Final Technical Report

Exploratory Synthesis for Reactive f-Element Separations without Solvent

DOE Award No. DE-SC0019426, August 1, 2018 – July 31, 2022

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Executive Summary

Solvent extraction is commonly used to separate different f-metals found in spent nuclear fuel, but this process results in large volumes of highly contaminated liquid waste that must be remediated or stored at significant expense. The project funded under this award was aimed at addressing solvent-related issues encountered in conventional f-metal separations. Our strategy focused on using solvent-free mechanochemical reactions to prepare lanthanide and actinide borohydride complexes so that they could be separated based on differences in their volatility. Key deliverables described in this report include proof-of-principle results demonstrating that borohydrides called aminodiboranates can be used for volatile lanthanide/lanthanide and lanthanide/uranium separations, as we proposed. Moreover, exploration of a closely related class of borohydrides called phosphinodiboranates allowed us to identify underlying chemical factors that control the volatility of trivalent lanthanide and uranium borohydride complexes with identical structures. Details of published and pending research products are provided, and these include comprehensive synthesis and characterization efforts required to support fundamental studies related to the proposed separations. These technical efforts supported the training of nine graduate students and three undergraduate researchers, and they established air-sensitive transuranic capabilities at the University of Iowa to enhance radiochemical workforce development.

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1. Major Activities and Objectives

The goal of this project was to develop lanthanide/actinide, lanthanide/lanthanide, and actinide/actinide separations by selective volatilization of *f*-element complexes with borohydride ligands. Our proposed separation strategy was aimed at using mechanochemistry and differences in the volatility of borohydride complexes to separate f-metals without using solvent. The principal advantage of this approach is that it avoids generating large volumes of contaminated solvent, a significant problem associated with conventional solvent extraction processes used for separating lanthanides and actinides (especially from spent nuclear fuel).

Achieving the goal of this project required fundamental understanding of how different borohydride ligands give rise to lanthanide and actinide complexes with different volatilities, especially with f-metals adopting a common +3 oxidation state. It has been shown previously that borohydride ligands such as $H_3BNMe_2BH_3^{1-}$ (*N,N*-dimethylaminodiboranate; DMADB) can yield isostructural trivalent lanthanide and actinide complexes with dramatic differences in volatility. For example, the actinide complex $U(H_3BNMe_2BH_3)_3$ and the lanthanide complex $Pr(H_3BNMe_2BH_3)_3$ are known to adopt the same structures in the solid state, but only the Pr complex sublimes when heated under vacuum. In the context of our proposed separations, it has also been shown that the lanthanide complexes can be prepared without solvent by grinding metal and ligand salts together.

Completed work described in this report was aimed at testing DMADB and other borohydride ligands for mechanochemical synthesis and volatile separation of f-metals. In addition to separations, fundamental studies were performed to elaborate chemical factors that give rise to f-element borohydride complexes with different volatility. Efforts completed during the award period can be organized into three categories:

1. Synthesis and characterization of new lanthanide and actinide borohydride complexes, including those with transuranic elements such as Np and Pu.
2. Fundamental studies of f-metal bonding with borohydride ligands to determine chemical factors that give rise to differences in lanthanide and actinide volatility.
3. Actinide/lanthanide and actinide/actinide separation studies using mechanochemistry and selective volatilization.

2. Key Accomplishments and Deliverables

2.1. Synthesis and characterization studies. Addressing the goals of this project required us to develop borohydride ligands for the mechanochemical synthesis and separation of f-metal complexes. To hasten the exploration of available chemical space, the Daly Group focused on the development of chelating borohydride ligands called phosphinodiboranates ($H_3BPR_2BH_3^-$, where R = alkyl or aryl) and the Girolami Group focused on the development of aminodiboranates ($H_3BNR_2BH_3^-$, where R = alkyl, H, or $SiMe_3$). Phosphinodiboranates are larger than aminodiboranates, and they were targeted because they can saturate more of coordination sphere of trivalent lanthanides and actinides (a key requirement for the synthesis of volatile complexes with these metals).

