Evaluation of *f*-Element Borate Chemistry: A Review

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Keywords: actinide borate, lanthanide borate, electronic spectroscopy, coordination chemistry

Abstract

The synthesis, structure elucidation, and spectroscopic measurements of a myriad of new, *f*-element borates has revealed the unusual effects that this electron-rich oxoanion has on the electronic properties of lanthanides and actinides. One purpose of these studies was to provide models for actinide compounds that may exist in either vitrified nuclear waste or in repositories located within salt deposits that have significant borate content. In addition, the radiation-damage resilience of polyborate networks positions these materials as suitable candidates for probing coordination chemistry and physical properties much deeper into the actinide series than is normally possible, and compounds with actinides up to californium ($Z = 98$) have been successfully prepared and characterized in exquisite detail. Structural determination of these materials show that both the lanthanide and actinide series display previously unknown coordination chemistry, but, more importantly, that the two series have little overlap in terms of structure and composition, and have few parallels. In addition, some of these compounds display unique physico-chemical properties, one example of which is the selective trapping of radionuclides. The foremost discovery first identified in actinide borates is that the chemistry of californium represents an onset of unprecedented chemical behavior that compares better with high-oxidation state, early transition metal complexes than it does with earlier *f*-elements.

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1. Introduction

The development of *f*-element borate chemistry was inspired, in part, from evidence that a significant boron concentration exists in the brine solutions found at the Waste Isolation Pilot Plant (WIPP) in Carlsbad, New Mexico.¹ WIPP is the world's only functioning nuclear waste

geological repository and contains significant quantities of uranium and plutonium as well as smaller quantities of other transuranium elements, especially americium.² The borate concentration in the intergranular brines at WIPP is 166 ppm, and ranks only behind chloride and sulfate.² The conditions at WIPP are unusual in that shortly after the repository is sealed, the conditions will become quite reducing. This scenario creates chemistry that had been previously considered as irrelevant, in that low oxidation states, such as Pu^{III} , contribute significantly to speciation.³ In addition, groundbreaking work by Reed and co-workers showed that not only are borate anions capable of coordinating *f*-element ions in these brines, but that under slightly acidic conditions, these actinide borates control actinide solubility.³ They therefore provide a mechanism for retarding actinide migration in salt-based repositories in the event of release from the storage containers, which has in fact already taken place at WIPP.⁴

Borate materials are known for their seemingly innumerable fundamental building blocks (FBB) that form both in solution and in the solid state. The two dominant subunits are trigonal planar BO_3^{3-} and tetrahedral BO_4^{5-} anions that are capable of polymerizing primarily via corner sharing under ambient conditions and edge-sharing at high pressures.⁵⁻⁷ Classification of the type of borate network is done in order to establish trends in the structures of the *f*-element materials (Figure 1).⁸ With adjustments in concentration, pH, temperature, or pressure, borates and polyborates exist as clusters, 1D chains, 2D scaffolds, or even 3D networks in these compounds.⁵ Borate systems can also accommodate the coordination of other anionic species in these structures.⁶ Finally, these materials have been found to form crystalline compounds with *f*-block metal ions in a variety of oxidation states despite the increasing specific activity of late actinide isotopes. These attributes qualify borate anions as excellent ligands for extensive research with lanthanide and actinide elements.

Figure 1: Illustrations of the variation in borate topologies within uranyl borates.

2. Lanthanide Borates

A variety of lanthanide borate materials have been synthesized, though only a few will be discussed in this review.⁹ The structural chemistry of these selected compounds is detailed to provide archetypal examples of *f*-block coordination chemistry. However, spectroscopic and magnetic evidence will be added where needed to illustrate the key differences between compounds. The lanthanide borate chlorides are presented for comparison in order to highlight differences with actinide borates prepared using the flux synthesis.⁹ These data point to differences in orbital contributions to bonding between 4*f* and 5*f* series.

Lanthanide borate materials are commonly found in formally trivalent oxidation states, while those compounds containing Ln^{II} are uncommon. Tetravalent lanthanide borate products are absent from the literature. Trivalent lanthanide borates exist in several forms⁹⁻¹² and can incorporate chloride,⁹ bromide,^{13,14} iodide,¹⁴ perchlorate,¹⁶ phosphate,¹⁷ and acetate¹⁸ into their structures, as well as crystallizing from different borate sources. Few divalent lanthanide borate products have been prepared with organoborate ligands in metathesis reactions, and we must refer the reader the small catalog of literature regarding these materials and their subsequent crystallographic and spectroscopic, as each analysis provides insight into the behavior of Sm^{II} , Eu^{II} , Tm^{II} , and Yb^{II} in bulk materials.¹⁹⁻²⁹ Table 1 displays characteristics of lanthanide borates, including their products formula, space group, and citation information.

2.1 Trivalent Lanthanide Chlorides

This series of lanthanide borates followed an optimized procedure used throughout the rest of this review, although slight adjustments in pH or anion character were made with the intent of observing the properties of new lanthanide and actinide borate materials.^{9,16} All lanthanide borate materials displayed spectroscopic properties characteristic of their respective trivalent lanthanide cation.

Table 1: Classification of lanthanide borates.

Compound	Space Group	Reference
$\text{Ln}[\text{B}_5\text{O}_9]$	$I2_1/acd$	Li, <i>et al.</i> ¹⁰
$\text{H}_3\text{LnB}_6\text{O}_{12}$	$R3c$	Li, <i>et al.</i> ¹⁰
$\text{Ln}[\text{B}_8\text{O}_{11}(\text{OH})_5]$	$P2_1/n$	Li, <i>et al.</i> ¹¹

$\text{Ln}[\text{B}_9\text{O}_{13}(\text{OH})_4] \cdot \text{H}_2\text{O}$	$P2_1/n$	Li, <i>et al.</i> ¹¹
$\text{Ce}[\text{B}_5\text{O}_8(\text{OH})]\text{NO}_3 \cdot 3\text{H}_2\text{O}$	$P2_1/n$	Li, <i>et al.</i> ¹¹
$\text{Ln}_2[\text{B}_6\text{O}_{10}(\text{OH})_4] \cdot \text{H}_2\text{O}$	$C2/c$	Cong, <i>et al.</i> ¹²
$\text{La}[\text{B}_7\text{O}_{10}(\text{OH})_3(\text{H}_2\text{O})\text{Br}]$	$P2_1/n$	Polinski, <i>et al.</i> ¹³
$\text{Ln}[\text{B}_6\text{O}_9(\text{OH})_2(\text{H}_2\text{O})_2\text{Br}] \cdot \frac{1}{2}\text{H}_2\text{O}$	$P2_1/n$	Polinski, <i>et al.</i> ¹³
$\text{Sm}_4[\text{B}_{18}\text{O}_{25}(\text{OH})_{13}\text{Br}_3]$	$P2_1/c$	Polinski, <i>et al.</i> ¹³
$\text{Ln}[\text{B}_7\text{O}_{11}(\text{OH})(\text{H}_2\text{O})_3\text{I}]$	$P2_1/n$	Polinski, <i>et al.</i> ¹³
$\text{Ln}[\text{B}_5\text{O}_8(\text{OH})(\text{H}_2\text{O})_2\text{Br}]$	$P2_1/n$	Polinski, <i>et al.</i> ¹⁴
$\text{Nd}_4[\text{B}_{18}\text{O}_{25}(\text{OH})_{13}\text{Br}_3]$	$P2_1/c$	Polinski, <i>et al.</i> ¹⁴
$\text{Ln}[\text{B}_5\text{O}_8(\text{OH})(\text{H}_2\text{O})_2\text{I}]$	$P2_1/n$	Polinski, <i>et al.</i> ¹⁴
$\text{Ln}_4\text{B}_{22}\text{O}_{36}(\text{OH})_6(\text{H}_2\text{O})_{13}$	$I23$	Parker, <i>et al.</i> ¹⁵
$\text{Ln}[\text{B}_8\text{O}_{10}(\text{OH})_6(\text{H}_2\text{O})(\text{ClO}_4)] \cdot 0.5\text{H}_2\text{O}$	$P2_1/n$	Polinski, <i>et al.</i> ¹⁶
$\text{Ln}[\text{B}_8\text{O}_{11}(\text{OH})_4(\text{H}_2\text{O})(\text{ClO}_4)]$	$P2_1/n$	Polinski, <i>et al.</i> ¹⁶
$\text{Ln}[\text{B}_7\text{O}_{11}(\text{OH})(\text{H}_2\text{O})_2(\text{ClO}_4)]$	$P2_1/n$	Polinski, <i>et al.</i> ¹⁶
$\text{K}_3\text{Ln}[\text{OB}(\text{OH})_2]_2[\text{HOPO}_3]_2$	$R-3$	Zhou, <i>et al.</i> ¹⁷
$\text{Ln}_2(\text{CH}_3\text{CO}_2)_2[\text{B}_5\text{O}_9(\text{OH})] \cdot \text{H}_2\text{O}$	Cc	Yang, <i>et al.</i> ¹⁸
$\text{Ln}_2(\text{CH}_3\text{CO}_2)_2[\text{B}_5\text{O}_9(\text{OH})]$	Cc	Yang, <i>et al.</i> ¹⁸
$\text{Lu}_2\text{B}_2\text{O}_5(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	$P-1$	Ortner, <i>et al.</i> ³⁰

Structural analysis of each material revealed a series with two structural and compositional changes occurring at neodymium and europium. The early lanthanide borates crystallize in the monoclinic space group, Cc , a noncentrosymmetric space group with a polar glide plane, with formula $\text{Ln}[\text{B}_4\text{O}_6(\text{OH})_2\text{Cl}]$ ($\text{Ln} = \text{La} - \text{Nd}$). Samarium and europium crystallize as $\text{Ln}_4[\text{B}_{18}\text{O}_{25}(\text{OH})_{13}\text{Cl}_3]$ ($\text{Ln} = \text{Sm}, \text{Eu}$) in the monoclinic space group, $P2_1/c$. Two products are

in fact found with occur with europium, and it represent an ionic radius where both the $\text{Ln}_4[\text{B}_{18}\text{O}_{25}(\text{OH})_{13}\text{Cl}_3]$ structure-type occurs, as well as the third and final composition $\text{Ln}[\text{B}_6\text{O}_9(\text{OH})_3]$ ($\text{Ln} = \text{Eu} - \text{Lu}$), are observed.¹⁰ Note that a transition from a polar structure with little point symmetry to a centrosymmetric structure to a relatively high-symmetry structure occurs as the ionic radius contracts. This is a direct reflection of the decreasing coordination number of the lanthanide cations (*vide infra*).

