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# New Neptunium(V) Borates That Exhibit the Alexandrite Effect

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Supporting Information

**ABSTRACT:** A new neptunium(V) borate, K[$(NpO_2)B_{10}O_{14}(OH)_4$], was synthesized using boric acid as a reactive flux. The compound possesses a layered structure in which $Np^V$ resides in triangular holes, creating a hexagonal-bipyramidal environment around neptunium. This compound is unusual in that it exhibits the Alexandrite effect, a property that is typically restricted to neptunium(IV) compounds.

Neptunium and plutonium possess extraordinarily complicated and rich redox chemistry with oxidation states ranging from 3+ to 7+.[1] The chemistry of neptunium is dominated by $Np^V$ in both solution and the solid state. However, the disproportionation of $Np^V$ into $Np^{IV}$ and $Np^{VI}$ occurs under a variety of conditions.[2] This process is known to be significantly affected by numerous factors that include concentration, temperature, counterions, radiolysis, pH, and hydrolysis.[2] As a consequence of the compromise between the disproportionation of $Np^V$ and comproportionation of $Np^{IV}$ and $Np^{VI}$, neptunium in multiple oxidation states can be trapped in some compounds, and examples of mixed-valent $Np^{IV}/Np^V$ and $Np^V/Np^{VI}$ solids are known.[3]

We have recently undertaken the study of the preparation, structure elucidation, and physicochemical property measurements of actinide borates with the aim of developing periodic trends that may be relevant to nuclear waste disposal.[4−6] We have demonstrated that the chemistry of actinides in molten boric acid is substantially different from that observed in aqueous media or high-temperature melts. In particular, we have provided evidence of neptunium borates that simultaneously contain $Np^{VI}$, $Np^V$, and $Np^{VI}$ using a combination of single-crystal X-ray diffraction, bond-valence-sum calculations, magnetism, and UV−vis−near-IR (NIR) spectroscopy.[6a] We also prepared a highly unusual mixed/intermediate-valent neptunium borate, $K_2[(NpO_2)_3B_{10}O_{16}(OH)_2(NO_3)_2]$, in which the structure shows the existence of $Np^V$ and $Np^{VI}$, while UV−vis−NIR spectroscopy indicates the potential presence of trace amounts of $Np^{IV}$ as well.[6b] To explain these observations, we propose three possibilities: one is that this compound is mixed-valent with $Np^{IV}$ partially occupying $Np^V$ sites; the other is that all Np sites are actually intermediate-valent; finally absorption spectroscopy of $Np^V$ may simply not be useful for the oxidation state assignment in these compounds.

Polyborate networks are structurally flexible enough to coordinate with neptunium in all possible oxidation states stable under standard conditions. The building units of borates, $BO_3$ triangles and $BO_4$ tetrahedra, tend to polymerize under a variety of conditions to form countless types of polyborates that provide numerous bonding modes to coordinate the metal centers with different geometric preferences. Moreover, borate itself is a non-redox-active ligand. This provides us an opportunity of controlling and predicting the oxidation states of actinides in desired products by controlling the initial oxidation states of the actinides. For example, when the strong oxidant $ClO_4^-$ is used as the counteranion, neptunium(VI) borate can be isolated; mixed/intermediate-valent neptunium borates can only be synthesized when $NO_3^-$ or chloride is present in the boric acid flux reactions.[6a,b] In this report, we describe the crystal structure and absorption spectra of two new neptunium(V) borates, K[$(NpO_2)B_{10}O_{14}(OH)_4$] (**1**) and $K_2[(NpO_2)_2B_{16}O_{25}(OH)_2]$ (**2**), which are prepared in boric acid flux reactions with $Cl^-$ present as a counteranion.

