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Cation−Cation Interactions between Neptunyl(VI) Units

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Supporting Information

ABSTRACT: The boric acid flux reaction of $NpO_2(ClO_4)_2$ with $NaClO_4$ affords $Na[(NpO_2)_4B_{15}O_{24}(OH)_5(H_2O)](ClO_4)\cdot 0.75H_2O$ (**NaNpBO-1**). **NaNpBO-1** possesses a layered structure consisting of double neptunyl(VI) borate sheets bridged by another Np^{VI} site through cation−cation interactions. The sole presence of Np^{VI} in **NaNpBO-1** is supported by absorption and vibrational spectroscopy.

Pentavalent and hexavalent actinides are typically found within a *trans*-dioxo unit, AnO_2^{n+}, namely, the actinyl cation. This unit forms as a consequence of hybridization of metal 5f/6p/6d and O 2p orbitals, yielding formally triple bonds between the actinide and oxygen.[1] The intrinsic Lewis base nature of the "yl" oxygen atoms and their ability to donate electron density to a Lewis acid center leads to a well-recognized bonding mode known as cation−cation interactions (CCIs); although these should simply be called bridging oxo's. These interactions were first observed in solutions containing NpO_2^{+} and UO_2^{2+},[2] but they are now known to occur in many neptunium(V) compounds.[3] CCIs play a key role in the disproportionation of actinide(V) because electron transfer occurs through the bridging oxo.[4] These oxo atoms also allow for superexchange that leads to magnetic ordering in neptunium(V) materials.[5]

The Lewis basicity of the "yl" oxygen atoms decreases dramatically from An^{V} to An^{VI}.[6] As a result, the oxos in uranium(VI) were thought to be chemically inert. For example, structural statistics show that more than 50% of inorganic neptunium(V) compounds contain CCIs, while only 2% of uranium(VI) compounds possess this bonding motif.[3,7] However, the number of uranium(VI) compounds that contain CCIs has increased rapidly in recent years, and both two- and three-center CCIs for uranium(VI) have been observed.[8]

While there is still considerable debate concerning periodic trends in the bond strength of $An^{VI}{=}O$, it is thought to decrease across the actinide series from U to Pu, and one conjecture is that the oxo atoms in NpO_2^{2+} are more basic than those in UO_2^{2+}.[9] This trend can also be understood based on the smaller electronegativity of neptunium compared to uranium (1.89 for U and 1.85 for Np).[10] One would therefore expect examples of neptunium(VI) compounds containing CCIs; however, none are known in the absence of neptunium(V).[11] One reason for this is that there are simply far fewer structurally characterized neptunium(VI) compounds compared to uranium(VI), and unlike uranium(VI), neptunium(VI) is both a strong oxidant and highly radioactive, making studies more challenging.

We recently demonstrated that a neptunium(VI) borate, $NpO_2[B_8O_{11}(OH)_4]$, can be synthesized from a boric acid flux reaction using $NpO_2(ClO_4)_2$ as the source of Np^{VI}, where ClO_4^{-} acts as a strong oxidizing reagent at elevated temperatures (e.g., 220 °C) to prevent Np^{VI} from being reduced.[12] By introducing Na^{+} into the neptunium(VI) borate system, we have successfully synthesized a new sodium neptunium(VI) borate with a complex structure that contains the first example of CCIs between neptunium(VI) centers. In this Communication, we will describe the synthesis, crystal structure, and electronic and vibrational spectra of $Na[(NpO_2)_4B_{15}O_{24}(OH)_5(H_2O)](ClO_4)\cdot 0.75H_2O$ (**NaNpBO-1**).

Nearly colorless crystals of **NaNpBO-1** were isolated as a pure phase from the boric acid flux reaction of $NpO_2(ClO_4)_2$ with $NaClO_4$ at 220 °C (see the Supporting Information, SI). Similar reactions using other alkali-metal perchlorates as starting materials only yielded $NpO_2[B_8O_{11}(OH)_4]$. Perchlorate is a strong enough oxidant that neptunium(V) perchlorate can be used as the starting material, and it still affords the neptunium(VI) product, $NpO_2[B_8O_{11}(OH)_4]$. Therefore, it seems unlikely that neptunium(V) will be produced in reactions starting with neptunium(VI) perchlorate owing to the oxidizing potential of ClO_4^{-}.

Single-crystal X-ray diffraction studies revealed that **NaNpBO-1** crystallizes in the triclinic space group $P\bar{1}$.[13] The structure of **NaNpBO-1** is represented by neutral slabs consisting of NpO_2^{2+}, BO_3 triangles, and BO_4 tetrahedra, and it bears many similarities with the slabs found in the mixed-valent neptunium compounds $K_4[(NpO_2)_{6.73}B_{20}O_{36}(OH)_2]$ and $Ba_2[(NpO_2)_{6.59}B_{20}O_{36}(OH)_2]$ (Figure 1a).[14] However, the Np^{IV} site found in the latter two is absent in **NaNpBO-1**. Another obvious difference is that the slabs in the two previously reported compounds are separated by K^{+} or Ba^{2+} cations; thus, the overall layers possess negative charge, while in **NaNpBO-1**, as can be seen from the chemical formula, Na^{+} cations and ClO_4^{-} anions are intercalated into the interlayer space.