The Daly Group completed a thorough synthetic exploration of phosphinodiboranate complexes with lanthanides and uranium. Phosphinodiboranate salts have been known since at least the 1960's, but they were not used to prepare lanthanide and actinide complexes until the first report with $H_3BP^tBu_2BH_3^-$ (^{t}Bu-PDB) by Daly and coworkers in 2018 (*Chem. Comm.* **2018**, 5602). The initial synthesis of lanthanide and uranium ^{t}Bu-PDB complexes relied on solution-based salt elimination reactions, which allowed the complexes to be prepared for the first time, but only in low and/or irreproducible yields. The synthesis of $U(H_3BP^tBu_2BH_3)_3$ also required UI_3

starting materials, which at the time were difficult to acquire because their synthesis relied on uranium metal (which is not commercially available).

The Daly Group addressed both problems as part of this project. In two reports, including one highlighted as an invited forum article in the American Chemical Society's journal *Inorganic Chemistry*, the Daly Group showed that PDB complexes can be prepared more reproducibly and isolated in significantly higher yields (>50%) using mechanochemical methods targeted for use in volatile separations (*Inorg. Chem.* **2020**, *59*, 48 and *Dalton Trans.* **2021**, *59*, 11472). These reactions also permitted access to a wider range of $H_3BPR_2BH_3^-$ complexes that showed how different substituents attached to phosphorus (R = ^{t}Bu, Ph, ^{i}Pr, Et, and Me) affects PDB metal binding and structure with lanthanides and uranium (*manuscript submitted*). The Daly Group also discovered and reported new methods to prepare important U(III) starting materials – including $UI_3(THF)_4$ – from commercially available uranium oxides (*Inorg. Chem.* **2021**, *60*, 7593). In addition to these efforts, a separate synthesis and characterization study of divalent Eu^{2+} complexes with PDB ligands is in progress.

Unfortunately, despite their promising mechanochemical reactivity, it was discovered that none of the phosphinodiboranate complexes sublime under vacuum, thereby eliminating their viability for volatile separation studies. However, as described in the next section, these complexes revealed important chemical insights that explain the origin of trivalent lanthanide/uranium volatility differences with other borohydride ligands like DMADB.

In parallel with efforts in the Daly Group, the Girolami Group completed several studies aimed at the synthesis of new aminodiboranate complexes with lanthanides and actinides. In 2020, the Girolami Group published a report on the synthesis and characterization of DMADB complexes with the divalent lanthanides Sm^{2+} and Tm^{2+} (*Inorg. Chem.* **2021**, *60*, 11164). This study revealed that DMADB is reducing enough to stabilize these lanthanides in their divalent oxidation states, thereby opening the door to redox facilitated lanthanide/lanthanide separations. In this context, it has been shown that all trivalent $Ln(H_3BNMe_2BH_3)_3$ complexes are volatile and sublime when heated under vacuum, whereas divalent $Ln(H_3BNMe_2BH_3)_2$ complexes do not. Related to these studies, Girolami and Daly collaboratively demonstrated the synthesis of $^{225}Ac(H_3BNMe_2BH_3)_3$ – a rare example of an Ac coordination complex – that can be sublimed using $Pr(H_3BNMe_2BH_3)_3$ as a carrier (*Inorg. Chem.* **2022**, *61*, 7217).

In work related to the DOE project, the Girolami Group developed synthetic routes to a wider range of $Na(H_3BNRR'BH_3)$ salts with NRR′ = NHMe, NHEt, $NH(SiMe_3)$, NEt_2, N^iPr_2, $N(SiMe_3)_2$, NMe(^{i}Pr), NMe(^{t}Bu), $NMe(SiMe_3)$, NC_4H_8, NC_5H_{10}, and NC_5H_8-cis-2,6-Me_2 (*Inorg. Chem.* **2022**, *61*, 18412). These results will allow future investigations aimed at determining how different nitrogen substituents influence the volatility of lanthanide and actinide aminodiboranate complexes.