**1** was prepared via the molten boric acid flux reaction of neptunium(V) chloride with KCl at 220 °C.[7] Crystals with a tablet habit were isolated for **1**, which appear to be light-yellow-green when illuminated by standard room fluorescence lighting; while under microscope lighting with a halogen lamp, the crystals show a coloration of dark brown (Figure 1). This phenomenon is referred to as the Alexandrite effect and is named so after the ability of the gemstone to change from green to red depending on the lighting. This effect is very common in neptunium(IV) compounds, but we have never observed it for neptunium(V). As a result, these crystals were originally thought to be a neptunium(IV) compound. Another similar neptunium borate phase, **2**, that is present as crystals with exactly the same habit as **1** was also isolated in the products. However, all crystals of **2** are severely twinned, and final refinement of the structural model is less than satisfactory. We only provide the unit cell parameters and discuss some general bonding aspects of **2**.[8]

The structure of **1** contains neptunium borate sheets that extend in the [*ab*] plane (Figure 2b), with $K^+$ cations residing between the neighboring sheets. There are significant numbers of $BO_3$ triangles that extend out perpendicularly on both sides of the sheets that form $B_2O_5^{4-}$ units on one side and $B_3O_6^{3-}$ units on the other side (Figure 2a). The combination of linear

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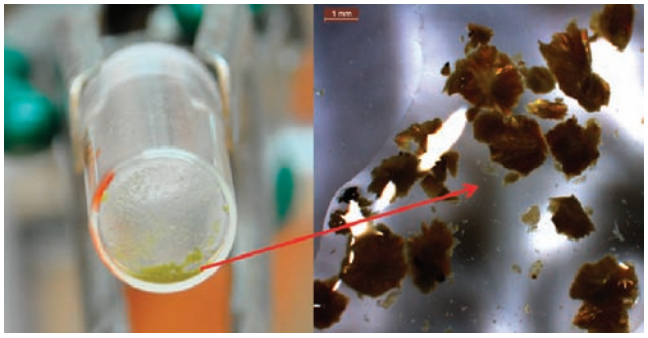

**Figure 1.** Photographs of crystals of **1** and **2** illuminated by standard room fluorescent lighting (left) and under microscope lighting (right) with a halogen lamp showing the Alexandrite effect.

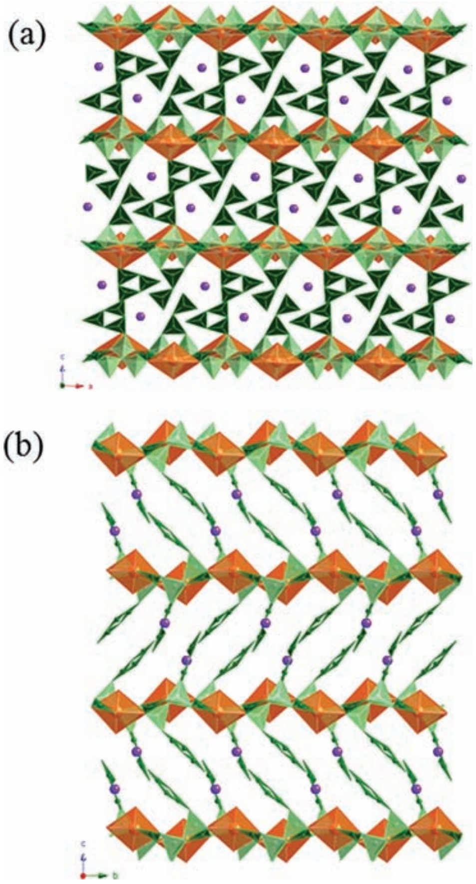

**Figure 2.** Views of part of the layered structure of **1** in the *ac* (a) and *bc* (b) planes. Np polyhedra are shown in orange, $BO_3$ triangles in dark green, $BO_4$ tetrahedra in light green, and K atoms in purple.

dimeric and cyclic trimeric groups has been observed for the first time in actinide borates.[4−6]

There is one crystallographically unique neptunium site existing in a $NpO_2^+$ unit with Np═O bond distances of 1.802(6) and 1.811(7) Å, which are close to the average Np═O distance of 1.83 Å found by surveying known neptunium(V) compounds.[9] It should be noted that these crystallographic data contrast sharply with the Alexandrite effect that is observed for the crystals of **1**, where no $Np^{IV}$ site is found. Also, no cation−cation interactions (CCIs) occur. The bond valence sum for neptunium is consistent with $Np^{V}$.[9]

