Actinoid Chemistry

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Capitalizing on Differing Coordination Environments and Redox Potentials to Prepare an Ordered Heterobimetallic U^{VI}/Np^{IV} Diphosphonate**

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The fine-tuning of both polymer-grafted and soluble phosphonates has played an essential role in the development of actinoid separation processes that are a critical feature of nuclear fuel cycles.[1] Despite the unusual nature of actinoid phosphonate interactions, which are strong even at low pH values, little is known about actinoid phosphonates in the solid-state outside of uranyl compounds, which are reasonably well represented.[2] In fact, it is from the uranyl phosphonate system that the first indications came that uranyl compounds could adopt nanotubular structures.[2b] Reports on the structural chemistry and physical properties of transuranium phosphonates have only appeared in the last year, and this work needs considerable expansion.[3,4]

The in situ hydrothermal reduction of Np^{VI} to Np^{IV} was recently discovered to facilitate the preparation and crystal growth of a variety of Np^{IV} materials.[3–5] While this work is in its infancy, it has already been used to prepare Np^{IV} compounds that do not have transition metal, lanthanoid, or uranium counterparts, which is exemplified by the polar layered structure of the Np^{IV} methylphosphonate $Np(CH_3PO_3)(CH_3PO_3H)(NO_3)(H_2O){\cdot}H_2O$ and by the three-dimensional framework compound $Np[CH_2(PO_3)_2](H_2O)_2$.[3,4] In the course of this work it was found that the reduction of U^{VI} to U^{IV} under mild hydrothermal conditions in the presence of diphosphonates proceeds only to a very small extent, whereas under identical conditions Np^{VI} is fully reduced to Np^{IV}.[4] In addition to a divergence in reactivity, there are substantial structural differences between U^{VI} and Np^{IV}. U^{VI} tends to adopt tetragonal-, pentagonal-, and hexagonal-bipyramidal geometries. Whereas Np^{IV} is typically found in eight-coordinate distorted dodecahedra and nine-coordinate tricapped trigonal prisms. Based on these observations, it became apparent that it might be possible to prepare heterobimetallic U^{VI}/Np^{IV} phosphonates by taking advantage of both the differences in hydrothermal redox chemistry and the substantial differences in coordination environments of U^{VI} and Np^{IV} to prepare crystalline solids containing these neighboring actinoids that are, nevertheless, ordered.[6]

The hydrothermal reaction of Np^{VI} nitrate with UO_3 and methylenediphosphonic acid (C1P2) results in the formation of clusters of acicular pale green crystals of $UO_2Np(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (UNpC1P2–1). The formation of UNpC1P2–1 relies on the ability of C1P2 to simultaneously bind U and Np, as well as the reduction of Np^{VI} to Np^{IV} under hydrothermal conditions. U^{VI} maintains its oxidation state in this reaction.

Single-crystal X-ray diffraction experiments on UNpC1P2–1 reveal a remarkable three-dimensional framework structure constructed from UO_6 tetragonal bipyramids, NpO_8 distorted dodecahedra, and monoprotonated methylenediphosphonate anions (Figure 1). A depiction of the fundamental building units in UNpC1P2–1 is shown in Figure 2.

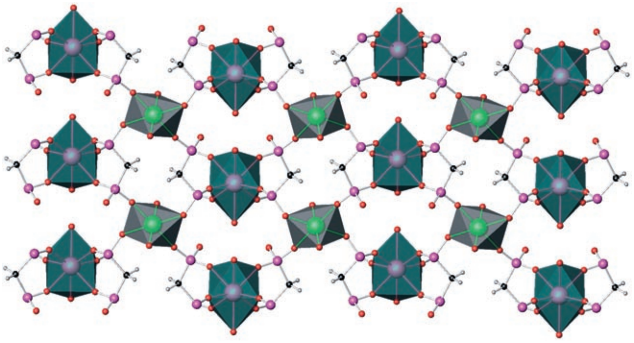

Figure 1. A view down the *a*-axis (in the [*bc*] plane) of the three-dimensional framework structure of the heterobimetallic U^{VI}/Np^{IV} diphosphonate $UO_2Np(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (UNpC1P2-1). U green, Np purple (large), O red, P purple (small), C black. UO_6 and NpO_8 coordination polyhedra are shown.