In all compounds of this series, dense, three-dimensional, borate frameworks are found that contain holes to incorporate lanthanide metalcenters. In the first lanthanide borate structure, triangular holes are created from one BO_3 unit and two BO_4 units, in a K-type borate network, where solely corner-sharing borate units exist (Figure 2a). Lanthanide centers are situated in a ten-coordinate environment described as a capped triangular cupola geometry (Figure 2b). The equatorial plane reaches near coplanar quality, with the six oxygen atoms from the three edge-sharing borates. The two basal oxygen atoms are those bound to two BO_4 units, while the capping and basal chloride anions are those bound to the lanthanide center in neighboring sheets, thereby creating the three-dimensional framework.

Figure 2: a) K-type borate sheet viewed along the $[ab]$ plane, and b) ten-coordinate capped triangular cupola geometry of Ln centers (La, Pr, and Nd). Lanthanide centers are light green, chlorine are yellow, BO_3^{3-} triangles are maroon, BO_4^{5-} are red, and oxygen are dark red.

Ln-O bond distances are typical of trivalent lanthanide materials, where between La – Nd the base oxygen bond distances are between 2.422(2) and 2.553(2) Å, and equatorial oxygen distances are between 2.524(3) and 2.733(3) Å. The capping and basal chloride bonds are at a distance between 2.852(3) and 2.925(1) Å then 2.909(4) and 2.927(1) Å, respectively throughout the family.

Figure 3: a) F-type borate sheet forming along $[ab]$ plane, and b) nine-coordinate hula-hoop geometry of Ln centers (Sm and Eu).

The structure of $\text{Ln}_4[\text{B}_{18}\text{O}_{25}(\text{OH})_{13}\text{Cl}_3]$ (Ln = Sm, Eu) contains an F-type borate network made up of corner-sharing BO_3 and BO_4 units (Figure 3a). The corner-sharing $\text{BO}_4\text{-BO}_4\text{-BO}_3$ polyborate unit can be seen diagonally along the $[ab]$ plane. Lanthanide centers are caught in a hula-hoop geometry within the triangular voids of two BO_4 and one BO_3 constituents (Figure 3b). Six oxygen atoms from two BO_4 units and one BO_3 unit are bound in a nearly coplanar equatorial arrangement.⁹ Additionally, a capping chloride bridges to the next lanthanide center, while the basal oxygen atoms are those bound to either two BO_4 bridge units or from one BO_3 unit and a nonbridging hydroxide moiety.

A different perspective of the final lanthanide borate structure-type $\text{Ln}[\text{B}_6\text{O}_9(\text{OH})_3]$ (Ln = Eu – Lu) is offered here by breaking down the B_6O_{15} FBB into its basic components.¹⁰ The polyborate network does not form in any characterized sheet (Figure 4a).⁹ Each lanthanide center is encapsulated in a nine-coordinate tricapped trigonal prism with slight distortion (Figure 4b).

Six BO_3 units corner-share to each of six BO_4 units and the metal-center, while three BO_4 tetrahedra edge-share and the other three units corner-share to the lanthanide. The three oxygen atoms that are bound to the edge-sharing BO_4 tetrahedra are not bound to a neighboring BO_3 unit and are those hydrogenated oxygen atoms. The three-dimensional polyborate network extends from each BO_3 unit and all corner-sharing BO_4 units. Ln–O bond distances of each triangle prism face and the capping oxygen distance are 2.387(5), 2.392(4), and 2.470(3) Å, respectively.

Figure 4: a) A view of the 3D borate network in $\text{Ln}[\text{B}_6\text{O}_9(\text{OH})_3]$ ($\text{Ln} = \text{Eu} - \text{Lu}$), and b) nine-coordinate tricapped trigonal prismatic geometry of the Ln^{III} centers.

2.2 Divalent $\text{Eu}[\text{B}_8\text{O}_{11}(\text{OH})_4]$

Preparation of a divalent europium borate material was performed from two different reductive methods, both of which were under aerobic and hydrated conditions.³¹ This compound not only adds to the spanning coordinating abilities of borate, now capable of crystallizing divalent *f*-elements, but adds to only a small family of air- and water-stable divalent europium materials.³²⁻³⁶

$\text{Eu}[\text{B}_8\text{O}_{11}(\text{OH})_4]$ was prepared under hydrothermal conditions using either HI or a Zn/Hg amalgam as a reductant. This compound adopts the polar, monoclinic space group, $P2_1$. The structure contains M-type sheets identified by a trimer formed from three, corner-sharing BO_4 units to a single oxygen atom. Borate sheets with triangular cavities are created from four BO_3 triangles and five BO_4 tetrahedra that corner-share to house Eu^{II} cations (Figure 5a).

Figure 5: a) M-type borate topology in $\text{Eu}[\text{B}_8\text{O}_{11}(\text{OH})_4]$, and b) nine-coordinate hula-hoop geometry of Eu^{II} -center.

Coordinating each europium atom in a nine-coordinate hula-hoop environment (Figure 5b) are three corner-sharing borate units, while two BO_3 units and one chelating BO_4 unit. The six oxygen atoms that are bound in the nearly coplanar equatorial plane are those to the borate units forming the triangular holes. The base and capping oxygen atoms are bound to BO_3 units above and below the $[bc]$ sheets. The much longer Eu–O bond lengths are observed that range

from 2.533(5) to 2.722(5) Å. These distances are consistent with Eu^{II} and support the divalent state and are further confirmed by bond-valence sum (BVS) calculations.³¹

Spectroscopic methods were employed to gather more information of this system. Divalent europium is a $4f^7$ system and has a ground state of $^8S_{7/2}$ with f^7 excited states and f^6d states, which are close in energy.^{37,38} UV-Vis-NIR absorption spectroscopy reveals a single broad peak maximizing at 329 nm that is characteristic of a $4f^7 \rightarrow 4f^65d$ transition. The intensity of this transition is much larger than that found with $4f-4f$ transitions because it is Laporte allowed (Figure 6a).³⁸⁻⁴⁰ Emission of blue light centered at 430 nm is also characteristic of this transition for Eu^{II} (Figure 6b). The intensity of this transition is further enhanced by the chiral structure and permanent dipole that exists in polar crystal structures.⁴¹⁻⁴³

Figure 6: a) UV-Vis-NIR absorption spectrum of Eu[B₈O₁₁(OH)₄], and b) emission spectrum of Eu[B₈O₁₁(OH)₄] from incident 430 nm light.

2.3 Nd₂[B₁₂O_{17.5}(OH)₅(H₂O)₄Br_{1.5}]Br_{0.5}·H₂O

Structural analysis of Nd₂[B₁₂O_{17.5}(OH)₅(H₂O)₄Br_{1.5}]Br_{0.5}·H₂O reveals the polar, orthorhombic space group, *Fdd2* (Figure 7a).¹³ Although several unusual structural

characteristics are found, the most interesting is the cationic framework of the material. Within this M-type borate framework, two crystallographically unique neodymium centers alternate in diagonal rows along the [011] axis, while two unusual voids, shaped like hourglasses and diamonds, alternate along the *b*-axis. The hourglass void contains co-crystallized water molecules, in addition to coordinating hydroxide and water moieties. The diamond-shaped holes houses single bromide anions (Figure 7b).

Figure 7: a) M-type borate sheet topology in $\text{Nd}_2[\text{B}_{12}\text{O}_{17.5}(\text{OH})_5(\text{H}_2\text{O})_4\text{Br}_{1.5}]\text{Br}_{0.5}\cdot\text{H}_2\text{O}$, and b) Bromide anions and water-filled voids within the cationic framework of $\text{Nd}_2[\text{B}_{12}\text{O}_{17.5}(\text{OH})_5(\text{H}_2\text{O})_4\text{Br}_{1.5}]\text{Br}_{0.5}\cdot\text{H}_2\text{O}$.

