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Boronic Acid Flux Synthesis and Crystal Growth of Uranium and Neptunium Boronates and Borates: A Low-Temperature Route to the First Neptunium(V) Borate

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Molten methylboronic acid has been used as a reactive flux to prepare the first neptunium(V) borate, $NpO_2[B_3O_4(OH)_2]$ (**NpBO-1**), and the first actinide boronate, $UO_2(CH_3BO_2)(H_2O)$ (**UCBO-1**). **NpBO-1** contains cation−cation interactions between the neptunyl units. In contrast, the presence of the methyl groups in the uranyl boronate leads to a one-dimensional structure.

The structural chemistry and electronic properties of actinide borates is exceedingly rich.[1] We have recently demonstrated that the chemistry of actinides in molten boric acid is substantially different from that observed in aqueous media or high-temperature melts.[2−8] In particular, we provided evidence for the simultaneous existence of Np^{IV}, Np^{V}, and Np^{VI} in a single compound via a combination of single-crystal X-ray diffraction, bond-valence-sum calculations, magnetism, and UV−vis−near-IR (NIR) spectroscopy.[3] The formation of mixed- or intermediate-valent neptunium compounds is driven by the ability of Np^{V} to disproportionate under a variety of conditions. The results of these studies provided an unusual challenge: how to obtain neptunium borates in single oxidation states that could be used for comparison with the mixed-valent compounds.

The melting point of boric acid is 170.9 °C, and this temperature must be exceeded for it to act as a reactive flux. In molten boric acid, Np^{V} partially disproportionates to Np^{IV} and Np^{VI}, leading to the formation of mixed-valent compounds. Because water competes very successfully with borate for inner-sphere coordination sites for actinides under most conditions, it is very difficult to synthesize actinide borates utilizing hydrothermal or room-temperature aqueous reactions. In order to prepare actinide borates at lower temperatures than the melting point of boric acid, we utilized methylboronic acid, the simplest boronic acid, as a new reactive flux. The melting point of methylboronic acid is within the range of 89−94 °C, which is considerably lower than the melting point of boric acid. In addition, the C−B bond is not thermally robust, and boronates are readily degraded to borates.[9] Finally, even if the C−B bond remains intact during the reaction, actinide boronates are completely unknown, and the solid-state chemistry of metal boronates in general is severely underexplored.[10] In this vein, we demonstrate that a neptunium(V) borate, $NpO_2[B_3O_4(OH)_2]$ (**NpBO-1**), has been successfully synthesized from the reaction of neptunium(VI) nitrate with a large excess of methylboronic acid at 120 °C. Under the same reaction conditions, uranyl nitrate reacts with methylboronic

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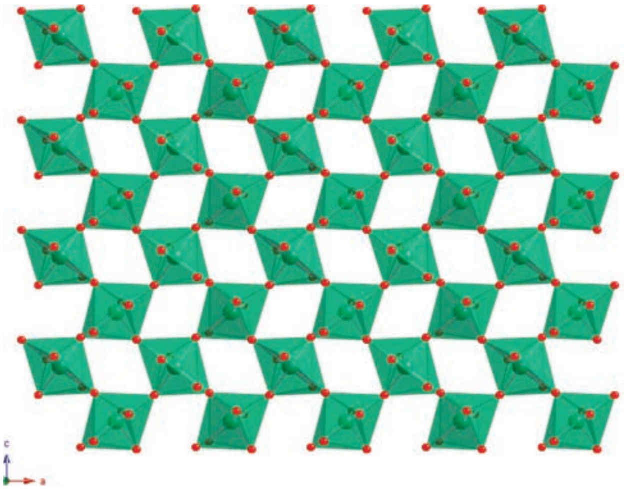
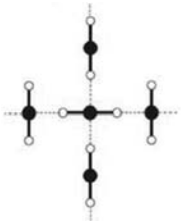


Figure 1. Illustration of the sheets created by CCIs in **NpBO-1**. Boron atoms are not shown for clarity.