The Girolami Group also reported the crystal structure of the binary borohydride $Th(BH_4)_4$ (*Inorg. Chem.* **2021**, *60*, 12489). This thorium complex is the analog of $U(BH_4)_4$, which was evaluated during World War II as the transporting agent in the separation of fissile ^{235}U from uranium mixtures by gas diffusion. Despite powder diffraction and spectroscopic data indicating that $Th(BH_4)_4$ and the tetragonal form of $U(BH_4)_4$ are isomorphous, their physical and chemical properties are rather different. For example, whereas $Th(BH_4)_4$ sublimes only with difficulty at 130 ºC (P_{vap} = 0.05 Torr at this temperature) and is thermally stable up to its melting point of 204 ºC, the uranium analogue sublimes readily at 30 ºC (P_{vap} = 0.19 Torr) and decomposes at 100 ºC. In addition, the thorium compound is far less soluble in nonpolar, non-coordinating solvents than its uranium analogue.

Our crystallographic study showed that $Th(BH_4)_4$ is in fact isomorphous with $U(BH_4)_4$. Two of the four BH_4^- ions are terminal and tridentate (κ^3) whereas the other two bridge between neighboring Th^{IV} centers in a κ^2,κ^2 (i.e., bis-bidentate) fashion. Thus, each thorium center is bound to six BH_4^- groups by 14 Th–H bonds. The six boron atoms describe a distorted octahedron in which the κ^3-BH_4^- ions are mutually *cis*; the 14 ligating hydrogen atoms define a highly distorted bicapped hexagonal antiprism. The thorium centers are linked into a polymer consisting of interconnected helical chains wound about four-fold screw axes. The structures of $An(BH_4)_4$ (An = Th, U) were also investigated by DFT. The geometries of $[An(BH_4)_6]^{2-}$, $[An_3(BH_4)_{16}]^{4-}$, and $[An_5(BH_4)_{26}]^{6-}$ fragments of the polymeric structures were optimized at the B3LYP and/or PBE levels. Most calculated geometries are 14-coordinate and agree with the experimental structures, but isolated $[Th(BH_4)_6]^{2-}$ units are predicted to feature 16-coordinate Th^{IV} centers.

Complementing borohydride ligand development efforts, a key objective related to our synthetic work was to develop infrastructure and collaborations to pursue the synthesis of transuranic borohydride complexes. This area is woefully underexplored relative to studies with uranium because of the increased radioactivity of transuranic isotopes of Np and Pu, and because of the unique handling challenges associated with air sensitive borohydride complexes. To address this objective, the Daly Group established air-sensitive transuranic capabilities at UIowa by installing a custom negative-pressure N_2-filled transuranic glovebox in the shared Radiochemistry Facility. The Daly Group also engaged in a collaboration with Los Alamos National Laboratory (LANL) to explore the chemistry of Pu borohydride complexes as Np capabilities were being developed at UIowa.

Completing experiments with Np and Pu required working out conditions needed to prepare phosphinodiboranate complexes at small scales (<10 mg) to accommodate the limited availability of Np and Pu starting materials. The Daly Group successfully demonstrated that uranium and lanthanide PDB complexes can be prepared on scales as small as 6 mg of metal starting material. The milliscale procedure and PDB starting materials were sent to collaborators at LANL, and they have crystals of what we believe is the first Pu phosphinodiboranate complex (they are awaiting time on the single-crystal diffractometer to confirm). Similar studies with Np are ongoing at UIowa.

Finally, the Girolami Group investigated other kinds of ligands in an effort to develop new volatile complexes of the f-elements. Some volatile f-element complexes with all-nitrogen coordination environments such as homoleptic lanthanide amidinates and guanidinates, are known. Closely related to amidinates and guanidinates are the triazenides; in the latter anions the central carbon atom has been replaced with nitrogen. Although several lanthanide triazenide complexes are known, all of them contain 1,3-diaryltriazenide ligands, and the large London forces and π-π stacking characteristic of aryl groups renders the complexes essentially non-volatile.

To make volatile complexes, the Girolami Group prepared the first dialkyltriazenide complexes of the lanthanide elements neodymium, europium, and erbium; these include the homoleptic complex $Er(Bu^tN_3Bu^t)_3$, the tetrahydrofuran monoadducts $Ln(Bu^tN_3Bu^t)_3(THF)$ where Ln = Nd or Eu, and the lithium salts $[Li(THF)][Ln(MeN_3Bu^t)_4]$ where Ln = Eu or Er (*Inorg. Chem.* **2022**, *61*, 16740). Crystal structures, NMR, and IR data are reported for all complexes. The di-*tert*-butyltriazenide complexes are thermally stable, sublime at reasonably low temperatures, and show smooth volatilization without decomposition by thermogravimetric analysis, which make them potentially useful in lanthanide separation processes and as chemical vapor deposition precursors for lanthanide nitrides and other phases.

