NEW INSIGHTS IN ACTINIDE BORATE CHEMISTRY

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Abstract

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The use of molten boric acid as a reactive flux for synthesizing actinide borates has been developed in the past three years providing access to a remarkable array of exotic materials with both unusual structures and unprecedented properties. [ThB$_5$O$_6$(OH)$_6$][BO(OH)$_2$]·2.5H$_2$O (NDTB-1) possesses a cationic supertetrahedral structure and displays remarkable anion exchange properties with high selectivity for TcO$_4^-$.

In addition, NDTB-1 was determined to show real utilities to solve the “Technetium Problem”. Uranyl borates form noncentrosymmetric structures with extraordinarily rich topological relationships. Neptunium borates are often mixed-valent and yield rare examples of compounds with one metal in three different oxidation states. Plutonium borates display new coordination chemistry for trivalent actinides. Finally, americium and curium borates show dramatic departures from plutonium borates, and form the first trivalent actinide compounds that do not have lanthanide analogues. There are scant examples of families of actinides compounds
that extend past plutonium to examine the bonding of later actinides. There are several grand challenges that this work addresses. The foremost of these challenges is the development of structure-property relationships in transuranium materials. A deep understanding of the materials chemistry of actinides will likely lead to the development of advanced waste forms for radionuclides present in nuclear waste that prevent their transport in the environment. This work may have also uncovered the solubility-limiting phases of actinides in some repositories such as the Waste Isolation Pilot Plant (WIPP), and allows for measurements on the stability of these materials.

The core of the this dissertation is focused on the crystal chemistry and the structure-property relationship of actinide borates that derived from the molten boric acid flux reactions including thorium borate (Chapter 3), uranium borates (Chapter 4-7,12,14), neptunium borates (Chapter 9-14), plutonium borates (Chapter 9,12,16,17), americium borate (Chapter 17), and curium borate (chapter 18). During the course of these studies, several important side results were also serendipitously discovered. These includes the anion exchange studies of NDTB-1 (Chapter 3), studies of iodine incorporation into uranyl borates (Chapter 8), the discovery of new cation-cation interaction bonding mode for Np(V) (Chapter 15), and investigations of novel interstitial incorporation of actinides into natural materials (Chapter 19).
This is dedicated to my parents Jianxin Wang and Ping Xia as backbones, and my love
Juan (Jenny) Diwu as mate in career, life, and soul.
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1.1 Overview

The terrestrial abundance of boron, mostly existing as borates, is 10 ppm.\(^1\) Giant borate deposits occur as the result of the evaporation of ancient oceans and seas. Uranium, the heaviest element that exists in natural environments, has a relatively low terrestrial abundance at 2.7 ppm.\(^2\) However, a variety of processes concentrate uranium in the Earth’s crust and numerous uranium minerals with most of the common oxo-anions have been discovered.\(^3-5\) Surprisingly, with variety of both borates and uranium deposits that well-known, the combination between the two is blank, i.e. there is no known uranium borate mineral existing on the earth. One of reasons for this is there is no such a natural geological site with both concentrated uranium and boron together on our planet. However, associated with the nuclear waste disposal, large amounts of actinides and borates have been artificially concentrated together under at least three ways.

First, except for Russia, which has produced phosphate glass for decades, borosilicate glass has become the only waste form for liquid high-level radioactive waste in the world now.\(^6,7\) In the United States, the vitrification of nuclear waste using
borosilicate glass started in year 1996 mainly at Savannah River Site and this process is estimated to continue for at least two decades.\(^8\) It has been recognized that both processing techniques and high actinide content in the glasses can lead to the formation of crystalline products such as silicates and borates within these glasses which may greatly lower the chemical durability and the integrity of the glass.\(^7,8\)

Second, one of well-known borate deposits is the Salado formation near Carlsbad, New Mexico where the concentration of borate, predominately in the form of \(\text{H}_3\text{BO}_3\), \(\text{B(OH)}_4^-\), and \(\text{B}_4\text{O}_7^{2-}\), reaches concentrations as high as 166 ppm in intergranular brines.\(^9\) Located within this deposit is the United States’ only repository for nuclear defense waste known as the Waste Isolation Pilot Plant (WIPP). WIPP presents a unique environment whereby large quantities of not only uranium, but also lesser amounts of the transuranium elements neptunium, plutonium, americium, curium, will eventually be able to react with the brines, potentially leading to the formation of actinide borate compounds. Recent solubility studies of neodymium(III), which acts as the surrogate of \(\text{An(III)}\) (actinides), in the environment of WIPP brines have shown that the borate competes with carbonate for \(\text{An(III)}\) complexation under the repository conditions.\(^10\) The presence of the decaying nuclear waste will lead to heating beyond the ambient conditions in the deposit, and therefore the reaction of actinides with borates at moderate temperatures (ca. 150 °C) are important reactions to study in order to predict the fate of actinides in the repository.

Third, what happened most recently, attacked by the great earthquake and the following tsunami, great alert was raised about safety at \textit{Fukushima Daiichi} plant in
Japan. Releasing and dispersion of radioactive materials are still under the way. In order to prevent the situation that the nuclear fuel rods being melting down, huge amounts of sea water and boric acid have been pumped into the reactors to shut down the undergoing fission reaction completely. Unlike the normal condition where boric acid was used in a small amount to modify the rate of the fission reactions, much larger scale of boric acid was used this time since the reactors involved will not operate again. As a result, actinide elements including uranium and transuraniums get a good chance to react with the boric acid hydrothermally to form the actinide borate species. Thus it will be ultra-important to understand the reactions between actinides and boric acid at such condition in order to rescue the environment problems in the geological time scale at these areas in Japan.

Despite the importance to understand all these potentially forming actinide borate species discussed above, there are very few examples of actinide borate compounds in the crystallographic database a year ago. There were even zero examples of transuranium borate compounds. The first crystalline actinide borate compound is \( \text{K}_6\{\text{UO}_2\{\text{B}_{16}\text{O}_{24}\text{(OH)}_8\}\}\cdot 12\text{H}_2\text{O} \) which was synthesized via the room temperature slow water evaporation method in the year 1985.\(^{11}\) This compound adopts a complicated molecular structure consisting of a uranyl core surrounded by a 16-borate ring.\(^{11}\) From 1986 to 1991, Gasperein synthesized seven actinide borate compounds, including \( \text{UO}_2(\text{B}_2\text{O}_4) \), \( \text{Li(UO}_2\text{)}\text{BO}_3 \), \( \text{Na(UO}_2\text{)}\text{BO}_3 \), \( \text{Ca(UO}_2\text{)}_2(\text{BO}_3)_2 \), \( \text{Mg(UO}_2\text{)}\text{B}_2\text{O}_5 \), \( \text{Ni}_7(\text{UO}_2\text{)}(\text{B}_4\text{O}_{14}) \), and \( \text{Th(B}_2\text{O}_5) \) by using molten \( \text{B}_2\text{O}_3 \) as a flux in the high temperature (>1000 °C) solid state reactions.\(^{12-18}\) All these actinide borates only contain anhydrated \( \text{BO}_3 \) triangles except
\[ \text{Ni}_7(\text{UO}_2)(\text{B}_4\text{O}_{14}) \] which contains both BO\(_3\) triangles and BO\(_4\) tetrahedra.\(^{16}\) Then no new actinide borates were reported for almost 20 years. More importantly, there is no actinide borate synthesized under the temperature range between room temperature and the extreme high temperature (1000 °C), i.e. the mild heating conditions.

1.2 Vitrification of Nuclear Wastes

Although there are a number of fission product radionuclides of high activity (\(^{137}\)Cs and \(^{90}\)Sr) and long half-life (\(^{99}\)Tc, 200,000 years; \(^{129}\)I, 1.6×10\(^7\) years) in spent nuclear fuel, actinides and their decay products account for most of the radiotoxicity of nuclear waste after the first 500 years of disposal.\(^{19}\) After several hundred years, radiotoxicity is dominated by \(^{239}\)Pu (half-life 24, 000 years) and \(^{237}\)Np (half-life 2,140,000 years).\(^{19}\) Thus, a major part of the long-term risk is directly related to the fate of actinides from uranium to curium in the geosphere.

Currently, the immobilization of actinides in solid matrixes is being used as an approach for preventing their release into the environment during long-term storage.\(^{20}\) Many waste forms have been suggested as being suitable for this including zircon, garnet, pyrochlore, synroc, and monazite, and there is an ongoing debate concerning the best waste form for actinides.\(^{21,22}\) Only two types of materials, glasses and ceramics, passed the U.S. and international peer reviews and waste form selection procedures.\(^{23}\) Referring to the report\(^{23}\) compiled by the Hench Committee, DOE selected only borosilicate glass for the defense waste at the Savannah River Site. Borosilicate glass is any silicate glass that contains more than 5 percent by weight of B\(_2\)O\(_3\). Meanwhile, DOE
has also applied this choice to all its sites for nuclear waste storage only except Idaho National Engineering Laboratory. Moreover, except for Russia, which has produced phosphate glass for decades, borosilicate glass has become the only waste form for liquid high-level radioactive waste in the world now.

The industrial-scale vitrification of high-level waste which adopts borosilicate glass waste form was initially developed in France in the 1970s. French and British companies operate the commercial reprocessing and vitrification plants. They reprocess domestic and foreign spent fuel from nuclear power reactors, vitrify the high-level waste, and return the glass. There are two noncommercial vitrification facilities in the United States: the West Valley Demonstration Project and Savannah’s Defense Waste Processing Facility. The high-level waste at the West Valley has already been vitrified and the melter had been shut down. The glass is loaded into 255 cylindrical canisters, each with 62 centimeters in diameter and about 3 meters long. These glass logs are stored on-site awaiting disposal in a geologic repository. The Savannah facility started radioactive operation in 1996. About fifteen hundred glass logs had been produced by 2004. A total of six thousand logs will be produced to convert all the high-level waste into borosilicate glass at Savannah River Site. At the current pace, the vitrification is estimated to continue for at least two decades.

Currently, the vitrification process (as shown in Fig. 1.1) requires that high-level waste be mixed with glass-forming additives, primarily SiO$_2$ and B$_2$O$_3$, heated up to higher than 1000 °C, melted, and poured into metallic containers. The melt then freezes and forms glass during the cooling process. As a result, most of the radioactive
elements become parts of the glass structure; some are just dispersed inside the glass as the mixtures. If there is insufficient alkali in the waste, sodium oxide, lithium oxide, or both are added. Other oxides are frequently added to fine-tune material properties which are important for the melting process, for instance, ZrO$_2$ is chosen as the additive to improve chemical durability- the most important property of glass.

A few fission products, such as ruthenium, rhodium, and palladium are insoluble in glass. They form small crystals embedded in the glass. These crystals can act as nucleation sites, that is, they can enhance the formation of other crystalline phases such as silicates and borates during the melting and on the cooling of the glass. It has been recognized that both processing techniques and high actinide content in the glasses can lead to the formation of crystalline products within these glasses which may greatly lower the chemical durability and the integrity of the glass. These crystals also possess long-range order, are generally less soluble than the glasses, and display physicochemical properties that sharply contrast with the original glasses. On the basis of dissolution studies on high borate content glasses, the actinides are apparently primarily interacting with the borate portion of the glass. The purpose of this research proposal is trying to synthesize and characterize a whole series of actinide borate compounds under a wide range of conditions, with the hope that they are reasonable models of the crystalline products in the vitrified nuclear waste.
Figure 1.1: A cartoon that shows the process of nuclear waste vitrification.
1.3 Waste Isolation Pilot Plant (WIPP)

Located near Carlsbad, New Mexico, in eastern Eddy County, the Waste Isolation Pilot Plant (WIPP) is the third deep geological repository (Morsleben and the Schacht Asse II Salt Mine in Germany are the first two) in the world that licensed for permanent disposal of transuranic (TRU) wastes left from the research and production of nuclear weapons. WIPP is a pioneering effort in the assessment of geological site suitability and design procedures for a waste repository and is the first geological repository in the nation for which an application to begin permanent geological isolation is being submitted for a regulatory decision. In 1957, the committee of Nation Research Council started to consider burying the waste in rock salt, either in salt domes or in thick salt beds. Selection of the present WIPP site came after rejection of a previous candidate site, an abandoned salt mine near Lyons, Kansas.25 The exploratory construction of WIPP began in 1974 and now it consists of eight different underground panels (Fig. 1.2) for the waste storage with one that has been excavated.

The salt bed repository is selected based on its several advantages: first of all, salt can be mined easily; second, it is known to flow slowly under the pressure of overlying beds, and so will consolidate around the waste and isolate it in place; third, it is essentially impermeable. A key argument for the WIPP as a TRU waste repository is that the self-sealing of the salt will limit the availability and transport of water into and through the repository, and correspondingly minimize the potential release of TRU from the repository. In all the undisturbed repository scenarios, no actinide release from the WIPP is predicted.26 There is, however, groundwater in the WIPP, even in undisturbed
Figure 1.2: A simplified map of WIPP showing the storage panels, salt beds, and brines.
scenarios, that is potentially available to interact with the TRU waste. The salt surrounding waste is groundwater-saturated with both intergranular and intragranular water, i.e. brines (blue area in Fig. 1.2). These brines can seep into the repository horizon and fill the excavated areas (TRU waste). Brine saturation of the repository is estimated to occur in less than 1000 years after repository closure. Therefore, those brines provide the most probable "escape route" of TRU waste to the public environment.

Two most important brines, namely GWB brine and ERDA-6 brine, are highly concentrated solutions (ionic strength up to 8 M) of predominantly sodium (Na\(^+\)), magnesium (Mg\(^{2+}\)), potassium (K\(^+\)), chloride (Cl\(^-\)), and sulfate (SO\(_4^{2-}\)), with smaller amounts of calcium (Ca\(^{2+}\)), carbonate (CO\(_3^{2-}\)), and borate (mostly B(OH)\(_4^-\) , B\(_4\)O\(_7^{2-}\), and H\(_3\)BO\(_3\)). These brines have been in contact with the Salado evaporite minerals since their deposition (estimated to be 250 million years) and are saturated with respect to these minerals.\(^{27}\)

The most important transuranic elements that related to WIPP are plutonium, the major component; americium, a moderate component; and neptunium, a minor component because of its relatively lower inventory.\(^{27}\) Thorium and uranium isotopes are the additional minor components of the WIPP inventory, smaller components than americium.\(^{27}\) Other radioactive elements are present in the waste but in amounts so small that they have a less significant influence on the determination of the performance of the proposed repository. Since the interaction of TRU waste with brines is the most probable way for the release of radioactive materials, it will be ultra-
important to study the solubility, the speciation diagram, and the chemical reaction of those actinides especially tranuranium elements from Np to Am in the WIPP brines.

One of the most important results recently is the investigation of trivalent actinide solubility in the WIPP brines conducted by Borkowski et al.\textsuperscript{10} In their studies, the neodymium(III) was selected as the surrogate of Actinide(III). The plot for the solubility of Nd(III) as function of tetraborate anion concentration in the presence of carbonate as shown in Fig. 1.3 demonstrates that the tetraborate anion is the primary complexant for Actinide(III) under the WIPP brine conditions. It was determined that Nd(III) is complexed by tetraborate with logarithm of the apparent stability constant ranging from 3.5 to 4.1 depending on the ionic strength. This implies actinide borates could be the most important solubility-limiting phases in the WIPP brine, which provides another motivation for the work in this dissertation.

1.4 Background I: Structural Chemistry of Actinides

The structural chemistry of actinides is very rich owing to the possibility of different oxidation states and the diversity of the actinide coordination geometries. The possible oxidation states of all actinides are shown in Table 1.1. The +1 oxidation state actinide was only reported for mendelevium, but the evidence is very doubtful.\textsuperscript{28} The +2 oxidation state for actinides first appears at Am in a few solid compounds but increasingly more stable in proceeding to mendelevium and nobelium where No(II) is the most stable oxidation states for nobelium in aqueous systems.\textsuperscript{29} With the exception of thorium and protactinium, all of the actinide elements can show a +3 state in
Figure 1.3: Plots for the solubility of Nd(III) as function of tetraborate anion concentration with different ionic strength.
### TABLE 1.1

OXIDATION STATES OF ACTINIDES (UNDERLINED, MOST STABLE; (), UNSTABLE; ?, CLAIMED BUT NOT SUBSTANTIATED)

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<tr>
<th>Actinide</th>
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Note: Underlined states indicate the most stable oxidation states.
aqueous solution, although the +3 state does not become the preferred under ordinary conditions until Am is reached. A stable +4 state is observed in the elements thorium through plutonium and in berkelium. The +5 oxidation state is well known in the elements from protactinium through americium, especially for protactinium and neptunium where Pa(V) and Np(V) are the most stable oxidation states. The +6 state is well established in the elements from uranium to americium. Only neptunium and plutonium are known to process An(VII) states while the evidence for existence of Pu(VIII) is very unsubstantiated.

Actinides in lower oxidation states (2, 3, and 4) sometimes mimic lanthanide elements in coordination geometry. The coordination number can be range from 6 to 12. Actinides in higher oxidation states (5, 6, and 7) adopt unique coordination geometry, mostly because of the tendency to form the linear dioxo actinyl ions (oxidation states of 5 and 6), with 4 to 6 additional donor atoms in the equatorial plane perpendicular to the actinyl axis to form tetragonal, pentagonal, and hexagonal bipyramids polyhedra shown in Fig. 1.4. These polyhedra can be condensed into dense structures via corner and edge-sharing, and are also bridged by various groups to yield isolated clusters, one-dimensional chains, two-dimensional sheets, and three-dimensional frameworks.

The structural chemistry of thorium is dominated by Th(IV) and the common thorium (IV) oxo-anion compounds including perchlorates, sulfates, nitrates, carbonates, phosphates, vanadates, molybdates, chromates, silicates, carbolxylates have been widely investigated. There are trace number of Th(III)
Figure 1.4: Depictions of (a) the actinyl ion, (b) and (e) actinyl square bipyramid, (c) and (f) actinyl pentagonal bipyramid, (d) and (g) actinyl hexagonal bipyramid.
compounds such as Th(C₅H₅)₃,⁴⁷ Th{η⁵-C₅H₃(SiMe₃)₂},⁴⁸ which have a 6d¹ ground state not 5f¹ showed by the EPR spectrum, although for the Th(III) free ion, the ground configuration was proved to be 5f¹ not 6d¹.⁴⁹

For the structural chemistry of uranium(VI), Burns reviewed crystal structures of 368 inorganic uranium(VI) compounds including minerals that contain a nearly linear uranyl ion UO₂²⁺, with U=O bond distances of ~1.79(4) Å.⁴⁶ The uranyl O atom, which has valence unit of ~1.7 v.u., usually does not have sufficient bond valence to further bond to other donor ligands, thus sheets type structures are found to dominate crystal chemistry of uranium(VI).⁴⁶ Until now, most of the common oxoanions have been used to bind uranyl, and large families of uranyl oxoanion compounds are known.⁴⁶ Recently, the focus of uranyl structural chemistry has moved from the characterization of known uranyl minerals for the new classed of uranium structures involving nanotubules and nanoclusters.⁵⁰-⁵⁵ The new syntheses have now led to the discovery of a large family of uranyl peroxide finite clusters with both fullerene and non-fullerene topologies and nanotubules consisting of uranyl polyhedra coordinated by various sulfates, selenates and phosphonates. Tetravalent uranium structures are also well studied and its crystal chemistry very similar with its Th(IV) counterpart.⁵⁶ There are very few example of U(V) crystal structures in the Inorganic Crystal Structure Database (ICSD), but the number of U(V) compounds increased dramatically in recent years.⁵⁷,⁵⁸

Similar with uranium, neptunium can adopt oxidation states of IV, V, and VI in the ordinary natural conditions while Np(V) dominates the structural chemistry of neptunium. Burns and coworkers recently reviewed the structural hierarchy of 59
inorganic neptunyl compounds including 43 Np(V) compounds and 16 Np(VI) compounds.\textsuperscript{59} Compared with uranium(VI), where the valence unit of the uranyl O atom is \(\sim 1.7\) v.u., the valence unit of the neptunium(V) O atom is \(\sim 1.5\) v.u.. As a consequence, the neptuyl(V) O atoms get a better chance to be further bonded to other atoms such as other neptunium atoms as co-called Cation-Cation Interactions (CCIs).\textsuperscript{59} In the solid-state the neptunyl O atom is bonded to another neptunyl unit in its equatorial plane as shown in Fig. 1.5. Roughly 50% known structures of Np(V) contain this phenomenon while it only occurs in 2% in all known U(VI) structures.\textsuperscript{59} Meanwhile, the neptunyl(VI) only differ with uranyl(VI) in the actinyl bond length, where the Np(VI) bond lengths of the neptunyl ion are about 0.05 Å shorter than the bond lengths of the uranyl ion in the same coordination polyhedra as the result of the actinide contraction.\textsuperscript{59} However, the bond lengths of the equatorial bonds appear unaffected by the actinide contraction, and are very similar for Np(VI) neptunyl and U(VI) uranyl in the coordination geometries square, pentagonal, and hexagonal bipyramids.\textsuperscript{59} The crystal chemistry of Np(IV) is also very limited and there is only a few Np(IV) sulfates, iodates, and phosphonates known in the ICSD.\textsuperscript{60-63}

Plutonium is known to possibly adopt four oxidation states in the aqueous systems at the same time: Pu(III), Pu(IV), Pu(V), Pu(VI).\textsuperscript{64} However, there are very few plutonium oxo-anion compounds that known, which is mostly dominated by Pu(IV). Recently, several Pu(IV) selenates, iodates, and phosphonates were synthesized and with these supplements, the bond-valence parameter of Pu(IV) has been developed.\textsuperscript{65-68}
Figure 1.5: Depiction of cation-cation interaction (CCI) bond for neptunyl units.
1.5 Background II: Structural Chemistry of Borates

Borates are being actively developed owing to their wide range of applications. In particular, they display remarkable transparency in the deep UV, high chemical stability, and for some materials, crystals with high optical quality can be obtained leading to the development of nonlinear optical materials when the borates adopt noncentrosymmetric space groups such as β-BaB$_2$O$_4$ (BBO),$^{69}$ LiB$_3$O$_5$ (LBO),$^{70}$ CsLiB$_6$O$_{10}$ (CLBO),$^{71}$ BiB$_3$O$_6$ (BiBO),$^{72}$ and La$_2$CaB$_{10}$O$_{19}$ (LCB)$^{73}$. From a structural chemistry point of view, boron atoms bound by oxygen atoms are found not only in three-fold (triangle, BO$_3$) coordination, but also in four-fold coordination (tetrahedron, BO$_4$). A twofold coordinated boron in BO$_2$ was only observed in boro-oxo-(or hydroxo) apatite structure, but never in other simple or complex borates.$^{74}$ Larger polyborate anions are formed by BO$_3$ and BO$_4$ sharing only corners so that a compact insular group generally results. These groups are called Fundamental Building Blocks (FBBs).$^{75,76}$ Only one exception was the structure of Dy$_4$B$_6$O$_{15}$ where BO$_4$ tetrahedra link together not only with common corners but also via common edges.$^{77}$ Because there is a vast number of different topological arrangements of the polyborate anions and Fundamental Building Blocks (FBBs), the solid-state and materials chemistry of borates is virtually unsurpassed.$^{78,79}$ Borates can be divided into three groups: main group and transition metal borates,$^{78}$ lanthanide and actinide borates, organic and transition metal complex templated borates.$^{80-83}$ Recent interest in borates has focused on mixed oxoanion systems that include B-O-P,$^{84-86}$ B-O-Ge,$^{87-89}$ B-O-Al,$^{90-95}$ B-O-Ga$^{96,97}$ and B-O-In$^{98}$ systems,
with a clear effort to prepare microporous zeolitic materials with new catalytic, ion exchange, and sorption properties.

1.6 Background III: Overview of all known Actinide Borate Compounds

There are many synthetic methods for making traditional borate compounds. The most important ones are hydrothermal methods, high temperature solid state fluxes and room temperature slow evaporation or solvothermal methods. Actinide borates are difficult to prepare by traditional hydrothermal methods, because water competes very successfully with borate for inner-sphere coordination sites for these metals under most conditions. In fact, many borates that occur naturally are found in evaporated deposits in arid regions. These known actinide borates compounds are synthesized by either removing water entirely from the system in high-temperature or slow water evaporation. In 1985, the first single crystal structure of uranium borate, $K_6[UO_2\{B_{16}O_{24}(OH)_8\}]\cdot 12H_2O$, was made by Behm from slow water evaporation. This compound consists of isolated clusters composed of molecular uranyl borates with a uranyl core surrounded by a 16-borates ring shown in Fig. 1.6. From 1986 to 1991, Gasperin synthesized seven actinide borates, including $UO_2(B_2O_4)$, $Li(UO_2)BO_3$, $Na(UO_2)BO_3$, $Ca(UO_2)_2(BO_3)_2$, $Mg(UO_2)B_2O_5$, $Ni_7(UO_2)(B_4O_{14})$ and $Th(B_2O_5)$ by using molten $B_2O_3$ as a flux in the high temperature (>1000 °C) solid state reactions. All these actinide borates only contain BO$_3$ triangles (Fig. 1.7) except $Ni_7(UO_2)(B_4O_{14})$ contains both BO$_3$ triangles and BO$_4$ tetrahedra. Then no new actinide borates were reported for almost 20 years until this work.
Figure 1.6: A view of 16 borate rings cluster of $K_6\left[\text{UO}_2\{\text{B}_{16}\text{O}_{24}\text{(OH)}_8\}\right]\cdot12\text{H}_2\text{O}$ ($\text{UO}_8$ hexagonal bipyramids are shown in yellow, $\text{BO}_3$ triangles in blue, and $\text{BO}_4$ tetrahedra in purple).
Figure 1.7: Views of the structure of UO$_2$(B$_2$O$_4$) in [ac] plane (a) and [bc] plane (b) (UO$_6$ hexagonal bipyramids are shown in green, BO$_3$ triangles in light purple).
1.7 Reference


    2009, 131, 16648.
    2005, 44, 1134.


2.1 Molten Boric Acid Flux Synthetic Technique

Boric acid is very soluble in boiling water; the melting point of it is 170.9 °C. When heated above this temperature, it melts and dehydrates, forming metaboric acid, HBO₂; when heated above about 230 °C it further dehydrates, forming tetraboric acid or pyroboric acid, H₂B₄O₇; further heating leads to boron oxide shown in the scheme below:

\[
\begin{align*}
\text{H}_3\text{BO}_3 & \xrightarrow{170.9^\circ \text{C}} \text{HBO}_2 \\
\text{HBO}_2 & \xrightarrow{230^\circ \text{C}} \text{H}_2\text{B}_4\text{O}_7 \\
\text{H}_2\text{B}_4\text{O}_7 & \xrightarrow{300^\circ \text{C}} \text{B}_2\text{O}_3
\end{align*}
\]

Boric acid flux method was first adopted by Williams and coworkers with the aim to synthesize new vanadium borate polymer materials, where large excess of boric acid acted as both the reaction medium and the reactant, \([\text{H}_2\text{en}]_4[\text{Hen}]_2[\text{V}_6\text{B}_{22}\text{O}_{53}\text{H}_8] \cdot 5\text{H}_2\text{O}\) was the first compound made via this technique.¹ Alternatively, Lin and coworkers also used boric acid flux method for the synthesis of boron-containing open-framework compounds such as aluminoborates, PKU-1 is the most fascinating example with 18-ring channels²; PKU-5 and PKU-6 were other examples of aluminoborates made from boric acid flux reactions.³ ⁴ Moreover, a series of novel rare earth polyborates were also synthesized by Lin and coworkers by adopting molten boric acid as a flux in the
Yu and coworkers applied this technique in the field of borophosphate compounds, where \( \text{Na}_2[\text{VB}_3\text{P}_2\text{O}_{12}\cdot(\text{OH})] \cdot 2.92\text{H}_2\text{O} \) and 
\[ \text{Na}_5(\text{H}_3\text{O})(\text{M}^\text{II}_3\text{[B}_3\text{O}_3(\text{OH})]_3(\text{PO}_4)_6) \cdot 2\text{H}_2\text{O} \ (\text{M}^\text{II} = \text{Mn, Co, Ni}) \] are recent examples.\(^8,^9\) There are also other borate materials made from boric acid flux methods such as transition metal borates, \( \text{NiB}_{12}\text{O}_{14}(\text{OH})_{10} \) which has ferromagnetic ordering, \( \text{Fe}_5\text{O}_5[\text{B}_6\text{O}_{10}(\text{OH})_3] \cdot n\text{H}_2\text{O} \) which shows anti-ferromagnetism in low temperature, and \( \text{MCuB}_7\text{O}_{12} \cdot n\text{H}_2\text{O} \ (\text{M} = \text{Na, K}) \) which is built with large 14-ring channels.\(^10-12\)

### 2.2 Systematic Synthesis of Actinide Borates

In this dissertation, the molten boric acid flux technique is utilized to synthesize a series of novel actinide borate compounds including thorium, uranium, neptunium, plutonium, americium, and curium borates. Typically, PTFE lined Parr reaction vessels is used to load large excess of boric acid, which acts as both the reaction media and the boron reagent, and actinide reagents usually actinide nitrate with or without the presence of other metal cations especially alkali metal cations, which are helpful with the crystallization and change of structural topologies by incorporating into crystal structures. Different from the traditional hydrothermal methods, water is still used but only in reagent-grade amounts. These vessels are then sealed in autoclaves, heated in a box-oven at the temperature above the melting point of boric acid for 1 to 7 days followed with programmable cooling back to room temperature. Crystallized products are washed with boiling water to remove the excess boric acid and rinsed with
methanol. In particular, there are several variables that greatly affect the syntheses of actinide borates from boric acid flux reactions:

1. **Reaction temperature:** From thermal decomposition scheme of boric acid shown above, the extent of dehydration of boric acid is determined by the temperature, this can further determine the topologies of final actinide borate products. In this work, 190 °C, 220 °C, 240 °C, 280 °C are chosen for conducting boric acid flux synthetic reactions.

2. **Additional metal cations:** It is already mentioned that additional metal cation can be incorporated into the systems. In this work, incorporation of alkali metal cations Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, and three pseudo alkali metal cations, NH₄⁺, Ag⁺, and Tl⁺ are the first systems to be explored and incorporation of alkali earth metal and transition metal cations are then conducted. Incorporation of +3 charge metal cations has been also under consideration such as the lanthanide series.

3. **Stoichiometry of starting materials:** Considering the principle of phase diagrams, the stoichiometry of the starting materials will greatly affect the number of phases of final products in the reactions. In this research, different stochiometries of reactions will be explored by changing two variables An:B molar ratio and An: A molar ratio (An: actinide; B: boric acid; A: additional cation) of starting materials. Since water is also in reagent-grade amount, the effect of water amount in the reactions is also investigated.

4. **Reaction time:** Reaction time is an important factor of boric acid reactions since some kinetically favorable products can only be isolated in short time reactions.
However, the yield of thermodynamically favorable products can be improved by longer time reactions. Thus, both yield and numbers of phases of products can be affected by the reaction time. 1 day, 3 days, 5 days, and 7 days reactions will be chosen for this research.

5. **Oxidation states of actinides**: In this research, presence of Th(IV), U(IV), U(VI), Np(IV), Np(V), Np(VI), Pu(III), Pu(IV), Pu(VI), Am(III), and Cm(III) in the borate matrix are all expected in either single actinide element with single valence for actinide borate compounds, or single actinide element with mixed/intermediate valence compounds, or even mixed-actinides borate compounds. Careful controlling of the oxidation states of actinides especially Np and Pu in the reactions is critical. This is realized by using different actinide starting materials and controlling of reaction temperature and pH.

Systematic reaction plans is designed by conducting experiment with all fixed variables listed above except that one will be systematically changed (see the supporting information in Chapter 7). All new actinide borate compounds are summarized in Table 2.1 and the unit cell parameter information are listed in Table 2.2.

2.3 Characterization Techniques

After the actinide borates are synthesized, characterization then ensues. Single Crystal X-ray Diffraction is utilized to determine crystal structures of actinide borate compounds that isolated. Powder X-ray Diffraction is employed to examine the purity and numbers of phases in the reaction products. UV-vis-NIR Absorption Spectroscopy
<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Formula</th>
<th>SG</th>
<th>Compound Name</th>
<th>Formula</th>
<th>SG</th>
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<td></td>
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<td>NDTB-1</td>
<td>Th[\text{B}_5\text{O}_6\text{(OH)}_6][\text{H}_2\text{BO}_3]\cdot2.5\text{H}_2\text{O}</td>
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<td></td>
<td></td>
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<tr>
<td><strong>Uranium Borate</strong></td>
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<td></td>
<td></td>
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<tr>
<td>UBO-1</td>
<td>β-\text{UO}_2\text{B}_2\text{O}_4</td>
<td>C2</td>
<td>UBO-2</td>
<td>α-(\text{UO}_2)_2[\text{B}<em>9\text{O}</em>{13}(\text{OH})_3]</td>
<td>P2_1</td>
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<tr>
<td>UBO-3</td>
<td>β-(\text{UO}_2)_2[\text{B}<em>9\text{O}</em>{13}(\text{OH})_3]</td>
<td>P-1</td>
<td>UBO-4</td>
<td>γ-(\text{UO}_2)_2[\text{B}<em>9\text{O}</em>{13}(\text{OH})_3]</td>
<td>C2/c</td>
</tr>
<tr>
<td>UBO-5</td>
<td>(\text{UO}<em>2)<em>2[\text{B}</em>{13}\text{O}</em>{21}(\text{OH})_3]\cdot\text{H}_2\text{O}</td>
<td>P-1</td>
<td>UBO-6</td>
<td>(\text{UO}_2)[\text{B}<em>8\text{O}</em>{11}(\text{OH})_4]</td>
<td>Cc</td>
</tr>
<tr>
<td>LiUBO-1</td>
<td>Li[(\text{UO}_2)\text{B}_9\text{O}_9]\cdot\text{H}_2\text{O}</td>
<td>Pn</td>
<td>NaUBO-1</td>
<td>Na[(\text{UO}_2)\text{B}<em>5\text{O}</em>{10}(\text{OH})]\cdot2\text{H}_2\text{O}</td>
<td>Cc</td>
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<tr>
<td>NaUBO-2</td>
<td>α-Na[(\text{UO}<em>2)\text{B}</em>{10}\text{O}_{15}(\text{OH})_5]</td>
<td>P3_2</td>
<td>NaUBO-3</td>
<td>β-Na[(\text{UO}<em>2)\text{B}</em>{10}\text{O}_{15}(\text{OH})_5]</td>
<td>Cc</td>
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<tr>
<td>NaUBO-4</td>
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<td>KUBO-1</td>
<td>K[(\text{UO}<em>2)<em>2\text{B}</em>{10}\text{O}</em>{15}(\text{OH})_5]</td>
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<td>KUBO-3</td>
<td>β-K_2[(\text{UO}<em>2)<em>2\text{B}</em>{12}\text{O}</em>{19}(\text{OH})_4]</td>
<td>C2/c</td>
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<tr>
<td>KUBO-4</td>
<td>K[(\text{UO}<em>2)<em>2\text{B}</em>{10}\text{O}</em>{16}(\text{OH})_3]\cdot\text{H}_2\text{O}</td>
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<td>KUBO-5</td>
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<td>RbUBO-1</td>
<td>Rb[(\text{UO}<em>2)<em>2\text{B}</em>{13}\text{O}</em>{20}(\text{OH})_3]</td>
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<td>Rb[(\text{UO}<em>2)<em>2\text{B}</em>{10}\text{O}</em>{16}(\text{OH})_3]\cdot\text{H}_2\text{O}</td>
<td>P21/m</td>
<td>RbUBO-3</td>
<td>Rb[(\text{UO}_2)\text{B}<em>6\text{O}</em>{10}(\text{OH})]\cdot0.5\text{H}_2\text{O}</td>
<td>Ama</td>
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<tr>
<td>CsUBO-1</td>
<td>α-Cs[(\text{UO}<em>2)<em>2\text{B}</em>{11}\text{O}</em>{16}(\text{OH})_6]</td>
<td>P-1</td>
<td>CsUBO-2</td>
<td>β-Cs[(\text{UO}<em>2)<em>2\text{B}</em>{11}\text{O}</em>{16}(\text{OH})_6]</td>
<td>Cc</td>
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<td>Cs\text{UO}_2\text{BO}_3</td>
<td>P21/n</td>
<td>AgUBO-1</td>
<td>Ag[(\text{UO}_2)\text{B}_6\text{O}_8(\text{OH})_2]</td>
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<td>AgUBO-2</td>
<td>Ag\text{UO}_2\text{BO}_3</td>
<td>Pbcm</td>
<td>TIUBO-1</td>
<td>Tl_2[(\text{UO}<em>2)<em>2\text{B}</em>{11}\text{O}</em>{19}(\text{OH})]</td>
<td>Cc</td>
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<tr>
<td>TIUBO-2</td>
<td>α-Tl_2[(\text{UO}<em>2)<em>2\text{B}</em>{11}\text{O}</em>{18}(\text{OH})_3]</td>
<td>P1</td>
<td>TIUBO-3</td>
<td>β-Tl_2[(\text{UO}<em>2)<em>2\text{B}</em>{11}\text{O}</em>{18}(\text{OH})_3]</td>
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<td>Cc</td>
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<td>Li_{0.07}\text{Tl}_{0.93}[(\text{UO}<em>2)<em>2\text{B}</em>{13}\text{O}</em>{16}(\text{OH})_6]</td>
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<td>SG</td>
<td>Compounds Name</td>
<td>Formula</td>
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<td>SrUBO-1</td>
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<td>NaUBOF-1</td>
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<td>KUBOF-2</td>
<td>K₁₁[(UO₂)₆B₂₄O₃₆F₂₂]·H₂BO₃</td>
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<td>RbUBOF-1</td>
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<td>Cc</td>
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<td>RbUBOF-2</td>
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<td>CsUBOF-1</td>
<td>Cs[(UO₂)B₅O₈(OH)F]</td>
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<td>Ag[(UO₂)B₅O₈(OH)F]</td>
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<td>TIUBOF-1</td>
<td>TI[(UO₂)B₅O₈(OH)F]</td>
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**Neptunium Borate**

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<th>Formula</th>
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<tbody>
<tr>
<td>Np(V)BO-1</td>
<td>(NpO₂)₂[B₃O₄(OH)₂]</td>
<td>Pca</td>
<td>KNp(V)BO-1</td>
<td>K₂[(NpO₂)₂B₁₀O₁₁(OH)₁₂]</td>
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<td>KNp(V)BO-2</td>
<td>K[(NpO₂)B₁₀O₁₄(OH)₄]</td>
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<td>Np(VI)BO-1</td>
<td>(NpO₂)[B₈O₁₁(OH)₄]</td>
<td>Cc</td>
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<td>Np(VI)BO-2</td>
<td>(NpO₂)₂[B₉O₁₃(OH)₅]</td>
<td>P1</td>
<td>NaNp(VI)BO-1</td>
<td>Na[(NpO₂)B₆O₁₀(OH)]·2H₂O</td>
<td>Cc</td>
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<tr>
<td>NaNp(VI)BOF-1</td>
<td>Na[(NpO₂)₂B₂O₅(OH)F]·H₂O</td>
<td>Cc</td>
<td>NaNp(V,VI)BO-1</td>
<td>Na<a href="ClO%E2%82%84">(NpO₂)₄B₁₅O₂₃(OH)₆(H₂O)</a>·0.75H₂O</td>
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<tr>
<td>KNp(V,VI)BO-1</td>
<td>K₂[(NpO₂)₂B₁₀O₁₆(OH)₂(NO₃)₂]</td>
<td>P21/n</td>
<td>Np(IV,VI)BO-1</td>
<td>(NpO₂)₄[(NpO₂)₆.₇₃B₂O₃₆(OH)₂]</td>
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<tr>
<td>KNp(IV,VI)BO-1</td>
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<td>P-1</td>
<td>BaNp(IV,VI)BO-1</td>
<td>Ba₂[(NpO₂)₆.₅₉B₂O₃₆(OH)₂]·H₂O</td>
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**Plutonium Borate**

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<th>Formula</th>
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<tr>
<td>Pu(III)BOCl-1</td>
<td>Pu[B₄O₆(OH)₂Cl]</td>
<td>Cc</td>
<td>Pu(III)BOCl-2</td>
<td>Pu₂[B₁₃O₁₉(OH)₅(H₂O)₃Cl₂]</td>
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<tr>
<td>Pu(III)BOBr-1</td>
<td>Pu₂[B₁₂O₁₈(OH)₄Br₂(H₂O)₃]·0.5H₂O</td>
<td>Pn</td>
<td>Pu(VI)BO-1</td>
<td>(PuO₂)[B₈O₁₁(OH)₄]</td>
<td>Cc</td>
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**Americium Borate**

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<tr>
<td>Am(III)BOCl-1</td>
<td>Am[B₉O₁₃(OH)₄]·H₂O</td>
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**Curium Borate**

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<td>Cm₂[B₁₆O₂₀(OH)₇(H₂O)₂Cl]</td>
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### TABLE 2.2

UNIT CELL LISTS OF ALL ACTINIDE BORATE COMPOUNDS THAT SYNTHESIZED IN THIS WORK

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α(deg)</th>
<th>β(deg)</th>
<th>γ(deg)</th>
<th>Space Group</th>
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<td>NDTB-1</td>
<td>17.4036</td>
<td>17.4036</td>
<td>17.4036</td>
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<td>90</td>
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measurements are used to identify the oxidation states of actinides especially Np and Pu in the crystal structures. Fluorescence Spectroscopy is applied as additional proof of existence of uranium in the crystal structure since luminescence is an important property for most of uranium(VI) compounds. Magnetic Susceptibility measurement is conducted for some pure transuranium borate products which may show interesting magnetism; this can also provide additional evidence for oxidation states of transuranium elements. Infrared Spectroscopy and Thermogravimetric Analysis is also used to provide supporting information about chemical forms in the crystal structures. If a pure actinide borate compound in non-centrosymmetric space group can be made, the Second-harmonic Generation measurements are also carried out.

2.4 Reference


CHAPTER 3:

NDTB-1: A SUPERTETRAHEDRAL CATIONIC FRAMEWORK THORIUM BORATE MATERIAL THAT CAN SOLVE THE TECHNETIUM PROBLEM

3.1 Abstract

[ThB₅O₆(OH)₆][BO(OH)₂]·2.5H₂O (Notre Dame Thorium Borate-1) is a purely inorganic supertetrahedral cationic framework material that derived from boric acid flux reactions. NDTB-1 exhibits facile single crystal to single crystal anion exchange with a variety of common anions such as Cl⁻, Br⁻, NO₃⁻, IO₃⁻, ClO₄⁻, MnO₄²⁻, CrO₄²⁻, etc. More importantly, NDTB-1 is selective for the removal of TcO₄⁻ from a simulated low-activity nuclear waste stream even though there are large excesses of competing anions such as Cl⁻, NO₃⁻, and NO₂⁻. Competing anion exchange experiments and MAS-NMR spectroscopy of anion-exchanged NDTB-1 demonstrate that this unprecedented selectivity originates from the ability of NDTB-1 to trap certain anions within cavities whereas others remain mobile within channels in the material. The exchange kinetics of TcO₄⁻ in NDTB-1 are second-order with the rate constant $k_2$ of 0.059 s⁻¹·M⁻¹.

Furthermore, we report the anion exchange capacity of NDTB-1 for TcO₄⁻ to be 162.2 mg/g (0.5421 mol/mol) and the maximum distribution coefficient $K_d$ of 1.0534×10⁴ mL/g. The latter is an order of magnitude larger than any other material. Finally, we
demonstrate that the exchange for TcO\textsubscript{4}\textsuperscript{−} in NDTB-1 to be reversible. TcO\textsubscript{4}\textsuperscript{−} trapped in NDTB-1 can be exchanged out using higher-charged anions with a similar size such as PO\textsubscript{4}\textsuperscript{3−} and SeO\textsubscript{4}\textsuperscript{2−}, and therefore the material can be easily recycled and reused.

3.2 Introduction

Due to its high fission yield (\(~6.03\%) from \textsuperscript{235}U, the radionuclide \textsuperscript{99}Tc is present as a large inventory in the nuclear waste. It is estimated that there is approximately 305 metric tons (\(~190\) PBq) of \textsuperscript{99}Tc that has been generated in both nuclear reactors and weapon tests from 1943 to 2010.\textsuperscript{1} \textsuperscript{99}Tc is a β emitter with a long half-life of \(2.13 \times 10^5\) years. As a result, \textsuperscript{99}Tc is one of the most important radiotoxicity contributors during the long-term waste storage. Unlike its congener MnO\textsubscript{4}\textsuperscript{−}, TcO\textsubscript{4}\textsuperscript{−} is not a strong oxidant and relatively unreactive. Technetium is therefore present mainly as TcO\textsubscript{4}\textsuperscript{−} under a large range of conditions from strongly oxidative to even mildly reductive environments.\textsuperscript{2} TcO\textsubscript{4}\textsuperscript{−} is highly soluble and extremely mobile in aqueous systems. The velocity of TcO\textsubscript{4}\textsuperscript{−} transportation in the subsurface was determined to be almost the same as the groundwater.\textsuperscript{3} In addition, compared to some other water-soluble radionuclides in the fission products such as \textsuperscript{137}Cs and \textsuperscript{90}Sr, TcO\textsubscript{4}\textsuperscript{−} is much more unlikely to be sorbed by the soil in the repositories.\textsuperscript{4} Finally, the volatile nature of some Tc(VII) compounds (e.g. Tc\textsubscript{2}O\textsubscript{7}) that are generated during nuclear waste vitrification makes technetium problematic in the off-gas system design for the vitrification facility.\textsuperscript{2} The combination of TcO\textsubscript{4}\textsuperscript{−} mobility in groundwater and technetium volatility during vitrification increases the risk of offsite release of Tc-99.
Currently, the major inventory of TcO$_4^-$ is present in the high-level nuclear wastes (LAW) stored at the Hanford Site in eastern Washington and the Savannah River Site in South Carolina. Almost all of the Tc-99 is present in the water-soluble fraction of the high level waste and is not removed by pretreatment processes that capture Cs-137, Sr-90 and alpha-emitting radionuclides. The decontaminated or low-activity waste (LAW) solutions containing the Tc-99, are incorporated into a grout wasteform at the Savannah River Site and will be incorporated into a borosilicate glass wasteform at Hanford. Effective removal of TcO$_4^-$ from the LAW stream prior to vitrification would eliminate problems associated with volatilization during the vitrification process.

At least two strategies for the technetium separation have already been proposed. One is using the commercial-available anion exchange resins to remove TcO$_4^-$ from the LAW stream before vitrification, the other is using a strong reducing agent such as zero-valent iron to reduce TcO$_4^-$ to lower-valence technetium species (e.g. TcO$_2$), which have much lower solubility in aqueous solutions and are much less volatile. At Hanford, the separated Tc-99 would be vitrified in the high-activity waste (HAW) melter. At present, a decision has not been made concerning the best method to remove or process the TcO$_4^-$ in the LAW stream. First, both the efficiency and the selectivity for removing TcO$_4^-$ in the LAW are poor especially for the commercially available anion exchange resins. Second, both separation strategies mentioned above would require processing either TcO$_4^-$-loaded ion-exchange materials or technetium-containing eluant into the HAW melther resulting in a volume increase for the HAW glass wasteform. Technetium
volatility would likely be an issue in the HAW melter unless technetium can be isolated from both LAW and HAW completely and incorporated in its own suitable waste form.

During the last two decades, significant efforts have been made in designing materials for removing $\text{TcO}_4^-$ from nuclear waste solutions with better selectivity and efficiency. Among these, several novel organic polymer based bifunctional anion-exchange resins with high exchange selectivity towards $\text{TcO}_4^-$ were reported. However, associated with their organic nature, the thermal and chemical stablity along with the resistance to the radiation damage for these resins are very limited. Furthermore, large excess of these exchange materials are used in the examinations for $\text{TcO}_4^-$ exchange, which questions the selectivity of the materials.

To address these drawbacks, a series of inorganic anion-exchangable materials have been prepared, which are mostly represented by the hydrotalcite clays, also known as layered double hydroxide (LDH), and its analogues. LDHs have been shown to exchange with a variety of anions including $\text{TcO}_4^-$ for the anions (usually halide, nitrate, or carbonate) that originally reside in its interlayer space. However, carbonate was proven to have the strongest affinity in LDHs, which leads to a poor exchange selectivity towards $\text{TcO}_4^-$. Very recently, Oliver and co-workers discovered a series of cationic materials with weakly bonded 1,2-ethanedisulfonate anions that undergo rapid anion exchange, examples of these include SLUG-21 and SLUG-26. In particular, SLUG-21 shows a high exchange capacity and affinity towards $\text{MnO}_4^-$, which would show potential applications to selectively remove $\text{TcO}_4^-$ from waste solutions although it still contains organic-based fragments.
We recently issued two communications on the synthesis, crystal structure of a pure inorganic supertetrahedral cationic framework material, NDTB-1, with fascinating anion exchange capabilities, and the $^{99}\text{Tc}$ MAS NMR spectroscopy of the $\text{TcO}_4^-$ exchanged NDTB-1 material showing $\text{TcO}_4^-$ can be trapped into the cavities of NDTB-1, which might lead to an unprecedented exchange selectivity.\textsuperscript{15,16} In this chapter, we will first re-emphasize the synthesis and the structural features of NDTB-1. We then report the details for the anion exchanges (mainly for $\text{TcO}_4^-$) of NDTB-1 including exchange kinetics, exchange capacity and the distribution coefficient, $K_d$. We will also demonstrate the exchange selectivity using a series of anion exchange competing experiments and MAS-NMR spectroscopy on the anion-exchanged NDTB-1 materials. Finally, we will present our $\text{TcO}_4^-$ removal experiments using a simulated Hanford low-activity melter recycle stream, which demonstrates that NDTB-1 can be used to remove $\text{TcO}_4^-$ in the presence of potentially competing anions such as nitrate, nitrite, and chloride.

3.3 Experimental section

*Synthesis of NDTB-1*: Procedure for making NDTB-1 can be followed in our previous communication\textsuperscript{15}. Typically, $\text{Th(NO}_3)_4\cdot4\text{H}_2\text{O}$ (0.2000 g), boric acid (0.6717 g), and DI-water (90 uL) were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 200 °C in a box furnace for 7 days. The autoclave was then cooled down to 160 °C at a rate of 1 °C/h followed by cooling at a rate of 9°C/h to the room temperature. The product was washed with boiling water to remove excess boric acid. Crystals in the
form of octahedra and their fractions can be isolated. Single crystal X-ray diffraction and powder X-ray diffraction studies reveal that NDTB-1 can be made as a pure phase with a yield of 72.8% based on Th (Fig. 3.S1).

*Exchange kinetics studies of NDTB-1:* 50 mg of TcO$_2$ was reacted with a large excess of 30% H$_2$O$_2$ to yield a solution containing TcO$_4^-$.

10 mg of NDTB-1 material and 3 mL of a solution containing 1.455×10$^{-4}$ M TcO$_4^-$ was mixed in a cuvette without shaking. UV-vis spectra were acquired using a Cary 6000i spectrometer every 20 minutes for 7 days to probe the concentration of TcO$_4^-$ in solution as a function of time.

*Exchange capacity and exchange coefficient studies of NDTB-1:* Six parallels of solutions (3 mL) containing 4.58×10$^{-4}$ M TcO$_4^-$ were mixed respectively with six NDTB-1 samples with six different TcO$_4^-$ : NDTB-1 molar ratios of 1:1 (0.75 mg), 1:2 (1.5 mg), 1:4 (3 mg), 1:8 (6 mg), 1:16 (12 mg), and 1:32 (24 mg) in cuvettes without shaking. UV-vis spectra were acquired using a Cary 6000i spectrometer at same time every day for 12 days to probe the concentration of TcO$_4^-$ in solution as a function of time.

*Exchange selectivity studies of NDTB-1:* Twelve parallels of solutions (1.5 mL) containing 9.16×10$^{-4}$ M TcO$_4^-$ and solutions (1.5 mL) containing 9.16×10$^{-4}$ M competing anions (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 mixed respectively with NDTB-1 (1.5 mg) with TcO$_4^-$ : competing anion : NDTB-1 molar ratios of 1:1:2 in cuvettes without shaking. UV-vis spectra were acquired using a Cary 6000i spectrometer at same time every day for 12 days to probe the concentration of TcO$_4^-$ as a function of time.
**Exchange experiments with simulated Hanford LAW melter recycle stream and**

**NDTB-1**: A simulated Hanford LAW melter recycle stream was prepared using reagent
grade chemicals and ultrapure water (MilliQ Element) comprised of the following anions,
Cl⁻, NO₃⁻, NO₂⁻, SO₄²⁻, CO₃²⁻, and TcO₄⁻. The molar concentration of the anions and
molar ratio of each anion to that of TcO₄⁻ is provided in Table 3.3. Measured quantities
of the simulated Hanford recycle stream were pipetted into plastic centrifuge tubes
containing a premeasured quantity of NDTB-1 to provide phase ratios of 200 mL/g (Expt
1) and 40 mL/g (Expt 2). A control test contained the simulant only. The centrifuge
tubes were tightly stoppered and tumbled for 4 hours at ambient laboratory
temperature. The test suspension was filtered through a 0.10-micron syringe filter
(Millex) and the clear filtrate collected in a clean polyethylene sample bottle. Tc-99
activity in the filtrate was determined by scintillation counting. A blank test served as
the control to determine the Tc-99 in the untreated simulant and to ensure Tc-99 was
not removed by sorption to the tube or filter media or by precipitation during the 4-
hour test period.

**MAS-NMR studies of anion-exchanged NDTB-1 materials**: The anion exchanged
NDTB-1 materials for MAS-NMR studies were prepared by the parallel anion exchange
reactions using 200 mg NDTB-1 each with 5 mL solutions containing 50 mg of TcO₄⁻,
H₂PO₄⁻, ClO₄⁻, SeO₄²⁻, MnO₄⁻, TeO₄²⁻, respectively, for approximately 7 days. The anion
exchanged NDTB-1 materials were then washed with DI-water and dried at 65°C for 5
hours. MAS-NMR spectra were collected on a Bruker AVANCE spectrometer equipped
with a widebore 11.7 Tesla magnet, corresponding to ν₀ = 202.446 MHz for ³¹P, 123.91
MHz for $^{55}$Mn, 157.782 MHz for $^{125}$Te, 112.56 MHz for $^{99}$Tc and 95.40 MHz for $^{77}$Se, respectively). For $^{99}$Tc-NMR, we used 1.3 $\mu$s nonselective pulses, a 5 s relaxation delay and a 62.5kHz spectral window. Experiments conducted with the relaxation delay time varying from 1 to 15 s showed that 5 s is long enough to prevent any signal saturation. The spectra were obtained by summation of 64 transients and processed with 200 Hz of line broadening. The chemical shift is referenced to TcO$_4^-$ solution (sealed in a quartz tube) at 0 ppm. $^{31}$P MAS NMR data were collected with 15 kHz and 30 kHz spinning rates and single-pulse excitation with, and without, proton-decoupling sequences. Proton decoupling made no important difference in the spectra. In a typical experiment, 45 degree pulses and 60 second relaxation delays were used. The chemical shift was externally reference to 85% H$_3$PO$_4$ at 0 ppm. $^{125}$Te MAS-NMR data were collected with 12 and 15 kHz spinning rates, 45 degree pulses and 60 second relaxation delays. The chemical shift was externally reference to crystalline ZnTe at -888 ppm. For $^{77}$Se NMR, the pulse length was 1.7 $\mu$s (corresponding to 60 degree tip angle), the recycle delay time was 60s, the number of transients was 960. The chemical shift is externally referenced to saturated H$_2$SeO$_3$ solution at 1288 ppm. Spectra were also collected on a NDTB-1 loaded with ClO$_4^-$ as the ion-exchanged species.

3.4 Synthesis and Structural Feature of NDTB-1

NDTB-1, with the formula of [ThB$_5$O$_6$(OH)$_6$][BO(OH)$_2$]·2.5H$_2$O, can be synthesized from boric acid flux reactions with Th(NO$_4$)$_2$·5H$_2$O or ThOCO$_3$ at 200 °C. NDTB-1 is obtained as a pure phase with in 72.8% based on Th. This can be confirmed by powder
X-ray diffraction data (Fig. S1). However, the morphology of the crystals is greatly improved by starting with ThOCO$_3$ instead of Th(NO$_4$)$_3$·5H$_2$O.

The crystal structure of NDTB-1 is a porous supertetrahedral three-dimensional framework that crystallized in the $Fd\bar{3}$ space group. The building blocks of this framework are twelve-coordinate Th$^{4+}$ polyhedra surrounded by BO$_3$ triangles and BO$_4$ tetrahedra. The BO$_4$ tetrahedra chelate the thorium centres, while the BO$_3$ groups share vertices with thorium polyhedra. Almost regular icosahedral coordination geometry is found for the thorium atoms. The borate units are polymerized, and form B$_{10}$O$_{24}$ clusters with three-fold symmetry that bridge between the thorium atoms, which results in a supertetrahedral framework structure shown in Fig. 3.1a.

