.547(9) Å.

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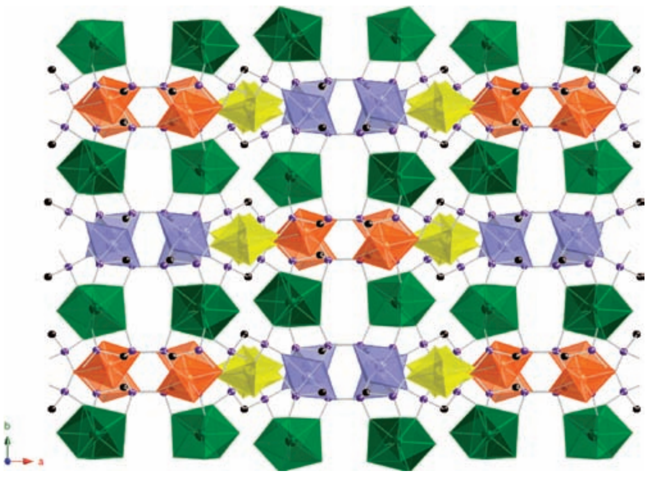

Figure 1. A view of the structure of $(H_3O)_2(UO_2)_3U(H_2O)_2[CH_2(PO_3)_2]_3 \cdot 6H_2O$ (**UC1P2S**) showing the framework that extends in the [*ab*] plane. The tetravalent uranium centers (U1) are shown in green. The three structurally distinct U(IV) centers are shown in blue (U2), yellow (U3), and orange (U4). The ligand atoms are shown in purple (P) and black (C). The disordered water molecules and hydroniums are omitted for clarity.

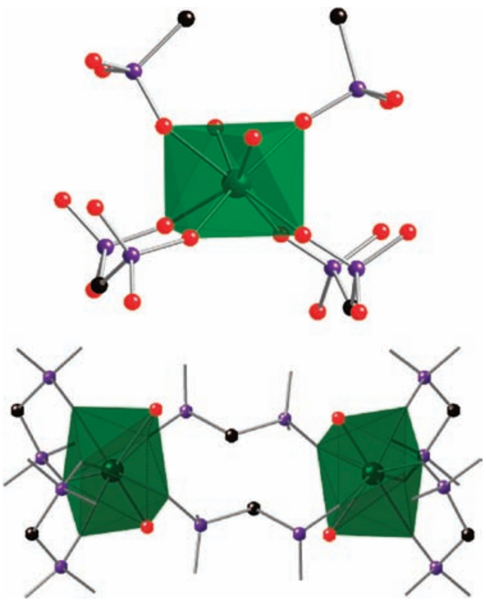

Figure 2. A view of the local coordination environment of U(IV) (top) and the bonding mode in the U(IV) dimer (bottom). Color code: green (U1), purple (P), black (C), and red (O).

The structure is pseudolayered with the U(IV) sites in one plane and the other three U(VI) centers in alternating layers. Both layers extend in the [*ac*] plane and are linked by the C1P2 ligand. The topology of the U(VI) layer is displayed in Figure 3. All three U(VI) centers are found as tetragonal bipyramids that are linked together by the C1P2 ligand. All four oxygen atoms in the equatorial plane are donated from four C1P2 units. For the four PO_3 moieties that are linked directly to U2, two of these are linked to three other U2 atoms, while the other two are linked to the adjacent U3 centers. For U3, the four oxygen atoms are also from four different C1P2 units. Of the four PO_3 moieties that bonded directly to U3, two are linked to U2 and two are bonded to the U4. The bonding for U4 is very similar to that for U2.

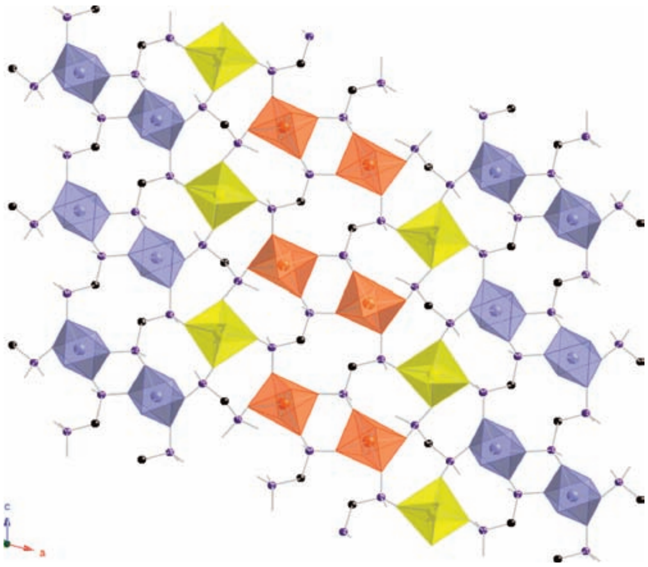

Figure 3. A view of the topology of the sheet formed by the three hexavalent uranium centers in the [*ac*] plane. The three structurally distinct U(VI) centers are shown in blue (U2), yellow (U3), and orange (U4). Purple spheres are phosphorus atoms, and the black spheres are carbon atoms.

