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In Situ Hydrothermal Reduction of Neptunium(VI) as a Route to Neptunium(IV) Phosphonates

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A lamellar neptunium(IV) methylphosphonate, $Np(CH_3PO_3)(CH_3PO_3H)(NO_3)(H_2O)\cdot H_2O$, has been prepared under hydrothermal conditions via the in situ reduction of Np^{VI} to Np^{IV}. The single crystal structure of this compound shows polar layers that are joined to one another via a hydrogen-bonding network involving interlayer water molecules. Magnetic susceptibility measurements demonstrate that the Np^{IV} ions are magnetically isolated from one another.

Phosphonates have played a critical role in f-element chemistry primarily from the perspective of their use in separation processes.[1] Many phosphonates have been developed for this purpose including geminally substituted diphosphonic acids that can be grafted to polymer matrixes, e.g., Diphonix resins.[2] Despite the importance of the formation of actinide phosphonates in nuclear waste treatment, little is known about the solid-state structures of these compounds or their physical properties. The only well-developed actinide phosphonate materials are known with thorium[3] and uranium.[4,5] The intricacies of uranium(VI) phosphonates are aptly illustrated by the uranyl phenylphosphonate system that undergoes a transformation from a cis (α-UPP) to a trans (β-UPP) confirmation at room temperature.[4b,c] Upon exposure to Na^+ or Ca^{2+} cations in an aqueous environment, both of these phases transform from linear chain structures into a hollow nanotubular form, γ-UPP.[4a]

The primary challenge in developing structure−property relationships in actinide phosphonates is that, other than the uranyl compounds, these phases are highly insoluble and generally precipitate as microcrystalline or amorphous powders. As a result, single crystal structure determinations are rare, thus forcing the use of ab initio powder diffraction methods when possible.[4h,5] One solution to this conundrum is to utilize reduction processes that transform actinides from the generally more soluble 6+ oxidation state to the much less soluble 4+ oxidation state. We have discovered that under mild hydrothermal conditions Np^{VI} can be reduced to Np^{IV} even in the presence of certain oxidation agents so long as this process is also driven by the formation of highly insoluble products.[6] In this vain, we demonstrate herein that the in situ reduction of Np^{VI} to Np^{IV} can be used to prepare the first well-characterized examples of transuranium phosphonates.

The hydrothermal reaction (180 °C, autogenously generated pressure, 3 days) of 333 μL of a 0.037 M stock solution of neptunium(VI) nitrate with methylphosphonic acid results in the formation of clusters of dichroic pale pink/green crystals of $Np(CH_3PO_3)(CH_3PO_3H)(NO_3)(H_2O)\cdot H_2O$ (**NpMeP-1**) as the only solid product.

Single crystal X-ray diffraction studies on **NpMeP-1** reveal a layered structure constructed from corner-sharing NpO_8 distorted dodecahedra that are bridged by $CH_3PO_3^{2-}$ and $CH_3PO_3H^-$ anions. The coordination sphere is completed by a chelating nitrate anion and a coordinating water molecule. These units form layers that extend into the *ac* plane. As indicated by the orthorhombic space group $Pca2_1$,

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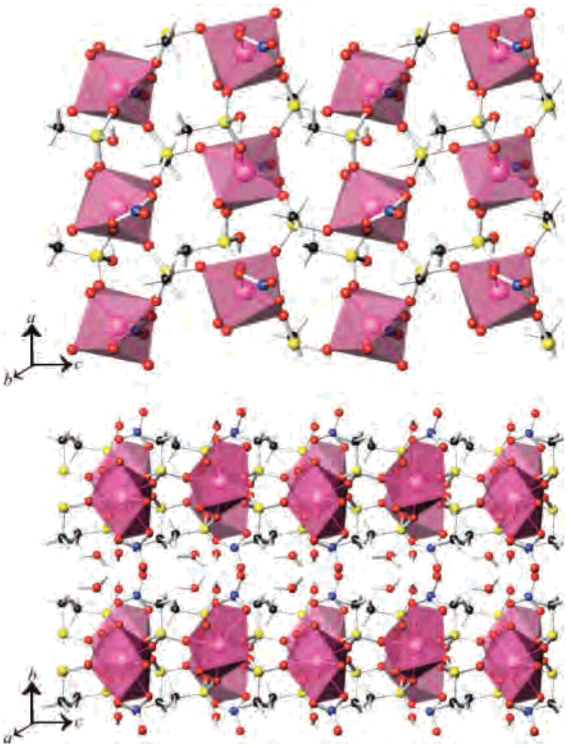

Figure 1. Two views of the polar, lamellar structure of **NpMeP-1**. Color code: NpO_8, pink; P, yellow; O, red; N, blue; H, white.

the structure is polar. The polarity of **NpMeP-1** is subtle. A portion of the structure of **NpMeP-1** is shown in Figure 1. The H atoms from the interlayer water molecules as well as those on the $CH_3PO_3H^-$ anions were located from difference maps. The nitrate and $CH_3PO_3H^-$ anions form a hydrogen-bonding network that stitches the layers together and provides stability for the overall structure. Both the hydrogen-bonding network and the tilt of the nitrate anions can be used to visualize the polarity of the structure along the *c* axis. The structure of **NpMeP-1** does not parallel that of other metal(IV) phosphonates.

The NpO_8 distorted dodecahedra have Np−O bond distances that range from 2.199(3) to 2.589(3) Å, yielding a bond-valence sum of 4.07, which is consistent with this compound containing Np^{IV}.[7] The P−O bond distances are normal, and the only one worth mentioning is the longest one of 1.579(4) Å, which corresponds to a P−OH moiety in the $CH_3PO_3H^-$ anions.