Thorium atoms and crown-like B$_{10}$O$_{24}$ groups do not fill all of the space in the supertetrahedra, and as a consequence of this architecture, a system of channels and cavities are observed in the structure of NDTB-1. The channels extend along cubic [110] directions (Fig. 3.1a) and intersect in the center of the supertetrahedra to form cavities with four equivalent gates (Fig. 3.1b). The gates into the intersecting chambers in the cavities have a hexagonal form with the size of 9.4 × 7.8 Å (Fig. 3.1c). The free void volume percentage in NDTB-1 is very high at 43%, which makes it the second most porous actinide compound known. A combination of single crystal X-ray diffraction, charge-balance considerations, and $^{11}$B MAS NMR spectroscopy shows that this supertetrahedral framework possesses a positive charge with disordered protonated BO$_3$ units (i.e. H$_2$BO$_3^-$) in the channels and cavities.
Figure 3.1: a) A view of the supertetrahedral framework structure of NDTB-1 with channels through cubic <110> directions (Th polyhedra are shown in green and borate are shown in yellow); b) Depiction of a supertetrahedral cavity formed by four hexagonal windows (gates); c) A view of hexagonal windows (gates).
All these structural features make **NDTB-1** one of the best candidates for applications of the selective anion exchange. First, boric acid is a very week acid with the first pKₐ of 9.23. As a result, H₂BO₃⁻ anions that originally reside within the structure readily hydrolyze back to H₃BO₃ in aqueous solutions under a wide range of pH. Other anions therefore tend to enter the structure of **NDTB-1** required by the principle of charge-balance. Second, H₂BO₃⁻ is unbound to the cationic framework and the interaction between them is solely provided by weak Coulombic forces. Third, within the cationic framework, the channels form a network that pierces the whole structure and allows facile anionic transport for the exchange processes. Finally, the cavities are able to trap the anions with suitable charge and size. Exchange selectivity is therefore provided based on the fact that small anions are mobile in the channels while larger anions are not able to enter the structure.

3.5 **¹¹B-MAS-NMR Spectra of NDTB-1**

Solid-state **¹¹B** MAS NMR spectra show distinct signals from well-ordered BO₃ and BO₄ groups, as found from the single-crystal XRD data. The ordered BO₃ groups yield a characteristic MAS powder pattern with horns that correspond to the steep edge near +15 ppm and the peak at +7.5 ppm, best fit with an isotropic chemical shift δ = 17.5 ppm and quadrupolar coupling parameters Cq = 2.65 MHz, η = 0 (Fig. 3.2). However, a powder pattern for a well-ordered site cannot account for the broad area of intensity from 14 to 10 ppm, between the sharper BO₃ features. This intensity can be explained by the presence of additional BO₃ environments that experience a distribution
Figure 3.2: $^{11}$B-MAS-NMR powder pattern of NDTB-1 at 160.45 MHz and 15 kHz spinning rate. The sharp peak near 0 ppm corresponds to tetrahedral borate. The broad, two-horned peak near 15 ppm corresponds to trigonal boron and has at least two sites. The integrated intensities of these two peaks gives the ratio of BO$_3$ to BO$_4$ of 0.82(5).
of electric-field gradients. Such additional features are in accord with the presence of a disordered BO$_3$ group as was suspected from the crystal structure. The ratio of BO$_3$ to BO$_4$ integrated intensity, 0.82(5), far exceeds that expected from the 2:3 crystallographic ratio of the framework and provides further support for the existence of additional, extra-framework BO$_3$ groups.

To better resolve the sources of this broad area of intensity, we collected Multi-Quantum Magic-Angle Spinning (MQMAS) spectra of the material, the BO$_3$ region of which is shown in Fig. 3.3. The full $^{11}$B MQMAS spectrum also contains a narrow, symmetrical peak for tetrahedrally coordinated boron at F1 = 1.3, F2 = 0.6 ppm that is omitted from Fig. 3.3 for clarity. The BO$_3$ region of the MQMAS spectrum contains multiple resolved signals and highlights the disordered nature of the corresponding BO$_3$ groups as was inferred from the MAS spectrum. The disordered BO$_3$ groups yield a broad peak in the isotropic dimension, centered near F1 = 19 ppm, corresponding to a correlated distribution of isotropic chemical shifts and quadrupolar coupling constants with decreasing intensity from $\delta = 17$ ppm and Cq = 2.55 MHz to $\delta = 14.5$ ppm and Cq = 2.35 MHz. The ordered framework BO$_3$ groups give a sharp F1 peak at 20.8 ppm and well-defined quadrupolar powder pattern in the anisotropic dimension (Fig. 3.3 inset, middle). The MQMAS spectrum also shows a third BO$_3$ signal at F1 = 21.9 ppm that is not resolved in the MAS spectrum. In the anisotropic dimension (Fig. 3.3 inset, bottom), this third peak shows an unusual, smoothed F2 lineshape that is not accompanied by a diagonal ridge of intensity that would be expected for a distribution of Cq values from structural disorder. The cause of this peak shape is uncertain, but
Figure 3.3: Contour plot of a $^{11}$B MQMAS NMR spectrum ($v_R = 35.0$ kHz, 11.74 T) of the **NDTB-1** material. The spectra at left and top are summed projections of the F1 (isotropic) and F2 (anisotropic) dimensions, respectively, and the upper inset shows both a sharp signal near 0 ppm (0.6 ppm in F2, +1.3 ppm in F1) corresponding to tetrahedrally coordinated boron (B$(O)_4$) and the broader signal at higher ppm values corresponds to trigonal boron (17-23 ppm in F2, 10-5 ppm in F2). This BO$_3$-region is expanded in the larger figure at the left and shows the presence of three distinct BO$_3$ signals. The lower inset shows F2-cross sections taken at the peak maxima in F1, at 21.9, 20.8, and 18.7 ppm, from bottom to top, respectively. The spectrum was acquired at spectral widths of 16.6 kHz (F2) and 35 kHz (F1) with 96 scans per slice. The three-pulse zero-quantum filter sequence was employed with 2.4 $\mu$s excitation and 0.78 $\mu$s conversion pulses at a 250 kHz RF field followed by a 56 $\mu$s selective 90° pulse.
could be relatively low-frequency, restricted motions, perhaps indicating the presence of more loosely bound BO$_3$ groups in the channels. Signals from apparently mobile groups were observed in NMR spectra of most anions exchanged into NDTB-1 (see below). These $^{11}$B-NMR data are consistent with a model of the NDTB-1 structure with several sites for boron, including ordered BO$_4$ and BO$_3$ sites in the framework along with two other disordered BO$_3$ groups that experience a range of local structures as expected for sites in the channels and cavities. The existence of these extra-framework BO$_3$ moieties is consistent with the results of anion-exchange experiments (see below).

3.6 Anion Exchange Properties of NDTB-1

Anion exchange experiments of NDTB-1 were conducted with a variety of common anions including halides (Cl$^-$, Br$^-$, I$^-$), and oxyanions such as MnO$_4$$^-$, TcO$_4$$^-$, ReO$_4$$^-$, PO$_4$$^{3-}$, CrO$_4^{2-}$, Cr$_2$O$_7^{2-}$, SO$_4^{2-}$, SeO$_4^{2-}$, SeO$_3^{2-}$, ClO$_4$$^-$, NO$_3$$^-$, IO$_3$$^-$, etc. The anion exchange experiments were confirmed by the combination of techniques including combined inductively coupled plasma mass spectrometry (ICP-MS), energy-dispersive X-ray spectroscopy (EDS), and UV-vis-NIR absorption spectroscopy. As determined by single-crystal and powder X-ray diffractions of anion-exchanged NDTB-1 materials, the whole structure remains intact throughout the exchange process (Fig. 3.51). More impressive is the fact that single crystals retain their integrity throughout the exchange, which results in a rare phenomenon of single crystal to single crystal anion exchange, although disordering of the exchanged anions in the channels remains a crystallographic problem. This is critical for the reusability of NDTB-1 in the utility of anion exchanges,
which contrasts sharply with the fact that most of LDH structures collapse after the exchange.\textsuperscript{9c} Exchange experiments conducted with a variety of highly colored anions, such as MnO$_4^-$, CrO$_4^{2-}$, and Cr$_2$O$_7^{2-}$, can result in the single crystals showing the color of the transition-metal anions within a few minutes (Fig. 3.4). UV-vis-NIR spectra were also collected for these colored anion exchanged crystals, which further demonstrate the presence of the colored anions in the crystals (Fig. 3.52).

The critical anion exchange experiments involve replacing the extraframework borate anions with TcO$_4^-$. The uptake of the TcO$_4^-$ by NDTB-1 was monitored using the charge-transfer bands (290 nm) in the UV region of the spectrum. In order to derive the exchange kinetics, large excesses of NDTB-1 were used. In particular, 10 mg of NDTB-1 and 3 mL of a solution containing 1.455×10$^{-4}$ M TcO$_4^-$ were mixed in a cuvette without shaking. UV-vis spectra were acquired every 20 minutes for 7 days to probe the concentration of TcO$_4^-$ in solution as a function of time. These studies of as-synthesized intact crystals of NDTB-1 show rapid uptake of TcO$_4^-$ from solution show in Fig. 3.5a (in day width) and the plots for the concentration of TcO$_4^-$ as a function of exchange time is shown in Fig. 3.5b. The plot of 1/Conc. for TcO$_4^-$ as a function of time was also examined (Fig. 3.53), where a proper linear fit can be applied. This is consistent with the fact that the exchange reaction is a second-order reaction with TcO$_4^-$. The rate law for the TcO$_4^-$ exchange reaction could be therefore described as:

\[ \nu = \frac{dc(TcO_4^-)}{dt} = k \times c(TcO_4^-)^2 \]  

(assuming NDTB-1 is always in excess), where the rate constant $k$ is the slope of the linear fit plot and was calculated to be 0.059 s$^{-1}$·M$^{-1}$. 

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Figure 3.4: Photos of crystals of NDTB-1, MnO$_4^-$ exchanged NDTB-1, CrO$_4^{2-}$ exchanged NDTB-1, and Cr$_2$O$_7^{2-}$ exchanged NDTB-1.
Figure 3.5: a) UV-vis spectra of TcO$_4$\textsuperscript{-} solution exchanged with NDTB-1; b) Plot of concentrations of TcO$_4$\textsuperscript{-} concentration as a function of exchange time.
The exchange capacity of NDTB-1 for TcO$_4^-$ was also examined using a series of exchange reactions with different molar ratios of TcO$_4^-$ to NDTB-1. Particularly, six different molar ratios (1:1, 1:2, 1:4, 1:8, 1:16, 1:32) was selected and their exchange curves are shown in Fig. 3.6. In the 1:1 exchange reaction, a maximum of about 54.21% of TcO$_4^-$ can be removed from the solution (Table 3.1). When the amount of NDTB-1 was doubled, the maximum amount of TcO$_4^-$ that is removed from solution increases sharply to 83.62%. Further increasing the amount of NDTB-1 does not result in a significant improvement for TcO$_4^-$ removing. About 96.07% of TcO$_4^-$ is found to be removed in the 1:32 reaction. The maximal exchange capacity of NDTB-1 can be calculated in the 1:1 reaction to be 162.2 mg/g and 0.5421 mol/mol. However, to achieve a better exchange completeness, a small excess of NDTB-1 is required.

In addition, the exchange results can also be described by the exchange coefficients $K_d$, which can be defined as:

$$K_d \left( \frac{ml}{g} \right) = \frac{\text{Equilibrium mass of Tc exchanged into NDTB-1}}{\text{Equilibrum mass of Tc in solution}} \times \left( \frac{\text{Volume of solution}}{\text{Mass of NDTB-1}} \right)$$  \hfill (2)

The maximal $K_d$ value is found in the 1:4 reaction to be $1.0534 \times 10^4$ mL/g (Table 3.1), which is significantly higher than any other anion exchange materials known up to date and thus a new record is provided for TcO$_4^-$ removing.$^{10,18}$

3.7 Anion exchange selectivity of NDTB-1

The anion exchange selectivity of NDTB-1 was probed by a series of TcO$_4^-$ exchange reactions with different kinds of secondary competing anions. 12 competing
Figure 3.6: Plots of concentrations of TcO$_4^-$ concentration as a function of time for reactions with six different molar ratios of TcO$_4^-$ to NDTB-1.
TABLE 3.1

RESULTS OF STUDIES ON EXCHANGE CAPACITY AND EXCHANGE EFFICIENCY OF NDTB-1

<table>
<thead>
<tr>
<th>Molar ratio TcO$_4^-$:NDTB-1</th>
<th>Maximal percentage of TcO$_4^-$ removed [%] [a]</th>
<th>Exchange capacity [mol/mol] [b]</th>
<th>Final percentage of TcO$_4^-$ removed [%]</th>
<th>$K_d$ [ml/g] [c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>54.21</td>
<td>0.5421</td>
<td>47.75</td>
<td>3656</td>
</tr>
<tr>
<td>1:2</td>
<td>83.62</td>
<td>0.4181</td>
<td>81.14</td>
<td>8604</td>
</tr>
<tr>
<td>1:4</td>
<td>91.33</td>
<td>0.2283</td>
<td>91.33</td>
<td>10534</td>
</tr>
<tr>
<td>1:8</td>
<td>95.08</td>
<td>0.1188</td>
<td>95.08</td>
<td>9663</td>
</tr>
<tr>
<td>1:16</td>
<td>96.01</td>
<td>0.0600</td>
<td>96.01</td>
<td>6016</td>
</tr>
<tr>
<td>1:32</td>
<td>96.07</td>
<td>0.0300</td>
<td>96.07</td>
<td>3056</td>
</tr>
</tbody>
</table>
anions (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 selected based on several considerations: first of all, none of these anions are able to produce transitions in the wavelength range used for identification of TcO\(_4\)^\(-\) in the UV-vis spectra; second, there should be no redox reaction involving the competing anions and TcO\(_4\)^\(-\); third, these anions provide wide distributions of size, configuration, and charge, therefore, the factors that determine the selectivity of NDTB-1 can be examined. To address the drawback of using large excesses of anion exchange materials, which might hide the real selectivity, a molar ratio of TcO\(_4\)^\(-\) : competing anion : NDTB-1 = 1:1:2 was strictly applied for all exchange reactions. The pH was also monitored for all reactions in the final to examine the effects of carbonate (Table 3.S1).

The exchange selectivity can be derived based on the comparison of the exchange kinetics and the exchange coefficients of TcO\(_4\)^\(-\) with different kinds of competing anions. In particular, the anion with a better ability to slow down the exchange kinetics and decrease the exchange coefficient of TcO\(_4\)^\(-\) has a stronger priority for being exchanged into NDTB-1. The exchange curves of TcO\(_4\)^\(-\) for all reactions are shown in Fig. 3.7 and the exchange results are listed in Table 3.2. It is not surprising that TcO\(_4\)^\(-\) exchange reaction without competing anions has the largest removing percentage and \(K_d\) value. Based on the distribution of final percentages of TcO\(_4\)^\(-\) removed and \(K_d\) values, we can simply divide these 12 competing exchange reactions into four groups.

The first group contains reactions of TcO\(_4\)^\(-\) + Cl\(^-\), TcO\(_4\)^\(-\) + I\(^-\), TcO\(_4\)^\(-\) + ClO\(_4\)^\(-\), and TcO\(_4\)^\(-\) + NO\(_3\)^\(-\). These reactions still have relatively high TcO\(_4\)^\(-\) exchange and \(K_d\) values, although these values are slightly smaller than those for the pure TcO\(_4\)^\(-\).
Figure 3.7: Plots of concentrations of $\text{TcO}_4^-$ concentration as a function of time for 13 different reactions with or without competing anions.
TABLE 3.2

RESULTS OF STUDIES ON EXCHANGE CAPACITY AND EXCHANGE EFFICIENCY OF NDTB-1

<table>
<thead>
<tr>
<th>Anions</th>
<th>Maximal percentage of TcO$_4^-$ removed [%] [a]</th>
<th>Final percentage of TcO$_4^-$ removed [%] [b]</th>
<th>$K_d$ [ml/g] [c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TcO$_4^-$</td>
<td>83.62</td>
<td>81.14</td>
<td>8604</td>
</tr>
<tr>
<td>TcO$_4^-$ + Cl$^-$</td>
<td>81.98</td>
<td>81.06</td>
<td>8560</td>
</tr>
<tr>
<td>TcO$_4^-$ + I$^-$</td>
<td>77.28</td>
<td>76.26</td>
<td>6424</td>
</tr>
<tr>
<td>TcO$_4^-$ + ClO$_4^-$</td>
<td>74.61</td>
<td>74.41</td>
<td>5816</td>
</tr>
<tr>
<td>TcO$_4^-$ + NO$_3^-$</td>
<td>74.37</td>
<td>72.89</td>
<td>5377</td>
</tr>
<tr>
<td>TcO$_4^-$ + HPO$_4^{2-}$</td>
<td>60.01</td>
<td>59.32</td>
<td>2916</td>
</tr>
<tr>
<td>TcO$_4^-$ + SeO$_3^{2-}$</td>
<td>57.97</td>
<td>53.83</td>
<td>2332</td>
</tr>
<tr>
<td>TcO$_4^-$ + ReO$_4^-$</td>
<td>58.87</td>
<td>52.61</td>
<td>2220</td>
</tr>
<tr>
<td>TcO$_4^-$ + IO$_3^-$</td>
<td>54.46</td>
<td>52.02</td>
<td>2168</td>
</tr>
<tr>
<td>TcO$_4^-$ + HAsO$_4^{2-}$</td>
<td>56.64</td>
<td>48.34</td>
<td>1871</td>
</tr>
<tr>
<td>TcO$_4^-$ + SO$_4^{2-}$</td>
<td>52.70</td>
<td>32.66</td>
<td>970</td>
</tr>
<tr>
<td>TcO$_4^-$ + SeO$_4^{2-}$</td>
<td>49.23</td>
<td>23.72</td>
<td>622</td>
</tr>
<tr>
<td>TcO$_4^-$ + PO$_4^{3-}$</td>
<td>23.08</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
The second group consists of HPO$_4^{2-}$, SeO$_3^{2-}$, ReO$_4^{-}$, IO$_3^{-}$, and HAsO$_4^{2-}$ as the competing anion. It has to be noted that although HPO$_4^{2-}$, SeO$_3^{2-}$, and HAsO$_4^{2-}$ was used as starting materials, based on the pH that monitored in the final (Table 3.51), their actual species in solution are dominated by H$_2$PO$_4^{-}$, HSeO$_3^{-}$, and H$_2$AsO$_4^{-}$, respectively. Thus, all these anions share a common character that they are all -1 charged anions and very close to TcO$_4^{-}$ in size (based on M-O bond distances in the anions). A reasonable prediction that TcO$_4^{-}$ and ReO$_4^{-}$ should share almost the same priority for being exchanged into NDTB-1 can be made based on the fact that they are almost identical in both charge and size. This prediction is also supported by comparing $K_d$ values between the competing reaction with molar ratio TcO$_4^{-}$ : ReO$_4^{-}$ : NDTB-1 of 1:1:2 and the reaction with molar ratio of TcO$_4^{-}$ : NDTB-1 of 1:1 (Table 3.1 and 3.2). A deduction of this prediction is that the competing anions showing a better competing ability than ReO$_4^{-}$ would also outcompete with TcO$_4^{-}$ for being exchanged into NDTB-1.

The third group includes competing anions of SO$_4^{2-}$ and SeO$_4^{2-}$, which are both -2 charged anions. It was observed that both anions outcompete with TcO$_4^{-}$ for being exchanged into NDTB-1. In addition, SeO$_4^{2-}$ is significantly larger than SO$_4^{2-}$, and possesses a better competing ability than SO$_4^{2-}$ as observed between Cl$^-$ and I$^-$, as well as H$_2$PO$_4^{-}$ and H$_2$AsO$_4^{-}$. More importantly, TcO$_4^{-}$ exchange into NDTB-1 is reversible, that is, TcO$_4^{-}$ that is initially exchanged into NDTB-1 is further exchanged back into solution using anions like SeO$_4^{2-}$. From here, a conclusion can be derived that the anion exchange selectivity of NDTB-1 is based on both the size and the charge of the anions.
Anions with larger size and charge will possess better priority for being exchanged into NDTB-1.

The last group only contains PO$_4^{3-}$ as the competing anion. Interestingly, this competing reaction shows a completely reversible exchange for TcO$_4^{-}$ after one day. All TcO$_4^{-}$ that initially exchanged into NDTB-1 is further exchanged back into solution, which results in the $K_d$ value being zero. It should be noted that the pH monitored in the final for this reaction is 7.92 (Table 3.S1). With PO$_4^{3-}$ being added initially will result in HPO$_4^{2-}$ as the dominated species at this pH. However, based on the previous conclusion, the fact that HPO$_4^{2-}$ is close to SO$_4^{2-}$ in size is not consistent with the completely reversible exchange. We propose that this completely reversible exchange is the consequence of a combination of two factors. First, excess of HCO$_3^{-}$ should be present at this condition, which could compete with TcO$_4^{-}$ for the exchange. Second, although HPO$_4^{2-}$ is the dominate species in solution, the equilibrium between HPO$_4^{2-}$ and PO$_4^{3-}$ still exists. According to the conclusion, PO$_4^{3-}$ should possess an extensive priority to enter and being trapped in NDTB-1, which would shift the equilibrium in the solution towards PO$_4^{3-}$ without significantly changing the pH because the borate that exchanged out from NDTB-1 is a good buffer in the pH range from 7.4 to 9.2. The later factor could play a major role, since HCO$_3^{-}$ should not be considered as a good competing anion based on the previous conclusion.

As a summary, the priority order for being exchanged into NDTB-1 can be listed as:

\[
\text{Cl}^- < \text{I}^- < \text{ClO}_4^- < \text{NO}_3^- < \text{H}_2\text{PO}_4^- < \text{HSeO}_3^- < \text{TcO}_4^- < \text{ReO}_4^- < \text{IO}_3^- < \text{H}_2\text{AsO}_4^- < \text{SO}_4^{2-} < \text{SeO}_4^{2-} < \text{PO}_4^{3-}
\]
3.8 MAS-NMR studies of anion-exchanged NDTB-1 materials

The phosphate- and tellurate-exchanged NDTB-1 samples showed two, and possibly three, signals in NMR spectra (Fig. 3.8). The $^{31}$P NMR spectra exhibited a strong, narrow signal at 2.3 ppm, and a broader shoulder spanning the 0 to -11 ppm range. The signal at 2.3 ppm becomes narrower at higher spinning rate, possibly owing to increased frictional heating of the rotor, while the weak broad signal at 0 to -11 ppm does not change. The $^{125}$Te NMR spectra display only a strong signal at 1086 ppm, together with a broader group of signals in the 1102-1190 ppm range (The $^{125}$Te standard is crystalline ZnTe, chemical shift at -888 ppm). None of these signals vary with spinning rate. The SeO$_4^{2-}$ and ClO$_4^{-}$-loaded NDTB-1 exhibited only a single sharp peak in the respective $^{77}$Se and $^{35}$Cl NMR spectra. Although, the $^{35}$Cl-MAS-NMR spectra contained a sharp peak near 0 ppm relative to the ClO$_4^{-}$ external standard, a large background signal from the probe might have obscured any additional $^{35}$Cl-NMR peaks. No NMR signal could be confidently resolved for $^{55}$Mn in the MnO$_4^{-}$-exchanged material because of a large $^{55}$Mn background signal.

The $^{99}$Tc MAS-NMR spectra (Fig. 3.9) indicate two distinct signals, with a possible third signal. The two most conspicuous signals have isotropic chemical shifts at near +0 ppm and upfield, in a range from -8 to -40 ppm. The downfield peak is sharp and narrow and diminishes profoundly in intensity with decreasing temperature. The characteristics of this sharp peak are consistent with those of the TcO$_4^{-}$ anion.
Figure 3.8: $^{31}$P- and $^{125}$Te-MAS-NMR spectra of anion-exchanged NDTB-1 material containing phosphate (top) and tellurate (bottom).
Figure 3.9: (top) A variable-temperature series of $^{99}$Tc-MAS-NMR spectra showing two clear sites, one of which becomes less prominent as temperature decreases. (bottom) The assignment of these two signals is a $^{99}$TcO$_4^-$ ion in a channel that can tumble freely at all but the lowest temperatures. The freedom to tumble, and thus the peak intensity near 0 ppm, declines with temperature. The upfield peak exhibits an intensity that does not change appreciably with temperature and is interpreted to correspond to a $^{99}$TcO$_4^-$ site bound more tightly to the framework.
The conspicuous upfield signal is much broader, does not diminish in intensity with temperature (Fig. 3.9), and exhibits spinning sidebands at all temperatures (weak peaks separated from the main peak by ±15 kHz). This broad peak could be fit with a second-order quadrupolar powder pattern for a single site with δ = -39 ppm, C_q ~0.16 MHz, η_q ≡ 0 (from a least-squares of the spectrum at 223 K), by including sufficient line broadening to smooth the fine-structure. The spectra and parameters are consistent with an interpretation that the chemical environment around the $^{99}$Tc nucleus is disturbed by bonding to the cationic framework. Furthermore, the $^{99}$Tc-NMR intensity contained in the conspicuous spinning sidebands indicates assignment to a dynamically rigid species, in contrast to the narrow downfield peak where evidence suggests mobility.

The relative intensity of the two major peaks (-39 and +0.1 ppm) are estimated by integrating signals from the low-temperature data. The smaller peak has about 6% (±1.5%) of the total intensity, so they differ in relative intensities by a ratio of ~ 20:1 at 193 K. The declining intensity of this narrow peak with decreasing temperature is interpreted to indicate that the molecule is dynamically averaging the $^{99}$Tc transitions into a narrow signal at room temperature. As the sample cools, the dynamic averaging diminishes, causing intensity from the satellite transitions to be lost from the single peak and broadened into the baseline.

Fine structure is evident in this peak near -20 ppm from ca 298 K to 323 K (Fig. 3.9) that resembles second-order quadrupolar broadening, however, the fact that the narrow feature appears to broaden as temperature is further reduced suggests instead...
the presence of a small amount of mobile $\text{TcO}_4^-$ in the cages. Some time variation in the intensities of the two most conspicuous peaks is observed, with the intensity of the narrow downfield peak growing with time over six weeks. The slow change in relative intensities of the $^{99}\text{Tc}$ signals indicates that movement between the two sites is much slower than the NMR time scale.

These results are consistent with the idea that both the channels and the cages in the NDTB-1 are taking up $\text{TcO}_4^-$ (aq) to balance the net cationic charge of the framework. The $\text{TcO}_4^-$ in the channels gives rise to the narrow peak near 0 ppm in the spectra. The broader upfield peak is assigned to $\text{TcO}_4^-$ in the cavities and accounts for most of the signal.

3.9 $\text{TcO}_4^-$ removal from a simulated Hanford LAW melter recycle stream

The simulated Hanford LAW melter recycle stream used in this test was comprised of four anions, $\text{NO}_3^-$, $\text{NO}_2^-$, $\text{Cl}^-$, and $\text{CO}_3^{2-}$, in addition to $\text{TcO}_4^-$. Three of the anions, $\text{NO}_3^-$, $\text{NO}_2^-$, and $\text{Cl}^-$, are present in large excess of the $\text{TcO}_4^-$, with mole ratios ranging from 314 ~ 873 (Table 3.3). The predominant cation in the simulant is $\text{Na}^+$ with smaller concentrations of $\text{NH}_4^+$, $\text{K}^+$, and $\text{Ca}^{2+}$. Given the large molar excess of $\text{NO}_3^-$, $\text{NO}_2^-$, and $\text{Cl}^-$, this solution represents a significant challenge to an ion exchange material for the effective removal of $\text{TcO}_4^-$. Despite the high concentration of potentially competing anions, $\text{TcO}_4^-$ removal was observed upon contact of the simulant with NDTB-1 at phase ratios of 200 and 40 mL/g. At a phase ratio of 200 mL/g, 13.0% of the Tc-99 was removed after a 4-hour
batch contact at ambient temperature. At a phase ratio of 40 mL/g, 44.8% of the Tc-99 was removed at the same conditions. From the measured Tc-99 removal, the calculated $K_d$ values are $2.99 \times 10^1$ and $1.62 \times 10^1$ mL/g at the phase ratios of 200 and 40 mL/g, respectively. The low $K_d$ values are not unexpected given the chemical composition of the simulated waste solution. Nevertheless, the test findings indicate that NDTB-1 serves as a highly selective ion exchanger for TcO$_4^-$ from a solution containing between two and three orders of magnitude higher concentrations of NO$_3^-$, NO$_2^-$, and Cl$^-$. 

**TABLE 3.3**

**COMPOSITION OF SIMULATED HANFORD LAW MELTER RECYCLE STREAM**

<table>
<thead>
<tr>
<th>Anion</th>
<th>Concentration (M)</th>
<th>Anion:TcO$_4^-$ Mole Ratio</th>
</tr>
</thead>
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<tr>
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<td>NO$_3^-$</td>
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</tr>
<tr>
<td>Cl$^-$</td>
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<tr>
<td>NO$_2^-$</td>
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<td>873</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
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<td>0.0343</td>
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<tr>
<td>CO$_3^{2-}$</td>
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<td>0.222</td>
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**3.10 Conclusions**

In conclusion, we have discovered a unique material, **NDTB-1**, which shows an extensive potential applications for removing pertechnetate from nuclear waste. This material possesses an ability to remove TcO$_4^-$ from aqueous solutions with both unprecedented selectivity and greatly improved efficiency. Furthermore, **NDTB-1** is
highly stable during the anion exchange processes thus provides a significant reusability for the real applications. More importantly, the completely reversible exchange of TcO$_4^{-}$ that observed in the exchange reaction using PO$_4^{3-}$ as the competing anion provides a good opportunity for isolating TcO$_4^{-}$ from both LAW and HAW. We have proposed a new model based on NDTB-1 as shown in Fig. 3.10 with the hope to help solve the “technetium problem” in nuclear wastes.
Figure 3.10: Presentation of the new model based on NDTB-1 to solve the “technetium problem”.
Figure 3.11: Powder diffraction patterns of **NDTB-1** (calculated, black), **NDTB-1** (experimental, red), and Cl$^-$ exchanged **NDTB-1** material (experimental, blue).
Figure 3.12: Solid state UV-vis-NIR spectra of crystals of **NDTB-1** (black), MnO$_4^-$ exchanged **NDTB-1** (red), CrO$_4^{2-}$ exchanged NDTB-1 (blue), and Cr$_2$O$_7^{2-}$ exchanged **NDTB-1** (green).
Figure 3.13: Plot of 1/concentrations of $\text{TcO}_4^-$ as function of time (black) and its linear fit (red). Parameters for linear fit: $R^2 = 0.99887$, Slope $= 0.05904 \pm 1.25493 \times 10^{-4} \text{ M}^{-1} \text{s}^{-1}$. 

\[ \text{Time (seconds)} \]

\[ \frac{1}{\text{Concentration of } \text{TcO}_4^-} (\text{M}^{-1}) \]
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<th>pH</th>
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<td>TcO$_4^-$ + Cl$^-$</td>
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<td>TcO$_4^-$ + I$^-$</td>
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<td>TcO$_4^-$ + ClO$_4^-$</td>
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3.12 Reference


CHAPTER 4:

POLARITY AND CHIRALITY IN TWO FAMILIES OF URANYL BORATES: INSIGHTS INTO UNDERSTANDING THE VITRIFICATION OF NUCLEAR WASTE AND THE DEVELOPMENT OF NONLINEAR OPTICAL MATERIALS

4.1 Abstract

Four new sodium uranyl borates, α-Na[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_5$] (NaUBO-$1$), β-Na[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_5$] (NaUBO-$2$), Na[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_5$]·3H$_2$O (NaUBO-$3$), and Na[(UO$_2$)$_6$B$_{10}$O$_{15}$(OH)$_5$]·3H$_2$O (NaUBO-$4$), and four new thallium uranyl borates Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{19}$(OH)$_3$] (TIUBO-$1$), α-Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$(OH)$_3$] (TIUBO-$2$), β-Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$(OH)$_3$] (TIUBO-$3$), and Tl[(UO$_2$)$_2$B$_{10}$O$_{16}$(OH)$_3$] (TIUBO-$4$) have been prepared via the reaction of sodium nitrate or thallium nitrate, uranyl nitrate, and excess boric acid at 190 °C. These compounds share a common structural motif consisting of a linear uranyl, UO$_2^{2+}$, cation surrounded by BO$_3$ triangles and BO$_4$ tetrahedra to create an UO$_8$ hexagonal bipyramidal environment around uranium. The borate anions bridge between uranyl units to create sheets. Additional BO$_3$ triangles extend from the polyborate layers, and are directed approximately perpendicular to the sheets. In some compounds, these units can link the layers together to yield three-dimensional networks with large pores to house the Na$^+$ or Tl$^+$ cations and water.
molecules. The structures are all noncentrosymmetric and are either polar or chiral. While the uranyl borate layers are noncentrosymmetric in and of themselves, there is also twisting of the interlayer BO$_3$ groups to reduce the interlayer spacing, producing helical features in some structures. Na[(UO$_2$)$_6$BO$_{10}$]·2H$_2$O and β-Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$](OH)$_3$, which can be obtained as pure phases, display second-harmonic generation of 532 nm light from 1064 nm light.

4.2 Introduction

Borates have attracted the attention of chemists, mineralogists, and materials scientists for decades, and the use of borates for a variety of applications dates back thousands of years. Borate compounds are often remarkably complex owing to the formation of clusters, chains, sheets, and even zeolite-like three-dimensional networks that contain polymerized BO$_3$ triangles and/or BO$_4$ tetrahedra in almost limitless combinations. While the astonishing crystal chemistry of borates is reason enough to investigate them, there are many practical applications for borates, only two of which will be mentioned here.

Many borates are highly transparent throughout the UV-visible-NIR spectrum. Since neither the BO$_3$ triangle nor the BO$_4$ tetrahedron can be placed on centers of inversion (without disorder), some borates adopt noncentrosymmetric structure types. When combined with their remarkable transparency, and the polarizability of the B–O bonds, they lend themselves well to the development of nonlinear optical materials, especially for deep UV applications. Beta-BaB$_2$O$_4$ is the most widely used of these
materials, and its commercial success has spawned the search for new and better noncentrosymmetric borates. These efforts have yielded borate materials with significantly improved properties such as CsLiB$_6$O$_{10}$.

There is also a second use for borates that is relevant to this present discussion, and that is the vitrification of nuclear waste in borosilicate and borophosphate glasses. The primary waste form for actinides in the United States is borosilicate glasses; in Russia, it is borophosphate glasses. While these waste forms are rather primitive, and are undoubtedly not an ideal waste form, they are the ones actually being used as opposed to the more advanced materials such as zircon, garnet, pyrochlore, synroc, and monazite at are the subject of current research and debate. It is known that high actinide loadings and slow cooling can lead to the formation of crystals within the glasses. Based on dissolution studies on high-borate content glasses, the actinides are apparently primarily interacting with the borate portion of the glass. We have undertaken the task of elucidating the synthesis, structures, and physico-chemical properties of actinide borates, and recently reported examples of uranyl, neptunyl, and plutonyl borates derived from boric acid flux reactions. Herein we disclose details on the entire families of sodium and thallium uranyl borates, $\alpha$-Na[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_3$] (NaUBO-1), $\beta$-Na[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_3$] (NaUBO-2), Na[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_3$]$\cdot$3H$_2$O (NaUBO-3), and Na[(UO$_2$)B$_6$O$_{10}$(OH)$_2$]2H$_2$O (NaUBO-4), and Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$(OH)$_3$] (TIUBO-1), $\alpha$-Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$(OH)$_3$] (TIUBO-2), $\beta$-Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$(OH)$_3$] (TIUBO-3), and Tl[(UO$_2$)$_2$B$_{10}$O$_{16}$(OH)$_3$] (TIUBO-4). With one exception, the small family of previously reported uranyl borates were prepared at high temperatures in B$_2$O$_3$ melts. These
high temperatures favor structures with BO$_3$ triangles, and BO$_4$ tetrahedra become less common. In contrast, the single uranyl borate prepared at room temperature via slow evaporation, K$_6$[UO$_2$(B$_{16}$O$_{24}$(OH)$_8$)]·12H$_2$O, is exceedingly complex, being composed of a cyclic cluster of BO$_3$ and BO$_4$ units with a central uranyl core. This present work makes use of the low melting point of boric acid, and its use as a reactive flux, to yield complex materials containing polyborates composed of both BO$_3$ and BO$_4$ units. Only one of the previously reported uranyl borates, Ca(UO$_2$)$_2$B$_2$O$_6$, is noncentrosymmetric (space group C2, polar). The compounds described in this work differ substantially from most uranyl borates in that all of them are noncentrosymmetric. The origin and consequences of the acentricity are detailed within.

4.3 Experimental Section

Syntheses: UO$_2$(NO$_3$)$_2$·6H$_2$O (98%, International Bio-Analytical Industries), H$_3$BO$_3$ (99.99%, Alfa-Aesar), NaNO$_3$ (99.3%, Fisher), and TlNO$_3$ (99.3%, Fisher) were used as received without further purification. Distilled and Millipore filtered water with resistance of 18.2 MΩ·cm was used in all reactions. PTFE-lined autoclaves were used for all reactions. While the UO$_2$(NO$_3$)$_2$·6H$_2$O used in this study contained depleted U, there is really not much difference between depleted uranium and natural abundance uranium, and standard precautions for handling radioactive materials should be followed at all times. There are very old sources of uranyl nitrate that may not be depleted, and enhanced care is warranted for these samples.
Synthesis of α-Na[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_5$] (NaUBO-1), 6-Na[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_5$] (NaUBO-2), Na[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_5$]·3H$_2$O (NaUBO-3), and Na[(UO$_2$)$_2$B$_6$O$_{10}$(OH)]·2H$_2$O

(NaUBO-4): UO$_2$(NO$_3$)$_2$·6H$_2$O, boric acid, sodium nitrate with ten different Na:U:B molar ratios (1:1:6, 1:1:10, 1:1:15, 2:1:8, 2:1:15, 3:1:8, 3:1:15, 4:1:15, 5:1:15, 6:1:15) (1mmol of UO$_2$(NO$_3$)$_2$·6H$_2$O for each reaction) were loaded into ten 23 mL autoclaves. The autoclaves were sealed and heated to 190 °C in a box furnace for 24 h. The autoclaves were then cooled down to room temperature at a rate of 5 °C/h. All the products were washed with boiling water to remove excess boric acid, followed by rinsing with methanol. Crystals in the form of tablets and prisms with light yellow-green coloration were collected for the first four reactions, and only prisms were found in the last six reactions. Single crystal X-ray diffraction and powder X-ray diffraction studies reveal that NaUBO-1 and NaUBO-2 form as the major products of the first four ratios. Whereas NaUBO-3 only occurs in 1:1:15 ratio reaction, and NaUBO-4 exists in all ten reactions, and can be found as a pure phase for the last six reaction ratios.

Synthesis of Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{19}$(OH)] (TIUBO-1), α-Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$(OH)$_3$] (TIUBO-2), β-Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$(OH)$_3$] (TIUBO-3), and Ti[(UO$_2$)$_2$B$_{10}$O$_{16}$(OH)$_3$] (TIUBO-4):

UO$_2$(NO$_3$)$_2$·6H$_2$O, boric acid, thallium nitrate with eight different Tl:U:B molar ratios (1:1:8, 1:1:15, 1:1:22, 2:1:8, 2:1:15, 2:1:22, 3:1:15, 3:1:22) (1 mmol UO$_2$(NO$_3$)$_2$·6H$_2$O for each reaction) were loaded into eight 23 mL autoclaves. The autoclaves were sealed and heated to 190 °C in a box furnace for 3 days. The autoclaves were then cooled down to room temperature at a rate of 5 °C/h. All the products were washed with boiling water to remove excess boric acid, followed by rinsing with methanol. Crystals in
the form of tablets, prisms, and blocks with light yellow coloration were collected for all eight reactions. Single crystal X-ray diffraction and powder X-ray diffraction studies reveal that TIUBO-3 occurs in all eight ratio reactions and is the only phase in the 1:1:22 and 2:1:22 reactions. TIUBO-4 can only be found in the 1:1:8 reactions, however, TIUBO-1 and TIUBO-2 exist in all reactions except the 1:1:22 and 2:1:22 reactions.

Crystallographic Studies: Single crystals of all eight NaUBO and TIUBO phases were mounted on glass fibers and optically aligned on a Bruker APEXII CCD X-ray diffractometer or a Bruker APEXII Quazar X-ray diffractometer using a digital camera. Initial intensity measurements were either performed using a μS X-ray source, a 30 W microfocused sealed tube (MoKα, λ =0.71073 Å) with high-brilliance and high-performance focusing Quazar multilayer optics, or a standard sealed tube with a monocapillary collimator. Standard APEXII software was used for determination of the unit cells and data collection control. The intensities of reflections of a sphere were collected by a combination of four sets of exposures (frames). Each set had a different φ angle for the crystal and each exposure covered a range of 0.5° in . A total of 1464 frames were collected with an exposure time per frame of 10 to 50 s, depending on the crystal. The SAINT software was used for data integration including Lorentz and polarization corrections. Semi-empirical absorption corrections were applied using the program SADABS. Selected data crystallographic information are listed in Tables 4.1 and 4.2.
TABLE 4.1
CRYSTALLOGRAPHIC DATA FOR A-NA[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_5$] (NAUBO-1), B-NA[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_5$] (NAUBO-2), NA[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_5$] • 3H$_2$O (NAUBO-3), AND NA[(UO$_2$)$_6$B$_6$O$_{10}$(OH)] • 2H$_2$O (NAUBO-4)

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$^a R(F) = \Sigma |F_o| - |F| / \Sigma |F_o|$

$^b R(F_0^2) = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma w(F_0^4)]^{1/2}$
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<td>0.0325</td>
</tr>
<tr>
<td>$2\sigma(F_o^2)^a$</td>
<td>0.0621</td>
<td>0.0561</td>
<td>0.0646</td>
<td>0.0755</td>
</tr>
<tr>
<td>$Rw(F_o^2)^b$</td>
<td>0.0621</td>
<td>0.0561</td>
<td>0.0646</td>
<td>0.0755</td>
</tr>
</tbody>
</table>

$^a R(F) = \Sigma |F_o|-|F_c|/\Sigma |F_o|$

$^b R(F_o^2) = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$
**Powder X-ray diffraction:** Powder X-ray diffraction patterns of the products of all ten reactions were collected on a Scintag theta-theta diffractometer equipped with a diffracted-beamed monochromatic set for Cu Kα (λ = 1.5418 Å) radiation at room temperature in the angular range from 10° to 80° (2θ) with a scanning step width of 0.05° and a fixed counting time of 1 s/step. The collected patterns were compared with those calculated from single crystal data using ATOMS (see Supporting Information).

**Thermogravimetric Analysis (TGA):** TGA measurements for the pure phase NaUBO$_4$ were conducted using a NetzschTG209F1 Iris thermal analyzer. A sample of NaUBO$_4$ was loaded into an alumina crucible and heated from 20 °C to 900 °C at a rate of 5 °C/min under flowing nitrogen gas. The thermogram can be found in the Supporting Information.

**Second-harmonic Generation Measurements:** Powder second-harmonic generation (SHG) measurements were performed on a Kurtz-Perry nonlinear optical system.$^{19}$ A Q-switched Nd:YAG laser (Continuum Surelite I-10), operated at 10 Hz, provided the 1064 nm light used for all measurements. The SHG intensity was recorded from a polycrystalline sample of NaUBO$_4$ and TIUBO$_3$. No index of refraction matching fluid was used in these experiments. The SHG light at 532 nm was collected in reflection, selected by a narrow band-pass interference filter (Pomfret) and detected by a photomultiplier tube (RCA 1P28). A near normal incidence beam splitter reflected a small fraction of the laser beam onto a pyroelectric detector (Molelectron J3-05) that was used as a laser pulse energy monitor. A digital storage oscilloscope (Tektronix TDS 640A) signal averaged and recorded both the SHG and incident laser energy signals.
Average laser power was measured separately with a calibrated Scientech volume absorber calorimeter. As an important note for other investigators interested in the nonlinear optical properties of radioactive materials: The practice of grinding and sieving powders so that comparisons can be made with reference materials of similar particle size is unsafe. We ground and sieved a less-radioactive thorium compound inside a glovebox and then surveyed the interior of the glovebox. There was a uniform contamination of 50 dpm on every surface tested. We recommend discontinuation of this practice immediately. It is enough to say that there is or is not SHG activity. The magnitude is not important enough to risk the health of researchers.

4.4 Synthesis Discussion

Molten boric acid is an exceedingly good reactive-flux for the preparation of borate compounds at relatively low-temperatures. We have tried for more than a decade to prepare actinide borates compounds, and have been largely unsuccessful because we employed hydrothermal conditions as the preparative method. Actinide borates are difficult to prepare by traditional methods in general because water competes very successfully for inner-sphere coordination sites with borate for these metals under most conditions. In fact, many borates that occur naturally are found in evaporate deposits in arid regions. This synthetic challenge can be overcome by either removing water entirely from the system in high-temperature solid-state reactions or slow evaporations, or by reducing the dielectric constant of water by heating to create hydrothermal conditions. Mild hydrothermal conditions are not
sufficient for preparing new uranyl borates. Supercritical water works better, but one has to question the sanity of heating radioactive materials to high temperatures and high pressures. Boric acid has proven to be an ideal solution to this problem, and we have more than thirty actinide borates in hand.

The formation of four phases in the NaUBO system is found to be a stoichiometrically driven reaction, which means that the formation of the four compounds is related to the molar ratio of sodium, uranium, and borate in the starting materials. The NaUBO-1, NaUBO-2, and NaUBO-3 phases have a Na:U ratio of 1:2, and are favored in the reactions that have a lower Na:U ratio. When increased amounts of sodium are present in the reaction mixture, NaUBO-4 becomes more favored, and can be made as a pure phase. The reaction yields increase with reaction time. One day reactions are appropriate for screening product composition, but only lead to low isolated yields. The yield maximizes after seven days at 72% for NaUBO-4. TGA analysis suggests that NaUBO-4 loses water near the synthesis temperature, but that there are not further changes until 500 °C.

As found in the sodium system, the formation of four phases in the TiUBO system is found to be a stoichiometrically driven reaction, which means that the formation of the four compounds is related to the molar ratio of thallium, uranium, and borate in the starting materials. The TiUBO-4 phase has a Ti:U ratio of 1:2, can only be made in the reaction that has a low Ti:U ratio (1:1) for the starting materials. When increased amounts of sodium are present in the reaction mixture, TiUBO-1, TiUBO-2, TiUBO-3 which have a high Ti:U ratio (1:1) becomes more favored, and TiUBO-3 can be made as a
pure phase in the high boron concentration reactions (U:B=1:22). The 1:1:22 (Tl:U:B) reaction has a moderate yield for TIUBO-3, of about 42% based on the uranium.

4.5 General Comments of Topology and Polymorphism in Sodium Uranyl Borates System

Fragments of the crystal structures of NaUBO-1, NaUBO-2, NaUBO-3, and NaUBO-4 are depicted in Fig. 4.1 a-d. Within these structures we can separate sheets directed perpendicular to c. All these sheets are based on boron oxo-groups (green tetrahedra and triangles) and sixfold coordinated uranyl groups (yellow hexagonal bipyramids). We will consider only the boron based part of these sheets because the uranyl groups are similar in all of them. There are four (in general) different type of sheets – A, A’, B, and B’ (the structure of these layers is taken from NaUBO-1 and presented in Fig. 4.2 in skeletal mode). All of them are strongly related (based on the same structural fragments) and can be transformed into each other using simple crystallographic operations. In these structures we can separate fragments that will be unique units, and at the same time represented in all the structural features. These fragments are shown in the Fig. 4.3a. In the center of these units are flat triangles BO₃ (on the topological symbols showed as black triangles). These groups connected by a vertex with groups consisting of three BO₄ tetrahedra. These groups are located differently in A and B, and it is shown in the topological description by solid lines. In each of these groups one BO₄ tetrahedra is directed “up” (arrow up on topology diagram) or “down” (arrow down on topology diagram), the other two are directed in to the opposite side. From the Fig. 4.3a we can see that groups A and A’ are mostly similar and defer only in
Figure 4.1: Views of the crystal structures of α-Na[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_5$] (NaUBO-1) (a), β-Na[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_5$] (NaUBO-2) (d), Na[(UO$_2$)$_2$B$_{10}$O$_{15}$(OH)$_5$] · 3H$_2$O (NaUBO-3) (c), and Na[(UO$_2$)$_6$B$_{8}$O$_{10}$(OH)] · 2H$_2$O (NaUBO-4) (b). UO$_8$ hexagonal bipyramids are shown in yellow, BO$_3$ and BO$_4$ units in green, Na$^+$ cations in blue, and water molecules in red.
Figure 4.2: A skeletal representation of the polyborate sheet found in the structure of $\alpha$-Na[($\text{UO}_2$)$_2$B$_{10}$O$_{15}$(OH)$_5$] (NaUBO-1).
Figure 4.3: The characteristic fragments of the oxoborate sheets (a) and views of the crystallographic transformations that relate the different sheets (b) in α-Na[\(\text{UO}_2\text{B}_{10}\text{O}_{35}(\text{OH})_5\)] (\textbf{NaUBO-1}), β-Na[\(\text{UO}_2\text{B}_{10}\text{O}_{35}(\text{OH})_5\)] (\textbf{NaUBO-2}), Na[\(\text{UO}_2\text{B}_{10}\text{O}_{35}(\text{OH})_5\] • 3H\(_2\)O (\textbf{NaUBO-3}), and Na[\(\text{UO}_2\text{B}_6\text{O}_{10}(\text{OH})\)] • 2H\(_2\)O (\textbf{NaUBO-4}).
direction of BO$_4$ tetrahedra. These two modifications are related by the mirror plane parallel to the sheets (see Fig. 4.3b). A and B layers types are enantiomorphic and can be transformed by the plane mirror plane that is perpendicular to the sheets (Fig. 4.3b). The relationship between B and B' is similar to the relationship between A and A'. Finally, A (or B) can be transformed to B' (or to A') by the simple 2-fold axis that are parallel to the plane of the sheets. All these transformations schematically presented in Fig. 4.3b.

From the Fig. 4.3a we can see that groups A and A' are mostly similar, and defer only in direction of BO$_4$ tetrahedra. These two modifications are related by the mirror plane parallel to the sheets (see Fig. 4.3b). A and B layers types are enantiomorphic and can be transformed by the plane mirror plane that is perpendicular to the sheets (Fig. 4.3b). The relationship between B and B' is similar to the relationship between A and A'. Finally, A (or B) can be transformed to B' (or to A') by the simple 2-fold axis that are parallel to the plane of the sheets.

If we look again at Fig. 4.1, we can find that phases NaUBO-1 and NaUBO-4 are crystallized in polar space groups that are based on both enantiomorphic sheets – A and B. Compounds NaUBO-2 and NaUBO-3 are crystallized in polar and chiral space groups, and consist only of A or B layers (and B'), and each third layers is formed by previous rotation of 120 degrees (see Fig. 4.1 c and d). The structural difference in polymorphic modifications (NaUBO-1 and NaUBO-2) has the same nature. The α-Na[[UO$_2$]$_2$B$_{10}$O$_{15}$(OH)$_5$] (NaUBO-1) phase is based on A,A'-B,B'-A,A'-... packing, and the β-Na[[UO$_2$]$_2$B$_{10}$O$_{15}$(OH)$_5$] (NaUBO-2) phase on B,B'-B,B'-B,B'-... packing.
Finally, in all four compounds there are BO$_3$ triangles that are directed between the layers. In all of the uranyl borates that we have prepared, we have not observed BO$_4$ units between the layers. In NaUBO-4, the BO$_3$ units are linked together to yield a rather open structure. This structure is depicted in Fig. 4.1b, and if one follows the polymerized BO$_3$ units, both bending and twisting can be seen. This helical feature reduces the interlayer space, and provides a less open, and presumably more stable structure than would be achieved in the BO$_3$ units were co-planar. Again, this feature is consistent with the noncentrosymmetric nature of these compounds. Given that NaUBO-4 can be prepared as a pure phase, we were able to provide external verification of the acentricity by second-order harmonic generation of 532 nm light from 1064 nm laser irradiation.

4.6 Topological Description of Thallium Uranyl Borates

Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{19}$](OH)] (TIUBO-1), α-Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$(OH)$_3$] (TIUBO-2), β-Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$(OH)$_3$] (TIUBO-3), and Tl[(UO$_2$)$_2$B$_{10}$O$_{16}$(OH)$_3$] (TIUBO-4). Within the structures of these compounds we can separate sheets fragments based on 2D polyborate nets and uranyl cations. One of the most interesting structural aspects of these phases is the topology of the polyborates nets within these sheets. There are five main types of topologies (A, B, C, D and E) and four additional sub-types (A′, B′, C′, D′). As shown in Fig. 4.4, the E topology is unique, and realized only in structure of TIUBO-1, we will describe this topology later.
The topologies A, B, C, and D (or the related forms A’, B’, C’, D’) are realized in 
**TIUBO-1**, **TIUBO-2**, and **TIUBO-3**. Fragments of sheets possess the new topologies 
showed on **Fig. 4.5** (topologies C-C’ and D-D’). In this figure we can see that the C and D 
topologies are a bit different from the A and B layers. These sheets are based on the 
fragments (**Fig. 4.2**) consisting of one BO₄ tetrahedron (in the center) and three super-
triangle groups connected with central tetrahedron by vertices in one plane. Each of 
the previously mentioned super-triangles consists of one BO₃ flat triangle and two BO₄ 
tetrahedra. The terminal oxygen atoms in these tetrahedra are oppositely directed (one 
“up” and one “down”). The symmetrical relationships in the groups of new sheets (for 
example C-C’ or D-C’ transformations) are same as those observed in sodium uranyl 
birates. All types of layers, realized in crystal structures of **TIUBO-2**, **TIUBO-3**, **TIUBO-4** 
are polar. Thus, all resulted structures based on alteration of different polar layer (**Fig. 4.1b-c**) are polar too (space group Cc). In general the C and D types of sheets are similar 
with oxo-borate sheets recently observed in PuO₂[B₆O₁₁(OH)₄]. The main point of 
difference between them is the direction of the terminal oxygen atom in the “central” 
tetrahedron – in Tl-uranyl borates all of these atoms are on one side (all “up” or all 
“down), but in the plutonyl borate, they alternate, and the resulting sheet is not polar. 

As we mentioned above, the topology type E is realized only in the structure of 
**TIUBO-1**. This topology is more complicate than all others that we have observed 
before in the chemistry of actinides borates. In **Fig. 4.6a,b**, we show the fragments of 
the poly-borate sheets we observed in the structures of neptunyl borates and plutonyl 
borate, respectively. We can separate in both net-types two different fragments.
Figure 4.4: Views of the crystal structures of $\alpha$-Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$(OH)$_3$] (TIUBO-1) (a), $\beta$-Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$(OH)$_3$] (TIUBO-2) (b), Tl[(UO$_2$)$_2$B$_{10}$O$_{16}$(OH)$_3$] (TIUBO-3) (c) and Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{19}$(OH)] (TIUBO-4) (e). UO$_8$ hexagonal bipyramids are shown in yellow, BO$_3$ and BO$_4$ units in green, Tl$^+$ cations in blue.
Figure 4.5: The characteristic fragments of the oxoborate sheets in (TIUBO-1), β-Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$(OH)$_3$] (TIUBO-2), Tl[(UO$_2$)$_2$B$_{10}$O$_{16}$(OH)$_3$] (TIUBO-3) and Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{19}$(OH)] (TIUBO-4).
Figure 4.6: The principal scheme of the formation of the oxoborate sheets in $\alpha$-Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$(OH)$_3$] (TIUBO-1): a) Sheet fragment in Ba/K neptunyl borates; b) Sheet fragment in plutonyl borate; c) Characteristic fragment of oxoborate sheet in $\alpha$-Tl$_2$[(UO$_2$)$_2$B$_{11}$O$_{18}$(OH)$_3$] (TIUBO-1).
These fragments are shown with red dashed lines in Fig. 4.6a,b (1 for the Np structures and 2 for the Pu structure). If we take these separated fragments and connect them to other with regular alternation in 2D space, then as a result of this operation we obtain complex topology E, realized in 1. Thus, in this structure two motives (Np and Pu) are observed simultaneously.

In comparison with Na-based uranyl borates the Tl-phases are more complicated and diverse. In the structures of the Na-containing uranyl borates, only one type of polyborate sheet with one principal topology variant (four with symmetrical transformations), was found. In the Tl-system, we observed three principal topology variants (nine with symmetrical transformation), and two of them are new.