Scheme 1. Illustration of the CCIs in **NpBO-1**



acid to yield the first known actinide boronate compound, $UO_2(CH_3BO_2)(H_2O)$ (**UCBO-1**), which can be made as a pure phase in good yield.[11]

Single-crystal X-ray diffraction studies reveal that **NpBO-1** crystallizes in the polar orthorhombic space group *Pca*2_1. The structure of **NpBO-1** contains only one crystallographically unique neptunyl cation, NpO_2^+, in a pentagonal-bipyramidal environment, NpO_7. This coordination geometry is very common for both U^{VI} and Np^V oxoanion compounds. Each oxygen atom of the NpO_2^+ unit is further bonded with neighboring neptunyl units through their equatorial planes to yield so-called cation−cation interactions (CCIs; Scheme 1). Each NpO_2^+ cation is bonded to four other neptunyl cations via these interactions. This CCI bonding mode can be described by the scheme below and is in accordance with CCI bonding modes summarized by Krot and Grigoriev and by Burns and co-workes.[12,13]

This CCI bonding mode is found to be the most common type for all neptunium(V) compounds that contain CCIs in the crystal structure.[13] As a result of this CCI bonding mode, all of the NpO_2^+ units are connected together to create neptunium(V) sheets within the *ac* plane, as shown in Figure 1.

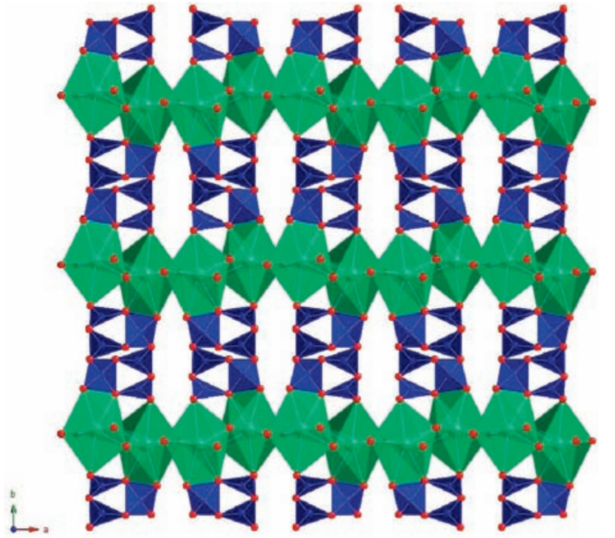


Figure 2. Depiction of the structure of **NpBO-1** showing sheets of neptunyl cations connected by polyborate chains.

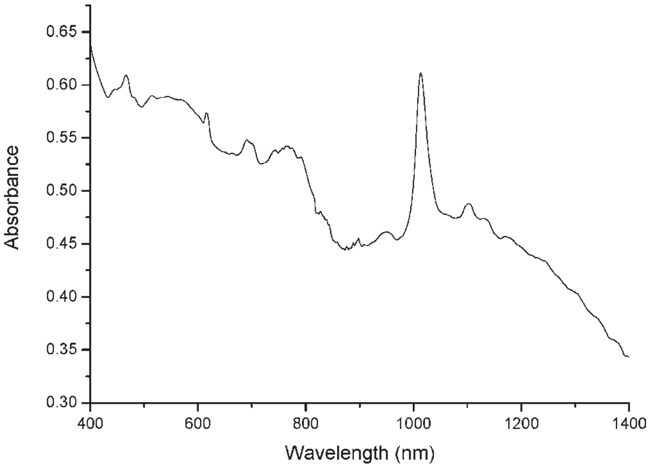


Figure 3. UV−vis−NIR spectrum of **NpBO-1** obtained from a single crystal. The transition at 1013 nm is demonstrative of Np^V.

The sheets are further stacked along the *b* axis via bridges created by both BO_3 and BO_4 units, as shown in Figure 2. As was previously mentioned, the structure is polar. The polarity of **NpBO-1** is subtle. As shown in Figure 2, both the orientation of the neptunium(V) sheets and the direction of the BO_3 triangles can be used to visualize the polarity of the structure along the *c* axis.

The NpO_2^+ cations have Np=O bond distances of 1.81(2) and 1.85(1) Å, which are within the normal range for the neptunyl bond distances for all other known neptunium(V) compounds.[12] Combined with the Np−O bond distances for the five interactions in the equatorial plane, which range from 2.39(1) to 2.53(1) Å, a bond-valence sum of 5.14 can be calculated.[13] This sum is consistent with this compound containing Np^V. All B−O bond distances are normal. Some oxygen atoms in the borate units are protonated, which can be confirmed by the bond-valence sums for these atoms and on the bond distances and coordination environments.