2.2. Fundamental studies of f-element borohydride bonding. A key question that this project aimed to address is: what is responsible for volatility differences observed in some actinide and lanthanide borohydride complexes? As discussed in Section 1, the Girolami Group previously showed that the DMADB complexes $U(H_3BNMe_2BH_3)_3$ and $Pr(H_3BNMe_2BH_3)_3$ adopt identical structures in the solid state, but only the latter sublimes. Both structures are polymers and contain DMADB ligands that bridge between adjacent metal centers, which indicates that the ligands must rearrange to form molecular complexes that can be sublimed. Theoretical studies suggest that the difference in sublimation behavior can be attributed to increased covalent U-H bonding in the actinide complex $U(H_3BNMe_2BH_3)_3$ compared to those with lanthanides like Pr. It has been proposed that the increased covalency prevents the bridging ligands in $U(H_3BNMe_2BH_3)_3$ from rearranging so that the complex can depolymerize and sublime, but there were no experimental data to corroborate this hypothesis.

The Daly Group recently reported that increased U-H-B covalency does indeed control depolymerization energies in diphosphinodiboranate complexes (*Angew. Chem., Int. Ed.* **2022**, *61*, e202211145). Unlike polymeric DMADB complexes, which only dissolve to form monomers in solution, dimeric ^{t}Bu-PDB complexes $U(H_3BP^tBu_2BH_3)_3$ and $Ln(H_3BP^tBu_2BH_3)_3$ depolymerize to different extents to form mixtures of dimers and monomers when dissolved. Variable-temperature NMR studies revealed that the U complex requires more energy to depolymerize, and the energy difference corresponded to shorter-than-expected bridging U-B distances in $U(H_3BP^tBu_2BH_3)_3$ when compared to Ln-B distances. The shorter U-B distances are a structural hallmark of increased covalency, which was corroborated by several types of theoretical calculations performed by the Vlaisavljevich Group at the University of South Dakota.

To further understand the role of metal-ligand covalency on the differential volatility of f-metal borohydride complexes, the Daly group recently began efforts aimed at collecting B K-edge X-ray absorption spectroscopy (XAS) data at the Canadian Light Source. Ligand K-edge XAS, where ligand refers an atom involved with bonding at the metal (in this case boron), is a spectroscopic technique that has proven remarkably valuable for quantifying differences in covalent metal-ligand bonding with transition metals, lanthanides, and actinides. Ligand K-edge XAS measurements have been performed on f-metal complexes at the Cl, O, and C K edges, but it has never been used to investigate metal borohydride complexes at the B K edge.

The Daly Group established the feasibility of B K-edge XAS for interrogating metal borohydride bonding by collecting data on $[M(H_3BR)_4]$ complexes with M = Zr and Hf and R = cyclohexyl, phenyl, and benzyl in July 2022. As is often the approach, high symmetry transition metal complexes were tested first because they have well-defined electronic structures and yield larger metal-dependent spectral differences that make spectroscopic assignments more reliable and easier to interpret. Moreover, metal borohydride complexes are highly air sensitive, and it was better to work out practical aspects of sample preparation and air-free measurements with non-radioactive complexes before proceeding to those containing actinides.

The B K-edge spectra for $[Zr(H_3BR)_4]$ and $[Hf(H_3BR)_4]$ complexes showed two pre-edge features as expected based on covalent M-H-B mixing and tetrahedral geometries that cause the d-orbitals to split into e and t_2 sets. A 0.3 eV increase in the energy of the two pre-edge features was also observed for the Hf complex, which follows the expected trend because of the higher energy 5d orbitals in Hf compared to 4d orbitals in Zr. These results represent the first B K-edge XAS spectra collected on air-sensitive transition metal borohydride complexes, and they demonstrate that similar data can be collected on lanthanide and actinide borohydride complexes. The Daly Group will be returning to the Canadian Light Source in January 2023 to complete measurements on lanthanide and actinide borohydride complexes.