4.7 Polymorphism and 2D – {2D-3D} – 3D Structural Evolution in Tl-uranyl borates

Phases TIUBO-1 and TIUBO-2 in the Tl-uranyl borate system are stoichiometrically identical, but crystallized in different space groups, and possess different structural motifs. The BO₃ and BO₄ units arranged within the oxo-borates sheets in TIUBO-1 and TIUBO-2 are quite different as described above. In the structure of TIUBO-1 only one type of such sheets is realized, but in the structure of TIUBO-2, we observe two main topologies and two derivatives of them. The most obvious change is the coupling of sheets in the structure of TIUBO-2. As the result of this coupling, the structure of TIUBO-2 changes from a pure 2D form to an intermediate {2D-3D} state. As a of this result, the diversity in these polymorphic modifications is larger in comparison with α-Na[(UO₂)₂B₁₀O₁₅(OH)$_5$] and β-Na[(UO₂)₂B₁₀O₁₅(OH)$_5$] polymorphs.
In the final point of the structure descriptions it is necessary to pay attention to structural modification along the line 2D (TIUBO-1) – {2D-3D} (TIUBO-2 and TIUBO-3) – 3D (TIUBO-4). The Tl-uranyl borate family is an example of systems with similar chemical composition and gradually increasing dimensionality. Between the phase TIUBO-1 (sheets based structure) to TIUBO-4 (classical 3D material), we have two intermediate states in the form of double layers in TIUBO-2 and TIUBO-3 (Fig. 4.4). The coupling of the sheets in TIUBO-2 goes via single BO$_3$ triangles (Fig. 4.4b), and in the structure of TIUBO-3 the sheets are connected by B$_3$O$_5$ dimers (Fig. 4.4c). We should mention that doubled layers (consisting of two linked sheets) are rare in actinide chemistry, and previously were observed only few times, but our research in the actinide borate system substantially expands this group. This is interesting in that in structure of TIUBO-4 we can separate fragments of doubled layers identical for both TIUBO-2 and TIUBO-3. The oxo-borate sheets in TIUBO-1 are connected by BO$_3$ triangles and B$_3$O$_5$ dimers in consecutive order, and as a result form a regular 3D framework (Fig. 4.1b).

4.8 Details on Coordination and Bonding Metrics in Uranyl Borates

In the previous discussion we have focused on the general crystallographic and topological relationships in the family of sodium uranyl borates. Here we provide some specific details bonding and coordination that aid in properly describing these compounds. First, the local coordination environment around the uranyl units is shown in Fig. 4.7. Here we use color to differentiate between the BO$_3$ triangles and the BO$_4$
Figure 4.7: Views of the local coordination environment around the uranium atoms in NaUBO-1, NaUBO-2, NaUBO-3, and NaUBO-4 (a), TlUBO-1 (b), and TlUBO-2, TlUBO-3, TlUBO-4 (a and c) leading to the formation of sheets. UO$_8$ hexagonal bipyramids are shown in yellow, BO$_3$ triangles in red, and BO$_4$ tetrahedra in green.
tetrahedra. The UO$_8$ hexagonal bipyramid is not a common building unit for uranyl compounds in general.$^{22}$ Uranyl compounds are dominated by UO$_7$ pentagonal bipyramids.$^{22}$ However, when small anions that are capable of chelating uranyl are employed, hexagonal bipyramids become much more common. This is known with nitrate and carbonate, for example.$^{23}$ Here we show that this general principle holds true with borate. There are nine borate units surrounding each uranyl cation as shown in Fig. 4.7. Six of these units are BO$_4$ tetrahedra and three of them are BO$_3$ triangles. Each of the BO$_3$ units is separated by two BO$_4$ units from each other.

Given the plethora of bond distances available on uranyl compounds, it would be a misuse of space to provide more details on the bond distances than are already available in the CIF’s. However, there are some noteworthy differences between these compounds and most other uranyl compounds. First, the uranyl oxo distances are very short and average 1.79(3) Å in uranyl compounds in general.$^{24}$ Some choose to express these bonds are double, some as triple, we will just leave it with them being short and strong. Normally they are also exactly equal because of imposed symmetry, or close to be equal even when the uranium atom is on a general position. However, in these compounds, the bonds are slightly asymmetric as a consequence of the noncentrosymmetric space groups. For example, in one of the uranyl cations in NaUBO-$\textbf{1}$, these distances are 1.75(1) and 1.79(1) Å. Second, the uranyl units are also slightly bent. Again, symmetry often dictates an O–U–O bond angle of exactly 180°. Here there are see slight deviations of linearity by a few degrees, which is not uncommon, but is a
requirement of the noncentrosymmetric space groups. The bond distances within the equatorial planes surrounding the uranyl units are also irregular, and in NaUBO-1, for example, range from 2.389(8) to 2.591(8) Å.

B–O bond distances show substantial variations, but are generally notably shorter in the BO$_3$ triangles than in BO$_4$ tetrahedra. Protonation of the oxygen atoms leads to noticeable bond lengthening, and B-OH bonds can be identified by both bond length considerations and bond-valence sum calculations.$^{25}$

4.9 Conclusions

We have, at least, uncovered a general, synthetic route to actinide borates. The boric acid flux method is a facile and safe way of preparing a large number of actinide borates, two families of which are reported here. The vast majority of these compounds are noncentrosymmetric. In our introduction we focused on two interesting applications of borate compounds, as NLO materials, and as materials for storing nuclear waste. We have demonstrated in this report that both are real possibilities. However, even though kilograms of uranium only represent radiation levels on a $\mu$Ci scale, scientists and the public in general have been raised in an environment where the mere mention of “uranium” inspires some degree of both fascination, and more importantly, fear. The idea of growing large crystals of uranium compounds, and cutting and polishing them into optics for lasers is unrealistic, and to suggest it as justification for work on actinide borates is disingenuous. There is, however, a caveat to this. These compounds might very well inspire researchers to investigate non-radioactive analogs of
uranyl compounds that will lead to real NLO applications. For example, we noted in our studies of actinide iodates that most were centrosymmetric despite the presence of an anion with a stereochemically-active lone pair of electrons.\textsuperscript{26-31} We were able to break the center of symmetry by replacing trans-$\text{UO}_2^{2+}$ with cis-$\text{MoO}_2^{2+}$, and thereby prepared a family of polar transition metal iodates whose NLO response was on par with some commercial materials.\textsuperscript{32}

The more important aspect of this work is perhaps the ability to glimpse into the large glass logs being prepared at Savannah River National Laboratory or the Hanford site for storing nuclear waste. A portion of these glasses has crystallized, but we do not know what these crystals are. This study provides models of how uranyl cations interact with polyborates in the presence of one the most common alkali metal cations found in nuclear waste ($\text{Na}^+$), and these materials are certainly relevant to the vitrification of nuclear waste. We also demonstrated that the pseudo-alkali metal $\text{Tl}^+$ is capable of directing the formation of uranyl borate topologies not found with $\text{Na}^+$. Finally, we have shown that this family of compounds is intrinsically interesting owing to the fascinating structures that these compounds adopt that differ in a number of ways from more mundane uranyl compounds. This is reason enough for engaging in this investigation.

4.10 Reference


CHAPTER 5:

HOW ARE CENTROSYMMETRIC AND NONCENTROSYMMETRIC STRUCTURES ACHIEVED IN URANYL BORATES?

5.1 Abstract

Four uranyl borates, \( \text{UO}_2\text{B}_2\text{O}_4 \) (UBO-1), \( \alpha-(\text{UO}_2)_2[\text{B}_9\text{O}_{14} (\text{OH})_4] \) (UBO-2), \( \beta-(\text{UO}_2)_2[\text{B}_9\text{O}_{14} (\text{OH})_4] \) (UBO-3), and \( \beta-(\text{UO}_2)_2[\text{B}_{13}\text{O}_{20} (\text{OH})_3]\cdot1.25\text{H}_2\text{O} \) (UBO-4), have been prepared from boric acid fluxes at 190 °C. UBO-3 and UBO-4 are centrosymmetric; whereas UBO-1 and UBO-2 are noncentrosymmetric (chiral and polar). These uranyl borates possess layered structures constructed from \( \text{UO}_8 \) hexagonal bipyramids, \( \text{BO}_3 \) triangles, and \( \text{BO}_4 \) tetrahedra. In the case of UBO-4, clusters of \( \text{BO}_3 \) triangles link the layers together to form open slabs with a thickness of almost 2 nm. The ability of uranyl borates to use very similar layers to yield both centrosymmetric and noncentrosymmetric layers is detailed in this work.

5.2 Introduction

Uranyl borates represent a fascinating group of zero-, two-, and three-dimensional materials. A variety of synthetic methods have been employed to prepare these compounds, and the conditions under which these solids form leads to their subdivision into three categories. The first group is a series of chiefly centrosymmetric borates that
are primarily constructed from $\text{UO}_6$ tetragonal bipyramids and/or $\text{UO}_7$ pentagonal bipyramids and $\text{BO}_3$ triangles.\textsuperscript{1-6} These compounds are derived from high-temperature $\text{B}_2\text{O}_3$ melts. The second category has a only a single representative, $\text{K}_6[\text{UO}_2\{\text{B}_{16}\text{O}_{24}(\text{OH})_8\}]\cdot 12\text{H}_2\text{O}$, and this compound consists of isolated clusters composed of a cyclic polyborate surrounding an uranyl core.\textsuperscript{7} It forms via the slow evaporation of aqueous solutions contain $\text{UO}_2^{2+}$ and borate at room temperature. The third group is prepared via the use of boric acid fluxes at relatively low temperatures (ca. 200 °C). These compounds blend features found in both previous categories in that they contain polyborate layers and frameworks that are built from both triangular $\text{BO}_3$ and tetrahedral $\text{BO}_4$ units that surround uranyl cations.\textsuperscript{8,9} All of these compounds contain $\text{UO}_8$ hexagonal bipyramids.

As a general class of compounds, borates are known from their applications in optics, especially for their large nonlinear optical responses in the deep UV, where they are much more transparent than most oxoanion compounds.\textsuperscript{10-12} In order for a compound to display a second-order nonlinear optical (NLO) response, it must lack a center of symmetry. While borates are known for achieving this, a survey of the space groups of borates reveals that noncentrosymmetric structures are not common, making the preparation of new borate NLO materials challenging.\textsuperscript{13,14} We have recently demonstrated that both sodium and thallium uranyl borates are either chiral or polar. Eight such compounds have been reported by us.\textsuperscript{8,9} These results are surprising because the presence of the uranyl cation has a propensity for yielding centrosymmetric structures because of the highly symmetric nature of $\text{UO}_2^{2+}$. Nevertheless, all of the
uranyl borates that we have prepared that contain additional monovalent cations are noncentrosymmetric. However, we know that centrosymmetric structures are possible in actinyl borates from the structures of the neptunyl and plutonyl borates, $K_4(NpO_2)_{6.73}B_{20}O_{36}(OH)_2$, $Ba_2(NpO_2)_{6.59}B_{20}O_{36}(OH)_2\cdot H_2O$, and $PuO_2[B_8O_{11}(OH)_4]$.

We have recently prepared pure uranyl borates from boric acid fluxes that lack additional cations. Two of these compounds are centrosymmetric; two are noncentrosymmetric. These compounds are $UO_2B_2O_4$ ($UBO-1$), $\alpha-\{UO_2\}_2[B_9O_{14}(OH)_4]$ ($UBO-2$), $\beta-\{UO_2\}_2[B_9O_{14}(OH)_4]$ ($UBO-3$), and $(UO_2)_2[B_{13}O_{20}(OH)_3]\cdot 1.25H_2O$ ($UBO-4$).

These uranyl borates are all new, and possess fascinating structures, and more importantly provide us with an opportunity to explore how uranyl borates can use similar structural motifs to yield both centrosymmetric and noncentrosymmetric structures, which is the purpose of this article.

5.3 Experimental Section

*Syntheses:* $UO_2(NO_3)_2\cdot 6H_2O$ (98%, International Bio-Analytical Industries), boric acid (99.99%, Alfa-Aesar), ammonium chloride (99.6%, Fisher), and cesium nitrate (99.8%, Alfa-Aesar) were used as received. All the reactions were run in PTFE-lined Parr 4749 autoclaves with a 23 mL internal volume. Distilled and Millipore filtered water with resistance of 18.2 MΩ·cm was used in all reactions. While the $UO_2(NO_3)_2\cdot 6H_2O$ used in this study contained depleted U, there is really not much difference between depleted uranium and natural abundance uranium, and standard precautions for handling radioactive materials should be followed at all times. There are very old sources of
uranyl nitrate that may not be depleted, and enhanced care is warranted for these samples.

\[ UO_2B_2O_4 (UBO-1): \] \[ UO_2(NO_3)_2 \cdot 6H_2O \ (0.5000 \text{ g}, 1 \text{ mmol}), \text{ boric acid, (0.4944 g, 8 mmol)}, \text{ and water (50 } \mu \text{L) were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 190 °C in a box furnace for 3 days. The autoclave was then cooled down to room temperature at a rate of 5 °C/h. The products were washed with boiling water to remove excess boric acid, followed by rinsing with methanol. Crystals in the form of needles and prisms with light yellow coloration were collected as a pure phase for } UO_2B_2O_4 (UBO-1). \text{ Yield: 123 mg (35% based on uranium)}

\[ \alpha-(UO_2)_2[B_9O_{14}(OH)_4] \text{ and } \beta-(UO_2)_2[B_9O_{14}(OH)_4] (UBO-2 \text{ and UBO-3}: \]

\[ UO_2(NO_3)_2 \cdot 6H_2O \ (0.5000 \text{ g}, 1 \text{ mmol}), \text{ boric acid, (1.3586 g, 22 mmol), ammonium chloride (0.0535 g, 1 mmol), water (50 } \mu \text{L) were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 190 °C in a box furnace for 3 days. The autoclave was then cooled down to room temperature at a rate of 5 °C/h. The products were washed with boiling water to remove excess boric acid, followed by rinsing with methanol. Crystals in the form of plates and blocks with light yellow-green coloration were collected for } \alpha-(UO_2)_2[B_9O_{14}(OH)_4] \text{ and } \beta-(UO_2)_2[B_9O_{14}(OH)_4] \text{ (UBO-2 and UBO-3).}

\text{UBO-1 is also present as a minor product.}

\[ (UO_2)_2[B_{13}O_{20}(OH)_3] \cdot 1.25H_2O (UBO-4): \] \[ UO_2(NO_3)_2 \cdot 6H_2O \ (0.5000 \text{ g}, 1 \text{ mmol}), \text{ boric acid, (0.4944 g, 8 mmol)}, \text{ cesium nitrate (0.3898 g, 2 mmol), and water (90 } \mu \text{L) were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 190 °C in a box furnace for 3 days. The autoclave was then cooled down to room temperature at a rate of 5 °C/h. The products were washed with boiling water to remove excess boric acid, followed by rinsing with methanol. Crystals in the form of plates and blocks with light yellow-green coloration were collected for } (UO_2)_2[B_{13}O_{20}(OH)_3] \cdot 1.25H_2O \text{ (UBO-4).}

\text{Yield: 112 mg (35% based on uranium).}
of 5 °C/h. The products were washed with boiling water to remove excess boric acid, followed by rinsing with methanol. Crystals in the form of needles with light yellow coloration were collected as a pure phase for \((\text{UO}_2)_2[\text{B}_{13}\text{O}_{20}(\text{OH})_3]\cdot 1.25\text{H}_2\text{O} \text{ (UBO-4)}\). Yield: 144 mg (27% based on uranium).

**Crystallographic Studies:** Single crystals of all four UBO phases were mounted on glass fibers and optically aligned on a Bruker APEXII CCD X-ray diffractometer or a Bruker APEXII Quazar X-ray diffractometer using a digital camera. Initial intensity measurements were either performed using a \(\mu\)S X-ray source, a 30 W microfocused sealed tube (MoK\(\alpha\), \(\lambda = 0.71073 \text{ Å}\)) with high-brilliance and high-performance focusing Quazar multilayer optics, or a standard sealed tube with a monocapillary collimator. Standard APEXII software was used for determination of the unit cells and data collection control. The intensities of reflections of a sphere were collected by a combination of four sets of exposures (frames). Each set had a different \(\varphi\) angle for the crystal and each exposure covered a range of 0.5° in \(\omega\). A total of 1464 frames were collected with an exposure time per frame of 10 to 50 s, depending on the crystal. The SAINT software was used for data integration including Lorentz and polarization corrections. Semi-empirical absorption corrections were applied using the program SADABS.\(^{15} \) Selected data crystallographic information are listed in Table 5.1. Atomic coordinates, bond distances, and additional structural information are provided in the Supplementary Material (CIF’s).

**Powder X-ray diffraction:** Powder X-ray diffraction patterns of products of pure UBO-1 and relatively pure UBO-4 were collected on a Scintag theta-theta diffractometer.
TABLE 5.1

CRYSTALLOGRAPHIC DATA FOR UO$_2$B$_2$O$_4$ (UBO-1), A-(UO$_2$)$_2$[B$_9$O$_{14}$(OH)$_4$] (UBO-2), B-(UO$_2$)$_2$[B$_9$O$_{14}$(OH)$_4$] (UBO-3), AND (UO$_2$)$_2$[B$_{13}$O$_{20}$(OH)$_3$]·1.25H$_2$O (UBO-4)

<table>
<thead>
<tr>
<th>Compound</th>
<th>UBO-1</th>
<th>UBO-2</th>
<th>UBO-3</th>
<th>UBO-4</th>
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<tr>
<td>Mass</td>
<td>355.65</td>
<td>925.35</td>
<td>925.35</td>
<td>1068.59</td>
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<td>Yellow-green, plate</td>
<td>Yellow-green, block</td>
<td>Yellow, needle</td>
</tr>
<tr>
<td>Space group</td>
<td>C2</td>
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<td>$P\bar{1}$</td>
<td>$P\bar{1}$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
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<td>6.4169(5)</td>
<td>6.4732(5)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
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<td>21.2535(12)</td>
<td>6.4494(5)</td>
<td>10.7981(8)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
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<td>6.4548(4)</td>
<td>11.0177(12)</td>
<td>19.6653(15)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
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<td>90</td>
<td>90.604(1)</td>
<td>85.711(1)</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>109.769(1)</td>
<td>119.874(1)</td>
<td>92.365(1)</td>
<td>82.660(1)</td>
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<tr>
<td>$\gamma$ (°)</td>
<td>90</td>
<td>90</td>
<td>119.475(1)</td>
<td>89.287(1)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>231.81(4)</td>
<td>767.68(8)</td>
<td>390.46(6)</td>
<td>1359.48(18)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>293(2)</td>
<td>100(2)</td>
<td>296(2)</td>
<td>293(2)</td>
</tr>
<tr>
<td>$\lambda$ (Å)</td>
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<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>$\rho$ calcld (g cm$^{-3}$)</td>
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<td>4.003</td>
<td>3.935</td>
<td>2.610</td>
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<td>$\mu$ (Mo Kα)</td>
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<td>212.00</td>
<td>208.41</td>
<td>120.05</td>
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<td>0.0139</td>
<td>0.0316</td>
<td>0.0200</td>
<td>0.0558</td>
</tr>
</tbody>
</table>

$^aR(F) = \Sigma |F_o| - |F_c| / \Sigma |F_o|$

$^bR(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)]^{1/2}$

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equipped with a diffracted-beamed monochromatic set for Cu Kα (λ = 1.54056 Å) radiation at room temperature in the angular range from 5° to 80° (2θ) with a scanning step width of 0.05° and a fixed counting time of 1 s/step. The collected patterns were compared with those calculated from single crystal data using ATOMS (see Supporting Information).

_Infrared spectroscopy:_ Infrared spectra were obtained from a single crystal of **UBO-4** using a SensIR technology IlluminatIR FT-IR microspectrometer. A single crystal of **UBO-4** was placed on a glass slide, and the spectrum was collected with a diamond ATR objective. Each spectrum was taken from 650 to 4000 cm\(^{-1}\) with a beam aperture of 100 mm. Infrared spectra are shown in the Supporting Information.

_Fluorescence Spectroscopy:_ Fluorescence data were acquired on all four compounds from single crystals using a Craic Technologies UV-vis-NIR microspectrophotometer with a fluorescence attachment. Excitation was achieved using 365 nm light from a mercury lamp. The fluorescence spectra are provided in the Supporting Information.

5.4 Synthesis Discussion

Boric acid becomes a reactive flux when the reaction temperature is raised above its melting point (170.9 °C). It is an ideal flux for prepared novel actinide borates.\(^8\,^9\,^{16}\) **UO\(_2\)B\(_2\)O\(_4\)** (**UBO-1**) is observed in reactions that contain high U:B ratios when alkali metal or alkaline-earth metal cations are also present. It can be made as a pure phase when the U:B ratio is higher than 1:8 when additional cations are not present. α-
(UO₂)₂[B₉O₁₄(OH)₄] (UBO-2) and β-(UO₂)₂[B₉O₁₄(OH)₄] (UBO-3) form simultaneously in the presence of ammonium chloride. We were surprised to find that NH₄⁺ does not directly incorporate into uranyl borates in the same way that alkali metal cations and Tl⁺ do. Although its presence plays a definitely role in crystallization. Similarly, (UO₂)₂[B₁₃O₂₉(OH)₃]·1.25H₂O (UBO-4) can only be isolated in the presence of trace amounts of Cs⁺. In contrast, cesium uranyl borates can be prepared, but these are the subject of a subsequent work. The yields reported in this work are with three day reaction times. We know that yields can be improved with substantially longer heating times (> 7 days).

5.5 Structure Descriptions

The structures of all synthesized phases are based on single (UBO-1) or double layers (UBO-2, UBO-3, and UBO-4). The simplest sheets are realized in crystal structure of UBO-1 (Fig. 5.1). They are based on BO₃ triangles linked by vertices into (BO₂)₁ₓ 1D zigzag-like chains (Fig. 5.1a). These chains are united into 2D layers by edge-sharing with UO₈ hexagonal bipyramids that also form a 1D chain with a (UO₆)₁ₓ composition. The resulting layers pack into a regular 3D structure (Fig. 5.1a) with weak connectivity (mostly via Van der Waals forces). UBO-1 is a second modification of a previously known uranyl borate with the UO₂B₂O₄ composition. However, this phase was synthesized using a high-temperature solid-state reaction at 1150° C. The temperature of preparation and symmetry are higher for the modification obtained by Gasperin, and we are referring to this modification as β-UO₂B₂O₄ in this work. Both modifications are
Figure 5.1: a) A view of the UBO-1 crystal structure. b) The structure of the uranyl borates sheets in UBO-1. c) The relative positions of the layers in α-UBO-1. d) The relative positions of the layers in β-UBO-1.
based on identical 2D-sheets (Fig. 5.1a), but the orientation of them is different in reviewing the modifications. In Fig. 5.1c it is demonstrated that the (BO₂)₁₆⁻ chains are arranged in identical positions in sequential layers in α-UO₂B₂O₄. However, as shown in Fig. 5.1d, the (BO₂)₁₆⁻ chains in β-UO₂B₂O₄ are arranged differently as the sheets are stacked. The layered structure of β-UO₂B₂O₄ is identical but oriented differently – the neighboring sheets are rotated by 180° each to other. This rotation is produced by doubling the c parameter in β-modification. This type of polymorphism can be referred to as rotational polytypism as described early on for micas.¹⁷

The UBO-2 and UBO-3 compounds have identical chemical compositions but crystallize in different space groups. We named UBO-2 as α-(UO₂)₂[B₉O₁₄(OH)₄] and UBO-3 as the β-modification. Both phases have layered structures, but are very different from UBO-1 in that they possess double layers that are based on two sublayers (Fig. 5.2a and b). These sublayers consist of 2D polyborate sheets that incorporate the nearly linear uranyl groups, UO₂²⁺, creating UO₆ hexagonal bipyramids. The borate sheets are based on BO₄ tetrahedra packed in a triangular manner (shown in green color in Fig. 5.2c) and BO₃ triangles (shown in red in Fig. 5.2c), which combine these triangular groups into a 2D network. These 2D sheets are united by perpendicular BO₃ groups into double layers. The resulting layers are packed with a slight shift into a 3D structure. The layers are connected by strong hydrogen bonds with a bond length of 2.42 Å between the O(15) and O(22) oxygen atoms.

The polymorphism in UBO-2 and UBO-3 is of a different nature than the polymorphism in UO₂B₂O₄. In general we can follow this in the same way that we used
Figure 5.2: a) A view of the UBO-1 crystal structure. b) The structure of the uranyl borates sheets in UBO-1. c) The relative positions of the layers in $\alpha$-UBO-1. d) The relative positions of the layers in $\beta$-UBO-1.
to describe the Na-uranyl borates and Tl-uranyl borates. In this work we illustrated several different types of borate sheets. In the structures of UBO-2 and UBO-3 three of these sheets – A, A′, and B (Fig. 5.2c) occur. In the α phase there are alternating enantiomorphic A′ and B layers, and the resulting structure is chiral and polar. In the β phase only similar A and A′ layers are found, and they create a symmetry center in UBO-3.

It is unusual that in all of the uranyl borates systems (U-B, Na-U-B, and Tl-U-B) that we have prepared, polymorphism is observed. These include: α,β-UO₂B₂O₄, α,β-(UO₂)₂[B₉O₁₄(OH)₄] (this work), α,β-Na[(UO₂)₂B₁₀O₁₅(OH)₅], and α,β-Tl₂[(UO₂)₂B₁₁O₁₈(OH)₃]. Such polymorphic richness is very surprising for uranyl chemistry, and makes the uranyl borate system unique within groups of binary and ternary uranyl compounds.

The layers in UBO-4 are also doubled as found in structures of UBO-2 and UBO-3 (Fig. 5.3a), but there are substantial differences as well because the layers in UBO-4 have a nano-scale thickness at ~19 Å. The thick slabs are the result of very unusual linkers and additional triangular BO₃ groups on both sides (top and bottom) of the layers as shown in Fig. 5.3a. The linkers in doubled layers consist of one BO₃ group connected with two BO₄ tetrahedra within the sublayers, and a supertriangle that is the second part of the linker. This supertriangle consists of three flat BO₃ groups combined by corners within the supertriangle, and with the BO₄ and BO₃ groups from layers (Fig. 5.3a). These supertriangles are perpendicular to the sublayer planes, and their position produces large free space within the layers that are occupied by disordered water.
Figure 5.3: a) An illustration of the **UBO-4** crystal structure. b) The structure of uranyl borates sheets in **UBO-4**. c) and d) The two topologies of uranyl borates sheets realized in **UBO-4**.
molecules. The sublayers in **UBO-4** are slightly corrugated, and as a result of this, the uranyl groups not strongly perpendicular to the plane of the layer. The topology of the sublayers is different from all previously known types in actinide borates sheets.\(^{1-9,18}\) The layers are based on two types of groups that we can call “building blocks” and “linkers.” The building blocks consist of two tetrahedral BO\(_4\) groups (directed on one side) and one BO\(_3\) triangle. All of these units share corners, and the projection of it onto the sublayer’s plane is triangular-like. The building blocks are united by two sorts of “linkers”; these are BO\(_3\) triangles and BO\(_4\) tetrahedra. These groups are linked together into building blocks that yield a regular 2D network, as shown in Fig. 5.3b, which we call F-type (Fig. 5.3c,d) layers. In the structure of **UBO-4** there are F type and symmetrically dependent F’ layers (for symmetry details see ref. 9). Both sheets take places in one double layer. The general topology of these sheets is new, but it can be represented as the superposition of the sheets realized in neptunyl and plutonyl borates.\(^8\) The scheme of this construction is shown on the Fig. 5.4. In Fig. 5.4a and b fragments of the sheets in neptunyl and plutonyl borates are shown, respectively. The dashed line shows selected 1D fragments separated from both structures. These are fragments 1 and 2. Fragment 2 can be transformed to 2’ by reflection in sheet plane (identical to the reverse view). In Fig. 5.4c it is demonstrated that the result of the 1 and 2’ 1D fragments are combined into the 2D structure where these fragments are regularly alternated. The resulting sheet is identical with F (or F’ after symmetrical transformation). By the same manner we can create the E-type sheets in uranyl borates
Figure 5.4: A schematic representation of F-types layers construction using neptunyl and plutonyl borates sheets. a) Neptunyl borates sheet structure b) plutonyl borate sheet structure c) Resulting sheet with F-type topology.
that are found in α-Tl₂[(UO₂)₂B₁₁O₁₈(OH)₃]. However, the E layer construction found the neptunyl borate sheets is the result of only one BO₄ tetrahedral linker.⁸

The layers in UBO-4 diverge sharply from other uranyl borates in other ways as well. There are two uranium sites in the layers, both of which are surrounded by nine borate groups. However, one site is surrounded by four BO₃ units and five BO₄ units. The other site is surrounded by three BO₃ units and six BO₄ units, which are also different from the typical uranyl borate coordination environment because these BO₃ units are not separated by two BO₄ units from each other. Interestingly, this coordination environment is exactly the same as the neptunyl borates.⁸ The primary difference between UBO-4 and K₄(NpO₂)₆.₇₃B₂₀O₃₆(OH)₂ and Ba₂(NpO₂)₆.₅₉B₂₀O₃₆(OH)₂·H₂O is that the neptunyl borates have additional neptunyl units in the voids that are held in place primarily through cation-cation interactions,⁸ which are exceedingly rare in U(VI) compounds. The channels that extend within the layers are large at 12.002 × 5.224 Å. In UBO-4, the channels are filled with disordered water.

Finally, there is a strong stoichiometric dependence from the reactions that is reflected in the B/U ratio found in the crystals: B/U = 2 (UBO-1), B/U = 4.5 (UBO-2, UBO-3), B/U = 6.5 (UBO-4). The packing principles show only small variations, and in all phases the layers pack to layers, and we observe only 2D structures. However, as the amount of boron is increased, the structures became more 3D-like. UBO-2 and UBO-3 (B/U = 4.5) have doubled layers, but very little free space between the layers. However, UBO-4 (B/U = 6.5) possesses a 3D framework with large voids within and between the
layers that are occupied by water molecules. Such structural behavior of the $\text{UO}_2^{2+}$ - $\text{B}_2\text{O}_3$ system is quite unusual because in other similar systems dimensionality decreased with increasing of $X/U$ ratios ($X = \text{Mo}, \text{W}, \text{P}, \text{As}$, etc.).

5.6 Conclusions

Of the twelve uranyl borates that we have now reported, ten are noncentrosymmetric, the majority of which adopt polar space groups. Of the seven previously reported uranyl borates derived from either $\text{B}_2\text{O}_3$ melts or room temperature crystallization, only one is noncentrosymmetric. What makes this result even more surprising is that in some of high-temperature phases the uranium coordination environment is an $\text{UO}_7$ pentagonal bipyramid. This building unit should show a greater propensity for acentric structures than the $\text{UO}_8$ hexagonal bipyramids that we have observed because in the former unit the uranium atoms can not be placed on centers of inversion (without disorder), whereas in the latter a center of symmetry is easily invoked. Of equal importance is the fact that similar layers that are capable of yielding noncentrosymmetric structures can also yield centrosymmetric structures as found in $\text{UBO-2}$ and $\text{UBO-3}$. In the future we will disclose other families of uranyl borates that will highlight these themes.

All of these actinide borates provide useful models for the crystallized portions of vitrified nuclear waste. These are likely to be one of the only ways that we can glimpse into vitrified nuclear waste because a typical glass log with high-level waste yields on the order 200,000 Ci (i.e. lethal doses within seconds).
5.7 Reference


6.1 Abstract

The reaction of uranyl nitrate with a large excess of molten boric acid in the presence of potassium or rubidium nitrate results in the formation of three new potassium uranyl borates, $K_2[(UO_2)_2B_{12}O_{19}(OH)_4]\cdot0.3H_2O$ (*KUBO*-1), $K[(UO_2)_2B_{10}O_{15}(OH)_5]$ (*KUBO*-2), and $K[(UO_2)_2B_{10}O_{16}(OH)_3]\cdot0.7H_2O$ (*KUBO*-3), and two new rubidium uranyl borates $Rb_2[(UO_2)_2B_{13}O_{20}(OH)_5]$ (*RbUBO*-1) and $Rb[(UO_2)_2B_{10}O_{16}(OH)_3]\cdot0.7H_2O$ (*RbUBO*-2). The latter is isotypic with *KUBO*-3. These compounds share a common structural motif consisting of a linear uranyl, $UO_2^{2+}$, cation surrounded by $BO_3$ triangles and $BO_4$ tetrahedra to create an $UO_8$ hexagonal bipyramidal environment around uranium. The borate anions bridge between uranyl units to create sheets. Additional $BO_3$ triangles extend from the polyborate layers, and are directed approximately perpendicular to the sheets. All of these compounds adopt layered structures. With the exception of *KUBO*-1, the structures are all centrosymmetric. All of these compounds fluoresce when irradiated with long-wavelength UV light. The fluorescence spectrum yields well-defined vibronically-coupled charge-transfer features.
6.2 Introduction

Actinide oxoanion compounds continue to fascinate and mystify researchers by virtue of the remarkable variety of unusual structures that they can adopt, and the vast array of properties that these compounds can display that include ion-exchange, mixed-valency, ionic conductivity, enhanced fluorescence, magnetic ordering, and nonlinear optical properties. These structures range from the extraordinary complexity of the uranium mineral Wölsendorfite, \( \text{Pb}_{6.16}\text{Ba}_{0.36}(\text{UO}_2)_{14}\text{O}_{19}(\text{OH})_4(\text{H}_2\text{O})_{12} \), whose layered topology is so complex that the length of the repeating \( c \) axis is nearly 56 Å, to both neutral and charged nanotubular structures adopted by uranyl phosphonates and selenates. There are also compounds that are difficult to rival in terms of the variability of the coordination around the metal centers, such as in \( \text{Na}_2\text{Li}_8[(\text{UO}_2)_{11}\text{O}_{12}(\text{WO}_5)_{2}] \) where \( \text{UO}_6\), \( \text{UO}_7\), and \( \text{UO}_8 \) tetragonal, pentagonal, and hexagonal bipyramids are all contained within one compound. Mixed- and intermediate valency are known in both uranium and neptunium compounds, and these materials combine both unprecedented structures with atypical electronic properties.

One example of actinide oxoanion compounds that are poorly explored are the actinide borates. This is surprising for several reasons, the first of which is that a thorium borate was reported in 1826 by Berzelius. Credible examples of well-defined actinide borates were absent until the 1980's when a series of crystal structures were reported for uranyl borates. These compounds were all synthesized via high temperature \( \text{B}_2\text{O}_3 \) melt reactions above 1000 K. These compounds share a common motif in that the boron atoms are typically found to have the \( \text{BO}_3 \) triangular
configuration, which is more thermodynamically favorable than BO$_4$ tetrahedra at high temperatures. The single exception to this is molecular system, K$_6$[UO$_2$B$_{16}$O$_{24}$(OH)$_8$]·12H$_2$O, which was prepared at room temperature via slow evaporation, and is composed of a cyclic cluster of BO$_3$ and BO$_4$ units with a central uranyl core. A single crystallographically characterized thorium borate, ThB$_2$O$_5$, can be added to this list. After these initial studies, additional actinide borates were not reported for 20 years.

Actinide borates are difficult to synthesize via commonly employed techniques, such as hydrothermal reactions, because water competes very successfully with borate for inner-sphere coordination sites with these metals under most conditions. Our strategy for preparing actinide borates is to capitalize on low temperature boric acid flux reactions that have yielded a thorium borate, [ThB$_5$O$_6$(OH)$_6$][BO(OH)$_2$]·2.5H$_2$O (NDTB-1), with a cationic framework structure and remarkable anion exchange capabilities, a large family of uranyl borates, three mixed-valent neptunium borates, and a single plutonium(VI) borate which is similar to its uranium counterparts. We have shown that boric acid fluxes are an excellent medium for preparing actinide borates in general. These conditions yield completely new coordination environments and topologies for actinide compounds. In addition, a significant percentage of uranyl borates adopt noncentrosymmetric structures, and these compounds may aid in the design of nonlinear optical materials. In this chapter, we substantially expand the uranyl borate family to include compounds that contain potassium and rubidium. These cations can yield structural features that have not been observed with other cations,
and provide important insights into how subtle changes in composition can lead to
dramatic changes in properties.

6.3 Experimental Section

*Syntheses:* \(\text{UO}_2(\text{NO}_3)_2\cdot6\text{H}_2\text{O}\) (98%, International Bio-Analytical Industries), \(\text{H}_3\text{BO}_3\) (99.99%, Alfa-Aesar), \(\text{KNO}_3\) (99.3%, Aldrich), and \(\text{RbNO}_3\) (99.8%, Alfa-Aesar) were used as received without further purification. Distilled and Millipore filtered water with resistance of 18.2 MΩ·cm was used in all reactions. PTFE-lined autoclaves were used for all reactions. *While the UO\(_2\)(NO\(_3\))\(_2\)·6H\(_2\)O used in this study contained depleted U, there is really not much difference between depleted uranium and natural abundance uranium, and standard precautions for handling radioactive materials should be followed at all times. There are very old sources of uranyl nitrate that may not be depleted, and enhanced care is warranted for these samples.*

*Synthesis of K\(_2\)((\text{UO}_2)_2\text{B}_{12}\text{O}_{19}(\text{OH})_4\)·0.3H\(_2\)O (KUBO-1), K\([\text{(UO}_2)_2\text{B}_{10}\text{O}_{15}(\text{OH})_5]\) (KUBO-2), and K\([\text{(UO}_2)_2\text{B}_{10}\text{O}_{16}(\text{OH})_3]\)·0.7H\(_2\)O (KUBO-3):* \(\text{UO}_2(\text{NO}_3)_2\cdot6\text{H}_2\text{O}\), boric acid, potassium nitrate with ten different K:U:B molar ratios (1:1:6, 1:1:10, 1:1:15, 2:1:8, 2:1:15, 3:1:8, 3:1:15, 4:1:15, 5:1:15, 6:1:15) (1 mmol of UO\(_2\)(NO\(_3\))\(_2\)·6H\(_2\)O was used in each potassium and rubidium reaction) were loaded into ten 23 mL autoclaves. The autoclaves were sealed and heated to 190 °C in a box furnace for 24 h. The autoclaves were then cooled down to room temperature at a rate of 5 °C/h. All the products were washed with boiling water to remove excess boric acid, followed by rinsing with methanol. Crystals in the form of tablets with light yellow-green coloration were collected for all reactions.
The tablets of \( \text{K}_2\text{UO}_2\text{B}_{12}\text{O}_{19}(\text{OH})_4\cdot0.3\text{H}_2\text{O} \) (\textbf{KUBO-1}) are remarkably well-formed triangles. The same conditions and procedures were used for both the potassium and rubidium reactions. Single crystal X-ray diffraction and powder X-ray diffraction studies reveal that \textbf{KUBO-2} forms as the major product of the first six ratios except for the 2:1:8 reaction where it is a minor product, it also exists in the 3:1:8 and 3:1:15 reactions. \textbf{KUBO-3} forms in the 2:1:8 reaction as the major product, and in the 2:1:15, 3:1:8, 3:1:15 reactions as the minor product. \textbf{KUBO-1} only occurs in high K\(^+\) ratio reactions for last five ratios, and can be found as a pure phase for the last three reaction ratios.

\textit{Synthesis of Rb}_2\text{[(UO}_2\text{)]}_2\text{B}_{13}\text{O}_{20}(\text{OH})_5\) \(\text{(RbUBO-1)}\), and Rb\(\text{[(UO}_2\text{)]}_2\text{B}_{10}\text{O}_{16}(\text{OH})_3\cdot0.7\text{H}_2\text{O}\) (\textbf{RbUBO-2}): Rb\(\text{[(UO}_2\text{)]}_2\text{B}_{13}\text{O}_{20}(\text{OH})_5\) \(\text{(RbUBO-1)}\) can be prepared using UO\(_2\)(NO\(_3\))\(_2\)·6H\(_2\)O, boric acid, rubidium nitrate at Rb:U:B molar ratio of 5:1:15. Rb\(\text{[(UO}_2\text{)]}_2\text{B}_{10}\text{O}_{16}(\text{OH})_3\cdot0.7\text{H}_2\text{O}\) \(\text{(RbUBO-2)}\) can be made in the reaction with a ratio of 2:1:15. Crystals in the form of tablets were isolated from the first reaction, and blocks for the second reaction. The crystals have light yellow-green coloration.

\textit{Crystallographic Studies}: Single crystals of all five \textbf{KUBO} and \textbf{RbUBO} phases were mounted on glass fibers and optically aligned on a Bruker APEXII CCD X-ray diffractometer or a Bruker APEXII Quazar X-ray diffractometer using a digital camera. Initial intensity measurements were either performed using a \(\mu\)S X-ray source, a 30 W microfocused sealed tube (MoK\(\alpha\), \(\lambda =0.71073\) Å) with high-brilliance and high-performance focusing Quazar multilayer optics, or a standard sealed tube with a monocapillary collimator. Standard APEXII software was used for determination of the unit cells and data collection control. The intensities of reflections of a sphere were
collected by a combination of four sets of exposures (frames). Each set had a different \( \phi \) angle for the crystal and each exposure covered a range of 0.5° in \( \omega \). A total of 1464 frames were collected with an exposure time per frame of 10 to 30 s, depending on the crystal. The SAINT software was used for data integration including Lorentz and polarization corrections. Semi-empirical absorption corrections were applied using the program SADABS. Selected crystallographic data are listed in Table 6.1. Selected bond distances are given in Tables 6.51–54. Atomic coordinates, bond distances, and additional structural information are provided in the Supplementary Material (CIF’s).

**Powder X-ray diffraction**: Powder X-ray diffraction patterns of the products of all KUBO reactions were collected on a Scintag theta-theta diffractometer equipped with a diffracted-beamed monochromatic set for Cu K\( \alpha \) (\( \lambda = 1.54056 \) \( \text{Å} \)) radiation at room temperature in the angular range from 10° to 80° (2\( \theta \)) with a scanning step width of 0.05° and a fixed counting time of 1 s/step. The collected patterns were compared with those calculated from single crystal data using ATOMS (see Supporting Information).

**UV-vis-NIR and Fluorescence Spectroscopy**: UV-vis-NIR data were acquired from single crystals using a Craic Technologies microspectrophotometer. Crystals were placed on quartz slides under oil, and the data was collected from 200 to 1700 nm. Fluorescence data were obtained using 365 nm light for excitation.

6.4 Syntheses Discussion

The formation of three phases in the KUBO system is found to be a stoichiometrically driven reaction, which means that the formation of the four
<table>
<thead>
<tr>
<th>Compound</th>
<th>KUBO-1</th>
<th>KUBO-2</th>
<th>RbUBO-1</th>
<th>RbUBO-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>1115.98</td>
<td>1007.26</td>
<td>1251.53</td>
<td>1048.83</td>
</tr>
<tr>
<td>Color and habit</td>
<td>Yellow-green, Triangle tablet</td>
<td>Yellow-green, tablet</td>
<td>Yellow-green, tablet</td>
<td>Yellow-green, block</td>
</tr>
<tr>
<td>Space group</td>
<td>P3(_1)2(_1)/c</td>
<td>C2/c</td>
<td>P2(_1)/n</td>
<td>P2(_1)/m</td>
</tr>
<tr>
<td>a (Å)</td>
<td>6.4418(4)</td>
<td>6.4637(4)</td>
<td>6.4449(3)</td>
<td>6.4063(7)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>6.4418(4)</td>
<td>11.1151(7)</td>
<td>11.0969(5)</td>
<td>26.028(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>47.457(3)</td>
<td>25.4185(16)</td>
<td>33.9974(16)</td>
<td>6.4573(7)</td>
</tr>
<tr>
<td>(\alpha) (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>90</td>
<td>96.3710(10)</td>
<td>92.2595(5)</td>
<td>119.7160(10)</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>120</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V (Å(^3))</td>
<td>1705.47(18)</td>
<td>1814.9(2)</td>
<td>2429.55(19)</td>
<td>935.10(17)</td>
</tr>
<tr>
<td>Z</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>T (K)</td>
<td>293(2)</td>
<td>293(2)</td>
<td>293(2)</td>
<td>296(2)</td>
</tr>
<tr>
<td>(\lambda) (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Maximum 2(\theta) (deg.)</td>
<td>28.92</td>
<td>28.62</td>
<td>28.78</td>
<td>28.75</td>
</tr>
<tr>
<td>(\rho)\text{calcld} (g cm(^{-3}))</td>
<td>3.260</td>
<td>3.686</td>
<td>3.422</td>
<td>3.725</td>
</tr>
<tr>
<td>(\mu) (Mo K(\alpha))</td>
<td>147.16</td>
<td>181.82</td>
<td>174.24</td>
<td>200.06</td>
</tr>
<tr>
<td>(R(F)) for (F_0^2 &gt; 2\sigma(F_0^2)) (a)</td>
<td>0.0212</td>
<td>0.0407</td>
<td>0.0419</td>
<td>0.0403</td>
</tr>
<tr>
<td>(R_w(F_0^2)) (b)</td>
<td>0.0552</td>
<td>0.1027</td>
<td>0.0917</td>
<td>0.0864</td>
</tr>
</tbody>
</table>

\text{TABLE 6.1}

CRYSTALLOGRAPHIC DATA FOR \(\text{K}_2[\text{UO}_2\text{]}_2\text{B}_{12}\text{O}_{19}$$\text{(OH)}_4\cdot0.3\text{H}_2\text{O}$ (\text{KUBO-1}), \(\text{K}[(\text{UO}_2\text{]}_2\text{B}_{10}\text{O}_{15}$$\text{(OH)}_3\) (\text{KUBO-2}), \text{Rb}_2[\text{UO}_2\text{]}_2\text{B}_{13}\text{O}_{20}$$\text{(OH)}_5\) (\text{RbUBO-1}, AND \text{Rb}[\text{UO}_2\text{]}_2\text{B}_{10}\text{O}_{16}$$\text{(OH)}_3\cdot0.7\text{H}_2\text{O}$ (\text{RbUBO-2})
compounds is related to the molar ratio of potassium, uranium, and boron in the starting materials (Table 6.55). The KUBO-2 and KUBO-3 phases possess a K:U ratio of 1:2, and are favored in the reactions that have a lower K:U ratio. When increased amounts of potassium are present in the reaction mixture, KUBO-1, which has a higher K:U ratio of 1:1, becomes more favored, and can be made as a pure phase. The reaction yields increase with reaction time. One day reactions are appropriate for screening product composition, but only lead to low isolated yields. The yield maximizes after three days at 57% for KUBO-1 in reaction of K:U:B= 5 : 1 : 15. The two RbUBO phases are more difficult to prepare. Both of the RbUBO phases can not be obtained as pure phases, and they always appear as minor products of the reaction along with β-UO₂B₂O₄ as the major product.

6.5 Crystal Structures and some General Topological Aspects

Portions of the crystal structures of KUBO-1, KUBO-2, RbUBO-1, and RbUBO-2 are shown in Fig. 6.1. The crystal structure of the KUBO-3 is not publishable owing to non-merohedral twinning. We have tried several crystals from two different syntheses but all of them contented two twinning components. We used Bruker software package (Cell_Now) for component separation, HKLF5 file creation and structure refinement. Using the HKLF5 file we got final R₁ value 2.87% but unfortunately displacement of two boron atoms have been not well refined. The structure model of KUBO-3 is isotypical with those in RbUBO-2, but it crystallized in triclinic syngony (space group P ̅1̅, unite cell parameters a=6.436(1), b=6.437(1), c=13.051(2), α=84.548(2), β=86.133(2),
Figure 6.1: Views of the crystal structures of K$_2$(UO$_2$)$_2$B$_{12}$O$_{19}$(OH)$_4$·0.3H$_2$O (KUBO-1) (a), K[(UO$_2$)$_2$B$_{16}$O$_{15}$(OH)$_5$] (KUBO-2) (c), Rb$_2$[(UO$_2$)$_2$B$_{13}$O$_{20}$(OH)$_5$]$\cdot$0.7H$_2$O (RbUBO-1) (b), Rb[(UO$_2$)$_2$B$_{16}$O$_{16}$(OH)$_3$]$\cdot$0.7H$_2$O (RbUBO-2) and K[(UO$_2$)$_2$B$_{16}$O$_{16}$(OH)$_3$]$\cdot$0.7H$_2$O (KUBO-3) (d). UO$_8$ hexagonal bipyramids are shown in yellow, BO$_3$ and BO$_4$ units in green, K$^+$ and Rb$^+$ cations in blue.
\( \gamma = 60.083(2) \). The powder X-ray diffraction data and unite cell parameters comparison (c parameter in RbUBO-2 is approximately \( 2^*c \) in KUBO-3) also confirming isotypism of RbUBO-2 and KUBO-3.

The crystal structures of all of the obtained phases are based on 2D borate sheets with similar topologies. In the structures of four of the phases (KUBO-1, KUBO-3, RbUBO-1, and RbUBO-2), these sheets are linked into double layers by BO\(_3\) triangles. In contrast, the structure of KUBO-2 is based on single layers. In all of the uranium borates, the uranium centers are contained within uranyl groups, UO\(_2\)\(^{2+}\), which are incorporated into the borate sheets. The resulting coordination of uranium atoms is as UO\(_8\) hexagonal bipyramids.

\( \text{K}_2(\text{UO}_2)_2\text{B}_{12}\text{O}_{19}(\text{OH})_4 \cdot 0.3\text{H}_2\text{O} \) (KUBO-1): KUBO-1 is based on double, negatively charged layers united in regular 3D structure by potassium cations distributed in the interlayer space (see Fig. 6.1a). Each double layer has a thickness of about 15.5 Å. The single sheets within the double layers in KUBO-1 have the A and B (in this case in form of B\(^{'}\)) types of topologies which were earlier founded in pure uranyl borates and sodium uranyl borate system.\(^{22,23}\) This topology is based on a single BO\(_3\) group linked with three groups each consisting of three BO\(_4\) tetrahedra. This is the simplest topologies we found in actinide borates. Each double layer consists of both types (A and B\(^{'}\)) of borate sheets. The sheets are linked into double layers by two BO\(_3\) triangles (B\(_2\)O\(_5\) groups) which act as columns, and the structures could be considered as being pillared. These groups are tilted away from the plane of the sheets because sheets are slighted shifted within one double layer with respect each to other (Fig. 6.1a). This tilting and shifting
reduces the interlayer space. The potassium cations and water molecules sites are in the pores of doubled layers between the $\text{B}_2\text{O}_5$ groups and borate sheets. These positions are split and partially occupied because of high volume of free space in the cavities (the same situation occurs in RbUBO-1). The single $\text{BO}_3$ triangles create a sawtooth-like configuration on the periphery of the double layers. Each double layer in the structure of KUBO-1 is rotated by 120° compared to the next layer. This is clearly visible from the single sheets positions in Fig. 6.1. Because of this orientational change three double layers exist in one unit cell with a total of 360° of turning, which is equivalent to a translation element. As we mentioned, one layer in KUBO-1 has 15.5 Å thickness, and as result we have a long unit cell parameter of $c = 47.747(3)$ Å (Table 6.1).

$K\{(\text{UO}_2)\text{B}_{10}\text{O}_{15}(\text{OH})_5\}$ (KUBO-2): This potassium uranyl borate has an identical chemical composition with $\alpha\text{-Na}\{(\text{UO}_2)\text{B}_{10}\text{O}_{15}(\text{OH})_5\}$ (NaUBO-1) and $\beta$-Na[($\text{UO}_2$)$_2\text{B}_{10}\text{O}_{15}(\text{OH})_5$] (NaUBO-2) and is related with the hydrated compound, Na[($\text{UO}_2$)$_2\text{B}_{10}\text{O}_{15}(\text{OH})_5$] · 3H$_2$O (NaUBO-3). The crystal structures of these phases are also quite similar (Fig. 6.1c). The structure of these compounds are based on 2D single layers constructed from polymerized borate clusters with A ($A'$) and B ($B'$) topologies. The layers rotated by 180° with respect to each other. The additional $\text{BO}_3$ triangle groups are only on one side of borate single sheets. These groups are directed into one side of neighboring layers (Fig. 6.1c), and as result a quasi doubled layer results without real linkages between the $\text{BO}_3$ groups. The potassium cations are in the voids between the single layers on the side where the $\text{BO}_3$ triangles are. The connection of the layers is
provided by K⁺ cations (in the places where they are) and by hydrogen bonds (on the opposite sides of single layers).

Chemically and topologically KUBO-2, NaUBO-1, and NaUBO-2 are practically identical. The main difference between them is in ordering and orientation of A (A') and B (B') sheet-types. In the sodium phases we have found A/A'/B/B' and B/B'/B/B' packing (in NaUBO-1 and NaUBO-2, respectively), but in the potassium phases the packing-type is different, A/B'/B/A'. These differences produced difference in number of layers in the unit cell and in the alkali metal cation environments.

*Rb₂[(UO₂)₂B₁₃O₂₀(OH)₅] (RbUBO-1)*: The rubidium uranyl borate RbUBO-1 has the most complicated crystal structure and a different borate sheet topology, and is shown in Fig. 6.1b. In general this structure is similar with structure of KUBO-1 because it is also based on doubled layers consisting of single borate sheets. However, these sheets are slightly different from A/A' – B/B' type topology, and they are based on a superposition of them. The schematic representation of the borate sheets in RbUBO-1 is given in Fig. 6.2a. The sheets as in the A and B types are based on flat BO₃ triangles linked by corners with the super triangular groups. These supertriangular groups consist of three BO₄ tetrahedra. Two of them are directed toward one side (“up” or “down”), and the third is directed opposite to them. In the structure of the A and B type sheets all three super triangles (surrounding flat BO₃ triangles) have same internal structure (for example two tetrahedrons “up” and one “down” in structure of A' and B'). In the structure of RbUBO-1 this order is not retained. In Fig. 6.2a it is shown that each single BO₃ triangle is interconnected with two identical super triangles (with identical internal
Figure 6.2: A skeletal representation of the polyborate sheet found in the structure of \( \text{Rb}_2[(\text{UO}_2)_2\text{B}_{13}\text{O}_{20}(\text{OH})_3] } (\text{RbUBO-1}) \): general view (a) and detailed view of two possible configuration (b) and (c).
structure) and one group with reversed structure. As the result of this a single triangle BO$_3$ can not be used for the topological description of the sheets in RbUBO-1. The topology of these new layers, is referred to as G in this work (after E and F) by the environment of the two neighboring BO$_3$ groups as is shown in Fig. 6.2b and 6.2c. The resulting topology of the G sheets is based on alternating A and A’ or B and B’ fragments as is shown in Fig. 6.2a. Because in one sheet there exists both variants of the orientation of the supertriangles, the G type sheet is not enantiomorphic. Transformation from the G conformation to G’ can be made by simple rotation around of the two-fold axis in figure plane (Fig. 6.2a). This is the first example of this sheet topology construction by combination of previously known topologies of uranyl borate phases. The topologies of other non- A/B or C/D sheets were combined from Np/Pu borates sheets topologies.$^{24}$

Each sheet, described above, within one layer is rotated by 180° in comparison with the other. The sheets linked by B$_2$O$_5$ groups into double layers (Fig. 6.1b). In contrast with KUBO-1, where B$_2$O$_5$ groups are linked with the sheets at two points (Fig. 6.1a), the B$_2$O$_5$ groups in RbUBO-1 are linked with sheets at three locations. The free space within one layer (between single sheets) is filled by Rb$^+$ cations, which partially compensate for the negative charge of the layers. The rubidium atoms positions within the layers are split between two sites, which are partially occupied in the same manner as in KUBO-1. The outer sides of double layers are covered by two types of groups – BO$_3$ single triangle and B$_2$O$_5$ dimers. These groups form an optimal environment for the Rb$^+$ cations in the interlayer space. The Rb atoms in the interlayer space are providing
the interconnection of the double layers as the potassium cations do in KUBO-1. Thus both structures are similar in packing (double layers, B₂O₅ as sheets linkers, A⁺ cations within and outside of the layers), but the difference in the ionic radius of K⁺ and Rb⁺ direct the structural fragments in different ways.

\[ \text{Rb}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{16}(\text{OH})_3]\cdot 0.7\text{H}_2\text{O} \] (RbUBO-2) and \[ K[(\text{UO}_2)_2\text{B}_{10}\text{O}_{16}(\text{OH})_3]\cdot 0.7\text{H}_2\text{O} \] (KUBO-3): The phases RbUBO-2 and KUBO-3 have the same chemical compositions and are isotypic. Here only the Rb phase is described because all of the potassium-containing crystals from several syntheses were twinned in manner that could be resolved (but structure was solved and refined). A portion of the RbUBO-2 crystal structure is shown in Fig. 6.1d. This structure is related to both of the previously described packing types – double layers from KUBO-1 and RbUBO-1 and “free” interlayer space as in KUBO-2. The double layers in KUBO-3 and RbUBO-2 are linked by B₂O₅ dimers with four points of connections to the single borate sheets. Here we see the difference from linking of borate sheets by B₂O₅ in KUBO-1 (two points of connection) and RbUBO-1 (three points of connection). As a result, projections of the single sheets within one double layer are identical without any kind of shift. The difference is only in the topology of the sheets – A/A', and rotation of the next double layers by 180° (Fig. 6.1d). There are not any additional groups (BO₃ or B₂O₅) on the outer side of double layers. This makes the structure of KUBO-3 and RbUBO-2 closer to the structure of KUBO-2. The structures of KUBO-3 and RbUBO-2 can be presented as a result of KUBO-2 structure condensation:

\[ K[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}(\text{OH})_3] \rightarrow K[(\text{UO}_2)_2\text{B}_{10}\text{O}_{16}(\text{OH})_3 + \text{H}_2\text{O}. \] This is clearly visible from structure comparison (Figs. 6.1c and 6.1d) – the single BO₃ triangles with
terminate with OH groups (in KUBO-2) and are condensed to B$_2$O$_5$ dimers (in KUBO-3 and RbUBO-2). Such processes are well known for layered silicate precursors for zeolite type materials.\(^{26}\)

6.6 Fluorescence Properties of Potassium and Rubidium Uranyl Borates

The term “fluorescence” was first coined in the late 1700’s in France to describe the green glow from uranyl salts that occurs when natural light irradiates them. This emission is in fact highly complex and is strongly vibronically-coupled charge-transfer emission. Emission from uranyl compounds has been carefully and extensively studied, especially by Denning and co-workers who assigned all of the vibronic transitions from single crystals containing the [UO$_2$Cl$_4$]$^{2-}$ anion.\(^{27}\) While it is generally thought that five broad features centered near 520 nm are generally observed for uranyl compounds at room temperature, far more bands are observed at low temperatures.