Although the coordination environments clearly indicate which sites are U(VI) and which are U(IV), the possibility that U(V) sites could exist in the compound cannot be excluded simply from the coordination environment because U(V) also forms a dioxo cation, UO_2^+. There are three lines of evidence that exclude U(V), two of which are based on bonding metrics. First, the U≡O distances are too short for U(V). The bond distances of the tetravalent U1 site range from 2.223(9) to 2.556(9) Å. In the three U(VI) sites, U2, U3, and U4, the uranyl bond distances are from 1.781(9) to 1.795(9) Å, and the bond distances in the equatorial plane range from 2.257(9) to 2.324(9) Å. These bond distances are within the normal range for U(VI). Second, bond-valence sum calculations for U1 yield a value of 4.36, while U2, U3, and U4 are 5.84, 5.84, and 5.77, respectively.[17]

The third line of evidence that both excludes U(V) and indicates both U(IV) and U(VI) is from the UV−vis−NIR absorption spectrum. U(IV) has an electron configuration of $5f^2$, and two of its characteristic f−f transitions are at 650 and 1020 nm, which can be observed in the spectrum in Figure 4.

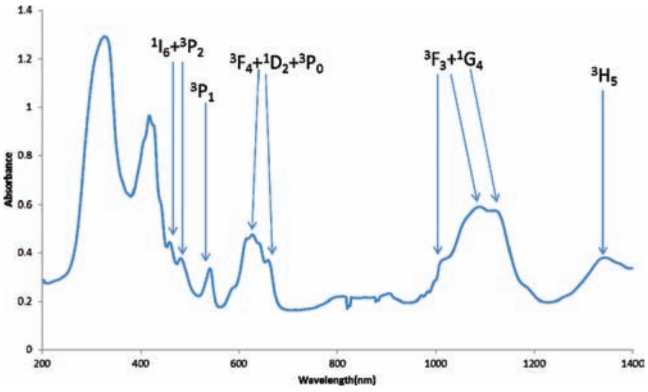

Figure 4. The UV−vis−NIR spectrum of **UC1P2S**, showing both the charge-transfer bands of U(VI) and the f−f transitions of U(IV).

These tetravalent uranium f−f transitions are assigned on the basis of Carnall et al.'s study.[18] The charge-transfer bands of uranyl centered at 250 and 430 nm were also observed along with characteristic fine-structure for the 430 nm peak for U(VI), indicating the mixed-valency in **UC1P2S**. U(V) transitions are absent. The fluorescence spectrum of **UC1P2S** was measured from 250 to 800 nm, but no emission was observed. The majority of U(VI) compounds fluoresce near 520 nm with strong vibronic coupling, yielding a five-peak pattern at room temperature. $UO_2M^{IV}(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (M = Np, Pu) do not fluoresce either, while $UO_2Th(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ does. The simple explanation for this is that the emission of the U(VI) units is absorbed by tetravalent sites that possess 5f electrons. Th(IV) is $5f^0$ and hence yields no absorption features in the visible region of the spectrum, and typical uranyl emission is observed.

This U(IV,VI) diphosphonate compound, **UC1P2S**, utilizes the same ligand as the previous reported actinide heterobimetallic family $UO_2M^{IV}(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (M = Ce, Th, Np, Pu).[12] In both structures, all of the U(VI) centers are tetragonal bipyramids, while the U(IV) and M(IV) sites are eight-coordinate, but $UO_2M^{IV}(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ is not isotypic with $(H_3O)_2(UO_2)_3U(H_2O)_2[CH_2(PO_3)_2]_3 \cdot 6H_2O$. In $UO_2Np(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$, for example, the NpO_8 group has C_{2v} symmetry, whereas the U(IV) center in **UC1P2S** is close to D_{4d}. In $UO_2M^{IV}(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$, the U/M ratio, which is also the VI/IV ratio, is 1:1, compared to that of **UC1P2S**, which is 3:1.

In conclusion, a mixed-valent U(IV/VI) diphosphonate, $(H_3O)_2(UO_2)_3U(H_2O)_2[CH_2(PO_3)_2]_3 \cdot 6H_2O$, has been prepared via partial reduction of U(VI). This compound is different from previously reported heterobimetallic diphosphonates in that it possesses a different stoichiometry of the different oxidation states and dissimilar symmetry of the M(IV) sites.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic file for $(H_3O)_2(UO_2)_3U(H_2O)_2[CH_2(PO_3)_2]_3 \cdot 6H_2O$ (**UC1P2S**) and the IR spectrum of this compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) Synthetic details: A uranyl nitrate $UO_2(NO_3)_2$ solution (0.5 M, 500 μL), $CH_2(PO_3H_2)_2$ solution (0.5M, 500 μL), (S)-2-butanol (99%, 500 μL), and 500 μL of H_2O were loaded in a PTFE liner and sealed in an autoclave. The reaction was heated to 180 °C for three days and then cooled down to room temperature. Green crystals of $(H_3O)_2(UO_2)_3U(H_2O)_2[CH_2(PO_3)_2]\cdot 4H_2O$ were isolated.

(15) Crystallographic data for UC1P2S: green prism, 0.063 × 0.042 × 0.039 mm, monoclinic, $C2/c$, $Z = 8$, $a = 25.903(5)$ Å, $b = 17.021(3)$ Å, $c = 16.723(3)$ Å, $\beta = 103.415(2)°$, $V = 7172(3)$ Å^3 ($T = 295$ K), $\mu = 183.82$ cm^{-1}, $R_1 = 0.0428$, $wR_2 = 0.1036$.

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