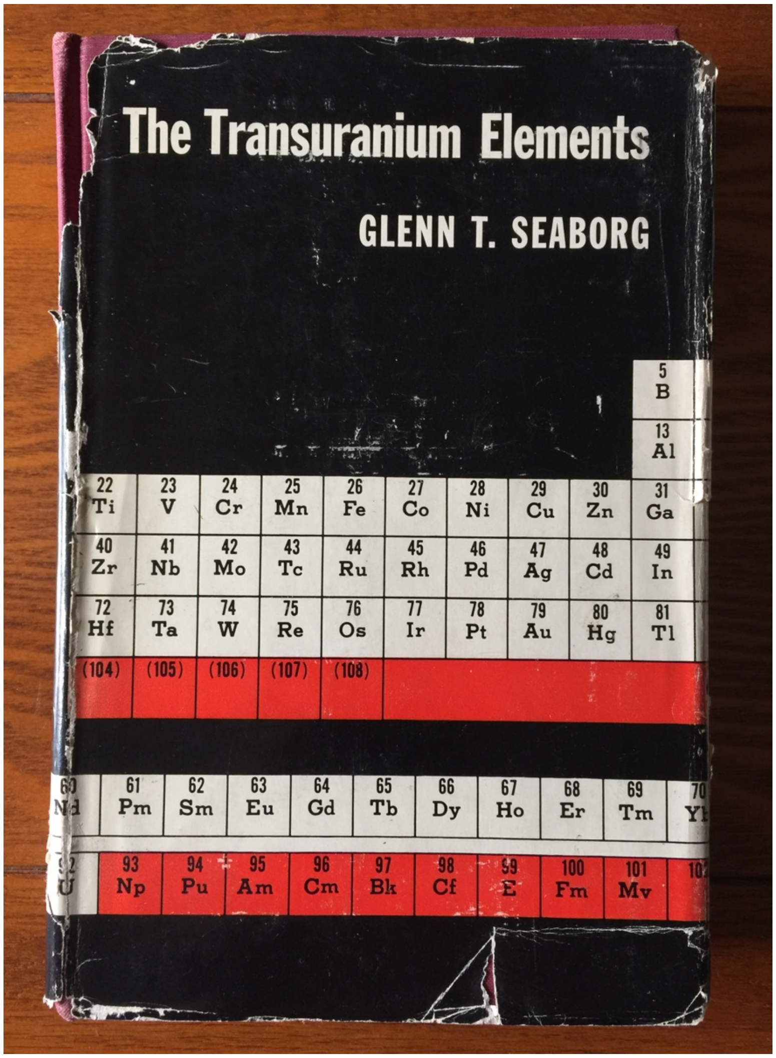
2019 Heavy Element Chemistry Principal Investigators' Meeting



Gaithersburg, MD
April 15–17, 2019

U.S. DEPARTMENT OF ENERGY | Office of Science

Office of Basic Energy Sciences (BES)
Chemical Sciences, Geosciences, and Biosciences Division

Program and Abstracts
for the

2019 Heavy Element Chemistry
Principal Investigators' Meeting

Gaithersburg Marriott
Washingtonian Center
Gaithersburg, MD
April 15–17, 2019

Chemical Sciences, Geosciences, and Biosciences Division
Office of Basic Energy Sciences
Office of Science
U.S. Department of Energy

Cover photo: Transuranium Book (Philip Wilk, 13 April 2019)

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Foreword

This abstract booklet provides a record of the tenth U.S. Department of Energy Principal Investigators' meeting in heavy element chemistry. The Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences and its predecessors have sponsored research in heavy element chemistry for over sixty years.

The objective of this meeting is to provide a fruitful environment in which researchers with common interests will present and exchange information about their activities, will build collaborations among research groups with mutually reinforcing strengths, will identify needs of the research community, and will focus on opportunities for future research directions. The agenda includes invited talks, oral presentations, and poster presentations, organized so that papers in related disciplines are loosely clustered together. With ample time for discussion and interactions, we emphasize that this is an informal meeting for exchange of information and building of collaborations; it is not a review of researchers' achievements or a forum to choose future directions.

It has been a privilege to serve as the manager of these research programs. In carrying out these tasks, I learn from the achievements and share the excitement of the research of the many sponsored scientists and students whose names appear on the papers in the following pages. I also hope that this meeting will enhance your research efforts and will nurture future collaborations and initiatives. I would like to thank all of the researchers whose dedication and innovation have advanced our research and made this meeting possible and, we hope, productive.

Philip Wilk

Agenda

2019 Heavy Element Chemistry Principal Investigators' Meeting

Gaithersburg Marriott, Washingtonian Center
Monday, April 15 - Wednesday, April 17

Meetings Notes:

The meeting fee includes breakfast and lunch provided at the meeting.

People who did not pay the registration fee will need to pay for their meals.

Sunday, April 14

	Arrival
7 -9 PM	Informal No-Host Meetup at "The Bench"
	Gaithersburg Marriott, Washingtonian Center

Monday, April 15

8:00 - 9:00	Breakfast
9:00	**Meeting Begins**

Philip Wilk
Program Manager
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Monday, April 15

8:00 - 9:00	Breakfast	
9:00	**Meeting Begins**	**Philip Wilk**
	Introduction, Agenda, Mini-Workshop Charge	
9:15	**Session 1a: Electronic structure and reactivity**	**Henry La Pierre**
9:15	Richard Wilson Heavy Element Speciation and Reactivity	
9:40	Karah Knope Harnessing Non-Bonding Interactions Towards the Isolation of Elusive An(IV) Species	
10:05	Andrew Gaunt Probing Electronic Structure and Redox Properties of Actinides through Inert Atmosphere Synthetic Chemistry	
10:20	break	
10:45	**Session 1b: Pu and trans-Pu chemistry**	**Benjamin Stein**
10:45	Rebecca Abergel Oxidizing, Recognizing, and Separating actinides, One Electron at a Time	
11:10	Jacklyn Gates Atom-at-a-time Chemistry with FIONA	
11:35	David Hobart Update on the Plutonium Handbook	
12:00	Working Lunch for Collaboration (poster room will be open)	
1:30	**Session 2: Theory**	**Wayne Lukens**
1:30	Jochen Autschbach Calculation of X-ray Absorption Spectra and Excited-State Bonding Analysis of Actinide Complexes	
1:55	Enrique Batista Theoretical Studies of Actinide-ligand Bonding Interactions: Covalency, Thermodynamics, and Spectroscopic Properties	
2:20	David Dixon The Role of ‘High’ Oxidation States in Actinide Chemistry	
2:45	Gustavo Scuseria Quantum Chemistry for Strong Correlation and Heavy Elements	
3:10	break	
3:25	**Chemical Sciences, Geosciences and Biosciences Division Update**	**Philip Wilk**
	Bruce Garrett, Division Director	
4:00	**Poster Slam**	**Philip Wilk**
	(Each poster presenter gets one minute and one slide, no questions)	
	Poster Session #1	
6:00	Dinner on your own and Collaborate (poster room will be open)	

Tuesday, April 16

8:00 - 9:00 Breakfast

9:00 Keynote Speaker

Rebecca Abergel

Marinella Mazzanti
Small Molecule Activation by Multimetallic Complexes of Uranium

break

10:15 Session 3: From Small Molecules to Hierarchical Structures

Amy Hixon

10:15 Stosh Kozimor
Aqueous Coordination Chemistry for +3 Actinides

10:40 Peter Burns
Hierarchical Arrangement of Inorganic Uranyl Compounds and Newly Discovered Uranium Minerals

11:05 Christopher Cahill
Restricted $[AnO_2]^{2+}$ speciation profiles and supramolecular assembly: a forum for probing electronic structure and bonding

11:30 Stefan Minasian
The Structure and 5f-Electron Behavior of Actinide Oxide Nanoparticles Embedded in Porous Frameworks

12:00 Working Lunch for Collaboration (poster room will be open)

1:30 Session 4: Spectroscopy to Probe Actinide Coordination and Reactivity

Anne E. V. Gorden

1:30 John Gibson
Towards Understanding Actinide Reactivity at the Molecular Level in Gas Phase

1:55 Justin Walensky
Exploring Covalency of the Actinides Using Soft Donor-Based Ligands and Metal-Ligand Multiple Bonding

2:20 Trevor Hayton
Use of ^{15}N NMR Spectroscopy to Probe 5f Covalency in a Thorium Nitride

2:45 break

3:00 Tim Steimle
High-resolution spectroscopic studies of Th and U containing molecules

3:25 Michael Neidig
Insight into Electronic Structure and Bonding in f-Element Chemistry via MCD Spectroscopy and Synthesis

3:50 Heavy Element Chemistry program and Separation Science program updates

Philip Wilk, Program Manager

4:15 break

4:30 Poster Session #2

6:00 Dinner on your own and Collaborate (poster room will be open)

Wednesday, April 17

8:00 - 9:00 Breakfast

9:00 Session 5: Molecular & Electronic Interactions — James Blakemore

9:00	Robin Rogers
	Exploring the Nature of f-Element Soft Donor Interactions Using Electronically Tunable Azolate Ionic Liquids
9:25	Ahmet Uysal
	Understanding the Role of Interfaces in Heavy Element Separations
9:50	Michael Heaven
	Electronic spectroscopy, electronic structure and ligand field theory for AnX diatomic actinides
10:15	break

10:30 Mini-Workshop

12:00 Lunch on your own / dismissal

Posters

Thomas Albrecht-Schmitt An Unexpected Plane of Covalency in Cerium and Berkelium Coordination Complexes	Florida State University
Peter Armentrout Hydration of Thorium Cations: Mechanisms and Energetics	University of Utah
Suzanne Bart Investigating the Role of Redox Chemistry in the Actinides	Purdue University
James Blakemore Uranyl Capture and Activation with Lewis Acids and Macrocyclic Hosts	University of Kansas
Corwin Booth Exploring local actinide bonding	Lawrence Berkeley National Laboratory
Kit Bowen Atomic and Molecular Anions of Uranium and Thorium studied by Negative Ion Photoelectron Spectroscopy	Johns Hopkins University
Herman Cho Spectroscopic Investigation of Electronic Structure in the Actinide Elements	Pacific Northwest National Laboratory
William Evans Exploring the Fundamental Chemistry of Actinide Metal Complexes	University of California, Irvine
Tori Forbes The peaks in your Raman spectra may be more difficult to assign than you think…	University of Iowa
Anne E. V. Gorden Tailoring Redox Active Ligands for Probing the Reactivity of Actinides	Auburn University
Amy Hixon Understanding Interactions between Uranium Polyoxometalates and Transuranic Elements	University of Notre Dame
Henry La Pierre Electron (De)localization in f-Block Complexes	Georgia Tech
Wayne Lukens Exploring f-orbital bonding with a Hubbard model	Lawrence Berkeley National Laboratory
Kirk Peterson Gas Phase Actinide Thermodynamics from Accurate Quantum Chemistry	Washington State University
Brian Powell Thermodynamics of U, Np, and Pu interactions with iron oxide and graphene oxide surfaces	Clemson University
Eric Schelter Kinetically-Driven Rare Earth Separations	University of Pennsylvania
Jenifer Shafer A Tale of Two Sulfurs	Colorado School of Mines
David Shuh Electronic Structure and Chemical Bonding in Actinide Materials	Lawrence Berkeley National Laboratory
Benjamin Stein Spectroscopic Studies of Actinide Coordination Chemistry	Los Alamos National Laboratory
Aaron Tondreau Developing Organometallic Actinide Chemistry	Los Alamos National Laboratory
Ping Yang Covalency of Actinide-Ligand Bonds and the Impact on Structural and Thermodynamic Properties	Los Alamos National Laboratory

Abstracts

Argonne National Laboratory Program in Heavy Element Chemistry and Separation Science

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Program Summary

It is the objective of our overall research program to provide a fundamental foundation to actinide chemistry within a broader context of the chemical trends that establish the periodic table. Underpinning this program is the impact of these trends as they manifest in separation science, specifically as they pertain to discovering the underlying drivers for *f*-element separations. From a fundamental standpoint, chemical separations are exquisitely sensitive to small energy differences that serve as the drivers of their performance and consequently their macroscopic behavior can be an effective bellwether of atomic- and molecular-scale metal-ion interactions.

Within this context, our efforts center on providing a basic platform upon which to describe the energy partitioning of actinide ions dissolved in solutions, both aqueous and organic, and the complementary roles of structural and electronic drivers as descriptors for the observable chemistry. Critical to these studies is our telescoping view of the energy landscape, extending from the molecular, enthalpic effects to the hierarchical structuring that present entropic contributions that may dominate observable chemistry. Defining and describing these complementary aspects of an energy landscape represent a critical component to be understood in order to advance our knowledge of actinide chemistry, separation science, and the chemical trends that provide the periodic table with its predictive impact.

Our program is divided into three subtasks, built to reflect our dual interest in actinide chemistry and separation science, (1) Heavy Element Speciation and Reactivity, (2) Speciation, Solution Structure, and Energy Partitioning in Chemical Separations, and (3) Understanding the Role of Interfaces in Heavy Element Separations. Resent advances and future directions are briefly described in the following abstracts.

1. Heavy Element Speciation and Reactivity

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Collaborators: Matthieu Autillo, Shanna Estes, Gengbang Jin, Ahmet Uysal, Mark Antonio, Stephen Southworth, Gilles Doumi, Argonne National Laboratory. John K. Gibson, Lawrence Berkeley National Laboratory. Valerie Vallet, Florent Real, CNRS, University of Lille, France, David A. Dixon, University of Alabama.

Overall research goals: This research program is aimed at understanding the chemistry, reactivity and speciation of actinide ions and molecules. The goals of this research program are to understand the fundamental properties of actinide f-electrons in terms of atomic and longer range interactions; their influence on the structure and reactivity of actinide complexes, and the interactions and reactivities of actinide molecules in solution beyond their first coordination sphere. This program uses a multifaceted approach combining chemical synthesis, structural characterization in solids and liquids, along with spectroscopic and computational studies to realize its goals.

Recent Progress: Our efforts have focused on isolating periodic series of inorganic actinide molecules. By exploiting the periodic properties of the early actinide ions, particularly the systematic filling of the 5f electronic shell, and coupling these trends with various ligand chemistries, we aimed to understand the influences that the f-electrons have on both the structure and reactivity of these molecules. We have exploited the entire series of the early actinide elements from Th to Cm, focusing on periodic series of the tetravalent and hexavalent actinides. Ligands of interest have spanned the halogens and nitrates, thiocyanate, and hydroxide. These ligand sets span trends in both electronic structure and complex formation thermodynamics.

Exploiting the periodic series hexavalent actinides, we have studied a comprehensive system of halogen complexes with the series U(VI), Np(VI) and Pu(VI). These synthetic and structural studies coupled with vibrational spectroscopy (FT-IR and Raman) have revealed systematic trends in the actinide oxygen bonding, trends that are inspiring future work in understanding the underlying electronic structure. These synthetic campaigns have been extended to include an isostructural series of An(VI) nitrate complexes, including a series of hydroxide bridge dimers as shown in Figure 1, and An(VI) hydroxide complexes isolated from alkaline solution. We have used these series of actinide molecules as model systems for computational studies with our collaborators to understand the systematics of the role of the 5f electrons across the early actinide series.

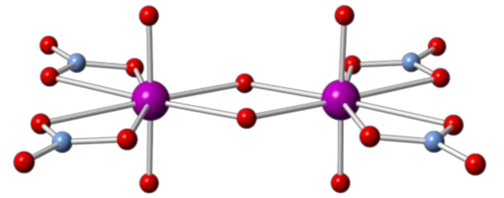

Figure 1. Representative structure of the isolated actinide hydroxide dimers for U(VI), Np(VI), and Pu(VI). $(Me_4N)_2AnO_2(OH)_2(NO_3)_4$.

While the systems mentioned have been primarily focused on the actinide metal center and the actinide-ligand bond, our earlier work in the thorium nitrate system highlighted the correlation of the hydration state and structure of the molecular complex with the hydration enthalpy of the counter-cation. Similar results have been demonstrated in the An(III) and Ln(III) thiocyanate systems where the structure of the synthesized molecule was largely dependent on both the counter-cation chemistry as well as the solvent the synthesis was conducted in. Such outer-sphere chemical interactions were also demonstrated to influence the redox stability of the metal center highlighting the significant thermodynamic influence of longer range chemical forces often overlooked. Inspired by this we have explored the An(IV) nitrate series extending these synthetic and structural studies to U(IV), Np(IV), and Pu(IV).

These synthetic and structural studies lay the foundation for studying the structure and speciation of these molecules in solutions. We have correlated the thermodynamic stability constants in the thorium nitrate system with its structure using the solid state complexes to guide the identification of the solution speciation, and these experiments are being extended to interrogate both longer-range interactions in solutions as well as correlations of metal complexes in non-aqueous solvents.

Science objectives for 2019-2021:

- Extend the synthesis of An(VI) and An(VII) complexes in alkaline solution including extreme conditions of alkalinity to investigate the chemistry of the high-valent oxidation states of the transuranium elements.
- Study, and correlate the solution speciation of actinide complexes in non-aqueous solvents using high-energy X-ray scattering techniques.
- Study the effect of longer-range chemical interactions on the structure and reactivity of actinide complexes, nitrates and thiocyanates in the solid state; investigating how these interactions drive speciation in solution and the solid state.
- Correlate these studies with other ongoing efforts in separations sciences and our understanding of the energy partitioning that drives separations processes.

2. Speciation, Solution Structure, and Energy Partitioning in Chemical Separations

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Collaborators: Renato Chiarizia, Mrinal Bera,§ Thomas Demars,§ Shanna Estes,§ Geng Bang Jin, Sang Soo Lee, CSE; Wei Jiang, Mathematics and Chemistry Computer Sciences; ANL

Marek Piechowicz,¶ Stuart Rowan, University of Chicago; Tori Forbes, A.W. Knight,¶ University of Iowa

Moritz Schmidt, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany
Valérie Vallet and Florent Réal, CNRS, University of Lille, France; Ryuhei Motokawa, Japan Atomic Energy Agency

§ Postdoctoral Fellows; ¶ Science Graduate Student Research (SCGSR) Program Awardee

Overall research goals: This program primarily focuses on quantifying solute and solvent speciation at lengthscales that span the atomic to the bulk, seeking to relate structural correlations in solution with competing equilibria and their associated free energies. It is our objective to probe the myriad influences on fluid architectures and their roles in ion phase-transfer phenomena of relevance to the thermodynamics of metal-ion partitioning in terms of selectivity, capacity, and phase stability. Our central paradigm is that the structural and dynamical aspects of separation science extend far beyond the realm of metal-extractant coordination chemistry. Namely, across the telescoping scales typical of solute aggregation and emergent solution behaviors, we seek to understand partitioning of the energy landscape (enthalpic vs entropic) underpinning and driving chemical separations of import to both ongoing and potential actinide- and lanthanide-separations processes.