K$_2$[(UO$_2$)$_2$B$_{12}$O$_{36}$(OH)$_4$]-0.3H$_2$O (KUBO-1) forms rather remarkable triangular tablets with a pale yellow-green coloration. Upon irradiation with 365 nm light, the crystals fluoresce with sufficient intensity that the emission from a few crystals is easily observed by the naked eye as shown in Fig. 6.3. The fluorescence spectrum of this compound shows very narrow features for a room temperature spectrum, and the five typical vibronic bands are observed as shown in Fig. 6.4. However, three additional weaker features can be clearly identified in this spectrum. The resolution of these additional features, and the sharpness of the spectrum can probably be attributed to
Figure 6.3: Single crystals of $\text{K}_2(\text{UO}_2)_2\text{B}_{12}\text{O}_{19}(\text{OH})_4\cdot 0.3\text{H}_2\text{O}$ (KUBO-1) showing their triangular habit (top). The black square aperture (size $6.3 \times 6.3 \ \mu\text{m}$) acts as a scale bar. The same crystals under irradiation with 365 nm light (bottom).
Figure 6.4: Fluorescence spectrum of $K_2[UO_2]_2B_{12}O_{19}(OH)_4\cdot0.3H_2O$ (KUBO-1) showing vibronically-coupled charge-transfer bands.
the remarkable quality of the crystals of this compound.\textsuperscript{28} All of the compounds described in this work yield fluorescence spectra similar to that shown in Fig. 6.4.

6.7 Conclusions

Uranyl borates derived from boric acid fluxes have yielded a total of seven different sheet topologies thus far despite the fact that they are all combination of the same three building units, UO\(_8\) hexagonal bipyramids, BO\(_3\) triangles, and BO\(_4\) tetrahedra. These sheets invariably possess additional BO\(_3\) triangles that extend into the interlayer space. In some cases these groups separate the layers, and in others they join them together to yield double layers or three-dimensional frameworks. The structures are typically noncentrosymmetric, and are often polar. The interlayer cations play structure-directing roles, and the size of the cations affects the type of structure of achieved. Finally, product composition, which is highly variable, is greatly influenced by reaction stoichiometry. In short, the uranyl borate system is one of the most complex actinide systems ever recorded.

Owing to the presence of the uranyl cations within the layers, all of these compounds fluoresce with sufficient intensity to be observed by the naked eye. The emission spectra show well-resolved vibronic coupling, and more features are observed for these compounds than are generally found, perhaps because the boric acid flux yields crystals of higher than normal quality. Other properties have also been observed such as second-harmonic generation of laser light. Therefore, the structure-property relationships in this family are also quite rich and potentially useful.
6.8 Reference


CHAPTER 7:
STRUCTURE-PROPERTY RELATIONSHIPS IN LITHIUM, SILVER, AND CESIUM URANYL BORATES

7.1 Abstract

Four new uranyl borates, Li[\(\text{UO}_2\text{B}_3\text{O}_9\)]\(\cdot\)\(\text{H}_2\text{O}\) (LiUBO-1), Ag[\(\text{UO}_2\text{B}_5\text{O}_8\text{(OH)}_2\)] (AgUBO-1), and \(\alpha\)-Cs[(\(\text{UO}_2\))\(_2\)\(\text{B}_{11}\text{O}_{16}\text{(OH)}_6\)] (CsUBO-1) and \(\beta\)-Cs[(\(\text{UO}_2\))\(_2\)\(\text{B}_{11}\text{O}_{16}\text{(OH)}_6\)] (CsUBO-2) were synthesized via the reaction of uranyl nitrate with a large excess of molten boric acid in the presence of lithium, silver, or cesium nitrate. These compounds share a common structural motif consisting of a linear uranyl, \(\text{UO}_2^{2+}\), cation surrounded by BO\(_3\) triangles and BO\(_4\) tetrahedra to create a \(\text{UO}_8\) hexagonal bipyramidal environment around uranium. The borate anions bridge between uranyl units to create sheets. Additional BO\(_3\) triangles extend from the polyborate layers, and are directed approximately perpendicular to the sheets. In Li[(\(\text{UO}_2\))\(_2\)\(\text{B}_3\text{O}_9\)]\(\cdot\)\(\text{H}_2\text{O}\), the additional BO\(_3\) triangles connect these sheets together to form a three-dimensional framework structure. Li[(\(\text{UO}_2\))\(_2\)\(\text{B}_5\text{O}_9\)]\(\cdot\)\(\text{H}_2\text{O}\) and \(\beta\)-Cs[(\(\text{UO}_2\))\(_2\)\(\text{B}_{11}\text{O}_{16}\text{(OH)}_6\)] adopt noncentrosymmetric structures, while Ag[(\(\text{UO}_2\))\(_2\)\(\text{B}_5\text{O}_8\text{(OH)}_2\)] and \(\alpha\)-Cs[(\(\text{UO}_2\))\(_2\)\(\text{B}_{11}\text{O}_{16}\text{(OH)}_6\)] are centrosymmetric. Li[(\(\text{UO}_2\))\(_2\)\(\text{B}_3\text{O}_9\)]\(\cdot\)\(\text{H}_2\text{O}\), which can be obtained as pure phase, displays second-harmonic
generation of 532 nm light from 1064 nm light. Topological relationships of all actinyl borates are developed.

7.2 Introduction

Borate materials are being actively developed owing to their wide range of applications. In particular, they display remarkable transparency in the deep UV, high chemical stability, and for some materials, crystals with high optical quality can be obtained leading to the development of nonlinear optical materials when the borates adopt noncentrosymmetric space groups such as $\beta$-BaB$_2$O$_4$ (BBO), $^1$LiB$_3$O$_5$ (LBO), $^2$CsLiB$_6$O$_{10}$ (CLBO), $^3$BiB$_3$O$_6$ (BiBO), $^4$and La$_2$CaB$_{10}$O$_{19}$ (LCB)$^5$. From a structural chemistry point of view, boron atoms bound by oxygen atoms are found not only in three-fold (triangle, BO$_3$) coordination, but also in four-fold coordination (tetrahedron, BO$_4$). These BO$_3$ and BO$_4$ units can further polymerize to create larger borate clusters by sharing common corners to create clusters, one-dimensional chains, two-dimensional sheets, and three-dimensional framework structures.$^6$ Because there is a vast number of different topological arrangements of the polyborate anions, the solid-state and materials chemistry of borates is virtually unsurpassed.$^6,7$ Borates can be divided into three groups: main group and transition metal borates,$^8-13$ lanthanide and actinide borates,$^{14-28}$ organic and transition metal complex templated borates.$^{29}$ Recent interest in borates has focused on mixed oxoanion systems that include B-O-P,$^9$ B-O-Ge,$^{10}$ B-O-Al,$^{11}$ B-O-Ga$^{11a,12}$ and B-O-In$^{13}$ systems, with a clear effort to prepare microporous zeolitic materials with new catalytic, ion exchange, and sorption properties.
There are a variety of fruitful methodologies for preparing borate compounds. The most important ones are traditional hydrothermal and solvothermal methods, high-temperature fluxes, and room temperature slow evaporation. Actinide borates are difficult to prepare by traditional hydrothermal methods, because water competes very successfully with borate for inner-sphere coordination sites for these metals under most conditions. In fact, many borates that occur naturally are found in evaporated deposits in arid regions. Actinide borates have been synthesized by either removing water entirely from the system in high-temperature reactions or slow water evaporation. The first single crystal structure of uranium borate, $K_6[\text{UO}_2\{\text{B}_{16}\text{O}_{24}\text{(OH)}_8\}]\cdot 12\text{H}_2\text{O}$, was obtained by Behm from crystals obtained from the slow evaporation of water.\textsuperscript{15} This compound consists of isolated clusters composed of molecular uranyl borates with a uranyl core surrounded by a 16-borate ring. Shortly after this report Gasperin synthesized seven uranyl borates, including $\text{UO}_2\{\text{B}_2\text{O}_4\}$, $\text{Li(UO}_2)\text{BO}_3$, $\text{Na(UO}_2)\text{BO}_3$, $\text{Ca(UO}_2)\text{BO}_3$, $\text{Mg(UO}_2)\text{B}_2\text{O}_5$, $\text{Ni}_7\text{(UO}_2)\text{(B}_4\text{O}_{14})$ and $\text{Th(B}_2\text{O}_3)$ by using molten $\text{B}_2\text{O}_3$ as a flux in high temperature reactions.\textsuperscript{16-22} No new actinide borates were then reported for almost 20 years.

Our strategy for preparing actinide borates is to capitalize on low temperature boric acid flux reactions that have yielded a thorium borate, $[\text{ThB}_5\text{O}_6\text{(OH)}_6][\text{BO(OH)}_2]\cdot 2.5\text{H}_2\text{O}$ (NDTB-1), with a cationic framework structure and remarkable anion exchange capabilities,\textsuperscript{23} a large family of uranyl borates,\textsuperscript{24-27} three mixed-valent neptunium borates,\textsuperscript{24,28} and a single plutonium(VI) borate which is similar to its uranium counterparts.\textsuperscript{24} We have shown that boric acid fluxes are an excellent
medium for preparing actinide borates in general. These conditions yield completely new coordination environments and topologies for actinide compounds.\textsuperscript{23-28} In addition, a significant percentage of uranyl borates adopt noncentrosymmetric structures, and these compounds may aid in the design of nonlinear optical materials. Among the 17 uranyl borates we have already reported, 11 of them adopt noncentrosymmetric space groups.\textsuperscript{24-27} In this chapter, we substantially expand the uranyl borate family to include compounds that contain lithium, silver, and cesium, completing the series of common monovalent cations. We show that uranyl borates are very sensitive to the cations in the crystal structures, i.e. subtle changes in composition can lead to dramatic changes in properties (herein, nonlinear optical properties and fluorescence). Finally, we summarize the topological relationships of the borate networks and general aspects of the synthetic conditions for all the actinide borates we have prepare.

7.3 Experimental Section

\textit{Syntheses:} \text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \text{ (98\%, International Bio-Analytical Industries)}, \text{H}_3\text{BO}_3 \text{ (99.99\%, Alfa-Aesar)}, \text{LiNO}_3 \text{ (99\%, Alfa-Aesar)}, \text{CsNO}_3 \text{ (99.8\%, Alfa-Aesar)} \text{ and AgNO}_3 \text{ (99.7\%, J. T. Baker)} \text{ were used as received without further purification. Distilled and Millipore filtered water with resistance of 18.2 MΩ-cm was used in all reactions. PTFE-lined autoclaves were used for all reactions. While the UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O used in this study contained depleted U, there is really not much difference between depleted uranium and natural abundance uranium, and standard precautions for handling radioactive materials should be followed at all times. There are very old sources of}
uranyl nitrate that may not be depleted, and enhanced care is warranted for these samples.

**Synthesis of Li[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O (LiUBO-1):** UO$_2$(NO$_3$)$_2$·6H$_2$O (0.5000 g, 1 mmol), boric acid (0.4944 g, 8 mmol), LiNO$_3$ (0.0690 g, 4 mmol) and water (50 µL) were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 190 °C in a box furnace for one day. The autoclave was then cooled down to room temperature at a rate of 5 °C/h. The products were washed with boiling water to remove excess boric acid, followed by rinsing with methanol. Crystals in the form of tablets with yellow-green coloration were collected as a pure phase for Li[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O (LiUBO-1) which is confirmed by the powder diffraction of the sample. One day reactions are appropriate for screening product composition, but only lead to low isolated yields. The yield maximizes after three days at 59% based on U.

**Synthesis of Ag[(UO$_2$)$_2$B$_5$O$_8$(OH)$_2$] (AgUBO-1):** AgUBO-1 can be prepared using UO$_2$(NO$_3$)$_2$·6H$_2$O, boric acid, AgNO$_3$ at different Ag:U:B molar ratios of 1:1:8, 1:1:15, 1:1:22, 2:1:8, 2:1:15, 2:1:22, 3:1:15, 3:1:22 by following the similar procedure for making the LiUBO-1. The reaction duration is three days. Crystals in the form of tablets were isolated from all reactions. The crystals have light yellow coloration. Powder diffraction data from these samples all show AgUBO-1 as a pure phase in all eight reactions. The highest yield is 65% based on U for the 2:1:15 reaction.

**Synthesis of α-Cs[(UO$_2$)$_2$B$_{11}$O$_{16}$(OH)$_6$] (CsUBO-1) and β-Cs[(UO$_2$)$_2$B$_{11}$O$_{16}$(OH)$_6$] (CsUBO-2):** CsUBO-1 and CsUBO-2 can be prepared using UO$_2$(NO$_3$)$_2$·6H$_2$O, boric acid, CsNO$_3$ at different Cs:U:B molar ratios of 3:1:8, 3:1:15 by following the similar procedure
for making the LiUBO-1. When the reaction duration was three days, CsUBO-1 and CsUBO-2 both existed in these two reactions as minor products while $\beta$-UB$_2$O$_6$ was the major product. When the reaction time was increased to seven days, CsUBO-1 and CsUBO-2 both existed in the reaction as the major products while $\beta$-UB$_2$O$_6$ was the minor product. Crystals were in form of prisms and tablets with yellow-green coloration. The prism crystals were proved to be CsUBO-1, while the tablet crystals were CsUBO-2.

Crystallographic Studies: Single crystals of all four LiUBO, AgUBO, and CsUBO phases were mounted on glass fibers and optically aligned on a Bruker APEXII CCD X-ray diffractometer or a Bruker APEXII Quazar X-ray diffractometer using a digital camera. Initial intensity measurements were either performed using a $\mu$S X-ray source, a 30 W microfocused sealed tube (MoK$\alpha$, $\lambda$ = 0.71073 Å) with high-brilliance and high-performance focusing Quazar multilayer optics, or a standard sealed tube with a monocapillary collimator. Standard APEXII software was used for determination of the unit cells and data collection control. The intensities of reflections of a sphere were collected by a combination of four sets of exposures (frames). Each set had a different $\varphi$ angle for the crystal and each exposure covered a range of 0.5° in $\omega$. A total of 1464 frames were collected with an exposure time per frame of 10 to 30 s, depending on the crystal. SAINT was used for data integration including Lorentz and polarization corrections. Semi-empirical absorption corrections were applied using the program SADABS. Selected crystallographic data and bond distances information are listed in
Table 7.1. Atomic coordinates and additional structural information are provided in the Supplementary Material (Tables 7.S1-7.S4).

**Powder X-ray diffraction:** Powder X-ray diffraction patterns of the products of pure LiUBO and AgUBO reactions were collected on a Scintag theta-theta diffractometer equipped with a diffracted-beamed monochromatic set for Cu Kα (λ = 1.54056 Å) radiation at room temperature in the angular range from 10° to 80° (2θ) with a scanning step width of 0.05° and a fixed counting time of 1 s/step. The collected patterns were compared with those calculated from single crystal data using ATOMS.

**UV-vis-NIR and Fluorescence Spectroscopy:** UV-vis-NIR data were acquired from single crystals of all phases using a Craic Technologies microspectrophotometer. Crystals were placed on quartz slides under Krytox oil, and the data was collected from 200 to 1700 nm. Fluorescence data were obtained using 365 nm light for excitation (see Supporting Information).

**Second-harmonic Generation Measurements:** Powder second-harmonic generation (SHG) measurements were performed on a Kurtz-Perry nonlinear optical system. A Q-switched Nd:YAG laser (Continuum Surelite I-10), operated at 10 Hz, provided the 1064 nm light used for all measurements. The SHG intensity was recorded from a polycrystalline sample of LiUBO-1. No index of refraction matching fluid was used in these experiments. The SHG light at 532 nm was collected in reflection, selected by a narrow band-pass interference filter (Pomfret) and detected by a photomultiplier tube (RCA 1P28). A near normal incidence beam splitter reflected a small fraction of the laser beam onto a pyroelectric detector (Molelectron J3-05) that was used as a laser pulse.
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TABLE 7.1

CRYSTALLOGRAPHIC DATA FOR Li[\(\text{UO}_2\)\(\text{B}_5\text{O}_9\)]·H₂O (LIUBO-1), AG[\(\text{UO}_2\)\(\text{B}_5\text{O}_8\)(OH)₂] (AGUBO-1), A-CS[\(\text{UO}_2\)\(\text{B}_{11}\text{O}_{16}\)(OH)₆] (CSUBO-1), AND B-CS[\(\text{UO}_2\)\(\text{B}_{11}\text{O}_{16}\)(OH)₆] (CSUBO-2)
energy monitor. A digital storage oscilloscope (Tektronix TDS 640A) signal averaged and recorded both the SHG and incident laser energy signals. Average laser power was measured separately with a calibrated Scientech volume absorber calorimeter. As an important note for other investigators interested in the nonlinear optical properties of radioactive materials: The practice of grinding and sieving powders so that comparisons can be made with reference materials of similar particle size is unsafe. We ground and sieved a less-radioactive thorium compound inside a glovebox and then surveyed the interior of the glovebox. There was a uniform contamination of 50 dpm on every surface tested. We recommend discontinuation of this practice immediately. It is enough to say that there is or is not SHG activity. The magnitude is not important enough to risk the health of researchers.

7.4 Some Aspects of Actinyl Borate Syntheses

There are many factors that control the boric acid flux syntheses of uranyl borates. First, the stoichiometry of the starting materials controls the number of products in the reaction. Small changes in stoichiometry can give rise to substantially different products. The phase diagrams and syntheses tables for all uranyl borates are provided in the Supporting Information, and these data show that each cation behaves differently. Compared to most other ligand systems, the uranyl borate system is much more sensitive to changes in the size of the cations, and there are few isostructural compounds that exist if the cation is changed (only RbUBO-2 and KUBO-3). In the LiUBO system, LiUBO-1 can only be made in a narrow range of stoichiometries. For the
NaUBO and KUBO systems, each of the different stiochiometries tested yields new NaUBO and KUBO phases. For the NaUBO system, low Na:U ratio reactions give a larger number of phases, and the product with higher Na:U ratio can be made pure in higher Na:U ratio reactions. In contrast the KUBO system is more complicated. Products with lower K:U ratios can be made pure in lower K:U reactions, while products with higher K:U ratio can be made pure in higher K:U ratio reactions, between these extremes, there are always mixtures of products. For the RbUBO and CsUBO systems, which are very similar to the LiUBO system, the products can only be made in a narrow range of stoichiometry. For the AgUBO system, each of the different stiochiometries tested yields only one pure product. For TIUBO system, which is the most complicated we have studied, each of the different stiochiometries tested yields different numbers of products. Only high B:U ratio reactions can give a pure product, TIUBO-2.

All these results are based on short reaction times (24 h), but the reaction duration is another important factor in the preparation of uranyl borates. Longer reactions lead to higher yields, and in some cases also change the number of products. For example, for the Li, Rb, and Cs systems, reaction stoichiometries that do not give rise to desired products in 24 hours do eventually yield new products if the heating is prolonger for several more days.

7.5 Crystal Structures and Topological Aspects

The structures of the four compounds described in this work are based on similar uranyl borate motifs. The polyborate sheets are based on both BO$_4$ tetrahedra and BO$_3$
triangles. These sheets incorporate linear uranyl groups, UO$_2^{2+}$. As the result of such incorporation the uranium atoms have hexagonal bipyramidal coordination, UO$_8$. This coordination is relatively rare in U(VI) chemistry (85% of uranyl compounds contain pentagonal bipyramidal coordination), but all uranyl borates synthesized from molten boric acid contain this type of uranium coordination.$^{24-28}$ This coordination generally requires small chelating ligands, and the borate anions serve this purpose well. Each UO$_8$ unit is surrounded by three BO$_3$ triangles and six BO$_4$ tetrahedra in the sheets showed in Fig. 7.1. Between the polyborate sheets are cations of alkali elements and BO$_3$ triangles (Fig. 7.2). The dramatic differences between these compounds are realized in the interlayer space rather than in the uranyl borate sheets. The phases can be separated into two groups based on the topological features: 1 – Li[(UO$_2$)B$_5$O$_9$]·H$_2$O (LiUBO-1) and Ag[(UO$_2$)B$_5$O$_8$(OH)$_2$] (AgUBO-1); 2 – α-Cs[(UO$_2$)$_2$B$_{11}$O$_{16}$(OH)$_6$] (CsUBO-1) and β-Cs[(UO$_2$)$_2$B$_{11}$O$_{16}$(OH)$_6$] (CsUBO-2). We will consider the structural features of these phases in more detail.

**LiUBO-1 and AgUBO-1:** The crystal structure fragments of Li and Ag uranyl borates are shown on Fig. 7.2a and b, respectively. The structure of LiUBO-1 is a 3D framework based on polyborates sheets linked by BO$_3$ triangles. The topology of these sheets was previously found only in the structure of Rb$_2$[(UO$_2$)$_2$B$_{13}$O$_{20}$(OH)$_3$],$^{27}$ and we named these sheets as G-type. The sheets are strongly corrugated along the c axis. A similar sheet distortion was observed in the structure of the pure uranyl borate (UO$_2$)$_2$[B$_{13}$O$_{20}$(OH)$_3$]·1.25H$_2$O.$^{26}$ The unit cell of LiUBO-1 contains only one uranyl borate sheet, and all of them in this structure are in identical positions. The BO$_3$ linkers
Figure 7.1: Depiction of local structure of uranyl borate sheets in all compounds. (UO$_8$ hexagonal bipyramids are shown in yellow, BO$_3$ triangles in dark green, and BO$_4$ tetrahedra in light green.)
Figure 7.2: The crystals structures of Li[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O (a), Ag[(UO$_2$)$_2$B$_5$O$_9$(OH)$_2$] (b), α-Cs[(UO$_2$)$_2$B$_{11}$O$_{16}$(OH)$_6$] (c), β-Cs[(UO$_2$)$_2$B$_{11}$O$_{16}$(OH)$_6$] (d). UO$_8$ hexagonal bipyramids are shown in yellow, BO$_3$ and BO$_4$ units in green, Li and Ag cations in blue, Cs cations in pink, and water molecules in red.
interconnect the borate sheets leading to the formation of open cages. Lithium cations are located between two neighboring BO$_3$ triangles, and have the contacts with oxygen atoms from uranyl groups, polyborate net, and water molecules. The resulting coordination of lithium atoms can be described as a distorted tetragonal pyramid. The water molecules are in open cages and strongly bonded with lithium (1.94 Å) and with oxygen atoms from borate network.

The structure of AgUBO-$1$ is based on 2D layers. These layers consist of borate sheets with a topology identical with the sheet topology in LiUBO-$1$ (G-type), and flat BO$_3$ triangles are directed perpendicular to the plane of the sheets (Fig. 7.2b). The neighboring layers in the structure are rotated 180° with respect to each other. Ag$^+$ cations link the uranyl borate layers into a regular 3D structure. The oxygen environment of the Ag$^+$ cations is a deformed tetrahedron with bond lengths from 2.31 Å to 2.50 Å. It is interesting that in the Ag$^+$ - UO$_2^{2+}$ - H$_3$BO$_3$ system that only one phase forms, whereas in Na$^+$ - UO$_2^{2+}$ - H$_3$BO$_3$ system four phases with a different topology of polyborate sheets was observed. Typically silver and sodium uranyl compounds demonstrate a high level of similarity.

The relationship between the two structure types is schematically presented in Fig. 7.3. The skeletal representations of the Ag and Li structure types have been plotted in this figure. Here are shown only 2D and 3D borate nets without UO$_8$ polyhedra, alkali atoms, and water molecules (for Li structure) are shown. In order to transform the structures from the Ag-type to Li-type, we need to turn each second layer by 180° in the plane of the sheets (shown by red dashed arrow), and shift these layers by 1/2 of x and
Figure 7.3: Schematic representation of LiUBO-1 and AgUBO-1 structure type relationships.
1/3 of z translations. As a result of these manipulations the BO\(_2\)OH triangles (shown in red) will occupy positions very close to BO\(_3\)OH tetrahedra (shown in red). The condensation of these groups with concomitant water formation links the layers and yields a 3D structure. The resulting structure has free space within open cages for all water molecules that are formed as is found in LiUBO-1. It is possible that the structure formation of LiUBO-1 was followed in this way through layered precursors, which is typical for zeolites-like structures.\(^{33}\)

**CsUBO-1 and CsUBO-2:** The Cs\(^+\)-containing structures have same chemical compositions and very similar crystal structures (Fig. 7.2c,d). They are based on single asymmetrical 2D layers composed of BO\(_4\) tetrahedra, BO\(_3\) triangles, and UO\(_8\) hexagonal bipyramids. These layers can be separated into borate sheets and teeth-like fragments. These fragments are practically perpendicular to the sheet's plane and consist of two BO\(_3\) triangles with a B\(_2\)O\(_5\) stoichiometry. The terminal BO\(_3\) triangles in each B\(_2\)O\(_5\) group are disordered over two sites with equal occupancy. The reason for this effect is the splitting of the Cs atom positions that appear because of large size of free space between uranyl borate layers. The distance between cesium atoms positions is only \(~\)2.19 Å, and these positions are each half occupied. As the results of such splitting the real structures of CsUBO-1 and CsUBO-2 based on both BO\(_3\) and B\(_2\)O\(_5\) groups simultaneously presented in the interlayer space, because if cesium atom settled in nearest position to B\(_2\)O\(_5\) group this group should not have a terminal BO\(_3\) triangle. Cs\(^+\) cations link the two uranyl borate layers into quasi double layers. Because of the layer asymmetry the nature of bonding on the different sides of these layers is different. If
Cs⁺ cations provide mainly ionic bonds (Cs – O) on the other side of the layers strong hydrogen bonds are observed (O – O distances ~ 2.43 Å). In structures of CsUBO-1 and CsUBO-2 are logical continuations of α-Na[(UO₂)₂B₁₀O₁₅(OH)₅] and β-Na[(UO₂)₂B₁₀O₁₅(OH)₅] structure types evolution. The cesium structures adopt additional space (this space appears because of the increase in size of the interlayer cations) with the addition of BO₃ groups and formation of teeth-like fragments.

The topology of the borate sheets in CsUBO-1 and CsUBO-2 are the same with A/B topology types we found in structures of several borates. The main difference between α- and β-Cs[(UO₂)₂B₁₁O₁₆(OH)₆] is in topologies alternation. In Fig. 7.2c we can see sheets packed in the structure of α modification. It contains only B and B’ type sheets which regularly alternate, B/B’/B/B’. The β modification consists from both A and B type sheets (Fig. 7.2d). These types are combined within quasi doubled layers, B/B’/A/A’. Such differences in topology and packing provide the unit cell doubling along of c direction and orientation of content within quasi double layers (Cs atoms position and teeth-like fragments, Fig. 7.2d). The addition of the A type layers to the centrosymmetric (P̅1) structure of α-Cs[(UO₂)₂B₁₁O₁₆(OH)₆] makes the new structure of β-Cs[(UO₂)₂B₁₁O₁₆(OH)₆] noncentrosymmetric (Cc). We have previously observed this in several uranyl borates.

Some aspects of actinyl borate topologies: We have thus far reported 25 actinide borates including those in this chapter. All of these compounds contain linear actinyl groups (O=An=O) contained within borate sheets except the Th[B₅O₆(OH)₆][BO(OH)₂]-2.5H₂O (NDTB-1). The borate sheets play the role of a matrix which
incorporates linear actinyl groups in triangular pores. Our recent results demonstrate
that such borate sheets can have different types of topologies because of complicated
ordering of BO$_3$ and BO$_4$ groups within them. This level of topology could be described
as a “fine topology” – detailed topology within finite clusters. But as we demonstrated
in our previous works borate sheets can be modified by the addition of BO$_3$ and BO$_4$
fragments directed perpendicular to the sheets plane. The result of such modification is
several types of structural motifs in actinyl borates - single layers, doubled layers, and
3D frameworks where BO$_3$ and BO$_4$ play the role of 2D sheet linkers. This feature makes
groups of actinide borates unique in all of actinide chemistry. Here we would like to
systemize the hierarchy of the structural motifs in actinyl borates based on sheets.

The simplest actinyl structures based on layers are constructed from polyborate
sheet with one additional BO$_3$ triangular group. Schematically this structure type is
shown in left side of first line in Table 7.2. These layers are asymmetric and have
different types of bonding on different sides – ionic with cations from side where
triangles are, and strong hydrogen bonds on the opposite side. To describe these layers
in the form of simple record we use descriptor **1L-1-0-0** where **1L** – means single layer,
1-0-0 demonstrates the number of additional BO$_3$ and/or BO$_4$ groups up/down on the
layers (first two digits), and number of inter-sheet linkers in the case if structure based
on double layers (for single layers it is 0, if double layers linked via one boron based
groups its is 1 and etc. up to 3). If we add the one additional BO$_3$ group to make layers
symmetrical we will have **1L-1-1-0** type, which is shown in the second row. These
phases are quite different, but are all based on similar 2D polyborate sheets with
# TABLE 7.2

THE HIGH-LEVEL TOPOLOGY IN ACTINYL BORATES

<table>
<thead>
<tr>
<th>Type</th>
<th>Descriptor</th>
<th>Compounds</th>
</tr>
</thead>
</table>
| 1    | 1L-1-0-0   | \(\alpha\)-Na\([\text{UO}_2\text{B}_{10}\text{O}_{15}(\text{OH})_3]\)\(^{25}\)  \\
|      |            | \(\beta\)-Na\([\text{UO}_2\text{B}_{10}\text{O}_{15}(\text{OH})_3]\)\(^{25}\)  \\
|      |            | Na\([\text{UO}_2\text{B}_{10}\text{O}_{15}(\text{OH})_3]\cdot3\text{H}_2\text{O}\)\(^{25}\)  \\
|      |            | K\([\text{UO}_2\text{B}_{10}\text{O}_{15}(\text{OH})_3]\)\(^{27}\) |
| 2    | 1L-1-1-0   | Ag\([\text{UO}_2\text{B}_5\text{O}_8(\text{OH})_2]\)\(^{25}\)  \\
|      |            | \(\alpha\)-Tl\([\text{UO}_2\text{B}_5\text{O}_8(\text{OH})_2]\)\(^{25}\)  \\
|      |            | K\(_4\)[\text{NpO}_2\text{B}_{20}\text{O}_{36}(\text{OH})_2]\cdot2\text{H}_2\text{O}\)\([2\text{L}-1-1-0]\)_\(2\text{Np}\)\(^{24}\)  \\
|      |            | Ba\(_2\)[\text{NpO}_2\text{B}_{20}\text{O}_{36}(\text{OH})_2]\cdot4\text{H}_2\text{O}\)\([2\text{L}-1-1-0]\)_\(2\text{Np}\)\(^{24}\)  \\
|      |            | K\(_2\)[\text{NpO}_2\text{B}_{11}\text{O}_{16}(\text{OH})_2\text{N}\text{O}_3\text{O}_2]\cdot2\text{H}_2\text{O}\)\([2\text{L}-1-1-0]\)_\(2\text{Np}\)\(^{28}\) |
| 3    | 1L-2/1-0-0 | \(\alpha\)-Cs\([\text{UO}_2\text{B}_{11}\text{O}_{15}(\text{OH})_3]\)_\(2\text{Np}\)\(^{25}\)  \\
|      |            | \(\beta\)-Cs\([\text{UO}_2\text{B}_{11}\text{O}_{15}(\text{OH})_3]\)_\(2\text{Np}\)\(^{25}\) |
| 4    | 2L-0-0-1   | \(\alpha\)-\([\text{UO}_2\text{B}_9\text{O}_4(\text{OH})_4]\)_\(2\text{Np}\)\(^{26}\)  \\
|      |            | \(\beta\)-\([\text{UO}_2\text{B}_9\text{O}_4(\text{OH})_4]\)_\(2\text{Np}\)\(^{26}\)  \\
|      |            | \(\gamma\)-\([\text{UO}_2\text{B}_9\text{O}_4(\text{OH})_4]\)_\(2\text{Np}\)\(^{26}\) |
| 5    | 2L-1-1-1   | \(\beta\)-Tl\(_2\)[\text{UO}_2\text{B}_{11}\text{O}_{18}(\text{OH})_3]\)_\(2\text{Np}\)\(^{25}\) |
| 6    | 2L-0-0-2   | K\([\text{UO}_2\text{B}_{10}\text{O}_{16}(\text{OH})_3]\cdot2\text{H}_2\text{O}\)\(^{27}\)  \\
|      |            | Rb\([\text{UO}_2\text{B}_{10}\text{O}_{16}(\text{OH})_3]\cdot0.7\text{H}_2\text{O}\)\(^{27}\)  \\
<p>|      |            | Tl([\text{UO}<em>2\text{B}</em>{10}\text{O}_{16}(\text{OH})_3]\cdot2\text{H}_2\text{O})(^{25}) |
| 7    | 2L-1-1-2   | K(<em>2)[\text{UO}<em>2\text{B}</em>{12}\text{O}</em>{19}(\text{OH})_4]\cdot0.3\text{H}_2\text{O})(^{27}) |
| 8    | 2L-2/1-2/1-2 | Rb(<em>2)[\text{UO}<em>2\text{B}</em>{13}\text{O}</em>{20}(\text{OH})_5])(^{27}) |</p>
<table>
<thead>
<tr>
<th>Type</th>
<th>Descriptor</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>2L-1-1-3</td>
<td>(UO₂)₂[B₁₃O₂₀(OH)₃]·1.25H₂O.²⁶</td>
</tr>
<tr>
<td>10</td>
<td>F-1-1</td>
<td>Li[(UO₂)B₅O₉]·H₂O.</td>
</tr>
<tr>
<td>11</td>
<td>F-2-1</td>
<td>Tl₂[(UO₂)₂B₁₁O₁₉(OH)].²⁵</td>
</tr>
<tr>
<td>12</td>
<td>F-2-2</td>
<td>Na[(UO₂)B₆O₁₀(OH)]·2H₂O.²⁵</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PuO₂[B₈O₁₁(OH)]₄.²⁴</td>
</tr>
</tbody>
</table>
symmetrical perpendicular BO$_3$ groups. In the structures of neptunium phases 1L-1-1-0 single layers are linked via cation-cation interactions of neptunyl groups into double layers, and a 3D framework. The biggest cations require more space, and yield the possibility of 1L-2/1-0-0 single layer formation in Cs uranyl borates (2/1 – is an alternation of BO$_3$ and B$_2$O$_5$ groups). The simplest double layers in reviewing these groups have the 2L-0-0-1 descriptor, and are shown in row four of Table 7.2. These layers are realized only in simplest modifications of pure uranyl borates (three forms – α, β, and γ). The other layers are formed with additional BO$_3$ and/or BO$_4$ groups in the external and internal positions. The double layers in actinyl borates can have from one to two BO$_3$ groups in external positions, and from one to three BO$_3$ and/or BO$_4$ groups as linkers (internal positions). The complexity of the phases based on double layers increases with increasing of the U/B ratios. This is obvious from Table 7.2. The U/B ratio in the simplest phases with double layers is less than in all others – 1/4.5 (row 6). When the ratio increased to 1/6.5 we have very complicate phases based on double layers with B$_2$O$_5$ and B$_3$O$_7$ linkers and BO$_3$ and B$_2$O$_5$ external groups (rows 8 and 9). It is interesting that structural complexity is not dependent on monovalent metal cation sizes.

For describing frameworks based on 2D sheets we used similar descriptors. In these descriptors the first letter has been changed from L to F (framework) and last digit was eliminated because frameworks do not have external positions (all are internal). The simplest framework realized in the discussed above is the Li uranyl borate. In this structure 2D borate sheets are linked by single BO$_3$ groups and the descriptor is F-1-1. If
one BO₃ group is added from only one side the F-2-1 structure is realized. Such a structure type was found in Tl₂[(UO₂)₂B₁₁O₁₉(OH)] (row 11). The symmetric framework with F-2-2 descriptor was realized in Na[(UO₂)B₆O₁₀(OH)]·2H₂O and PuO₂[B₈O₁₁(OH)₄] where the last phase demonstrated largest ration An/B – 1/8.

The approach to high-level topology presentation described above is easily modified and can be applied to various actinyl phases which have similar structural features.

7.6 Nonlinear Optical Properties

**LiUBO-1** crystallizes in the noncentrosymmetric space group *Pn*, and can be obtained as a pure phase. This space group is also polar, and this being the case the compound is capable of exhibiting a wide range of physical properties include the second-harmonic generation of light when irradiated with a laser. Indeed when a polycrystalline sample of LiUBO-1 is irradiated with 1064 nm light, 532 light is clearly observed as shown in Fig. 7.4.

7.7 Fluorescence Properties

The term “fluorescence” was created in the 18th century to describe the green glow from uranyl salts that occurs when natural light irradiates them. This emission is in fact highly complex and is strongly vibronically-coupled charge-transfer emission. Emission from uranyl compounds has been carefully and extensively studied, especially by Denning and co-workers who assigned all of the vibronic transitions from single
Figure 7.4: Second-harmonic generation of 532 nm laser light from 1064 nm laser light getting from a polycrystalline sample of LiUBO-1.
crystals containing the \([\text{UO}_2\text{Cl}_4]^{2-}\) anion.\(^{34}\) While five broad features centered near 520 nm are generally observed for uranyl compounds at room temperature, far more bands are resolved at low temperatures.

Li\([(\text{UO}_2)\text{B}_5\text{O}_9]\cdot\text{H}_2\text{O} \, (\text{LiUBO-1}),\ \alpha\text{-Cs}\([(\text{UO}_2)_2\text{B}_{11}\text{O}_{16}(\text{OH})_6] \, (\text{CsUBO-1}),\ \text{and } \beta\text{-Cs}\([(\text{UO}_2)_2\text{B}_{11}\text{O}_{16}(\text{OH})_6] \, (\text{CsUBO-2})\) all form crystals with the pale yellow-green coloration. Upon irradiation with 365 nm light, these crystals fluoresce with sufficient intensity that the emission from a few crystals is easily observed by the naked eye. The fluorescence spectra are all provided in the Supporting Information, and given that all of the uranyl borates contain very similar site symmetry around the uranium atoms \((D_{6h})\), it is not surprising that there are little differences among these data. However, Ag\([(\text{UO}_2)\text{B}_5\text{O}_8(\text{OH})_2] \, (\text{AgUBO-1})\) forms crystals with light yellow coloration, and these crystals do not show any fluoressce signal upon the 365 nm irradiation. It is expected that the Ag\(^{+}\) quenches the fluoressce feature from the uranyl units. Thallium also quenches the fluorescence in all of the thallium uranyl borates.

7.8 Conclusions

Our original interest in actinide borates stemmed from their potential formation in vitrified nuclear waste, and in fact, some of these phases are of sufficient thermal stability that they might form in molten borosilicate glasses.\(^{24,25}\) Such compounds may also be produced as vitrified waste is altered on a geologic time-scale in a nuclear waste repository. However, it became immediately clear on a more fundamental level that actinide borates were structurally unique among actinide oxoanion families. The
complexity of the polyborate sheets and frameworks is unparalleled, and of equal importance the family is dominated by the formation of acentric structures. We have developed syntheses that lead to the formation of pure crystalline phases, and these compounds show nonlinear optical properties, and most of them also fluoresce. While we think it is unlikely uranyl borates will be used as nonlinear optical materials, the principles learned about the structures of these materials may instruct us in how to prepare non-radioactive analogs that are truly useful in this application. This report completes the series of uranyl borates with common monovalent cations, and we have developed a simple graphical representation for organizing these complex materials.

7.9 Reference


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CHAPTER 8:
INCORPORATION OF IODATE INTO URANYL BORATE AND ITS IMPLICATION FOR THE IMMOBILIZATION OF $^{129}$I IN NUCLEAR WASTE REPOSITORIES

8.1 Abstract

A series of uranyl borates, $\text{UO}_2\text{B}_2\text{O}_4$, $\text{Na}[(\text{UO}_2)\text{B}_6\text{O}_{10}(\text{OH})_3] \cdot 2\text{H}_2\text{O}$, and $\text{K}_2[(\text{UO}_2)\text{B}_{12}\text{O}_{19}(\text{OH})_4] \cdot 0.3\text{H}_2\text{O}$, with different topologies have been prepared and tested for the incorporation of iodate, one of the chemical forms that $^{129}$I should have in nuclear waste. Laser ablation ICP-MS was used to determine the iodine content in single crystals of the three different uranyl borates. Iodine levels can be greater than 3200 ppm in crystals synthesized in the presence of iodate. The intercalation of iodic acid is one possible mechanism for iodate uptake in these solids.

8.2 Introduction

Borosilicate glasses are being used as a long-term storage material for containing used nuclear fuel and other nuclear wastes. These glasses are of different compositions and include R7T7, AVM, VRC, SNO8, and SM513$^{1-3}$. In order to evaluate the performance of repositories in the long term, it is necessary to study the corrosion behavior of nuclear waste. Alteration phases are expected to form during the corrosion of waste glass$^{4-7}$ and used nuclear fuel$^{8-12}$. Uranyl borates may form during the cooling
and storage of borosilicate glasses containing nuclear waste. They may also form as alteration products. A series of actinide borates have recently been prepared by a facile route in enabling subsequent physical property measurements 13–17.

Burns et al. 18 and Chen et al. 19 predicted the possibility that actinides and selenium could be incorporated into the alteration uranyl phases in trace quantities, which might be a mechanism for immobilizing 79Se. Several experimental studies have confirmed that 237Np can be incorporated into uranyl silicates, hydroxides, and phosphates 20–26. Owing to its long half-life and bioavailability, 129I is a radionuclide of special concern in repositories. Our previous studies have shown that 129I can be incorporated into a uranyl silicate and three uranyl phosphate in the form of iodate 27, 28. Recently, we reported the coupled substitution of Np5+ and iodate into a uranyl phosphate 29. Since uranyl borates might form or be initially present in a repository 13–17, iodine uptake by these compounds is of interest. Therefore, the uptake of iodate during the formation of three typical uranyl borates, UO$_2$B$_2$O$_4$ (UB), Na[(UO$_2$)$_3$B$_6$O$_{19}$]$\cdot$2H$_2$O (NaUB) and K$_2$[(UO$_2$)$_3$B$_{12}$O$_{19}$]$\cdot$0.3H$_2$O (KUB) under mild hydrothermal conditions was investigated.

8.3 Experimental Section

*Synthesis:* UO$_2$(NO$_3$)$_2$$\cdot$6H$_2$O (98%, International Bio-Analytical Industries), H$_3$BO$_3$(99.99%, Alfa-Aesar), NaNO$_3$(99.3%, Fisher), KNO$_3$(99.3%, Fisher), and HIO$_3$(99.5%, Alfa-Aesar) were used as received without further purification. Distilled and Millipore filtered water with resistance of 18.2 MΩ·cm was used in all reactions. PTFE-
lined autoclaves were used for all reactions. **Caution! While the UO$_2$(NO$_3$)$_2$·6H$_2$O used in this study contained depleted U, there is really not much difference between depleted uranium and natural abundance uranium, and standard precautions for handling radioactive materials should be followed at all times. There are very old sources of uranyl nitrate that may not be depleted, and enhanced care is warranted for these samples.**

UO$_2$B$_2$O$_4$ (UBO-1), Na[(UO$_2$)$_2$B$_6$O$_{10}$(OH)$_3$]·2H$_2$O (NaUB), and K$_2$[(UO$_2$)$_2$B$_{12}$O$_{19}$(OH)$_4$]·0.3H$_2$O (KUB) were synthesized using the methods of Wang et al. with molar ratios of B : U = 8 : 1 in UB, Na : B : U = 5 : 15 : 1 in NaUB and K : B : U = 5 : 15 : 1 in KUB. All autoclaves were sealed and heated to 190 °C in a box furnace for 2 days.

**Incorporation of Iodate into Uranyl Borate:** In order to compare iodate uptake results from crystals grown in the presence of iodate versus those that are added back into iodate solutions, two different experiments were designed as follows: (1) UB, NaUB, and KUB were synthesized in the presence of HIO$_3$ with the U:I molar ratio of 20:1 and 10:1, and labeled as UB1, UB2, NaUB1, NaUB2, KUB1 and KUB2. (2) 0.0050 g, 0.0350 g and 0.0053 g of pure UB, NaUB and KUB were reacted with suitable amount of boric acid and iodic acid solutions under mild hydrothermal condition. The stoichiometric ratios of uranium to iodate in all reactions were kept as 20:1 and 10:1. The samples were labeled as UB3, UB4, NaUB3, NaUB4, KUB3 and KUB4, respectively. The iodate incorporated samples were washed and dried using the same method as previous described. $^{127}$I was used as an analogue for $^{129}$I in this study.
Powder X-ray Diffraction: Power X-ray diffraction patterns of all products were collected on a Scintag $\theta$-$\theta$ diffractometer equipped with a diffracted-beammed monochromatic set for Cu Kα ($\lambda=1.54056$ Å ) radiation at room temperature in the angular range from 5° to 80°(2θ) with a scanning step width of 0.05° and a fixed counting time of 1 s/step.

Crystallographic studies: Single crystals of all samples were selected and mounted on glass fibers with epoxy and aligned on a Bruker APEXII Quazar CCD X-ray diffractometer with a digital camera to determine unit cell parameters. The unit cells of iodine incorporated samples were checked prior to Laser-Ablation Inductively Coupled Plasma Mass Spectrometer (LA-ICPMS) analysis.

Laser-Ablation Inductively Coupled Plasma Mass Spectrometer (LA-ICP-MS) Analysis: Laser ablation analysis of single crystals from the three samples were conducted using a ThermoFinnigan high resolution magnetic sector Element2 ICP-MS instrument coupled to a UP213 Nd:YAG laser ablation system (New Wave Research). Selected crystals were fixed on 1-inch glass slides with double-sided tape. Individual analyses consisted of a 60 seconds measurement of background ion signals followed by a 60 seconds interval of measurement of ion signals subsequent the start of lasering. Each analysis represents a total of 93 scans (93 runs x 1 pass) with a sample (dwell) time of 0.01 second with 20 samples per ion signal peak. Analyses were conducted in medium mass resolution mode (Resolution = Mass/Peak Width $\sim$4,000) in order to eliminate possible spectral interferences. The ablated particles were transported from the ablation cell to the ICP-MS instrument using He carrier gas at a flow rate of 0.7
L/min. Crystals were ablated using a range of spot size between 40 to 55μm, repetition rate of 2 Hz and 70% power output corresponding to an energy density of 12-15 J/cm2. And in these conditions, the depth of penetration of the laser is between 5 to 15 microns. Because of the high content of $^{238}\text{U}$ in the crystals, $^{235}\text{U}$ was chosen to determine the ratios, and the total uranium content was calculated according to the abundance of $^{235}\text{U}$ in depleted uranium. Based on the known U content in UB, NaUB and KUB, the iodine concentrations were estimated on the basis of the ratios of the counts for I/U.

8.4 Structures Descriptions

The structures of UB, NaUB, and KUB are shown in Fig. 8.1. UB is light yellow and NaUB is yellow-green, and their structures have been reported recently by Wang et al. UB is composed of (BO$_2$)$_1$∞1D zigzaglike chains and UO$_8$ hexagonal bipyramids via edge-sharing to form 2D layer. It is remarkable that there are no cations or water molecules between the sheets (Fig.8.1a), thus these sheets are held together only by van der Waals forces. KUB is based on double, negatively charged layers united in regular 3D structure by potassium cations distributed in the interlayer space. It is interesting that KUB has a yellow-green color and the crystals adopt a triangular habit. The color does not change when iodine is incorporated into the structure. The basic structure of NaUB is composed of uranyl bipyramids, BO$_3$ and BO$_4$ polyhedra, which is similar to KUB. However, each uranyl cation in NaUB was surrounded by B$_9$O$_{24}$ to form [(UO$_2$)(B$_9$O$_{10}$)(OH)]$^{-}$ framework which is not found in UB and KUB. Na$^+$ cations and
Figure 8.1: General views of the structure of UB (a), KUB (b) and NaUB (c). UO$_8$ hexagonal bipyramids are shown in green, BO$_3$ units in pink, BO$_4$ units in purple, K and Na cations in black and O anions in red.
water were found within the pores of framework \textsuperscript{16}. The detailed structures of UB, NaUB, and KUB have been reported by Wang \textit{et al.} \textsuperscript{15-17}.

8.5 Chemical Phases

The XRD patterns of all products were shown in Fig. 8.2. The patterns of samples synthesized in iodate-free systems are identical to those reported by Wang \textit{et al.} \textsuperscript{15-17} for UBO, NaUB, and KUB, respectively, indicating that pure phases of these compounds were obtained. On the other hand, when iodate was present, some undesired phases were observed in UB1, UB2, and KUB4 and were analyzed using electron microscope and single crystal XRD. Sample UB1 consists of UO\textsubscript{2}B\textsubscript{2}O\textsubscript{4} and uranyl iodate, UO\textsubscript{2}(IO\textsubscript{3})\textsubscript{2}(H\textsubscript{2}O), while samples UB2 and KUB4 are pure uranyl iodate, which indicates that iodate is a strong ligand that may substitute for borate in uranyl phases if the structure is feasible. The presence of UO\textsubscript{2}(IO\textsubscript{3})\textsubscript{2}(H\textsubscript{2}O) was identified using electron microscope and single crystal XRD. The unit cell parameters of each crystal were listed in Table 8.1.

\begin{table}[h]
\centering
\caption{Crystallographic information of UB, NaUB, KUB and uranyl iodate}
\begin{tabular}{lcccccccc}
\hline
Sample & Color & \(a(\text{Å})\) & \(b(\text{Å})\) & \(c(\text{Å})\) & \(\beta(\degree)\) & \(V(\text{Å}^3)\) & Space group & Reference \\
\hline
UB & Yellow & 10.46 & 4.19 & 15.63 & 109.77 & 231.81 & C\text{2} & (13) \\
NaUB & Yellow & 6.39 & 11.14 & 15.99 & 92.77 & 1136.7 & Cc & (14) \\
KUB & Yellow-green & 6.43 & 6.43 & 47.43 & 120 & 1699.8 & P\text{3}1\text{2} & (29) \\
Uranyl iodate & Yellow & 8.45 & 7.71 & 12.27 & 90 & 799.3 & P\text{bcn} & (32) \\
\hline
\end{tabular}
\end{table}
8.6 LA-ICP-MS

LA-ICP-MS is well-suited for in situ chemical analysis of trace element in small crystals, and hence was used to detect the incorporated iodine within the synthesized uranyl borate crystals. Our previous studies have shown that this method can supply information on the chemical makeup of crystals at high spatial resolution (≈ 50 μm wide at surface and ≈ 15 μm depth; Fig. 8.3). Obviously, such information cannot be
Figure 8.2: Powder X-ray patterns of UB, KUB and NaUB and the iodate incorporated samples.
Figure 8.3: Photomicrograph of KUB crystal before (a) and after (b) laser ablation.
obtained by bulk sample digestion and subsequent solution mode analysis. As shown in the time-resolved laser ablation spectrum (Fig. 8.4), background ion signals are very low and smooth prior the start of lasering. Subsequent lasering, $^{127}$I ion signals were detected, in particular for crystals UB1 and UB4 (Fig. 8.4) indicating that iodine was incorporated into these crystals. The average molar I/U ratios and the calculated iodine concentrations are listed in Table 8.2.

Samples UB2 and KUB4 are pure uranyl iodate phases and thus were not analyzed by LA-ICP-MS. For the analysis of the uranyl borates, single crystals were hand-picked carefully using a binocular microscope and verified with single XRD. Generally, the incorporated iodine in UB ranges from 253.19 ppm to 3211.38 ppm, contrasting with 0.33 ppm to 4.60 ppm in KUB.

As is discussed in our previous study, IO$_3^-$ trigonal pyramid could substitute for PO$_4^{3-}$ tetrahedron if there is a terminal oxygen in PO$_4^{3-}$ [28, 29]. If this rule can be used in uranyl borates, the iodine concentration in KUB should be much higher than that in UB because KUB has terminal oxygen in BO$_3$ polyhedra. Based on the LA-ICPMS data, it is unlikely that BO$_3$ polyhedra are substituted for by IO$_3^-$ anions. The trace amount of iodine in KUB samples may be contributed by iodine inclusion, or intercalated between the layers. Generally, anions with similar valences and geometries can easily substitute for one another, such as (IO$_4^-$(OH$^-$)$_2$ $\leftrightarrow$ (SiO$_4$OH)$_3^-$ and IO$_3^-$ $\leftrightarrow$ HPO$_4^{2-}$ [27, 28]. However, the length of I–O bond range between 1.77 Å and 1.86 Å and is much longer than the B–O bond (1.36–1.49 Å). This may therefore account for the very limited substitution between IO$_3^-$ and BO$_3$ or BO$_4$ polyhedra UO$_2$(IO$_3$)$_2$·2H$_2$O+2HIO$_3$ $\rightarrow$ UO$_2$(IO$_3$)$_2$·2H$_2$O·2HIO$_3$.
Figure 8.4: Typical LA-ICP-MS spectrum for UB1, UB4, NaUB2 and KUB2. $^{127}\text{I}$ was shown in open circle and $^{235}\text{U}$ in square.
# TABLE 8.2

**CONCENTRATION OF IODINE IN URANYL BORATE**

<table>
<thead>
<tr>
<th>Sample</th>
<th>I/U (molar)</th>
<th>Iodine (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB1</td>
<td>0.01464±0.00476</td>
<td>5227.23±1699.98</td>
</tr>
<tr>
<td></td>
<td>0.00680±0.00219</td>
<td>2428.77±783.55</td>
</tr>
<tr>
<td></td>
<td>0.00109±0.00033</td>
<td>390.88±116.87</td>
</tr>
<tr>
<td></td>
<td>3.95E-5±2.34E-5</td>
<td>14.12±8.36</td>
</tr>
<tr>
<td>UB3</td>
<td>0.00188±0.00053</td>
<td>671.77±190.33</td>
</tr>
<tr>
<td></td>
<td>0.00021±9.1E-5</td>
<td>73.67±32.33</td>
</tr>
<tr>
<td></td>
<td>0.01408±0.00420</td>
<td>5028.46±1498.42</td>
</tr>
<tr>
<td></td>
<td>0.00446±0.00073</td>
<td>1592.72±260.50</td>
</tr>
<tr>
<td></td>
<td>0.00844±0.00144</td>
<td>3012.72±513.67</td>
</tr>
<tr>
<td>UB4</td>
<td>4.43E-6±3.53E-6</td>
<td>1.00±1.26</td>
</tr>
<tr>
<td></td>
<td>1.16E-08±5.9E-8</td>
<td>0.004±0.02</td>
</tr>
<tr>
<td>KUB1</td>
<td>1.84E-05±7.60E-6</td>
<td>4.19±2.72</td>
</tr>
<tr>
<td></td>
<td>1.06E-05±5.85E-6</td>
<td>2.42±2.09</td>
</tr>
<tr>
<td></td>
<td>3.18E-05±1.21E-5</td>
<td>7.19±4.31</td>
</tr>
<tr>
<td>KUB2</td>
<td>9.37E-06±5.32E-6</td>
<td>2.12±1.90</td>
</tr>
<tr>
<td></td>
<td>6.98E-06±3.60E-6</td>
<td>1.58±1.29</td>
</tr>
<tr>
<td></td>
<td>9.96E-07±2.28E-6</td>
<td>0.22±0.81</td>
</tr>
<tr>
<td>KUB3</td>
<td>3.16E-06±2.98E-6</td>
<td>0.70±1.07</td>
</tr>
<tr>
<td></td>
<td>1.47E-07±7.04E-7</td>
<td>0.03±0.25</td>
</tr>
<tr>
<td></td>
<td>8.18E-07±7.09E-7</td>
<td>0.18±0.25</td>
</tr>
<tr>
<td>NaUB1</td>
<td>3.16E-06±2.98E-6</td>
<td>0.70±1.07</td>
</tr>
<tr>
<td></td>
<td>1.24E-05±6.48E-6</td>
<td>2.77±2.31</td>
</tr>
<tr>
<td></td>
<td>0.00700±0.00035</td>
<td>155.84±126.41</td>
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<tr>
<td></td>
<td>0.00206±0.00094</td>
<td>458.13±336.20</td>
</tr>
<tr>
<td></td>
<td>0.00013±6.15E-5</td>
<td>28.44±21.96</td>
</tr>
<tr>
<td></td>
<td>0.00011±5.44E-5</td>
<td>25.44±19.43</td>
</tr>
<tr>
<td>NaUB2</td>
<td>7.82E-06±4.15E-6</td>
<td>1.74±1.48</td>
</tr>
<tr>
<td></td>
<td>4.70E-06±3.70E-6</td>
<td>1.05±1.32</td>
</tr>
<tr>
<td></td>
<td>4.45E-06±3.55E-6</td>
<td>0.99±1.26</td>
</tr>
<tr>
<td>NaUB3</td>
<td>1.10E-05±5.56E-6</td>
<td>2.44±1.99</td>
</tr>
<tr>
<td></td>
<td>1.81E-06±8.73E-7</td>
<td>0.40±0.31</td>
</tr>
<tr>
<td></td>
<td>6.63E-07±9.05E-7</td>
<td>0.15±0.32</td>
</tr>
</tbody>
</table>
in uranyl borates. Ling and Albrecht-Schmitt demonstrated the intercalation of iodic acid into the layered uranyl iodate to yield \( \text{UO}_2(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{HIO}_3 \) in crystalline form, and the reaction was described by the following equation \(^{33}\). As described above, there is no direct linkage between adjacent sheets, which are held together only by van der Waals forces. In addition, the interlayer space within UB is about 2 Å, which is large enough for the emplacement of \( \text{HIO}_3 \) molecules. Thus, the intercalation mechanism of iodate into UB is expected, which accounts for the substantial iodine detected in samples UB1, UB3 and UB4. The intercalation of \( \text{HIO}_3 \) into UB layers can be described as follows.

\[
\text{UO}_2\text{B}_2\text{O}_4 + n\text{HIO}_3 \rightarrow \text{UO}_2\text{B}_2\text{O}_4 \cdot n\text{HIO}_3 \ (n \ll 1)
\]

According to the experiments conducted by Ling and Albrecht-Schmitt, when large excess iodic acid is present, \( \text{UO}_2(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O} \) will transform into a new structure, \( \text{UO}_2(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{HIO}_3 \) \(^{33}\). In this study, pure uranyl borate (UB2) was synthesized when U: I ratio at 10:1, but phase transformation did not occur in UB4 when UB reacted with iodate-bearing solution under similar conditions.