The most important feature of the structure of **1** is the neptunium borate sheet topology. As observed in a typical uranyl borate,[5] within the sheets, each $NpO_2^+$ hexagonal bipyramid is surrounded by nine nearest-neighbor borate units (Figure 3). Four of them are $BO_3$ triangles, and five of them are $BO_4$ tetrahedra. This ratio of $BO_3$ triangles versus $BO_4$ tetrahedra within the sheet has not been observed in uranyl borates. There is a second unusual feature: a $\mu_3$-O atom shared by three $BO_4$ tetrahedra. These new features result in a new sheet topology (M type) for actinide borates.[5,6] However, it should be noted that significant numbers of trivalent lanthanide borates also adopt this sheet topology.[6,10] Large differences exist between $Np^{V}$ and $An^{III}/Ln^{III}$ in relation to their respective coordination numbers and environments. However, this work shows that both the highly anisotropic actinyl cation coordination and the more isotropic $RE^{3+}$ environments reside in the same type of polyborate sheet. Therefore, the supposition that $Np^{IV}$ might substitute onto $Np^{V}$ sites is not as outlandish as it first appears because $An^{III}$ and $An^{IV}$ possess similar coordination chemistry.

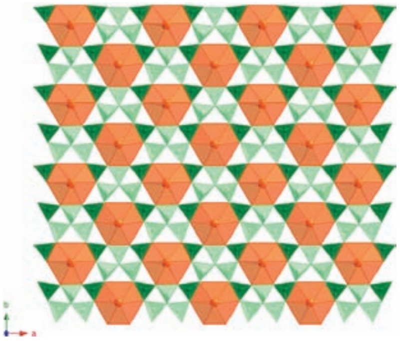

**Figure 3.** Views of the sheet topology (M type) in **1** and **2**.

The structure of **2** is based upon the same types of 2D borate sheets and has a certain similarity to **1**. The sheets are linked into a 3D framework by the $B_2O_5$ and $[(B_3O_6)(BO(OH)_2]$ groups.

The UV−vis−NIR absorption spectrum of **1** is shown as the black curve in Figure 4. These data were acquired from the same single crystal that was used for the structure determination using a microspectrophotometer. The crystals were oriented along [010] for data collection; i.e., the light is orthogonal to the polyborate layers. They are too small to obtain data in different orientations. The spectrum of **2** is essentially the same as that of **1**. It is well-known that the main transition for a typical neptunium(V) compound appears as a sharp feature at 980 nm (blue curve, Figure 4). When $Np^{V}$ units are involved in CCIs, this feature is red-shifted to the higher wavelength region around 1010 nm (green curve, Figure 4). For $Np^{IV}$, the most important transitions that can be used for distinguishing it from $Np^{V}$ are those at 730 and 960 nm (pink curve, Figure 4). There are two important features in the spectrum of **1**. First, the main transition that is used to characterize $Np^{V}$ is blue-shifted to 947 nm and significantly broadened. Second, the transition at 736 nm is attributed to $Np^{IV}$. Thus, there is a conflict between crystallographic and optical data that was previously observed in $K_2[(NpO_2)_3B_{10}O_{16}(OH)_2(NO_3)_2]$.[6b] However, there is a difference between the spectrum of **1** and that of $K_2[(NpO_2)_3B_{10}O_{16}(OH)_2(NO_3)_2]$ in that the main transition

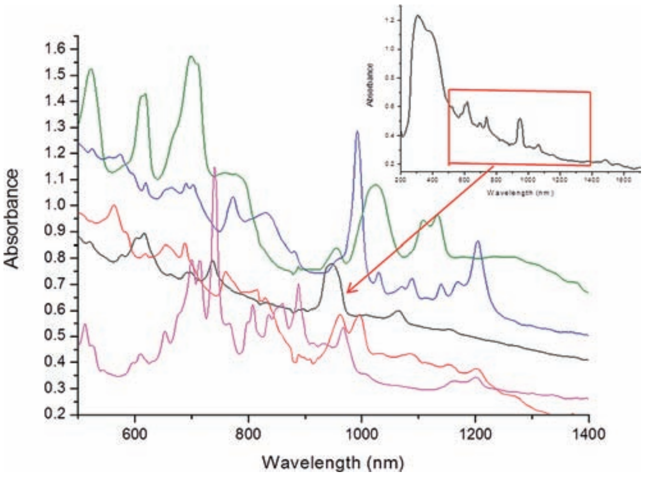

**Figure 4.** UV−vis−NIR spectra of **1** (black), $K_4[(NpO_2)_{6.73}B_{20}O_{36}(OH)_2]$ (blue), $K_2[(NpO_2)_3B_{10}O_{16}(OH)_2(NO_3)_2]$ (red), $NpO_2(IO_3)$ (green), and $Np[C_6H_4(PO_3H)_2]_2 \cdot 2H_2O$ (pink).