Significant achievements during 2017-2019:

Unraveling telescoping (multiscale) structures in oil phases from liquid-liquid extraction (LLE). We are casting LLE as soft matter science of complex fluids in order to understand and predict actinide separations using concepts and methods from soft matter science. This is a new paradigm for LLE of actinides. It allows us to address assumptions and unexplained issues from a century of LLE tradition, including 70 years of PUREX (Plutonium Uranium Reduction EXtraction). The current understanding of LLE from inorganic coordination chemistry alone (structure at left in Figure 1 is a TBP solvate of a $M(NO_3)_4$ complex) is insufficient to explain myriad complex physical/extractive properties. Our combined synchrotron radiation research and LLE experimentation reveals that all length-scales (micro-to-meso-to-macroscopic) and all energy-scales (from weak intermolecular

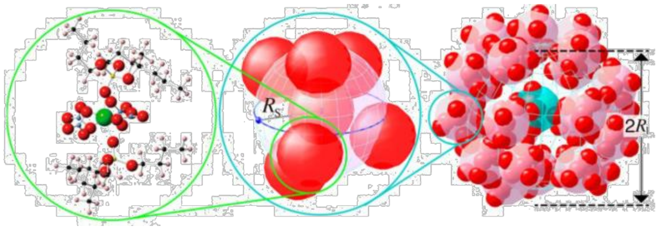

Figure 1. A telescoping, multimodal approach has been used to reveal multi-lengthscale structuring in the oil phase of a solvent-extraction process, in which M(IV)-loaded organic phases show hierarchical aggregation built from coordination complexes (left) that self-assemble as primary clusters (middle) that further organize into super-

forces to strong interatomic bonding) are relevant to oil phase behaviors. This newfound understanding of scalar hierarchies (Figure 1) enables innovations vis-à-vis selectivity, efficiency, phase stability, and informs development of advanced, high performance LLE systems.

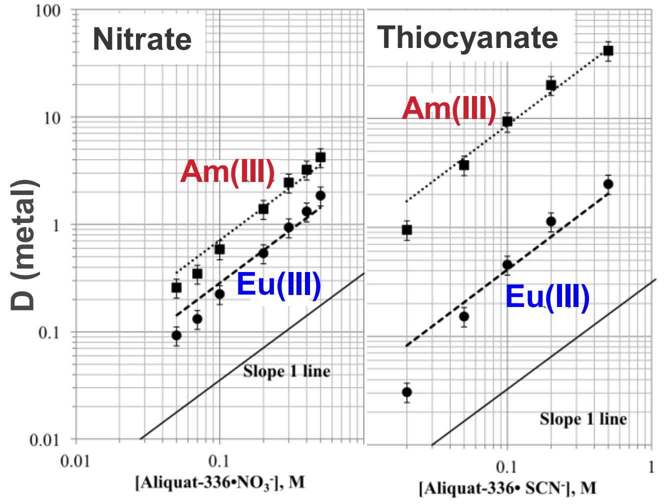

Figure 2. Extraction dependency plots for distribution ratios (D) versus concentrations of the extractant, Aliquat-336 as the nitrate (left) or thiocyanate (right). Data reveal an increased selectivity for Am(III) in the presence of thiocyanate over that for nitrate media. Results are linked to average extract-aggregation numbers, shown to be

Linking solution structuring and solute aggregation with LLE selectivity. The underlying mechanism(s) driving enhanced selectivity of actinides over lanthanides, sometimes observed in solvent-extraction processes, has remained unclear. The result of very small energy differences (~kT), this enhancement is generally attributed to soft-donor interactions that strengthen 5*f*- over 4*f*-extractant bond strengths, often discussed in conjunction with changes in inner- vs outer-sphere complexation. We have begun a study to probe the complementary roles of enthalpic, localized selectivity drivers such as bonding strengths, with entropic drivers arising from longer-range solute and solvent ordering. The results of our initial studies (Figure 2) reveal the enhanced selectivity in thiocyanate over nitrate media is directly associated with a difference in the average number of extractant molecules in organic-phase aggregates. The solution results are complemented by solid-state structures of lanthanide- and actinide- thiocyanate complexes, which indicate little difference in bonding energies between solvent and thiocyanate for inner-sphere coordination.

Science objectives for 2017-2019:

- Use our multimodal, telescopic experimental approach, in conjunction theory, to probe the energy landscape of LLE, with the specific goal of decoupling enthapic from entropic contributions to the free-energy drivers for the chemical separation metrics of selectivity and capacity.
- Employ new experimental advances for probing temporal correlations over length scales relevant to reverse-micelle structures to uncover the role of dynamics to nanoscale to mesoscale mechanistic phenomena that impact liquid separations.

3. Understanding the Role of Interfaces in Heavy Element Separations

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Collaborators: Kaitlin Lovering, Srikanth Nayak, William Rock, Chemical Sciences & Engineering Division, Argonne National Laboratory

Aurora E. Clark, Department of Chemistry and the Material Science and Engineering Program, Washington State University

Overall research goals: Our efforts are mainly focused on developing a molecular-scale understanding of interfacial processes of heavy elements, specifically as they pertain to separations sciences. Interfaces play a crucial role in chemical separations, as the selective adsorption and transfer of ions happen at phase boundaries; and a predictive understanding of interfacial phenomena in heavy element separations require a molecular-scale description of all these factors under relevant, in situ conditions. We address these needs by combining state-of-the-art interfacial X-ray scattering and vibrational spectroscopy tools, integrated with molecular dynamics simulations.

Significant achievements during 2017-2019:

Separation of target ion species from a mixture of ions in an aqueous solution requires target ions' favorable access to the interface. Interestingly, there has been unrealized contradictions between some successful solvent extraction (SX) processes and the widely accepted theories and models in surface science community on this interpretation. For instance, extraction of minute amount of platinum group metals (PGMs) from highly concentrated chloride solutions, in the form of anionic complexes, is one of the most common SX process used in their refinery. However, according to the most recent theories of competitive adsorption of ions with different sizes and valencies, the aqueous side of the interface should be occupied with Cl^- ions, making these process very inefficient.

Our efforts to resolve this apparent contradiction started with one of the simplest model systems, an atomically flat amine functionalized surface in contact with an aqueous solution of $PtCl_6^{2-}$ in highly concentrated Cl^-. Interface specific x-ray reflectivity (XR) experiments showed that chlorometalate ions, indeed, adsorb at the interface favorably even at four order of magnitude less bulk concentration compared to Cl^-, directly demonstrating that both mean field theories and empirical Hofmeister series fail to describe the molecular scale processes in this system.

A monolayer of extractants at the air/water interface was used to further investigate this peculiar adsorption behavior. By using a combination synchrotron x-ray and sum frequency generation (SFG) spectroscopy experiments we showed that $PtCl_6^{2-}$ ions adsorb in a two-step process as a function of their bulk concentration. At very low bulk concentrations, chlorometalate ions prefer to adsorb with full hydration shell, in the diffuse layer, without directly interacting with extractants. However, as the bulk (hence the diffuse layer) concentration of $PtCl_6^{2-}$ increases, ion-ion interactions start to become significant and help chlorometalate ions to adsorb in the Stern layer, directly interacting with the extractants.

The peculiar adsorption behavior described here is also connected to a unique and complex interfacial water structure that can be clearly observed in SFG experiments. However a comprehensive explanation required a novel MD simulation sub-ensemble analysis, which was done in collaboration with Aurora E. Clark (Washington State University). As the figure below depicts, the water molecules in different colored regions exhibit different orientational structures and/or hydrogen bonding strengths. The integration of various experimental probes and computational methods provide a great accuracy in the model we developed to explain the observations.

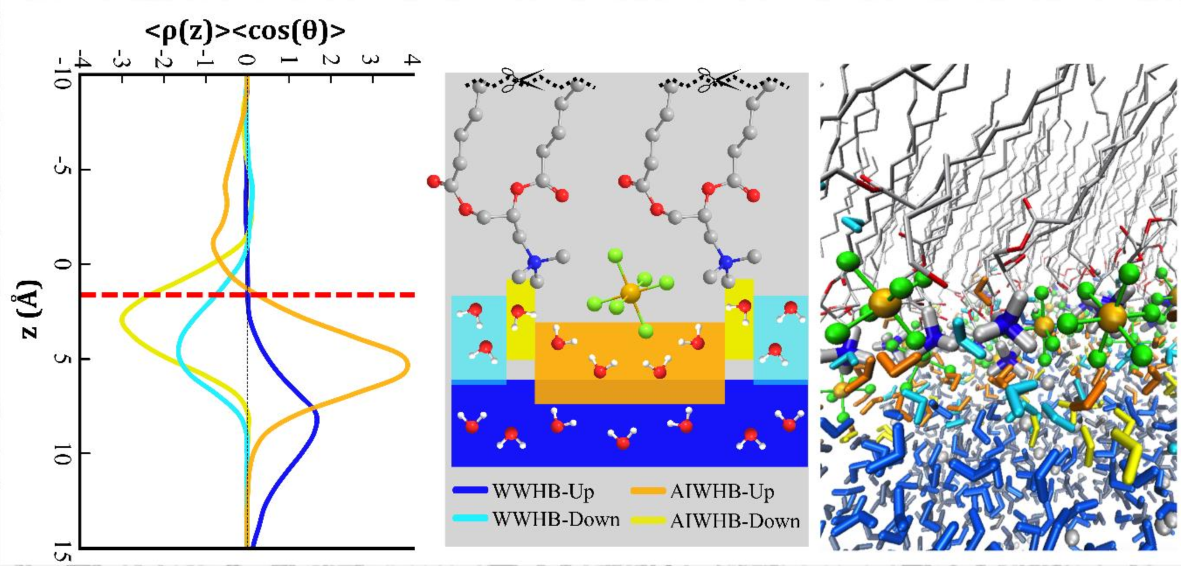

Figure 1: A unique interfacial water structure observed by SFG spectroscopy is explained by MD simulations and sub-ensemble analysis. Four different water sub-ensembles are identified, and labeled with different colors according to their interactions with the metalate anion and the extractant headgroups. The left panel shows average number density times average orientation of water molecules in each sub-ensemble, visualized in the middle panel. The right panel is an actual snapshot from MD simulations.

Science objectives for 2019-2021:

- Direct investigations of the water-hydrophobic interface under process conditions, especially in the context of interfacial water structure and the water transfer into the organic phase in SX.
- Understanding the periodic trends in interfacial adsorption of heavy elements and their complexes, in the general picture of specific ion effects. Especially, designing competitive adsorption studies in the presence of highly concentrated backgrounds, and understanding the effects of background ions, such as nitrate and thiocyanate, to the selectivity among lanthanide ions.
- Translating the established experience into interfacial actinide adsorption studies and establishing a comparisons between lanthanides and actinides.

Heavy Element Chemistry and Separation Science Subtask 1. Publications supported by this project 2017-2019

M. Autillo, R. E. Wilson. *Molecular Hydroxo-bridged dimers of U(VI), Np(VI), and Pu(VI):* $[Me_4N]_2(AnO_2)_2(OH)_2(NO_3)_4$. *Inorganic Chemistry.* DOI: 10.1021/acs.inorgchem.8603304. (2019)

S. Estes, B. Qiao, G. B. Jin. *Ion association with tetra-n-alkyammonium cations stabilizes higher-oxidation-state neptunium dioxo-cations*. *Nature Communications*. DOI: 10.1038/s41467-018-07982-5 (2019)

D. D. Schnaars, R.E. Wilson, *Synthesis, structure and vibrational properties of* $[Ph_4P]_2NpO_2Cl_4$ *and* $[Ph_4P]_2PuO_2Cl_4$ *complexes.* *Inorganic Chemistry*. DOI: 10.1021/acs.inorgchem.7b02382. (2018).

R. E. Wilson, S. M. DeSio, Valerie Vallet. *Protactinium and the intersection of transition metal and actinide chemistry. Nature Communications* DOI: 10.1038/s41467-018-02972-z (2018)

B. Qiao, S. Skanthakumar, L. Soderholm. *Comparative CHARMM and AMOEBA Simulations of Lanthanide Hydration Energetics and Experimental Aqueous-Solution Structures.* *Journal of Chemical Theory and Computation*. DOI: 10.1021/acs/jctc.7b01018 (2018)

M. Autillo, R. E. Wilson, *Phase Transitions in Tetramethylammonium Hexachlorometalate Compounds,* $(TMA)_2MCl_6$ *(M = U, Np, Pt, Sn, Hf, Zr).* *European Journal of Inorganic Chemistry*. DOI: 10.1002/ejic.201700764.

S. Skanthakumar, G. B. Jin, J. Lin, V. Vallet, L. Soderholm. *Linking solution structures and energetics: Thorium nitrate complexes*. Journal of Physical Chemistry, B. DOI: 10.1021/acs.jpcb.7b06567 (2017)

G. B. Jin, J. Lin, S. Estes, S. Skanthakumar, L. Soderholm. *Influence of counter-cation hydration enthalpies on the formation of molecular complexes: A thorium nitrate example.* *Journal of the American Chemical Society*. DOI: 10.1021/jacs.7b09363. (2017).

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Heavy Element Chemistry and Separation Science Subtask 2. Publications supported by this project 2017-2019

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Antonio, M. R.; Bera, M. K., pH-Dependent Interactions between Keggin Heteropolyanions in Dilute Solutions. *Eur. J. Inorg. Chem.* **2019,** *2019* (3-4), 367-373.

Piechowicz, M.; Chiarizia, R.; Soderholm, L., Insight into selectivity: uptake studies of radionuclides $^{90}S^{r2+}$, $^{137}Cs^{+}$, and $^{233}UO_2^{2+}$ with bis-amidoxime polymers. *Dalton Trans.* **2018,** *47* (15), 5348-5358.

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Probing Electronic Structure and Redox Properties of Actinides through Inert Atmosphere Synthetic Chemistry

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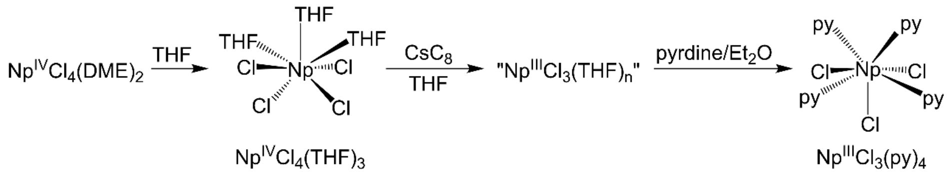
Postdoctoral/Student Active Collaborators: C. A. P. Goodwin, J. Su (LANL), J. Brewster (UT-Austin), S. Staun (UCSB), S. A. Pattenaude (Purdue).

Overall research goals: To advance knowledge and control of transuranium electronic structure, bonding and redox behavior. The approach is to utilize rare inert atmosphere synthetic chemistry capability with transuranium isotopes to selectively target molecules that will yield novel insight into those above properties. The task spans development of non-aqueous precursors, new synthetic methodology, generation of Np and Pu molecules with metal-ligand multiple-bonding character, homologous series of organometallic complexes from Th to Cf to elucidate reactivity and electronic structure trends, and pursuit of unusual oxidation states in molecular form. The research takes advantage of collaborations with other DOE Heavy Element Chemistry funded groups and external groups to capture a wide range of elements and ligand/chelator types that can be studied in a systematic manner from lanthanides (Ln) to uranium to the transuranium elements. Below, two key areas are highlighted, expanding in some detail on recent progress.

Recent Progress:

1. Access routes into Np(III) and Pu(III) non-aqueous synthetic chemistry. In uranium chemistry, a common entry point into U(III) molecular synthesis is via oxidation of uranium metal with reagents such as iodine in coordinating organic solvents. Analogous starting materials can be prepared for Np(III) and Pu(III) using neptunium and plutonium metal. However, these metals are either scarce (especially for neptunium) and/or difficult to obtain outside of the few institutions that produce metallic forms. In addition, the metals are highly susceptible to oxidation, meaning that storage requires long unbroken periods of rigorous exclusion of air and moisture. Conversely, aqueous solutions (and oxides that can be readily dissolved into aqueous form) are more widely available for Np and Pu. Therefore, if well-defined non-aqueous, organic-soluble, precursors can be reproducibly synthesized in reasonable yields from acidic stock solutions that are 'dried-out', the number of research groups and institutions able to conduct synthetic Np and Pu chemistry can potentially be greatly expanded. The field of uranium non-aqueous chemistry has flourished this century, and for the actinide community to capitalize on the wealth of new uranium electronic structure, bonding and reactivity information (with the aim of uncovering trends and changes across the 5f series), the ability to perform similar chemistry with a comparable 'tool-box' for Np and Pu would enable this goal.



Scheme 1. Reduction of an Np(IV) starting material to an Np(III) trichloride THF-adduct, followed by addition of pyridine to 'trap' the '$NpCl_3$' in crystallisable form for structural determination.

Following on from our development of $NpCl_4(DME)_2$ and $PuCl_4(DME)_2$ (DME = 1,2-dimethoxyethane) as new non-aqueous starting materials in the +4 oxidation state, we have now demonstrated (in collaboration with Bart) that $NpCl_4(DME)_2$ can be reduced by CsC_8 to a putative $NpCl_3(THF)x$ complex, as a yellow microcrystalline solid in moderate yield. Further evidence for reduction to Np(III) was provided by addition of pyridine (py) and single-crystal X-ray diffraction structural confirmation of the resultant $NpCl_3(py)_4$ molecule (scheme 1).

Both the THF and pyridine adducts should prove useful in the future syntheses of a wide range of air- and moisture-sensitive Np(III) molecules. Very recently, this approach has been extended to show that the more common KC_8 reductant can also be employed to generate the $NpCl_3(THF)x$ complex, and preliminary reactions confirm that organometallic Np(III) molecules can be synthesized using this THF-adduct as a starting material. The analogous reduction of $PuCl_4(DME)_2$ to Pu(III) also proceeds in a facile manner. The process of optimizing reaction conditions and exploring further reactivity is underway, but as with Np, preliminary usage suggests that organometallic Pu(III) complexes can be prepared from the presumed '$PuCl_3$-THF' complex.