The environment of the first Nd center (Nd^1) is a nine-coordinate hula-hoop, where its equatorial plane is made up of six oxygen atoms bound from two edge-sharing BO_3 units and one edge-sharing BO_4 unit, one water molecule capping Nd^1 , and either two bromide anions or one bromide and one hydroxide moiety, respectively, coordinating at the base (Figure 8a and b).⁴⁴ The second Nd environment (Nd^2) is ten-coordinate and appropriately described as a capped triangular cupola (Figure 8c).⁴⁵ The equatorial plane contains six oxygen atoms from two edge-

sharing BO_3 units and one edge-sharing BO_4 unit, while one bound water molecule caps Nd^2 , and two water molecules and one corner-sharing BO_3 unit coordinate from below.¹³ It is this BO_3 unit which connects each borate sheet together by coordinating to one of three BO_4 tetrahedra comprising the central polyborate trimer. The equatorial oxygen bond lengths of Nd^1 are between 2.494(5) and 2.651(5) Å, while the capping water bond distance is 2.453(8) Å and the two base bromide and hydroxide distances are 2.905(1), 2.968(2), and 2.559(1) Å, respectively. The bond distances between Nd^2 and the equatorial oxygen bond distances are found between 2.547(6) and 2.676(6) Å, while the capping water bond distance is 2.706(8) Å, the base water distances are 2.423(6) and 2.438(7) Å, and the bond distance between the oxygen bound to the BO_3 unit is 2.618(3) Å.

Figure 8: a) Nine-coordinate hula-hoop geometry of Nd^1 centers with two basal bromides, or b) one basal bromide and one basal hydroxide, and c) capped triangular cupola geometry of Nd^2 center.

3. Higher-Valent Actinyl Borates

Uranium, neptunium, and plutonium display redox chemistry that is more similar to that found with early transition metals in that oxidation states as low as 3+ and as high as 7+ are well-known.⁴⁶ A linear, dioxo species, known the actinyl cation, usually occurs with penta- and hexavalent oxidation states. Although Behm⁴⁷ and Gasperin⁴⁸⁻⁵⁴ reported a total of eight uranyl borates, little is known about these compounds beyond their structural chemistry. Transuranium borates were absent in the literature until quite recently. These materials have extraordinary structural richness and are among the most complex uranyl oxoanion systems reported. Many of these compounds form noncentrosymmetric structure types, and second-harmonic generation has been measured for some of these compounds. The neptunium compounds add considerable complexity beyond the structural features because mixed-valency is endemic to this system.

3.1 Uranyl Borates

Uranyl borates were prepared in the 1980's primarily via high-temperature solid-state synthesis.⁴⁸⁻⁵⁴ Using this method, seven uranyl borates were isolated that contain a wide variety of structural motifs, but in general the BO_4 building unit is rare, and the structures are assembled from almost entirely from BO_3 triangles. The compounds are typically layered as is the norm for uranyl oxoanion materials. $\text{K}_6[\text{UO}_2\{\text{B}_{16}\text{O}_{24}(\text{OH})_8\}]\cdot 12\text{H}_2\text{O}$ represents the sole exception to this and was prepared by the evaporation of a concentrated solution at room temperature. Its structure and composition is quite different from that obtained from high-temperature reactions in that it contains molecular clusters of UO_2^{2+} units surrounded by 16-borate rings (Figure 9) and BO_4 units are prevalent.⁴⁷⁻⁵⁴

Figure 9: A view of the molecular $[\text{UO}_2(\text{BO}_3)_8(\text{BO}_4)_8]^{6-}$ anion found in $\text{K}_6[\text{UO}_2\{\text{B}_{16}\text{O}_{24}(\text{OH})_8\}]\cdot 12\text{H}_2\text{O}$.⁴⁷

After twenty years, this area of research was quickly revitalized with the production of twenty-six new uranyl borates using low-temperature boric acid flux reactions.⁵⁴⁻⁶² Of merit is the fact that many of these crystallize in noncentrosymmetric space groups. Coupled to the fact that borate materials are known to not absorb deep UV light,⁶³ these material's optical properties were sought more rigorously compared to other actinide borate materials. More specifically, second-harmonic generation measurements were taken in order to characterize the nonlinear optical properties of these materials. Table 2 lists these uranyl borate materials prepared and includes borate derivatives such as fluoroborates.

Table 2: Uranyl borates, boronates and fluoroborates.

Product Formula	Space Group	Citation
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$(\text{UO}_2)\text{B}_2\text{O}_4$	$C2$	Wang, S. <i>et. al.</i> ⁵⁵
$\alpha\text{-(UO}_2)_2[\text{B}_9\text{O}_{14}(\text{OH})_4]$	$P2_1$	Wang, S. <i>et. al.</i> ⁵⁵
$\beta\text{-(UO}_2)_2[\text{B}_9\text{O}_{14}(\text{OH})_4]$	$P-1$	Wang, S. <i>et. al.</i> ⁵⁵
$(\text{UO}_2)_2[\text{B}_{13}\text{O}_{20}(\text{OH})_3] \cdot 1.25\text{H}_2\text{O}$	$P-1$	Wang, S. <i>et. al.</i> ⁵⁵
$\alpha\text{-Na}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}(\text{OH})_5]$	$P3_2$	Wang, S. <i>et. al.</i> ⁵⁶
$\beta\text{-Na}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}(\text{OH})_5]$	Cc	Wang, S. <i>et. al.</i> ⁵⁶
$\text{Na}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}(\text{OH})_5] \cdot 3\text{H}_2\text{O}$	$P3_121$	Wang, S. <i>et. al.</i> ⁵⁶
$\text{Na}[(\text{UO}_2)\text{B}_6\text{O}_{10}(\text{OH})] \cdot 2\text{H}_2\text{O}$	Cc	Wang, S. <i>et. al.</i> ⁵⁶
$\text{Ti}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{16}(\text{OH})_3]$	Cc	Wang, S. <i>et. al.</i> ⁵⁶
$\alpha\text{-Ti}_2[(\text{UO}_2)_2\text{B}_{11}\text{O}_{18}(\text{OH})_3]$	$P1$	Wang, S. <i>et. al.</i> ⁵⁶
$\beta\text{-Ti}_2[(\text{UO}_2)_2\text{B}_{11}\text{O}_{18}(\text{OH})_3]$	Cc	Wang, S. <i>et. al.</i> ⁵⁶
$\text{Ti}_2[(\text{UO}_2)_2\text{B}_{11}\text{O}_{19}(\text{OH})]$	Cc	Wang, S. <i>et. al.</i> ⁵⁶
$\text{Li}[(\text{UO}_2)\text{B}_5\text{O}_9] \cdot \text{H}_2\text{O}$	Pn	Wang, S. <i>et. al.</i> ⁵⁷
$\text{Ag}[(\text{UO}_2)\text{B}_5\text{O}_8(\text{OH})_2]$	$P2_1/n$	Wang, S. <i>et. al.</i> ⁵⁷
$\alpha\text{-Cs}[(\text{UO}_2)_2\text{B}_{11}\text{O}_{16}(\text{OH})_6]$	$P-1$	Wang, S. <i>et. al.</i> ⁵⁷
$\beta\text{-Cs}[(\text{UO}_2)_2\text{B}_{11}\text{O}_{16}(\text{OH})_6]$	Cc	Wang, S. <i>et. al.</i> ⁵⁷
$\text{Na}[(\text{UO}_2)\text{B}_5\text{O}_8(\text{OH})\text{F}] \cdot \text{H}_2\text{O}$	Cc	Wang, S. <i>et. al.</i> ⁵⁸
$\text{K}[(\text{UO}_2)\text{B}_5\text{O}_8(\text{OH})\text{F}]$	$P2_1/n$	Wang, S. <i>et. al.</i> ⁵⁸
$\text{K}_{11}[(\text{UO}_2)_6\text{B}_{24}\text{O}_{36}\text{F}_{22}](\text{H}_2\text{BO}_3)$	$P6_3/m$	Wang, S. <i>et. al.</i> ⁵⁸
$\text{Rb}[(\text{UO}_2)\text{B}_5\text{O}_8(\text{OH})\text{F}]$	Cc	Wang, S. <i>et. al.</i> ⁵⁸
$\text{Ti}[(\text{UO}_2)\text{B}_5\text{O}_8(\text{OH})\text{F}]$	$P1$	Wang, S. <i>et. al.</i> ⁵⁸
$\text{K}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}(\text{OH})_5]$	$C2/c$	Wang, S. <i>et. al.</i> ⁵⁹
$\text{K}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{16}(\text{OH})_3] \cdot 0.7\text{H}_2\text{O}$	$P-1$	Wang, S. <i>et. al.</i> ⁵⁹

$\text{K}_2[(\text{UO}_2)_2\text{B}_{12}\text{O}_{19}(\text{OH})_4]\cdot 0.3\text{H}_2\text{O}$	$P3_121$	Wang, S. <i>et. al.</i> ⁵⁹
$\text{Rb}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{16}(\text{OH})_3]\cdot 0.7\text{H}_2\text{O}$	$P2_1/m$	Wang, S. <i>et. al.</i> ⁵⁹
$\text{Rb}_2[(\text{UO}_2)_2\text{B}_{13}\text{O}_{20}(\text{OH})_5]$	$P2_1/n$	Wang, S. <i>et. al.</i> ⁵⁹
$\text{Ba}_5[(\text{UO}_2)(\text{PO}_4)_3(\text{B}_5\text{O}_9)]\cdot x\text{H}_2\text{O}$	$P4_2/n$	Wu, S. <i>et. al.</i> ⁶⁰
$\text{Rb}_2[(\text{UO}_2)_2\text{B}_8\text{O}_{12}\text{F}_6]\cdot \text{H}_2\text{B}_4\text{O}_7$	$P1$	Wang, S. <i>et. al.</i> ⁶¹
$\text{UO}_2(\text{CH}_3\text{BO}_2)(\text{H}_2\text{O})$	$Pnma$	Wang, S. <i>et. al.</i> ⁶²

Four of these twenty-nine uranyl borates are second-harmonic generators (SHG), producing 532 nm light when irradiated with a 1064 nm laser.⁵⁶⁻⁵⁸ Of these twenty-nine compounds in Table 2, seventeen are noncentrosymmetric materials, all of which should be capable of being a SHG.^{54-59,61,62} Unfortunately, thirteen do not crystallize as pure phases.