of $Np^{V}$ is split into two peaks at both 960 and 980 nm (red curve, Figure 4), which belong to $Np^{IV}$ and $Np^{V}$, respectively, while in **1**, this transition is extensively shifted to the region that is even below that of $Np^{IV}$. It is therefore possible that $Np^{IV}$ is also disordered within **1**.

In conclusion, **1** provides a further example of the complexity of the mixed/intermediate valency that is found in several neptunium compounds. This is represented by $\beta$-$AgNpO_2(SeO_3)$, where low-temperature electron spin resonance data also indicate the presence of $Np^{IV}$ in crystals even though the structure only appears to contain $Np^{V}$.[12] Much like **1**, crystals of $\beta$-$AgNpO_2(SeO_3)$ are brown instead of the unusual blue-green coloration of neptunium(V) compounds. The large differences in the coordination environments within polyborates that were thought to differentiate between $Np^{IV}$ and $Np^{V}$ are based on the hypothesis that the linear dioxoneptunyl(IV) unit would not occupy the same kinds of sites as lower oxidation states of neptunium. However, with observation of this unit in the structures of $K_4[(NpO_2)_{6.73}B_{20}O_{36}(OH)_2]$ and $Ba_2[(NpO_2)_{6.59}B_{20}O_{36}(OH)_2]$[6a] and the fact that $RE^{3+}$ cations can reside in the same sites as actinyl cations, it now appears that disordering of $Np^{IV}$ at $Np^{V}$ sites is at least plausible. $Np^{V}$ disproportionation leads to $Np^{IV}$ trapped within the crystals of $\beta$-$AgNpO_2(SeO_3)$, and potentially in $K_2[(NpO_2)_3B_{10}O_{16}(OH)_2(NO_3)_2]$, and **1**.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

X-ray crystallographic data file for $KNpO_2[B_{10}O_{14}(OH)_4]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) **Synthetic details:** A stock solution of 237-neptunium(V) chloride 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. A large excess of $NaNO_2$, followed by an excess of $NH_4OH$, was added to this solution, resulting in the precipitation of neptunium(V) hydroxide. The precipitate was then filtered and dried at 120 °C for about 30 min. Neptunium(V) hydroxide was then dissolved in a dilute HCl solution. A stock solution of 237-neptunium(V) chloride (containing 10 mg of $Np^{V}$) was transferred to a 10 mL Teflon liner and was reduced to a tiny droplet by heating at 140 °C. Large excesses of boric acid (47.2 mg) and KCl (7.7 mg) were then added directly to the droplet containing $Np^{V}$. The mixture was then sealed in an autoclave and heated at 220 °C for 3 days, followed by cooling to room temperature over a 1 day period. The autoclave was opened, and boiling water was added to dissolve the excess boric acid; tablet crystals with light-green/dark-brown coloration were then isolated for both compounds **1** and **2**.

(8) Crystallographic data for **1**: light-green/dark-brown tablet, 0.085 × 0.079 × 0.006 mm, monoclinic, $P2_1/n$, $Z = 4$, $a = 9.933(2)$ Å, $b = 8.1985(17)$ Å, $c = 21.041(4)$ Å, $\beta = 91.302(3)°$, $V = 1713.1(6)$ Å$^3$ [$T = 293(2)$ K], $\mu = 64.13$ cm$^{-1}$, R1 = 0.0511, wR2 = 0.1179. Partial crystallographic data for **2**: light-green/dark-brown tablet, 0.099 × 0.065 × 0.005 mm monoclinic, $Pn$, $a = 8.3214(17)$ Å, $b = 15.876(3)$ Å, $c = 9.889(2)$ Å, $\beta = 90.008(2)°$, $V = 1306.4(5)$ Å$^3$.

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