The UO_6 tetragonal bipyramids contain a standard uranyl core resting on an inversion center with two U≡O bond lengths of 1.776(7) Å. Of the remaining four U−O bonds, two are 2.289(7) Å and two are 2.317(6) Å. From these data a bond-valence sum for the U center can be calculated to be 6.07, which is consistent with this compound containing U^{VI}.[7,8] The NpO_8 units are found as distorted dodecahedra and reside on a single mirror plane. The Np−O bond lengths range from 2.245(7) to 2.500(9) Å, with two particularly long bonds of 2.474(11) and 2.500(9) Å. Both of these oxygen atoms are terminal and are thought to be from coordinating

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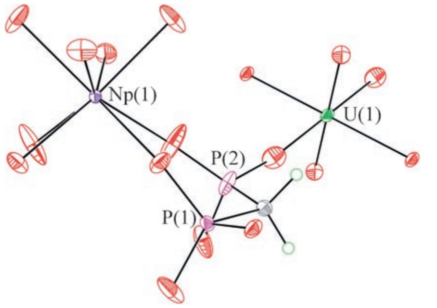

Figure 2. A depiction of the fundamental building units in $UO_2Np(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (UNpC1P2-1).

water molecules as have been found in the two previous Np^{IV} phosphonates. An additional interesting feature of the structure of UNpC1P2–1 is a single terminal oxygen atom bound to P(2) of the methylenediphosphonate with a P–O bond length of 1.568(8) Å. This distance suggests the oxygen atom is protonated. As can be noted in Figure 1, there are small channels extending down the *a* axis that are ideally configured for a series of hydrogen-bonding interactions between the P-OH group and coordinating water molecules.

Confirmation of the presence of both U and Np in UNpC1P2–1, while bolstered by reactivity and bonding arguments, can not be demonstrated unequivocally on the basis of X-ray scattering alone because U and Np differ by only a single electron. Evidence for the inclusion of both elements in the crystals is provided by a variety of spectroscopic techniques starting with energy dispersive X-ray analysis that clearly indicates the presence of both U and Np in the crystals. Further clarity concerning the oxidation states of the actinoids in question is provided by visible diffuse reflectance spectroscopy (Figure 3). The spectrum shows characteristic charge-transfer features (centered at 422 nm) for the UO_2^{2+} cation, as well as strong f-f absorption bands (with the most intense feature at 740 nm) consistent with the presence of Np^{4+}.[9]. Fluorescence from UNpC1P2–1 is not observed because the paramagnetic Np^{4+} centers quench the emission from the UO_2^{2+} moieties. Using a Raman microscope, vibrational data were collected from UNpC1P2–1. The ν_1-symmetric stretching mode of the UO_2^{2+} ion was found at 832 cm^{-1}.

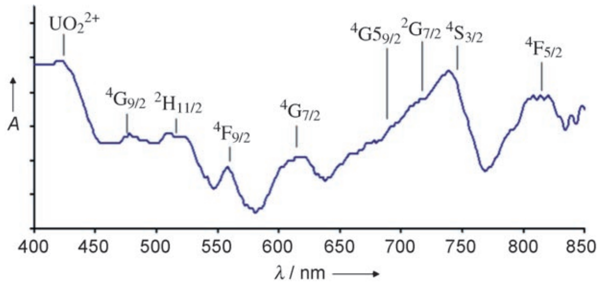

Figure 3. Visible diffuse reflectance spectrum of $UO_2Np(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (UNpC1P2-1) demonstrating the presence of both U^{VI} and Np^{IV} (see text for details).

UNpC1P2–1 provides an exceedingly rare example of a well-characterized and ordered heterobimetallic U^{VI}/Np^{IV} material. This compound points to the potential preparation of other novel mixed-actinoid compounds that capitalize on the divergent structural and solution chemistry of actinoids in different oxidation states.

Experimental Section

Synthesis of $UO_2Np(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (UNpC1P2–1): a solution of Np^{VI} nitrate (333 µL, 0.037 M) was heated with UO_3 (11 mg, 0.037 mmol) and methylenediphosphonic acid (12 mg, 0.068 mmol) at 180 °C for three days in a PTFE-lined autoclave, followed by slow cooling to room temperature over 24 h.

Crystallographic data for UNpC1P2–1: pale green needle, crystal dimensions $0.020 \times 0.042 \times 0.076$ mm^3, monoclinic, $P2_1/m$, $Z = 2$, $a = 5.5279(5)$, $b = 20.3381(19)$, $c = 6.9321(6)$ Å, $\beta = 98.703(2)°$, $V = 770.38(12)$ Å^3 ($T = 193$ K), $\mu = 177.03$ cm^{-1}, $R_1 = 0.0340$, $wR2 = 0.1021$. Data were measured on a Bruker APEX CCD diffractometer: $\theta_{max} = 56.62°$, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, 0.3° ω scans, 7471 reflections measured, 1945 independent reflections all of which were included in the refinement. The data was corrected for Lorentz-polarization effects and for absorption. The structure was solved by direct methods, anisotropic refinement of F^2 by full-matrix least-squares, 110 parameters.[10] Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-419434.

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