2.3. Separation studies. One of the most exciting discoveries of the project was confirmation of a key hypothesis of this project: borohydride ligands can indeed be used to selectively volatilize and separate different f-metals. In a representative experiment, the Girolami Group showed that treating one-to-one mixtures of UCl_4 and $SmCl_3$ with 7 eq. of the

DMADB salt $Na(H_3BNMe_2BH_3)$, followed by sublimation of the mixture at 70 °C at 10^{-2} Torr, yielded sublimates with Sm/U ratios of >30:1. Similar studies showed that we can also separate mixtures of early and late lanthanide elements. For example, treating a 1:1 mixture of $PrCl_3$ and $ErCl_3$ with 6 eq. of $Na(H_3BNMe_2BH_3)$ followed by sublimation at 95 °C at 10^{-2} Torr yielded an Er-enriched sublimate with an 8:1 Er/Pr ratio in a single step. Sublimation of the Er-enriched material at lower temperature (70 °C) increased the Er/Pr ratio further to ca. 30:1.

Though the separations were successful, a drawback of the approach is the low % metal recovery in the sublimate (≤ 30%) compared to sublimation recoveries of pure $Ln(H_3BNMe_2BH_3)_3$ complexes under identical conditions (70 – 90%). Our hypothesis is that the low recovery is due to the formation of mixed metal oligomers in the solid-state when different lanthanides and actinides are combined in the same mixture. We suspect that these mixed-metal oligomers suppress volatility and must be broken up by sustaining the mechanochemical reactions during the sublimation process. This would allow ligands and metals in the mixture to continue to exchange until the volatile lanthanide complexes are formed and can escape into the gas phase via sublimation. Several new reactor prototypes were being developed to test this hypothesis for DMADB separations as the project and funding expired.

Attempts to use other borohydride ligands for separations were unsuccessful. As mentioned in Section 2.1, newly discovered phosphinodiboranate complexes had insufficient volatility for our proposed volatile separations. More traditional borohydrides like tetrahydroborate (BH_4^-) were also unsuitable. Although $An(BH_4)_4$ complexes are some of the most volatile actinide complexes known, and $Ln(BH_4)_3$ complexes do not sublime, the Daly Group discovered that the chemistry of tetravalent actinides differs in the presence of lanthanide salts. Specifically, although highly volatile $U(BH_4)_4$ can be prepared from UCl_4 and 4 equiv of $Li(BH_4)$ in isolated yields of >60% by mechanochemical synthesis (*Inorg. Chem.* **2021**, *60*, 7593), attempting the same ball milling reaction in the presence of $NdCl_3$ catalyzed the reduction of $U(BH_4)_4$ to non-volatile $U(BH_4)_3$ with formation of diborane and H_2 gas, according to the following equation:

$$U^{IV}(BH_4)_4\ (s) \rightarrow U^{III}(BH_4)_3\ (s) + \tfrac{1}{2}\ H_2\ (g) + \tfrac{1}{2}\ B_2H_6\ (g)$$

It is not clear why lanthanides catalyze the reduction of $U(BH_4)_4$ in the solid state, but the results highlight the need to carry out studies with technologically relevant mixtures; the behavior of the pure components may be very different. This was also shown to be the case in separation studies with DMADB, but the presence of different metal ions did not appear to affect the separation (only metal recovery). We consider the low metal recoveries to be a more tractable problem that can be addressed with new reactor prototypes and subsequent optimization studies in future work.

3. Student Training and Professional Development

This project provided crucial training and professional development opportunities for nine chemistry graduate students (7 PhD and 2 MS). This includes a Black PhD graduate who is now an Assistant Professor of Chemistry at Augustana College in Rock Island, IL (Dr. A. Rayford Harrison) and two female PhD graduates currently working at Los Alamos National Laboratory (LANL) in Los Alamos, NM (Drs. Anastasia Blake and Taylor Fetrow). Based on her work with phosphinodiboranates, Dr. Anastasia Blake subsequently received an Office of Science Graduate Student Research (SCGSR) Program Fellowship to work at LANL with Dr. Stosh Kozimor. There she performed research with transuranic elements up to and including Am and Cm, which helped facilitate her conversion to permanent staff. Similarly, Dr. Taylor Fetrow was awarded a Seaborg Postdoctoral Fellowship to work at LANL after graduating from UIowa.