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(11) Synthesis details: A stock solution of ^{237}neptunium(VI) nitrate was prepared by first digesting NpO_2 in 8 M HNO_3 for 3 days at 200 °C (in an autoclave). The solution was reduced to a moist residue and redissolved in water, forming a neptunium(VI) nitrate solution. UV−vis−NIR spectroscopy indicates that only Np^{VI} is present. **NpBO-1**: neptunium(VI) nitrate (10 mg in 10 μL of water) and methylboronic acid (46.1 mg) were mixed together in a Teflon-lined autoclave. The mixture was heated at 120 °C for 3 days and then cooled at 5 °C/h to room temperature. The products consisted of light-green needle crystals of **NpBO-1**. **UCBO-1**: $UO_2(NO_3)\cdot 6H_2O$ (200 mg), methylboronic acid (360 mg), and H_2O (20 μL) were mixed together in a Teflon-lined autoclave. The mixture was heated at 120 °C for 3 days and then cooled at 5 °C/h to room temperature. The products consisted of light-yellow needle crystals of **UCBO-1**, which exist as a pure phase. Yield: 76% based on uranium.

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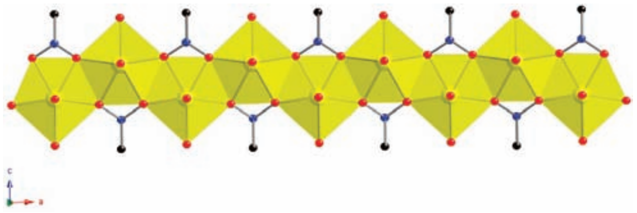

Figure 4. View along the *b* axis of the one-dimensional structure of **UCBO-1**.

The existence of Np^{V} in **NpBO-1** can be further confirmed by the UV−vis−NIR spectra of single crystals of **NpBO-1**, as shown in Figure 3. As expected, the most important f−f transition for Np^{V} at 980 nm is shifted to a longer wavelength at 1013 nm owing to the CCIs.[12] It is also important to note the absence of a strong transition at 1200 nm that would be indicative of Np^{VI}. This transition was observed in all other neptunium borates. Key transitions for Np^{IV} are also absent.

Np^{VI} is a strong oxidant ($E^0_{Np^{VI/V}} = 1.16$ V) and likely oxidizes methylboronic acid by attacking the C−B bond to yield borate. Nevertheless, the goal of preparing a neptunium borate with neptunium in a single oxidation state was achieved by this method. A similar reaction does not occur with U^{VI} owing to its much lower oxidizing potential ($E^0_{U^{VI/IV}} = 0.32$ V), and the first actinide boronate, **UCBO-1**, was subsequently isolated.

A single-crystal X-ray diffraction study of **UCBO-1** shows that it adopts a simple one-dimensional chain structure, as shown in Figure 4. This structure consists of edge-sharing pentagonal bipyramids. The methylboronate anions chelate the uranyl cations and also bridge between the uranium centers via μ_3-oxygen atoms. There is only one crystallographically unique U^{VI} site in the crystal structure that has a pentagonal-bipyramidal coordination environment much like that found in **NpBO-1**, except that the CCIs are completely absent, as expected. It should be noted that, although pentagonal-bipyramidal coordination is the most common one found for actinyl compounds, all of the uranium(VI) borates prepared from boric acid flux reactions adopt a hexagonal-bipyramidal environment.[2−8]

The methyl groups of the $CH_3BO_2^{2-}$ anions play a critical role in this structure in that they terminate the edges of the chains. If these moieties were replaced either by oxygen to yield BO_3 triangles or with two oxygen atoms to yield BO_4 tetrahedra, the structure would likely extend in at least one more dimension, as found for all actinyl borates.

In conclusion, we have successfully synthesized the first pure neptunium(V) borate, and the first actinide boronate by using molten methylboronic acid as a reactive flux. The temperature is likely to be a key factor for the disproportionation of Np^{V} in the borate system. A new way is provided to control the oxidation states of neptunium in a borate matrix. It is also expected that the methylboronic acid flux reaction can be used as a new technique to synthesize not only a new family of metalboronate compounds but also a new family of borate compounds with interesting structures and properties by introducing an oxidizing reagent into this system.

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