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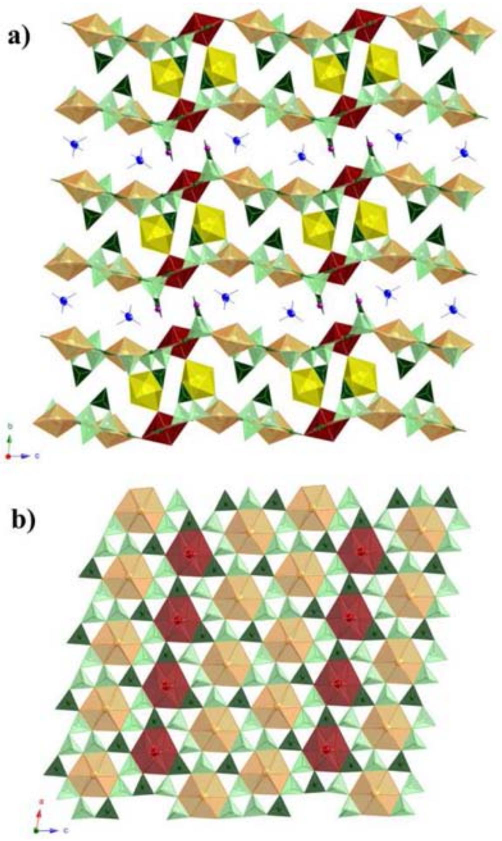

Figure 1. (a) Depiction of the layered structure of **NaNpBO-1**. (b) Depiction of sheet topology of **NaNpBO-1**. Np(1) sites providing one bridging oxo are shown in dark brown. Np(3) sites accepting one oxo are shown in yellow. Np(2) and Np(4) sites are shown in light pink, BO_3 triangles in dark green, BO_4 tetrahedra in light green, sodium atoms in purple, and perchlorates in blue.

One of the reasons for the complexity of the structure of **NaNpBO-1** is that it contains four crystallographically distinct neptunium sites. The neptunyl borate sheets extend parallel to the [*ac*] plane as shown in Figure 1b, the three neptunium atoms found within the sheets are eight-coordinate hexagonal bipyramids, and each hexagonal bipyramid is surrounded by nine neighboring borate units, as observed in a typical actinyl borate compound.[15] However, all previously reported actinyl borates only include one or, more rarely, two distinct actinide sites within the sheets. Therefore, the sheets in **NaNpBO-1** provide the most complicated topology found in actinyl borates and are assigned as N-type sheets according to the nomenclature that we have developed.[15] Np(1) polyhedra are coordinated by four BO_3 triangles and five BO_4 tetrahedra, while Np(2) and Np(4) are both surrounded by three BO_3 triangles and six BO_4 tetrahedra, but the ordering of the different borate units is not the same in Np(2) and Np(4) (Figure 1b).

The most important structural feature of **NaNpBO-1** is the bridges that connect the sheet substructures, which are provided by bridging oxo's between the Np(1) and Np(3) centers. Np(3) is seven-coordinate and has a pentagonal-bipyrimid geometry. One BO_3 triangle, two BO_4 tetrahedra, one water molecule, and the oxo atom from Np(1) provide the first coordination sphere of the Np(3) sites. The CCI bonding mode is found to be the simplest form; i.e., each Np(1) center donates only one oxo, while the Np(3) center accepts only one oxo (Figure 2). This mode is also the most common case for uranium(VI)[7,8] but is very rare in neptunium(V) compounds.[3,16] The bridging oxo forms in a relatively asymmetric neptunyl unit for Np(1) with neptunyl distances of 1.80(1) and 1.87(1) Å, where the latter is involved in CCI. Notably, although it is known that "yl" oxo atoms for uranium(VI) involved in CCIs can have significantly longer uranyl bond distances, the oxo atom not involved in CCIs in the Np(1) unit still possesses a neptunyl distance longer than the average neptunyl(VI) distance of 1.75 Å,[3b] which leads to the presumption that Np(1) is pentavalent. The bond valence sum (BVS) of Np(1) using neptunium(VI) parameters is calculated to be 5.61, and this further questions the real valence state of the Np(1) centers.[3b] In contrast, the neptunyl distances for the other three neptunium centers range from 1.73 (1) to 1.76(1) Å. The BVS calculations and spectroscopic data for the assignments of the hexavalent state to these neptunium sites are straightforward.