3.2 The Inverse Uranyl Unit or Tetraoxo Core

Two uranyl borates, $\text{K}_{12}[(\text{UO}_2)_{19}(\text{UO}_4)(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6(\text{BO}_2\text{OH})\text{O}_{10}]\cdot x\text{H}_2\text{O}$ and $\text{K}_{13}[(\text{UO}_2)_{19}(\text{UO}_4)(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6(\text{OH})_2\text{O}_5]\cdot \text{H}_2\text{O}$, have been prepared that display tetraoxo-coordinated uranyl centers.^{64,65} This can be viewed as the inverse of a $\text{UO}_2(\text{OH})_4$ unit in that instead of two trans oxo atoms and four equatorial hydroxide groups, there are two trans hydroxides and four equatorial oxos, i.e. $\text{UO}_4(\text{OH})_2$. This is the typical environment found for actinides in the 7+ oxidation state.^{66,67} What makes these compounds more unusual is that they contain uranium in both the 6+ and 5+ oxidation states. The second compound forms atypically colored, dichroic, black/amber tablets. These structures are different from most of actinyl borates in that they contain layers are much richer in uranyl content as shown in Figures 10a and

b. It should be noted that these structures lack BO_4 tetrahedral units, an effect of the higher temperatures and the reaction.

Figure 10: a) View of uranyl sheets down a -axis in $\text{K}_{12}[(\text{UO}_2)_{19}(\text{UO}_4)(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6(\text{BO}_2\text{OH})\text{O}_{10}]\cdot x\text{H}_2\text{O}$, and b) c -axis in $\text{K}_{13}[(\text{UO}_2)_{19}(\text{UO}_4)(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6(\text{OH})_2\text{O}_5]\cdot \text{H}_2\text{O}$. UO_2^{2+} and pentagonal bipyramids are yellow, UO_2^{2+} tetragonal bipyramids are yellow-green, UO_2^+ tetragonal bipyramids are yellow-orange, BO_3 units are dark red, BO_4 units are red, and potassium ions are purple.

Each material propagates as BO_3 -studded uranyl sheets along a major crystallographic plane, with an inner layer of K^+ cations and water molecules (Figure 11). In $\text{K}_{12}[(\text{UO}_2)_{19}(\text{UO}_4)(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6(\text{BO}_2\text{OH})\text{O}_{10}]\cdot x\text{H}_2\text{O}$, each sheet contains eight crystallographically unique uranyl sites, seven of which are UO_7 pentagonal bipyramids and the eighth being a UO_6 tetragonal bipyramid (yellow-green). $\text{K}_{13}[(\text{UO}_2)_{19}(\text{UO}_4)(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6(\text{OH})_2\text{O}_5]\cdot \text{H}_2\text{O}$ features eleven crystallographically unique uranyl sites, classified into seven UO_7 pentagonal bipyramids and four UO_6 tetragonal

bipyramidal units. One of these tetragonal bipyramids is a tetraoxo-coordinated UO_2^+ site (yellow-orange). In both materials, all equatorial U-O and axial $\text{U}\equiv\text{O}$ bonds of all other pentagonal and tetragonal bipyramids are of typical bond lengths. The hexavalent tetraoxo uranyl site in $\text{K}_{12}[(\text{UO}_2)_{19}(\text{UO}_4)(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6(\text{BO}_2\text{OH})\text{O}_{10}]\cdot x\text{H}_2\text{O}$ has axial U–O bond lengths of 1.793(8) Å ($\times 2$) and equatorial bond U=O distances of 2.22(1) Å ($\times 2$) and 2.34(1) Å ($\times 2$) (Figure 12a). This unique site can be classified as having two short axial, and two pairs of longer equatorial bonds. However, the pentavalent tetraoxo site in $\text{K}_{13}[(\text{UO}_2)_{19}(\text{UO}_4)(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6(\text{OH})_2\text{O}_5]\cdot\text{H}_2\text{O}$ features U–O bonds to hydroxide moieties of length 2.33(3) Å ($\times 2$), while the four equatorial bonds are divided in two sets of bonds to oxygen atoms at 1.999(13) and 2.134(13) Å (Figure 12b). Under the same criterion, this UO_2^+ site has two pairs of shorter equatorial bonds and one pair of long axial bonds.

Figure 11: a) View of interlayer spacing down c -axis in $\text{K}_{12}[(\text{UO}_2)_{19}(\text{UO}_4)(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6(\text{BO}_2\text{OH})\text{O}_{10}]\cdot x\text{H}_2\text{O}$, and b) a -axis in $\text{K}_{13}[(\text{UO}_2)_{19}(\text{UO}_4)(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6(\text{OH})_2\text{O}_5]\cdot\text{H}_2\text{O}$. UO_2^{2+} hexagonal and pentagonal bipyramids are yellow, UO_2^{2+} tetragonal bipyramids are yellow-green, UO_2^+ tetragonal bipyramids are

yellow-orange, BO_3 units are dark red, BO_4 units are red, potassium ions are purple, and oxygen atoms from water molecules are light blue.

Figure 12: a) Tetragonal bipyramidal geometries of a) uranyl^{VI} in $\text{K}_{12}[(\text{UO}_2)_{19}(\text{UO}_4)(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6(\text{BO}_2\text{OH})\text{O}_{10}] \cdot x\text{H}_2\text{O}$, and b) uranyl^V in $\text{K}_{13}[(\text{UO}_2)_{19}(\text{UO}_4)(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6(\text{OH})_2\text{O}_5] \cdot \text{H}_2\text{O}$.

Spectroscopic analysis of the dichroic $\text{K}_{13}[(\text{UO}_2)_{19}(\text{UO}_4)(\text{B}_2\text{O}_5)_2(\text{BO}_3)_6(\text{OH})_2\text{O}_5] \cdot \text{H}_2\text{O}$ crystals exposes the mixed-valent nature of this uranyl borate (Figure 13). At 350 and 450 nm, the well-known excitations of UO_2^{2+} can be seen. Additionally, a third peak maximizes at 550 nm, a characteristic of a pentavalent uranyl center. This broad peak is a charge-transfer feature of UO_2^+ , as any Laporte forbidden f - f transitions would be too weak to observe (especially as this uranium sits on an inversion center).

Figure 13: UV-Vis-NIR absorption spectrum of $K_{13}[(UO_2)_{19}(UO_4)(B_2O_5)_2(BO_3)_6(OH)_2O_5] \cdot H_2O$ (orange) compared to $K_{10}[(UO_2)_{16}(B_2O_5)_2(BO_3)_6O_8] \cdot 7H_2O$ (red-orange), a pure UO_2^{2+} compound.

3.3 Intermediate- and Mixed-Valent Neptunium Borates

Three different neptunium borate materials have been prepared that stabilize multiple oxidation states by unusual means. $K_4(NpO_2)_{6.73}[B_{20}O_{36}(OH)_2]$ and $Ba_2(NpO_2)_{6.59}[B_{20}O_{36}(OH)_2] \cdot H_2O$ crystallize in the triclinic space group, $P-1$, with the only difference in structure being their interlayer cations (Figure 14a and b, respectively).⁶⁸ $K_2[(NpO_2)_3B_{10}O_{16}(OH)_2(NO_3)_2]$ is the first actinide nitratoborate compound synthesized, though lanthanide nitratoborates have been well documented, and it crystallizes in $P2_1/n$, a centrosymmetric space group (Figure 14c).⁶⁹ The incorporation of multiple oxidation states in these materials displays how yielding neptunium is to disproportionation. Common in these structures are the borate sheets containing exclusively NpO_8 sites (Figure 15).

Figure 14: Interlayer spacing between NpO_x sheets in a) $\text{K}_4(\text{NpO}_2)_{6.73}[\text{B}_{20}\text{O}_{36}(\text{OH})_2]$, b) $\text{Ba}_2(\text{NpO}_2)_{6.59}[\text{B}_{20}\text{O}_{36}(\text{OH})_2] \cdot \text{H}_2\text{O}$, and c) $\text{K}_2[(\text{NpO}_2)_3\text{B}_{10}\text{O}_{16}(\text{OH})_2(\text{NO}_3)_2]$.

Figure 15: NpO₈ studded sheets shared between a) $\text{K}_4(\text{NpO}_2)_{6.73}[\text{B}_{20}\text{O}_{36}(\text{OH})_2]$, b) $\text{Ba}_2(\text{NpO}_2)_{6.59}[\text{B}_{20}\text{O}_{36}(\text{OH})_2] \cdot \text{H}_2\text{O}$, and c) $\text{K}_2[(\text{NpO}_2)_3\text{B}_{10}\text{O}_{16}(\text{OH})_2(\text{NO}_3)_2]$.

Unique amongst all other actinide materials that form in sheets are $\text{K}_4(\text{NpO}_2)_{6.73}[\text{B}_{20}\text{O}_{36}(\text{OH})_2]$ and $\text{Ba}_2(\text{NpO}_2)_{6.59}[\text{B}_{20}\text{O}_{36}(\text{OH})_2] \cdot \text{H}_2\text{O}$, each forming thick layers (≈ 1.6 nm) with four distinct neptunium sites. These sites range in coordination environment, from hexagonal bipyramids (NpO₈) to tetragonal bipyramids (NpO₆), while maintaining almost-linear dioxo bonds. In $\text{Ba}_2(\text{NpO}_2)_{6.59}[\text{B}_{20}\text{O}_{36}(\text{OH})_2] \cdot \text{H}_2\text{O}$, the axial Np^{IV}=O bond distance measures 1.938(14) Å, which is significantly longer than the average axial Np^V=O bond distance of 1.83(2) Å, an effect from the lower formal oxidation state in the tetravalent metal-center.⁷⁰ BVS

calculations support oxidation states NpO_2^{2+} , NpO_2^+ , and Np^{IV} , which is unusual as no tetravalent neptunium dioxo species has been witnessed. In its tetragonal bipyramidal environment, Np^{IV} is coordinated entirely by cation-cation interactions (CCI) from “yl” oxo atoms of four corner-sharing NpO_7 and two corner-sharing NpO_8 units, a first in neptunium chemistry (Figure 16). The complex borate sheets extend from purely corner-sharing BO_3 and BO_4 units, some of which are protonated to balance charge.