The iodine ion signals within KUB and NaUB are concentrated within a few seconds of the ablation interval; a feature that is characteristic of when ablating crystals containing inclusions. As the laser hits an iodine-containing inclusion, the mass spec records some iodine and the remaining part of the interval is blank. This is precisely what is shown in the time-resolved spectra.

In the reported iodate substitution, both the SiO\(_4\) and PO\(_4\) polyhedra are isolated with other SiO\(_4\) or PO\(_4\) polyhedra \(^{27-29}\). In contrast, the BO\(_3\) or BO\(_4\) polyhedra in KUB and NaUB structure are connected to other BO\(_3\) or BO\(_4\) polyhedra to form framework. And in UB the BO\(_3\) polyhedra are connected to other BO\(_3\) to form \((\text{BO}_2)_{1\infty} \) zigzag-like
chains. Thus, the substitutions of \(\text{IO}_3 \leftrightarrow \text{BO}_3\) or \(\text{IO}_3 \leftrightarrow \text{BO}_4\) will disrupt the structural connectivity and are unlikely to occur.

8.7 Implication for the Immobilization of \(^{129}\text{I}\) in Nuclear Waste Repositories

One of the structural characteristics of \(\text{UO}_2(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O}\) and \(\text{UO}_2\text{B}_2\text{O}_4\) is that the space between the sheets is empty, which is easily filled by other neutral molecules. In this case, the intercalated molecule is \(\text{HIO}_3\). As shown in Fig. 8.5, the structure of rutherfordine, \(\text{UO}_2\text{CO}_3\) \(^{34}\), as well as \(\text{UO}_2\text{SeO}_3\) \(^{35}\), and \(\text{UO}_2\text{TeO}_3\) \(^{36}\) also have unoccupied spaces between the sheets. Considering the similarity of the structure, the intercalation of iodic acid into the layers of \(\text{UO}_2\text{CO}_3\), \(\text{UO}_2\text{SeO}_3\), \(\text{UO}_2\text{TeO}_3\) and other similar structures is also expected, but experimental investigation is required. Therefore, intercalation may be a plausible mechanism for immobilizing \(^{129}\text{I}\) in nuclear waste repositories.

8.8 Conclusions

As one of the forms for disposing of high level waste, borosilicate glass is very important for immobilizing the radionuclides in repositories. Uranyl borate may be initially present or form during the long-term storage and subsequent alteration. According to the differences of bond distances between \(\text{IO}_3\) and \(\text{BO}_3\) and different geometry, it is unlikely that \(\text{IO}_3\) will substitute for \(\text{BO}_3\) polyhedra in uranyl borates. Furthermore, \(\text{IO}_3\) units will not substitute for \(\text{BO}_4\) based on the LA-ICP-MS results. The trace iodine found in KUB and NaUB should be contributed by iodine inclusion while iodine may intercalate in significant level into layered UB in the form of iodic acid. It is
Figure 8.5: Views of the structure of UO$_2$(IO$_3$)$_2$(H$_2$O) (a), UO$_2$CO$_3$ (b), UO$_2$SeO$_3$ (c) and UO$_2$TeO$_3$ (d). UO$_8$ hexagonal bipyramids are shown in green, Se and Te in blue and O in red.
expected that iodic acid can also incorporate into the interlayers of some layered structures such as UO$_2$CO$_3$, UO$_2$SeO$_3$, and UO$_2$TeO$_3$.

8.9 Reference


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CHAPTER 9:

NEPTUNIUM DIVERGES SHARPLY FROM URANIUM AND PLUTONIUM IN CRYSTALLINE BORATE MATRIXES: INSIGHTS INTO THE COMPLEX BEHAVIOR OF THE EARLY ACTINIDES RELEVANT TO NUCLEAR WASTE STORAGE

9.1 Abstract

A large family of uranium, neptunium, and plutonium borates was synthesized via molten boric acid flux reactions. Uranium and plutonium borates were determined to be in hexavalent and very similar with each other, while neptunium borates contrast sharply and are intermediate- or mixed-valent compounds with three different oxidation states as determined using single crystal X-ray diffraction, bond-valence sum calculations, magnetism, and UV-vis-NIR spectroscopy.

9.2 Introduction

The immobilization of actinides, such as neptunium and plutonium, in solid matrixes is being used as an approach for preventing their release into the environment during long-term storage. Many waste forms have been suggested as being suitable for this including zircon, garnet, pyrochlore, synroc, and monazite, and there is an ongoing debate concerning the best waste form for actinides. Among the earliest and most widely utilized solids for the storage and transport of actinides are borosilicate glasses.
Some of these glasses are phase segregated and are really glasses-in-glasses (e.g. Vycor® types) where there is a silica portion and a sodium borate portion. Ironically, some of these glasses have been tested as a safe transportation form for $^{237}$Np because their ease of releasing this radionuclide upon contact with acidic media.\textsuperscript{6}

It has been recognized that both processing techniques and high actinide content in the glasses can lead to the formation of crystalline products within these glasses.\textsuperscript{6} These original glasses. Despite the importance of understanding the chemical nature of these crystals, very little is known about crystalline transuranium borates. In fact, there is not a single example present in crystallographic databases. In an effort to begin the process of understanding structure-property relationships in uranium, neptunium, and plutonium borates relevant to the development of advanced waste forms for the long-term storage of these radionuclides, we have prepared a large family of U(VI) borates, several highly unusual intermediate- or mixed-valent neptunium compounds, and a Pu(VI) borate that differs in bonding from its U(VI) counterparts.

9.3 Experimental Section

0.037 M stock solutions of $^{237}$Np(VI) nitrate or $^{242}$Pu(VI) nitrate were prepare by first digesting NpO$_2$ or PuO$_2$ in 8M HNO$_3$ for 3 days at 200 °C (in an autoclave). The solutions were reduced to moist residues and redissolved in water. For plutonium, the solution was then ozonated for approximately 5 hours to ensure complete oxidation of the plutonium to +6. UV-vis-NIR spectroscopy indicates that only Pu(VI) is present. Np(V) stock solutions were prepared via reduction with nitrite, followed by precipitation
with hydroxide, washing, and dissolution in dilute HCl. Standard precautions were performed for handling radioactive materials during work with uranium. \(^{237}\)Np \((t_{1/2} = 2.14 \times 10^6 \text{ y})\) and \(^{242}\)Pu \((t_{1/2} = 3.76 \times 10^5 \text{ y})\) represents a serious health risks owing to their \(\alpha\) and \(\gamma\) emission. All studies with neptunium and plutonium were conducted in a lab dedicated to studies on transuranium elements. This lab is equipped with a HEPA filtered hoods and negative-pressure gloveboxes. A series of counters continually monitor radiation levels in the lab. The lab is licensed by the Nuclear Regulatory Commission. All experiments were carried out with approved safety operating procedures. All free-flowing solids are worked with in gloveboxes, and products are only examined when coated with either water or Krytox oil and water.

9.4 Synthesis Discussion

Actinide borates are difficult to prepare by traditional methods in general because water competes very successfully for inner-sphere coordination sites with borate for these metals under most conditions. In fact, many borates that occur naturally are found in evaporate deposits in arid regions.\(^7\) This synthetic challenge can be overcome by either removing water entirely from the system in high-temperature solid-state reactions\(^8-13\) or slow evaporations,\(^14\) or by reducing the dielectric constant of water by heating to create hydrothermal conditions. We were interested in studying high-valence actinides, either An(VI) or An(V) \((\text{An} = \text{U, Np, Pu})\) initially, and therefore avoided the potentially thermally reducing conditions of high-temperature solid-state reactions, and diminished the potential for radiolytic reduction of the neptunium or plutonium in
slow evaporation crystallizations that can take months to occur. Instead, we utilized a boric acid flux as the reaction medium by adding excess boric acid and various alkali metal or alkaline-earth nitrates to small droplets (ca. 5-20 uL) of 1.8 M Np(V), Np(VI), or Pu(VI) chloride or nitrate. Much larger scale (ca. 1 g) reactions were performed with uranium using a similar methodology. After three days of heating at approximately 220 °C in an autoclave followed by cooling, a single translucent crystalline mass was isolated. Within this mass, crystals were observed for all actinides studied. These crystals were freed from the matrix by the addition of hot water, which dissolved the excess boric acid flux, but even with repeated washing leaves the crystals unaltered. Single crystal and powder X-ray diffraction and spectroscopic measurements of these crystals then ensued.

9.5 Uranium Borates

The uranyl borates prepared thus far number in excess of twenty. We have selected one of these for this discussion, Na[(UO$_2$)$_6$B$_6$O$_{10}$(OH)]·2H$_2$O.$^{15}$ Despite the complexity of this large family there is a single fundamental building unit that exists for all of these compounds; that of a linear uranyl, UO$_2$,$^{2+}$, cation surrounded by nine borate anions. This topology is substantially different from the topology observed when other triangular anions (e.g. carbonate) are combined with uranyl cations.$^{16}$ The borate anions, which occur as both BO$_3$ and BO$_4$ polymerized units bridge between uranyl cations to create layers as shown in Fig. 9.1a. Additional BO$_3$ units extend perpendicular to these layers, and link the layers together into a polar three-dimensional framework.
Figure 9.1: Views of the uranyl (a), neptunyl (b), and plutonyl (c) layers found in Na(UO$_2$)[B$_6$O$_{10}$(OH)$_2$]-2H$_2$O, K$_4$(NpO$_2$)$_{6.73}$B$_{20}$O$_{36}$(OH)$_2$, and PuO$_2$[B$_{8}$O$_{11}$(OH)$_4$] showing the hexagonal bipyramidal environments around the An(VI) (An = U-yellow, Np-green, Pu-orange) as well as the BO$_3$ triangles (blue) and BO$_4$ tetrahedra (purple).
with relatively large channels to house the Na\(^+\) cations and the water molecules (Fig. 9.5). Despite the open-framework nature of this compound it shows good thermal stability, loosing water at 180 °C, and remaining intact until 500 °C.

9.6 Neptunium Borates

The behavior of neptunium contrasts substantially with that of uranium. Two neptunium borates have been prepared that differ essentially only in their interlayer cations. The structures of K\(_4\left(\text{NpO}_2\right)_{6.73}\text{B}_{20}\text{O}_{36} \left(\text{OH}\right)_{2}\) and Ba\(_2\left(\text{NpO}_2\right)_{6.59}\text{B}_{20}\text{O}_{36} \left(\text{OH}\right)_{2}\cdot\text{H}_2\text{O}\) are extraordinary in all regards.\(^{15}\) The overall structure is layered with slabs of neptunyl borate separated by K\(^+\) or Ba\(^{2+}\) cations. The layers diverge sharply from what is typically observed in high-valence actinyl oxoanion materials. They are approximately 1.6 nm thick. Most actinyl sheets have their thickness determined by a single polyhedron, and are on the order of 4-5 Å. Here, however, there are four distinct neptunium sites. In all cases the neptunium is found in the form of an approximately linear dioxo cation, NpO\(_2\)\(^{n+}\). An evaluation of both the neptunyl Np=O bond distances, and the bond-valence sums indicates that all four sites do not simply contain Np(V). In two of the sites the NpO\(_2\)\(^{n+}\) cations are coordinated by six oxygen atoms in the equatorial plane to form NpO\(_8\) hexagonal bipyramidal geometries. One NpO\(_2\)\(^{n+}\) cation is bound by five oxygen atoms to form a NpO\(_7\) pentagonal bipyramid. Bond-valence sum calculations suggest the NpO\(_8\) units being primarily +6 and the NpO\(_7\) units primarily +5. The final NpO\(_2\)\(^{n+}\) cation is bonded to four oxygen atoms to yield a tetragonal bipyramid. The core neptunyl unit has Np=O bond distances that average 1.938(14) Å, which are
considerable longer than those found in Np(V) compounds, which average 1.83(2) Å.\textsuperscript{17} The neptunyl bond distances and the bond-valence sum calculations indicate Np(IV).\textsuperscript{17} However, it should be noted that a dioxo Np(IV) unit has never been observed before. The barium compound shows bond-valence sums more consistent with single oxidation states for each site, whereas there is slightly more intermediate-valency in the potassium compound. Thus, in a single compound all possible coordination environments for neptunyl are realized, and there is evidence for three oxidation states for neptunium.

The neptunyl polyhedra are interconnected by both BO\textsubscript{3} and BO\textsubscript{4} units in the cases of the the NpO\textsubscript{7} and NpO\textsubscript{8} units. However, the NpO\textsubscript{6} site is solely held in place by so-called cation-cation interactions (CCI’s). These interactions form via the coordination of the “yl” oxo atoms from one neptunyl cation into the equatorial plane of a neighboring neptunium polyhedron. This Np site is flanked on two sides by NpO\textsubscript{7} units and two sides by NpO\textsubscript{8} units that provide the CCI oxo atoms. The NpO\textsubscript{6} unit uses its oxo atoms to also form CCI’s with the NpO\textsubscript{7} pentagonal bipyramids. While CCI’s are known in approximately half of Np(V) oxoanion compounds,\textsuperscript{[17]} this is the first example where neptunium is solely held in place by CCI’s. The bond-valence sum for this site of 4.0 valence units again suggests Np(IV) in the barium compound. The CCI’s yield clusters of eleven neptunium centers within the layers as shown in Fig. 9.3 (and Fig. 9.6).

The BO\textsubscript{3} and BO\textsubscript{4} units share corners to create highly complex sheets shown in Fig. 9.2. Some of the oxygen atoms in these sheets are protonated to maintain charge balance for the structure. The joining of the NpO\textsubscript{6}, NpO\textsubscript{7}, NpO\textsubscript{8}, BO\textsubscript{3}, and BO\textsubscript{4} units
Figure 9.2: A depiction of the structure of $K_4[[\text{NpO}_2]_{6.73}\text{B}_{20}\text{O}_{36}(\text{OH})_2]$ showing Np$^{VI}$O$_8$ (green), Np$^V$O$_7$ (dark blue), and Np$^{IV}$O$_6$ (light blue) units linked by BO$_3$ triangles and BO$_4$ tetrahedra, and by bridging oxo atoms to form 1.6 nm thick slabs that are separated by K$^+$ cations. Some of the disordered cations between the layers have been omitted for clarity.
Figure 9.3: UV-vis-NIR spectrum of $K_4[(\text{NpO}_2)_{6.73}\text{B}_{20}\text{O}_{36}(\text{OH})_2]$ showing regions of f-f transitions that indicate the presence of Np(IV), Np(V), and Np(VI). Corresponding Np$^{\text{VI}}$O$_8$ (green), Np$^{\text{V}}$O$_7$ (dark blue), and Np$^{\text{IV}}$O$_6$ (light blue) polyhedra are placed above each region of the spectrum.
creates the remarkable layers with nano-scale features depicted in Fig. 9.2. The layers are separated from one another by \( K^+ \) or \( \text{Ba}^{2+} \) cations, some of which are ordered and some of which are disordered.

Bond-valence sum calculations while effective in most cases can only suggest possible oxidation states. The cavity size of the \( \text{NpO}_6 \) site might simply be too large, resulting in an anomalously low calculated charge. However, this does not explain the lengthening of the neptunyl bonds. An excessively large cavity would probably result in a slight contraction of the neptunyl unit, not an expansion. The magnitude of the lengthening of the neptunyl bond is consistent with reduction of the oxidation state to a formal valence of +4. Nevertheless, much stronger evidence for \( \text{Np(IV)} \) comes from UV-vis-NIR spectroscopic measurements taken from crystals of \( \text{K}_4[(\text{NpO}_2)_{6.73}\text{B}_{20}\text{O}_{36}(\text{OH})_2] \) and \( \text{Ba}_2[(\text{NpO}_2)_{6.59}\text{B}_{20}\text{O}_{36}(\text{OH})_2]\cdot\text{H}_2\text{O} \) using a microspectrophotometer. One convenient feature of the optical spectra of neptunium in different oxidation states is that they are very distinct from one another.\(^{18,19}\) Absorption features are present that clearly identify \( \text{Np(IV)}, \text{Np(V)}, \) and \( \text{Np(VI)} \) as shown in Fig. 9.3. The most important f-f transitions for \( \text{Np(IV)} \) are the transitions near 700 nm and 800 nm; whereas the \( \text{Np(V)} \) and \( \text{Np(VI)} \) transitions are observed near 990 and 1200 nm, respectively. When calculations based on the known extinction coefficients of the f-f transitions, and the measured intensities of the primary peaks for each oxidation state in the UV-vis-NIR spectrum are compared with the crystal structures, the following formula based on formal oxidation states can be derived, \( \text{K}_4[(\text{Np}^{\text{IV}}\text{O}_2)_{0.73}(\text{Np}^{\text{V}}\text{O}_2)_2(\text{Np}^{\text{VI}}\text{O}_2)_3\text{B}_{20}\text{O}_{36}(\text{OH})_2] \) and \( \text{Ba}_2[(\text{Np}^{\text{IV}}\text{O}_2)_{0.59}(\text{Np}^{\text{V}}\text{O}_2)_2(\text{Np}^{\text{VI}}\text{O}_2)_3\text{B}_{20}\text{O}_{36}(\text{OH})_2]\cdot\text{H}_2\text{O}. \) In short, the bond-valence sum
calculations determined from the X-ray diffraction data are consistent with the spectroscopic measurements, and both indicate the first examples of a Np(IV) dioxo unit. Based on comparative studies using Np(VI) and Np(V) as the source of neptunium in these syntheses, it has been determined that this compound forms via the disproportionation of some of the Np(V) to yield Np(VI) and Np(IV). The fact that this compound forms with many different interlayer cations, and from different oxidation states of neptunium suggests that it represents an energetic well.

The magnetic response from K$_4$[(NpO$_2$)$_{6.73}$B$_{20}$O$_{36}$(OH)$_2$] was obtained from a powdered sample using a Quantum Design MPMS 7 SQUID magnetometer. Magnetization data as a function of temperature obtained under an applied field of 50 Gauss showed no evidence of any ordering down to the lowest measured temperature, 3.5 K. Field measurements at low temperature (5 K; 0 – 0.5 T) and higher temperature (300 K; 0 – 2 T) were linear, supporting the conclusion from the low-field, variable-temperature experiment. Zero-field cooled and field cooled data obtained as a function of temperature overlapped at all temperatures. Taken together, these results show the sample to be paramagnetic down to the lowest temperature measured. Because of the small sample size, and hence small magnetic signal, the susceptibility data used to obtain an effective moment (Fig. 9.7) were obtained at 0.5 T. Fitting these susceptibility data assuming Curie-Weiss behavior of non-interacting, localized moments, produces an effective moment of 3.08 ± 0.15 μ$_B$ per Np ion. Data obtained at 0.05 and 0.2 T yield the same effective moments. The theoretical, free-ion effective moments, based on Russell-Saunders coupling, are 3.62, 3.58, and 2.54 μ$_B$ for Np(IV), Np(V), and Np(VI),
respectively. These values represent maximum observables because the crystal-field is expected to reduce the measured moment. The measured moment represents an average over all the crystallographically distinct Np, weighted by their multiplicity, and as such cannot be analyzed in depth without extensive further experiments. However, it is interesting to note that if the susceptibilities are calculated assuming the free-ion moments weighted by the ratios of crystallographic multiplicities, yields a calculated effective moment of $3.01 \mu_B$ per Np ion, well within the error of the experiment. The presence of neptunyl (V) and/or (IV) is confirmed by these results because these valence states are required to increase the measured value above the $2.54 \mu_B$ theoretical value for Np(VI). This behavior is similar to the mixed-valent Np(IV)/Np(V) selenite, Np(NpO$_2$)$_2$(SeO$_3$)$_3$, and contrasts sharply with most pure Np(V) compounds that either ferromagnetically order <10 K or antiferromagnetically order near 20 K.$^{21,22}$

9.7 Plutonium Borates

The first Pu(VI) borate prepared forms in the presence of additional cations, such as Ba$^{2+}$, although these diminish the size of the crystallites. Dichroic peach/pink crystals of PuO$_2$[B$_8$O$_{11}$(OH)$_4$] were isolated as the sole product of the boric acid flux reactions$^{15}$. UV-vis-NIR studies clearly show only Pu(VI) in the compounds (i.e. no reduction has taken place) (Fig. 9.8)$^{18}$. At first glance the structure of this compound appears similar to that of many of the uranyl borates because it also contains a hexagonal bipyramidal environment around the Pu(VI) centers. However, while there are still nine borate groups around the equatorial plane of the plutonium, the number of BO$_3$ and BO$_4$
groups differs between U(VI) and Pu(VI) (see Fig. 9.1c). In PuO$_2$[B$_8$O$_{11}$(OH)$_4$] there are seven BO$_4$ units and two BO$_3$ units; whereas in Na[[UO$_2$]B$_6$O$_{10}$(OH)]·2H$_2$O there are six BO$_4$ units and three BO$_3$ units. In the neptunium compounds the layers are also subtly different as shown in Fig 9.1b. One way of viewing these layers is to consider them as being composed of chains of BO$_4$ tetrahedra that are linked into sheets by BO$_3$ triangles. There are further differences in the interlayer borate units where in all uranyl compounds there are only BO$_3$ triangles connecting layers, whereas in PuO$_2$[B$_8$O$_{11}$(OH)$_4$] there are BO$_4$ tetrahedra between the layers as shown in Fig. 9.4. The three-dimensional network found for this material is also polar as indicted by the monoclinic space group Cc. The origin of the acentricity is likely the helical nature of chains of BO$_3$ triangles (see Fig. 9.5 and 9.4), whose twisting reduces the interlayer space in these materials.

9.8 Conclusions

In conclusion, these data point to the mounting body of evidence that indicates the need to conduct research on the actual actinide in question, and not on a less radioactive surrogate like uranium. Great caution needs to be exercised in predicting the chemistry of transuranium materials based on the behavior of uranium compounds; they can be quite different. However, this is not the primary message of this work. What we have now observed in K$_4$[(NpO$_2$)$_{6.73}$B$_{20}$O$_{36}$(OH)$_2$] and Ba$_2$[(NpO$_2$)$_{6.59}$B$_{20}$O$_{36}$(OH)$_2$]·H$_2$O are materials that can successfully sequester all stable oxidation states of neptunium, not just one. Therefore, we have the ability to design
Figure 9.4: A depiction of the polar, three-dimensional network found for \( \text{PuO}_2[\text{B}_9\text{O}_{11}(\text{OH})_8] \). \( \text{PuO}_8 \) hexagonal bipyramids are shown in orange, \( \text{BO}_3 \) triangles in blue, and \( \text{BO}_4 \) tetrahedra in purple. Unlike the uranyl and neptunyl borate phases, there are \( \text{BO}_4 \) tetrahedra between the layers.
advanced materials that target not just one oxidation state of a radionuclide, but all possible oxidation states. The low-symmetry, polymeric nature of the borate anions is the key to achieving this goal and therefore other polyanions (e.g. silicates and borophosphates) may also be appropriate for materials design. The neptunium borates underscore the need for more versatile storage materials most strongly because unlike other actinides, neptunium’s most stable oxidation state under normal environmental conditions is +5, in the form of NpO$_2^+$. This cation is notorious for only being weakly bound by anions and mineral surfaces, and easily migrating in the environment. Neptunium is of particular importance because $^{237}$Np has a long half-life ($t_{1/2} = 2.14 \times 10^6$ years), and in the long-term will be the primary contributor to the calculated dose from spent nuclear fuel stored in repositories.$^{27}$

9.9 Supporting Information
Figure 9.5: An illustration of the polar three-dimensional framework found in Na(UO$_2$)$_2$[B$_6$O$_{10}$(OH)]·2H$_2$O showing the hexagonal bipyramidal environments around U(VI) (yellow) as well as the BO$_3$ triangles (blue) and BO$_4$ tetrahedra (purple). The BO$_4$ units are only found within the same plane as the UO$_2^{2+}$ cations; whereas the BO$_3$ units are observed to link the layers together. Na$^+$ cations (aqua) and water molecules (red) occupy the channels within the framework.
Figure 9.6: A view of the cluster of eleven neptunyl units that result from the formation of cation-cation interactions.
Figure 9.7: Magnetic susceptibility of $K_4(NpO_2)_{6.73}B_{20}O_{36}(OH)_2$ obtained under an applied field of 0.5 T. The best fit to the data, shown as a solid line, yields a Curie constant of 1.19, which corresponds to an effective moment of 3.08 $\mu_B$. 
Figure 9.8: UV-vis-NIR spectrum of PuO$_2$[B$_8$O$_{11}$(OH)$_4$] obtained from a crystal using a Craic technologies microspectrophotometer.
9.10 Reference


15. Crystallographic data for Na[(UO$_2$)B$_8$O$_{10}$(OH)$_4$]·2H$_2$O: Yellow-green block, 0.162 x 0.154 x 0.126 mm, monoclinic, $Cc$, $Z = 4$, $a = 6.3905(9)$ Å, $b = 11.1390(15)$ Å, $c = 15.987(2)$ Å, $\beta = 92.777(2)^\circ$, $V = 1136.7(3) Å^3$ ($T = 293(2)$ K), $\mu = 144.08$ cm$^{-1}$, $R_1 = 0.0416$, $wR_2 = 0.1042$. K$_{4}$(NpO$_2$)$_6$B$_{20}$O$_{36}$(OH)$_2$: Drab plate, 0.105 x 0.042 x 0.011 mm, triclinic, $P-1$, $Z = 1$, $a = 6.5341(15)$ Å, $b = 10.908(2)$ Å, $c = 16.042(4)$ Å, $\alpha = 95.946(3)^\circ$, $\beta = 96.240(3)^\circ$, $\gamma = 90.162(3)^\circ$, $V = 1130.3(4) Å^3$ ($T = 293(2)$ K), $\mu = 158.35$ cm$^{-1}$, $R_1 = 0.0607$, $wR_2 = 0.1491$. Ba$_2$(NpO$_2$)$_{6.59}$B$_{20}$O$_{36}$(OH)$_2$·H$_2$O: Drab plate, 0.088 x 0.063 x 0.009 mm, triclinic, $P-1$, $Z = 1$, $a = 6.5582(13)$ Å, $b = 11.016(2)$ Å, $c = 17.071(3)$ Å, $\alpha = 100.927(3)^\circ$, $\beta = 100.497(3)^\circ$, $\gamma = 90.178(3)^\circ$, $V = 1189.7(4) Å^3$ ($T = 293(2)$ K), $\mu = 160.33$ cm$^{-1}$, $R_1 = 0.0490$, $wR_2 = 0.0853$. PuO$_2$[B$_8$O$_{11}$(OH)$_4$]: Dichroic peach/pink plate, 0.110 x 0.081 x 0.008 mm, monoclinic, $Cc$, $Z = 4$, $a = 6.4391(8)$ Å, $b = 16.714(2)$ Å, $c = 10.9648(13)$ Å, $\theta =$
90.744(1)°, \( V = 1180.0(3) \, \text{Å}^3 \) \( (T = 100(2) \, \text{K}) \), \( \mu = 56.97 \, \text{cm}^{-1} \), \( R_1 = 0.0198 \), \( wR_2 = 0.0438 \). Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (crysdata@fiz-karlsruhe.de) on quoting numbers CSD 420984, 420985, 420986, and 420987.


CHAPTER 10:

FURTHER INSIGHTS INTO INTERMEDIATE- AND MIXED-VALENCY IN NEPTUNIUM

OXOANION COMPOUNDS: STRUCTURE AND ABSORPTION SPECTROSCOPY OF

\[ \text{K}_2[(\text{NPO}_2)_3\text{B}_{10}\text{O}_{16}(\text{OH})_2(\text{NO}_3)_2] \]

10.1 Abstract

The reaction of Np(V) chloride with molten boric acid results in the disproportionation of Np(V) into Np(IV) and Np(VI), and the crystallization of \( \text{K}_2[(\text{NPO}_2)_3\text{B}_{10}\text{O}_{16}(\text{OH})_2(\text{NO}_3)_2] \). UV-vis-NIR spectroscopy demonstrates that in addition to the Np(VI) and Np(V) found in the crystal structure, that Np(IV) is also present.

10.2 Introduction

The chemistry of neptunium and plutonium can be markedly different from earlier actinides like thorium and uranium.\(^1\) This impacts how we design materials for storing these radionuclides, and how we model the behavior of these elements in the environment.\(^2\)

We have recently demonstrated that the chemistry of actinides in molten boric acid is substantially different from that observed in aqueous media.\(^3-6\) In particular, we provided evidence for the simultaneous existence of Np(IV), Np(V), and Np(VI) in a single compound via a combination of single crystal X-ray diffraction, bond-valence sum
calculations, magnetism, and UV-vis-NIR spectroscopy.\(^3\) The formation of mixed- or intermediate-valent neptunium compounds is driven by the ability of Np(V) to disproportionate under a variety of conditions. This reaction can be strongly favored in the presence of strong complexants, leading to the isolation of both Np(IV) and Np(VI) compounds.\(^7\)\(^-\)\(^{10}\) A very small group of mixed-valent Np(IV)/Np(V)\(^{11}\) and Np(V)/Np(VI)\(^{12}\) compounds exist. In the former compounds the presence of two oxidation states is easily determined by the presence or absence of short oxo bonds to form linear, dioxo cations of the form NpO\(_2\)\(^{n+}\). In the latter systems where Np(V) and Np(VI) both display similar neptunyl units, determination of multiple oxidation states becomes more difficult using X-ray diffraction alone.

In an attempt to prepare a borate compound containing both thorium and neptunium, a new mixed-valent neptunium nitratoborate was serendipitously discovered. This compound, K\(_2\)[(NpO\(_2\))\(_3\)B\(_{10}\)O\(_{16}\)(OH)\(_2\)(NO\(_3\))\(_2\)], forms small pale pink tablets on the surface of thorium borate glasses derived from boric acid flux reactions. Although lanthanide nitratoborates are known,\(^{13}\) this is the first example in this oxoanion family with an actinide.

10.3 Experimental Section

*Synthesis:* Np(V) chloride (10 mg in 30 \(\mu\)L water), Th(NO\(_3\))\(_4\)·5H\(_2\)O (22.7 mg), KNO\(_3\) (9.8 mg), and H\(_3\)BO\(_3\) (47.4 mg) were mixed together in a teflon-lined autoclave. The mixture was heated at 220 °C for 3 days, and then cooled at 1 °C per hour to 160 °C, and
then quenched. The product consisted of a colorless glass of thorium borate coated with pale pink crystals of $K_2[(\text{NpO}_2)_3\text{B}_{10}\text{O}_{16}(\text{OH})_2(\text{NO}_3)_2]$.

Crystallography of $K_2[(\text{NpO}_2)_3\text{B}_{10}\text{O}_{16}(\text{OH})_2(\text{NO}_3)_2]$: pale pink tablet, crystal dimensions 0.047 x 0.041 x 0.009 mm, monoclinic, $P2_1/n$, $Z = 2$, $a = 6.599(5)$ Å, $b = 16.026(12)$ Å, $c = 11.053(9)$ Å, $\beta = 90.922(13)^\circ$, $V = 1168.7(16)$ Å$^3$ ($T = 100$ K), $\mu = 114.15$ cm$^{-1}$, $R_1 = 0.0518$, $wR_2 = 0.1350$. Bruker APEXII Quazar diffractometer: $\theta_{\text{max}} = 49.76^\circ$, MoK$\alpha$, $\lambda = 0.71073$ Å, 0.5° $\omega$ scans, 10978 reflections measured, 2026 independent reflections all of which were included in the refinement. The data was corrected for Lorentz-polarization effects and for absorption, structure was solved by direct methods, anisotropic refinement of $F^2$ by full-matrix least-squares, 214 parameters.$^{20}$

10.4 Crystal Structure

Single crystal X-ray diffraction studies reveal a complex three-dimensional network whereby layers of Np(V) borate that extend in the $[ac]$ plane are interconnected by Np(VI)-containing moieties. The mode of connection is via so-called cation-cation interactions (CCI’s), where the oxo atoms of the Np$O_2^+$ units directly coordinate the interlayer Np(VI) ions. While CCI’s are known in approximately 50% of Np(V) structures,$^{14}$ these interactions are almost always between neighboring Np$O_2^+$ units. Interactions with other oxidation states of neptunium, or other metal ions in general are still quite rare.$^{3,11,15}$ The linking of the Np(V) borate sheets by the neutral Np$^{VI}O_2(\text{NO}_3)_2$ units creates the three-dimensional network shown in Fig. 10.1.
Figure 10.1: A view of the three-dimensional network structure of $\text{K}_2[(\text{Np}^\text{VI}_\text{O}_2)(\text{Np}^\text{VII}_\text{O}_2)_2\text{B}_{10}\text{O}_{16}(\text{OH})_2(\text{NO}_3)_2]$. $\text{Np}^\text{VII}_\text{O}_8$ and $\text{Np}^\text{VI}_\text{O}_8$ hexagonal bipyramids are shown in green and pink, respectively. $\text{BO}_3$ and $\text{BO}_4$ triangles and tetrahedra are shown in dark blue. The nitrate groups contain the light blue atoms. $\text{K}^+$ cations are shown in purple.
The presence of Np(V) versus Np(VI) can be ascertained on the basis of the length of the Np=O bonds in the dioxo cations. The neptunium atoms within the borate layers have Np=O bond distances of 1.805(10) and 1.828(12) Å, which are close to the average Np=O distance of 1.83 Å found by surveying known Np(V) compounds. In contrast, the interlayer neptunyl units have much shorter Np=O distances of 1.736(12) Å (×2) that are consistent with Np(VI). Bond-valence sum calculations that also incorporate the six equatorial Np–O bonds in the NpO$_8$ hexagonal bipyramids yield sums that are consistent with this oxidation state assignment. This yields a formula with formal oxidation states of $K_2[(\text{Np}^{VI}O_2)_2(\text{Np}^{V}O_2)_2B_{10}O_{16}(OH)_2(NO_3)_2]$.

The environment around the NpO$_2^+$ units within the layers is new to actinide borates. Here the neptunyl units are bound by nine borate anions. While this general description applies to all of the actinide borates with layered motifs that we have structurally characterized, the number of BO$_3$ and BO$_4$ units that surround the neptunium ions differs between compounds. Here there are five BO$_3$ triangles and four BO$_4$ tetrahedra. Normally there are more tetrahedra than triangles. A view of these layers is shown in Fig. 10.2.

10.5 UV-VIS-NIR Spectrum of $K_2[(\text{Np}O_2)_3B_{10}O_{16}(OH)_2(NO_3)_2]$

While the assignment of oxidation states based on the X-ray diffraction data appears to be straightforward, UV-vis-NIR absorption spectroscopy reveals a more complex story. In Fig. 10.3 we show the absorption features of a series of
Figure 10.2: A view of the three-dimensional network structure of K$_2$[(Np$^\text{V}$O$_2$)(Np$^\text{V}$O$_2$)$_2$B$_{10}$O$_{16}$(OH)$_2$(NO$_3$)$_2$]. Np$^\text{V}$O$_8$ and Np$^\text{VI}$O$_8$ hexagonal bipyramids are shown in green and pink, respectively. BO$_3$ and BO$_4$ triangles and tetrahedra are shown in dark blue. The nitrate groups contain the light blue atoms. K$^+$ cations are shown in purple.
Figure 10.3: UV-vis-NIR spectra of single crystals of $K_2[(\text{NpO}_2)_3\text{B}_{10}\text{O}_{16}\text{(OH)}_2(\text{NO}_3)_2]$ (black), Np(VI) in NpO$_2$(IO$_3$)$_2$(H$_2$O) (green), Np(V) in NpO$_2$(IO$_3$) (blue), and Np(IV), Np(V), and Np(VI) in $K_4(\text{NpO}_2)_{6.73}\text{B}_{20}\text{O}_{36}\text{(OH)}_2$ (red).
neptunium compounds where the oxidation state is known with a high degree of confidence. These data were acquired from single crystals and not solutions. In the solid state, there is both enhancement and reduction of certain transitions that leads to more overlap between various transitions of different oxidation states that are usually not problematic for solutions.

As can be seen in this figure, $K_2[(\text{NpO}_2)_3\text{B}_{10}\text{O}_{16}(\text{OH})_2(\text{NO}_3)_2]$, displays f-f transitions that are appropriate for both Np(V) and Np(VI). However, an additional feature is also present at 770 nm that can not be explained by either Np(V) or Np(VI). In fact, this band is characteristic for Np(IV). While it is evident that disproportionation of Np(V) from the original starting material is indicated by the presence of the Np(VI) units, an additional unique crystallographic site for Np(IV) is not indicated in this structure in contrast with $K_4(\text{NpO}_2)_{6.73}\text{B}_{20}\text{O}_{36}(\text{OH})_2$ and $\text{Ba}_2(\text{NpO}_2)_{6.59}\text{B}_{20}\text{O}_{36}(\text{OH})_2$, where such a site exists.

10.6 Conclusions

It must be kept in mind that crystal structures represent averages of the total composition of the crystal. One explanation for location of Np(IV) sites is that they are disordered with the Np(V) sites. A second option is that the site is in fact intermediate-valent between Np(IV) and Np(V). The second is more satisfying because the coordination geometry for Np(IV) is substantially different than that of Np(V). A similar explanation needs to be invoked for $\beta$-AgNpO$_2$(SeO$_3$) where low-temperature ESR data also indicate the presence of Np(IV) in crystals even though the structure only appears...
to contain Np(V). This is a cautionary note: Perhaps other neptunium compounds that we believe to contain only Np(V) are actually mixed- or intermediate-valent. If this is true, some of the physical properties that have been measured may have more complex explanations than we currently think.

10.7 Reference


11.1 Abstract

Molten methylboronic acid has been used as a reactive flux to prepare the first neptunium(V) borate, NpO₂[B₃O₄(OH)₂] (NpBO-1), and the first actinide boronate, UO₂(CH₃BO₂)(H₂O) (UCBO-1). NpBO-1 contains cation-cation interactions between the neptunyl units. In contrast, the presence of the methyl groups in the uranyl boronate leads to a one-dimensional structure.

11.2 Introduction

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

The melting point of boric acid is 170.9°C, and this temperature must be exceeded
for it to act as a reactive flux. In molten boric acid Np(V) partially disproportionates to
Np(IV) and Np(VI) leading to the formation of mixed-valent compounds. Because water
competes very successfully with borate for inner-sphere coordination sites for actinides
under most conditions, it is very difficult to synthesize actinide borates utilizing
hydrothermal or room-temperature aqueous reactions. In order to prepare actinide
borates at lower temperatures than the melting point of boric acid, we utilized methyl
boronic acid, the simplest boronic acid, as a new reactive flux. The melting point of
methyl boronic acid is within the range of 89~94°C, which is a considerably lower than
the melting point of boric acid. In addition, the C−B bond is not thermally robust, and
boronates are readily degraded to borates.9 Finally, even if the C−B bond remains intact
during the reaction, actinide boronates are completely unknown, and the solid-state
chemistry of metal boronates in general is severely underexplored.10 In this vein, we
demonstrate that a Np(V) borate, NpO₂[B₃O₄(OH)₂] (NpBO-1) has been successfully
synthesized from the reaction of Np(VI) nitrate with large excess of methyl boronic acid
at 120 °C. Under the same reaction conditions uranyl nitrate reacts with methyl boronic
acid to yield the first known actinide boronate compound UO₂(CH₃BO₂)(H₂O) (UCBO-1),
which can be made as a pure phase in good yield.
11.3 Experimental Section

A stock solution of $^{237}$Np (VI) perchlorate 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 the Np (VI) nitrate solution. UV-vis-NIR spectroscopy indicates that only Np(VI) is present.

**NpBO-1**: Np(VI) nitrate (10 mg in 10 μL water), methyl boronic acid (46.1 mg) were mixed together in a a teflon-lined autoclave. The mixture was heated at 120 °C for 3 days, and then cooled at 5°C per hour to room temperature. The products consisted of light green needle crystals of **NpBO-1**.

**UCBO-1**: UO$_2$(NO$_3$)$_2$.6H$_2$O (200mg), methyl boronic acid (360mg), H$_2$O(20μL) were mixed together in a a teflon-lined autoclave. The mixture was heated at 120 °C for 3 days, and then cooled at 5°C per hour to room temperature. The product consisted of light yellow needle crystals of **UCBO-1** which exist as a pure phase. Yield: 76% based on U.

11.4 The First Np(V) Boate

Single crystal X-ray diffraction studies reveal that **NpBO-1** crystallizes in the polar orthorhombic space group Pca2$_1$. The structure of **NpBO-1** contains only one crystallographically unique neptunyl cation, NpO$_2^+$, in a pentagonal bipyramidal environment, NpO$_7$. This coordination geometry is very common for both U(VI) and Np(V) oxoanion compounds. Each oxygen atom of the NpO$_2^+$ units is further bonded with neighboring neptunyl units through their equatorial planes to yield so-called...
cation-cation interactions (CCIs). Each NpO$_2^+$ cation is bonded to four other neptunyl cations via these interactions. This CCI bonding mode can be described by the scheme below, and is in accord with CCI bonding modes summarized by Grigoriev et al. and Burns and co-workers.$^{11,12}$ This CCI bonding mode is found to be the most common type for all Np(V) compounds that contain CCIs in the crystal structure.$^{12}$ As a result of this CCI bonding mode, all the NpO$_2^+$ units are connected together to create Np(V) sheets within the [ac] plane as shown in Fig. 11.1.

The sheets are further stacked along the $b$ axis via bridges created by both BO$_3$ and BO$_4$ units showed in Fig. 11.2. As previously mentioned the structure is polar. The polarity of NpBO-$1$ is subtle. As shown in Fig. 11.2, both the orientation of Np(V) sheets and the direction of BO$_3$ triangles can be used to visualize the polarity of the structure along the $c$ axis.

The NpO$_2^+$ cations have Np=O bond distances of 1.81(2) and 1.85(1) Å, which are within the normal range for the neptunyl bond distances for all other known Np(V) compounds.$^{11}$ Combined with the Np−O bond distances for the five interactions in the equatorial plane, which range from 2.39(1) to 2.53(1) Å, a bond-valence sum can be calculated of 5.14.$^{12}$ This sum is consistent with this compound containing Np(V). All B−O bond distances are normal. Some oxygen atoms in the borate units are protonated which can be confirmed by the bond-valence sums for these atoms and on the bond distances and coordination environments.

The existence of Np(V) in NpBO-$1$ can be further confirmed by the UV-Vis-NIR spectra of single crystals of NpBO-$1$ as shown in Fig. 11.3. As expected, the most
Figure 11.1: UV-vis-NIR spectra of single crystals of $K_2[(\text{NpO}_2)_3\text{B}_{10}\text{O}_{16}(\text{OH})_2(\text{NO}_3)_2]$ (black), Np(VI) in $\text{NpO}_2(\text{IO}_3)_2(\text{H}_2\text{O})$ (green), Np(V) in $\text{NpO}_2(\text{IO}_3)$ (blue), and Np(IV), Np(V), and Np(VI) in $K_4(\text{NpO}_2)_{6.73}\text{B}_{20}\text{O}_{36}(\text{OH})_2$ (red).
Figure 11.2: A depiction of the structure of NpO$_2$[B$_3$O$_4$(OH)$_2$] (NpBO-1) showing the sheets of neptunyl cations connected by the polyborate chains.
Figure 11.3: UV-vis-NIR spectrum of NpO$_2$[B$_3$O$_4$(OH)$_2$] (NpBO-1) obtained from a single crystal. The transition at 1013 nm is demonstrative of Np(V).
important f-f transition for Np(V) at 980 nm is shifted to a longer wavelength at 1013 nm owing to the cation-cation interactions.\textsuperscript{11} It is also important to note the absence of a strong transition at 1200 nm that would be indicative of Np(VI). This transition was observed in all other neptunium borates. Key transitions for Np(IV) are also absent.

11.5 The First U(VI) Boronate

Np(VI) is a strong oxidant ($\text{E}^{0}_{\text{Np(VI/V)}}=1.16\text{V}$) and likely oxidizes the methyl boronic acid by attacking the C–B bond to yield borate. Nevertheless, the goal of preparing a neptunium borate with neptunium in a single oxidation state was achieved by this method. A similar reaction does not occur with U(VI) owing to its much lower oxidizing potential ($\text{E}^{0}_{\text{U(VI/I)}}=0.32\text{V}$), and the first actinide boronate, UO$_2$(CH$_3$BO$_2$)(H$_2$O) (UCBO-1), was subsequently isolated.

A single crystal X-ray diffraction study of UCBO-1 shows that it adopts a simple one-dimensional chain structure shown in Fig. 11.4. This structure consists of edge-sharing pentagonal bipyramids. The methyl boronate anions chelate the uranyl cations, and also bridge between the uranium centers via $\mu_3$ oxygen atoms. There is only one crystallographically unique U(VI) site in the crystal structure that has a pentagonal bipyramidal coordination environment much like that found in NpBO-1, except that the CCIs are completely absent as expected. It should be noted that although pentagonal bipyramidal coordination is the most common one found for actinyl compounds, all the U(VI) borates prepared from boric acid flux reactions adopt a hexagonal bipyramidal environment.\textsuperscript{2-8}
Figure 11.4: A view along the $b$ axis of the one-dimensional structure of $\text{UO}_2(\text{CH}_3\text{BO}_2)(\text{H}_2\text{O})$ (UCBO-1).
The methyl groups of the CH$_3$BO$_2^{2-}$ anions play a critical role in this structure in that they terminate the edges of the chains. If these moieties were replaced by oxygen to yield either BO$_3$ triangles or with two oxygen atoms to yield BO$_4$ tetrahedra, the structure would likely extend in at least one more dimension as found for all actinyl borates.

11.6 Conclusions

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

11.7 Reference


CHAPTER 12:

ROLE OF ANIONS AND REACTION CONDITIONS IN THE PREPARATION OF URANIUM, NEPTUNIUM, AND PLUTONIUM BORATES

12.1 Abstract

U(VI), Np(VI), and Pu(VI) borates with the formula AnO₂[B₈O₁₁(OH)₄] (An = U, Np, Pu) have been prepared via the reactions of U(VI) nitrate, Np(VI) perchlorate, or Pu(IV) or Pu(VI) nitrate with molten boric acid. These compounds are all isotopic and consist of a linear actinyl(VI) cation, AnO₂²⁺, surrounded by BO₃ triangles and BO₄ tetrahedra to create an AnO₈ hexagonal bipyramidal environment. The actinyl bond lengths are consistent with actinide contraction across this series. The borate anions bridge between actinyl units to create sheets. Additional BO₃ triangles and BO₄ tetrahedra extend from the polyborate layers and connect these sheets together to form a three-dimensional chiral framework structure. UV-vis-NIR absorption and fluorescence spectroscopy confirms the hexavalent oxidation state in all three compounds. Bond-valence parameters are developed for Np(VI).

12.2 Introduction

The terrestrial abundance of boron, and therefore borates, is quite low at 10 ppm. However, borate deposits occur as the result of the evaporation of ancient
oceans and seas. One such deposit is the Salado formation near Carlsbad, New Mexico where the concentration of borate, predominately in the form of $\text{H}_3\text{BO}_3$, $\text{B(OH)}_4^-$, and $\text{B}_4\text{O}_7^{2-}$, reaches concentrations as high as 166 ppm in intergranular brines.\textsuperscript{2} Located within this deposit is the United States’ only repository for nuclear defense waste known as the Waste Isolation Pilot Plant (WIPP). Much like boron, uranium has a relatively low terrestrial abundance at 2.7 ppm.\textsuperscript{3} However, a variety of processes concentrate uranium in the Earth’s crust, and large deposits of uranium are found throughout the world. Despite the fact that vast quantities of uranium are dissolved in oceans and seas, there are no known naturally occurring uranium borate minerals that form as the result of evaporation of ancient bodies of water.\textsuperscript{4} WIPP presents a unique environment whereby large quantities of not only uranium, but also lesser amounts of the transuranium elements neptunium, plutonium, americium, curium, will eventually be able to react with the brines, potentially leading to the formation of actinide borate compounds. The presence of the decaying nuclear waste will lead to heating beyond the ambient conditions in the deposit, and therefore the reaction of actinides with borates at moderate temperatures (ca. 150 °C) are important reactions to study in order to predict the fate of actinides in the repository.

The structural chemistry of both borates and actinides is very rich. Borate occurs as both $\text{BO}_3$ triangles and $\text{BO}_4$ tetrahedra, and these units fuse in limitless combinations to create clusters, chains, sheets, and three-dimensional frameworks of remarkable complexity.\textsuperscript{5} Likewise, the coordination chemistry of actinides is exceedingly rich with tri- and tetravalent actinide cations being found with coordination numbers ranging
from six to fifteen,\(^6\) and penta- and hexavalent actinide cations forming the ubiquitous linear actinyl units, AnO\(_{2n^+}\) (An = U, Np, Pu, Am; n = 1 or 2), that are further ligated by four to six donor groups to create tetragonal, pentagonal, and hexagonal bipyramids.\(^7\) The combination of the structural flexibility of actinides with borates should lead to countless novel materials, some of which will have relevance to the disposition and fate of nuclear waste. Despite these motivations, the first uranyl borate for which a crystal structure is known was not reported until 1985, when Behm disclosed the remarkable structure of K\(_6[\text{UO}_2\{\text{B}_{16}\text{O}_{24}(\text{OH})_8\}]\cdot12\text{H}_2\text{O},\) an extraordinarily complex cluster composed of a cyclic \(\text{BO}_3\) and \(\text{BO}_4\) units with a central uranyl core.\(^8\) This work was quickly followed by that of Gasperin, who utilized high-temperature \(\text{B}_2\text{O}_3\) melts to prepare seven different uranyl borates, one of which contains an early example of uranyl cations using oxo atoms to coordinate one another, a so-called cation-cation interaction.\(^9-15\) For twenty years the field lay dormant until the use of boric acid flux reactions was introduced providing access to thorium,\(^16,17\) uranium,\(^18-21\) neptunium,\(^22-24\) and plutonium\(^22\) borates with both unprecedented structural richness and complex electronic structures.

One of the challenges in working with these elements is to find synthetic methods that allow for isolation of single oxidation states across a series of neighboring actinides (e.g. U(VI), Np(VI), Pu(VI)).\(^25\) This can be difficult to achieve because the redox potentials for uranium, neptunium, and plutonium are very different, and plutonium is well known to equilibrate as many as four different oxidation states in solution at the same time.\(^26\) Concentration,\(^27\) temperature,\(^28\) counter ions,\(^29\) radiolysis,\(^30\) and
hydrolysis\(^{31}\) can all significantly alter the course reactions involving actinides. If proper conditions can be created for preparing a series of actinide compounds with the same formula and oxidation state systematic comparisons of these compounds can be made.

We have recently discovered that molten boric acid is a unique medium for preparing crystalline actinide borates. We have reported a large family of U(VI) borates, many of which adopt noncentrosymmetric structures.\(^{18-21}\) In a boric acid flux Np(V) partially disproportionates to Np(IV) and Np(VI) allowing for the isolation of neptunium borates, such as \(K_4[(\text{NpO}_2)_{6.73}\text{B}_{20}\text{O}_{36}(\text{OH})_2]\) and \(K_2[(\text{NpO}_2)_{3}\text{B}_{10}\text{O}_{36}(\text{OH})_2(\text{NO}_3)_2]\), that simultaneously contain three different oxidation states.\(^{22,23}\) Lowering the reaction temperature and changing the flux to methyl boronic acid allows for the isolation of a neptunium borate, \(\text{NpO}_2[\text{B}_{3}\text{O}_4(\text{OH})_2]\), that only contains Np(V).\(^{24}\) When Pu(VI) is reacted with molten boric acid the hexavalent oxidation state is maintained, and we have briefly communicated the synthesis and structure of \(\text{PuO}_2[\text{B}_{8}\text{O}_{11}(\text{OH})_4]\).\(^{22}\)

In this work we will show how anions present in the reactions influence the formation of neptunium and plutonium borates. We demonstrate that by judicious choice of counter ions and careful control of reaction conditions that a series of uranium, neptunium, and plutonium borates can be synthesized that all contain actinides in the hexavalent oxidation state allowing for the development of periodic trends.
12.3 Experimental Section

_Syntheses:_ UO$_2$(NO$_3$)$_2$·6H$_2$O (98%, International Bio-Analytical Industries), H$_3$BO$_3$ (99.99%, Alfa-Aesar), Pb(NO$_3$)$_2$ (99%, Alfa-Aesar), and KBO$_2$ (Alfa-Aesar) were used as received. Reactions were run in PTFE-lined Parr 4749 autoclaves with a 23 mL internal volume for uranium, and with 10 mL internal volume autoclaves for neptunium and plutonium. Distilled and Millipore filtered water was used in all reactions. Standard precautions were performed for handling radioactive materials during work with thorium and uranium. _Caution!_ $^{237}$Np ($t_{1/2} = 2.14 \times 10^6$ y) represents a serious health risk owing to its $\alpha$ and $\gamma$ emission, and especially because of its decay to the short-lived isotope $^{233}$Pa ($t_{1/2} = 27.0$ d), which is a potent $\beta$ and $\gamma$ emitter. $^{242}$Pu ($t_{1/2} = 3.76 \times 10^5$ y) represents a serious health risk owing to its $\alpha$ and $\gamma$ emission. All studies with neptunium and plutonium were conducted in a laboratory dedicated to studies on transuranium elements. This laboratory is located in a nuclear science facility and is equipped with a HEPA filtered hoods and negative pressure gloveboxes that are ported directly into the hoods. A series of counters continually monitor radiation levels in the laboratory. The laboratory is licensed by the Nuclear Regulatory Commission. All experiments were carried out with approved safety operating procedures. All free-flowing solids are worked with in gloveboxes, and products are only examined when coated with either water or Krytox oil and water. There are significant limitations in accurately determining yield with neptunium and plutonium compounds because this requires drying, isolating, and weighing a solid, which poses certain risks, as well as manipulation difficulties given the small quantities employed in the reactions.
A stock solution of $^{237}$Np (VI) perchlorate 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 Np(VI) nitrate solution. A large excess of NaNO$_2$ followed by an excess of NH$_4$OH were added to this solution resulting in the precipitation of Np(V) hydroxide. The precipitate was then filtered and dried in 120 °C for about 30 minutes. Np(V) hydroxide was then dissolved in a dilute HClO$_4$ solution. This solution was then ozonated for approximately 1 hour to ensure complete oxidation of the neptunium to +6. UV-vis-NIR spectroscopy indicated that only Np(VI) was present.