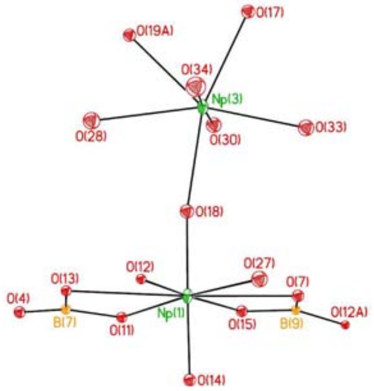

Figure 2. View of the bridging oxo in **NaNpBO-1**.

Compared to the crystallographic data, where the assignment of the valence state to neptunium can be ambiguous, electronic spectroscopy can provide more straightforward information because neptunium in different oxidation states produces characteristic electronic transitions that are well separated from each other.[17]

These transitions undergo relatively small shifts with different coordination environments and can thus be used as fingerprints for oxidation-state identification. The solid-state UV–vis–NIR absorption spectrum of **NaNpBO-1** measured from a single crystal is shown in Figure 3. The peak at 1200 nm is characteristic for neptunium(VI), which corresponds to the f–f transition from the ground state of $5f^1$ to the third excited state.[18] The transition near 980 nm characteristic for neptunium(V) is absent in the spectrum. Rao et al. reported a series of highly symmetric neptunium(V) compounds, where the neptunium(V) centers reside on inversion centers.[19] The characteristic transitions for neptunium(V) are "silent" in their spectra according to Laporte's rule. However, given the highly asymmetric coordination environment of Np(1) centers in **NaNpBO-1**, the possibility of a "silent neptunium(V) band" is very unlikely. Therefore, the electronic spectrum strongly suggests the absence of neptunium(V) in **NaNpBO-1**, because a sharp feature at around 1010 nm would be expected for a neptunium(V) involved in CCI bonding.[3a]

Finally, Raman spectroscopy is also useful for the oxidation-state assignment of neptunium because the symmetric stretching modes of pentavalent and hexavalent neptunyl

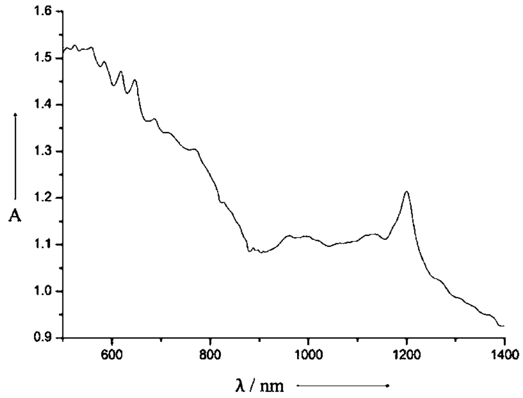

Figure 3. Solid-state UV−vis−NIR absorption spectrum of **NaNpBO-1**.

units are well separated from each other.[20] The solid-state Raman spectrum of **NaNpBO-1** taken from a cluster of crystals covered with Krytox oil (for safety reasons) compared to the oil background are shown in Figure S2 (in the SI along with data collection parameters). The major peak at 881 cm^{-1} can be unambiguously assigned to the symmetric stretching mode of neptunyl(VI) units because it is comparable to that of $NpO_2(IO_3)_2(H_2O)$ at 872 cm^{-1}.[21] It appears that all four symmetric stretching modes of the neptunyl units overlap. Very recently, symmetric stretching modes of neptunyl(V) were shown to be sensitive to CCI bonding modes in the solid state by Jin et al.[5f] The frequencies for neptunyl(V) units that are not involved in CCIs, donating one oxo, and donating two oxo's are near 773, 730, and 670 cm^{-1}, respectively, in the selenate system.[5f] The 730 cm^{-1} feature is weak because of the highly asymmetric nature of the neptunyl(V) unit in $Na(NpO_2)(SeO_4)(H_2O)$, which is donating one oxo atom, whereas the other features are strong and sharp.[5f] Notably, no features are observed in the range between 700 and 800 cm^{-1} in the spectrum of **NaNpBO-1**.

In conclusion, a pure hexavalent assignment for all neptunyl units present in **NaNpBO-1** is strongly supported by the reaction conditions and reagents and by the electronic and Raman spectra, although one of the neptunium(VI) sites possesses relatively long neptunyl bond distances. This site donates an oxo atom to another neptunium(VI) site, which provides the first example of CCIs between neptunium(VI) centers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details, solid-state Raman spectra, SEM−EDS measurement, and X-ray crystallographic files in CIF format for **NaNpBO-1**. 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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(13) Crystallographic data for **NaNpBO-1**: nearly colorless needles, 0.073 × 0.015 × 0.007 mm^3, triclinic, $P\bar{1}$, $Z = 2$, $a = 6.466(4)$ Å, $b = 15.816(9)$ Å, $c = 16.644(10)$ Å, $\alpha = 84.229(12)°$, $\beta = 78.955(8)°$, $\gamma = 86.853(9)°$, $V = 1661.0(17)$ Å^3 [$T = 100(2)$ K], $\mu = 126.53$ cm^{-1}, R1 = 0.0579, wR2 = 0.1222.

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