Figure 16: Polyhedral view of Np^{IV} coordination via cation-cation interactions.

Absorption analysis (Figure 17) of these materials provides more conclusive evidence of tetra-, penta-, and hexavalent oxidation states than BVS calculations, with fingerprint *f-f* transitions occurring near 700 and 820, 980, and 1223 nm for the aforementioned oxidation states, respectively.⁴⁶ Consideration of all diffraction, BVS, and spectroscopic evidence allows for a reassignment of each material's chemical formula to $\text{K}_4(\text{Np}^{\text{IV}}\text{O}_2)_{0.73}(\text{Np}^{\text{V}}\text{O}_2)_2(\text{Np}^{\text{VI}}\text{O}_2)_4[\text{B}_{20}\text{O}_{36}(\text{OH})_2]$ and $\text{Ba}_2(\text{Np}^{\text{IV}}\text{O}_2)_{0.59}(\text{Np}^{\text{V}}\text{O}_2)_2(\text{Np}^{\text{VI}}\text{O}_2)_4[\text{B}_{20}\text{O}_{36}(\text{OH})_2] \cdot \text{H}_2\text{O}$.

Figure 17: UV-Vis-NIR absorption spectra of $\text{K}_4(\text{Np}^{\text{IV}}\text{O}_2)_{0.73}(\text{Np}^{\text{V}}\text{O}_2)_2(\text{Np}^{\text{VI}}\text{O}_2)_4[\text{B}_{20}\text{O}_{36}(\text{OH})_2]$.

The magnetic susceptibility of a powdered sample of $\text{K}_4(\text{NpO}_2)_{6.73}[\text{B}_{20}\text{O}_{36}(\text{OH})_2]$ was measured at 0.5 T. The calculated free-ion moments, with Russell-Saunders coupling factored, are found to be 3.62, 3.58, and 2.54 μ_{B} for Np^{IV} , NpO_2^+ and NpO_2^{2+} , respectively. Accounting for the ratios of crystallographic multiplicities of the tetra- through hexavalent states, a calculated effective moment of 3.01 μ_{B} is then expected. Despite showing purely paramagnetic ordering throughout the entire range of temperatures (1.8 – 300 K), once fitted to assume Curie-Weiss behavior of localized moments, the effective moment is $3.08 \mu_{\text{B}} \pm 0.15 \mu_{\text{B}}$ per Np cation. This accounts for the NpO_2^{2+} cations in the sample, as well as lower valent cations whose free-ion moment would raise the effective moment for the sample overall in this measurement.

$\text{K}_2[(\text{NpO}_2)_3\text{B}_{10}\text{O}_{16}(\text{OH})_2(\text{NO}_3)_2]$ comprises sheets of NpO_2^+ borate extending along the $[ac]$ plane connected by NpO_2^{2+} nitrate moieties. Bridging oxo's from the NpO_2^+ sheets are responsible for the connection to the NpO_2^{2+} cations (Figure 18). Nine borate, five BO_3 and four BO_4 , units surround each NpO_2^+ site.

Figure 18: NpO_2^{2+} coordination via bridging oxos in $\text{K}_2[(\text{NpO}_2)_3\text{B}_{10}\text{O}_{16}(\text{OH})_2(\text{NO}_3)_2]$.

Assessing the UV-Vis-NIR absorption spectrum (Figure 19), complexity arises as many features are drowned out from the overlap of certain transitions which overlap in the solid state. Additionally, intense features, like the $f-f$ transition at 1200 nm for NpO_2^{2+} , are significantly reduced. The most intense signals near 760, 960, and 980 nm have been attributed to Np^{IV} and NpO_2^+ ; however, Np^{IV} is not accounted for in the single crystal data. Recalling that SC-XRD data is an averaged representation of the actual structure could mean that disordered Np^{IV} sites are masked by NpO_2^+ in the borate sheets. A more plausible explanation would be that the NpO_2^+ site exhibits intermediate-valent behavior, between the tetravalent and pentavalent states. This would require that Np^{IV} reside in a linear dioxo environment, but the aforementioned materials, $\text{K}_4(\text{NpO}_2)_{6.73}[\text{B}_{20}\text{O}_{36}(\text{OH})_2]$ and $\text{Ba}_2(\text{NpO}_2)_{6.59}[\text{B}_{20}\text{O}_{36}(\text{OH})_2]\cdot\text{H}_2\text{O}$, are known to display that feature as well. By placing Np^{IV} in a strong axial crystal field, a decrease in the transition energy should occur from the accepted to 723 nm to the observed 760 nm. This transition matches between all three structures presented here.

Figure 19: UV-Vis-NIR spectrum of $K_2[(NpO_2)_3B_{10}O_{16}(OH)_2(NO_3)_2]$.

3.4 $AnO_2[B_8O_{11}(OH)_4]$ – Trends from UO_2^{2+} - PuO_2^{2+}

An isotopic series of actinyl borates, $AnO_2[B_8O_{11}(OH)_4]$, has been synthesized with specific adjustments made to the molten boric acid flux that has been used throughout to prepare the borate materials discussed.⁷¹ In the case of $UO_2[B_8O_{11}(OH)_4]$, the temperature of the reaction was the only adjustment made. At 220 °C, $UO_2[B_8O_{11}(OH)_4]$ could be isolated, while at 190 °C, the aforementioned uranyl borates form. Anions present in the reaction solutions have an effect on the products crystallized. Especially is this the case for $NpO_2[B_8O_{11}(OH)_4]$, which is susceptible to being reduced in aqueous solutions. The preparation of neptunyl^{VI} perchlorate allows dissociated perchlorate anions to act as an oxidizing agent in the reaction. This maintains NpO_2^{2+} concentrations throughout the process, allowing $NpO_2[B_8O_{11}(OH)_4]$ to form. No changes were necessary in preparing $PuO_2[B_8O_{11}(OH)_4]$, but it was found that regardless of whether to hexavalent or tetravalent nitrate species was used, this product formed as a pure phase.

$\text{AnO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]$ ($\text{An} = \text{U} - \text{Pu}$) crystallizes in the monoclinic, noncentrosymmetric space group, Cc . A three-dimensional H-type polyborate framework creates hexagonal voids for actinyl cations to reside (Figure 20a). As a result, each actinyl unit is coordinated in a hexagonal bipyramidal geometry, with two BO_3 triangles and seven BO_4 tetrahedra bonding by a corner-sharing. The basic borate fragment consists of three BO_4 units corner-sharing to a central BO_3 unit. Within the sheets, the tetrahedra in each fragment flip, where adjoining fragments feature a two-down/one-up:two-up/one-down enantiomerism (Figure 20b).

Figure 20: a) H-type borate sheet topology, and b) alternating BO_4 tetrahedra connectivity in $\text{AnO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]$.

The two-dimensional actinyl borate sheets extend along the $[ac]$ plane, while additional borate units bridge these sheets, extending them in the b -axis. The noncentrosymmetric quality of this structure can be comprehended by the helical twisting of the polyborate chain between the actinyl borate sheets, reducing the interlayer spacing and making a denser borate material.

The actinide contraction can be seen when traversing the unit cell parameters and bond lengths of these compounds.⁷² $\text{An}\equiv\text{O}$ bond distance decrease by $0.02 \text{ \AA}$ on average from uranyl to plutonyl, while the volume of the shrinks from $1183.4(5)$ to $1180.0(3) \text{ \AA}^3$, respectively.

4. Lower-Valent Actinide Borates

The success in synthesizing and studying two series of actinide borate materials has provided much insight into the bonding behavior of these heavy elements. The first series displayed deviations in structure compared to the lanthanide borates as a result of including $5f$, $6d$, $7s$, and $7p$ orbital character in bonding. This is in contrast to the second series of cubic borates, whose structure-type holds between lanthanide and actinide borate materials. This shows the unique capabilities of $5f$ and higher energy orbitals compared to those of the $4f$ orbitals, and supports the observations of covalency in actinide complexes, in addition to displaying the adaptive nature of borate as a ligand. A novel thorium borate material has displayed unique selectivity for pertechnetate, TcO_4^- , exceeding the exchange coefficients of presently used layered-double hydroxides by an order of magnitude.

4.1 $[\text{ThB}_5\text{O}_6(\text{OH})_6][\text{BO}(\text{OH})_2]\cdot\text{H}_2\text{O}$, the first, selective TcO_4^- trapping material

Analysis of $[\text{ThB}_5\text{O}_6(\text{OH})_6][\text{BO}(\text{OH})_2]\cdot\text{H}_2\text{O}$, the second known crystallographically characterized thorium borate compound,⁷³ concluded with a unique property of any borate material thus far. This material, also known as **NDTB-1**, forms a porous supertetrahedral 3D framework capable of withholding monatomic and polyatomic anions.^{74,75} Of significant importance is **NDTB-1**'s ability to selectively exchange the pertechnetate (TcO_4^-) anion, a radioactive compound of high concentration in a few nuclear facilities, such as Savannah River or Hanford.