Joshua Zgrabik, who is currently the graduate student lead on the project at UIowa, is currently interviewing for postdoctoral positions at LANL.

This project also supported three undergraduate researchers who continue to demonstrate remarkable success. All three undergraduate researchers are published co-authors on manuscripts stemming from work described in this report. One of these students is now an officer in the US Army (Grabow), and the other two have moved on to medical and graduate school (Theiler and Eckstrom, respectively).

Despite the lack of in-person presentation opportunities due to the COVID-19 pandemic for a significant portion of the project period, graduate and undergraduate students supported on this project successfully attended regional, national, and international conferences and delivered 15 presentations on the work with acknowledged DOE support (see list in section 9).

Collectively, these outcomes demonstrate how the project provided important student training and workforce development in chemical synthesis and radiochemistry to meet emerging technical need, especially to support mission-critical National Laboratories like LANL. It also demonstrates how the project supported students from underrepresented backgrounds.

4. List of Students Supported

Graduate Students (9 total): Anastasia V. Blake (PhD, UIowa; now staff scientist at Los Alamos National Laboratory), Taylor V. Fetrow (PhD, UIowa; now Seaborg Postdoctoral Scholar at Los Alamos National Laboratory), A. Rayford Harrison (PhD, UIowa; now Assistant Professor at Augustana College in Rock Island, IL), Holly Huther (MS program, UIowa; graduating May 2023), Jacob Schuely (PhD program, UIowa), Joshua C. Zgrabik (PhD program, UIowa; graduating May 2023), Nels T. Anderson (MS, UIUC; employed at TipTek in Savoy, IL), Joseph C. Wright (left PhD program in June 2021 for family reasons), Christopher M. Caroff (PhD program, UIUC; graduating 2022 and will be employed by Gelest in Morrisville, PA)

Undergraduate Researchers (3 total): Francesca Eckstrom (BS, UIowa; now PhD student at Colorado State University), Zachary J. Theiler (BS, UIowa; now in medical school at Kansas City University), J. Pete Grabow (BA, UIowa; now an officer in the US Army)

5. List of Peer-Reviewed Manuscripts Published

Fetrow, T. V.; Zgrabik, J.; Bhowmick, R.; Eckstrom, F. D.; Crull, G.; Vlaisavljevich, B.; Daly, S. R. "Quantifying the Influence of Covalent Metal-Ligand Bonding on Differing Solution Reactivity of Trivalent Uranium and Lanthanide Complexes." *Angewandte Chemie, International Edition* **2022**, e202211145.

Caroff, C. M.; Bellott, B. J.; Daly, C. I.; Daly, S. R.; Dunbar, A. C.; Mallek, J. L.; Nesbit, M. A.; Girolami, G. S. "Sodium Aminodiboranates Na($H_3BNR_2BH_3$): Structural and Spectroscopic Studies of Steric and Electronic Substituent Effects." *Inorganic Chemistry* **2022**, *61*, 18412-18423.

Caroff, C. M.; Girolami, G. S. "Synthesis, Structure, and Properties of Volatile Lanthanide Dialkyltriazenides." *Inorganic Chemistry* **2022**, *61*, 16740-16749.

Daly, S. R.; Bellott, B. J.; McAlister, D. R.; Horwitz, E. P.; Girolami, G. S. "Pr($H_3BNMe_2BH_3$)$_3$ and Pr(thd)$_3$ as Volatile Carriers for Actinium-225. The Deposition of Actinium-Doped Praseodymium

Boride Thin Films for Potential Use in Brachytherapy." *Inorganic Chemistry* **2022**, *61*, 7217-7221.

Fetrow, T. V.; Bhowmick, R.; Achazi, A. J.; Blake, A. V.; Eckstrom, F. D.; Vlaisavljevich, B.; Daly, S. R. Correction and Addition to Chelating Borohydrides for Lanthanides and Actinides: Structures, Mechanochemistry, and Case Studies with Phosphinodiboranates. *Inorganic Chemistry* **2022**, *61*, 5440-5441.

Fetrow, T. V.; Daly, S. R. "Mechanochemical Synthesis and Structural Analysis of Trivalent Lanthanide and Uranium Diphenylphosphinodiboranates." *Dalton Transactions* **2021**, 50, 11472-11484.