A stock solution of $^{242}$Pu (VI) nitrate was prepared by first digesting PuO$_2$ 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. This solution was then ozonated for approximately 5 h to ensure complete oxidation of the plutonium to +6. UV-vis-NIR spectroscopy indicated that only Pu(VI) was present. A stock solution of $^{242}$Pu(IV) nitrate was made by treating $^{242}$Pu(VI) nitrate stock solution with a small excess of H$_2$O$_2$ followed by mild heating.

$\text{UO}_2[B_8\text{O}_{11}(\text{OH})_4]$: UO$_2$(NO$_3$)$_2$·6H$_2$O (0.5000 g, 1 mmol), boric acid (1.3596 g, 22 mmol), Pb(NO$_3$)$_2$ (0.3317 g, 1 mmol) and water (50 μL) were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 220 °C in a box furnace for 500 hours. The autoclave was then cooled down to room temperature at a rate of 5 °C/h. The products were washed with boiling water to remove excess boric acid, followed by rinsing with methanol. Crystals in the form of tablets with light yellow-green coloration
were collected for $\text{UO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]$ as a minor phase. $\beta$–$\text{UO}_2\text{B}_2\text{O}_4$ (UBO-1) was also found as the main product.$^{19}$

$\text{NpO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]$: A stock solution of Np(VI) perchlorate containing 20 mg of Np(VI) perchlorate was loaded into a 10 mL autoclave and dried in the oven at 120 °C until the whole solution appeared to be a drop (about 20 μL in volume). Boric acid (0.094 g, 1.5mmol) and KBO$_2$ (0.0154 g, 0.18mmol) were then added to the autoclave. The autoclave was sealed and heated to 220 °C in a box furnace for 3 days. The autoclave was then cooled down to room temperature at a rate of 9 °C/h. The products were washed with boiling water to remove excess boric acid, followed by rinsing with methanol. Crystals in the form of tablets with light peach-pink coloration were collected for $\text{NpO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]$ as the only product.

$\text{PuO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]$: A stock solution of Pu(VI) nitrate containing 10 mg of Pu(VI) nitrate was loaded into a 10 mL autoclave and dried in the oven at 120 °C until the whole solution appeared to be a drop (about 20 μL in volume). Boric acid (0.0472 g, 0.7mmol) was then added to the autoclave. The autoclave was sealed and heated to 220 °C in a box furnace for 3 days. The autoclave was then cooled down to room temperature at a rate of 9 °C/h. The products were washed with boiling water to remove excess boric acid, followed by rinsing with methanol. Crystals in the form of tablets with peach-pink coloration were collected for $\text{PuO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]$ as a pure product.

Crystallographic Studies: Single crystals of all three $\text{UO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]$, $\text{NpO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]$, and $\text{PuO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]$ phases were mounted cryoloops with viscous
Krytox and optically aligned on a Bruker APEXII CCD X-ray diffractometer or a Bruker APEXII Quazar X-ray diffractometer using a digital camera. Initial intensity measurements were either performed using a 1µS X-ray source, a 30 W microfocused sealed tube (MoKα, λ =0.71073 Å) with high-brilliance and high-performance focusing Quazar multilayer optics, or a standard sealed tube with a monocapillary collimator. Standard APEXII software was used for determination of the unit cells and data collection control. The intensities of reflections of a sphere were collected by a combination of four sets of exposures (frames). Each set had a different φ angle for the crystal and each exposure covered a range of 0.5° in ω. A total of 1464 frames were collected with an exposure time per frame of 10 to 30 s, depending on the crystal. The SAINT software was used for data integration including Lorentz and polarization corrections. Semi-empirical absorption corrections were applied using the program SADABS.  

*UV-vis-NIR and Fluorescence Spectroscopy:* UV-vis-NIR data were acquired from single crystals of all phases using a Craic Technologies microspectrophotometer. Crystals were placed on quartz slides under Krytox oil, and the data was collected from 400 to 1400 nm. Fluorescence data were obtained using 365 nm light for excitation (see Supporting Information).

12.4 Controlling the Oxidation States of Neptunium and Plutonium Borates.

In the previous chapters, we described the syntheses of K₄(NpO₂)₆.7₃[B₂₀O₃₆(OH)₂] and Ba₂(NpO₂)₆.₅₉[B₂₀O₃₆(OH)₂]·H₂O, which contain Np(IV), Np(V), and Np(VI). These
compounds are synthesized by the reactions of Np(VI) nitrate with molten boric acid. When chloride is the only counter ion in the reaction \([\text{NpO}_2]_4[(\text{NpO}_2)_{6.73}\text{B}_{20}\text{O}_{36}(\text{OH})_2]\) forms.\(^{22}\) This demonstrates that Np(VI) is first reduced to Np(V) followed by disproportionation. We noted, however, that when Np(VI) perchlorate is heated in water at 200 °C that initially Np(V) grows into the reaction, but that after prolonged heating the neptunium is predominately in the +6 oxidation state. Likewise, when Np(VI) perchlorate is reacted with molten boric acid, the first Np(VI) borate, \(\text{NpO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]\) is isolated.

The reaction chemistry of plutonium in boric acid is much more straightforward than with neptunium. Both Pu(IV) and Pu(VI) nitrate react with boric acid to yield \(\text{PuO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]\). Unlike uranyl and neptunyl borates, additional cations are not readily incorporated into the structure. \(\text{PuO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]\) also crystallizes in the presence of \(\text{Ba}^{2+}\) and \(\text{K}^+\). The isolation of a Pu(VI) borate from a Pu(IV) source is surprising in light of the fact that Pu(IV) compounds are generally far less soluble than Pu(VI) compounds.\(^{26}\)

The isolation of an uranium analog of the aforementioned Np(VI) and Pu(VI) compounds, \(\text{UO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]\), requires the use of higher temperatures than we have typically employed in uranyl borate syntheses. At 190 °C an entirely different set of compounds forms that possess very different polyborate networks.\(^{18-21}\) However, by increasing the reaction temperature to 220 °C, \(\text{UO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4]\) can be isolated.
12.5 Structure and Topology Description

Single crystal X-ray diffraction studies of $\text{UO}_2[\text{B}_8\text{O}_{11}\text{(OH)}_4]$, $\text{NpO}_2[\text{B}_8\text{O}_{11}\text{(OH)}_4]$, and $\text{PuO}_2[\text{B}_8\text{O}_{11}\text{(OH)}_4]$ show that $\text{AnO}_2[\text{B}_8\text{O}_{11}\text{(OH)}_4]$ crystal structures are all isotopic and crystallize in the chiral monoclinic space group $Cc$. A view of the overall structure is shown in Fig. 12.1. There is one crystallographically unique actinyl cation, $\text{AnO}_2^{2+}$, that resides in a hexagonal hole within the polyborate sheets to create a hexagonal bipyramidal environment, $\text{AnO}_8$. This coordination environment dominates the entire family of actinyl borates derived from molten boric acid, and is a consequence of having small chelating anions. Similar environments can be found with other small chelating anions such as nitrate and carbonate.$^7a$ This coordination environment is actually quite rare in extended structures when compared with the prevalence of $\text{AnO}_7$ pentagonal bipyramids that are found in 85% of actinyl compounds.$^7a$

Each $\text{AnO}_8$ unit is surrounded by nine borate groups in $[ac]$ plane to form an actinyl borate sheet as shown in Fig. 12.2. Among these nine borate groups, there are two $\text{BO}_3$ triangles and seven $\text{BO}_4$ tetrahedra. The terminal oxygen of five $\text{BO}_4$ tetrahedra are directed “up”/“down” corresponding to the sheet plane and other two are directed in the opposite - “down”/“up” direction. This is the same number of surrounding $\text{BO}_3$ triangles and $\text{BO}_4$ tetrahedra we found in $\text{C/D}$ and $\text{E}$ types of uranyl borate sheets which were observed in Tl-uranyl borates.$^{18}$ However, the topology of the layers in the new U, Np and Pu borates are different, and has not been seen in any other actinide borate that we have observed.$^{11-17}$ The basic fragment of the borate sheets is shown in Fig. 12.3. It consists of two symmetrical parts I and II related via a mirror reflecting in sheet plane.
Figure 12.1: A depiction of the chiral, three-dimensional network structure found for AnO$_2$[B$_8$O$_{11}$(OH)$_4$] (An=U, Np, Pu). AnO$_8$ hexagonal bipyramids are shown in yellow, BO$_3$ triangles in red, and BO$_4$ tetrahedra in green.
Figure 12.2: A view along the $b$ axis of the actinyl borate sheets in $\text{AnO}_2\,[\text{B}_8\text{O}_{11}(\text{OH})_4]$ (An = U, Np, Pu). AnO$_8$ hexagonal bipyramids are shown in yellow, BO$_3$ triangles in red, and BO$_4$ tetrahedra in green.
Figure 12.3: A skeletal view of the actinyl borate sheets in AnO\textsubscript{2}[B\textsubscript{8}O\textsubscript{11}(OH)\textsubscript{4}] (An = U, Np, Pu). Solid-line tetrahedra directed “up”, dashed-line “down”.
Such configuration makes layers in these new phases nonpolar and we call this sheet type as \textbf{H-type} (relatively to sheets classifications of uranyl borates)\textsuperscript{18-21}.

There are additional BO\textsubscript{3} triangles and BO\textsubscript{4} tetrahedra connecting these actinyl borate sheets together, and the sheets stack along the \textit{b} axis to form a three-dimensional framework structure. Based on the classification of actinyl borates these structures can be described as \textbf{F-2-2} compounds\textsuperscript{21}. It should be noted that this is the only actinyl borate structure type from boric acid reactions where BO\textsubscript{4} tetrahedra are located between the sheets\textsuperscript{18-23}. As indicated by the space group \textit{Cc}, the \textit{b} axis is chiral, and this can be understood by the helical nature of the polyborate chains between the actinyl borate sheets. The twisting of the interlayer borate groups with respect to one another reduces the interlayer space, and yields a less open, denser structure.

The actinide contraction in this series of compounds can be demonstrated with a variety of metrics. The unit cell parameters given in \textbf{Table 12.1}, and the bond distances provided in \textbf{Table 12.2} all provide evidence of this.

The unit cell volumes for UO\textsubscript{2}[B\textsubscript{8}O\textsubscript{11}(OH)\textsubscript{4}], NpO\textsubscript{2}[B\textsubscript{8}O\textsubscript{11}(OH)\textsubscript{4}], and PuO\textsubscript{2}[B\textsubscript{8}O\textsubscript{11}(OH)\textsubscript{4}] are 1183.4(5) Å\textsuperscript{3}, 1182.1(2) Å\textsuperscript{3}, and 1180.0(3) Å\textsuperscript{3}, respectively. More importantly the actinyl An≡O bond distances shrink by 0.02 Å on average from uranium to plutonium. The Np≡O bond distances are within normal range and compare well with neptunyl bond distance found in the [NpO\textsubscript{2}(NO\textsubscript{3})\textsubscript{3}]\textsuperscript{1−}, which also contain neptunium in hexagonal bipyramidal environment\textsuperscript{33}. There are very few plutonyl crystal structures; far too few to make broad comparisons. However, the average Pu≡O bond length in PuO\textsubscript{2}[B\textsubscript{8}O\textsubscript{11}(OH)\textsubscript{4}] is within 3σ of the plutonyl bonds in PuO\textsubscript{2}(IO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O\textsuperscript{34}. It is important
TABLE 12.1
CRystallographic Data For \( \text{UO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4] \), \( \text{NpO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4] \), and \( \text{PuO}_2[\text{B}_8\text{O}_{11}(\text{OH})_4] \)

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<th>( \text{NpO}_2[\text{B}<em>8\text{O}</em>{11}(\text{OH})_4] )</th>
<th>( \text{PuO}_2[\text{B}<em>8\text{O}</em>{11}(\text{OH})_4] )</th>
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<td>( Cc )</td>
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<td>6.4426(8)</td>
<td>6.4391(8)</td>
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<td>28.79</td>
</tr>
<tr>
<td>( \rho \text{ calcd (g cm}^{-3}) )</td>
<td>3.348</td>
<td>3.346</td>
<td>3.380</td>
</tr>
<tr>
<td>( \mu (\text{Mo } K\alpha) )</td>
<td>138.27</td>
<td>89.02</td>
<td>56.97</td>
</tr>
<tr>
<td>( R(F) ) for</td>
<td>( F_o^2 &gt; 2\sigma (F_o^2)^a )</td>
<td>0.0300</td>
<td>0.0247</td>
</tr>
<tr>
<td>( R_w(F_o^2) )</td>
<td>0.0612</td>
<td>0.0531</td>
<td>0.0473</td>
</tr>
</tbody>
</table>
TABLE 12.2

SELECTED BOND DISTANCES FOR ANO$_2$[B$_8$O$_{11}$(OH)$_4$] (AN = U, NP, PU)

<table>
<thead>
<tr>
<th>Distance (Å)</th>
<th>An = U</th>
<th>An = Np</th>
<th>An = Pu</th>
</tr>
</thead>
<tbody>
<tr>
<td>An(1)-O(3)</td>
<td>1.733(5)</td>
<td>1.737(5)</td>
<td>1.720(4)</td>
</tr>
<tr>
<td>An(1)-O(10)</td>
<td>1.767(5)</td>
<td>1.746(5)</td>
<td>1.733(4)</td>
</tr>
<tr>
<td>An(1)-O(7)</td>
<td>2.405(7)</td>
<td>2.399(13)</td>
<td>2.399(11)</td>
</tr>
<tr>
<td>An(1)-O(6)</td>
<td>2.436(8)</td>
<td>2.440(9)</td>
<td>2.438(7)</td>
</tr>
<tr>
<td>An(1)-O(2)</td>
<td>2.468(6)</td>
<td>2.468(5)</td>
<td>2.454(4)</td>
</tr>
<tr>
<td>An(1)-O(8)</td>
<td>2.529(7)</td>
<td>2.527(13)</td>
<td>2.527(10)</td>
</tr>
<tr>
<td>An(1)-O(5)</td>
<td>2.532(7)</td>
<td>2.544(8)</td>
<td>2.527(6)</td>
</tr>
<tr>
<td>An(1)-O(1)</td>
<td>2.622(6)</td>
<td>2.639(5)</td>
<td>2.634(4)</td>
</tr>
</tbody>
</table>
to note that actinyl bonds distances are close enough to each other across the uranium, neptunium, and plutonium series that the actinide contraction is difficult to detect between different types of compounds (i.e. the errors in the bond lengths produce overlap if one uses $3\sigma$ on the calculated errors). The actinide contraction is only detectable if the errors are small, the residuals are low, and the compounds are isostructural.\(^{35}\)

12.6 Bond-Valence Parameters for Neptunium(VI)

The bond valence parameters for $\text{Np}^{6+}$ were derived before the 1970’s,\(^{36}\) however, as more and more structures of $\text{Np}^{6+}$ have been reported it is important to improve on the original parameters using the 23 structures in total found in ICSD (Table 12.3)\(^{37}\) and synthesized by us. In order to derive the values of $R_0$ and $b$ at the same time for $\text{Np}^{6+}$ neptunyl polyhedra, it is critical to establish the ideal bond distance of the neptunyl ions which corresponds to 2.0 v.u. (valence unit). Burns and coworkers have derived the bond valence parameters for $\text{U}^{6+}$ and $\text{Np}^{5+}$ using this method.\(^{7b,38}\) Here, taking only well refined anhydrous structures into consideration, the bond strengths of the neptunyl bonds were calculated by subtracting the bond valence of other bonds to a given neptunyl O ion using the published parameters\(^{39}\) from the formal valence of 2.0 for O, and then plotted as a function of the bond length. The interception of the linear fit for these points corresponding to the ideal distance is 1.717\(\text{Å}\) ($R^2 = 0.9948$). Thus, the relationship between $R_0$ and $b$ follows the equation below:

$$2.0 = \exp[(R_0 - 1.717)/b]$$
TABLE 12.3
RESULTS FROM THE CALCULATION OF BOND-VALENCE PARAMETERS

<table>
<thead>
<tr>
<th>Compound</th>
<th>CN</th>
<th>S</th>
<th>ICSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_2$(NpO$_2$(SO$_4$)$_2$)</td>
<td>7</td>
<td>5.99</td>
<td>51501$^{37a}$</td>
</tr>
<tr>
<td>(NpO$_2$)(CrO$_4$(CO(NH$_2$)$_2$)$_2$</td>
<td>7</td>
<td>5.94</td>
<td>93940$^{37b}$</td>
</tr>
<tr>
<td>NH$_4$(NpO$_2$)(NO$_3$)$_3$</td>
<td>8</td>
<td>6.06</td>
<td>95921$^{37c}$</td>
</tr>
<tr>
<td>K(NpO$_2$)(NO$_3$)$_3$</td>
<td>8</td>
<td>6.12</td>
<td>95922$^{37c}$</td>
</tr>
<tr>
<td>(NpO$_2$)$_2$(TcO$_4$)$_4$(H$_2$O)$_3$</td>
<td>7</td>
<td>6.15</td>
<td>98417$^{37d}$</td>
</tr>
<tr>
<td>((CH$_3$)$_4$N)$_4$(NpO$_2$(CO$_3$)$_3$)(H$_2$O)$_8$</td>
<td>8</td>
<td>5.97</td>
<td>110324$^{37e}$</td>
</tr>
<tr>
<td>K(NpO$_2$)(PO$_4$(H$_2$O)$_3$</td>
<td>6</td>
<td>6.02</td>
<td>157297$^{37f}$</td>
</tr>
<tr>
<td>Na(NpO$_2$)(PO$_4$(H$_2$O)$_3$</td>
<td>6</td>
<td>6.06</td>
<td>157298$^{37f}$</td>
</tr>
<tr>
<td>Rb(NpO$_2$)(PO$_4$(H$_2$O)$_3$</td>
<td>6</td>
<td>5.79</td>
<td>157299$^{37f}$</td>
</tr>
<tr>
<td>NH$_4$(NpO$_2$)(PO$_4$)(H$_2$O)$_3$</td>
<td>6</td>
<td>5.91</td>
<td>157300$^{37f}$</td>
</tr>
<tr>
<td>Na$_{14}$(Na$_2$(NpO$_2$)$_2$(GeW$<em>9$O$</em>{34}$)$_2$(H$<em>2$O)$</em>{37}$</td>
<td>7</td>
<td>5.76</td>
<td>173174$^{37g}$</td>
</tr>
<tr>
<td>NpO$_2$(CH$_3$PO$_3$)</td>
<td>7</td>
<td>6.02</td>
<td>173370$^{37h}$</td>
</tr>
<tr>
<td>(NpO$_2$)(SO$_4$)$_2$(H$_2$SO$_4$(H$_2$O)$_4$</td>
<td>7</td>
<td>5.94</td>
<td>201192$^{37i}$</td>
</tr>
<tr>
<td>Rb(NpO$_2$)(NO$_3$)$_3$</td>
<td>8</td>
<td>6.08</td>
<td>201232$^{37j}$</td>
</tr>
<tr>
<td>K$_2$(NpO$_2$)$_2$(CrO$_4$)$_3$(H$_2$O)$_4$</td>
<td>7</td>
<td>6.23</td>
<td>250164$^{37k}$</td>
</tr>
<tr>
<td>(NpO$_2$)(IO$_3$)$_2$(H$_2$O)</td>
<td>7</td>
<td>5.90</td>
<td>281463$^{37l}$</td>
</tr>
<tr>
<td>(NpO$_2$)(IO$_3$)$_2$(H$_2$O)</td>
<td>7</td>
<td>5.92</td>
<td>281464$^{37l}$</td>
</tr>
<tr>
<td>K(NpO$_2$)(IO$_3$)$_3$(H$<em>2$O)$</em>{1.5}$</td>
<td>7</td>
<td>6.10</td>
<td>413240$^{31m}$</td>
</tr>
<tr>
<td>(NpO$_2$)(IO$_3$)$<em>2$(KCl)$</em>{0.5}$(H$<em>2$O)$</em>{3.25}$</td>
<td>7</td>
<td>6.16</td>
<td>413331$^{31n}$</td>
</tr>
<tr>
<td>NpO$_2$(C$_2$H$_5$PO$_3$)</td>
<td>7</td>
<td>5.80</td>
<td></td>
</tr>
<tr>
<td>NpO$_2$(B$<em>8$O$</em>{11}$(OH)$_4$)</td>
<td>8</td>
<td>5.86</td>
<td>This work</td>
</tr>
</tbody>
</table>

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With this constraint, the values of $R_0 = 2.025$ and $b = 0.444$ are obtained by optimizing the values to give the bond valence sum of 6.0 v.u. for 23 compounds. The results are shown in Table 12.3. This set of parameters works very well for most compounds giving an average bond valence sum of 6.00 v.u. and the standard deviation is 0.13 v.u., while the previous reported parameters of $R_0 = 2.07$ and $b = 0.35$ give the completely unreasonable average bond-valence sum of 7.12 v.u. and the standard deviation 0.21 v.u.

12.7 UV-Vis-NIR Absorption Spectroscopy

The 5f$^1$ electron configuration typically yields a single somewhat broad Laporte-forbidden f-f transition in addition to higher energy charge-transfer bands.\textsuperscript{40} For U(V) the f-f transition is in the visible region of spectrum.\textsuperscript{40} For isoelectronic Np(VI), this transition occurs in the NIR near 1200 nm. The UV-vis-NIR spectra of NpO$_2$[B$_8$O$_{11}$(OH)$_4$] acquired from a single crystal is shown in Fig. 12.4. We have found that this peak can be shifted from where it typically occurs in solution when compared to solid samples. For example, data acquired from single crystals of NpO$_2$(NO$_3$)$_2$·6H$_2$O shows this peak is located at 1100 nm. NpO$_2$[B$_8$O$_{11}$(OH)$_4$] shows a transition at 1140 nm. In contrast, in single crystals of NpO$_2$(IO$_3$)$_2$(H$_2$O) the transition is at 1230 nm, which is similar to where it is found in perchlorate and nitrate solutions.\textsuperscript{41} An explanation for the differences in the energy of this transition is found the coordination environments. In NpO$_2$[B$_8$O$_{11}$(OH)$_4$] and NpO$_2$(NO$_3$)$_2$·6H$_2$O the neptunium center is in a hexagonal
Figure 12.4: UV-vis-NIR absorption spectra of the Np(VI) compounds, NpO₂[B₈O₁₁(OH)₄] (black), NpO₂(NO₃)₂·6H₂O (blue), and NpO₂(IO₃)₂·H₂O (red).
Figure 12.5: UV-vis-NIR absorption spectrum of PuO$_2$[B$_8$O$_{11}$(OH)$_4$] from a single crystal aligned along the $b$ axis in the same direction as the plutonyl units.
bipyramidal environment; whereas in NpO$_2$(IO$_3$)$_2$(H$_2$O) and solutions of neptunyl perchlorate the neptunium is in a pentagonal bipyramidal geometry.\textsuperscript{25} It appears that the addition of a larger number of donor atoms in the equatorial plane, and presumably more electron density at the neptunium center, shifts the f-f transition to higher energy. The reverse effect is observed in the shift of the main transition at 980 nm in Np(V) compounds. Upon the formation of cation-cation interactions, the f-f transition shifts to longer wavelengths.\textsuperscript{42}

Pu(VI) yields a spectrum that is far more complex than Np(VI) because of its 5f$^2$ electron configuration. Superficially the spectrum is similar to isoelectronic Np(V) with a single strong f-f transition at approximately 830 nm. A series of much weaker transitions also occur. The UV-Vis-NIR spectrum of single crystals of PuO$_2$[B$_8$O$_{11}$(OH)$_4$] is shown in Fig. 12.5. This spectrum was acquired from a single crystal where the plutonyl axis is aligned in the excitation direction. The main f-f transition is at 800 nm.\textsuperscript{40} However if the crystal is rotated by 90° so that excitation is perpendicular to the plutonyl axis then the intensity of this transition is significantly diminished with respect to all of the other transitions. This pleochroism can be significant in other transuranium compounds, such as $K_2[(\text{NpO}_2)_3\text{B}_{10}\text{O}_{16}(\text{OH})_2(\text{NO}_3)_2]$,\textsuperscript{23} and is visible to the naked eye without polarized light. Crystals of both PuO$_2$[B$_8$O$_{11}$(OH)$_4$] and PuO$_2$(IO$_3$)$_2$·H$_2$O are dichroic being pink when viewed in one direction and peach in the other two directions.
12.8 Conclusions

In summary, we have successfully synthesized the first Np(VI) borate in molten boric acid by using Np(VI) perchlorate as the starting material. This compound has uranium and plutonium analogues that are accessible by carefully controlling the reaction conditions. The actinide contraction can be detected in this system because of the high quality of the X-ray diffraction data even though all of the crystals are pseudo-merohedrally twinned. Bond-valence parameters for Np(VI) have been developed that when used in conjunction with Np(IV)\(^{43}\) and Np(V)\(^{7b,44}\) parameters derived by us and others can be used to rapidly and accurately determine the oxidation state(s) of neptunium from the crystal structure alone. UV-vis-NIR data acquired from single crystals demonstrates that there can be substantial shifts in the f-f transitions when solids with one coordination environment are compared with solutions containing actinides in a different coordination environment. Taken together these data provide a series of general tools that illuminate differences between solution and the solid state for actinide compounds.

12.9 Reference


CHAPTER 13:
NEW NEPTUNIUM(V) BORATES THAT EXHIBIT THE ALEXANDRITE EFFECT

13.1 Abstract

A new neptunium(V) borate K[(NpO$_2$)$_2$B$_{10}$O$_{14}$(OH)$_4$] was synthesized using the boric acid flux reaction. Only one Np(V) metal center is found in the crystal structure. However, this compound shows an unusual Alexandrite effect which can be observed for only previous Np(IV) compounds. In addition, the UV-vis-NIR absorption spectra further indicates the presence of Np(IV) in the crystals.

13.2 Introduction

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, counter ions, 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.\textsuperscript{3}

We have recently undertaken the study of the preparation, structure elucidation, and physico-chemical property measurements of actinide borates with the aim of developing periodic trends that may be relevant to nuclear waste disposal.\textsuperscript{4-8} 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-NIR spectroscopy.\textsuperscript{6a} We also prepared a highly unusual mixed-/intermediate-valent neptunium borate, K\textsubscript{2}[(NpO\textsubscript{2})\textsubscript{3}B\textsubscript{10}O\textsubscript{16}(OH)\textsubscript{2}(NO\textsubscript{3})\textsubscript{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.\textsuperscript{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 be not useful for oxidation state assignment in these compounds. Explanations that require placing Np(IV) on crystallographic sites that are likely only compatible with neptunyl cations are not particularly satisfying.

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.\footnote{9}

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 counter-anion, a Np(VI) borate can be isolated,\footnote{6d} mixed-/intermediate-valent neptunium borates can only be synthesized when NO$_3^-$ or chloride is present in the boric acid flux reactions.\footnote{6a,6b} In this chapter, we describe the crystal structure and the absorption spectra of two new Np(V) borates, K[(NpO$_2$)$_2$B$_{10}$O$_{14}$(OH)$_4$] (1) and K$_2$[(NpO$_2$)$_2$B$_{16}$O$_{25}$(OH)$_2$] (2), which are prepared in boric acid flux reactions with Cl$^-$ present as a counter-anion.

### 13.3 Experimental Section

**Caution** $^{237}$Np ($t_{1/2} = 2.14 \times 10^6$ y) represents a serious health risk owing to its $\alpha$ and $\gamma$ emission, and especially because of its decay to the short-lived isotope $^{233}$Pa ($t_{1/2} = 27.0$ d), which is a potent $\beta$ and $\gamma$ emitter.

A stock solution of $^{237}$Np (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 Np(VI) nitrate solution. Large excess of NaNO$_2$ followed by excess of NH$_4$OH were added to this solution resulting in the precipitation
of Np(V) hydroxide. The precipitate was then filtered and dried at 120 °C for about 30 minutes. Np(V) hydroxide was then dissolved in a dilute HCl solution.

A stock solution of $^{237}\text{Np (V)}$ 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 three days followed by cooling to room temperature over one 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.

13.4 Synthesis Discussion

$\text{K}[\text{(NpO}_2\text{)}\text{B}_{10}\text{O}_{14}(\text{OH})_4]$ (1) was prepared via the molten boric acid flux reaction of Np(V) chloride with KCl at 220 °C. 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 (Fig. 13.1). This phenomenon is referred to as 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 Np(IV) compounds (it occurs in all Np(IV) compounds that we have prepared), but we have never observed it for Np(V). As a result, these crystals were originally thought to be a Np(IV) compound. Another similar neptunium borate phase $\text{K}_2[\text{(NpO}_2\text{)}_2\text{B}_{16}\text{O}_{25}(\text{OH})_2]$ (2) that are present as crystals
Figure 13.1: Photographs of crystals of $K[(\text{NpO}_2)\text{B}_{10}\text{O}_{14}(\text{OH})_3]$ (1) and $K_2[(\text{NpO}_2)\text{B}_{16}\text{O}_{25}(\text{OH})_2]$ (2) illuminated by standard room fluorescent lighting (left) and under microscope lighting (right) with a halogen lamp showing the Alexandrite effect.
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.  

13.5 Crystal Structure Depiction

Single crystal X-ray diffraction studies reveal that K[(NpO$_2$)B$_{10}$O$_{14}$(OH)$_4$] (1) crystallizes in the monoclinic centrosymmetric space group $P2_1/n$. The structure of 1 contains neptunium borate sheets that extend in the $[ab]$ plane (Fig. 13.2b) 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$_2$O$_5$$^4$- units on one side and B$_3$O$_6$$^3$- units on the other side (Fig. 13.2a). As a result, the structural hierarchy of this compound can be described as 1L-2-2-0, according to our symbol representations summarized for actinide borate compounds. The combination of linear dimeric and cyclic trimeric groups has been observed for the first time in actinide borates.

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 Np(V) compounds. It should be noted that this crystallographic data contrasts 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 occur, although CCI’s are very common in Np(V) compounds, and occur in
Figure 13.2: Views of part of the layered structure of $K[(NpO_2)B_{10}O_{14}(OH)_4]$ (1) in [ac] plane (a) and [bc] plane (b), and $K_2[(NpO_2)_2B_{16}O_{25}(OH)_2]$ (2) in [ac] plane (c). Np polyhedra are shown in orange, BO$_3$ triangles in dark green, BO$_4$ tetrahedra in light green, and potassium atoms in purple.
approximately 53% of known structures. The bond-valence sum for neptunium is consistent with Np(V).

The most important feature of the structure of 1 is the neptunium borate sheet topology. As observed in a typical uranyl borate, within the sheets, each NpO$_2^+$ hexagonal bipyramid is surrounded by nine nearest borate units (Fig. 13.3). 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 u$_3$-oxo atom shared by three BO$_4$ tetrahedra. These new features result in a new sheet topology (M type) for actinide borates. However, it should be noted that significant numbers of trivalent lanthanide borates also adopt this sheet topology. Large differences exist between Np(V) and An/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 both reside in the same type of polyborate sheets. 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.

The structure of K$_2$[(NpO$_2$)$_2$B$_{16}$O$_{25}$(OH)$_2$] (2) is based upon the same types of 2D borate sheets and has a certain similarity to 1 (Fig. 13.2c). The sheets are linked into a 3D framework by the B$_2$O$_5$ and [(B$_3$O$_6$)(BO(OH)$_2$)] groups. We can ascribe the F-2-2 descriptor to polyborate framework of 2. The additional BO(OH)$_2$ has only corner connections to the B$_3$O$_6$ trimer. A similar geometry is also observed in phases of AnO$_2$[B$_8$O$_{11}$(OH)$_4$] (An = U, Np, Pu).
Figure 13.3: Views of the sheet topology (M-type) in $\text{K}[(\text{NpO}_2)\text{B}_{10}\text{O}_{14}(\text{OH})_4]$ (1) and $\text{K}_2[(\text{NpO}_2)_2\text{B}_{16}\text{O}_{25}(\text{OH})_2]$ (2).
13.6 UV-vis-NIR Spectrum

The UV-vis-NIR absorption spectrum of $K[(\text{NpO}_2)\text{B}_{10}\text{O}_{14}(\text{OH})_4]$ (1) is shown as the black curve in Fig. 13.4. 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 the 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 Np(V) compound appears as a sharp feature at 980 nm (blue curve, Fig. 13.4). When Np(V) units are involved in cation-cation interactions, this feature is red-shifted to the higher wavelength region around 1010 nm (green curve, Fig. 13.4). For Np(IV), the most important transitions that can be used for distinguishing from Np(V) are at 730 nm and 960 nm (pink curve, Fig. 13.4). 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 $K_2[(\text{NpO}_2)_3\text{B}_{10}\text{O}_{16}(\text{OH})_2(\text{NO}_3)_2]$. However, there is a difference between the spectrum of 1 and that of $K_2[(\text{NpO}_2)_3\text{B}_{10}\text{O}_{16}(\text{OH})_2(\text{NO}_3)_2]$, in that the main transition of Np(V) is split into two peaks at both 960 nm and 980 nm (red curve, Fig. 13.4), which belong to Np(IV) and Np(V), respectively. While in 1, this transition is extensively shifted to the
Figure 13.4: UV-vis-NIR spectra of K[(NpO$_2$)$_{10}$O$_{14}$(OH)$_4$] (1) (black), K$_4$[(NpO$_2$)$_{6.73}$B$_{20}$O$_{36}$(OH)$_2$] (blue), K$_2$[(NpO$_2$)$_3$B$_{10}$O$_{16}$(OH)$_2$(NO$_3$)$_2$] (red), NpO$_2$(IO$_3$) (green), Np[C$_6$H$_4$(PO$_3$H)$_2$]$_2$·2H$_2$O (pink).
region that is even below that of Np(IV). It is therefore possible that there is also Np(IV) disordered within 1.

13.7 Conclusions

In conclusion, K[(NpO$_2$)$_{10}$O$_{14}$]$_4$(OH)$_4$ (1) provides a further example of the complexity of the mixed-/intermediate-valency that is found in several neptunium compounds. This is represented by β-AgNpO$_2$(SeO$_3$) where low-temperature ESR data also indicates the presence of Np(IV) in crystals even though the structure only appears to contain Np(V). Much like 1, crystals of β-AgNpO$_2$(SeO$_3$) are brown instead of the unusual blue-green coloration of Np(V) compounds. The large differences in the coordination environments within polyborates that was thought to differentiate between Np(IV) and Np(V) is based on the hypothesis that the linear dioxo neptunyl(IV) unit would not occupy the same kind of sites as lower oxidation states of neptunium. However, with the 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)$_2$], 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 β-AgNpO$_2$(SeO$_3$), and potentially in K$_2$[(NpO$_2$)$_3$B$_{10}$O$_{16}$(OH)$_2$(NO$_3$)$_2$], and 1.

13.8 Reference


11. Crystallographic data for K[(NpO$_2$)B$_{10}$O$_{14}$(OH)$_4$] (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, $\beta = 91.302(3)^\circ$, $V = 1713.1(6)$ Å$^3$ ($T = 293(2)$ K), $\mu = 64.13$ cm$^{-1}$, $R_1 = 0.0511$, $wR2 = 0.1179$.
Partial crystallographic data for K$_2$[(NpO$_2$)$_2$B$_{16}$O$_{25}$(OH)$_2$] (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, $\beta = 90.008(2)^\circ$, $V = 1306.4(5)$ Å$^3$.


CHAPTER 14:

FUNCTIONALIZATION OF BORATE NETWORKS BY THE INCORPORATION OF FLUORIDE:
SYNTHESSES, CRYSTAL STRUCTURES, AND NONLINEAR OPTICAL PROPERTIES OF NOVEL
ACTINIDE FLUOROBORATES

14.1 Abstract

The boric acid flux reactions of uranyl nitrate with sodium, potassium, rubidium or thallium fluoride result in the formation of a novel family of uranyl(VI) fluoroborate materials. These compounds are Na[(UO₂)B₅O₈(OH)F]·H₂O (NaUBOF-1), K[(UO₂)B₅O₈(OH)F] (KUBOF-1), K₁₁₁[(UO₂)₆B₂₄O₃₆F₂₂]·(H₂BO₃) (KUBOF-2), Rb[(UO₂)B₅O₈(OH)F] (RbUBOF-1), and Tl[(UO₂)B₅O₈(OH)F] (TlUBOF-1). A new neptunium(VI) fluoroborate isotypic with NaUBOF-1, Na[(NpO₂)B₅O₈(OH)F]·H₂O (NaNpBOF-1), was synthesized via the boric acid flux reaction of neptunium(VI) nitrate with sodium fluoride. These new actinide fluoroborates share a common structural motif consisting of a linear actinyl, U(Np)O₂²⁺, cation surrounded by BO₃ triangles and BO₄ tetrahedra to create an U(Np)O₆ hexagonal bipyramidal environment around uranium or neptunium. The borate anions bridge between actinyl units to create layers. B–F bonds were formed during the reactions to yield BO₃F tetrahedral units. The BO₃F tetrahedra and additional BO₃ triangles extend from the actinyl polyborate layers, and
are directed approximately perpendicular to the layers. A novel actinyl borate layered topology was found in $K_{111}[(UO_2)_6B_{24}O_{36}F_{22}](H_2BO_3)$ (KUBOF-2). Except for $K[(UO_2)B_5O_8(OH)]$ (KUBOF-1) and $K_{111}[(UO_2)_6B_{24}O_{36}F_{22}](H_2BO_3)$ (KUBOF-2), all of the other actinide fluoroborate phases adopt noncentrosymmetric space groups. $Tl[(UO_2)B_5O_8(OH)]$ (TIUBOF-1), which can be obtained as pure phase, displays second-harmonic generation of 532 nm light from 1064 nm light.

14.2 Introduction

The nonlinear optical applications of borate materials have been heavily investigated over the past several decades.\(^1\) $\beta$-BaB$_2$O$_4$ (BBO) is one of earliest and best developed examples,\(^1^a\) and improved second-harmonic generation have been realized in other materials such as $\alpha$-BiB$_3$O$_6$.\(^2\) The success of these borate crystals can be largely attributed to the unique structural characteristics of borate building units since the most common borate units are BO$_3$ triangles and BO$_4$ tetrahedra, and neither of these units can possess an inversion center. In a typical polyborate structure, BO$_3$ triangles and BO$_4$ tetrahedra share corners to form larger polyborate clusters, although rare examples of edge-sharing by two BO$_4$ tetrahedra have been found.\(^3,^4\) Because there are a vast number of different topological arrangements of the polyborate clusters, the solid-state and materials chemistry of borates is very rich.\(^5,^6\)

One of the least explored borate systems is the actinide borates.\(^7^-1^4\) We recently adopted the boric acid flux synthetic technique to synthesize a thorium borate, $[\text{ThB}_5\text{O}_6(\text{OH})_6][\text{BO(OH)}_3] \cdot 2.5\text{H}_2\text{O}$ (NDTB-1), with a cationic framework structure and
remarkable anion exchange capabilities,\textsuperscript{15,16} a large family of uranyl borates,\textsuperscript{17-20} several neptunium borates with variety of combinations of single valence states or mixed/intermediate valence states, and a single Pu(VI) borate.\textsuperscript{21-24} In particular, a significant percentage of these uranyl borates adopt noncentrosymmetric structures, and these compounds may aid in the design of other nonlinear optical materials.\textsuperscript{17-20} Among the 21 uranyl borates we have already reported, 13 of them adopt noncentrosymmetric space groups.\textsuperscript{17-20} Li[(UO\textsubscript{2})B\textsubscript{5}O\textsubscript{9}]\cdot H\textsubscript{2}O, Na[(UO\textsubscript{2})B\textsubscript{6}O\textsubscript{10}]\cdot 2H\textsubscript{2}O, K[(UO\textsubscript{2})\textsubscript{2}B\textsubscript{10}O\textsubscript{16}(OH)\textsubscript{3}]\cdot H\textsubscript{2}O, and \(\beta\)-Tl\textsubscript{2}[(UO\textsubscript{2})\textsubscript{2}B\textsubscript{11}O\textsubscript{18}(OH)\textsubscript{3}], which can be obtained as pure phases, display second-harmonic generation of 532 nm light from 1064 nm light.\textsuperscript{17-20}

The term “fluoroborate” is predominantly represented by the tetrafluoroborate anion BF\textsubscript{4}\textsuperscript{-} which often acts as an out-sphere, charge-balancing anion. However, fluoroborates have been largely expanded by the recent observations of partial substitution of oxygen atoms by fluorine atoms in the BO\textsubscript{4} units to form BOF\textsubscript{3}\textsuperscript{2-}, BO\textsubscript{2}F\textsubscript{2}\textsuperscript{3-} or BO\textsubscript{3}F\textsubscript{4}\textsuperscript{-} anions.\textsuperscript{25-30} The first example of BOF\textsubscript{3}\textsuperscript{2-} was shown in the structure of BaBOF\textsubscript{3}, but the bond distance information turns out to be very suspicious.\textsuperscript{25} A more reliable description of the BO\textsubscript{2}F\textsubscript{2}\textsuperscript{3-} anion first appeared in an organically templated borophosphate compound, (C\textsubscript{2}H\textsubscript{10}N\textsubscript{2})[BPO\textsubscript{4}F\textsubscript{2}], where reasonable evidence for the partial substitution of O atoms by F atoms in the BO\textsubscript{4} units was shown.\textsuperscript{26} Finally, the BO\textsubscript{3}F\textsubscript{4}\textsuperscript{-} unit was first reported in the compound NH\textsubscript{4}[BPO\textsubscript{4}F],\textsuperscript{27} and was rapidly expanded in the structures of NH\textsubscript{4}[BAsO\textsubscript{4}F],\textsuperscript{28} BiB\textsubscript{2}O\textsubscript{4}F,\textsuperscript{29} and LiB\textsubscript{6}O\textsubscript{9}F.\textsuperscript{30} In these compounds, B–F bonds are reasonably shorter than the B–O bonds in the same BO\textsubscript{3}F\textsubscript{4}\textsuperscript{-} units which can be used as an important evidence for identifying the presence of F\textsuperscript{-} in the structures.
We started to consider actinide fluoroborate compounds for several reasons. Firstly, compared to the BO$_4$ tetrahedra, the partial substitution of oxygen atoms by fluoride atoms will further reduce the symmetry, thus a noncentrosymmetric structure could yield a larger nonlinear optical response based on the polarization of the B–F bond. Actually, except for BaBOF$_3$, whose description is questionable, all of the aforementioned fluoroborate compounds crystallize in noncentrosymmetric space groups.$^{26-30}$ Secondly, compared to oxide anions, fluoride anions are more likely to be terminal instead of bridging, thus the incorporation of fluoride can be used to functionalize the structure of actinide borate sheets and frameworks, and novel actinide borate topologies should be observed. Finally, the redox chemistry of transuranium borates could be affected by further incorporation of fluoride. In this chapter, we will describe the syntheses, structures, and properties of a novel actinide fluoroborate family, and how these goals are realized.

14.3 Experimental Section

**Syntheses:** UO$_2$(NO$_3$)$_2$·6H$_2$O (98%, International Bio-Analytical Industries), $^{237}$NpO$_2$ (99.9%, Oak Ridge, t$_{1/2}$ = 2.14×10$^6$ yr, made by the oxidation of triple electrolytically refined Np metal), H$_3$BO$_3$ (99.99%, Alfa-Aesar), NaF (99%, Alfa-Aesar), KF (99%, Acros), RbF·xH$_2$O (99%, Alfa-Aesar), and TlF (99%, Strem) were used as received without further purification. Distilled and Millipore filtered water with resistance of 18.2 MΩ·cm was used in all reactions. PTFE-lined autoclaves were used for all reactions. *Caution!* $^{237}$Np ($t_{1/2} = 2.14 \times 10^6$ y) represents a serious health risk owing to its $\alpha$ and $\gamma$ emission, and
especially because of its decay to the short-lived isotope $^{233}\text{Pa}$ ($t_{1/2} = 27.0\text{ d}$), which is a potent β and γ emitter. All studies with neptunium were conducted in a laboratory dedicated to studies on transuranium elements. This laboratory is located in a nuclear science facility and is equipped with a HEPA filtered hoods and negative pressure gloveboxes that are ported directly into the hoods. A series of counters continually monitor radiation levels in the laboratory. The laboratory is licensed by the Nuclear Regulatory Commission. All experiments were carried out with approved safety operating procedures. All free-flowing solids are worked with in gloveboxes, and products are only examined when coated with either water or Krytox oil and water. There are significant limitations in accurately determining yield with neptunium compounds because this requires drying, isolating, and weighing a solid, which poses certain risks, as well as manipulation difficulties given the small quantities employed in the reactions.

Synthesis of $\text{Na}[(\text{UO}_2)\text{B}_5\text{O}_8(\text{OH})\text{F}]\cdot\text{H}_2\text{O}$ (NaUBOF-1): $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.1000 g, 0.2 mmol), boric acid (0.2720 g, 4.4 mmol), NaF (0.0250 g, 0.6 mmol) and water (20 μL) were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 220 °C in a box furnace for 5 days. The autoclave was then cooled down to room temperature at a rate of 5 °C/h. The products were washed with boiling water to remove excess boric acid, followed by rinsing with methanol. Crystals in the form of tablets with yellow-green coloration were collected for NaUBOF-1 with other light-yellow amorphous phases as side products. NaUBOF-1 can be made from the reaction of $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$,
boric acid, NaF at different NaF:U:B molar ratios of 1:1:8, 1:1:15, 3:1:8, and 3:1:15, but none of these reactions yield a pure NaUBOF-1 phase.

**Synthesis of K[(UO$_2$)$_2$B$_5$O$_8$(OH)F] (KUBOF-1) and K$_{11}$[(UO$_2$)$_6$B$_{24}$O$_{38}$F$_{22}$)](H$_2$BO$_3$) (KUBOF-2):** UO$_2$(NO$_3$)$_2$·6H$_2$O, H$_3$BO$_3$, KF with eight different KF:U:B molar ratios (4:1:8, 4:1:15, 5:1:8, 5:1:15, 6:1:15, 8:1:15, 10:1:15, 12:1:15) (0.1 g, 0.2 mmol of UO$_2$(NO$_3$)$_2$·6H$_2$O for each reaction) and 20 μL of water were loaded into eight 23 mL autoclaves. The autoclaves were sealed and heated to 220 °C in a box furnace for 5 days. The autoclaves were then cooled down to room temperature at a rate of 5 °C/h. All the products were washed with boiling water to remove excess boric acid, followed by rinsing with methanol. Crystals in the form of tablets and colorless glass phase were found for all reactions, and additional prism-like crystals were only found in the 8:1:15 reaction. Single crystal X-ray diffraction studies reveal that the tablet crystals are KUBOF-1 and the prism crystals are KUBOF-2.

**Synthesis of Rb[(UO$_2$)$_2$B$_5$O$_8$(OH)F] (RbUBOF-1):** RbUBOF-1 can be prepared using UO$_2$(NO$_3$)$_2$·6H$_2$O, H$_3$BO$_3$, RbF·xH$_2$O at different RbF:U:B molar ratios of 4:1:15, 6:1:15, and 8:1:15 by following the similar procedure for making the NaUBOF-1. Yellow-green crystals in the form of tablets and colorless amorphous phases as side products for all the reactions. A pure phase of RbUBOF-1 was not achieved.

**Synthesis of Tl[(UO$_2$)$_2$B$_5$O$_8$(OH)F] (TIUBOF-1):** TIUBOF-1 can be prepared using UO$_2$(NO$_3$)$_2$·6H$_2$O, H$_3$BO$_3$, TlF at different TlF:U:B molar ratios of 1:1:15, 1:1:22, 3:1:8, 3:1:15, and 3:1:22 by following the similar procedure for making the NaUBOF-1. Light
yellow crystals of **TlUBOF-1** in the form of prisms were collected as a pure phase only in the 1:1:22 reaction with the yield of 29% based on U. Colorless and yellow amorphous phases were found in all other reactions.

*Synthesis of Na\[(NpO_2)B_2O_8(OH)F\]·H_2O (NaNpBOF-1):* A 0.372 M stock solution of Np(VI) nitrate was prepared by first digesting 60 mg of NpO_2 in 8 M HNO_3 for 3 days at 200 °C in an autoclave. The resulting solution was reduced to a residue, during which all neptunium is oxidized to Np(VI). The residue was redissolved in 600 μL of water to form a 0.372 M stock solution of Np(VI) nitrate. 100 μL of Np(VI) nitrate stock solution was loaded into a 10 mL volume PTFE autoclave liner and then heated at 140 °C to be reduced to a droplet. NaF (3.07 mg, 0.073 mmol) and a large excess of H_3BO_3 (47.2 mg, 0.77 mmol) were added to the droplet in the autoclave followed by the similar procedure for making the NaUBOF-1. Dark green crystals of NaNpBOF-1 in the form of tablets were collected with brown and colorless amorphous phases as side products.

*Crystallographic Studies:* Single crystals of all six actinide fluoroborate phases were mounted on glass fibers and optically aligned on a Bruker APEXII CCD X-ray diffractometer or a Bruker APEXII Quazar X-ray diffractometer using a digital camera. Initial intensity measurements were either performed using a μS X-ray source, a 30 W microfocused sealed tube (MoKα, λ =0.71073 Å) with high-brilliance and high-performance focusing Quazar multilayer optics, or a standard sealed tube with a monocapillary collimator. APEXII software was used for determination of the unit cells and data collection control. The intensities of reflections of a sphere were collected by a combination of four sets of exposures (frames). Each set had a different φ angle for the
crystal and each exposure covered a range of 0.5° in $\omega$. A total of 1464 frames were collected with an exposure time per frame of 10 to 80 s, depending on the crystals. SAINT was used for data integration including Lorentz and polarization corrections. Semi-empirical absorption corrections were applied using the program SADABS. Selected crystallographic data and bond distances information are listed in Table 14.1 and Tables 14.S1-14.S6. Atomic coordinates and additional structural information are provided in the Supplementary Material (CIF’s). The assignment of the fluoride sites is challenging because of the nearly identical scattering of oxygen and fluorine. Four lines of evidence support our assignments. First, B–F and B–O bonds are slightly different in length. Second, when the sites that we have assigned as fluoride are replaced with oxygen the thermal parameter becomes non-positive definite. Third, EDX has been used to measure the amount of fluoride in the crystals, and the An/F ratios from EDX are consistent with the formula derived from the crystal structures. Finally, the structures are different from compounds that lack fluoride.

**Powder X-ray diffraction:** Powder X-ray diffraction patterns of the products of pure TIUBOF-1 reaction was collected on a Bruker powder diffractometer with a Lynxeye one-dimensional detector at room temperature in the angular range from 5° to 80° ($2\Theta$) with a scanning step width of 0.05° and a fixed counting time of 1 s/step. The collected patterns were compared with those calculated from single crystal data using ATOMS shown in the supporting information.

**SEM/EDS:** SEM/EDS images and data were collected using a LEO EVO 50 with an Oxford INCA Energy Dispersive Spectrometer (EDS). The energy of the electron beam
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<th>KUBOF-2</th>
<th>RbUBOF-1</th>
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was 29.02 kV, and spectrum acquisition time was 120 seconds. All of the data were calibrated with standards and all EDS results are provided in the supporting information. Fluorine was found in all phases. KUBOF-2 showed a much higher F/U ratio than all other phases which coincides with the proposed formula of KUBOF-2.

UV-vis-NIR and Fluorescence Spectroscopy: UV-vis-NIR data were acquired from a single crystal of NaNpBOF-1 using a Craic Technologies microspectrophotometer. Crystals were placed on quartz slides under Krytox oil, and the data were collected from 500 to 1400 nm. Fluorescence data were obtained for all uranium phases using 365 nm light for excitation (see Supporting Information).

Second-Harmonic Generation Measurements: Powder second-harmonic generation (SHG) measurements were performed on a Kurtz-Perry nonlinear optical system. A Q-switched Nd:YAG laser (Continuum Surelite I-10), operated at 10 Hz, provided the 1064 nm light used for all measurements. The SHG intensity was recorded from a pure polycrystalline sample of TlUBOF-1. No index of refraction matching fluid was used in these experiments. The SHG light at 532 nm was collected in reflection, selected by a narrow band-pass interference filter (Pomfret) and detected by a photomultiplier tube (RCA 1P28). A near normal incidence beam splitter reflected a small fraction of the laser beam onto a pyroelectric detector (Molelectron J3-05) that was used as a laser pulse energy monitor. A digital storage oscilloscope (Tektronix TDS 640A) signal averaged and recorded both the SHG and incident laser energy signals. Average laser power was measured separately with a calibrated Scientech volume absorber calorimeter. As an important note for other investigators interested in the
nonlinear optical properties of radioactive materials: The practice of grinding and sieving powders so that comparisons can be made with reference materials of similar particle size is unsafe. We ground and sieved a less-radioactive thorium compound inside a glovebox and then surveyed the interior of the glovebox. There was a uniform contamination of 50 dpm on every surface tested. We recommend discontinuation of this practice immediately. It is enough to say that there is or is not SHG activity. The magnitude is not important enough to risk the health of researchers.

14.4 Synthesis Discussion

The boric acid flux reactions of actinide(VI) nitrates with alkali metal or pseudo-alkali metal fluorides is a facile way to prepare novel actinide fluoroborates. However, unlike the uranyl borate system, where Li, Cs, and Ag uranyl borates can be made, the same effort to synthesize Li, Cs, and Ag uranyl fluoroborates was not successful. Also, compared to actinide borate systems, isolating pure phases is much more difficult in the actinide fluoroborate system, all the reactions tested failed to yield pure phases except for one reaction with a specific stoichiometry that yielded a pure thallium uranyl fluoroborate, \( \text{Tl} [(\text{UO}_2)\text{B}_5\text{O}_8(\text{OH})\text{F}] \) (\text{TUBOF-1}) as confirmed by powder X-ray diffraction (see Supporting Information).

The B–F bonds were formed in situ during the boric acid flux reactions. It is surprising that actinide fluoride compounds were not formed since fluoride is a strong ligand for actinides in all oxidation states according to the Pearson acid base concept, and actinide fluoride compounds in most oxidation states are well known. However,
this can be explained by the fact that the bond dissociation energy of B–F bonds (732 kJ/mol) is considerably larger than U–F bonds (648 kJ/mol), which indicates that the actinide fluoroborate compounds with B–F bonds instead of U–F bonds are the thermodynamic products.

It is also interesting that in Na[(NpO₂)B₅O₈(OH)F]·H₂O (NaNpBOF-1), neptunium retains the +6 oxidation state. In our previous report, we described the syntheses of K₄(NpO₂)₆.7₃[B₂₀O₃₆(OH)₂] and Ba₂(NpO₂)₆.₅₉[B₂₀O₃₆(OH)₂]·H₂O, which contain Np(IV), Np(V), and Np(VI).²¹ These compounds are synthesized by the reactions of Np(VI) nitrate with molten boric acid. When chloride is the only counter ion in the reaction (NpO₂)₄[(NpO₂)₆.₇₃B₂₀O₃₆(OH)₂] forms.²¹ This demonstrates that Np(VI) is first reduced to Np(V) followed by disproportionation. We noted later, however, in order to retain neptunium in the +6 oxidation state, neptunium(VI) perchlorate could be used as the starting materials, where perchlorate is likely acting as an oxidant that prevents neptunium from being reduced from VI to V.²⁴ The Np(VI) fluoroborate, Na[(NpO₂)B₅O₈(OH)F]·H₂O (NaNpBOF-1) likely crystallizes more rapidly than the reduction of Np(VI) to Np(V) takes place.