In **NDTB-1**, twelve-coordinate Th^{4+} cations are ligated by vertices-connecting BO_3 triangles and bidentate BO_4 tetrahedra with a near-icosahedral geometry (Figure 21a). The

crystalline structure forms in the space group $Fd-3$, where the borate units polymerize into a larger $B_{10}O_{24}$ cluster that links coordinated thorium cations while creating channels that widen into large cages in the supertetrahedra (Figure 21b). These pores account for 43% of the volume in this material, leading to the quality of anion exchange involving halides or oxoanions, like MnO_4^- , CrO_4^{2-} , and TcO_4^- (Figure 22).

Figure 21: a) Twelve-coordinate near-icosahedral geometry of Th^{IV} , and b) porous framework in **NDTB-1**.

A comprehensive anion exchange study involving several different monatomic and polyatomic anions and pertechnetate was pursued, with UV-Vis-NIR absorption spectroscopy, energy-dispersive X-ray spectroscopy, and inductive-coupled plasma mass spectrometry techniques used to characterize and quantify each solid sample. The integrity of the crystal lattice of **NDTB-1** was maintained between studies, a particularly useful property which this

material has compared to layered-double hydroxide (LDH) materials typically used for pertechnetate sorption.⁷⁵

Figure 22: UV-Vis-NIR absorption spectra of **NDTB-1** (blue), and **NDTB-1** exchanged with MnO₄⁻ (purple), CrO₄²⁻ (yellow) and Cr₂O₇²⁻ (red).

Figure 23: UV-Vis-NIR absorption spectra of TcO_4^- sorption by **NDTB-1** immediately (dark blue), in 8 hours (blue), and in 36 hours (light blue).

In order to quantify the exchange kinetics of pertechnetate with **NDTB-1**, solution state absorption studies were conducted, where 10 mg of **NDTB-1** was placed in a cuvette with 3 mL of 1.455×10^{-4} M TcO_4^- . The UV region ($\lambda = 290$ nm is the site of pertechnetate's charge-transfer band) was monitored every 20 minutes for one week in order to quantify the concentration of the TcO_4^- left in solution (Figure 23), then to determine what has been absorbed into **NDTB-1**. Consistent with a second-order reaction, the rate constant of the reaction is determined by the equation:

$$v = dc(\text{TcO}_4^-)/dt = kc(\text{TcO}_4^-)^2$$

(coupled with the assumption that **NDTB-1** is always in excess). Additionally, exchange capacity measurements were made, using a series of different molar ratios of TcO_4^- : **NDTB-1**. The optimal exchange capacity value of $0.5421 \text{ mol mol}^{-1}$ was found at a ratio of 1:1, though the maximal exchange coefficient, K_d , of $1.0534 \times 10^4 \text{ mL g}^{-1}$ was found at 1:4. This material exhibits pertechnetate exchange at a higher rate than any other anion exchange material presently known.^{76,77}

To further the understanding of the anion exchange **NDTB-1** has with pertechnetate, anion exchange selectivity with a wide variety of anions was pursued. Cl^- , I^- , ClO_4^- , NO_3^- , HPO_4^{2-} , SeO_3^{2-} , ReO_4^- , IO_3^- , HAsO_4^{2-} , SO_4^{2-} , SeO_4^{2-} , and PO_4^{3-} were chosen with the criterion of leaving TcO_4^- 's absorption at 290 nm unaffected in solution. The diversity in size, charge, and

atomic configuration provides for a comprehensive analysis of the anion exchange selectivity of TcO_4^- with expected anions in nuclear waste. A 1:1:2 (TcO_4^- :competing anion:**NDTB-1**) proportion was used throughout this analysis, and selectivity can be determined from the exchange kinetics and coefficients of the TcO_4^- study. With little effect, anions Cl^- , I^- , ClO_4^- , and NO_3^- show little competition for exchange into **NDTB-1**. These anions share a monovalent charge with TcO_4^- , and it is not until the anions become more equal in volume before they become more competitive. IO_3^- , ReO_4^- , SeO_3^{2-} , HPO_4^{2-} , HAsO_4^{2-} are more competitive, with each anion's size emerging as a dominant factor in the exchange. It will be noted here that the pH of the solutions involving SeO_3^{2-} , HPO_4^{2-} , and HAsO_4^{2-} allowed for the dominant species to be the protonated species of each anion. The monovalent charge ultimately has an effect which causes discrepancies in the analysis and the true placement of these anions within the series in Table 3. It is not until TcO_4^- exchange with SO_4^{2-} and SeO_4^{2-} , each being divalent nature and being similar in size, does it become conclusive that these anions are beyond the tipping point and TcO_4^- is outcompeted for sorption into **NDTB-1**. Not only that, but it is at this point when the exchange between TcO_4^- and **NDTB-1** becomes reversible. The largest effect on TcO_4^- exchange is charge, where PO_4^{3-} competition shows a completely reversible exchange of TcO_4^- . HPO_4^{2-} does exist as the dominant species at the pH measured; however, the equilibrium rate between PO_4^{3-} and its mono-protonated species favors PO_4^{3-} as it is sorbed into **NDTB-1**.

Table 3: Identities of anion exchange reactions and their respective distribution coefficients.

Anions	Maximal percentage of TcO_4^- removed [%]	Final percentage of TcO_4^- removed [%]	K_d [mL g^{-1}]
TcO_4^-	83.62	81.14	8604

$\text{TcO}_4^- + \text{Cl}^-$	81.98	81.06	8560
$\text{TcO}_4^- + \text{I}^-$	77.28	76.26	6424
$\text{TcO}_4^- + \text{ClO}_4^-$	74.61	74.41	5816
$\text{TcO}_4^- + \text{NO}_3^-$	74.37	72.89	5377
$\text{TcO}_4^- + \text{HPO}_4^{2-}$	60.01	59.32	2916
$\text{TcO}_4^- + \text{SeO}_3^{2-}$	57.97	53.83	2332
$\text{TcO}_4^- + \text{ReO}_4^-$	58.87	52.61	2220
$\text{TcO}_4^- + \text{IO}_3^-$	54.46	52.02	2168
$\text{TcO}_4^- + \text{HAsO}_4^{2-}$	56.64	48.34	1871
$\text{TcO}_4^- + \text{SO}_4^{2-}$	52.7	32.66	970
$\text{TcO}_4^- + \text{SeO}_4^{2-}$	49.23	23.72	622
$\text{TcO}_4^- + \text{PO}_4^{3-}$	23.08	0	0

Finally, a case study of **NDTB-1**'s ability to exchange TcO_4^- in a simulated Hanford waste stream was sought. A solution of Cl^- , NO_2^- , NO_3^- , CO_3^{2-} , K^+ , Ca^{2+} , NH_4^+ , and TcO_4^- was prepared with large molar excess of the former three anions compared to pertechnetate. Despite the large excess of these anions, **NDTB-1** still showed significant exchange coefficient of TcO_4^- ($K_d = 29.9$ and 16.2 mL g^{-1} for 200 and 40 mL g^{-1} , respectively) in this simulated waste material.

4.2 Plutonium, Americium, and Curium Borates

Plutonium is often regarded as the first transition point in the actinide series, where a combination of its unique redox activity and placement in the actinide atomic radii trend makes it a truly bewildering element.⁴⁶ It was thought that the bonding beyond plutonium would be

limited in orbital character, and the mid-late actinides will bond similar to the lanthanides. Additionally, americium and curium are regarded as electronically interesting elements, as trivalent americium has a nonmagnetic ground state ($J = 0$), and curium's magnetic interactions can control its crystal structure.^{78,79}

Five trivalent actinide borates have been prepared; however, to maintain accurate comparisons between the lanthanide chloride series, $\text{Pu}_2[\text{B}_{12}\text{O}_{18}(\text{OH})_4\text{Br}_2(\text{H}_2\text{O})_3] \cdot 0.5\text{H}_2\text{O}$ will not be discussed in depth.⁸⁰ $\text{Pu}[\text{B}_4\text{O}_6(\text{OH})_2\text{Cl}]$, $\text{Pu}_2[\text{B}_{13}\text{O}_{19}(\text{OH})_5\text{Cl}_2(\text{H}_2\text{O})_3]$, $\text{Am}[\text{B}_9\text{O}_{13}(\text{OH})_4] \cdot \text{H}_2\text{O}$, and $\text{Cm}_2[\text{B}_{14}\text{O}_{20}(\text{OH})_7(\text{H}_2\text{O})_2\text{Cl}]$ were prepared by the similar methods as those used to prepare uranyl borates.^{9,81} The major plutonium product, $\text{Pu}[\text{B}_4\text{O}_6(\text{OH})_2\text{Cl}]$ (80%), is isotopic with the lanthanide borate structure, $\text{Ln}[\text{B}_4\text{O}_6(\text{OH})_2\text{Cl}]$ ($\text{Ln} = \text{La} - \text{Pr}$).⁹

The minor product in this reaction, $\text{Pu}_2[\text{B}_{13}\text{O}_{19}(\text{OH})_5\text{Cl}_2(\text{H}_2\text{O})_3]$, crystallizes in the monoclinic space group, $P2_1/n$.⁸¹ This compound has no lanthanide analogue. The three-dimensional network features triangular polyborate units with voids to fit plutonium centers (Figure 24a). The voids provide six equatorial oxygen atoms from two BO_3 units and one BO_4 unit, which is opposite of that in the $\text{Ln}[\text{B}_4\text{O}_6(\text{OH})_2\text{Cl}]$ network.⁹ A capping chloride anion resides in the apical position, and the three basal bonds are formed to one water molecule and two corner-sharing BO_3 triangles (Figure 24b). In the $\text{Ln}[\text{B}_4\text{O}_6(\text{OH})_2\text{Cl}]$, these basal borate units are in fact the BO_4 tetrahedra, that extend the structure in the third dimension.⁹ Similarly, each plutonium site is ten-coordinate, and the geometry is best described as capped triangular cupola. All Pu–O and Pu–Cl bond distances are similar to those found in $\text{Pu}[\text{B}_4\text{O}_6(\text{OH})_2\text{Cl}]$.