Dunbar, A. C.; Wright, J. C.; Grant, D. J.; Girolami, G. S. “X-ray Crystal Structure of Thorium Tetrahydroborate, $Th(BH_4)_4$, and Computational Studies of $An(BH_4)_4$ (An = Th, U).” *Inorganic Chemistry* **2021**, *60*, 12489-12497.

Anderson, N. T.; Wright, J. C.; Girolami, G. S. “Synthesis and Characterization of Divalent Samarium and Thulium N,N-Dimethylaminodiboranates.” *Inorganic Chemistry* **2021**, *60*, 11164-11176.

Fetrow, T. V.; Grabow, J. P.; Leddy, J.; Daly, S. R. "Convenient Syntheses of Trivalent Uranium Starting Materials without Uranium Metal." *Inorganic Chemistry* **2021**, 60, 7593-7601.

Meyer, R. L.; Greer, S. M.; Blake, A. V.; Cary, S. K.; Ditter, A. S.; Daly, S. R.; Li, F.; Kozimor, S. A.; Matson, E. M.; Mocko, V.; Seidler, G. T.; Stein, B. W.; Weinstein, S. D. "Characterizing Polyoxovanadate-Alkoxide Clusters Using Vanadium K-Edge X-Ray Absorption Spectroscopy." *Chemistry – A European Journal* **2021**, *27*, 1592-1597.

Fetrow, T. V.; Bhowmick, R.; Achazi, A. J.; Blake, A. V.; Eckstrom, F. D.; Vlaisavljevich, B.; Daly, S. R. "Chelating Borohydrides for Lanthanides and Actinides: Structures, Mechanochemistry, and Case Studies with Phosphinodiboranates." *Inorganic Chemistry* **2020**, *59*, 48-61.

6. List of Book Chapters Published

Daly, S. R. "Actinide Borohydrides." In *The Heaviest Metals: Science and Technology of the Actinides and Beyond;* Hanusa, T. P. and Evans, W. J., Eds.; **2018**, John Wiley & Sons, Ltd: West Sussex, UK. pp. 319–334.

7. List of Manuscripts Submitted

Zgrabik, J. C.; Bhowmick, R.; Eckstrom, F. D.; Harrison, R. A.; Fetrow, T. V.; Blake, A. V.; Vlaisavljevich, B.; Daly, S. R. “Comparative Study of Alkyl Substituent and Metal Size on the Structures of Trivalent f-Element Phosphinodiboranates.”

Dunbar, A. C.; Gozum, J. E.; Lin, W.; Flores, V. J.; Girolami, G. S. “Synthesis and Characterization of Ether Adducts of Thorium Tetrahydroborate, $Th(BH_4)_4$, and Chemical Vapor Deposition of Thorium Boride Thin Films.”

8. List of PI and co-PI Presentations

2022 29th Rare Earth Research Conference, Quantifying the Influence of Covalent Metal-Ligand Bonding on Differing Reactivity of Trivalent Actinide and Lanthanide Phosphinodiboranates, Philadelphia, Pennsylvania. Presenter: Daly

2022 New Horizons in Molecular f-Element Chemistry, Thermochemical and Structural Comparison of f-Metal Phosphinodiboranates, Virtual. Presenter: Daly

2022 Grinnell College, The Grind with Nuclear: Mechanochemical Synthesis of Borohydride Complexes. Grinnell, Iowa. Presenter: Daly

2022 Truman State University, Mechanochemical Synthesis and Separation of f-Element Borohydride Complexes. Kirksville, Missouri. Presenter: Daly

2021 IMS Mechanochemistry Symposium, Mechanochemical Synthesis and Separation of f-Element Borohydride Complexes, Los Alamos National Lab, Los Alamos, New Mexico. Presenter: Daly

2021 Eastern Illinois University, Mechanochemical Synthesis and Separation of f-Element Borohydride Complexes, Charleston, Illinois. Presenter: Daly

2021 Pacifichem 2021, Thermochemical and Structural Comparison of f-Metal Phosphinodiboranates, Honolulu, Hawaii (virtual). Presenter: Daly