2. Identification and characterization of the formal +2 oxidation state of Np and Pu in molecular form and uncovering trends in An(III) organometallic complexes. Over the last several years, a range of ligand scaffolds have been shown to support formal Ln^{2+}, Th^{2+} and U^{2+} complexes, including the use of several cyclopentadienyl (Cp) rings by our collaborator (Evans). In 2017, we reported that reduction of $Pu^{III}Cp''_3$ [$Cp'' = C_5H_3(SiMe_3)_2$] (itself the first reported full single-crystal structural determination of a Pu–C bond) with KC_8 in the presence of 2.2.2.-cryptand (crypt) generates the Pu^{2+}-containing salt [K(crypt)][$Pu^{II}Cp''_3$]. The molecular compound was structurally verified, spectroscopically characterized, and analyzed by Density Functional Theory, The results indicated that plutonium represents an intriguing 'crossover' case with a small energy difference between $5f^n6d^1$ or $5f^{n+1}d^0$ electronic configuration (with the conclusion of a predominantly $5f^66d^0$ ground state with some $5f^56d^1$ configuration mixing). This work has now been extended to neptunium, with synthesis, structural, spectroscopic and computational characterization of [K(crypt)][$Np^{II}Cp''_3$], the first confirmation of a discrete molecule containing Np in the formal +2 oxidation state (Figure 1). Results suggest the $5f^46d^1$ configuration is favored as the ground state in the case of the Np^{2+} complex.

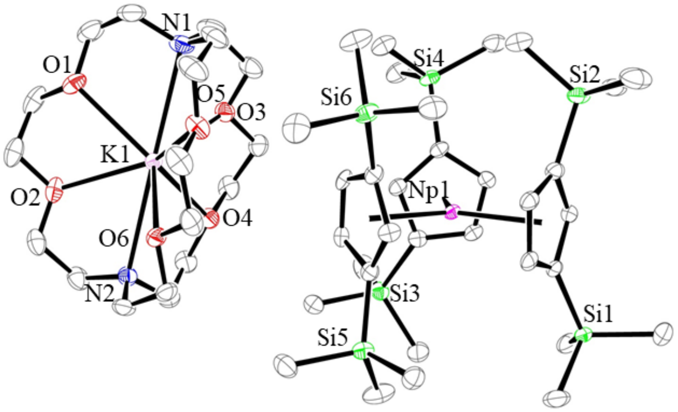


Figure 1. Solid-state structure of the anion in [K(crypt)][$Np^{II}Cp''_3$], containing Np in the formal +2 oxidation state.

A series of An(III) molecules with ‘Cp-type’ ligands are also being prepared and characterized as part of an effort to decipher reactivity and bonding trends across the series. A plutonium complex of the form $Pu(Cp^{tet})_3$ ($Cp^{tet} = C_5HMe_4^{1-}$) has been generated and characterized, whereas a similar reaction with californium(III) led to isolation and structural determination of a different ‘bis-Cp’ product form.

In addition to the highlighted topic areas above, progress has also been realized towards rare examples of transuranium metal-ligand multiple bonds, building upon earlier success in generating a Np(V) bis(imido) species in collaboration with Boncella. Collaboration with Liddle led to an Np(III) complex with ‘Np-CH’ bonding interactions as an intermediate towards Np=C multiply bonded interactions. Collaboration with Hayton employing silyl amide scaffolds facilitated the targeting of imido moieties with Np with successful generation of intermediates. In collaboration with Sessler, neptunyl and Np(IV) complexes have been synthesized with expanded porphyrin rings uncovering interesting redox chemistry and in-plane coordination of a transuranium tetravalent cation into the ring cavity, ripe for electronic structure probing.

Future Plans:

- Capitalize upon collaborative progress towards metal-ligand multiple bonds in Np and Pu molecules by synthesizing examples of carbenes, nitridos, and imidos in order to assess relative contributions of 5f and 6d orbitals to the bonding, and establish covalency trends as the 5f series is traversed from uranium into the transuranic realm.
- Employ heteroatom substituted five-membered analogs of cyclopentadienyl rings in order to assess how changes in electronic structure imparted by the heteroatom effect electronic structure and redox properties and the ability to access unusually low oxidation states.
- Compare and contrast bonding in series of trivalent organometallic complexes spanning Ln, U, Np, and Am in order to assess both the effects of cation size and ability of the 5f and 6d orbitals to engage in covalent interactions with ligand-based orbitals.

Recent Publications Resulting from this Project

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Actinide Electronic Structure, Bonding, and Coordination Chemistry

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Active Collaborators: Rebecca J. Abergel (LBNL), Thomas Albrecht-Schmitt (FSU), Jochen Autschbach (University at Buffalo), Suzanne C. Bart (Purdue University), Enrique R. Batista (LANL), John Berry (University of Wisconsin), James M. Boncella (LANL), Herman C. Choi (PNNL); William Evans (UCI), Andrew J. Gaunt (LANL), Nik Kaltsoyannis (University of College London), Karah Knope (Georgetown), Andrew Keridge (Lankaster Univeristy), Ellen M. Matson (Rochester), Stefan Minasian (LBNL), Michael Neidig (Rochester), Jeff J. Rack (University of New Mexico), Eric Schelter (University of Pennsylvania), Gerald T. Seidler (University of Washington), David K. Shuh (LBNL); Timothy H. Warren (Georgetown), Ping Yang (LANL).

Overall Research Goals: The central goal of the Los Alamos Heavy Element Chemistry program is to advance understanding of unexpected covalency on the chemistry and physics of actinide containing compounds. Objectives include advancing fundamental understanding of actinide coordination chemistry and assessing roles of 5*f*- vs. 6*d*-orbitals in bonding for actinide ions in a variety of oxidation states. This includes evaluating electronic structure and reactivity changes across the actinide series and as a function of 3*d*, 4*d*, 5*d*, 4*f*/5*d*, and 5*f*/6*d*-orbitals.

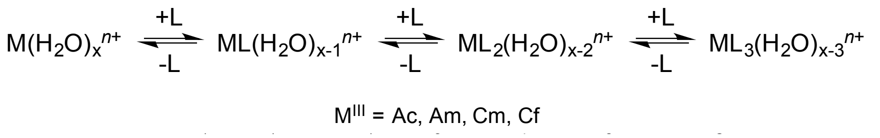
Recent Progress:

ACS Central Science journal cover that highlights Kozimor, Stein, Batista, et al. *ACS Central Sci* **2017**, *3*, 176.

1. Actinide +3 Coordination Chemistry: Actinides in the +3 oxidation state occupy central roles in many areas that are important for our quality of life. These range from developing targeted alpha therapy in treating cancer to processing spent nuclear fuel. Hence, there is need to advance fundamental understanding of +3 actinide coordination chemistry. While numerous efforts have advanced An^{III} chemistry, two main technical challenges have impeded the general scientific advancements. These include (1) obtaining sufficient quantities of highly radioactive actinides for study, and (2) safely handling the highly-radioactive actinide isotopes. Since the last contractors meeting, we made substantial progress in overcoming these two obstacles and commenced efforts to advance understanding of how coordination chemistry varies as a function of actinide identity across the 5*f*-element series. These efforts included characterizing the coordination chemistry of a broad range of inorganic and organic ligands with some of the most difficult to access (and handle) actinide(III) isotopes, including ^{227}Ac, ^{243}Am, ^{248}Cm, and ^{249}Cf (***Scheme 1***). The results generated hard data that are essential for advancing our ability to control and predict actinide coordination chemistry.

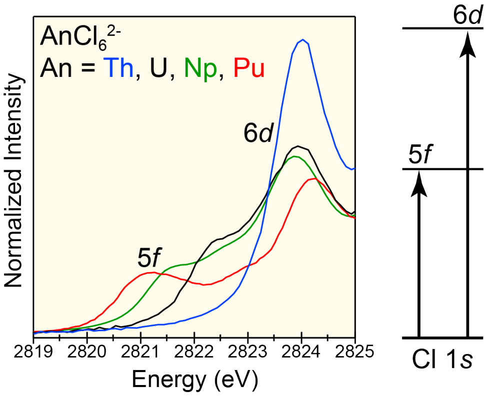
The coordination chemistry of An^{III} cations has been interrogated with a series of ligands that were selected based on their relevance towards chemical processing and environmental/biological complexation. These results include the first measurement of an Ac–ligand bond distance ever. We also contributed the characterization of arguably the most fundamentally important actinium coordination complex, namely the actinium aquo ion. These results were accompanied by characterization of other fundamental An–ligand interactions, many of which were characterized for the first time. This list includes the ***An–Cl*** interaction for An = Ac and the ***An–NO₃*** interaction for An = Ac and Cm.

Scheme 1



2. Electronic Structure and Bonding: The An^{III} aqueous studies described above were supported by our expertise and previous campaigns focused on understanding actinide electronic structure and bonding. We have taken a deep dive over the last few years in characterizing covalency in bonding for the actinide–halide interactions. This includes quantifying 5*f*- and 6*d*-covalent bonding in An–Cl bonds for $AnCl_6^{x-}$ (An = Th, Un, Np, Pu, Am), $LnCl_6^{x-}$ (x = 2 for Ln = Ce^{IV}; x = 3 for Ce^{III}, Nd, Sm, Eu, Gd), and MCl_6^{x-} (M = Ti, Zr, Hf, Nb, Mo, Tc) compounds. Highlights since the last contractors meeting include advancing understanding of actinide covalency, which represents one of the most important and long-standing fundamental areas associated with actinide science. However, actinide covalency has historically been difficult to experimentally measure and computationally model. As such, its existence has been a highly debated since Seaborg first proposed (while studying americium chlorides) that 5*f*-orbitals participate in covalent bonding. We recently contributed the first unambiguous confirmation of Seaborg's original claim for Np, Pu, and Am. The efforts included the first reported synthesis and structural characterization of $AmCl_6^{3-}$. This $AmCl_6^{3-}$ is the first molecular octahedral compound structurally characterized for americium. Its high symmetry provided an ideal test bead for evaluating electronic structure by a wide range of physical methods. We reported (1) UV-Vis-NIR absorbance spectroscopy, (2) Am M-edge XAS, the second such measurement ever reported for americium, and (3) ligand K-edge X-ray absorption spectroscopy (XAS). The latter represented the first ligand K-edge XAS measurement ever for a trans-uranium element. Moreover, it enabled us to measure covalency in the americium–ligand covalent bond for the first time. The spectral interpretations were guided by state-of-the-art DFT calculations focused on providing accurate description of Am–Cl bonding. The experimental data was accompanied by with high-powered DFT calculations that incorporated relativistic effects and spin-orbit coupling. Both theory and experiment suggested that the Am^{III} 5*f*- and 6*d*-orbitals participate in covalent bonding with Cl-3*p* orbitals. To place the study in historical context, we compared the data with the isoelectronic lanthanide analogue, $EuCl_6^{3-}$. The comparison showed the Am 5*f*-orbitals contribute to a larger extent in covalent bonding than the analogous Eu 4*f*-orbitals and was consistent with Seaborg's original 1954 proposition.

Complementary to the $AmCl_6^{3-}$ study was a parallel effort to characterize the electronic structure and bonding of plutonium and the other early actinides (Th, U, Np). This study was similar to that for $AmCl_6^{3-}$ in that it also focused on quantitatively characterizing actinide covalency. It differs in that it focused on actinides in the +4 oxidation state. The results revealed that the 6*d*-orbitals participated in covalent bonding to a larger extent than the 5*f*-orbitals. Additionally, 5*f*-participation in covalent bonding was largest for Pu, intermediate for Np and U, and lowest for Th. The results have been presented in the context of an energy-degeneracy driven covalency concept, which provides understanding of roles that 5*f*- and 6*d*-orbitals play in chemical bonding.



Chlorine K-edge XANES spectra of actinide hexachlorides showing greater involvement of 6d orbitals in covalent bonding.

Future plans:

Future goals for this project are to continue efforts in advancing understanding of actinide electronic structure, covalent bonding, and reactivity. Particular effort will be placed on evaluating transuranic elements. By combining our capabilities in actinide synthesis with expertise in actinide photoluminescence, magnetic resonance, synchrotron-based spectroscopies, and actinide theory, we will organize a multidisciplinary effort to better define the concepts of ***energy driven covalency*** and ***unexpected covalency*** in actinide-ligand bonds. We anticipate that the covalency studies will help define how orbital mixing changes across the light actinide series from Ac to Cf. Moreover, the work will help to frame the degree of covalency in light actinide complexes within the context of the rest of the periodic table.

Relevant Publications:

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2. Ferrier, M. G.; Batista, E. R.; Berg, J. M.; Birnbaum, E. R.; Cross, J. N.; Engle, J. W.; La Pierre, H. S.; Kozimor, S. A.; Lezama Pacheco, J. S.; Stein, B. W.; Stieber, S. C. E.; Wilson, J. J. "Spectroscopic and computational investigation of actinium coordination chemistry" *Nature Commun.* **2016**, *7*, 12312. DOI: 10.1038/ncomms12312

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Theoretical Studies of Actinide-ligand Bonding Interactions: Covalency, Thermodynamic and Spectroscopic Properties

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Overall research goals: The ovearching goal of our program is in studing the nature of chemical bonds between actinide elements and their ligands in a variety of coordination environments. In this subtask we focus on theoretical studies of actinide-ligand bonding across the series as a functional of oxidation state and identity of the ligands using quantum chemistry methodologies. The computational studies are carried out in close cooperation with experimental probes of the electronic structure of the synthesized compounds, in the form of a variety of spectroscopic techniques and thermodynamic measurements. Together we aim at unraveling the chemical signatures of actinide-ligand bonds.

Recent Progress: Several advances on actinide-ligand bonding interactions have been made using closely integrated theoretical and spectroscopic techniques that has also lead to the sharpening of our computational approaches. This has allowed us to tackle more challenging systems than in the past and reach better agreement between experiment and theory. Herein we highlighted a few examples on spectroscopy and thermodynamics as a function of covalency, metal identity and oxidation states. Complete details can be founded in the publications section.

1. Formal Ln^{II} ions; XANES spectroscopy and DFT calculations.[17] Experimental advances by the Evans group (UC Irvine) in rare-earth metal reduction chemistry unearthed a series of formally +2 rare-earth metal complexes. In order to decifer wether the extra electron is actually localized in the metal, rendering it a Ln^{II}, or in the ligand, yielding a $Ln^{III}L^-$ our team, measured X-ray absorption near edge spectroscopy (XANES), calculated ground-state electronic structure and transition dipole momentum to understand the correlation between oxidation state and XANES spectra. Our results suggest that the Ln ions are with $4f^n5d^1$ configuration, not $4f^{n+1}5d^0$. In these $4f^n5d^1$ complexes, the C_{3h}-symmetric ligand environment provides a highly shielded 5d-orbital of a' symmetry that made the $4f^n 5d^1$ electronic configurations lower in energy than the more typical $4f^{n+1}5d^0$ configuration.

2. Identification of Np^{II}.[5] In a similar but not obvious extension of the work described on item 1 above, Gaunt and coworkers synthesized the long sought a new formal oxidation state for neptunium, namely, Np^{2+} in a crystallographically characterizable molecular complex in $[K(crypt)][Np^{II}Cp''_3]$ [crypt = 2.2.2-cryptand, $Cp'' = C_5H_3(SiMe_3)_2$]. Similarly to the LnII compounds, whereas the formal oxidation state is clear the actual metal oxidation state is not. Our relativistic density functional theory calculations identify the Np center in this complex to be, indeed, a +2 ion. The further identified the Np^{2+} electronic state as $5f^46d^1$ in analogy with the early actinides. Np, therefore, represents a transition from $5f^n6d^1$ configuration to the later actinides +2 that "prefer" the $5f^{n+1}6d^0$ electronic state.

3. Covalency in $(\mathrm{Am^{III}Cl_6})^{3-}$.[14] On a similar vain as the studies described above, we have delved into the interaction between the $\mathrm{Am^{III}}$ and Cl ligands. We were attracted to this study for two reasons. First, moving right on the actinide series leads to trivalent ions that are expected to form very ionic bonds much as the lanthanide +3 ions. At the same time, a 60-year old report from Seaborg and coworkers proposed that covalency from 5*f*-orbitals contributed to the unique behavior of americium. Our study involved a combination of ligand K-edge X-ray absorption spectroscopy (XAS) and electronic structure calculations to quantify the extent of covalent bonding in – arguably – one of the most difficult systems to study, the Am–Cl interaction within $\mathrm{AmCl_6^{3-}}$. We observed both 5*f*- and 6*d*-orbital mixing with the Cl-3*p* orbitals; however, contributions from the 6*d*-orbitals were more substantial. Comparisons with the isoelectronic $\mathrm{EuCl_6^{3-}}$ indicate similar bonding for the $\mathrm{Am^{III}}$ 6*d*- and $\mathrm{Eu^{III}}$ 5*d*-orbitals with a 5f participation in bonding ever so slightly larger than that of the 4f electrons in Eu. Meanwhile, the results confirmed Seaborg's 1954 hypothesis that $\mathrm{Am^{III}}$ 5*f*-orbital covalency was more substantial that 4*f*-orbital mixing for $\mathrm{Eu^{III}}$.

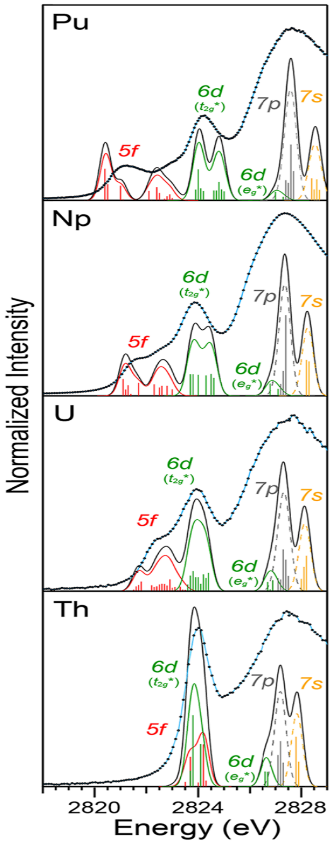


Figure 1: Experimetal and theoretical calculation of the ligand Cl k-edge spectra for $(\mathrm{AnCl_6})^{2-}$. All details of the calculations and interpretation can be read in Ref. 1

4. Energy-Degeneracy-Driven Covalency in Actinide Bonding.[1] A systematic study of the bonding and electronic structure for the $(\mathrm{An^{IV}Cl_6})^{2-}$ (An=Th, U, Np, Pu) series was carried out in a combined experimental (spectroscopy) and theoretical effort (relativistic density functional theory), see Figure 1. We directly address this challenge and contribute a Cl K-edge X-ray absorption spectroscopy and relativistic density functional theory study that quantitatively evaluates An−Cl covalency. The results showed significant mixing between Cl 3p- and $\mathrm{An^{IV}}$ 5f- and 6d-orbitals (t_{1u}*/t_{2u}* and t_{2g}*/e_g*), with the 6d-orbitals showing more pronounced covalent bonding than the 5f-orbitals. Moving from Th to U, Np, and Pu markedly changed the amount of M−Cl orbital mixing, such that $\mathrm{An^{IV}}$ 6d- and Cl 3p-mixing decreased and metal 5f- and Cl 3p-orbital mixing increased across this series. Critical for the proper theoretical reproduction of the experimental spectra was the inclusion of fully relativistic corrections which were key in modeling peak splittings in the excited state

5. Understanding the origin of covalency across the actinide series as a function of oxidation state and ligand.[7] Covalency lies at the heart of actinide coordination chemistry, that drives the chemistry controlling decorporation efficacy and separation efficiency. We investigated the bonding interactions of An(III) and An(IV) ions with 3,4,3-LI(1,2-HOPO), which is a promising agent for biological decorporation of radionuclides, to address their structure, thermodynamics, redox and electronic structure. The complexation of actinide ions generally becomes more favorable as the series is traversed. Notably, as the series is traversed, the 5f orbitals become more contracted in concurrence with the energy of 5f orbitals decreases resulting in reduced orbial overlap and increased energy degeneracy covalency, illustrated in Figure 2. This phenomenon is also observed with a different ligand, dipicolinate, and the thermodynamic measurements validated the theoretical predictions.