14.5 Structure Descriptions and Topological Aspects

The crystal structures of all of these compounds contain layered motifs and are based on similar functional groups. Uranium and neptunium atoms have similar oxygen coordination U(Np)O₈ with a hexagonal bipyramidal geometry. The pyramids are based on axial uranyl/neptunyl groups (UO₂²⁺/NpO₂²⁺), and six oxygen atoms coordinate the
$\text{UO}_2^{2+}/\text{NpO}_2^{2+}$ groups in the equatorial plane. The bond lengths of $\text{U(Np)}-\text{O}$ in $\text{UO}_2^{2+}$ and $\text{NpO}_2^{2+}$ groups are practically identical and in the range from 1.74 Å to 1.78 Å. The boron environments are more diverse than what were previously observed in the crystal structures of actinide borates.$^7$-$^{24}$ The structures of $\text{NaUBOF-1}$, $\text{KUBOF-1}$, $\text{RbUBOF-1}$, $\text{TIUBOF-1}$, and $\text{NaNpBOF-1}$ are based on the same oxo- and fluorooxo-boron groups – $\text{BO}_3$ triangles, $\text{BO}_4$ and $\text{BO}_3\text{F}$ tetrahedra (Fig. 14.1). The crystal structure of $\text{KUBOF-2}$ is quite different from other phases and is formed by two types of $\text{BO}_3$ triangles and one type of tetrahedron – $\text{BO}_3\text{F}$ fluorooxo group (Fig. 14.2). The $\text{B–O}$ bond distances in the $\text{BO}_3$ triangles of all obtained structures are in the normal range from 1.34 Å to 1.39 Å. Bond lengths in $\text{BO}_4$ tetrahedra are also standard, and range from 1.44 Å to 1.50 Å. The $\text{B–F}$ bond lengths in $\text{KUBOF-2}$ are in the range of 1.41 Å to 1.46 Å, which are slightly longer than in the other phases where the same bonds are in range from 1.40 Å to 1.43 Å. Such differences are probably a result of the different environment of the fluorine atoms. In the structure of $\text{KUBOF-2}$, fluorine atoms are contacted only with potassium atoms in the interlayer space, while in all other compounds, the environments of fluorine atoms are more complicated as the hydrogen bonding is involved. Based on the general aspects of the layered structures and organization of the interlayer space, we can separate the six actinide fluoroborate phases into three groups. The first group includes $\text{NaUBOF-1}$, $\text{RbUBOF-1}$, $\text{TIUBOF-1}$, and $\text{NaNpBOF-1}$, while the second and third groups have only one member each – $\text{KUBOF-1}$ and $\text{KUBOF-2}$, respectively.

All compounds in the first group contain layers with the same type of topologies (A/B-type layers) which were first observed in sodium uranyl borates.$^{17}$ However,
Figure 14.1: The fragments of NaUBOF-1 and NaNpBOF-1 (a), KUBOF-1 (b), RbUBOF-1 (c), TIUBOF-1 (d) crystal structures. (U shown in yellow, B in green, F, Na-Tl and water molecules are red, blue and violet spheres respectively)
Figure 14.2: (a) Fragment of KUBOF-2 crystal structure, (b) and (c) structures of layers in KUBOF-2. (U shown in yellow, B in green, F and K shown in red and blue respectively, BO$_3$ groups in layers are red triangles, BO$_3$$^-$ anions are violet lines)
alternating orders and the orientations of these layers strongly vary among these phases which leads to different space groups adopted by these phases (chiral, polar space group \( P1 \) for \( \text{TIUBOF-1} \) and noncentrosymmetric space group \( \text{Cc} \) for \( \text{NaUBOF-1}, \text{NaNpBOF-1}, \) and \( \text{RbUBOF-1} \)). The simplest one is \( \text{TIUBOF-1} \), which is formed by only one type of layer (Fig. 14.1d). The layers are packed together without further rotation, which results in the unit cell with only one layer for \( \text{TIUBOF-1} \). \( \text{NaUBOF-1} \) and \( \text{NaNpBOF-1} \) are isotypic and similar with \( \text{RbUBOF-1} \). All of these phases are based on two types of alternating layers shown in Fig. 14.1a and Fig. 14.1c. The difference between \( \text{NaUBOF-1} / \text{NaNpBOF-1} \) and \( \text{RbUBOF-1} \) is only in the layer orientations. Each second layer is turned 120° with respect to the nearest layer in structures of \( \text{NaUBOF-1} \) and \( \text{NaNpBOF-1} \), while in the structure of \( \text{RbUBOF-1} \), the angle is only 60°. Also, the interlayer content is different since the sodium phase is hydrated while the rubidium phase is anhydrous. Each layer in the structures of \( \text{NaUBOF-1, RbUBOF-1, TIUBOF-1,} \) and \( \text{NaNpBOF-1} \) has “additional” \( \text{BO}_3 \) triangles perpendicular to the plane of the layer. The general topology of such layers is identical with \( \alpha-\text{Na}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}(\text{OH})_5], \beta-\text{Na}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}(\text{OH})_5], \text{Na}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}(\text{OH})_5]\cdot3\text{H}_2\text{O}, \text{and K}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}(\text{OH})_5] \) and can be described with \( 1\text{L}-1-0-0 \) descriptor. However, the way the layers pack in the mentioned phases and in \( \text{NaUBOF-1, RbUBOF-1, TIUBOF-1,} \) and \( \text{NaNpBOF-1} \) is different. In the structures of \( \alpha-\text{Na}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}(\text{OH})_5], \beta-\text{Na}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}(\text{OH})_5], \text{Na}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}(\text{OH})_5]\cdot3\text{H}_2\text{O}, \text{K}[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}(\text{OH})_5] \), the layers are packed “face-to-face”, which means “additional” \( \text{BO}_3 \) triangles in two nearest layers are directed towards each other. The bonding between them is provided by alkali metal cations. The other sides
of the layers which do not have “additional” BO$_3$ unit are also turned to each other but they are bound by strong hydrogen bonds provided by terminal B–OH groups. In the structures of NaUBOF-1, RbUBOF-1, TIUBOF-1, and NaNpBOF-1, these B–OH bonds are substituted by B–F bonds and hydrogen bonding disappears between these fragments. Thus, the orientation of the layers has to be modified to provide the bonding via monovalence metal cations. The only way to achieve this is turning the sides of layers with “additional” BO$_3$ triangles to the sides with terminal B–F groups which can be observed in NaUBOF-1, RbUBOF-1, TIUBOF-1, and NaNpBOF-1. Such modification is an example of how a new structure type is formed by functionalized structural units plus the old topology of main structural fragments.

The second group includes only one phase which is KUBOF-1. The layer topology is different from the A/B types observed in the phases of the first group. In general, the layers in KUBOF-1 are very similar with the structure of silver uranyl borate (Ag[(UO$_2$)$_5$B$_5$O$_8$(OH)$_2$], G-type layer topology) and can be described with 1L-1-1-0 descriptor (Fig. 14.1b). The corrugated layers of KUBOF-1 are linked into a quasi 3D-framework via K⋯O, K⋯F interactions and hydrogen bonds between terminal B-OH groups in additional BO$_3$ triangles perpendicular to the layers. The layer packing mode in KUBOF-1 is also identical with the structure of Ag[(UO$_2$)$_5$B$_5$O$_8$(OH)$_2$] and based on the same layer types (G-type) which rotates by 180° with respect to one another between neighboring layers (Fig. 14.1b). The G-type topology in the structure of KUBOF-1 allowed the formation of symmetrical layers where terminal functional B–F groups appear on both sides of the layers. This makes the layers non-polar and the structural
modifications we observed in $\alpha$-Na$[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}$(OH)$_5$], $\beta$-Na$[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}$(OH)$_5$], Na$[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}$(OH)$_5$]$\cdot$3H$_2$O, K$[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}$(OH)$_5$]$ \rightarrow (\text{NaUBOF-1, RbUBOF-1, TIUBOF-1 and NaNpBOF-1})$ are not required. Interestingly, KUBOF-1 does not have an analogue in the group of potassium uranyl borates including K$[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}$(OH)$_5$], K$[(\text{UO}_2)_2\text{B}_{10}\text{O}_{15}$(OH)$_5$]$\cdot$H$_2$O, K$_2$[(UO$_2$)$_2$B$_{12}$O$_{19}$(OH)$_4$]$\cdot$0.3H$_2$O. This could be another effect of BO$_4$ to BO$_3$F tetrahedra modification. The K···F bonds are stronger than K···O interactions and helps with the stabilization of Ag$[(\text{UO}_2)\text{B}_5\text{O}_8$(OH)$_2$]$ structure type with K$^+$ as an interlayer cation.

The third group also has only one member – KUBOF-2. The crystal structure of this phase is very unusual in all regards which combines structural aspects from groups of uranyl borates obtained from both high- and mild-temperature synthetic methods. The general view of the KUBOF-2 structure is shown on Fig. 14.2a. The 2D layered structure of KUBOF-2 is based on BO$_3$ triangles appearing only in the layers and BO$_3$F tetrahedra. The layers are asymmetric since on one side there are twice as many terminal B–F groups (Fig. 14.2b) than the other side (Fig. 14.2c). All of BO$_4$ tetrahedra were substituted by BO$_3$F units in the layers of KUBOF-2 and there are no additional BO$_3$ groups oriented perpendicularly to the layer planes. The structure can be described with 1L-0-0-0 descriptor. This is the first difference between KUBOF-2 and all other phases reviewed in this work. The second difference is the topology of fluorooxo-borate layers. In the Fig. 14.2b and 14.2c triangles are shown in red, tetrahedra are in green, and we can observe only one BO$_3$ triangle and eight BO$_3$F tetrahedra around each UO$_2$$^{2+}$ hexagonal bipyramid. This is the lowest ratio BO$_3$/BO$_4$(BO$_3$F) observed to date in the
actinide borate system. The layers observed in the structure of KUBOF-2 are named as I-type. Skeletal representations of this layer topology are shown on Fig. 14.3a (I-type) and Fig. 14.3b (I'-type). Three BO$_3$F tetrahedra are linked via vertices into supertriangle-like groups. Two of them directed “up” (in I-type) or “down” (in I'-type) which provides the main difference between I and I' geometries, and is very similar with orientations of the same supertriangles in A/B- and A'/B'- type layers. The difference between A/B-types and I-type layers is in the method of the supertriangles linkage. The supertriangles in the structures of A/B-types layers are linked into 2D layers by BO$_3$ triangles only while 2/3 of the BO$_3$ triangles are now substituted by BO$_3$F tetrahedra in I-type layers as shown in Fig. 14.3a, 14.3b. One of these BO$_3$F tetrahedra is directed “up” (shown in green in Fig. 14.3a and blue in Fig. 14.3b) while others are directed “down” (green in Fig. 14.3a and blue in Fig. 14.3b, respectively). I-type and I'-type layers are enantiomorphic and have the same symmetrical relationship as we demonstrated in A/B type layers system. Described layers alternate in the structure of KUBOF-2 with the following packets ... (I/I')(I+180°/I'+180°)(I/I')... (Fig. 14.2a). The layers in each packet face each other via the side shown in Fig. 14.2c. The layers from different packets face each other via the other side which contains twice as many B–F groups on the surface (demonstrated in Fig. 14.2b). This is the third difference between KUBOF-2 and other phases discussed in this paper. Thus, we have two types of interlayer constituents, and the nature of these constituents is also different. There are only K$^+$ cations in the interlayer space between (I/I') and (I+180°/I'+180°) packets (Fig. 14.2a). These cations are connected only by fluorine atoms (case of K1) or by fluorine and oxygen atoms from
Figure 14.3: Schematic representation of layer topology in KUBOF-2.
B–F groups and uranyl groups (case of K4). The interlayer content within packets consists of both K\(^+\) cations and H\(_2\)BO\(_3^-\) anions with the ratio of K : H\(_2\)BO\(_3\) = 4 : 1 (Fig. 14.2a, H\(_2\)BO\(_3^-\) anions are violet). The same anionic groups (H\(_2\)BO\(_3^-\)) were also found in the structure of Th[B\(_5\)O\(_6\)(OH)\(_6\)](H\(_2\)BO\(_3\))·2.5H\(_2\)O (NDTB-1) where it only appeared in the cages and channels.\(^{15}\) The H\(_2\)BO\(_3^-\) anions are located right on the top of BO\(_3\) triangles from the neighboring layers within one package (coordinates x,y,z: B6 in H\(_2\)BO\(_3^-\) anions 0.33333,0.66667,-0.12018; B7 in the layers 0.33333,0.66667,-0.25000) through the c axis. The oxygen atoms from H\(_2\)BO\(_3^-\) are also bound to the K\(_3\) cations. It is impossible to localize of H\(^+\) positions on the H\(_2\)BO\(_3^-\) anions since all these oxygen atoms in the H\(_2\)BO\(_3^-\) anions are crystallographically equivalent. Most probably, they are delocalized as an effect of H\(_2\)BO\(_3^-\) rotations among equivalent structural positions. The structure of Ni\(_7\)UB\(_4\)O\(_{16}\) shares certain similarities with KUBOF-2. There are both nickel cations and BO\(_3^{3-}\) anions between uranyl borate chains.\(^{12}\) However, this phase was obtained by the high-temperature solid state B\(_2\)O\(_3\) flux reactions.

The structure of KUBOF-2 is a logically final point in the process of borate network functionalization within uranyl borate layers. The replacement of all terminal oxygen atoms with fluorine atoms provides substantial changes in the structure formation which leads to multifunctional interlayer contents.

14.6 Nonlinear Optical Properties

As mentioned above, the partial substitution of BO\(_4\) by BO\(_3\)F tetrahedra can further reduce the symmetry. TIUBOF-1 crystallizes in the chiral and polar space group \(P1\)
without any symmetry elements present in the crystal structure, and is the only phase that can be obtained in pure form. Thus, this compound is capable of exhibiting a wide range of physical properties including the second-harmonic generation of light when irradiated with a high wavelength NIR-laser. When a pure polycrystalline sample of **TIUBOF-1** is irradiated with 1064 nm light, a sharp strong signal with 532 nm light is clearly observed as shown in Fig. 14.4.

14.7 UV-Vis-NIR Absorption Spectroscopy

U(VI) compounds usually show charge-transfer bands in the UV region of the spectrum without f-f transitions since there is no 5f electrons in U(VI), while Np(VI), which has a 5f\(^1\) electron configuration, yields a single broad Laporte-forbidden f-f transition in addition to higher energy charge-transfer bands.\(^{34}\) Typically for Np(VI) this transition occurs in the NIR near 1200 nm.\(^{34}\) The UV-vis-NIR spectrum of **NaNpBOF-1** acquired from a single crystal is shown in Fig. 14.5, the transition is at 1120 nm. We noted again this transition peak position is closely associated with the coordination geometries of Np(VI) when in solid state. For example, as we previously observed, the f-f transition peak for single crystals of NpO\(_2\)(NO\(_3\))\(_2\)-6H\(_2\)O is located at 1100 nm and NpO\(_2\)[B\(_8\)O\(_{11}\)(OH)\(_4\)] shows a transition at 1140 nm.\(^{24}\) The transition of NpO\(_8\) units are blue shifted compared to NpO\(_7\) units.\(^{24,35}\) In the higher energy visible region, the fine vibronically-coupled charge-transfer bands are shown for neptuyl units NpO\(_2\).\(^{24,36}\)
Figure 14.4: Second-harmonic generation of 532 nm laser light from 1064 nm laser light getting from the pure polycrystalline sample of TIUBOF-1.
Figure 14.5: UV-vis-NIR absorption spectrum of a single crystal of Na[(NpO$_2$)$_5$B$_5$O$_8$(OH)]·H$_2$O (NaNpBOF-1) showing both f-f transition and vibronic-coupled charge-transfer bands.
14.8 Fluorescence Properties

Denning and co-workers have carefully and extensively studied the emission from uranyl compounds, and assigned all of the vibronic transitions from single crystals containing the \([\text{UO}_2\text{Cl}_4]^{2-}\) anion. While five broad features centered near 520 nm are generally observed for uranyl compounds at room temperature, far more bands are resolved at low temperatures.

\[
\text{Na}[\text{(UO}_2\text{)}\text{B}_5\text{O}_8\text{(OH)}\text{F}]\cdot\text{H}_2\text{O (NaUBOF-1)}, \quad \text{K}[\text{(UO}_2\text{)}\text{B}_5\text{O}_8\text{(OH)}\text{F} ] (\text{KUBOF-1}),
\]

\[
\text{K}_{11}[\text{(UO}_2\text{)}_6\text{B}_{24}\text{O}_{36}\text{F}_{22}]\cdot\text{H}_2\text{BO}_3 (\text{KUBOF-2}), \quad \text{and Rb}[\text{(UO}_2\text{)}\text{B}_5\text{O}_8\text{(OH)}\text{F} ] (\text{RbUBOF-1})
\]

all form crystals with the pale yellow-green coloration. Upon irradiation with 365 nm light, these crystals fluoresce with sufficient intensity that the emission from a few crystals is easily observed by the naked eye. The fluorescence spectra are all provided in the Supporting Information. Given that all of the uranyl borates contain very similar site symmetry around the uranium atoms (\(D_{6h}\)), it is not surprising that they are all very similar to the alkali metal uranyl borates synthesized by us. However, \(\text{Tl}[\text{(UO}_2\text{)}\text{B}_5\text{O}_8\text{(OH)}\text{F} ]\) (TIUBOF-1) forms crystals with a light yellow coloration, and these crystals do not fluoresce when irradiated with 365 nm light. It is expected that the \(\text{Tl}^+\) quenches the fluorescence features from the uranyl units, which has also been observed in all thallium uranyl borate compounds.

14.9 Conclusions

In summary, we have demonstrated that the boric acid flux reactions of actinide starting materials with the alkali metal or pseudo-alkali metal fluorides is a facile
method for preparing novel actinide fluoroborates containing the BO$_3$F unit. Compared with the actinide borate family, the modification of BO$_4$ to BO$_3$F tetrahedra further reduces the symmetry, and improves the probability of achieving a noncentrosymmetric phase. Pure phases can be synthesized in this family through careful control of reaction composition. More importantly, the replacement of B−OH bonds with B−F bonds should substantially enhance the stability of these materials, and the borate networks can now be greatly modified to yield novel actinide borate layered topologies and layer packing modes that are further enrichments of the actinide borate system. Finally, as observed in NaNpBOF-1, the redox chemistry of transuranium elements is greatly affected by counter ions, and Np(VI) is stabilized in the presence of fluoride. Perhaps the greatest surprise in this family is the lack of U−F and Np−F bonds. B−F bonds are simply much stronger, and this is one of very few families of fluoride-containing compounds with actinides where An−F bonds do not occur. There are in fact other systems where fluoride could potentially be incorporated without forming An−F bonds. For example, the beryllium fluoroborate compounds, ABe$_2$BO$_3$F$_2$ (A = K, Rb, Cs, Tl),$^{38}$ are among the best optical materials for deep UV applications.$^{39}$ In these compounds B−F bonds do not exist, and the fluoride is solely bound to beryllium. Therefore, actinide compounds that contain both beryllium and fluoride may also lack An−F bonds. We will be exploring this system shortly.
14.10 Reference


CHAPTER 15:

K(NpO$_2$)$_3$(H$_2$O)Cl$_4$: A CHANNEL STRUCTURE ASSEMBLED BY TWO- AND THREE-CENTER CATION-CATION INTERACTIONS OF NEPTUNYL CATIONS

15.1 Abstract

A Np(V) compound containing three-center cation-cation interactions,
K(NpO$_2$)$_3$(H$_2$O)Cl$_4$, has been prepared by reacting Np(V) with KCl in molten boric acid. This compound forms a three-dimensional channel structure that is constructed from both two- and three-center cation-cation interactions. Three new bonding modes for cation-cation interactions are added to the summary of all known Np(V) compounds.

15.2 Introduction

Cation-cation interactions (CCI’s) in actinide compounds describe the scenario where the oxo atom of an actinyl unit can further bond to another actinide center in its equatorial plane. More generally these would be called bridging oxo atoms. CCI’s between UO$_2^{2+}$ and NpO$_2^+$ were first observed in solution studies by Sullivan et al. in 1961, and have subsequently been detected using a variety of techniques including absorption, vibrational, and Mossbauer spectroscopy as well as X-ray scattering. CCI’s in the solid state were first described from the crystal structure of Na(NpO$_2$)$_2$(C$_{12}$O$_{12}$)(H$_2$O)$_8$ which contains a slipped dimer of NpO$_2^+$ connected through...
CCI’s.² It is now known that 53% of Np(V) compounds contain these interactions in the solid state.³ This bonding motif also exists in other An(V) compounds such as U(V),⁴ Pu(V),⁵ and Am(V).⁶ This linkage plays an important role in both the disproportionation of An(V),⁷ and in the magnetic ordering in some Np(V) compounds.⁸ Although it is very rare, CCI’s can also be found in U(VI) compounds.⁹ From an applied standpoint these interactions are important because they affect neptunium partitioning during the reprocessing of used nuclear fuel, i.e. neptunium can be transferred to streams where it is not desired during PUREX-type processes.

The most common CCI bonds involve two actinide centers, where the oxo atoms of an actinyl unit bond to only one secondary actinide atom. This is called a two-center cation-cation interaction. However, CCI bonds can also involve three actinide centers, where the oxo atoms of an actinyl unit coordinates to two adjacent actinide centers, i.e a u₃-oxo. Although CCI’s are rare in U(VI) compounds, a three-center CCI was first reported in a U(VI) hydroxide compound, Sr₅(UO₂)₂₀(UO₆)₂O₁₆(OH)₆(H₂O)₆, in which only one oxo atom is involved in the three-center CCI, and the corresponding U≡O distance is very long at 1.967(9) Å compared to the normal length of 1.79(3) Å for an oxo atom not involved in further bonding.¹⁰ Three-center CCI’s were further detected in the structures of (K,Na)Na₃[(UO₂)₅O₆(SO₄)]¹¹ and Li₄[(UO₂)₁₀O₁₀(Mo₂O₈)].¹² These four compounds are the only examples of U(VI) compounds that contain three-center CCI’s. Despite the fact that CCI’s are much more common in Np(V) compounds than in U(VI) materials, there is only one example of the three-center CCI’s for Np(V) in the solid state, and these are found in the structure of Np₂O₅.¹³ These interactions in Np₂O₅ result
in a relatively complex magnetic structure at low temperatures.\textsuperscript{13} Herein, we report the crystal structure and the optical spectrum of the second example of Np(V) compounds containing three-center CCl’s: K(NpO\textsubscript{2})\textsubscript{3}(H\textsubscript{2}O)Cl\textsubscript{4}.

15.3 Experimental Section

\textit{Caution!} \textsuperscript{237}Np (t\textsubscript{1/2} = 2.14 \times 10\textsuperscript{6} y) represents a serious health risk owing to its \(\alpha\) and \(\gamma\) emission, and especially because of its decay to the short-lived isotope \textsuperscript{233}Pa (t\textsubscript{1/2} = 27.0 d), which is a potent \(\beta\) and \(\gamma\) emitter.

A stock solution of \textsuperscript{237}Np (V) chloride was prepared by first digesting NpO\textsubscript{2} in 8 M HNO\textsubscript{3} for 3 days at 200 °C (in an autoclave). The solution was reduced to a moist residue and redissolved in water forming a Np(VI) nitrate solution. Large excess of NaNO\textsubscript{2} followed by excess of NH\textsubscript{4}OH were added to this solution resulting the precipitation of Np(V) hydroxide. The precipitate was then filtered and dried in 120 °C for about 30 minutes. Np(V) hydroxide was then dissolved in a dilute HCl solution.

A stock solution of \textsuperscript{237}Np (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 (46.2 mg) and KCl (14.5 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 three days followed by cooling to room temperature over one day period. The autoclave was opened and boiling water was added to dissolve the excess boric acid revealing bright green crystals with an acicular habit as the major product.
15.4 Synthesis Discussion

\[ \text{K(NpO}_2\text{)}_3(\text{H}_2\text{O})\text{Cl}_4 \] was synthesized by reacting Np(V) chloride in a molten boric acid flux with an excess of KCl at 220 °C.\textsuperscript{14} The product was washed by boiling water and acicular crystals with bright green coloration were isolated. Surprisingly, K(NpO\textsubscript{2})\textsubscript{3}(H\textsubscript{2}O)Cl\textsubscript{4} is not soluble in water while all other Np(V) chloride compounds that have been reported are water-soluble, and have been prepared by room-temperature slow evaporation of water.\textsuperscript{15}

15.5 Crystal Structure Depiction

Single crystal X-ray diffraction studies\textsuperscript{16} revealed that K(NpO\textsubscript{2})\textsubscript{3}(H\textsubscript{2}O)Cl\textsubscript{4} crystallizes in the polar orthorhombic space group \textit{Pna\textsubscript{2}}\textsubscript{1}. The structure of K(NpO\textsubscript{2})\textsubscript{3}(H\textsubscript{2}O)Cl\textsubscript{4} contains three crystallographically unique Np(V) sites. All of these Np(V) sites are found to have a pentagonal bipyramidal coordination environment containing Cl\textsuperscript{−} in their equatorial planes. One of the Np(V) sites is also bound by additional H\textsubscript{2}O in the equatorial plane. These Np(V) pentagonal bipyramids are connected through CCl\textsuperscript{−}’s and bridging Cl\textsuperscript{−} to form a remarkable three-dimensional channel structure with potassium cations in the channels, as shown in \textbf{Fig. 15.1}.

The Np(1)O\textsubscript{2}\textsuperscript{+} and Np(2)O\textsubscript{2}\textsuperscript{+} sites are very similar, with average neptunyl bond distances of 1.836(7) and 1.834(7) Å, and bond angles of 177.3(3) and 178.0(3), respectively. All of the oxygen atoms on their neptunyl units are further bonded to another Np(V) site to form two-center CCl\textsuperscript{−}’s. Np(1)O\textsubscript{2}\textsuperscript{+} sites have two neptunyl oxo atoms donating to Np(2)O\textsubscript{2}\textsuperscript{+} sites and Np(3)O\textsubscript{2}\textsuperscript{+} sites; while Np(2)O\textsubscript{2}\textsuperscript{+} sites donates two
Figure 15.1: A view of part of the three-dimensional structure of $\text{K(NpO}_2\text{)}_3\text{(H}_2\text{O)}\text{Cl}_4$ showing the channels extends along the $c$ axis. Np polyhedra are shown in red-brown, chlorine in green, oxygen in red, and potassium atoms in purple.
CCI’s to the Np(1)O$_2^+$ sites and the Np(3)O$_2^+$ sites, respectively. The only difference between Np(1)O$_2^+$ and Np(2)O$_2^+$ sites is that Np(1)O$_2^+$ sites are bound by two Cl atoms and one water molecule besides the oxo atoms from CCI’s in the equatorial planes, while Np(2)O$_2^+$ sites have three Cl atoms in the equatorial planes (Fig. 15.2).

The most remarkable aspect of the structure of K(NpO$_2$)$_3$(H$_2$O)Cl$_4$ lies at the Np(3)O$_2^+$ sites. Np(3)O$_2^+$ sites contain quite asymmetric neptunyl units with the neptunyl bond distances of 1.908(7) Å (O4) and 1.819(7) Å (O2), and a bond angle of 175.9(3)$^\circ$. One of the neptunyl oxo atoms, O4, which has the longer Np≡O distance, is further bonded to two other Np(V) sites simultaneously to form a three-center CCI. The bond-valence sum was calculated at 1.93 for O4. The other neptunyl oxygen atom, O2, forms two-center CCI’s to another adjacent Np(3)O$_2^+$ site. The Np(3)O$_2^+$ sites also accept three CCI bonds in the equatorial planes from a Np(1)O$_2^+$ site, a Np(2)O$_2^+$ site, and another Np(3)O$_2^+$ site, respectively. As a result, all oxo atoms coordinating to Np(3) are involved in the CCI’s. With two other Cl atoms, a pentagonal bipyramidal geometry is formed for the Np(3)O$_2^+$ sites as shown in Fig. 15.2.

15.6 New Summary of the CCI Bonding Modes

Grigoriev et al. summarized all the bonding modes of CCI’s that existed in the all known neptunium compounds as of 2004. However, this review needs to be amended in light of the discovery of the new three-center CCI’s. For example, the bonding mode of Np(3)O$_2^+$ sites in the title compound can be described as the new type listed in Fig. 15.3, case $k$. Both Np(1)O$_2^+$ and Np(2)O$_2^+$ sites still adopt the known CCI bonding type.
Figure 15.2: Depiction of the coordination environments of the three neptunium sites and the cation-cation interactions in $\text{K(NpO}_2\text{)}_3\text{(H}_2\text{O)}\text{Cl}_4$. 
Figure 15.3: New summary of the CCI bonding modes for all known neptunium compounds, the dash lines represent the CCI bonds.
listed as case $h$. Moreover, in the structure of $\text{Np}_2\text{O}_5$, two of the three Np sites adopt the new type listed as case $i$, while the third Np site containing the three-center CCI neptunyl has the type of $j$.$^{13}$ The two mixed/intermediate-valent neptunium borates, $\text{K}_4(\text{Np}^{\text{IV}}\text{O}_2)_{0.73}(\text{Np}^{\text{V}}\text{O}_2)_{2}(\text{Np}^{\text{VI}}\text{O}_2)_{4}\text{B}_{20}\text{O}_{36}(\text{OH})_2$ and $\text{Ba}_2(\text{Np}^{\text{IV}}\text{O}_2)_{0.59}(\text{Np}^{\text{V}}\text{O}_2)_{2}(\text{Np}^{\text{VI}}\text{O}_2)_{4}\text{B}_{20}\text{O}_{36}(\text{OH})_2\cdot\text{H}_2\text{O}$, contain neptunium tetragonal bipyramidal sites that are surrounded by only by CCI’s.$^{23}$ As a result, these neptunium sites also adopt a new CCI bonding type listed as case $i$.

15.7 UV-vis-NIR Spectrum

Cation-cation interactions result in changes in the f-f transitions for neptunium(V). The UV-vis-NIR spectrum acquired from single crystals of $\text{K}(\text{NpO}_2)_{3}(\text{H}_2\text{O})\text{Cl}_4$ is shown in Fig. 15.4. The existence of CCI’s in a compound shift the primary transition at 980 nm to longer wavelengths, typically around 1010 nm.$^{17-19}$ This transition is in fact found at 1010 nm for $\text{K}(\text{NpO}_2)_{3}(\text{H}_2\text{O})\text{Cl}_4$. However, the peak is broader than normal, most likely because $\text{K}(\text{NpO}_2)_{3}(\text{H}_2\text{O})\text{Cl}_4$ contains both two- and three-center CCI’s and there are multiple overlapping transitions. The intensities of Np(V) transitions have been carefully examined by several groups.$^{20}$ Krot and co-workers concluded that when the intensity of the ca. 980 nm transition is relatively higher that a pentagonal bipyramidal environment is typically observed.$^{21}$ Absorption studies on single crystals are complicated by the potential for an orientational dependence on which transitions are allowed. The acicular nature of the crystals of $\text{K}(\text{NpO}_2)_{3}(\text{H}_2\text{O})\text{Cl}_4$ is not amenable to a detailed study of pleochroism. However, the spectrum taken from a single crystal,
Figure 15.4: UV-vis-NIR spectrum of K(NpO$_2$)$_3$(H$_2$O)Cl$_4$ obtained from a single crystal. The primary f-f transition for Np(V) is at 1010 nm.
shown in Fig. 15.4, reveals some important observations. First, the transitions near 616 and 980 nm have been found to obey Beer-Lambert behavior in solution and can be used to calculate the concentration of Np(V). The transitions between 616 and 980 are typically too weak to utilize, the same is true for the transitions after 980 nm.

For K(NpO$_2$)$_3$(H$_2$O)Cl$_4$, we find that these typically neglected transitions are of nearly equal intensity to 1010 nm transition, which should be as much as 400× more intense owing to the mixing of 5fϕ and 6dϕ orbitals, which relaxes the selection rules for this transition (f-f transitions are Laporte-forbidden).$^{22}$ In fact, there is a transition near 720 nm that is suspiciously like the key transition for Np(IV), however, other necessary transitions are lacking. Given the prevalence of mixed-valent neptunium compounds that result from Np(V) disproportionation,$^{23}$ it is becoming increasingly clear that these compounds require very detailed characterization to be confident about oxidation state assignments. Bond-valence sum calculations are particularly useful in this regard, and for K(NpO$_2$)$_3$(H$_2$O)Cl$_4$ all of the Np(V) yield sums consistent with Np(V) only.

15.8 Conclusions

In conclusion, we have provided an example of a Np(V) compound containing a new type of three-center cation-cation interaction. The channel structure is built from both two- and three-center CCI’s. With the discovery of the three-center CCI’s in Np(V) compounds, three new CCI bonding modes can now be added to the summary of known interactions.$^{17}$ Moreover, as observed in the actinide borate system,$^{23,24}$ the chemistry
of actinides in molten boric acid is proving to be substantially different from that observed in aqueous media or high temperature fluxes. This rare example of a Np(V) chloride compound containing three-center CCI’s has thus far only been prepared in the molten boric acid.

15.9 Reference


16. Crystallographic data for $\text{K(NpO}_2\text{)}_3\text{(H}_2\text{O)Cl}_4$: bright green needle, $0.050 \times 0.015 \times 0.012$ mm, orthorhombic, $Pnma$, $Z = 4$, $a = 19.49(2)$ Å, $b = 11.295(12)$ Å, $c = 5.654(6)$ Å, $V = 1245(2)$ Å$^3$ ($T = 100(2)$ K), $\mu = 260.56$ cm$^{-1}$, $R_1 = 0.0217$, $wR_2 = 0.0387$.


CHAPTER 16:
SURPRISING COORDINATION FOR PLUTONIUM IN THE FIRST PLUTONIUM(III) BORATE

16.1 Abstract

The first plutonium(III) borate, \( \text{Pu}_2[\text{B}_{12}\text{O}_{18}(\text{OH})_4\text{Br}_2(\text{H}_2\text{O})_3] \cdot 0.5\text{H}_2\text{O} \), has been prepared by reacting plutonium(III) with molten boric acid under strictly anaerobic conditions. This compound contains a three-dimensional polyborate network with triangular holes that house the plutonium(III) sites. The plutonium sites in this compound are 9- and 10- coordinate and display atypical geometries.

16.2 Introduction

Structural intricacy and complexity are achieved at a remarkable level in lanthanide and actinide borates owing to unsurpassed flexibility of the coordination chemistry of both rare earth elements and boron. The former have coordination numbers ranging from six to fifteen with a strong preference for seven-, eight- and nine-coordinate geometries,\(^1\) and the latter occurs as both \( \text{BO}_3 \) triangle and \( \text{BO}_4 \) tetrahedra that polymerize in a seemingly limitless variety of cluster, chains, sheets, and frameworks.\(^2-4\) The structural chemistry of borates with trivalent cations has been well-developed over the past decade for the lanthanide series with both hydrothermal conditions and boric acid fluxes being utilized as synthetic methods. The first of these
studies yielded the hydrated gadolinium hexaborate $\text{H}_3\text{GdB}_6\text{O}_{12}$ that can be decomposed to the pentaborate, $\text{GdB}_5\text{O}_9$.\textsuperscript{5} In fact the entire series of $\text{H}_3\text{LnB}_6\text{O}_{12}$ ($\text{Ln} = \text{Sm–Lu}$) can be decomposed to pentaborate phases.\textsuperscript{6} Lanthanide borates yield extremely rich polyborate networks containing both $\text{BO}_3$ triangles and $\text{BO}_4$ tetrahedra, and phases such $\text{Ln[B}_8\text{O}_{13}(\text{OH})_5]$ ($\text{Ln} = \text{La – Nd}$) and $\text{Ln[B}_9\text{O}_{13}(\text{OH})_4]\cdot\text{H}_2\text{O}$ have been prepared, structural characterized, and their luminescent properties elucidated.\textsuperscript{7}

Interest in trivalent actinide (e.g. Pu(III), Am(III), and Cm(III)) borates does not stem from their potential applications as optical materials as it does with lanthanide compounds, but rather from their potential formation in the geological repository for nuclear defense waste known as the Waste Isolation Pilot Plant (WIPP) near Carlsbad, NM. In this salt deposit the concentration of borate species in intergranular brines can be as high as 166 ppm. There is not a single example of a well-characterized trivalent actinide borate in the literature. Although studies of the complexation of Nd(III) by borates in solution have been performed where the neodymium is serving as a surrogate for trivalent actinides.\textsuperscript{8,9} We have recently undertaken the study of actinide borates starting with high oxidation states for the actinides,\textsuperscript{10-18} but in this work we demonstrate the first access to a low oxidation state actinide borate with the synthesis, structural characterization, and absorption spectroscopy of the Pu(III) borate, $\text{Pu}_2[\text{B}_{12}\text{O}_{18}(\text{OH})_4\text{Br}_2(\text{H}_2\text{O})_3]\cdot0.5\text{H}_2\text{O}$. 

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16.3 Experimental Section

A stock solution of $^{242}\text{Pu(VI)}$ nitrate was prepare by first digesting $\text{PuO}_2$ in 8 M HNO$_3$ for 5 days at 200 °C (in an autoclave). The solution was ozonated for an hour and reduced to a moist residue and redissolved in water forming a Pu(VI) nitrate solution. UV-vis-NIR spectroscopy indicates that only Pu(VI) is present. An aliquot containing 5 mg of plutonium was taken from this solution and reduced to a residue. 50 µL of conc. HBr was added to this residue resulting in the immediate formation of bromine gas and a red solution. The red solution was reduced to a residue and transferred into an argon-filled glovebox. The residue was redissolved in 30 µL of argon-sparged water producing a navy blue/purple solution characteristic of Pu(III). The droplet of Pu(III) was then transferred to a PTFE autoclave liner that had been previous heated in the glovebox for two days at 200 °C for two days to drive the oxygen out of the PTFE. The catalyst for the glovebox was then regenerated. Large excess of boric acid (63 mg) was then added directly to the droplet containing Pu(III). The mixture was then sealed in an autoclave and heated at 240 °C for seven days followed by slow cooling to room temperature over a two day period. The furnace for heating the autoclave was also inside the glovebox. The autoclave was opened and cold water was added to dissolve the excess boric acid revealing navy blue/purple crystals with a plate-like habit as the sole product. The unit cells of many crystals were examined, and there is only one Pu(III) compound present.
16.4 Synthesis Discussion

Unlike trivalent lanthanides, Am(III), or Cm(III), Pu(III) is air-sensitive and is often oxidized to Pu(IV) by oxygen. Although it must be kept in mind that there are some systems (e.g. monazites) where Pu(IV) is thermally reduced to Pu(III) at high temperatures. The oxidation of Pu(III) to Pu(IV) can be very rapid at elevated temperatures. When Pu(III) is reacted with molten boric acid at 200 °C or higher it rapidly oxidizes to Pu(IV) and Pu(VI). In order to prevent this oxidation, strictly anaerobic conditions had to be maintained, and it was found that in the absence of oxygen, Pu(III) (as the bromide salt) is maintained in molten boric acid, and we were able to crystallize the first Pu(III) borate, \( \text{Pu}_2[B_{12}O_{18}(OH)4\text{Br}_2(\text{H}_2\text{O})_3] \cdot 0.5\text{H}_2\text{O} \) as thin navy blue/purple tablets as the sole product of the reaction.

16.5 Crystal Structure Depiction

Single crystal X-ray diffraction experiments on \( \text{Pu}_2[B_{12}O_{18}(OH)4\text{Br}_2(\text{H}_2\text{O})_3] \cdot 0.5\text{H}_2\text{O} \) proved to be very challenging for many reasons. First, the crystals were small (ca. 30 um). Second, the crystals had a tendency to stack on one another. Third, owing to the small \( \beta \) angle, all of the crystals were pseudo-merohedrally twinned, and this twinning creates pseudo-orthorhombic symmetry leading one down the false path of trying to solve the structure in the orthorhombic space group \( \text{Pnn}2 \) where a suitable twin law does not exist. Even when the correct crystal system of monoclinic is selected the centrosymmetric space group of \( \text{P2}_1/\text{n} \) is suggested by the systematic absences. This space group requires a single crystallographically unique plutonium site, but in fact
there are two distinct sites with different coordination environments. All of these features are only compatible with the noncentrosymmetric space group $Pn$ where a reasonable solution and refinement of the structure was finally achieved.

Part of the structure of $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3] \cdot 0.5H_2O$ is shown in Fig. 16.1. The structure consists of layers created by $BO_3$ triangles and $BO_4$ tetrahedra that extend in the $[ac]$ plane. These sheets do not occur in the actinide borates that contain actinides in higher oxidation states, and contain an unusual cluster of three $BO_4$ units that share a common corner. This type of polyborate network is also found in the lanthanide octaborates, $Ln[B_8O_{11}(OH)_5]$. These sheets are linked together by interlayer $BO_3$ triangles to create a three-dimensional framework as shown in Fig. 16.2.

The most remarkable feature of the structure of $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3] \cdot 0.5H_2O$ is the coordination of the Pu(III). As previously mentioned the plutonium ions reside in triangular holes in the polyborate sheets and there are six oxygen donor atoms in these holes that bind the Pu(III) cations. There are two crystallographically unique Pu(III) sites. One of these, Pu(1), is nine-coordinate, and the other, Pu(2), is ten-coordinate with the remaining donor atoms above and below the plane of the polyborate sheet. These two coordination environments are shown in Fig. 16.3. Both sites are capped on one side by bromide anions. While the immediate thought would be that the low oxidation state is stabilized in part by having a soft donor in the inner coordination sphere, but this is in fact unnecessary for stabilizing Pu(III). For Pu(1) there are two water molecules opposite from the bromide anion, and for Pu(2) there are three such water molecules. These coordination geometries are not typical for plutonium. The most prevalent
Figure 16.1: A view of part of the structure of Pu$_2$[B$_{12}$O$_{18}$(OH)$_4$Br$_2$(H$_2$O)$_3$]$\cdot$0.5H$_2$O showing the polyborate framework that extends in the [ac] plane that has triangular holes that are filled with the Pu(III) cations. Pu polyhedra are shown in blue-purple, BO$_3$ triangles in dark green, BO$_4$ tetrahedra in light green, bromine atoms in brown.
Figure 16.2: A depiction of the structure of Pu$_2$[B$_{12}$O$_{18}$(OH)$_4$Br$_2$(H$_2$O)$_3$]·0.5H$_2$O showing the linking of the polyborate sheets by interlayer BO$_3$ triangles. Pu polyhedra are shown in blue-purple, BO$_3$ triangles in dark green, BO$_4$ tetrahedra in light green, bromine atoms in brown, and unbound water in red.
Figure 16.3: Views of the coordination environments for Pu(III) in Pu$_2$[B$_{12}$O$_{18}$(OH)$_6$Br$_2$(H$_2$O)$_3$]-0.5H$_2$O showing the nine- and ten-coordinate geometries.
coordination environment for nine-coordinate lanthanides and actinides is a tricapped trigonal prism. However, in this compound six of the oxygen atoms are close to being in a plane. Therefore, this geometry is very different from a tricapped trigonal prism.

Likewise, a ten-coordinate geometry was found for plutonium in the Pu(IV) compound, [Pu(NO$_3$)$_3$]$_3$[2-][(C$_6$H$_5$)$_2$P(O)CH$_2$C$_5$H$_4$NO]$_2$][Pu(NO$_3$)$_6$]$_{0.5}$. There are two idealized geometries for coordination number ten, the bicapped square antiprism and sphenocorona.$^{22}$ The Pu(2) site in Pu$_2$[B$_{12}$O$_{18}$(OH)$_4$Br$_2$(H$_2$O)$_3$]·0.5H$_2$O is neither of these. Having six nearly co-planar oxygen atoms distorted both Pu(1) and Pu(2) from having more typical coordination geometries. Although, it should be noted that there are few examples of ten-coordinate metal centers so perhaps we simply do not have enough examples to yet known what is typical and what is not.

The bond distances around the plutonium sites are highly variable. The Pu−O bond distances to the borate donor oxygen atoms are range from 2.502(6) to 2.721(6) Å. Pu−O bonds to the water molecules and range from 2.304(8) to 2.546(6) Å. Finally, the Pu−Br bonds are expectedly long at 2.887(1) and 2.902(2) Å.

16.6 UV-vis-NIR Spectrum

The absorption spectrum of Pu$_2$[B$_{12}$O$_{18}$(OH)$_4$Br$_2$(H$_2$O)$_3$]·0.5H$_2$O as obtained from a twinned crystal using a microspectrophotometer and is shown in Fig. 16.4. The absorption spectrum of Pu(III) is very rich and displays are series of weak Laporte-forbidden f-f transitions throughout the UV-vis-NIR region of the spectrum. Pu(III) has a $^6$H$_{5/2}$ ground state, and its f-f transitions have been carefully assigned by Carnall and co-
Figure 16.4: Absorption spectrum of Pu$_2$[B$_{12}$O$_{18}$(OH)$_4$Br$_3$(H$_2$O)$_3$]$\cdot$0.5H$_2$O showing f-f transitions that are diagnostic for Pu(III).
workers.\textsuperscript{23} We have used Carnall’s analysis of the absorption spectrum of Pu(III) to assign the transitions for Pu\(_2\)[B\(_{12}\)O\(_{18}\)(OH)\(_4\)Br\(_2\)(H\(_2\)O)\(_3\)]\(\cdot\)0.5H\(_2\)O. The most important transitions that distinguishes Pu(III) from Pu(IV) are the \(^6\)H\(_{5/2}\)→\(^6\)H\(_{13/2}\) transitions near 900 nm. Fortunately this region is barren for Pu(IV).\textsuperscript{24} The \(^4\)L\(_{13/2}\) and \(^4\)M\(_{15/2}\) transitions are also used routinely to identify the presence of Pu(III).

16.7 Conclusions

In conclusion, we have successfully synthesized the first Pu(III) borate by using boric acid as a reactive flux under strictly anaerobic conditions. The Pu(III) sites in this compound display atypical geometries for actinides, and a rare ten-coordinate plutonium site is found in this compound. We continue to work on this system and plan to replace the bromide with smaller donor atoms such chloride and oxygen from nitrate. The synthesis and structures of the Am(III) and Cm(III) borates will also be forthcoming.

16.8 Reference


21. Crystallographic data for Pu$_2$B$_2$O$_{18}$(OH)$_4$Br$_2$(H$_2$O)$_3$·0.5H$_2$O: purple-blue plate, 0.030 × 0.020 × 0.002 mm, monoclinic, $Pn$, $Z = 1$, $a = 8.0995(15)$ Å, $b = 14.635(3)$
Å, c = 9.8248(18) Å, β = 90.028(2)°, V = 1164.6(4) Å³ (T = 100(2) K), μ = 91.55 cm⁻¹,
R₁ = 0.0334, wR₂ = 0.0693.

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CHAPTER 17:

BONDING CHANGES IN PLUTONIUM(III) AND AMERCIUM(III) BORATES

17.1 Abstract

Two Pu(III) borate compounds, \( \text{Pu}[\text{B}_4\text{O}_6(\text{OH})_2\text{Cl}] \) and \( \text{Pu}_2[\text{B}_{13}\text{O}_{26}(\text{OH})_5\text{Cl}_2(\text{H}_2\text{O})_3] \), and a single Am(III) borate compound, \( \text{Am}[\text{B}_9\text{O}_{13}(\text{OH})_4] \cdot \text{H}_2\text{O} \), were synthesized under similar conditions via boric acid flux reactions. It was determined that Am(III) shows a dramatic change from Pu(III) in both crystal structures and coordination environments.

17.2 Introduction

Interest in trivalent actinide (e.g. Pu(III), Am(III), and Cm(III)) borates stems from their potential formation in the geological repository for nuclear defense waste known as the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico, USA.\(^1\) A similar repository is being considered in Germany. In this salt deposit the concentration of borate species in intergranular brines can be as high as 166 ppm.\(^1\) Studies of the complexation of Nd(III) by borates in solution have been performed indicating that borate is the primary complexant in WIPP for trivalent cations.\(^2\) Furthermore, WIPP is self-sealing, and once closed will be saturated with hydrogen and methane, making it a highly reducing environment that will favor lower oxidation states for plutonium.
There are few systems that have been developed that extend between plutonium and americium where detailed structural information is known. The differences in bonding between plutonium and americium in the same oxidation state (e.g. Pu(III) and Am(III)) is expected to be small enough that the ligand set that binds these two cations would have to be exquisitely sensitive to the differences in bonding between plutonium and americium to detect any divergence. In fact, the few systems where corresponding compounds are known such as the halides\(^3\) and triflates\(^4\) do not respond to the changes in bonding between plutonium and americium by exhibiting substantially different structures; although the actinide contraction is certainly found between these two elements.\(^5\)

The formation of different polyborate networks is profoundly affected by numerous factors that including minute changes in pH, reaction temperature, stoichiometry, cation size, and counterions. We have recently explored the syntheses, structures, spectroscopy, and stability of actinide borates from thorium to plutonium. These investigations have uncovered a pertechnetate-selective anion exchange material,\(^6,7\) spectacularly complex acentric topologies in uranyl borates,\(^8-12,15,17\) mixed-valency in neptunium borates,\(^12-15,17\) and new coordination environments in plutonium borates.\(^12,15,16\) It occurred to us that as these studies progressed that Pu(III) and Am(III) polyborates might be an ideal system for observing changes in bonding that occur across the actinide series when all other variables are held constant except for the identity of the actinides because the polyborate network should be hyper-responsive to subtle changes in the metal centers. Herein we report the syntheses, structures,
coordination chemistry, and spectroscopy of new Pu(III) and Am(III) borates that achieve the goal of observing substantial different structures between these two elements.

17.3 Experimental Section

Pu[B_4O_6(OH)_2Cl] and Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3] was synthesized using weapons-grade (94% ^{239}Pu and 6% ^{240}Pu along with trace amounts of the other Pu isotopes and ^{241}Am) PuCl_3. Anhydrous PuCl_3 that results from the recycling and electro-refining of plutonium metal was used as received. 10.6 mg of PuCl_3 was placed in an autoclave and then transferred into an argon-filled glovebox. 30 µL of argon-sparged water and 63 mg of boric acid were added into the autoclave. The mixture was then sealed and heated at 240 °C for seven days followed by slow cooling to room temperature over a two day period. The furnace for heating the autoclave was also inside the glovebox to prevent oxygen from re-entering the autoclave because oxygen is not excluded by PTFE. The resulting product was washed using cold water and consisted of large blue crystals of Pu[B_4O_6(OH)_2Cl] (80%) and a few clusters of much smaller crystals of Pu_2[B_{13}O_{19}(OH)_5Cl_2(H_2O)_3] which are lighter in color and have an acicular habit (20%). Both compounds are not air-sensitive.

Am[B_9O_{13}(OH)_4]·H_2O was synthesized using ^{243}AmO_2 as received. 6.6 mg AmO_2 was dissolved in 100 µL 5M HCl in an autoclave. The solution was dried by heating at 130 °C, ending with a yellow solid of AmCl_3. The autoclave was then transferred into an argon-filled glovebox and the same procedure was followed forthwith as was done with PuCl_3.
The resulting product consisted of large pink tablets of Am[B$_9$O$_{13}$(OH)$_4$]·H$_2$O as a pure phase.

$^{239}$Pu ($t_{1/2} = 24,110$ y) and $^{243}$Am ($t_{1/2} = 7380$ y) represents a serious health risks owing to their $\alpha$ and $\gamma$ emission. All studies with plutonium and americium were conducted in a lab dedicated to studies on transuranium elements. This lab is equipped with a HEPA filtered hoods and negative-pressure gloveboxes. A series of counters continually monitor radiation levels in the lab. The lab is licensed by the Nuclear Regulatory Commission. All experiments were carried out with approved safety operating procedures. All free-flowing solids are worked with in gloveboxes, and products are only examined when coated with either water or Krytox oil and water.

17.4 Synthesis Discussion

The reactions of PuCl$_3$ and AmCl$_3$ with molten boric acid at 240 °C under strictly anaerobic conditions leads to the formation of Pu[B$_4$O$_6$(OH)$_2$Cl] and Pu$_2$[B$_{13}$O$_{19}$(OH)$_5$Cl$_2$(H$_2$O)$_3$], and Am[B$_9$O$_{13}$(OH)$_4$]·H$_2$O, respectively. Pu[B$_4$O$_6$(OH)$_2$Cl] forms blue crystals that can exceed 1 mm in size. Pu$_2$[B$_{13}$O$_{19}$(OH)$_5$Cl$_2$(H$_2$O)$_3$] forms smaller more lightly colored blue crystals. Am[B$_9$O$_{13}$(OH)$_4$]·H$_2$O is isolated as large pink tablets. Pictures of these crystals can be found in the Supporting Information. The crystals are not degraded by oxygen or water. Curiously the crystals of Pu[B$_4$O$_6$(OH)$_2$Cl] are extremely hard and cannot be cut with steel tools. This might be a function of the multiple ways in which the structure is cross-linked (vide infra). These crystals were used directly for structural and spectroscopic investigations.
17.5 Crystal Structure Depiction

Single crystal X-ray diffraction experiments on all three compounds yielded models for the structures with low residuals.\textsuperscript{18} There are very few single crystal structures known for americium compounds.\textsuperscript{3a,4b,19} Crystals of Am[B\textsubscript{9}O\textsubscript{13}(OH)\textsubscript{4}]:H\textsubscript{2}O are of remarkable quality, and the residuals for the model of the structure are the lowest reported for an americium compound, providing very precise metrics for the structure. All three compounds form dense, three-dimensional structures shown in Fig. 17.1. Pu\textsubscript{2}[B\textsubscript{13}O\textsubscript{19}(OH)\textsubscript{5}Cl\textsubscript{2}(H\textsubscript{2}O)\textsubscript{3}] and Am[B\textsubscript{9}O\textsubscript{13}(OH)\textsubscript{4}]:H\textsubscript{2}O both contain similar polyborate sheets as shown in Fig. 17.2b,c. These sheets contain an unusual unit of three BO\textsubscript{4} tetrahedra that share a common corner. These clusters share corners with BO\textsubscript{3} triangles to create sheets with triangular holes where the An(III) (An = Pu, Am) cations reside. For comparison, this sheet topology can be also found in the Ln(III) borate systems, Ln[B\textsubscript{8}O\textsubscript{11}(OH)\textsubscript{5}] (Ln = La - Nd) and Ln[B\textsubscript{9}O\textsubscript{13}(OH)\textsubscript{4}] (Ln = Pr - Eu).\textsuperscript{20} Pu[B\textsubscript{4}O\textsubscript{6}(OH)\textsubscript{2}Cl] possesses a very different sheet topology that lacks the clusters, and only contains corner-sharing BO\textsubscript{3} and BO\textsubscript{4} units (Fig. 17.2a). Once again there are triangular holes to house the Pu(III) cations. These layers are very similar to those found with penta- and hexavalent actinides (e.g. U(VI), Np(V), Np(VI), and Pu(VI)).\textsuperscript{8-17} Both types of sheets are joined together by BO\textsubscript{3} or BO\textsubscript{4} units to create three-dimensional networks as shown in Fig. 17.1.

The most remarkable features of the Pu(III) and Am(III) borates are the local coordination environments of the metal centers. In all three compounds the polyborate layers provide six oxygen donors that are close to being co-planar. This forces these
Figure 17.1: Depiction of three-dimensional framework structures of Pu[B₄O₆(OH)₂Cl] (a), Pu₂[B₁₃O₂₉(OH)₅Cl₂(H₂O)₃] (b), and Am[B₉O₁₃(OH)₄]·H₂O (c). Pu polyhedra are shown in blue (a) or light purple blue (b), Am polyhedra in pink, BO₃ triangles in dark green, BO₄ tetrahedra in light green, chlorine atoms in purple, and unbound water in red. The color of the actinide polyhedra is similar to the color of the crystals.
Figure 17.2: Depiction of sheet topologies of Pu[B₄O₆(OH)₂Cl] (a), Pu₂[B₁₃O₁₉(OH)₅Cl₂(H₂O)₃] (b), and Am[B₉O₁₃(OH)₄]·H₂O (c). Pu polyhedra are shown in blue (a) or light purple-blue (b), Am polyhedra in pink, BO₃ triangles in dark green, BO₄ tetrahedra in light green, and chlorine atoms in purple.
cations to have geometries that are not typically found for actinides in the trivalent oxidation state. Pu\([\text{B}_4\text{O}_6\text{(OH)}_2\text{Cl}]\) and Pu\([\text{B}_{13}\text{O}_{19}\text{(OH)}_5\text{Cl}_2\text{(H}_2\text{O})_3]\) both contain ten-coordinate Pu(III) in a geometry that is best described as a capped triangular cupola.\(^{[21]}\)

The capping group is a chloride anion, and the triangular base is created by either water molecules and borate anions in Pu\([\text{B}_{13}\text{O}_{19}\text{(OH)}_5\text{Cl}_2\text{(H}_2\text{O})_3]\), or borate and an additional chloride anion in Pu\([\text{B}_4\text{O}_6\text{(OH)}_2\text{Cl}]\). Both chloride anions in Pu\([\text{B}_4\text{O}_6\text{(OH)}_2\text{Cl}]\) bridge between Pu(III) centers, and these bridges span between the sheets. This type of connectivity is absent in all of the actinide borates that we have prepared and may be responsible for the hardness of the crystals. These bridges are lacking in Pu\([\text{B}_{13}\text{O}_{19}\text{(OH)}_5\text{Cl}_2\text{(H}_2\text{O})_3]\), and the chloride anion is terminal, much like the bromide anions in Pu\([\text{B}_{12}\text{O}_{18}\text{(OH)}_4\text{Br}_2\text{(H}_2\text{O})_3]\cdot 0.5\text{H}_2\text{O}^{[16]}\) As given by the formula, Am\([\text{B}_9\text{O}_{13}\text{(OH)}_4]\cdot \text{H}_2\text{O}\) lacks chloride entirely, and this is a significant departure from the reactivity of Pu(III) halide starting materials where we observe halides bound to Pu(III) in the final products. The capping group where the halide would have been is instead occupied by a BO\(_3\) unit that bridges to the next layer. The two sites beneath the borate layer are two oxo atoms from one chelating BO\(_4\) unit. Therefore, the groups above and below the polyborate plane are different between Pu(III) and Am(III). This another point of distinction between the Pu(III) borates herein and Am\([\text{B}_9\text{O}_{13}\text{(OH)}_4]\cdot \text{H}_2\text{O}\) because the Am(III) is nine-coordinate instead of ten, and the geometry is best described as hula-hoop.\(^{[22]}\)
Figure 17.3: Views of coordination environments of actinide(III) sites in Pu[B₄O₆(OH)₂Cl] (a), Pu₂[B₁₃O₁₉(OH)₅Cl₂(H₂O)₃] (b), and Am[B₉O₁₃(OH)₄·H₂O] (c).
17.6 Conclusions

The central question is why are the Pu(III) and Am(III) borates so different? There are several answers to this question. First, the actinide contraction between Pu(III) and Am(III) is larger than one might expect. Pu(III) has a ionic radius of 1.00 Å; whereas Am(III) has a radius 0.975 Å (CN = 6).\(^5\) The typical change in ionic radius between neighbouring actinides in the same oxidation state with the same coordination number is approximately 0.01 Å,\(^5\) and this is enough of a difference to induce structural changes.\(^{23}\) Therefore, the formation of a different structure is not completely surprising based on this rather large change. Second, while exclusion of chloride from the inner coordination sphere is a bit more perplexing, it is also a reflection of the increased Pearson hardness of the Am(III) cation versus the Pu(III) cation.\(^{24}\) Am(III) shows a preference for all oxo donors. Finally, Pu\(_2\)[B\(_{13}\)O\(_{19}\)(OH)\(_3\)Cl\(_2\)(H\(_2\)O)\(_3\)] does not have a lanthanide analog whereas lanthanide borates with similar structures to Am[B\(_9\)O\(_{13}\)(OH)\(_4\)]·H\(_2\)O are known.\(^{25}\) We suggest that this represents a sharp demarcation between the chemistry of Pu(III) and Am(III).