The isolation of **NpMeP-1** as a pure crystalline material and subsequent structural characterization allows us to address potential structure−property correlations. In particular, the magnetic properties of Np^{IV} compounds can be particularly intriguing because of its $5f^3$ electron configuration that has a $^4I_{9/2}$ ground state. The magnetic behavior of Np^{IV} compounds sharply contrasts with that of U^{IV} ($5f^2$, $^3H_4$) compounds that have a tendency of becoming nonmagnetic or only exhibiting temperature-independent paramagnetism at low temperatures owing to a singlet ground state. The

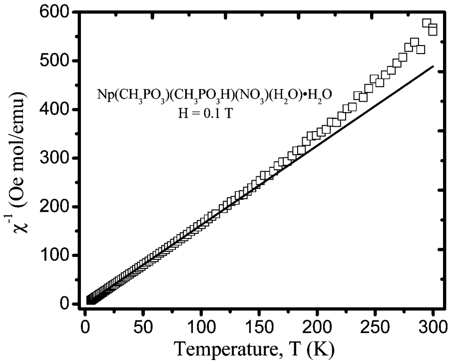

Figure 2. Temperature dependence of the reciprocal molar magnetic susceptibility for **NpMeP-1** under an applied magnetic field of 0.1 T between 5 and 300 K. The straight line represents the fit to the Curie−Weiss law in the range of 5−100 K.

Np···Np distance is greater than 5.3 Å in **NpMeP-1**, and there are no μ_3-O groups in the structure, and therefore no opportunity for superexchange. Therefore, the prediction is that the Np^{IV} centers will behave as isolated ions and Curie−Weiss behavior should be observed without long-range magnetic ordering. The inverse magnetic susceptibility is plotted versus the temperature in Figure 2. As can be observed from these data, this prediction proves to be true as Curie−Weiss behavior is exhibited at low temperatures. The susceptibility data were least-squares fit to $\chi(T) = C/(T + \theta) + \chi_0$, where C is the Curie constant, θ is the Weiss constant, and χ_0 is the temperature-independent susceptibility. We have fit the data from 5 to 100 K to arrive at a θ value of 0.53(6) K, indicating no strong interactions between Np^{IV} ions. The value of μ_{eff} is 2.213(1) μ_B. While this value is considerably lower than that predicted for the free ion (3.62 μ_B), it compares well with other Np^{IV} compounds such as $Np(IO_3)_4$ (2.22 μ_B).[6] This reduced moment is not a reflection of the covalency of the 5f orbitals but rather arises from crystal-field effects.[6]

The beauty of utilizing Np as the core metal ion in phosphonate materials is the ability to tune the oxidation state of Np as demonstrated by the formation of **NpMeP-1**. By using a large excess of nitrite in the aforementioned reaction, the oxidation state of Np can be maintained at 6+,[8] enabling the isolation of the neptunium(VI) methylphosphonate, $NpO_2(CH_3PO_3)$ (**NpMeP-2**), as orange-brown microcrystals. A view of part of the structure of **NpMeP-2** is shown in Figure 3. This lamellar compound is isostructural with its uranium(VI) analogue.[4h] However, the structure of $UO_2(CH_3PO_3)$ was obtained from high-resolution powder X-ray diffraction data.[4h]

Despite the very small size (largest dimension ~2 μm) of the crystals of **NpMeP-2**, the use of a single crystal X-ray diffractometer with a CCD detector with long exposure times allowed for the elucidation of a high-resolution structure for **NpMeP-2** (see the Supporting Information). The structure of this compound consists of NpO_7 pentagonal bipyramids containing a nearly linear NpO_2^{2+}, neptunyl, core. The critical bond distances are the two neptunyl Np═O bonds that

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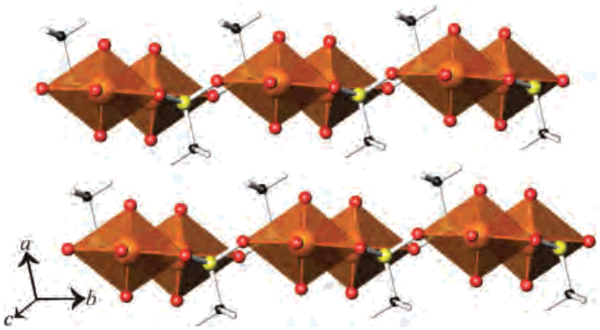

Figure 3. View down the *c* axis of the layered structure of the neptunium(VI) methylphosphonate **NpMeP-2**. Color code: NpO_7 pentagonal bipyramids, orange; P, yellow; O, red; H, white.

average 1.736(7) Å. This distance is statistically shorter than that typically found in uranyl compounds, which averages 1.79(3) Å.[9] The NpO_7 pentagonal bipyramids form one-dimensional chains via edge-sharing and are, in turn, bridged by $CH_3PO_3^{2-}$ anions to yield layers that extend into the [*bc*] plane. The methyl groups are oriented approximately perpendicular to this plane and point between the layers, as shown in Figure 3.

This is the first report on structure–property relationships in transuranium phosphonates. We have demonstrated that the redox capabilities of neptunium, which are *not* paralleled by uranium or other lighter actinides, provide access to new neptunium(IV) and neptunium(VI) phosphonates. Neptunium(V) phosphonates should also be available in the near future. The high coordination numbers of Np in these compounds provide access to structural motifs not available from transition metal phosphonate materials.[10]

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Supporting Information Available: X-ray crystallographic files for **NpMeP-1** and **NpMeP-2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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