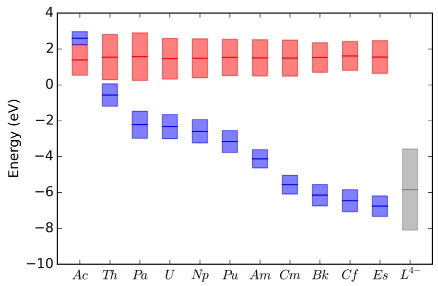
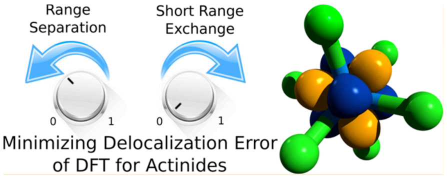


Figure 2: Energy levels of 5f(blue), 6d(red) and ligand (grey) orbitals in the An^{IV}(HOPO) complexes.

6. Revisiting complexation thermodynamics of transplutnium elements up to einsteinium.[2] Einsteinium (Es) is among the heaviest elements for which off-line experimental studies are possible. The number of metal–ligand stability constants with Es is limited. Previously reported data for Es^{3+} with nitrilotriacetic acid (NTA), trans-1,2-cyclohexanediamine-tetraacetic acid (CDTA), and ethylenediamine-tetraacetic acid (EDTA) suggest actinide interactions with aminopolycarboxylate (APC) ligands are unexpectedly much weaker than lanthanide (Ln) interactions with the same ligands. This manuscript reports on experimentally determined actinide–APC binding for americium (Am), berkelium (Bk), californium (Cf) and einsteinium (Es). Computational stability constant studies of the same actinides with diethylenetriamine-pentaacetic acid (DTPA) are also completed. The experimental and computational results of actinide complexation are compared to each other and with previous Ln–APC complexation results. Literature casts einsteinium as a departure from earlier transplutonium actinides, with a decrease in stability constants with aminopolycarboxylate ligands. This report studies transplutonium chemistry – including Am, Bk, Cf, and Es – with aminopolycarboxylate ligands. Interestingly, Es complexation follows similar thermodynamic and structural trends to the earlier actinides, consistent with our calculations.

7. Assessment of Tuned Range Separated Exhange Funcitonals for Spectrosocpies and Propterties of Uranium Complexes.[13] The Kohn−Sham delocalization error (DE) is quantified in select uranium compounds for various functionals and shown to correlate with the magnitude of dative ligand donation into the 5f shell. Range separated exchange functionals are reparametrized to minimize the DE and analyzed for their spectroscopic predictive capabilities. Valence excitation spectra of occupied 5f systems exhibit noticeable improvement upon reparametrization, e.g. UCl_6^-, UCl_6^{2-}, and UO_2^+. Less sensitivity to the reparameterization was observed for closed shell 5f systems and core excitation spectra. A general parametrization is proposed to perform well for valence excitation spectra with small DE.



Future Plans:

Expand theoretical efforts on the electronic structure of transuranic molecules containing new metal-ligand bonds, in parallel to the synthetic and spectroscopic characterization efforts, aiming to understand the origin of covalency across the actinide series. Investigate actinide-ligand bonding interactions in solution and their dynamic behaviors using quantum mechanics based methods and compare with experimental measurements carried by our experimental collaborators.

Recent Publications Resulting from this Project in the last three years

1. J Su, ER Batista, DL Clark, SA Kozimor, SG Minasian, HS La Pierre, P Yang, et al, "*Energy-Degeneracy-Driven Covalency in Actinide Bonding", J. Am. Chem. Soc.* **140***, 17977* (2018)
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4. AM Tondreau, TJ Duignan, BW Stein, J Autschbach, ER Batista, JM Boncella, SA Kozimor, P Yang, et al, "*A Pseudotetrahedral Uranium(V) Complex*" *Inorg. Chem*. **57**, 8106 (2018)
5. J Su, CJ Windorff, ER Batista, WJ Evans, AJ Gaunt, SA Kozimor, P Yang, et al, "*Identification of formal +2 oxidation state of Np:Synthesis and Structure of* $\{Np[C_5H_3(SiMe_3)_2]_3\}^{1-}$*,*" *J. Am. Chem. Soc.* **140***, 7425* (2018)
6. P Rungthana, TJ Duignan, J Autschbach, ER Batista, P Yang, JR Walensky, et al, "*Influence of substituents on electronic structure of Mono and Bis (phosphido) Th(IV) complexes*," *Inorg. Chem*. **57**, 7270 (2018)
7. MP Kelley, GJP Deblonde, J Su, CH Corwin, RJ Abergel, ER Batista, P Yang, "*Bond Covalency and Oxidation State of Actinide Ions Complexes with 3,4,3-LI(1,2-HOPO),*" *Inorg Chem*. **57**, 5352 (2018)
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10. AE Clark, P Yang, JC Shafer "*Coordination of Actinides and the Chemistry behind solvent extraction*", Ch 5, Epxerimental and Theoretical Approaches to Actinide Chemistry. Ed. JK Gibson, WA de Jong (2018)
11. SK Cary, J Su, SS Galley TE Albrecht-Schmitt, ER Baista MG Ferrier, SA Kozimor, V Mocko, BL Scott, CE Alstine, FD White, P Yang "*A series of dithiocarbamates for Am, Cm, and Cf,*" Dalton Trans. **93**, 323 (2018)
12. SG Minasian, ER Batista, CH Booth, DL Clark, JM Keith, SA Kozimor, et al, "*Quantitative Evidence for Lanthanide-Oxigen Orbital Mixing in* CeO_2*,* PrO_2*, and* TbO_2*,*" *J. Am. Chem. Soc.* **139**, 18052 (2017)
13. TJ Duignan, J Autschbach, ER Batista, P Yang "*Assessment of tuned range separated exchange functionals for spectroscopies and properties of uranium complexes*," *J. Chem. Theor. Comp.* **8***, 3614* (2017)
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21. M Sturzbecher-Hoehne, P Yang, A D'Aléo, RJ Abergel, "*Intramolecular Sensitization of Am Luminescence in Solution: Shining Light on Short-lived Forbidden 5f Transitions*," *Dalton Transactions*, **2016**, 45, 9912-9919,
22. WW Lukens, M Speldrich, P Yang, P Kögerler, "*The Roles of 4f and 5f Orbitals in Bonding: a Magnetochemical, Crystal Field and Density Functional Theory-based Study*," *Dalton Trans.* **45**, 11508 (2016)
23. KP Browne, DE Morris, P Yang, JL Kiplinger, MJ Veauthier, et al "*Synthesis, Characterization, and DFT Analysis of N-rich Complexes of U and Th Containing 5-methyltetrazolate*," *Inorg Chem,* **55**, 4941 (2016)
24. MP Kelley, P Yang, SB Clark, AE Clark, "*Structural and Thermodynamic Properties of the Curium(III) Ion Solvated by Water and Methanol*,"*Inorg. Chem.* **55**, 4992 (2016)
25. MS Winston, ER Batista, P Yang, AM Tondreau, J.M. Boncella, "*Extending Stannyl Anion Chemistry to the Actinides: Synthesis and Characterization of a U-Sn Bond*." *Inorg. Chem.* **55**, 5534 (2016)
26. MG Ferrier, ER Batista, JM Berg, SA Kozimor et al "*Spectroscopic and Computational Investigation of Actinium Coordination Chemistry,*" *Nat. Comm.* **7**, 12312 (2016)

Assessing Influences of Actinide and Transactinide Electronic Structures on Reactivity
FWP CH030203 – Thrust 1

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Overall Research Goals

This Thrust seeks to determine, understand, and ultimately control reactivity of actinide (An) and transactinide elements, for systems ranging in complexity from small molecules to large poly-nuclear and multi-metallic complexes. An overarching objective is to define characteristics that govern distinctive chemistry of these elements, including 5f-electron participation and relativistic effects. Interactions with theory serve to elucidate experimental results, and to assess and refine theory. Experiments are designed to provide information that will assess the validity and generality of central hypotheses; results for several elements reveal trends and provide new insights.

Recent Progress

Development of New Supporting Ligands to Control Electronic Structure and Reactivity. Actinide ions can use their 5f-orbitals to bind ligands and substrates in ways that are impossible for main group elements and transition metals and, as a result, they have the potential to mediate new chemical transformations. Moreover, because subtle changes to the coordination environment around a metal can dramatically alter its reactivity, supporting ligand design in An chemistry is critical to discovering and harnessing these unique modes of reactivity. Some recent accomplishments are reported in publications **1-9**.

Understanding and Controlling Actinide Reactivity at the Molecular Level in Gas Phase. Gas phase projects span three broad themes: (1) reactivity of An-ligand bonds; (2) coordinating ligands modify reactivity; and (3) high oxidation states (OS). These topics naturally intersect, such as when An-ligand bond reactivity is modified by ancillary coordination. Some recent results are described in publications **10-20**. Upper limits of An OS reveal the extent of 5f-electron involvement in chemistry, either directly in covalent bonding or indirectly via charge transfer in ionic bonding. Pentavalent chemistry has now been extended farther into the An series with curyl(V), CmO_2^+, berkelyl(V), BkO_2^+, and californyl(V), CfO_2^+ (**10**). These pentavalent actinides were also produced in nitrate complexes $AnO_2(NO_3)_2^-$ for An = Cm, Bk and Cf (**11**). These new An(V) species demonstrate that late An are not "lanthanide-like", as lore would have it; instead, such high OS reveal that the 5f-electrons of late An are chemically engaged to a greater extent than previously thought. We also reported Np(VII) in $NpO_3(NO_3)_2^-$ and Pu(VII) in square-planar PuO_4^- (**12**). A remarkable conclusion from the latter result is that adding an electron to neutral PuO_4 results in *oxidation* from Pu(V) to Pu(VII). This seemingly odd phenomenon—oxidation of a metal center concomitant with net reduction of a complex—reflects the low stability of Pu(VIII) versus Pu(V), and demonstrates O_2 as a redox-active ligand. In the realm of fundamental reactivity, activation of an actinyl AnO_2^{n+} (n=1 or 2) by H_2O yields hydroxide $AnO(OH)_2^{n+}$, either as a hydrolysis product or as an oxo-exchange intermediate, as shown in Figure 1. This activation was studied by experiment and CCSD(T) computations (with D. Dixon and K. Peterson). Surprisingly, An-O activation is predicted to be most facile for PaO_2^+, which exhibits the highest of all known actinyl(V) bond dissociation energies. Both the hydrolysis energy, ΔH(hydrol), and the transition state barrier, *E*(TS1), are predicted to increase from PaO_2^+ to AmO_2^+, coincident with a decrease in bond dissociation energy from 186 kcal/mol for D[OPa^+-O], to 98 kcal/mol for D[OAm^+-O]. We have verified this counterintuitive relationship - more facile activation of stronger bonds - for PaO_2^+, UO_2^+, NpO_2^+ and PuO_2^+. Very recent results show that AmO_2^+ does not oxo-exchange, while CmO_2^+ does. Referring to *E*(TS1) values in Fig. 1**B**, it is apparent that these new results confirm the reactivity minimum (i.e. maximum TS1 kinetic barrier) at AmO_2^+; and the subsequent "turn" towards lower *E*(TS1) from AmO_2^+ to CmO_2^+, which is manifested as enhanced exchange reactivity for CmO_2^+.

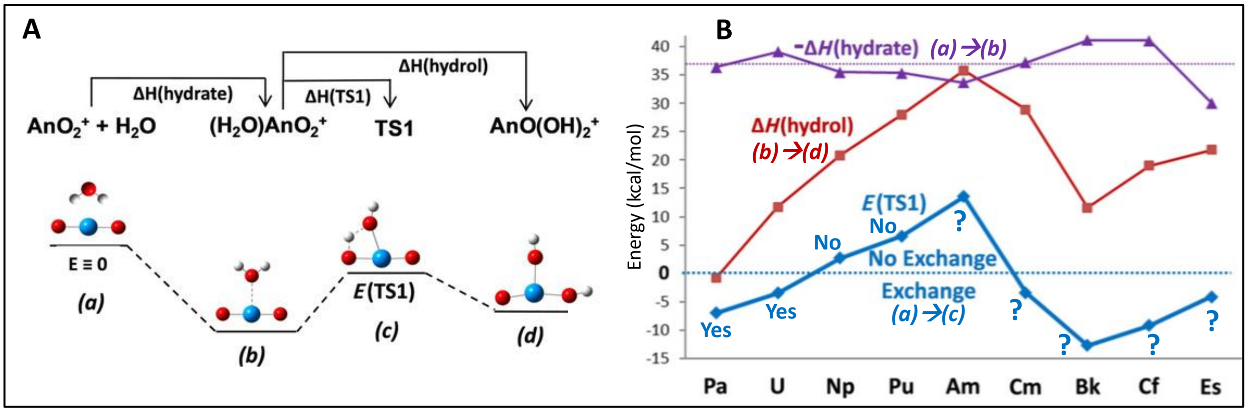

Figure 1. (**A**) Species; and (**B**) computed energies for association of An(V) and H_2O ***(a)*** to yield hydroxide ***(d)*** that is the intermediate in oxo-exchange. Experimental results for observation of oxo-exchange are indicated in **B** as "Yes"; "No"; or "?" (to-be-determined). Results are from (**13**).

Gas Phase Superheavy Element Chemistry. Other than a few (impressive) previous experiments, chemical understanding of superheavy elements (SHE; Z ≥ 100) is limited to theoretical predictions and qualitative experimental comparisons to lighter elements, such as Sg ($Z = 106$) forming volatile carbonyl complexes as does W. Using the FIONA (**F**or the **I**dentification **O**f **N**uclide **A**) SHE mass analysis device recently installed at the exit of the BGS (**B**erkeley **G**as-filled **S**eparator) at the LBNL 88" Cyclotron (referred to as "BGS+FIONA"), we have initiated a program to expand chemical knowledge of SHEs by examining elementary ion-molecule reactions that can occur in the quadrupole ion trap of FIONA. Initial experiments have demonstrated that Lr^{2+} abstracts an electron from O_2 whereas No^{2+} does not, providing the first experimental assessment of second ionization energies (IEs) of these heaviest actinides. The results establish a relatively low IE[No^+], for removal of the lone 7s electron from the expected $[Rn]5f^{14}7s^1$ configuration. The demonstration of a higher IE[Lr^+] is in accord with removal of a spin-paired 7s electron from the supposed $[Rn]5f^{14}7s^2$ configuration.

Future Plans

Development of New Supporting Ligands to Control Electronic Structure and Reactivity. We will investigate new coordination compounds bearing novel ligands with An metals in a range of oxidation states. A key strategy is to aim for systems based on use of a single ligand, i.e. *homoleptic* systems, and to examine trends in electronic structure and reactivity across the An series as these ligand motifs are deployed. We hypothesize that a focus on control of sterics and electronics via ligand design will engender new opportunities to regulate electronic structure within the 6d, 5f manifold, which will, in turn, lead to new types of reactivity. In-depth analysis of these compounds through reactivity studies, as well as physical and theoretical characterization, will be completed to expand our understanding of An fundamental properties, including bonding trends as they relate to metal and ligand oxidation state, coordination number, and geometry.

Understanding and Controlling Actinide Reactivity at the Molecular Level in Gas Phase. We will search for new high An OS to probe upper limits of 5f-electron participation in chemistry. Targets include species with coordination environments that are likely to stabilize such extreme OS as Cm(VI), Am(VII) and Pu(VIII). We previously demonstrated heptavalent actinides in NpO_4^- and PuO_4^-. Preliminary DFT calculations suggest that AmO_4^- may similarly comprise Am(VII), though lower Am OS are energetically competitive. A possible synthetic route to AmO_4^- is based on reaction (1) for an actinyl(V) oxalate with oxygen via an association intermediate (*INT)*:

$$AnO_2(C_2O_4)^- + O_2 \rightarrow \{(O_2)AnO_2(C_2O_4)^-\}_{INT} \rightarrow AnO_4^- + 2CO_2 \quad (1)$$

Extraordinary reactions such as (1) are thermodynamically facilitated by stable products like CO_2. Another planned direction is rational alteration of reactivity by ligation. As noted above, bare actinyl activation does not reasonably correlate with bond strength. In pursuit of an alternative and rational explanation for observed differences in reactivity, in collaboration with D. Dixon and K. Peterson we have found from Natural Bond Order (NBO) analysis that a decrease in reactivity occurs in parallel with increasing bond covalency and decreasing charge, $q(An^{\delta+})$. Between different actinyls, such key characteristics as covalency and $q(An^{\delta+})$ simultaneously change, thus complicating reliable assignment of causation for observed reactivity disparities. To circumvent this confusion that is inherent to simple molecular oxides, we will study reactivity of complexes that afford more diverse and controlled variations in properties. The studied systems and reactions will however retain sufficient simplicity to allow for rational analysis. For example, an An(III) coordinated by anion ligands X and Y can react with an acid HZ via an elementary proton-transfer intermediate as in reaction (2):

$$X_3AnY^- + HZ \rightarrow \{X_3An(ZHY)^-\}_{INT} \rightarrow X_3AnZ^- + HY \quad (2)$$

In reaction (2), such properties as atomic charge and bond covalency can be coherently varied by substitution of spectator donor ligands X, and/or exchanged ligands Y and Z. For example, replacing Y=Cl by Y=F should result in decreases in both An-Y bond covalency and $q(An^{\delta+})$. In preliminary work, we found lower reaction efficiency for Y=Cl versus Y=F, which may reflect less facile activation of the more covalent An-Cl bonds. Expanded studies of such variations in reactivity for different spectator donor ligands and exchanged ligands, and also for different An, will provide insights into underlying characteristics that govern An bond activation.

Gas Phase Superheavy Element Chemistry. Using the new BGS+FIONA setup at the Berkeley 88" Cyclotron, we will study ion-molecule reactions for SHE, performed "one-atom-a-time" in the FIONA quadrupole ion trap. In an initial foray into this realm, we plan to consider the elementary and exemplary reaction of monopositive transactinide element 105, Db^+, with O_2. This reaction will provide an assessment of the essential chemistry of 6d transition metal Db, for comparison with that of lighter homologs from the 5d-, 4d- and 3d-series transition metals. Of particular interest is whether pentavalent DbO_2^+ (i.e. $O=Db^+=O$) is produced in a similar manner—kinetically and thermodynamically—as homologous TaO_2^+, NbO_2^+ and VO_2^+. Such very basic information as characteristic reactivity and OS is needed to establish similarities and differences in chemical trends for the heaviest known elements, and thereby further expand understanding of the periodic table.