In conclusion, the coordination chemistry of Pu(III) and Am(III) can be highly different even when synthetic parameters and crystallization conditions are held constant. Bond distances of Pu–O and Am–O are quite different, and the hope would be that future theory will be able to account for the differences in the bonding behavior.

17.7 Supporting Information
Figure 17.4: Photo of crystals of Pu\([B_4O_6(OH)_2Cl]\).
Figure 17.5: Photo of crystals of Am[BeO$_{13}$(OH)$_{4}$]$\cdot$H$_2$O.
Figure 17.6: Absorption spectra of Pu[B₄O₆(OH)₂Cl] (black) and Pu₂[B₁₃O₁₉(OH)₅Cl₂(H₂O)₃] (red) showing f-f transitions that are diagnostic for Pu(III). (f-f transitions are assigned based on the reference: Carnall, W. T.; Fields, P. R.; Pappalardo, R. G. J. Chem. Phys. 1970, 53, 2922.)
Figure 17.7: Absorption spectra of Am\([\text{B}_9\text{O}_{13}\text{(OH)}_4]\)·\(\text{H}_2\text{O}\) showing f-f transitions that are diagnostic for Am(III). (f-f transitions are assigned based on the reference: Pappalardo, R. G.; Carnall, W. T.; Fields, P. R. *J. Chem. Phys.* **1969**, *51*, 1182.)
Reference


18. Crystallographic data for Pu[B₄O₆(OH)₂]Cl: Blue block, 0.064 x 0.056 x 0.052 mm, monoclinic, Cc, Z = 4, a = 6.491(2) Å, b = 11.184(4) Å, c = 9.630(3) Å, β = 105.175(9)º, V = 674.7(4) Å³ (T = 100(2) K), μ = 101.76 cm⁻¹, R₁ = 0.0223, wR² = 0.0408. Pu₂[B₁₃O₁₉(OH)₅Cl₂(H₂O)₃]: Light purple-blue needle, 0.080 x 0.010 x 0.002 mm, monoclinic, P₂₁/n, Z = 2, a = 8.0522(17) Å, b = 14.568(3) Å, c = 9.820(2) Å, β = 90.120(2)º, V = 1151.8(4) Å³ (T = 100(2) K), μ = 60.29 cm⁻¹, R₁ = 0.0547, wR² = 0.1284. Am[B₉O₁₃(OH)₄]·H₂O: Pink tablet, 0.078 x 0.061 x 0.007 mm, monoclinic, P₂₁/n, Z = 2, a = 7.7030(15) Å, b = 16.688(3) Å, c = 9.872(2) Å, β = 90.073(6)º, V = 1269.7(4) Å³ (T = 100(2) K), μ = 61.60 cm⁻¹, R₁ = 0.0143, wR² = 0.0370. Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (crysdata@fiz-karlsruhe.de) on quoting numbers 423058, 423059, and 423060.


CHAPTER 18:

CURIUM(III) DISPLAYS BONDING INTERMEDIATE BETWEEN THAT OF PLUTONIUM(III) AND AMERCIUM(III) IN BORATE MATERIALS

18.1 Abstract

A Cm(III) borate compound, Cm$_2$[B$_{14}$O$_{20}$(OH)$_7$(H$_2$O)$_2$Cl], was synthesized in the boric acid flux reaction. Single crystal X-ray diffraction shows that there are two different Cm(III) sites in the crystal structure of Cm$_2$[B$_{14}$O$_{20}$(OH)$_7$(H$_2$O)$_2$Cl], and they displays bonding intermediate between that of Pu(III) and Am(III). Furthermore, the two different Cm(III) sites was confirmed by the low-temperature luminescence spectroscopy.

18.2 Introduction

Curium is the heaviest element that is relevant to the nuclear fuel cycle being produced by neutron capture by lighter actinides followed by $\beta$ decay in nuclear reactors. It is desireable to separate it from americium during the reprocessing of used nuclear fuel. However, Am(III) and Cm(III) possess extraordinarily similar ionic radii that only differ by 0.005 Å, making the separation of these two elements challenging.$^{[1]}$ Curium is an underexplored element for several reasons. First, for several decades after its discovery the only available isotope was $^{244}$Cm. $^{244}$Cm has a short half-life of only 18
years and radiation damage in its compounds is very rapid. $^{242}$Cm was also available, but is even shorter-lived with a half-life of 163 days.$^{[2]}$ The highly neutron-rich isotope, $^{248}$Cm, became available in small qualities in the late 1970’s. This isotope too has serious issues despite its long half-life of $3.48 \times 10^5$ years because 8.3% of its decay is via spontaneous fission, and therefore even milligram amounts of $^{248}$Cm release large fluxes of neutrons. The lack of availability of material combined with the hazards of working with the different isotopes of curium has greatly curtailed the development of the fundamental and applied chemistry of curium. Evidence for this is that CmCl$_3$$^{[3]}$, Cm(IO$_3$)$_3$$^{[4]}$, Cm[M(CN)$_2$]$_3$·3H$_2$O (M = Ag, Au)$^{[5]}$ and [Cm(H$_2$O)$_3$][SO$_3$CF$_3$]$_3$$^{[6,7]}$ are the only inorganic compounds of curium for which single crystal structures are known. The development of the chemistry and physical properties of curium compounds is important because like Gd(III), Cm(III) has a half-filled f shell with seven unpaired electrons. However, unlike Gd(III), Cm(III) typically has a split ground state,$^{[8]}$ so its electronic properties are absolutely unique. It is the only f-block element whose magnetic interactions can control its crystal structure.$^{[9]}$

We have recently undertaken the study of the preparation of actinide borates with the aim of developing periodic trends that may aid in predicting the fate of actinides in nuclear waste repositories that are in salt deposits, such as the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico, USA.$^{[10]}$ A similar repository is being considered in Germany. These deposits contain borate in high concentrations in intergranular brines, and landmark work by Reed and co-workers has shown that
borate, not carbonate, is the primarily complexant for trivalent cations in these repositories.\cite{11}

We recently demonstrated that Pu(III) and Am(III) borates possess substantially different compositions, structures, and local coordination environments at the metal centers.\cite{12} Our prediction was that the chemistry of Cm(III) would closely parallel that of Am(III), and that the borate compounds would be very similar given their nearly identical ionic radii and lack of redox activity. Herein we demonstrate that this hypothesis is incorrect and that Cm(III) borate displays bonding characteristics intermediate between that of Pu(III) and Am(III). The curium compound reported in this work is the only curium compound that lacks both lanthanide and actinide analogs.

18.3 Experimental Section

\[ \text{Cm}_2[B_{14}O_{20}(OH)_7(H_2O)_2\text{Cl}] \] was synthesized using \(^{248}\text{CmCl}_3 (3\% \ ^{246}\text{Cm})\) as the starting material. 5 mg of CmCl\(_3\) was placed in an autoclave and then transferred into an argon-filled glovebox. 30 µL of argon-sparged water and 63 mg of boric acid were added into the autoclave. The mixture was then sealed and heated at 240 °C for seven days followed by slow cooling to room temperature over a two day period. This is the same procedure used to synthesize Pu(III) and Am(III) borates. The resulting product was washed with boiling water and consisted of pale yellow tablets of \[ \text{Cm}_2[B_{14}O_{20}(OH)_7(H_2O)_2\text{Cl}] \] as the sole product.
18.4 Crystal Structure Depiction

Crystals of $\text{Cm}_2\text{[B}_{14}\text{O}_{20}\text{(OH)}_7\text{(H}_2\text{O)}_2\text{Cl]}$ were isolated from the reaction of $^{248}\text{CmCl}_3$ with molten boric acid at 240°C. The crystals take the form of small tablets (ca. 50 μm) with very pale yellow coloration. Single crystal X-ray diffraction experiments on $\text{Cm}_2\text{[B}_{14}\text{O}_{20}\text{(OH)}_7\text{(H}_2\text{O)}_2\text{Cl]}$ pose a number of interesting challenges based on the fact that this compound combines one of the heaviest elements in the periodic table with some of the lightest elements. Clearly curium is responsible for the majority of the X-ray scattering. We have found in layered borates that the heavy elements can be arranged with higher symmetry than the rest of the extended network. For example, in $\text{Pu}_2\text{[B}_{12}\text{O}_{18}\text{(OH)}_4\text{Br}_2\text{(H}_2\text{O)}_3\cdot0.5\text{H}_2\text{O]}$, which has some structural similarities with $\text{Cm}_2\text{[B}_{14}\text{O}_{20}\text{(OH)}_7\text{(H}_2\text{O)}_2\text{Cl]}$, the two different Pu(III) centers appear to be crystallographically related, but in fact differ by one coordinating water molecule.\textsuperscript{[13]}

The relationship between the plutonium centers leads to the erroneous conclusion that the structure possesses higher symmetry than it actually does. We find very similar phenomenon in $\text{Cm}_2\text{[B}_{14}\text{O}_{20}\text{(OH)}_7\text{(H}_2\text{O)}_2\text{Cl]}$ in that there appears to be two different curium sites with different coordination environments in the low symmetry space groups $P2_1$ and $Pn$. However, unlike $\text{Pu}_2\text{[B}_{12}\text{O}_{18}\text{(OH)}_4\text{Br}_2\text{(H}_2\text{O)}_3\cdot0.5\text{H}_2\text{O]}$, the thermal parameters for some light atoms (B and O) were unreasonable in these space groups as are, more importantly, the B–O bond distances. In order to achieve a suitable refinement where both of the curium site(s) and the borate network possess reasonable metrics, the structure had to be solved and refined in $P2_1/n$, which forces the two Cm sites into a single site with mixed coordination environments. The induced disorder is
easily accounted for, and the resulting model for the structure has low residuals, especially for a curium compound where it is expected the spontaneous fission should induce rapid radiation damage.[14]

The crystal structure of Cm\(_2\)[B\(_{14}\)O\(_{20}\)(OH)\(_7\)(H\(_2\)O)\(_2\)Cl] contains a complicated 3D-framework that is similar to several other An(III) borates (Fig. 18.1a).\([12,13]\) The framework is formed from a series of Cm(III) borate sheets that extend in the \([ac]\) plane bridged by additional BO\(_3\) triangles and BO\(_4\) tetrahedra that extend from the sheets. The Cm(III) borate sheets adopt the same topology as those found in Pu\(_2\)[B\(_{12}\)O\(_{18}\)(OH)\(_4\)Br\(_2\)(H\(_2\)O)\(_3\)]·0.5H\(_2\)O, Pu\(_2\)[B\(_{13}\)O\(_{19}\)(OH)\(_5\)Cl\(_2\)(H\(_2\)O)\(_3\)], and Am[B\(_9\)O\(_{13}\)(OH)\(_4\)]·H\(_2\)O as shown in Fig. 18.1b. Within this sheet, a \(\mu_3\)-oxo atom can be found in clusters formed by three corner-sharing BO\(_4\) tetrahedra. These clusters share corners with BO\(_3\) triangles to create sheets with triangular holes where the An(III) (An=Pu, Am, Cm) cations reside.

Although the same sheet type implies the similarity of reactivity for Pu, Am, and Cm in the borate system, these An(III) borate compounds are all different as can be seen from their chemical formula. The structural differences among these compounds can be observed in the sheet-bridging units. In Cm\(_2\)[B\(_{14}\)O\(_{20}\)(OH)\(_7\)(H\(_2\)O)\(_2\)Cl] and Am[B\(_9\)O\(_{13}\)(OH)\(_4\)]·H\(_2\)O, both BO\(_3\) triangles and BO\(_4\) tetrahedra connect the sheets together, while in Pu\(_2\)[B\(_{12}\)O\(_{18}\)(OH)\(_4\)Br\(_2\)(H\(_2\)O)\(_3\)]·0.5H\(_2\)O and Pu\(_2\)[B\(_{13}\)O\(_{19}\)(OH)\(_5\)Cl\(_2\)(H\(_2\)O)\(_3\)], only BO\(_3\) triangles are found between the sheets. In addition, compared with Cm\(_2\)[B\(_{14}\)O\(_{20}\)(OH)\(_7\)(H\(_2\)O)\(_2\)Cl], the lack of the halide moiety in Am[B\(_9\)O\(_{13}\)(OH)\(_4\)]·H\(_2\)O results in more complicated bridging borate units. This can also be probed by the atomic ratio of An:B in the formulas (1:9 for Am, 1:7 for Cm, and 1:6/1:6.5 for Pu). Again, the
Figure 18.1: (a) Depiction of three-dimensional framework structure of Cm$_2$[B$_{14}$O$_{20}$(OH)$_7$(H$_2$O)$_2$Cl]. (b) Depiction of sheet topologies of Cm$_2$[B$_{14}$O$_{20}$(OH)$_7$(H$_2$O)$_2$Cl]. Cm polyhedra are shown in pale yellow, BO$_3$ triangles in dark green, BO$_4$ tetrahedra in light green, chlorine atoms in purple.
polyborate network is found to be a powerful ligand that can be used to structurally probe small differences among actinides.\textsuperscript{[12]}

The local coordination environments of the Cm(III) centers in Cm\textsubscript{2}[B\textsubscript{14}O\textsubscript{20}(OH)\textsubscript{7}(H\textsubscript{2}O)\textsubscript{2}Cl] are unusual. There are two different coordination environments for Cm(III) in Cm\textsubscript{2}[B\textsubscript{14}O\textsubscript{20}(OH)\textsubscript{7}(H\textsubscript{2}O)\textsubscript{2}Cl] as shown in Fig. 18.2. One is a nine-coordinated Cm(III) polyhedron with six almost co-planar oxo atoms provided by the borate sheets and a capping chloride anion. This type of coordination environment can be referred to as the hula-hoop geometry\textsuperscript{[15]} and can be also found in one of the Pu(III) sites in Pu\textsubscript{2}[B\textsubscript{12}O\textsubscript{18}(OH)\textsubscript{4}Br\textsubscript{2}(H\textsubscript{2}O)\textsubscript{3}]\cdot 0.5H\textsubscript{2}O, which is bound by a capping bromide anion. Am(III) centers in Am[B\textsubscript{9}O\textsubscript{13}(OH)\textsubscript{4}]\cdot H\textsubscript{2}O also adopt this geometry, but lack the capping halide moiety.\textsuperscript{[12]} The other is ten-coordinate Cm(III) also with six almost co-planar oxo atoms, however, the capping group is an oxo atom from a bridging BO\textsubscript{3} triangle instead of the chloride anion. The same coordination environment can be only found in Ce[B\textsubscript{5}O\textsubscript{8}(OH)]NO\textsubscript{3}\cdot 3H\textsubscript{2}O and Ln[B\textsubscript{8}O\textsubscript{11}(OH)\textsubscript{5}] (Ln = La - Nd).\textsuperscript{[16]} The geometry of this coordination environment is best described as a capped triangular cupola\textsuperscript{[17]} and can also be found in most of the Pu(III) centers in the Pu(III) borates with capping halide ions.\textsuperscript{[12,13]} Therefore, Cm(III) displays bonding intermediate between that of Pu(III) and Am(III) not only in the coordination numbers, but also with the bonding nature to the halide moieties.
Figure 18.2: Views of two different coordination environments of Cm(III) sites in 
$\text{Cm}_2\text{[B}_{14}\text{O}_{20}(\text{OH})_2(\text{H}_2\text{O})_2\text{Cl}]$. 
18.5 Luminescence Properties

Cm(III) is known to produce intense orange luminescence when irradiated with blue light.\textsuperscript{[18]} Owing to the fact that there are two different coordination environments with different ligand sets in this compound, it is expected that spectroscopic studies should also indicate the presence to two distinct crystallographic sites. Laser-induced and time- and energy-resolved excitation and luminescence spectra were utilized to reveal the two sites of Cm\textsuperscript{3+} in the crystalline lattice of Cm\textsubscript{2}[B\textsubscript{14}O\textsubscript{20}(OH)\textsubscript{7}(H\textsubscript{2}O)\textsubscript{2}Cl]. There is clear evidence showing that Cm\textsuperscript{3+} has different local environments. However, the spectroscopic difference between Cm\textsuperscript{3+} at the two different sites is small, so our experiments had to be carried out at liquid helium temperature to eliminate thermal dynamics that obscure the energy levels of Cm\textsuperscript{3+} at different sites. It is understood that the crystal field interaction of Cm\textsuperscript{3+} in 5f\textsuperscript{7} configuration is weak especially in the ground state and low-lying excited states.\textsuperscript{[8]} The energy levels of these states are relatively insensitive to the lattice environment. \textbf{Fig. 18.3} shows the site-resolved fluorescence emission spectra of Cm\textsuperscript{3+} excited resonantly from the ground multiplet \textsuperscript{8}S\textsubscript{7/2} into the emitting state of \textsuperscript{6}D\textsubscript{7/2} mixed with \textsuperscript{6}P\textsubscript{5/2}. Apparently, the two spectra are partially overlapped and with similar structures. They were recorded at 4 K with laser excitation at 601.4 nm and 602 nm, respectively, measuring the lowest level of the excited state for Site-A and Site-B. Four lines marked in both spectra measure the crystal field splitting of the ground state \textsuperscript{8}S\textsubscript{7/2}. From the spectra, we know that the ground state splitting for the two Cm\textsuperscript{3+} sites have similar patterns with a total splitting approximately of 1.2 nm, and that the difference in the energy of the \textsuperscript{8}S\textsubscript{7/2} - \textsuperscript{6}D\textsubscript{7/2} excitation between...
Figure 18.3: Luminescence spectra of Cm$^{3+}$ at two different sites in Cm$_{2}$[B$_{14}$O$_{20}$(OH)$_{2}$(H$_{2}$O)$_{2}$Cl] recorded at 4 K in resonant excitation at 601.4 nm and 602 nm, respectively.
the two sites is only 0.6 nm. These characteristics are determined by the electronic properties of Cm$^{3+}$, and its interaction with the surrounding ligands as shown in Fig. 18.2. However, there is no exclusive information obtained from the spectroscopic experiments to allow us to assign the spectra to the structures.

The two-site structure of Cm$^{3+}$ and its dynamics are further investigated in luminescence decay measurements. At low temperature when thermal population and phonon assisted energy transfer are eliminated, excitation energy transfer occurs only from the donor sites at higher energies to the acceptor sites at lower energies.$^{[19]}$ As shown in Fig. 18.4, in the system we studied, two very different fluorescence decay curves were recorded. When Site-A was excited, emission from both Site-A and Site-B was observed. Site-A luminescence which exhibits a non-exponential behavior has a much shorter decay time than that of the Site-B luminescence. The Site-B luminescence has an initial rising before it approaches to an exponential decay. These results clearly indicate energy transfer from Site-A to Site-B, and that the relaxation of Site-A excitation is predominantly quenched through energy transfer. The effect of Site-A to Site-B energy transfer is seen also in the emission spectrum shown in Fig. 18.3. When Site-A was excited at 601.4 nm, luminescence from Site-B was induced in addition to the Site-A emission lines. The efficient energy transfer confirms the structure in which Cm$^{3+}$ ions at Site-A and Site-B are paired with each other as shown in Fig. 18.1.
Figure 18.4: Luminescence decay curves of Cm$^{3+}$ at Site-A and Site-B in Cm$_2$[B$_{14}$O$_{20}$(OH)$_7$(H$_2$O)$_2$Cl] monitored at 601.5 nm and 602.3 nm respectively. The decay curves were recorded at 4 K after laser excitation of Site-A.
18.6 Conclusions

In conclusion, crystallographic and spectroscopic studies provide complementary information about this complex Cm(III) borate. Both confirm two distinct crystallographic sites. The data that we have now gathered on Pu(III), Am(III), and Cm(III) borates when combined with parallel studies on lanthanide borates demonstrates three key conclusions. First, lanthanide borates undergo systematic changes as a function of the size of the lanthanides. Second, Ln$^{3+}$ and An$^{3+}$ (An = Pu, Am, Cm) do not form the same compounds when reacted under the same conditions in boric acid. Third, trivalent actinide borates do not vary simply as a function of the ionic radius of the metal ion; the behavior is far more complex. Our current hypothesis is that actinide borate compounds yield such distinct chemistry among 5f elements because of the large polarizability of BO$_3$ units. This yields unusual bonding with 5f orbitals that is absent in most other ligand systems. This supposition is currently being probed with high-level quantum theory.

18.7 Supporting Information
Figure 18.5: Photo of crystals of Cm$_2$[B$_{14}$O$_{20}$(OH)$_7$(H$_2$O)$_2$Cl].
Figure 18.6: Photo of a crystal of Cm$_2$[B$_{14}$O$_{20}$(OH)$_7$(H$_2$O)$_2$Cl] under irradiation of 420 nm light.
Figure 18.7: UV-vis-NIR absorption spectrum of Cm$_2$[B$_{14}$O$_{20}$(OH)$_7$(H$_2$O)$_2$Cl].
18.8 Reference


14. Crystallographic data for Cm$_2$[B$_{14}$O$_{20}$(OH)$_7$[(H$_2$O)$_2$Cl]: Pale yellow tablet, 0.044 x 0.035 x 0.007 mm, monoclinic, P2$_1$/n, Z = 2, a = 7.9561(17) Å, b = 14.212(3) Å, c = 9.836(2) Å, $\theta$ = 90.013(2)$^\circ$, V = 1112.2(4) Å$^3$ (T = 100(2) K), $\mu$ = 75.37 cm$^{-1}$, $R_1$ = 0.0645, wR$^2$ = 0.1452. Bruker APEXII Quazar diffractometer: $\theta_{\text{max}}$ = 49.42$^\circ$, MoK$\alpha$, $\lambda$ = 0.71073 Å, 0.5$^\circ$ $\omega$ scans, 10454 reflections measured, 1899 independent reflections all of which were included in the refinement. The data was corrected for Lorentz-polarization effects and for absorption, the structure was solved by direct methods, anisotropic refinement of F$^2$ by full-matrix least-squares on 184 parameters.


CHAPTER 19:

INTERSTITIAL INCORPORATION OF PLUTONIUM INTO A LOW-DIMENSIONAL POTASSIUM BORATE

19.1 Abstract

The molten boric acid flux reaction of PuBr$_3$ with KBO$_2$ at 200 $^\circ$C results in the formation of large light-yellow crystals of K[B$_5$O$_7$(OH)$_2$]-H$_2$O:Pu$^{4+}$. Single crystal X-ray diffraction experiments on the Pu-doped K[B$_5$O$_7$(OH)$_2$]-H$_2$O demonstrate two features: (1) K[B$_5$O$_7$(OH)$_2$]-H$_2$O:Pu$^{4+}$ adopts a one-dimensional borate chain structure with large void spaces between the chains; (2) The doping plutonium atoms do not reside on the potassium sites. The latter are not fully occupied. Both laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and energy dispersive spectrometer (EDS) analyses indicate that plutonium atoms are uniformly distributed in crystals of K[B$_5$O$_7$(OH)$_2$]-H$_2$O with an atomic K:Pu ratio of approximately 65:1 measured by LA-ICP-MS. UV-vis-NIR spectra taken from both freshly-made and one-day old crystals show that the plutonium present within the crystals is predominantly characterized by an oxidation state of IV. A small amount of Pu(III) is also present initially, but slowly oxidized to Pu(IV) via interaction with oxygen in the air. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopic
measurements confirm that plutonium is mainly present as a form similar to that of a PuO$_2$ cluster. The combined results suggest that the clusters containing Pu(VI) ions are uniformly distributed in the void spaces between the borate chains.

K[B$_5$O$_7$(OH)$_2$]·H$_2$O·Pu$^{4+}$ provides a mechanism for incorporating heavy metal contaminants, including actinides, into natural materials.

19.2 Introduction

Nuclear weapon testing and plutonium production during the cold war, and recent events such as the catastrophe at the Fukushima Daiichi nuclear plant in Japan, resulted in the contamination of large areas of oceans, ground-water, soils, and sediments by actinides, such as uranium and plutonium, along with their fission and decay products. Thus, possible migration of actinides within contaminated sites becomes an important environmental concern$^{1-3}$. Generally, the incorporation of actinides into natural materials retards their transport in the environment. Knowledge of the incorporation mechanisms of actinides into different types of natural materials is therefore required both for predicting the migration of radionuclides at repositories and at contaminated sites, and for designing/manufacturing of suitable radioactive waste forms$^{4-6}$.

During the last two decades, significant efforts have been made to better understand the incorporation of early actinide elements (namely Th, U, Np, and Pu) into a variety of mineral phases, such as calcite$^{7-15}$, zircon$^{4,16-17}$, monazite$^{4,17-18}$, zirconolite$^{4,18-22}$, perovskite$^{4,22}$, garnet$^4$, pyrochlore$^{4,23-25}$, brucite$^{26}$, and several other systems$^{27-30}$. Particularly for transuranium elements (Np and Pu), it was determined that these can
also be incorporated into a series of uranium- or thorium- based minerals such as 
brannerite\(^4\), ianthinite\(^{31}\), schoepsite, becquerelite, compleignacite, and boltwoodite\(^{32}\) 
or even synthetic phases such as \(\text{Th}_{2-x/2}\text{An}^{IV}_{x/2}(\text{PO}_4)_2(\text{HPO}_4)_2\text{H}_2\text{O} \ (\text{An} = \text{U, Np, Pu})\)\(^{33}\), 
\(\text{ThSiO}_4\)\(^{34}\), and \(\text{Ba}_3(\text{UO}_2)_2(\text{HPO}_4)_2(\text{PO}_4)_2\)\(^{35}\). The majority of these studies focus on 
examining incorporation mechanisms based on the presence of a suitable 
crystallographic site in the lattice for actinide units to reside in the incorporated 
materials; i.e. the actinide units substitute into lattice sites that are occupied by other 
cations that have similar crystal chemistry. This commonly occurring mechanism is 
termed “substitutional incorporation.” For example, numerous studies indicate that 
trace amounts of uranium, present as both U(VI) and U(IV), can be incorporated into 
natural calcite\(^7\)-\(^{14}\). U(IV) was found to have a stable location on the sites of divalent 
calcium\(^7\), while U(VI) occupies mainly calcium sites along with other possible defects or 
disordered sites\(^8\)-\(^9\). For cases of plutonium incorporation, Pu(IV) substitutes into calcium 
sites in zirconolites\(^{19}\), and Pu(III) can enter the structure of monazite in the position of 
La(III)\(^{18}\). Furthermore, Pu(VI) can readily occur in many structures containing U(VI) by 
substituting onto the U(VI) sites\(^{31-32}\). In light of all these observations, one could 
conclude that the high level incorporation of actinides requires suitable crystallographic 
sites in the lattice of materials.

We have recently undertaken a study involving the preparation, structural 
elucidation, and physico-chemical property measurements of actinide borates\(^{36-47}\) with 
the aim of uncovering the solubility-limiting phases of actinides in some repositories 
such as the Waste Isolation Pilot Plant (WIPP)\(^{48}\). In an attempt to prepare a
plutonium(IV) borate compound, a potassium borate that is doped with Pu(IV) was discovered. This compound, with a formula of $K[B_5O_7(OH)_2] \cdot H_2O$, contains no suitable lattice sites for plutonium substitution. However, it was determined that high levels of Pu(IV) are capable of entering the structure of $K[B_5O_7(OH)_2] \cdot H_2O$ with an atomic ratio $K:Pu$ around 65:1, as measured by LA-ICP-MS. We have used single crystal X-ray diffraction, X-ray absorption near-edge structure (XANES), and extended X-ray absorption fine structure (EXAFS) to demonstrate that Pu(IV) can enter the interstitial spaces between neighboring borate chains while removing some lattice potassium to maintain charge-balance. Interstitial incorporation suggests an approach for understanding how actinides can enter natural materials, although interstitial incorporation was found in a few other, non-actinide-bearing systems\textsuperscript{49-51}, as well as in NZP (sodium zirconium phosphate) type materials\textsuperscript{52}.

There are several objectives for this work. First, we demonstrate that plutonium can incorporate into interstitial sites in naturally occurring phases that have low-dimensional networks. Second, we show that while plutonium can be detected visually, as well as with a variety of spectroscopic techniques, its presence can only be inferred from X-ray diffraction data. Finally, we address the broader environmental implications of interstitial incorporation of actinides into low-dimensional minerals.

19.3 Experimental Section

*Syntheses:* Specialized facilities and procedures are needed for this work. All free-flowing solids were handled within negative-pressure gloveboxes, and products were
examined when coated with either water or Krytox oil and water. $^{242}\text{PuO}_2$ (99.98% isotopic purity, Oak Ridge National Laboratory, $t_{1/2} = 3.76 \times 10^5$ y) was used as received. While the plutonium is of very high isotopic purity, there are trace amounts of $^{238}\text{Pu}$, $^{240}\text{Pu}$, $^{241}\text{Pu}$, $^{244}\text{Pu}$, and $^{241}\text{Am}$. The majority of the radioactivity comes from the $^{241}\text{Pu}$ even though it represents only 0.008% of the plutonium. $^{242}\text{Pu}$ still represents a serious health risk owing to its $\alpha$ and $\gamma$ emission. This isotope was selected because of its long half-life, which increased the longevity of the crystals. A 0.365 M stock solution of $^{242}\text{Pu(VI)}$ nitrate was prepared by first digesting $\text{PuO}_2$ in 8 M HNO$_3$ for 3 days at 200 °C in an autoclave. The solution was then reduced to a moist residue and redissolved in water. This solution was then ozonated for approximately 5 hours to ensure complete oxidation of the plutonium to +6.

An aliquot containing 5 mg of plutonium(VI) was taken from the above stock solution and reduced to a residue. 50 μL of concentrated HBr was added to this residue resulting in the immediate formation of bromine gas and a red solution (the red color is from the dissolved bromine which masks the color of Pu(III)). The red solution was reduced to a purple-black residue at 130 °C. The residue was redissolved in 30 μL of argon-sparged water producing a navy blue/purple solution characteristic of Pu(III). A droplet of Pu(III) was then transferred to a PTFE autoclave liner. A large excess of boric acid (47 mg) and KBO$_2$ (7.8 mg) was then added directly to the droplet containing Pu(III). The mixture was then sealed in an autoclave and heated at 200 °C for three days followed by slow cooling to room temperature over a period of two days. The autoclave was then opened and boiling water was added to dissolve the excess boric acid.
wash solution was almost colorless which indicates that an insignificant amount of Pu was released upon washing. Plutonium in solution was not detected by UV-vis spectroscopy. Yellow crystals of \( K[B_5O_7(OH)_2]\cdot H_2O:Pu^{4+} \) with a tablet habit were then isolated as a pure product.

Crystallographic studies: A crystal of \( K[B_5O_7(OH)_2]\cdot H_2O:Pu^{4+} \) was mounted on a CryoLoop with Krytox oil and optically aligned on a Bruker APEXII Quazar X-ray diffractometer using a digital camera. Initial intensity measurements were performed using a \( \mu S \) X-ray source, a 30 W microfocused sealed tube (MoK\( \alpha \), \( \lambda = 0.71073 \) Å) with high-brilliance and high-performance focusing Quazar multilayer optics. Standard APEXII software was used for determination of the unit cells and data collection control. The intensities of reflections of a sphere were collected by a combination of four sets of exposures. Each set had a different \( \phi \) angle for the crystal and each exposure covered a range of 0.5° in \( \omega \). A total of 1464 frames were collected with an exposure time per frame of 30 s. SAINT software was used for data integration including Lorentz and polarization corrections. Semiempirical absorption corrections were applied using the program SCALE (SADABS).\(^53\)

The crystal structure of \( K[B_5O_7(OH)_2]\cdot H_2O:Pu^{4+} \) was solved by direct methods. All atoms were refined anisotropically. The site occupancy factor refinement on the potassium sites showed that the sites are not fully occupied with approximately 2.0% defects. However, this number is not reliable. Instead the occupancy of the K sites was fixed based on the ICP-MS data (vide infra). Also, the substitutional disorder refinement on the potassium sites based on both K and Pu atoms failed to provide a reasonable
occupancy, indicating the doping Pu atoms do not occupy K sites. However, it was still not possible to locate the doping Pu atoms in the final difference Fourier map, which indicates Pu atoms are highly disordered within the void space between the borate chains.

*Laser-ablation inductively coupled plasma mass spectrometer (LA-ICP-MS) analysis:*

Laser ablation analysis of nine different crystals of $K[B_5O_7(OH)_2]·H_2O:Pu^{4+}$ were conducted using a ThermoFinnigan high resolution magnetic sector Element2 ICP-MS instrument coupled to a UP213 Nd:YAG laser ablation system (New Wave Research).

Selected crystals were fixed on 1-inch round glass slides with double-sided tape. Individual analyses consisted of 60 seconds measurement of background ion signals followed by a 60 seconds interval of measurement of ion signals ($^{11}\text{B}, \ ^{39}\text{K}, \ ^{242}\text{Pu}$) subsequent the start of lasering. Each analysis represents a total of 93 scans (93 runs x 1 pass) with a sample (dwell) time of 0.01 second with 20 samples per ion signal peak.

Analyses were conducted in medium mass resolution mode (Resolution = Mass/Peak Width $\sim 4,000$) in order to eliminate possible spectral interferences. The ablated particles were transported from the ablation cell to the ICP-MS instrument using He carrier gas at a flow rate of 0.7 L/min. Crystals were ablated using a range of spot sizes between 40 and 55 μm, repetition rate of 2 Hz and 70% power output corresponding to an energy density of 12-15 J/cm$^2$. Using these ablation conditions, the depth of penetration of the laser is between 5 and 15 microns$^{54-55}$.

*Scanning electron microscopy and energy dispersive spectrometer (SEM/EDS) analysis:*

SEM/EDS images and data were collected using a LEO EVO 50 with an Oxford
INCA Energy Dispersive Spectrometer. The energy of the electron beam was set at 29.02 kV, and spectrum acquisition time was 120 seconds. All of the data were calibrated with standards and all EDS results are provided in the supporting information. Plutonium in the K[B₅O₇(OH)₂]·H₂O:Pu⁴⁺ was easily identified in the energy dispersive spectrum (Supporting Information).

**UV-vis-NIR absorption spectroscopy:** UV-vis-NIR data were acquired from both freshly-made and one day old crystals of K[B₅O₇(OH)₂]·H₂O:Pu⁴⁺ using a Craic Technologies microspectrophotometer. Crystals were placed on quartz slides under Krytox oil, and the data were collected from 500 to 1400 nm. The exposure time was optimized automatically by the Craic software.

**X-ray absorption spectroscopy:** A sample of crystalline K[B₅O₇(OH)₂]·H₂O:Pu⁴⁺ was measured at the Pu L₃ edge on beamline 11-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) using a Si(220) double monochromator (φ = 0°) detuned by 50% to avoid unwanted harmonics. Data were collected in fluorescence mode using a multi-element Ge detector and corrected for dead time. The data were also corrected for self-absorption assuming 5% of the K atoms are replaced by Pu. The EXAFS data were reduced and fit using the RSXAP analysis suite in r-space using standard procedures. The XANES data are shown in Fig. 19.5 and both the EXAFS data and fit are shown in Fig. 19.6. EXAFS fits utilize scattering amplitudes and phases calculated with the FEFF8.1 code based on a PuO₂ fluorite structure.
19.4 Synthesis Discussion

The pure phase of K[B₅O₇(OH)₂]·H₂O·Pu⁴⁺ can be synthesized by the molten boric acid flux reaction of PuBr₃ with KBO₂ at 200 °C. Apparently, Pu(III) was slowly oxidized to Pu(IV) by O₂ in the atmosphere during the reaction. We found that a similar reaction in the absence of KBO₂ in the starting materials will result in the formation of a Pu(IV) borate. Thus, the presence of KBO₂ will kinetically eliminate the formation of plutonium(IV) borates. K[B₅O₇(OH)₂]·H₂O·Pu⁴⁺ forms large yellow crystals with a tablet habit and are shown in Fig. 19.1. The crystals can be cut, and the interior shows the same color as the surface, which excludes the case of surface absorption of Pu(IV) on the crystals of K[B₅O₇(OH)₂]·H₂O. Given that pure, non-doped K[B₅O₇(OH)₂]·H₂O crystals are expected to be colorless, the yellow coloration indicates high levels of plutonium incorporation.

19.5 Crystallographic Studies

The synthesis and crystal structure of K[B₅O₇(OH)₂]·H₂O was recently reported by Zhang et al. The structure of K[B₅O₇(OH)₂]·H₂O contains a series of double helical one-dimensional borate chains shown in Fig. 19.2a. The potassium atoms reside in the void space within the double helical borate chains. There are larger void spaces present between the neighboring double chains (Fig. 19.2b). The vertical distance for these void spaces along a axis is approximately 3.9 Å, which is compatible for trapping the eight-coordinated Pu(IV)O₈ cubic polyhedra (Fig. 19.2b). It should be noted that although K[B₅O₇(OH)₂]·H₂O does not have an exact natural mineral analogue and can only be
Figure 19.1: Photo of crystals of $\text{K}[\text{B}_5\text{O}_7(\text{OH})_2]\cdot\text{H}_2\text{O}:\text{Pu}^{4+}$. 
Figure 19.2: (a) Skeletal structure of double helical one-dimensionl borate chains in K[B$_5$O$_7$(OH)$_2$]·H$_2$O. (b) A cartoon representation of the incorporation mechanism of Pu(IV) into crystals of K[B$_5$O$_7$(OH)$_2$]·H$_2$O. Potassium atoms are shown in purple, borate units (both BO$_3$ triangles and BO$_4$ tetrahedra) are shown in blue, and plutonium are shown as yellow polyhedra.
synthesized in the lab, the structure of larderellite, with the formula of

\[ \text{NH}_4[\text{B}_5\text{O}_7(\text{OH})_2]\cdot\text{H}_2\text{O} \]  

is isotypic with \( K[\text{B}_5\text{O}_7(\text{OH})_2]\cdot\text{H}_2\text{O} \) (Table 19.1). By incorporating Pu(IV), the unit cell parameters for \( K[\text{B}_5\text{O}_7(\text{OH})_2]\cdot\text{H}_2\text{O}:\text{Pu}^{4+} \) are slightly smaller than those for \( K[\text{B}_5\text{O}_7(\text{OH})_2]\cdot\text{H}_2\text{O} \) reported by Yang et al. (Table 19.1). Approximate 2.0% defects was shown on K1 sites based on the site occupancy factor refinement. However, we have fixed the occupancy to that of the ICP-MS data, which is far more reliable. More importantly, the substitutional disorder refinement on K1 sites based on both K and Pu atoms fails to give a reasonable second free variable for occupancy determination. Together, these facts indicate that the doping Pu atoms are not occupying the K sites. This conclusion is reasonable from the point of view that there are large differences between Pu(IV) and \( K^+ \) in both coordination geometries and ionic radius \(^62\). Thus, the doping by Pu(IV) is only possible by allowing it to reside in the void spaces between the neighboring double borate chains (Fig. 19.2b). As a consequence of Pu(IV) entering the structure, some of the \( K^+ \) cations are lost in order to maintain charge-balance, which results in the 2.0% defects on the K sites.

19.6 LA-ICP-MS Studies

Fig. 19.3 demonstrates a typical time-resolved spectrum (i.e., ion signal measured in counts per second (cps) vs. time (seconds)) for a LA-ICP-MS analysis of a single \( K[\text{B}_5\text{O}_7(\text{OH})_2]\cdot\text{H}_2\text{O}:\text{Pu}^{4+} \) crystal in medium mass resolution mode. It is evident from Fig. 19.3 that \( ^{242}\text{Pu} \) is incorporated into the crystal (and not solely onto the crystal’s surface) since its ion signal measured during the lasering interval is concomitant with those
TABLE 19.1

CRYSTALLOGRAPHIC INFORMATION FOR K[B_5O_7(OH)_2]·H_2O\(^{60}\), K[B_5O_7(OH)_2]·H_2O·Pu\(^{4+}\),
AND LARDERELLITE (NH\(_4\)[B_5O_7(OH)_2]·H_2O\(^{61}\))

<table>
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<th>Sample</th>
<th>K[B_5O_7(OH)_2]·H_2O</th>
<th>K[B_5O_7(OH)_2]·H_2O·Pu(^{4+})</th>
<th>Larderellite</th>
</tr>
</thead>
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<td>Yellow</td>
<td>Colorless</td>
</tr>
<tr>
<td>Space group</td>
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<td>(P2_1/c)</td>
<td>(P2_1/c)</td>
</tr>
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<td>9.4619(12)</td>
<td>9.47(1)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>7.5180(6)</td>
<td>7.4691(10)</td>
<td>7.63(1)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>11.4154(6)</td>
<td>11.3740(15)</td>
<td>11.65(1)</td>
</tr>
<tr>
<td>(\alpha) (deg)</td>
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<td>90</td>
</tr>
<tr>
<td>(\beta) (deg)</td>
<td>97.277(3)</td>
<td>97.412(1)</td>
<td>97.08(25)</td>
</tr>
<tr>
<td>(\gamma) (deg)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(V) (Å(^3))</td>
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<td>797.1(2)</td>
<td>835.37</td>
</tr>
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<td>Reference</td>
<td>Zhang et al.(^{60})</td>
<td>This work</td>
<td>Merlino et al.(^{61})</td>
</tr>
</tbody>
</table>
Figure 19.3: Illustration of a typical time-resolved spectrum (ion signal vs. time) for a LA-ICP-MS analysis of a single K[B_{5}O_{7}(OH)_{2}]-H_{2}O:Pu^{4+} crystal. Time interval between 0 and ~60 seconds represents background measurement, whereas subsequent interval represents measurement of ion signals after the start of lasering.
recorded for $^{11}$B and $^{39}$K, and importantly does not decrease rapidly with time; the latter feature is consistent for atoms incorporated solely within the surface of the crystal (~first micron of depth). Moreover, repeated analysis (n=9) by LA-ICP-MS of individual K[$B_5O_7(OH)_2$]·$H_2$O:Pu$^{4+}$ crystals yielded an average, calculated K:Pu ‘mass’ ratio of 3.37 ±0.7. However, a more accurate assessment of the K:Pu ratio should take into account the lower ionization efficiency or lower ‘ion yield’ (ion signal – counts per second/concentration unit) of K versus that for Pu in a plasma environment. In general, the ‘ion yield’ for elements analyzed by an ICP-MS instrument is mass dependent, with ‘heavier’ elements (>80 amu$^{-1}$) recording higher values compared to those for lighter elements. The differential ion yield for K versus Pu was assessed in medium mass resolution via the measurement of 4 solutions each containing 1:1 mass ratio of K:U at variable concentrations (~10 to 50 ppb). For ease of sample preparation, uranium was used as a valid proxy for Pu given their similar atomic masses. The average, measured K:U mass ratio obtained for the solutions was 1:3.12. Hence, this result when applied to the laser ablation values yields an average ‘normalized’ K:Pu mass ratio of ~10.5:1, and a corresponding atomic ratio for K:Pu of ~65:1 for the K[$B_5O_7(OH)_2$]·$H_2$O:Pu$^{4+}$ crystals.

19.7 UV-vis-NIR Absorption Spectroscopy

By possessing complicated f electron configurations, both Pu(IV) and Pu(III) are known to produce a series of weak, Laporte-forbidden f-f transitions in the vis-NIR region in both solution and the solid state$^{63-64}$. In solution, the spectrum of Pu(IV) consists of characteristic transitions such as the peaks near 477, 660, 800, 1080 nm$^{63}$. 

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For Pu(III), the most important transition that can be used for distinguishing from Pu(IV) is at 920 nm. The UV-vis-NIR absorption spectra taken from both freshly-made and one-day old crystals of K[B$_5$O$_7$(OH)$_2$]·H$_2$O:Pu$^{4+}$ are shown in the Fig. 19.4. It is found that the freshly-made crystals contain predominantly Pu(IV), whereas a very small amount of Pu(III) is also present based on the weak peak at 926 nm. In the spectrum of one-day old crystals, the 926 peak disappears, which indicates that the tiny amount of remaining Pu(III) incorporated into the crystals is rapidly oxidized by ambient O$_2$ in the air.

Nevertheless, the results indicate that both Pu(III) and Pu(IV) are capable of entering the structure of K[B$_5$O$_7$(OH)$_2$]·H$_2$O. It should be noted that the incorporation of Pu(III) into K[B$_5$O$_7$(OH)$_2$]·H$_2$O still does not prevent the oxidation of Pu(III). This oxidation contrasts sharply with the fact that many Pu(III) compounds are not air-sensitive. Apparently, Pu(III) can be further stablized by the lattice energy in most Pu(III) compounds while the lattice energy is lacking for Pu(III) in crystals of K[B$_5$O$_7$(OH)$_2$]·H$_2$O since plutonium atoms are highly disordered in the void space.

19.8 XANES and EXAFS Studies

The XANES data shown in Fig. 19.5 are clearly consistent with a Pu(IV) state for the K[B$_5$O$_7$(OH)$_2$]·H$_2$O:Pu$^{4+}$ sample, as indicated by the consistent position of the white line when compared to data from PuO$_2$. Moreover, the first EXAFS oscillation (peak at ~ 18100 eV) is practically identical to that of PuO$_2$. The increased peak height of the data indicates differences in the long-range structure, for instance, due to particle or cluster size, which tends to increase the amplitude of the white line for smaller clusters.
Figure 19.4: UV-vis-NIR absorption spectra taken from both freshly-made (black) and one-day old (red) crystals of $K[B_5O_7(OH)_2] \cdot H_2O:Pu^{4+}$. 
Figure 19.5: Pu $L_{III}$-edge XANES of K[B$_5$O$_7$(OH)$_2$]$\cdot$H$_2$O:Pu$^{4+}$ at 30 K, together with that of PuO$_2$ collected at room temperature. Data in this and Figure 6 are displayed with error bars estimated by collecting several scans.
Some of this difference could be due to the difference in the measurement
temperatures between the borate and the PuO$_2$ sample.

The EXAFS data in Fig. 19.6 are also quite similar to that expected from PuO$_2$ (not
shown in the figure), although the Pu-Pu peak at $\sim$ 3.7 Å in the spectra (corresponding to
a Pu-Pu distance of about 3.8 Å) is actually less than half the expected amplitude. The
fit results listed in Table 19.2 clearly indicate the similarity between the measured local
structure and that of PuO$_2$, as the number of Pu-Pu neighbors is 3.9 ± 0.9, as opposed to
the 12 Pu-Pu neighbors in PuO$_2$, the measured Pu-O bond length of 2.325 ± 0.8 Å is
typical for a Pu(IV) compound$^{65}$, and the amplitude reduction factor $S_0^2$ is reasonable
given an oxygen coordination of 8 around the Pu atoms. It should be noted, however,
that the estimated error in $S_0^2$ allows for 9 Pu-O nearest-neighbors.

These data are not compatible with a significant number of Pu atoms occupying
the K position in the structure of K[B$_5$O$_7$(OH)$_2$]·H$_2$O. In that structure, the K-O near
neighbor shell has 10 neighbors with bond lengths between 2.76 and 3.22 Å, which
would generate an EXAFS peak approximately 15% of the amplitude at centered about
0.4 Å further in the Fourier transform of Fig. 19.6. Even if one allows for a local
rearrangement of O around Pu when Pu occupies a K site, one would not expect a Pu-Pu
pair at 3.8 Å in this structure, where the K-K nearest distance is about 5.0 Å with only
two neighbors. These data are therefore more consistent with PuO$_2$ clusters, rather than
a random distribution of Pu on K positions within the K[B$_5$O$_7$(OH)$_2$]·H$_2$O structure.
Figure 19.6: Pu $L_{III}$-edge EXAFS data from $K[B_3O_3(OH)_2]·H_2O$:Pu$^{4+}$ at 30 K in both (a) $k$-space and (b) $r$-space. The Fourier transform (FT) in (b) shows the amplitude (outer envelope) and the real part (modulating line) of the transform, and is taken between 2.5-15.0 Å$^{-1}$, Gaussian narrowed by 0.3 Å$^{-1}$. The fit shown in (b) is between 1.8 and 3.9 Å. Fit results are summarized in Table 19.2.
TABLE 19.2

FIT RESULTS FOR PU $L_{III}$-EDGE EXAFS DATA ON K[B$_3$O$_7$(OH)$_2$]-H$_2$O:PU$^{4+}$ AT T = 30 K. FIT RANGE IS BETWEEN 1.8 AND 3.9 Å. THE $K^3$-WEIGHTED DATA ARE TRANSFORMED BETWEEN 2.5-15.0 Å$^{-1}$ AND ARE GAUSSIAN NARROWED BY 0.3 Å$^{-1}$. THE DEGREE OF FREEDOM OF THE FIT IS ESTIMATED TO BE 11.7$^{67}$. ERROR ESTIMATES USE A MONTE CARLO METHOD$^{68}$. THE AMPLITUDE REDUCTION FACTOR FOR THESE FITS IS DETERMINED TO BE $S_0^2 = 1.14 \pm 0.14$ AND THE EDGE SHIFT IS $\Delta E_0 = -11.0 \pm 0.9$ EV

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<th>$N$</th>
<th>$\sigma^2$(Å$^2$)</th>
<th>$R$(Å)</th>
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<td>Pu-O</td>
<td>8</td>
<td>0.010(1)</td>
<td>2.325(8)</td>
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<tr>
<td>Pu-Pu</td>
<td>3.9(9)</td>
<td>0.0027(5)</td>
<td>3.808(4)</td>
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<tr>
<td>$\Delta E_0$</td>
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<td>-11.0(9)</td>
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<tr>
<td>$S_0^2$</td>
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<td>1.14(14)</td>
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<tr>
<td>$R$(%)</td>
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19.9 Implications for the Migration of Radionuclides at Repositories

It is well known that the release of radionuclides at repositories is retarded by the incorporation of radionuclides into natural materials. However, predictions of actinide incorporation based solely on the old lattice substitution mechanism now seem to be very limited. With our observation of incorporation occurring in $\text{K[B}_5\text{O}_7\text{(OH)}_2\cdot\text{H}_2\text{O}}:\text{Pu}^{4+}$, many natural materials that lack suitable sites for lattice substitution but that possess void spaces of suitable dimensions may also show the capacity for trapping certain radionuclides. Furthermore, studies focused on the incorporation of actinides into borate minerals are scarce. This study is pertinent and significant for the Waste Isolation Pilot Plant (WIPP) located at the Salado formation near Carlsbad, NM, where the concentration of borates, predominately in forms of $\text{H}_3\text{BO}_3$, $\text{B(OH)}_4^-$, and $\text{B}_6\text{O}_7^{2-}$, attains concentrations as high as 166 ppm in intergranular brines$^{69}$. Borate minerals are known to have a very complicated and rich structural chemistry, and countless structural topologies have been observed in the borate mineral family$^{70-71}$. A variety of borate minerals including larderellite (natural analogue of $\text{K[B}_5\text{O}_7\text{(OH)}_2\cdot\text{H}_2\text{O}}$) as well as other one-dimensional materials such as vimsite, colemanite, calciborite, hydroboracite, probertite, ezcurrite, kaliborite, kernite, aristarainite etc.$^{71}$ are expected to form in the WIPP that can provide a series of structures containing void space with a wide range of dimensions. These void spaces could trap actinides, which would slow down their migration.
19.10 Supporting Information

Figure 19.7: EDS spectrum of $\text{K[B}_3\text{O}_5\text{(OH)}_2]\cdot\text{H}_2\text{O:Pu}^{4+}$
19.11 Reference


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CHAPTER 20:

CONCLUSIONS AND OUTLOOK

Driven by the curiosity about the crystalline portion of actinides in the vitrification products of nuclear wastes, we have already made a large family of novel actinide (including Th, U, Np, Pu, Am, and Cm) borates using molten boric acid flux reactions. The chemistry involved with this topic is unique and rich in all regards. First of all, we have proved that the behavior of actinide elements in molten boric acid is substantially different from that observed in aqueous solutions. An extremely rare cationic framework thrioum borate that can selectively remove TcO$_4^-$ in simulated nuclear waste, several extraordinarily complicated mixed/intermediate valence neptunium borates that can simultaneously contain neptunium in three different oxidation states, the reversed relative favorability between Pu(IV) and Pu(VI), structural evidences to probe the difference among Pu(III), Am(III), and Cm(III), none of these have ever observed in the aqueous solution system. Second, the actinide borate system show an exceeding diversity in the structures that probably never been seen in any other ligand systems in the solid state. Borate is a perfect non-redox-active ligand that can be used to structurally probe the tiny difference among different elements, oxidation states, or
even reaction conditions while providing strong abilities to coordinate different metal centers in all cases using its numerous bonding modes.

As one of the messages taken from the actinide borate system, great caution needs to be exercised in predicting the chemistry of transuranium materials based on the behavior of uranium compounds; they can be quite different. Even the neighbouring elements in same oxidation states can show obviously different structure and coordinate geometries. However, this is not the primary message of this work. What we have now observed in $\text{K}_4[(\text{NpO}_2)_{6.73}\text{B}_{20}\text{O}_{36}(\text{OH})_2]$ 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 materials that can successfully sequester all stable oxidation states of neptunium, not just one. Therefore, we have the ability to design advanced materials that target not just one oxidation state of a radionuclide, but all possible oxidation states. More importantly, we have discovered most of our actinide borate compounds are radiation-resistant even for transuranic element borates including neptunium, plutonium and americium borates although great amount of radiations are generated by these isotopes (including $^{237}\text{Np}$, $^{239}\text{Pu}$, $^{240}\text{Pu}$, $^{242}\text{Pu}$, $^{243}\text{Am}$, and $^{248}\text{Cm}$) we have used for syntheses.
APPENDIX A:

PAPERS AND CONFERENCES

A.1 Peer-Viewed Journal Papers


(16) “Deviation Between the Chemistry of Ce(IV) and Pu(IV) and Routes to Ordered and Disordered Heterobimetallic 4f/5f and 5f/5f Phosphonates” J. Diwu, S. Wang, J. Good, D. Victoria, T. E. Albrecht-Schmitt, *Inorg. Chem.*, 2011, 50, 4842-4850;


A.2 Conference Presentations and Lectures

(12) S. Wang, “From Thorium to Curium: Unprecedented Structures and Properties in Actinide Borates” invited talk, Lawrence Berkeley National Laboratory and University of California-Berkeley, Berkeley, CA, November 16, 2011;


(9) S. Wang, J. Diwu, E. V. Alekseev, T. E. Albrecht-Schmitt, “Recent Progress in Actinide Borate Chemistry”, poster presentation at Rare Earth Research Conference 2011, Santa Fe, NM, June 20, 2011;


(3) S. Wang, “New insights into Actinide Borate Materials Relevant to Nuclear Waste Storage”, invited talk, Shaanxi Normal University, Xi’an, Shaanxi, China, December 28, 2009;

(2) S. Wang, “New insights in Actinide Borates”, oral presentation at PINDU (Purdue, Indiana, Notre dame Universities) Annual Inorganic Symposium, University of Notre Dame, Notre Dame, IN, November 17, 2009;

(1) S. Wang, “Actinide Chemistry at the University of Notre Dame”, poster presentation at Chemistry fun event, University of Notre Dame, Notre Dame, IN, October 24, 2009.