2019 Michigan State University, Ligand Scaffolds with Boron and Phosphorus: Synthetic Investigations for Metallodrug Imaging and Solvent-Free f-Element Separations, East Lansing, Michigan. Presenter: Daly

2019 Separation Science PI Contractors Meeting, Department of Energy, Toward the Selective Volatilization of f-Element Complexes using Mechanochemistry and Chelating Borohydrides, Gaithersburg, Maryland. Presenter: Girolami

9. List of Student Presentations

2022 Synthesis and Thermal Properties of f-Metal Complexes with Fluorinated β-Ketoiminate Ligands. Oral presentation. Student Presenter: Huther, Holly (UIowa)

2022 Synthesis and Thermal Behavior Properties of Lanthanide Complexes with Fluorinated Heptadentate β-Ketoiminate Ligands. Oral presentation. Student Presenter: Zgrabik, Joshua C. (UIowa)

2022 Inorganic Chemistry Gordon Research Conference, Influence of Metal Identity and Phosphorus Substituents on the Thermodynamic and Structural Properties of f-Metal Phosphinodiboranates, Newport, Rhode Island. Poster presentation. Student Presenter: Zgrabik, Joshua C. (UIowa)

2022 Inorganic Chemistry Gordon Research Seminar, Influence of Metal Identity and Phosphorus Substituents on the Thermodynamic and Structural Properties of f-Metal Phosphinodiboranates, Newport, Rhode Island. Poster presentation. Student Presenter: Zgrabik, Joshua C. (UIowa)

2021 Angular Momentum: A Virtual f-Element Symposia Series. Mechanochemical Synthesis and Exploration of f-Element Phosphinodiboranates. Oral Presentation. Student Presenter: Fetrow, T. V. (UIowa)

2021 262nd ACS National Meeting, Synthesis and thermal properties of lanthanide complexes with fluorinated heptadentate β-ketoiminate ligands, Atlanta, Georgia (virtual). Student Presenter: Zgrabik, Joshua C. (UIowa)

2019 54th ACS Midwest Regional Meeting, Homoleptic Lanthanide and Uranium Phosphinodiboranates, Ames, Iowa. Student Presenter: Fetrow, Taylor V. (UIowa)

2019 257th ACS National Meeting, Influence of Phosphorus Substituents on Homoleptic Lanthanide and Actinide Phosphinodiboranate Structures, Orlando, Florida. Poster presentation. Student Presenter: Harrison, A. Rayford (UIowa)

2019 1st American Mexican Symposium on Supramolecular Materials Design, Pushing the Boundaries of Phosphinodiboranates, Iowa City, Iowa. Oral Presentation. Student Presenter: Fetrow, Taylor V. (UIowa)

2018 Inorganic Chemistry Gordon Research Conference, Synthesis, Structures, and XAS Studies of Neutral Soft-Donor Ligands, Phosphinodiboronates, and Polyoxovanadates with Uranium and Lanthanides, Biddeford, Maine. Poster Presentation. Student Presenter: Blake, Anastasia V. (UIowa)

2018 53rd ACS Midwest Regional Meeting, Synthesis and Structural Characterization of Divalent Lanthanide and Actinide Complexes for the Solvent-Less Separation of f-Elements by Sublimation, Ames, Iowa. Student Presenter: Anderson, Nels (UIUC)

2018 53rd ACS Midwest Regional Meeting, Homoleptic Dimethylphosphinodiboranate Uranium and Lanthanide Complexes, Ames, Iowa. Student Presenter: Eckstrom, Francesca (UIowa)

2018 53rd ACS Midwest Regional Meeting, Solution Studies of Homoleptic Uranium and Lanthanide Phosphinodiboranate Complexes: Insight into Monomer/Dimer Equilibrium Dictated by Metal Size, Ames, Iowa. Student Presenter: Fetrow, Taylor V. (UIowa)

2018 UIowa Spring Undergraduate Research Festival, Homoleptic Neodymium(III) and Uranium(III) Phosphinodiboranates, Iowa City, Iowa. Poster Presentation. Student Presenter: Theiler, Zachary T. (UIowa)

2018 255th ACS National Meeting, Homoleptic Uranium and Lanthanide Phosphinodiboranate Complexes, New Orleans, Louisiana. Poster Presentation. Student Presenter: Fetrow, Taylor V. (UIowa)