Selected Recent Publications Resulting from this Project (2017-Present)

1. “Isolation of a TMTAA-Based Radical in Uranium bis-TMTAA Complexes.” S. Hohloch, M.E. Garner, C.H. Booth, W.W. Lukens, C.A. Gould, D.J. Lussier, J. Arnold, *Angew. Chem.*, 130 **2018** 16368 DOI: 10.1002/anie.201810971
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5. "Insertion, protonolysis and photolysis reactivity of a thorium monoalkyl amidinate complex" N.S. Settineri, J. Arnold, *Chem. Sci.,* 9 **2018** 2831 DOI:10.1039/C7SC05328B
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20. “Crown ether complexes of actinyls: A computational assessment of AnO_2(15-crown-5)$^{2+}$ (An = U, Np, Pu, Am, Cm),” S.-X. Hu, *et al.*, *Dalton Trans*. 46 **2017** 12354 DOI: 10.1039/C7DT02825C

Role of f Orbital Interactions in Determining Heavy Element Physical Properties
FWP CH030203 – Thrust 2

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Overall Research Goals

A central issue in coordination chemistry is the effect of orbital interactions on electronic structure, which in turn affects complex stability, ionic radii, magnetic behavior, reactivity, and luminescence. In the actinide (An) series, the effective nuclear charge of a given oxidation state increases from Th through Lr, which leads to both stabilization and contraction of the 5f orbitals. These changes have profound and contradictory effects on An-ligand interactions. Contraction of 5f orbitals decreases overlap (S), which decreases orbital mixing (λ), while stabilization reduces the difference in energy between the An and ligand orbitals ($\Delta E_{M\text{-}L}$), which increases λ. From MO theory, λ is proportional to $S/\Delta E_{M\text{-}L}$, while stabilization is proportional to $S^2/\Delta E_{M\text{-}L}$, so an increase in λ due to small $\Delta E_{M\text{-}L}$ creates less stabilization than an increase in λ due to larger overlap. The consensus is that f-orbital stabilization increases λ for later An ions (energy degeneracy driven covalency). How increased orbital mixing affects other properties, especially ground state stabilization, is less clear since S decreases for later An ions. Our goals are to quantify orbital mixing, λ, and determine how changes in λ affect other properties, especially bond stabilization and magnetic behavior.

Recent Progress

Hard X-Ray Spectroscopy. The spectroscopic and magnetic properties of Ce TriNOx imido, anilide, and oxide-based molecules (with E. Schelter, U. Penn) have been intensely studied. A highlight includes the separation of the effects of various orbitals on L_3-edge spectra via high-energy resolution fluorescence detection (HERFD) measurements that provide confidence in n_f measurements for these and future An L_3 experiments. We have also explored using M_{IV} and M_V edge HERFD measurements on U compounds, including UCd_{11}, UF_4 and UO_2, in a way that utilizes the absolute emission intensity to isolate the $5f_{5/2}$ and $5f_{7/2}$ occupancies. In addition, we have developed methods for routine EXAFS measurements of the local structures of transPu solutions, including An(DTPA)[1] (Fig. 1) and An(HOPO)[2], finding that the An-O bond length in An(DTPA) abruptly changes as one passes through Bk to Cf in the An series. This change is ascribed to a water molecule loss in the Cf system.

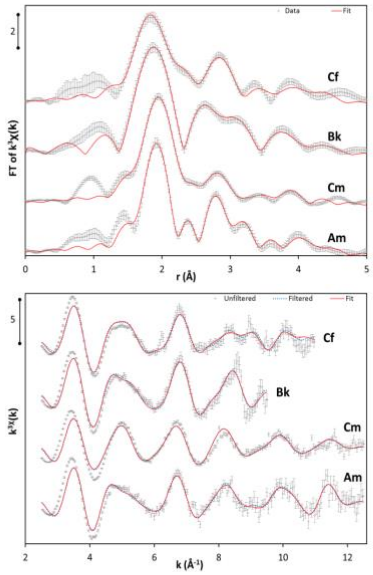


Figure 1. An^{III}(DTPA) EXAFS spectra.

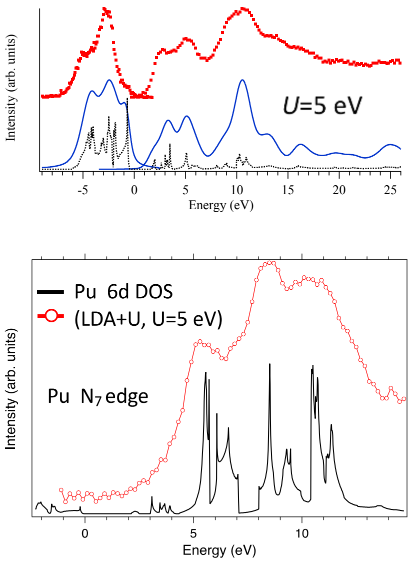


Figure 2. (Top) O K-α XES and O K-edge XAS of PuO_2 (red), LDA+U simulations (blue) and O 2p density of states (black). (Bottom) The Pu N_7 XAS of PuO_2 (red) and density of states *from LDA+U (black).*

Soft X-Ray Spectroscopy. High-resolution soft X-ray spectroscopy has been combined with theory to determine the electronic structures and the chemical bonding characteristics of transuranic dioxides (Figure 2). UO_2, NpO_2, and PuO_2 were studied at the O K-edge using XANES and XES to measure the densities of unoccupied and occupied O 2p states, respectively. Local density approximation plus Hubbard U (LDA+U) DFT methods were used to simulate the experimental data (XES and XANES) and determine U, the intra-atomic Coulomb interaction for 5f electrons.

Direct evidence of O 2p mixing with 4f orbitals was obtained by O K-edge XAS of CeO_2, PrO_2, and TbO_2, which agree quantitatively with measurements at Ln L_3-edges.[14] This work determined the O K-edge transition dipole integral, which allows quantification of 5f orbital mixing in actinide-oxygen bonds using O K-edge XAS.

Lanthanide and actinide dialuminides ($LnAl_2$ and $AnAl_2$) were studied using Al K-edge XAS. The combined experimental and theoretical study shows that the 5f electrons facilitate mixing of Al 3p character into the 6d conduction bands, which affects quenching of magnetic moments. Pre-edge features observed at low energy provide irrefutable evidence for mixing between the Al 3p and lanthanide 5d or actinide 6d orbitals. This mixing is correlated with both the f-orbital occupancies and changes in magnetic behavior.

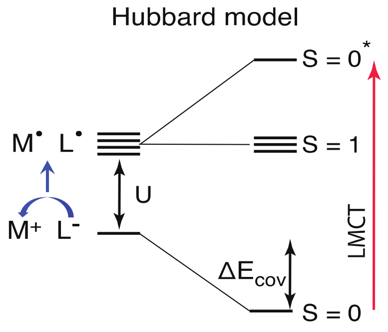
Future plans

Hard X-Ray Spectroscopy. Problems with relying only on HERFD measurements for determining orbital mixing have been identified, and we are exploring how to alleviate these problems. A systematic exploration of the new M_4 and M_5 high-resolution measurements on model compounds will focus initially on Th, U and Pu systems, with immediate application to the hidden order material URu_2Si_2. EXAFS measurements on transplutonium systems and the analysis of Am through Cf carboxylates should provide a significant boost in understanding of bonding in such systems, especially Bk and Cf. A long-term goal is to use this structural information to determine bond-valence sum parameters for comparisons to future materials data. In conjunction with the O K-edge XAS studies described below, AnO_2 will be studied at the An L_3, M_4 and M_5 edges to understand how changes in orbital mixing affect these spectra.

Soft X-Ray Spectroscopy. Studies of electronic structure and the nature of the chemical bonding in the light actinide oxides at the O K-edge will be extended to AmO_2, CmO_2, and BkO_2. Using the O K-edge transition dipole integral determined from LnO_2 spectra, orbital mixing will be quantified in AnO_2 compounds. Ligand K-edge studies will be extended to actinide borides, carbides and nitrides. Ligand K-edge XAS will also be used to study actinide complexes including oxalates, cyclooctatetraenyl complexes (actinocenes), and fluoride complexes. The fluoride complexes should be especially interesting due to the ability to directly compare the results to those of actinide chloride complexes, which have been previously studied by researchers from LANL and LBNL.

Electron Energy Loss Spectroscopy. Spectra of An ions at the M, N, and O absorption edges can also be obtained by EELS using a TEM (with A. Minor, LBNL). The information obtained by XAS and EELS is analogous and can be used to explore electronic structure and electron delocalization as describe above. The first known EELS spectra of Bk were acquired of the $O_{4,5}$-, $N_{4,5}$- and $M_{4,5}$-core loss edges. s. EELS data will be obtained on Ac, Pa, and Cf compounds. This study will be extended to Es, Fm, and Md if they become available.

Effects of Orbital Mixing on Bond Strength and Magnetic Properties. In conjunction with the hard and soft XAS studies of AnO_2, the UV-vis spectra of An-doped CeO_2 and ThO_2 will be measured to determine the energies of the ligand to metal change transfer (LMCT) bands. Using the LMCT energy and the orbital mixing, the U (electron repulsion) and t (electron hopping) parameters can be calculated for a Hubbard molecule model (Figure 3). In turn, U and t can be used to determine the amount of stabilization due to 5f-orbital mixing with the oxygen 2p orbitals.



$$\Psi_{S=0} \cong N(\Psi_{M^{+}L^{-}} + \lambda\Psi_{M\text{-}L})$$

$$t = H \approx S\left(E_M + E_L\right), \quad \lambda \cong \sqrt{2}\frac{t}{U}$$

$$\Delta E_{cov} = 2\Delta E_L \cong 2\frac{t^2}{U}$$

Figure 3. Hubbard molecule model.

Using this model, ligands with enhanced orbital mixing will be identified and characterized using ligand and metal XAS spectroscopy to determine the stabilization due to orbital mixing. The relative strengths of these ligands and analogous ligands with similar ionic bonding but much less orbital mixing will be measured by setting up appropriate equilibria.

In a similar vein, the exchange coupling between unpaired electrons on an An center and unpaired electrons on a ligand will be measured. The value of the exchange coupling, J, in the simple Heisenberg, Dirac, van Vleck Hamiltonian is given by $\mathcal{H} = -J\mathbf{S}_{\mathbf{M}} \bullet \mathbf{S}_{\mathbf{L}}$, where $\mathbf{S}_{\mathbf{M}}$ and $\mathbf{S}_{\mathbf{L}}$ are the spins on the metal ion and ligand, respectively. The magnitude of J is the same as ΔE_{cov} in the Hubbard model. In other words, the magnitude of the exchange coupling is directly related to the overlap between the metal and ligand orbitals and U.

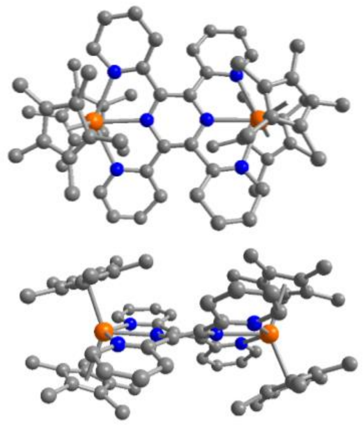


Figure 4. Crystal structure of $[(Cp^*_2U)_2(\mu_2\text{-tppz})][BPh_4]_2$. BPh_4^- and hydrogens removed for clarity.

Work with U systems is underway, and one of the complexes with two U centers coordinated to a $tppz^{\bullet-}$ ligands is shown in Figure 4. In general, uranium in these complexes prefers to be tetravalent, f^2, which results in a singlet (S=0) ground state for the U(IV) center. The goals in this project are to extend this work to Np(IV), which will have a Kramer's doublet ground state with an effective spin, $\hat{S}$, of ½. In addition, U(III) and U(V) complexes with ligands having unpaired spin density will be pursued.

Selected Recent Publications Resulting from this Project (2017-Present)

(I) Exclusively funded by this grant

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(II) Jointly funded by this grant and other grants with relatively major intellectual contribution from this grant

1. Tobin, J. G.; Yu, S. W.; Qiao, R.; Yang, W. L.; Shuh, D. K., Oxidant K edge x-ray emission spectroscopy of UF_4 and UO_2. *J. Vac. Sci. Technol., A* **2018,** *36*, 03E101/1-03E101/5.
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Designing New Structural Platforms for Heavy Element Chemistry
FWP CH030203 – Thrust 3

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Overall Research Goals

Much of our current understanding of the *5f-electron challenge* has been developed through studies of model compounds, which are often small and highly symmetric molecular systems. A major focus of the LBNL Heavy Element Chemistry group is to move beyond the inherent limitations of small molecules and develop predictive models for chemical processes in complex molecules and hierarchical structures by synthesizing new structural platforms for actinide (An) chemistry. The research is based on a hypothesis that controlling actinide chemical structure in multiple dimensions and length-scales will reveal new aspects of 5f-electron behavior that are otherwise difficult or impossible to observe. Because the synthetic targets are complex systems, a comprehensive characterization effort is required to show how multidimensional and/or hierarchical structure creates emergent properties that are not observed in homogeneous materials.

Research Progress

Nature-Inspired Ligands for An Coordination Chemistry. Liquid-liquid extraction methods were developed to determine conditional stability constants for complexes formed between 3,4,3-LI(1,2-HOPO) and the heavier actinide ions Am^{3+}, Cm^{3+}, Bk^{4+}, Cf^{3+}, and Es^{3+}, with minute amounts of ligand and tracer levels of the metal ions. Such methods were particularly useful for Es, only available in hundreds of ng quantities at best, and were verified with spectroscopic and titration techniques that leveraged specific absorption and fluorescence spectral signatures, which we had previously established with Cm and Am complexes. We are now able to derive conditional stability trends along the Ln and An series, which will inform us of the potential of these ligands for element separation based on metal identity and oxidation state. We prepared series of ligands through a combinatorial approach using peptoid scaffolds, which allows for the sequential addition of chosen binding groups in a systematic manner. A total of 16 octadentate combinations were characterized for their Cm(III) luminescence sensitization properties, drastically enhancing the effects of different functional groups on luminescence properties that were previously observed with Eu(III) and Tb(III). Metal coordination will be probed by EXAFS for the Am to Cf systems.

Porous Aromatic Frameworks. Unusual and selective coordination sites for An ions have promise for use in f-element separations depending on their tunable characteristics, and are chemically-robust materials in comparison to general framework materials. The highly-interpenetrated carboxylic acid-functionalized PAF, Berkeley Porous Polymer-7 (BBP-7), was prepared and reacted with trivalent Nd and Am to yield stable PAF complexes. The nature of metal ion coordination and bonding in the polycrystalline PAFs was determined from complementary Langmuir adsorption site modeling and structural characterization by extended X-ray absorption fine structure (EXAFS) spectroscopy. The strong and selective binding interaction, similar for Nd and Am, was shown to originate from more than one metal ion binding site along with the unusual coordination mode resulting from multiple interactions with the interpenetrating ligands.

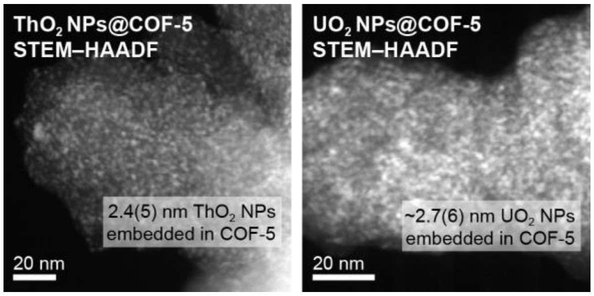

Figure 1. STEM–HAADF images of ThO_2 and UO_2 NPs confined to pores of COF-5 particles. The images show that the NP diameters are on the order of the pore size of COF-5 (2.7 nm), suggesting that the COF-5 templates effectively limit the NP growth.

Synthesis of Well-Defined Actinide Nanoparticles. We invented new synthetic methodologies and demonstrate the impact of actinide nanoparticle (NP) size and composition on physical properties. The synthesis of well-defined ThO_2 and UO_2 NPs (Fig. 1) was achieved beginning with fluorinated β-diketonate precursors, $An(hfa)_4$ (hfa = hexafluoroacetylacetonate), and a COF-5 template (COF = covalent organic framework). Comparisons in the XANES region of the U L_3-edge XAFS spectra for bulk UO_2 and UO_2 NPs@COF-5 provided a qualitative confirmation of composition, while actinide L_3-edge extended XAFS (EXAFS) spectroscopy was used to probe composition including the local coordination environment, bond distances, and the identities of neighboring atoms. In addition, 2-5 nm Pu oxide nanoparticles (NPs) synthetically prepared by precipitation from aqueous solutions by either a sonichemical technique or a standard hydrolysis method were probed using STXM. Comparison of the O K-edge STXM-XANES spectrum obtained from NPs originating from sonolysis closely resembled the spectrum of bulk-like PuO_2.

Future Plans

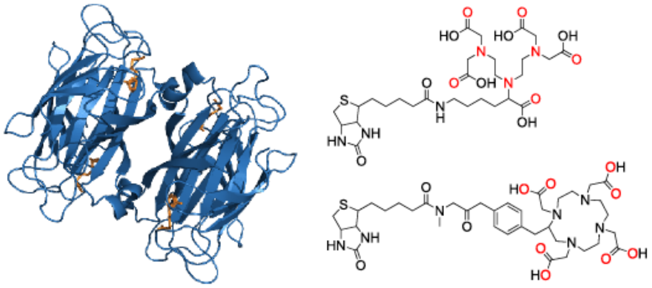

Figure 2. The streptavidin protein (left) can bind to up to four biotin small molecules, which are easily modified to carry ligands such as DTPA (top right) or DOTA (bottom right). Streptavidin /biotin/ligand/actinide constructs will be used for structural characterization and in crystallo reactivity studies.

Molecular Recognition of An Small Molecules. Over the past few decades, a number of natural small molecules have been identified as modern structural platforms in transition-metal coordination chemistry and separation processes. By extending the number of ligands and complexes available for protein crystallization, we hope to build on the first series of trends obtained with 3,4,3-LI(1,2-HOPO) complexed to each of the lanthanides, as well as Am, Cm, and Cf. This will also enable the probing of tetravalent metal ions dioxo cations as the ligand structure is tuned. Beyond the use of siderophore-specific proteins, we will also exploit known systems that exhibit tight binding between a protein and a small molecule by linking actinide-ligand complexes to the recognized entity. We will pursue structural investigations of streptavidin/biotin/ligand/actinide constructs (with A. Borovik, UC Irvine), and start investigating metal reactivity *in crystallo* (Fig. 2).