Figure 24: a) Borate sheet topology, and b) capped triangular cupola geometry of Pu^{III} centers in $\text{Pu}_2[\text{B}_{13}\text{O}_{19}(\text{OH})_5\text{Cl}_2(\text{H}_2\text{O})_3]$.

$\text{Am}[\text{B}_9\text{O}_{13}(\text{OH})_4]\cdot\text{H}_2\text{O}$ exhibits the same structure as $\text{Ln}[\text{B}_9\text{O}_{13}(\text{OH})_4]\cdot\text{H}_2\text{O}$ ($\text{Ln} = \text{Pr}, \text{Sm}, \text{Eu}$). A polyborate framework similar to the $\text{Pu}_2[\text{B}_{13}\text{O}_{19}(\text{OH})_5\text{Cl}_2(\text{H}_2\text{O})_3]$ exists in this structure (Figure 25a), though, without a capping chloride anion,⁸² each Am^{III} -center is left nine-coordinate. The geometry at the Am^{III} site is a hula-hoop (Figure 25b), with the six equatorial oxygen atoms coming from the borate sheet, the two basal oxygen atoms from an edge-sharing BO_4 , and one oxygen atom from the capping, corner-sharing BO_3 unit.

Figure 25: a) Polyborate network of, and b) nine-coordinate hula-hoop geometry of Am^{III} in $\text{Am}[\text{B}_9\text{O}_{13}(\text{OH})_4] \cdot \text{H}_2\text{O}$.

$\text{Cm}_2[\text{B}_{14}\text{O}_{20}(\text{OH})_7(\text{H}_2\text{O})_2\text{Cl}]$ is a new actinide borate material, though the formula resembles the minor plutonium product, $\text{Pu}_2[\text{B}_{13}\text{O}_{19}(\text{OH})_5\text{Cl}_2(\text{H}_2\text{O})_3]$.⁸³ This material also crystallizes in the $P2_1/n$ space group and has the same sheet topology as $\text{Pu}_2[\text{B}_{13}\text{O}_{19}(\text{OH})_5\text{Cl}_2(\text{H}_2\text{O})_3]$ and $\text{Am}[\text{B}_9\text{O}_{13}(\text{OH})_4] \cdot \text{H}_2\text{O}$ compounds (Figure 26a). Despite this similarity, the curium cations reside in two different coordination environments. The first environment features the same six equatorial oxygen atoms alike the previous actinide structures, with an apical chloride anion, and two oxygen atoms bonding from two BO_4 units at the base (Figure 26b). This qualifies the nine-coordinate curium site as hula-hoop, while the ten-coordinate site is best described as having the capped triangular cupola geometry (Figure 26c). For this site, a BO_3 -bound oxygen caps curium, while the triangular base is composed of three oxygen atoms from one BO_3 and two BO_4 units. Though the chloride anions are terminal, like in

$\text{Pu}_2[\text{B}_{13}\text{O}_{19}(\text{OH})_5\text{Cl}_2(\text{H}_2\text{O})_3]$, the three-dimensional structure extends from the BO_3 and BO_4 units in the americium and curium borates, while $\text{Pu}_2[\text{B}_{13}\text{O}_{19}(\text{OH})_5\text{Cl}_2(\text{H}_2\text{O})_3]$ propagates by BO_3 triangles alone. $\text{Pu}[\text{B}_4\text{O}_6(\text{OH})_2\text{Cl}]$ extends via the capping and base chloride anions.

Figure 26: a) Borate sheet topology, b) nine-coordinate hula-hoop geometry, and c) ten-coordinate capped triangular cupola geometry of $\text{Cm}_2[\text{B}_{14}\text{O}_{20}(\text{OH})_7(\text{H}_2\text{O})_2\text{Cl}]$.

A quantum mechanical analysis revealed that varying involvement of the $5f/6d$ orbitals is the largest factor in causing the observed differences between lanthanide and actinide borate structures. The models used includes the f -metal-center, capping or basal BO_3 , BO_4 , Cl , or H_2O moieties, and two spheres of equatorial BO_3 and BO_4 at full valency (protonating BO_3/BO_4 groups to balance charge) were submitted for DFT, CASSCF, CASPT2 calculations.⁸⁴⁻⁸⁷ $\text{Ce}[\text{B}_4\text{O}_6(\text{OH})_2\text{Cl}]$, $\text{Pu}[\text{B}_4\text{O}_6(\text{OH})_2\text{Cl}]$, $\text{Pu}_2[\text{B}_{13}\text{O}_{19}(\text{OH})_5\text{Cl}_2(\text{H}_2\text{O})_3]$, $\text{Am}[\text{B}_9\text{O}_{13}(\text{OH})_4] \cdot \text{H}_2\text{O}$, and $\text{Cm}_2[\text{B}_{14}\text{O}_{20}(\text{OH})_7(\text{H}_2\text{O})_2\text{Cl}]$ models were used with the intent of studying the differences in the electronic structures in trivalent lanthanide and actinide borates.

Several observations should be taken from these analyses, but first it should be mentioned that DFT can over-delocalize electron and orbital density in heavy-element calculations compared to CASSCF. In all cases, the seven *f* orbitals were localized on the metal-center, with each element's respective number of *f*-electron populating those orbitals. In the case of the Ce[B₄O₆(OH)₂Cl], a 5*p* orbital sits lower in energy than the singly occupied 4*f* orbital and remains noninteracting with any coordinating atom (Table 4). The same phenomenon is witnessed in the 6*p* orbital of Pu₂[B₁₃O₁₉(OH)₅Cl₂(H₂O)₃], but does not occur in the Pu-analogue of the cerium borate. It can be seen, rather, that the 6*p* orbital delocalizes electron density into a 2*p* orbital of a basal oxygen atom in Pu[B₄O₆(OH)₂Cl]. In Am[B₉O₁₃(OH)₄]·H₂O and Cm₂[B₁₄O₂₀(OH)₇(H₂O)₂Cl], the 2*p* orbital of a base oxygen atom delocalizes electron density to the 6*d* orbital of each metal-center.

Natural bond order (NBO) and natural population analysis (NPA) calculations were done at the CASSCF and DFT levels with the intent of determining the ionic charge and spin population at each metal site. Although the spin population yielded expected results, charge values deviated from (+3) and provided averaged values of 2.47 (LoProp), 2.12 (Mulliken), and 1.55 (NPA). Compared to the NPA charges for Am and Cm, the charges on Pu was determined to be $\approx 0.42e$ less, a result from a larger transfer of electron density from the coordinating oxygens in the plutonium borates compared to the americium and curium borates. This phenomenon is accounted for in the electronic configuration analysis performed by NPA which notes a larger electron occupation in the Pu 5*f* orbitals compared to Am and Cm (Table 5). This is concurrent with the ionic contraction when proceeding from Pu^{III} to Cm^{III} coupled with the localization and noninteraction of the 5*f* orbitals of Am and Cm. Additionally, the electron

configuration analysis determined a larger $6d$ orbital population in each Pu borate by $\approx 0.1e$ compared to the Am and Cm $6d$ orbitals.

Table 4: Spin and atomic population information of f -element borate materials using various DFT approaches.

Compound	CASSCF			PBE
	Mülliken spin	Mülliken	LoProp	Natural
	population	atomic	atomic	population
		charges	charges	atomic charges
Ce[B ₄ O ₆ (OH) ₂ Cl]	1.00	2.08	2.43	1.53
Pu[B ₄ O ₆ (OH) ₂ Cl]	4.98	2.07	2.42	1.29
Pu ₂ [B ₁₃ O ₁₉ (OH) ₅ Cl ₂ (H ₂ O) ₃]	4.98	2.18	2.49	1.30
Am[B ₉ O ₁₃ (OH) ₄] $\cdot$ H ₂ O	5.98	2.14	2.47	1.73
Cm ₂ [B ₁₄ O ₂₀ (OH) ₇ (H ₂ O) ₂ Cl] ¹	6.98	2.08	2.48	1.67
Cm ₂ [B ₁₄ O ₂₀ (OH) ₇ (H ₂ O) ₂ Cl] ²	6.98	2.19	2.52	1.77

¹- Cm^{III} residing in nine-coordinate hula-hoop geometry

²- Cm^{III} residing in ten-coordinate capped triangular cupola geometry

Table 5: $5f$ orbital population of f -element borate materials.

Compound	Natural Population Analysis Orbital Population							
	$5f^0$	$5f^1$	$5f^{1-}$	$5f^2$	$5f^{2-}$	$5f^3$	$5f^{3-}$	Total $5f$
Ce[B ₄ O ₆ (OH) ₂ Cl]	0.093	0.216	0.162	0.175	0.154	0.115	0.191	1.106
Pu[B ₄ O ₆ (OH) ₂ Cl]	0.593	0.856	0.783	0.956	0.637	0.542	0.984	5.351

$\text{Pu}_2[\text{B}_{13}\text{O}_{19}(\text{OH})_5\text{Cl}_2(\text{H}_2\text{O})_3]$	0.905	0.566	0.853	0.813	0.867	0.965	0.588	5.557
$\text{Am}[\text{B}_9\text{O}_{13}(\text{OH})_4]\cdot\text{H}_2\text{O}$	0.974	0.99	0.739	0.865	0.801	0.853	0.994	6.216
$\text{Cm}_2[\text{B}_{14}\text{O}_{20}(\text{OH})_7(\text{H}_2\text{O})_2\text{Cl}]^1$	1.021	1.021	1.025	1.017	1.028	1.029	1.030	7.171
$\text{Cm}_2[\text{B}_{14}\text{O}_{20}(\text{OH})_7(\text{H}_2\text{O})_2\text{Cl}]^2$	1.024	1.02	1.026	1.035	1.027	1.034	1.020	7.186

¹- Cm^{III} residing in nine-coordinate hula-hoop geometry

²- Cm^{III} residing in ten-coordinate capped triangular cupola geometry

4.3 A Glimpse of the Late Actinides in $\text{Cf}[\text{B}_6\text{O}_8(\text{OH})_5]$

Only seven single-crystal structures containing californium have been published in the literature: CfCp_3 (Cp = cyclopentadienyl),⁸⁸ CfCl_3 ,⁸⁹ $\text{Cf}(\text{IO}_3)_3$,⁹⁰ $[\text{Cf}(\text{H}_2\text{O})_9][\text{CF}_3\text{SO}_3]_3$,⁹¹ $\text{Cf}(\text{HDPA})_3\cdot\text{H}_2\text{O}$,⁹² and the californium borates to be discussed in this and the proceeding sections.^{93,94} The same boric acid flux synthesis led to the production of pale green microcrystals of formula, $\text{Cf}[\text{B}_6\text{O}_8(\text{OH})_5]$, which crystallizes in the monoclinic space group, $C2/c$. This structure is not shared by any of the earlier trivalent actinides or lanthanides, an anomaly which demanded further attention in order to understand.⁹

Single-crystal diffraction analysis yields one-dimensional polyborate chains, featuring a new borate FBB (Figure 27a). This FBB comprises four corner-sharing BO_4 tetrahedra and two BO_3 triangle units (Figure 27b and c). These FBBs coordinate each Cf^{III} in a distorted square antiprismatic geometry, thereby creating two-dimensional sheets (Figure 28). More noticeably is the almost exclusive coordination from nine BO_4 units, two that are edge-sharing and the other seven corner-sharing. With only two BO_3 triangles that also coordinate, this represents the largest ratio between $\text{BO}_4:\text{BO}_3$ witnessed in *f*-element borate materials.

Figure 27: a) One-dimensional chains, b) view of new FBB down a -axis, and c) view down c -axis.

Figure 28: Square antiprismatic geometry of Cf^{III} centers in $\text{Cf}[\text{B}_6\text{O}_8(\text{OH})_5]$.

It is unexpected that californium borate should structurally diverge from previously reported f -element borate materials, more so for the actinide borates than the lanthanide borates, without accounting for an accompanying change in the bonding between metal and ligand. Magnetic measurements were taken via VSM-SQUID with the intent of gathering information

regarding the unpaired $5f$ electrons in $\text{Cf}[\text{B}_6\text{O}_8(\text{OH})_5]$. When fitting the data to a modified Curie-Weiss law, in order to account for temperature-independent paramagnetism, a decrease in the effective moment (μ_{eff}) is observed. This experimental $\mu_{\text{eff}} = 6.7(4) \mu_{\text{B}}$, and fails to account for the entire $10.65 \mu_{\text{B}}$ calculated for Cf^{III} with a Hund's rule ground term of $^6\text{H}_{15/2}$. With there being no evidence of any long-range ordering or direct Cf–Cf interactions, significant covalency between Cf^{III} and the polyborate network was postulated to be the cause of the missing magnetism.

It is agreed upon by actinide scientists that covalency occurs in trivalent actinide complexes.⁹⁵ Though always present, its contributions in bonding decrease at plutonium and remain a subordinate to ionicity in materials involving americium and later actinides. However, a spectroscopic analysis of $\text{Cf}[\text{B}_6\text{O}_8(\text{OH})_5]$ reveals the return of covalency as the dominant contributor in bonding.⁹³ Temperature-variable photoluminescence spectroscopy shows a unique broadening of the emission from trivalent californium in $\text{Cf}[\text{B}_6\text{O}_8(\text{OH})_5]$ when excited with light of the visible region. This phenomenon, that is absent in the photoluminescence spectra of $\text{Cm}_2[\text{B}_{14}\text{O}_{20}(\text{OH})_7(\text{H}_2\text{O})_2\text{Cl}]$, begins when the ligand-to-metal charge-transfer creates a metastable Cf^{II} -hole pair in $\text{Cf}[\text{B}_6\text{O}_8(\text{OH})_5]$.⁹⁶ Photoluminescence from this charge-transfer state results from the recombination of this hole occurs through both radiative and non-radiative pathways. This comes with the depression in reduction potential of trivalent actinides beginning with $\text{Cf}^{\text{III}}/\text{Cf}^{\text{II}}$ ($E^\circ = -1.4 \text{ V}$). This continues and is a new theory which may explain the blue glow of einsteinium.

4.4 Cubic Borates – $\text{M}_4[\text{B}_{16}\text{O}_{26}(\text{OH})_4(\text{H}_2\text{O})_3\text{Cl}_4]$ ($\text{M} = \text{Sm} - \text{Gd}, \text{Pu} - \text{Cm}, \text{Cf}$)

Complete characterization of the structural and bonding orbital dynamics of the lanthanide and actinide borate series came with the suspicion that an isostructural f -element borate series

could be prepared and characterized.⁹⁴ This would provide a chance to probe the differences in bonding compared to the initial borate series. In addition to the borate flux synthesis, the system was also saturated with chloride anions, in attempt to stir interactions from the metal-centers. Holding all other conditions constant, large octahedral-shaped crystals of formula $M_4[B_{16}O_{26}(OH)_4(H_2O)_3Cl_4]$ ($M = Sm - Gd, Pu - Cm, Cf$) formed in low yield (30-40 % for $Sm - Gd$). This isostructural series is only the third type known to include SC-XRD analysis with samples up to californium (excluding berkelium due to its short half-life, $\lambda=330$ days).⁴⁶

SC-XRD analysis revealed a complex cubic crystal structure of polar and chiral space group, $P2_13$ (Figure 28a). The structure-type features two crystallographically-unique f -element centers, regardless of them both being in nine-coordinate tricapped trigonal prismatic geometries. Corner-sharing BO_3 triangles and BO_4 tetrahedra comprise a dense, three-dimensional framework to bind f -element centers. The first site has six BO_3 and three BO_4 tetrahedra that each corner-share to become the base and capping unit of each trigonal prism, while three water molecules coordinate to become the top (Figure 28b). This site resides on a three-fold rotational axis, therefore, all oxygen atoms are symmetry-related. The second metal-center bonds by corner-sharing to five BO_3 and two BO_4 units, to create the bottom and capping groups of the trigonal prisms (Figure 28c). Two crystallographically-unique chloride anions bond from the top in this site. The first chloride (Cl1) participates as a μ_3 -chloride, bonding three metal-centers while sitting on a threefold rotational axis. As a result of the two μ_2 -chlorides (Cl2), edge-sharing metal-centers connect to symmetry equivalent sites, propagating 2_1 helical strains parallel to the four different polar threefold axes of the cubic space group.

Figure 28: a) Three-dimensional polyborate network featuring μ_3 -chloride, b) nine-coordinate f -element centers.

With there being no deviations in M-O or M-Cl bond distances between the cubic borates and other f -element borates, UV-Vis-NIR absorption analysis followed. In lanthanide materials, crystal-field effects of the cations are expected to be minimal, due to the f orbitals being inaccessible. However, spin-orbit coupling is expected to take over, causing “field-free” levels to exist that provide spectroscopists a means of determining elemental and oxidation state identification, regardless of the ligand environment and bonding.⁹⁷⁻⁹⁹

Apparent differences in the intensity of color between the each Pu^{III} and Am^{III} borates is attributed to the different space groups in which they crystallize. In the nonpolar, centrosymmetric space groups of the aforementioned actinide borates, the electric field is dynamic. This weakens f - f transitions (Laporte forbidden). Regardless, because the metal-centers occupy general positions in their lattices, the selection rules are relaxed slightly, allowing for the observed transitions in the absorption spectra. For the present cubic borates, the noncentrosymmetric nature of the space group establishes a permanent electric field. This has an effect on certain f - f transitions in these

polar crystals because the magnetic field remains unaffected, adding in part to relief of the selection rules. Additionally, mixing of 5*f* orbitals with ligand orbitals would lead to broadened transitions due to vibronic coupling as a result of the selection rules being relaxed further.

Experimentally, the cubic borates display more intense, slightly bathochromically-shifted peaks in nigh-on identical regions compared to the centrosymmetric actinide borates. A correct answer as to why this occurs in these cubic materials will only come with higher levels of theory, for which does not exist presently. Higher-quality basis sets for Pu – Cf, which is of no easy task, are years from being acceptable and applicable.

5. Conclusions

Borates containing *f*-block metals have provided insight into bonding differences between lanthanides and actinides and revealed the participation of a variety of frontier orbitals in bonding, even with late actinides. Borate networks have proven themselves effective in maintaining *f*-elements of different oxidation states, as well as providing a stable matrix for interrogating isotopes with short half-lives.

6. References

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