Unusual Coordination Environments in An-Based Metal-Organic Frameworks. We will synthesize and characterize the first series of actinide-based MOFs bearing coordinatively-unsaturated metal centers. Varying the metal center across the An series, including transU elements, together with the adsorbate species, we will then provide valuable new insights into the fundamental coordination chemistry of An elements, much as it has already for high-spin transition metals. Experimental results will serve as the basis for quantum chemical analysis of the observed metal–adsorbate interactions. Because actinides can achieve high coordination numbers, there is potential for added framework flexibility and other unique advantages that are difficult to achieve for transition metals. Metal-organic frameworks with open metal sites have proven to be a powerful tool for the investigation of unusual and unprecedented metal–adsorbate interactions. Based on the initially characterized uranium MOFs, it is envisioned to then isolate and characterize isostructural Th, Np, and Pu materials, to identify trends across a comparable series of actinide-adsorbates. Open metal sites in crystalline MOF materials will be introduced via the post synthetic desolvation of metal nodes (Fig. 3). The electronic and physical properties of the resulting materials with coordinatively-unsaturated actinide sites will be probed by H_2, N_2, O_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, Ar, and Xe gas adsorption experiments in combination with *in situ* single-crystal X-ray diffraction methods. Actinide L_3-edge XANES experiments on the proposed compounds will allow the direct quantification of actinide electronic structure and the covalency in An-ligand bonds (with C. Booth, LBNL).

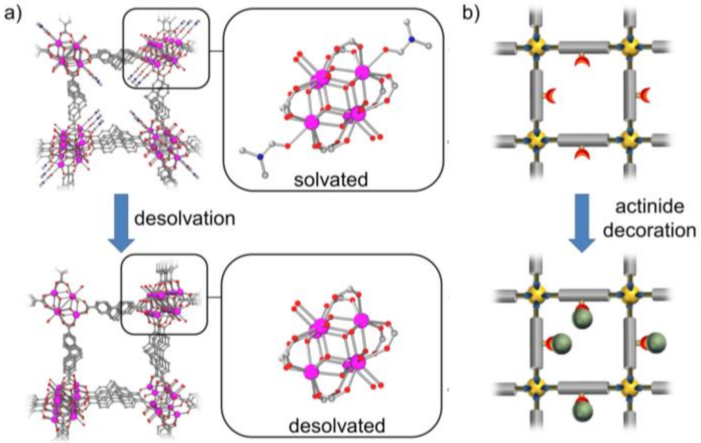

Figure 3. (a) Introduction of open metal sites at SBUs of $U_6O_4(OH)_8(Me_2bpdc)_4(DMF)_2$ via post synthetic solvent removal. (b) Schematic representation of open metal site introduction via post synthetic actinide decoration of MOFs with secondary binding sites.

Bridging Molecular-Level and Nanoscale An Chemistry. Our approach involves establishing new methods to synthesize actinide NPs in a manner that provides control over size and composition, and leverages several unique and previously unutilized methods for physical characterization. The synthetic strategy was designed to accelerate the pace of discovery for transU An systems by targeting specific methodologies that are adaptable for milligram and microgram-scale experiments. Because size-controlled syntheses for Np and Pu-based NPs are exceedingly uncommon, and to the best of our knowledge there are no examples of Am, Cm, Bk, or Cf-based NPs, these studies will add significantly to our understanding of transuranic actinide nanoscale chemistry. Our initial work with ThO_2 and UO_2 NPs have shown that the template-directed synthetic approach is versatile: it accommodates both 2D and 3D COF templates and a range of coordination compounds. Formation of NPs will be corroborated by transmission electron microscopy (TEM), which will confirm NP formation and evaluate NP size and structure (shape, crystallinity, and interparticle spacing), and by small-angle X-ray scattering (SAXS) to obtain a statistically-significant measurement of NP sizes in the 3D inorganic-organic hybrid materials. Following confirmation of size control, the most important task is to determine the chemical (elements and stoichiometry) and structural (phase and disorder) compositions of NPs. Preliminary Np L_3-edge XANES and EXAFS studies with Np(hfa)$_4$@COF-5 showed a similar XANES spectrum and characteristic Np–O bond lengths as compared with pure Np(hfa)$_4$. VT magnetic susceptibility and resonant X-ray emission (RXES) measurements will be used to evaluate oxidation state, ground state electronic configuration, and changes in phase or magnetic ordering that occur at low temperature (with C. Booth, LBNL).

Selected Recent Publications Resulting from this Project (2017-Present)

1. "Chemical and Morphological Inhomogeneity of Aluminum Metal and Oxides from Soft X-ray Spectromicroscopy." Altman, A. B.; Pemmaraju, C. D.; Alayoglu, S.; Arnold, J.; Booth, C. H.; Braun, A.; Bunker, C. E.; Herve, A.; Minasian, S. G.; Prendergast, D.; Shuh, D. K.; Tyliszczak, T. *Inorg. Chem.* **2017**, *56*, 5710-5719. DOI: 10.1021/acs.inorgchem.7b00280
2. “Cleaving Off Uranyl Oxygens through Chelation: A Mechanistic Study in the Gas Phase” Abergel R. J., de Jong W. A., Deblonde G. J.-P., Dau P. D., Captain I., Eaton T. M., Jian J., van Stipdonk M. J., Martens J., Berden G., Oomens J., Gibson J. K. *Inorg. Chem.* **2017**, *56*, 12930-12937.
3. “Chelation and stabilization of berkelium in oxidation state +IV” Deblonde G. J.-P., Sturzbecher-Hoehne M., Rupert P. B., An D. D., Illy M. C., Ralston C. Y., Brabec J., de Jong W. A., Strong R. K., Abergel R. J. *Nat. Chem.* **2017**, *9*, 843-849.
4. C.-T. Yeung, K.-H. Yim, H.-Y. Wong, R. Pal, W.-S. Lo, S.-C. Yan, M. Y.-M. Wong, D. Yufit, D. E. Smiles L. J. McCormick, S. Teat, D. K. Shuh, W.-T. Wong, and G.-L. Law, "Chiral Transcription in Self-Assembled Tetrahedral Eu_4L_6 Chiral Cages Displaying Sizable Circularly Polarized Luminescence," *Nat. Commun.* **2017** *8*, 1128. DOI: 10.1038/s41467-017-01025-1
5. "Homoleptic U(III) and U(IV) Amidate Complexes." Straub, M. D.; Hohloch, S.; Minasian S. G; Arnold, J. A. *Dalton Trans.,* **2018**, 47, 1772 - 1776. DOI: 10.1039/c7dt04813k
6. "Development of small particle speciation for nuclear forensics by soft X-ray scanning transmission spectromicroscopy." Pacold, J. I.; Altman, A. B.; Knight, K. B.; Holliday, K. S.; Kristo, M. J.; Minasian, S. G.; Tyliszczak, T.; Booth, C. H.; Shuh, D. K. *Analyst* **2018**, *143*, 1349-1357. DOI: 10.1039/c7an01838j
7. “Reductive activation of neptunyl and plutonyl oxo species with a hydroxypyridinone chelating ligand” Carter K. P., Jian J., Pyrch M. M., Forbes T. Z., Eaton T. M., Abergel R. J., de Jong W. A., Gibson J. K. *Chem. Comm.* **2018**, *54*, 10698-10701, DOI: 10.1039/C8CC05626A.
8. “Investigating subtle 4f vs. 5f coordination differences using kinetically inert Eu(III), Tb(III), and Cm(III) complexes of a coumarin-appended 1,4,7,10-tetraazacyclododecane-1,4,7-triacetate (DO3A) ligand” Junker A. K. R., Deblonde G. J.-P., Abergel R. J., Sorensen T. J. *Dalton Trans*. **2018**, *47* (21), 7362-7369, DOI: 10.1039/C8DT01547C.
9. "Chemical Vapor Deposition of Stoichiometric UO_2 Thin Films from U(IV) Amidate Precursors." Straub, M. D.; Leduc, J.; Frank, M.; Raauf, A.; Lohrey, T.; Minasian, S. G.; Mathur, S.; Arnold, J. *Angew. Chem. Intl. Ed.*, *in press*. DOI: 10.1002/anie.201901924

Unexpected Covalency in the *f*-Block and Routes to It

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Overall research goals: *Our hypothesis is that the chemistry of trivalent californium is dominated by charge transfer from complexants owing to the metastability of the 2+ oxidation state.* If correct, this phenomenon is more pronounced in einsteinium because the 2+ state increases in thermodynamic stability between californium and nobelium. Many of our projects directed at both understanding and fine-tuning the CT features in Cf(III) complexes and benchmarking these data with large families of earlier actinide complexes. We seek to gain a deep understanding of the electronic structure of these compounds as means for understanding the origin of their unusual physical properties.

Recent Progress: We have prepared and characterized families of Pu^{III}, Am^{III}, Cm^{III}, Bk^{III}, and Cf^{III} compounds including the first seven crystal structures determined for berkelium compounds. In particular, the family of the compounds described below contains a truly unusual surprise that we are currently capitalizing on. We have also brought online HP diamond anvil capabilities with transU compounds. We are going to knock your socks off when we show you what happens to certain curium coordination complexes when they are pressurized.

Example of both previous and current work ongoing in our group. $M(TpyNO_2)(NO_3)_3(H_2O)\cdot THF$ (M = Ln, Am, Cm, Bk, Cf); $TpyNO_2$ = 4'-nitrophenyl terpyridyl) have been prepared from the reaction of $M(NO_3)_3\cdot nH_2O$ with $TpyNO_2$ in THF. Structural analysis shows that the metal centers are ten-coordinate, providing the first examples of Am^{III}, Cm^{III}, Bk^{III}, and Cf^{III} with this coordination number. Further spectroscopic and theoretical evaluation of these complexes reveals utilization of the 5*f* orbitals in bonding in the actinide complexes and even more surprisingly with Ce^{III}. Comparison of Nd–L, Eu–L, and Am–L bond distances demonstrates that some caution should be taken in comparing Eu^{III} versus Am^{III} in extraction experiments. The structure of

$M(TpyNO_2)(NO_3)_3(H_2O)\cdot THF$ is shown in Figure 1. Will demonstrate that these complexes actually change the symmetry of the ground states expected for certain *f*-ions. For example, we can induce axial symmetry in Ce^{III} complexes. Berkelium is the closest electrochemical analog of cerium and we have expanded this family to include a well characterized berkelium complex. We will provide examples of the stabilization/destabilization of the III/IV oxidation states in these systems.

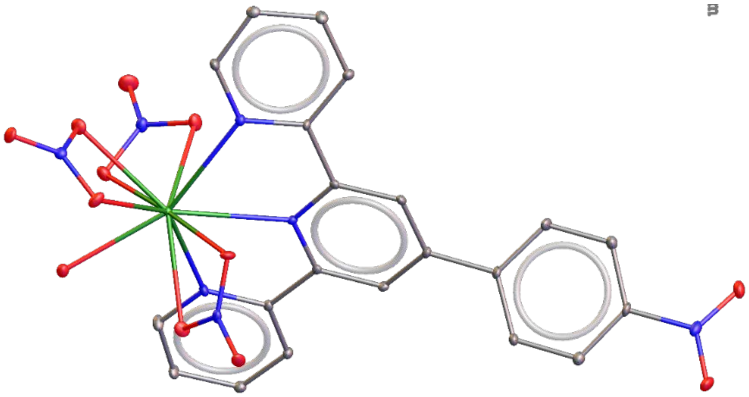

Figure 1. Crystal structure of $[M(TpyNO_2)(NO_3)_3(H_2O)]\cdot THF$ (M = Ln, Am, Cm, Bk, Cf) shown with the 50% ellipsoid probability. Hydrogen atoms and the co-crystallized THF molecule have been omitted for clarity.

Future Goals (this is the basis of our renewal):

Our hypotheses are that 1) the bonding, and perhaps even the intrinsic nature of the ground states, of actinide coordination complexes can be modified through ligation by chelators that possess large hyperpolarizabilities because the polarization of electron density allows for the creation of covalent bonds even in systems that are normally mostly ionic. 2) In both these and simpler complexes the nature of the An–L bonds can be demonstrably altered by compression under high pressures because frontier metal orbitals can be engaged to a greater degree than possible under ambient conditions and orbital mixing can also be enhanced. Thus, both hypotheses are aimed at deliberate augmentation of covalent bonding in actinide molecules. If these postulates are correct we should observe spectroscopic features, magnetic behavior, and bond distances different from that found in currently known in actinide complexes. Furthermore, the origin of these alterations should be identifiable by theoretical examination of electronic structure. The projects and associated questions that we seek to answer within these hypothetical envelops are as follows:

- 1) Can conjugated, donor/acceptor ligands with large hyperpolarizabilities be used to create covalent bonds with *f*-block elements where they are normally absent and enhance them where they are already present?
- 2) Can the nature of actinide-ligand bonds be experimental quantified and theoretically buttressed?
- 3) Can the pressures that are achievable using diamond-anvil cells (DACs) be used to decrease An–L bond lengths and increase hybridization of metal frontier orbitals with ligand orbitals?

Selected publications supported by this project 2017-2019

1. S. S. Galley, J. M. Sperling, C. J. Windorff, M. Zeller, T. E. Albrecht-Schmitt, S. C. Bart, "Conversion of Americia to Anhydrous Trivalent Americium Halides," *Organometallics*, **2019**, *38*, 606-609. **DOI:** 10.1021/acs.organomet.8b00840
2. F. D. White, C. Celis-Barros, J. Rankin, E. Solís-Céspedes, D. Dan, A. N. Gaiser, Y. Zhou, J. N. Colangelo, D. Páez-Hernández, R. Arratia-Pérez, T. E. Albrecht-Schmitt, "Molecular and Electronic Structure, and Hydrolytic Reactivity of a Samarium(II) Crown Ether Complex," *Inorg. Chem.*, **2019**, *ASAP*. **DOI:**10.1021/acs.inorgchem.8b03566
3. E. Warzecha, C. Celis-Barros, T. E. Albrecht-Schmitt, "High-Pressure Studies of Cesium Uranyl Chloride," *Inorg. Chem.*, **2019**, *58*, 228-233. **DOI:** 10.1021/acs.inorgchem.8b02300
4. S. S. Galley, S. A. Pattenaude, C. A. Gaggioli, Y. Qiao, J. M. Sperling, M. Zeller, S. Pakhira, J. L. Mendoza-Cortes, E. J. Schelter, T. E. Albrecht-Schmitt, L. Gagliardi, S. C. Bart, "Synthesis and Characterization of Tris-Chelate Complexes for Understanding *f*-Orbital Bonding in Later Actinides," *J. Am. Chem. Soc.*, **2019**, *141*, 2356-2366. **DOI:** 10.1021/jacs.8b10251
5. F. D. White, A. N. Gaiser, E. J. Warzecha, J. M. Sperling, C. Celis-Barros, S. R. Salpage, Y. Zhou, T. Dilbeck, A. J. Bretton, D. S. Meeker, T. E. Albrecht-Schmitt, "Examination of Structure and Bonding in 10-Coordinate Europium and Americium Terpyridyl Complexes," *Inorg. Chem.*, **2018**, *57*, 12969-12975. **DOI:** 10.1021/acs.inorgchem.8b02085
6. M. A. Silver, S. K. Cary, A. J. Garza, R. E. Baumbach, A. A. Arico, G. A. Galmin, K.-W. Chen, J. A. Johnson, J. C. Wang, R. J. Clark, A. Chemey, T. M. Eaton, M. L. Marsh, K. Seidler, S. S. Galley, L. van de Burgt, A. L. Gray, D. E. Hobart, K. Hanson, S. M. Van Cleve, F. Gendron, J. Autschbach, G. E. Scuseria, L. Maron, M. Speldrich, P. Kögerler, C. Celis-Barros, D. Páez-Hernández, R. Arratia-Pérez, M. Ruf, T. E. Albrecht-Schmitt, "Electronic Structure and Properties of Berkelium Iodates," *J. Am. Chem. Soc.*, **2017**, *139*, 13361-13375. **DOI:** 10.1021/jacs.7b05569
7. S. K. Cary, R. E. Baumbach, J. N. Cross, J. T. Stritzinger, M. J. Polinski, T. E. Albrecht-Schmitt, "Incipient Class II Mixed-Valency in a Plutonium Solid-State Compound," *Nature Chemistry*, **2017**, *9*, 856-861. **DOI:** 10.1038/nchem.2777

Thermochemistry and Reactivity of Atomic and Molecular Actinides

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Overall research goals: The objective of this project is to measure thermodynamic information on small gas-phase molecules containing the actinides, thorium and uranium, using guided ion beam tandem mass spectrometry (GIBMS). The results act as benchmarks for comparison to high level ab initio calculations performed in-house and by our collaborators.

Recent Progress during 2014-2019: The project has focused initially on the chemistry of thorium and reactions with H_2, D_2, HD, O_2, CO, CH_4, CD_4, and D_2O have been characterized.

1. Kinetic energy dependent reactions of Th^+ with H_2, D_2, and HD were studied using GIBMS.[2] Formation of ThH^+ and ThD^+ was endothermic in all cases with similar thresholds. Branching ratio results for the reaction with HD indicate that Th^+ reacts via a statistical mechanism, which is similar to its third-row transition metal congener Hf^+. The kinetic energy dependent cross sections for formation of ThH^+ and ThD^+ were evaluated to determine a 0 K bond dissociation energy (BDE) of $D_0(Th^+\text{-}H) = 2.45 \pm 0.07$ eV. Compared to its transition metal congeners, TiH^+, ZrH^+, and HfH^+, the ThH^+ BDE is larger, a result attributed to the effects of lanthanide contraction. Spin-orbit (SO) contributions to the BDE were calculated empirical and explicitly, and agree nicely (0.18 and 0.17 eV, respectively), suggesting that effective SO corrections can be made without requiring a detailed high-level calculation for all systems. Theory also provided the potential energy surfaces for the $Th^+ + H_2$ reaction, and conclude that the reaction can proceed without a barrier in excess of the reaction endothermicity, requires avoided crossings between surfaces of different electronic configurations.

2. Kinetic energy dependent reactions of Th^+ with O_2 and CO were studied using GIBMS.[4] The formation of ThO^+ in the reaction of Th^+ with O_2 is observed to be exothermic, barrierless, and efficient. Formation of ThO^+ and ThC^+ in the reaction of Th^+ with CO is endothermic in both cases and can be evaluated to determine $D_0(Th^+\text{-}O) = 8.57 \pm 0.14$ eV and $D_0(Th^+\text{-}C) = 4.82 \pm 0.29$ eV. Our value for ThO^+ is within experimental uncertainty of literature values and can be combined with very precise values for IE(Th) and IE(ThO) to give $D_0(Th\text{-}O) = 8.87 \pm 0.14$ eV. This value suggests that the lower values of $D_0(Th\text{-}O)$ in the literature are probably more accurate. A number of theoretical approaches to describing the thermochemistry of these species was also included in this work.[4] The most accurate came from composite thermochemistry outlined in the Feller-Peterson-Dixon method (FPD), which includes complete basis set extrapolations, core correlation contributions, explicit SO corrections, quantum electrodynamic effects (Lamb shift), and triple and quadruple excitations (CCSDTQ) with values for ThC^+, ThO^+, and ThO that agree with the present experimental values within their uncertainties.

3. The reaction of atomic thorium cations with CH_4 (CD_4) and the collision-induced dissociation (CID) of $ThCH_4^+$ with Xe were studied using GIBMS.[1] In the methane reactions at low energies, $ThCH_2^+$ ($ThCD_2^+$) is the only product; however, the energy dependence of the cross section is inconsistent with a barrierless exothermic reaction as previously assumed on the basis of ICR-MS results; however, the present results are consistent with the very small reaction efficiencies (0.009 ± 0.005 and 0.02 ± 0.01) found in those previous studies, as shown in Figure 1 where our

cross sections have been converted to rate coefficients, as described elsewhere. The dominant product at higher collision energies is ThH^+ (ThD^+) with $ThCH_3^+$ ($ThCD_3^+$) having a similar threshold energy. The latter product subsequently decomposes at still higher energies to $ThCH^+$ ($ThCD^+$). CID of $ThCH_4^+$ yields atomic Th^+ as the exclusive product. The cross sections of all product ions are modeled to provide 0 K bond dissociation energies (in eV) of $D_0(Th^+\text{-}H) \geq 2.25 \pm 0.18$, $D_0(Th^+\text{-}CH) = 6.19 \pm 0.16$, $D_0(Th^+\text{-}CH_2) \geq 4.54 \pm 0.09$, $D_0(Th^+\text{-}CH_3) = 2.60 \pm 0.30$, and $D_0(Th^+\text{-}CH_4) = 0.47 \pm 0.05$. Quantum chemical calculations at several levels of theory are used to explore the potential energy surfaces for activation of methane by Th^+ and the effects of SO coupling are carefully considered. The highest level of theory yields results in good agreement with experiment. Without considering SO coupling, no barrier for dehydrogenation of methane by Th^+ is found, inconsistent with the present experimental results. When explicit consideration of SO interactions are included, a barrier for C-H bond activation that matches the threshold measured for $ThCH_2^+$ formation (0.17 ± 0.02 eV) is found. The observation that CID of the $ThCH_4^+$ complex produces Th^+ as the only product with a threshold of 0.47 eV indicates that this species has a $Th^+(CH_4)$ structure, which is also consistent with a barrier for C-H bond activation. This barrier was explained as resulting from the mixed (^4F,^2D) electronic character of the Th^+ $J = 3/2$ ground level combined with extensive SO effects. Notably, our theoretical results agreed reasonably well with two previous theoretical studies, although these studies came to different conclusions regarding the origins of the low reactivity of Th^+ with CH_4. The discrepancies among the studies are largely resolved by including SO interactions, which had not been considered in the previous theoretical work).

4. The reaction of atomic thorium cations with D_2O were studied using GIBMS.[5] At thermal energies, both $ThO^+ + D_2$ and $DThO^+ + D$ are formed in a ratio that reproduces previous ICR-MS experiments. As the energy available is increased, the dominant product changes from ThO^+ to $DThO^+$ and back to ThO^+ until the $ThD^+ + OD$ channel opens and dominantes, Figure 1. The complicated kinetic energy dependent branching ratio is interpreted successfully using phase space theory (PST) (in which angular momentum is explicitly conserved) and the allows the measurement of the energies for two competing transition states that lead to the final products. These energies are compared with those obtained theoretically, and good agreement requires including SO efforts. These reactions provide the first step in the hydration of the thorium cation.

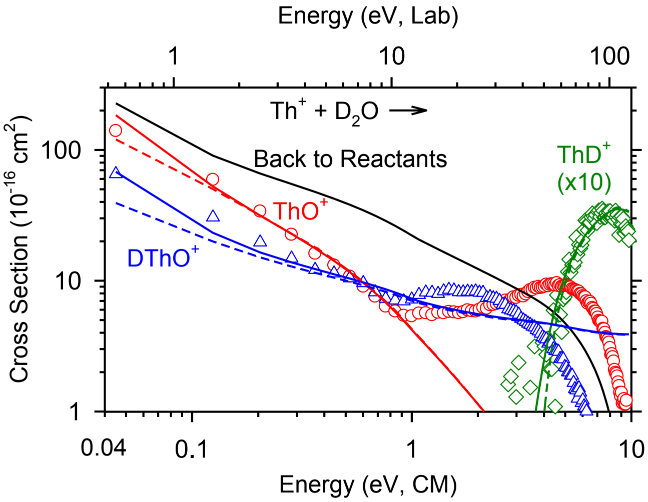

Fig. 1. Reaction rate for $Th^+ + D_2O$ plotted as a function of kinetic energy. Experimental data (points) are compared to PST (lines).

5. Further hydration of Th^+ has been examined using GIBMS.[6] Both ThO^+ and ThO_2^+ are found to react with D_2O to form $OThOD^+$ as the dominant product in barrierless, exothermic reactions. $OThOD^+$ then reacts with D_2O to form $ThO_3D_3^+$ in an association reaction. The CID of $OThOD^+$ with Xe is also examined. Analysis of the kinetic energy dependence of these cross sections leads to thermochemistry for $OTh^+\text{-}D$, $OTh^+\text{-}O$, $OTh^+\text{-}OD$, and $OThOD^+\text{-}D_2O$ bonds. Theory provides bond energies in reasonable agreement with experiment and is also used to examine the potential energy surfaces for these reactions. This comparison also establishes that the $ThO_3D_3^+$ species is the tri-hydroxide, $Th(OD)_3^+$. Thus, the mechanisms for hydration of Th^+ to eventually form the $Th(OH)_3^+$ species have been fully elucidated with complementary energetics measured for all major steps.

Future Plans for 2019-2020:

- Experiments have been completed for the hydration energies of $Th(OH)_3^+$ with up to three added water molecules. This bridges the gas-phase work with solution phase chemistry. This work and associated theory is being written up for publication.
- Collision-induced dissociation studies of $Th^+(CO)_n$ where $n = 1 – 6$ with Xe have been completed. This work and associated theory is being written up for publication.
- Experiments have also been completed for reactions of U^+ with H_2, D_2, HD, O_2, CO, and CF_4, which will provide thermochemistry for UH^+, UC^+, UO^+, UF_x^+ and UF_x ($x = 1 – 3$).

Recent Publications Resulting from This Project 2014-2019

1. "Activation of CH_4 by Th^+ as Studied by Guided Ion Beam Mass Spectrometry and Quantum Chemistry" Cox, R. M.; Armentrout, P. B.; de Jong, W. A. *Inorg. Chem.* **2015**, *54*, 3584–3599. DOI: 10.1021/acs.inorgchem.5b00137
2. "Reactions of $Th^+ + H_2$, D_2, and HD Studied by Guided Ion Beam Tandem Mass Spectrometry and Quantum Chemical Calculations" Cox, R. M.; Armentrout, P. B.; de Jong, W. A. *J. Phys. Chem. B* **2016**, *120*, 1601-1614. DOI: 10.1021/acs.jpcb.5b08008
3. "Activation of Carbon Dioxide by a Terminal Uranium-Nitrogen Bond in the Gas-Phase: A Demonstration of the Principle of Microscopic Reversibility" Dau, P. D.; Armentrout, P. B.; Michelini, M. C.; Gibson, J. K. *Phys. Chem. Chem. Phys.*, **2016**, *18*, 7334-7340. DOI: 10.1039/C6CP00494F
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5. "Activation of Water by Thorium Cation: A Guided Ion Beam and Quantum Chemical Study" Cox, R. M; Armentrout, P. B. *J. Am. Soc. Mass Spectrom.* in press.
6. "Mechanism and Energetics of the Hydration of Th^+ to Form $Th(OD)_3^+$: Guided Ion Beam and Theoretical Studies of ThO^+, ThO_2^+, and $OThOD^+$ Reacting with D_2O" Kafle, A.; Armentrout, P. B. in preparation.

Computational studies of magnetism and spectra of actinide complexes

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Overall research goals:

In this project, we investigate the electronic structures as well as spectroscopic and magnetic properties of chemical compounds with 5f-elements, i.e. actinides, by quantum theoretical calculations. The main objective is to learn how the observable magnetic and spectroscopic properties are related to the geometrical structure of the molecules, their chemical bonding, and the nature of the ground and excited electronic states. We develop and apply state-of-the-art relativistic theoretical methods for computations of magnetic resonance parameters (electron paramagnetic resonance = EPR, nuclear magnetic resonance = NMR), magnetic susceptibilities, as well as valence and core excitation spectra (UV-vis spectroscopy & XAS) and magnetic field-induced circular dichroism (MCD). A major focus is the involvement of the actinide 5f shell in the chemical bonds. The project goals include developments of new relativistic quantum chemical methods in the open-source NWChem and Molcas quantum chemistry packages, along with new stand-alone open-source software.

Recent Progress:

A few months ago we reported a study of X-ray absorption spectra (XAS) of actinide complexes, AnO_2^{2+} with An = U, Np, Pu, (metal M edges) and $AmCl_6^{3-}$ (metal M edge and Cl K edge), based on relativistic multi-reference wavefunction calculations that include spin-orbit coupling (SOC) effects. A newly developed program allowed us to analyze the chemical bonding in the ground state and in the core-excited states directly based on the relevant wavefunctions. We showed that the experimental spectra for the actinyl species, reported in 2017, had been incorrectly interpreted as showing a loss of 5f overlap covalency when going from U to Pu. In agreement with prior assumptions derived from experiments and calculations, we found that in the ground states the overlap covalency increases from U to Pu. However, the core-excited states undergo strong orbital relaxations, which reduce the covalent bonding. When this is not taken into account, the experimental spectra are easily misinterpreted.

In 2017 we started to develop new theoretical methods that allow for the calculation of magnetic field-induced circular dichroism (MCD) in electronic transitions. The methods utilize multi-reference wavefunctions with SOC and are therefore ideally suited for actinide research. Unlike natural circular dichroism, MCD is not limited to chiral molecules, i.e. it can be observed generally. The MCD signal is often able to resolve multiple electronic transitions within a broad UV-vis absorption band. Therefore, MCD is among the primary experimental tools for assigning complicated valence excitation spectra of open-shell metal complexes. It is also possible to extract excited-state EPR g-factors from MCD data. However, the spectra can be difficult to interpret and their analysis benefits greatly from theoretical support. Our collaborator Michael Neidig (Rochester U.) performs the measurements. As a proof of concept, we calculated the low-temperature MCD spectrum of the $5f^1$ complex UCl_6^-. The calculations reproduced the measured spectrum well and allowed us to assign the observed bands predominantly as ligand-to metal charge transfer. However, one of the observed bands is likely caused by 5f to 6d metal-centered transitions. A second application of the new MCD program focused on the spectra of [K(2.2.2-cryptand)][LnCp'$_3$] (Ln = Y, La, Pr, Eu, Gd; Cp' = $C_5H_4SiMe_3^-$) synthesized in the laboratory of W. J. Evans, which contain ions in the formal +2 oxidation state. These complexes were assigned having a $4f^n5d^1$ electron configuration, unlike the traditional $4f^{n+1}$ configuration of the long known Eu(II) ion. Transitions with f-orbital character were observed in the NIR MCD spectra of the $4f^25d^1$ complex $[PrCp'_3]^-$. These signals are much broader than would be predicted for pure f-f transitions, suggesting significant 4f/5d mixing. This is supported by the calculations.

Another new theoretical method development focused on dipole-forbidden 5f-5f transitions in the near-infrared spectral region. Multi-reference wavefunction calculations with SOC, in combination with Kohn−Sham density functional calculations of vibrational modes, were used to determine the vibronic and electronic absorption intensities of the near-infrared electric dipole-forbidden 5f−5f transitions of representative uranium(V) hexa-halide complex ions. The agreement with experimentally assigned vibronic and electronic was reasonable overall, and excellent for the experimentally best-resolved E 5/2u → E′ 5/2u bands. We showed that the intensity of the vibronic transitions may be borrowed from ligand-to-metal charge-transfer excitations as well as 5f-to-6d metal-centered transitions. The experimental spectra also show purely electronic peaks, which we reproduced and assigned as magnetic dipole transitions.

We performed ab-initio molecular dynamics simulations, accompanied by NMR calculations, in order to study solvent and dynamical effects on the ^{13}C and ^{17}O chemical shifts and 17O quadrupolar line widths of uranyl and uranyl carbonate complexes in aqueous solution. One takeaway from the study is that the quadrupolar broadening of the ^{17}O signals of the carbonate ligands is dominated by the internal dynamics of the complexes, not by the solvent dynamics. The 'yl'-oxygen NMR shifts are strongly altered by solvent effects.

In collaboration with E. Batista and P. Yang, and with additional financial support of my student Tom Duignan by Los Alamos National Laboratory (LANL), we performed a joint investigation of the impact of the DFT delocalization error (DE) on core and valence excitation spectra of uranium complexes. A non-empirical 'tuning' approach designed to minimize the DE was found to improve the valence spectra considerably, without deteriorating the core excitation spectra. The procedure is therefore a suitable workaround for commonly encountered problems in DFT calculations that will eventually need to be address at a more fundamental level by the developers of density functionals. Two additional collaborative studies with experimental groups resulted from the visit of Tom Duignan at LANL. For one study, with J. M. Boncella and coworkers, we performed wavefunction calculations of the EPR g-tensor of a pseudo-tetrahedral U(V) complex, along with DFT calculations of core and valence excitation spectra. For another study, with J. R. Walensky and coworkers, we calculated and analyzed electronic spectra of a series of mono- abd bis-phosphido Th(IV) complexes in order to rationalize their observed changes in color upon varying substituents in the ligands.

A series of joint experimental-theoretical publications resulted from a collaboration with C. L. Cahill, his student R. G Surbella, III, and others, on the supramolecular assembly of uranium and trans-uranium materials, and how hydrogen and halogen bonding directs the structure of the molecular crystals. In a study of uranyl thiocyanates, the calculations helped linking an observed thermochromism to the temperature-dependent structural interactions in the solid influencing the absorption spectra.

In collaboration with T. Albrecht-Schmitt and his team, we studied the electronic structure, magnetic properties, and chemical bonding in berkelium III and IV iodate complexes, using SOC multi-reference wavefunction calculations. The Bk(III) centers showed an extremely strong magnetic anisotropy. The Bk(IV) centers exhibited some degree of covalency with the iodate oxygen atoms.

In a joint experiment-theory collaboration with N. Cheng, J. Li, and others, we studied the U—C bonding in the interesting system UCU@C_{80}. The calculations assign the U centers in the encapsulated UCU moiety as weakly coupled U(V) ions.

In a long article published in Chem. Sci., we investigated the similarities and differences between the metal-ligand bonding in the 5f1 system $U(C_7H_7)_2^-$ (`Ucene') and the transition metal sandwich complexes $M(C_5H_5)_2$ with M = V, Co, Ni. It was speculated previously that the metal-ligand bonding in Ucene is very similar to cobaltocene, because both have a negative isotropic ligand proton hyperfine coupling constant (HCC) around ca. -2.5 MHz. If the HCC is interpreted in terms of metal to ligand or ligand to metal spin declocalization, this would indeed require similar bonding. However, the electron spin contribution to the HCC in Ucene is positive, like in vanadocene, while there is a large negative contribution from the orbital angular momentum at U which is induced by SOC. Such a SOC effect is not present in the metallocenes, as they have much smaller nuclear charges. The study contributes to a better understanding of actinide 5f vs. transition metal 3d covalency, and highlights potential pitfalls when interpreting experimental magnetic resonance data in terms of covalent bonding for actinide complexes.

Future plans:

The new theoretical methods for analyzing the bonding in multi-reference SOC wavefunction calculations will be applied to other available XAS spectra of actinide complexes, in order to confirm whether the spectra indeed indicate 5f covalency, or a lack thereof. These theoretical tools will also be used extensively in our on-going collaborations with experimental groups in order to assign the bonding in open-shell actinide complexes based on accurate wavefunction calculations. In the collaboration with Neidig on MCD, we will investigate UL_6^{2-} (L = aryl or alkyl) complexes for which the experimental data are already available, and how charge-transfer MCD spectra change when going from highly symmetric complexes such as UCl_6^- or UL_6^{2-} to complexes with mixed ligands. Another focus will be on the magnetically (or quadrupole-) allowed and vibronically allowed MCD of 5f-5f transitions. These studies will be important to establish the interpretation of MCD spectra for actinide complexes more generally. We will continue our investigations of the magnetic susceptibilities of AnO_2 materials with the help of multi-reference wavefunction calculations based on cluster models. There are also on-going experimental efforts to measure the quadrupole transitions of An and ligand isotopes (`NMR without a magnetic field') that we support with calculations of the associated electric field gradient tensors.

Recent Publications Resulting from this Project (a selection)

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Uranyl Capture and Activation with Lewis Acids and Macrocyclic Hosts

Award DE-SC0019169
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Overall Research Goals

The overall objective of this project is to harness knowledge of chemical structure and bonding to develop a useful and predictive understanding of the fundamental parameters that govern bond activation at a common form of uranium, the unique uranyl ion (UO_2^{2+}). Quantitative control of these parameters is being pursued by elucidation of the electrochemical properties of targeted uranyl-containing compounds, plus related lanthanide complexes that are providing insight into strategies for tightly binding large ions. Assembly of molecular structures containing the uranyl ion in close proximity to a second metal ion is also being pursued, a strategy inspired by metal-containing cofactors found in nature that engage in bond making and breaking with high efficiency. Electron- and group transfer reactions involving uranium are targeted for study in this work, including detailed electrochemical studies of diffusional heterobimetallic species in solution as well as more elaborate analogues immobilized on electrode surfaces.

Recent Progress

Electrochemical properties of surface-immobilized molecular lanthanide and uranyl complexes

One area of heavy-element chemistry that has received less attention than it deserves is that of surface immobilization of molecular complexes on electrode surfaces. Such compounds could serve as models for study of electron transfer, and as prototype assemblies for separation of challenging ions from mixtures. Moreover, capabilities associated with selective immobilization of complexes on surfaces could be useful in advancement of materials science relying on f-elements. As most prior surface-immobilization work has been carried out with complexes containing d-block metals,[1] we are turning toward a newer area by examining the surface immobilization of complexes containing metals from the f-block.[2]

Recently, we have synthesized and characterized four new tripodal lanthanide complexes, denoted **M(LTP)** (M = Ce, Nd, Sm, or Eu; see Chart 1) capable of undergoing noncovalent immobilization on graphitic surfaces. In the new lanthanide compounds that have been prepared, we have used the modular pyrene moiety to enable noncovalent immobilization on the surface. Characterization of the complexes by solution NMR has confirmed successful preparation of the compounds, while X-ray photoelectron (XP) spectroscopic studies carried out on electrodes prepared with the new compounds support that the lanthanide complexes retain their molecular structure after immobilization. Photoelectron peaks associated with all the expected elements have been measured in XP spectra (see Figure 2), and inspection of relevant high resolution data confirm the expected elemental ratios for the molecular compounds.

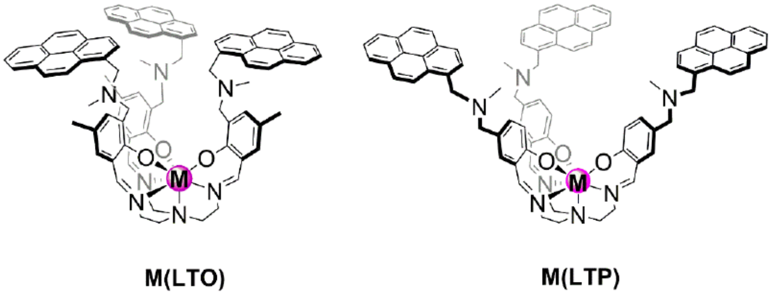

Chart 1. Representation of pyrene-appended lanthanide complexes discussed here. M = Ce, Nd, Sm, or Eu; **LTO** = Ligand, tripodal, *ortho*-position; **LTP** = Ligand, tripodal, *para*-position.

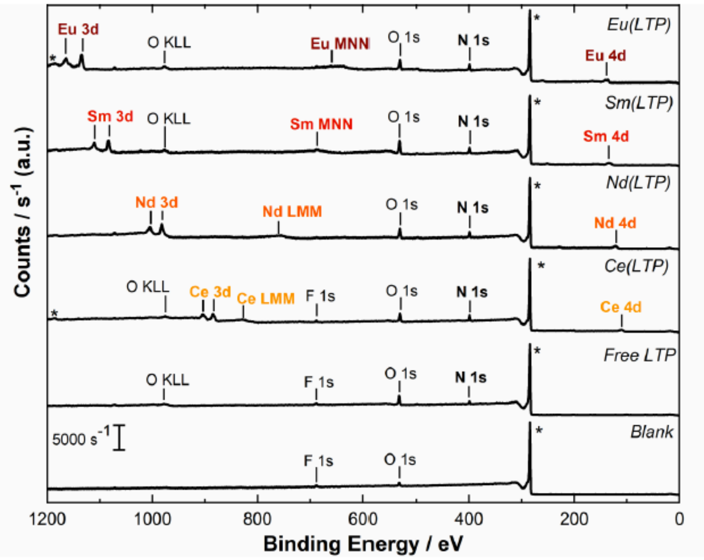

Figure 1. Stacked Al-source XP survey spectra for a blank carbon electrode and electrodes functionalized with free **LTP** and **M(LTP)** (M = Ce, Nd, Sm, Eu) complexes. Signals corresponding to the surface-bound complexes are highlighted in bold. Signals corresponding to carbon (C 1s photoelectron emission and C KLL Auger processes) are marked with (*).

Electrochemical studies of the redox-active cerium complex **Ce(LTP)**, which displays a reversible process at $E(\mathrm{Ce^{IV}/Ce^{III}}) = -0.19$ V vs. the ferrocenium/ferrocene couple, have enabled us to study the surface stability and interfacial electron transfer rate. In prior work from our group in this area,[2] the complexes **Ce(LTO)** was found to have only moderate stability on the electrode surface. Specifically, electrochemical studies of the **Ce(LTO)** complex revealed that the currents associated with the $\mathrm{Ce^{IV}/Ce^{III}}$ redox process significantly diminish in electrochemical experiments conducted over the course of minutes-to-hours. To explain this surface behavior, we previously hypothesized that the pyrene groups of the **LTO** framework prefer to interact with one another rather than participating in noncovalent interactions with the surface. The **LTP** framework was thus designed to disfavor the suspected aggregation of pyrene groups. Gratifyingly, the **Ce(LTP)** complex displays significantly improved surface stability, but a similar electron transfer rate. This finding supports the exciting notion that molecular design can be used to improve the stability of noncovalently immobilized molecular assemblies on electrode surfaces.

Building on experience gained from working with the lanthanide complexes described above, we have also been investigating the assembly and electrochemical properties of molecular uranyl complexes on electrode surfaces. For this undertaking, we have synthesized and characterized two new $[UO_2]^{2+}$ complexes (see Chart 2) using NMR and single-crystal X-ray diffraction (XRD). Notably, to the best of our knowledge, this work is the first to investigate the properties of molecular uranyl compounds immobilized on electrodes. We have found that the coordination of the uranyl moiety significantly contributes to the electrochemical properties of the immobilized compounds, much like in other classes of metal complexes that have been immobilized on electrode surfaces. Electrochemical methods have been used to probe the properties of the uranyl complexes using redox cycling association with the U^{VI}/U^{V} reductions for the compounds at ca. –1.6 V vs. ferrocenium/ferrocene. Appealingly, the complexes display enhanced surface stabilities compared to the tripodal lanthanide complexes, as well as high rates of interfacial electron transfer that we attribute to closer association with the surface than in the case of the tripodal **Ce(LTP)**.

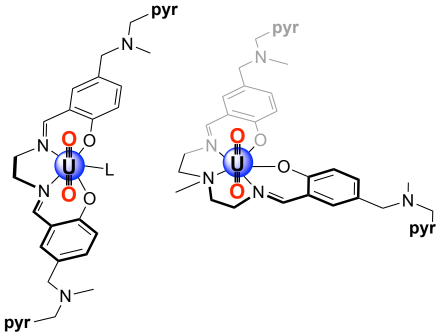

Chart 2. Representation of pyrene-appended uranyl complexes discussed here. L = dimethylformamide, pyr = pyrene.

Future Plans

X-ray photoelectron (XP) spectra have been collected for the entire family of immobilized lanthanide complexes **M(LTP)**, as well as for the ligands supporting the pyrene-appended uranyl complexes. However, arrangements are being made to collect XP spectra for the uranyl complexes. As XP spectroscopy is a high-vacuum technique, safety precautions center on the possible, but unlikely, volatility of the compounds and radiation considerations. Related work is also underway on preparation of heterobimetallic compounds containing the uranyl ion. This portion of the work is leveraging experience gained here with redox cycling of the monometallic uranyl complexes as well as related prior work from our group in studies of heterobimetallic systems,[3] to make progress on quantitively controlling the electrochemical properties of these uranyl-based systems.

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ATOMIC AND MOLECULAR ANIONS OF URANIUM AND THORIUM STUDIED BY NEGATIVE ION PHOTOELECTRON SPECTROSCOPY (DE-SC0019317)

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OVERALL RESEARCH GOALS

Our main research goals are to map both the ground and electronically-excited states of both neutral uranium and thorium atoms/molecules and their atomic/molecular anions using negative ion photoelectron spectroscopy. As a consequence, both electron affinities as well as copious electronic structure information about the anions' *neutral* counterparts will be provided. Our research goals focus on three categories of systems: (1) atomic anions of uranium and thorium, (2) small uranium- and thorium-containing molecular anions, and (3) exploratory investigations of vibronic coupling in polyatomic U- and Th-containing molecular anions.

(1) **Atomic Anions** Because of near-degeneracies among open atomic sub-shells as well as very strong spin-orbit interactions, one anticipates complex anion photoelectron spectra, these made even more challenging by the likely presence of long-lived electronically-excited anions. Using a unique combination of Rydberg electron transfer and anion photoelectron spectroscopy and tuning through Rydberg quantum numbers, one of our goals is to determine whether transitions originated from ground versus excited anion states, thus simplifying spectral assignments. These measurements will provide an extraordinary opportunity for our theoretical collaborators (Laura Gagliardi and Lan Cheng) to benchmark/validate computational methods used to study actinides.

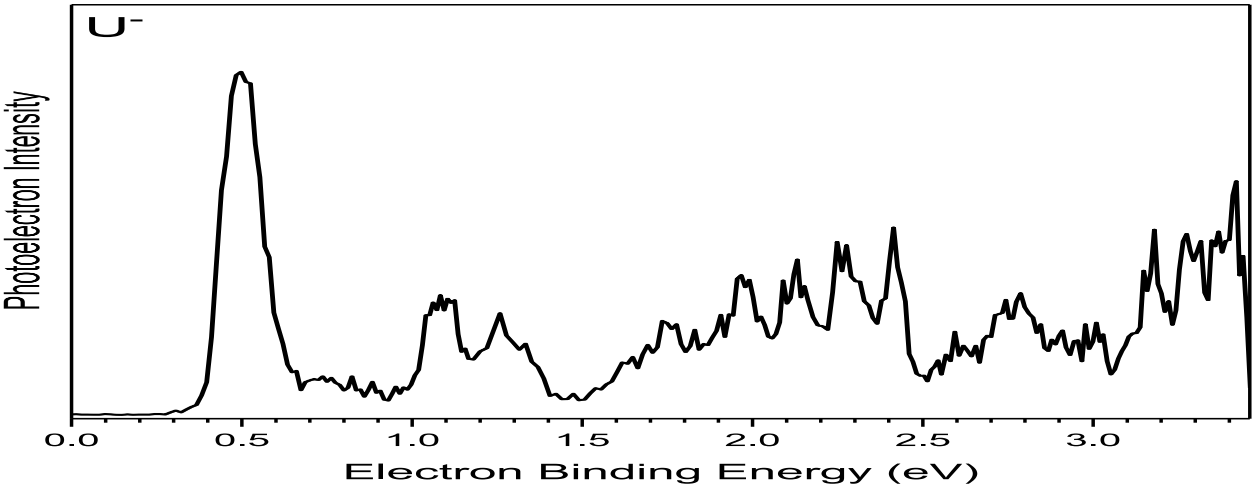
(2) **Small Molecular Anions** Even though anion photoelectron spectroscopy is conducted on anions, it also maps the ground and excited electronic states of the anions' *neutral* counterparts. Surveying the energies of the excited electronic states of U- and Th-containing *neutral* molecules will support the high-resolution spectroscopic studies of our collaborator, Tim Steimle, by greatly reducing the time it takes him to search for those states. Additionally, the photoelectron spectra of small molecular anions will provide our theory collaborators with even more opportunities to test and to develop their methods.

(3) **Vibronic Coupling in Polyatomics: Exploratory Studies** The role of vibronic coupling in the excited states of uranium- and thorium-containing polyatomic molecules is under-explored. Strong vibronic coupling effects are expected to reveal themselves in anion photoelectron spectra. By working symbiotically with our theoretical collaborators, we expect to shed light on this challenging topic.

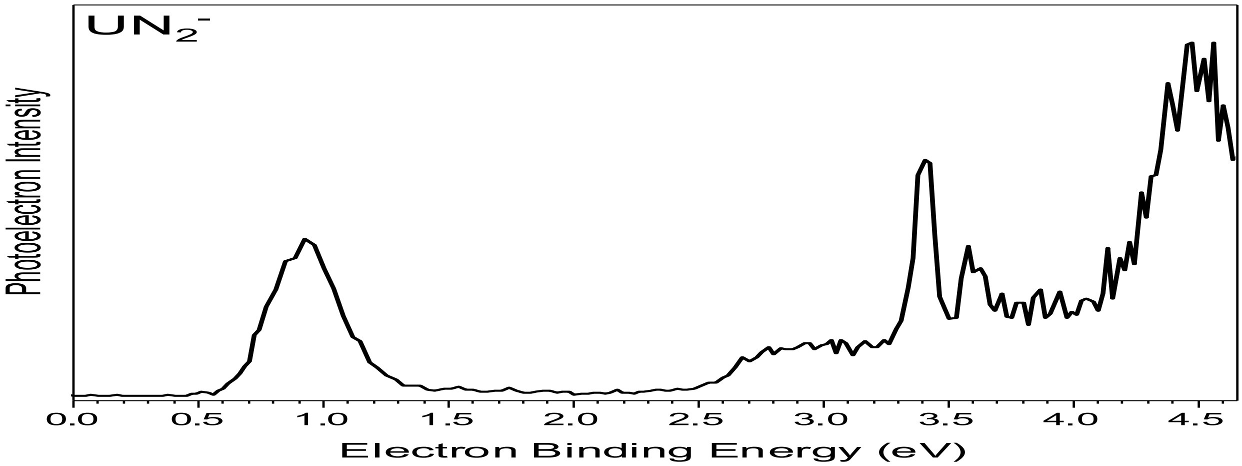
RECENT PROGRESS

We are still in the early stages of this project. Thus far, we have focused on obtaining appropriate uranium and thorium materials and on measuring mass spectra and *preliminary* negative ion photoelectron spectra using several ion sources. Below, there are two lists. In the first one, we tabulate anionic species for which we have both taken their mass spectra and measured their anion photoelectron spectra. In the second list, we tabulate anionic species for which we have taken only mass spectra thus far. The observation of their mass spectra indicates that we can make those specific species in molecular beams.

Anionic species for which we have measured anion photoelectron spectra thus far include the following; $\mathbf{U^-}$, $\mathbf{U_3^-}$, $\mathbf{U_4^-}$, $\mathbf{U_5^-}$, $\mathbf{U_6^-}$, $\mathbf{U_7^-}$, $\mathbf{U_8^-}$, $\mathbf{UH^-}$, $\mathbf{UC^-}$, $\mathbf{UC_2^-}$, $\mathbf{UO_2N^-}$, $\mathbf{UN^-}$, $\mathbf{UN_2^-}$ and $\mathbf{UO_2(C_2H_3O_2)]^-}$. The photoelectron spectrum of the atomic uranium anion, U^-, is shown below. It has permitted us to measure the electron affinity of the uranium atom *for the first time*. While preliminary, the simplest assignment would imply its electron affinity to be ~0.5 eV.



While the uranyl dication, UO_2^{2+}, is among the most important species in uranium chemistry, controversy surrounds theory's ability to characterize its electronic structure.[1] Moreover, there is no experimental electronic spectrum of bare UO_2^{2+} with which to benchmark and improve computational results. The uranyl dication, UO_2^{2+}, however, is isoelectronic to neutral UN_2. Both $[O{\equiv}U{\equiv}O]^{2+}$ and $N{\equiv}U{\equiv}N$ are linear molecules with two triple bonds each[2] and with the uranium atom in each in its VI (highest and most computationally tractable) oxidation state. The electronic spectrum of neutral UN_2 would thus be useful in validating calculations on UO_2^{2+}, these being carried out by increasingly sophisticated theoretical methodologies. The electronic spectrum of neutral UN_2 is revealed through the anion photoelectron spectrum of its anion, UN_2^-, since the photoelectron spectrum of an anion provides a mirror image of the electronic spectrum of its neutral counterpart, albeit at the structure of the anion and offset by the electron affinity of the neutral molecule. Our recently measured anion photoelectron spectrum of UN_2^- is presented below. My Hopkins faculty colleague and one of my theoretical collaborators, Lan Cheng, has conducted high level calculations on this system, finding the UN_2^- anion to have a bent structure (~155°) and a vertical detachment energy (VDE) of 0.8 – 0.9 eV. Inspection of our photoelectron spectrum of UN_2^- shows that it has a vertical detachment energy of ~0.9 eV and an estimated electron affinity (EA) for neutral UN_2 of ~0.7 eV. Previous calculations found the electron affinity of UN_2 to be 0.69 eV.[3] The spectral features to the high electron binding energy side of the EA/VDE-determining peak reflect the excited electronic states of neutral UN_2. Although computational adjustments will be required because of the differing structures of the UN_2^- anion (bent) and neutral UN_2 (linear), this anion photoelectron spectrum provides the electronic spectrum of neutral UN_2, from which calculations on the electronic spectrum of UO_2^{2+} can be benchmarked.



1. S. Zhang and F. Wang, *J. Phys. Chem. A* **121**, 3966 (2017).
2. While the classic bonding description for UO_2^{2+} is $[O=U=O]^{2+}$, it has three pairs of electrons in bonding orbitals, and is generally described as having two sets of triple bonds, i.e., as $[O{\equiv}U{\equiv}O]^{2+}$. (Among the two triple bonds between U and O, one of their bonds may be viewed as a dative bond in each case.) See P. Pyykko, j. li, and N. Runeberg, *J. Phys. Chem.* **98**, 4809 (1994).
3. P. Tecmer, A. S.P. Gomes, S. Knecht, and L. Visscher, *J. Chem. Phys.* **141**, 041107 (2014).

Anionic species for which we have observed mass spectra alone include; **UO_2^-, UO_3^-, UO_3N^-, $U_3O_n^-$, $U_4O_n^-$, $U_5O_n^-$, $U_6O_n^-$, $U_7O_n^-$, and $U_8O_n^-$** .

Interestingly, we make only negligible intensities of U_2^-. Given that the electronic configuration of U as $f^3d^1s^2$, we suspect that U_2 and U_2^- are much like Mg_2 and Mg_2^-. The neutral magnesium dimer has only a van der Waals bond (no covalent bond). The magnesium dimer anion has not been not observed.

FUTURE PLANS

In addition to pursuing our proposed goals as outlined above, we also have several new directions that we plan to explore.

Ligands can change the relative ordering of high lying orbitals. Having had success in tuning the electronic properties of cobalt sulfide super-atoms by ligand substitution,[4] we plan to employ this tactic to tune electronic properties of uranium and thorium.

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Gallic acid is a bidentate chelating agent which binds well with hydrated uranyl ions and which has been used in nuclear site clean-up and human detoxification efforts. It is known to be even more effective when binding plutonium complexes. We have plans to study gallate-uranyl anionic complexes as isolated (gas-phase) species, generating them via electrospray and characterizing them using anion photoelectron spectroscopy and synergetic computations.

Uranium hexafluoride, UF_6, remains the principal compound used in isotope separation. UF_6 is unusual in several ways. It possesses a high electron affinity, it appears to have a plasmon resonance, access to which leads to its rapid dissociation in multiply-charged atomic cations, and it does not attach low energy free electrons, despite the fact that both charge transfer and surface ionization make copious amounts of UF_6^-. We plan to study several aspects of this mysterious molecule, starting with investigating whether state-tuned Rydberg electron transfer will be able to attach ultra-slow electrons to it to form its anion, UF_6^-.

PUBLICATIONS

None yet, but one in preparation.

Neptunyl and Uranyl Oxide Clusters, Uranyl Structures from Nature, and Thermodynamic Studies Extending into the Transuranium Elements

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Overall research goals

The objectives of this project are to synthesize U(VI) and Np(V)/Np(VI) nanoclusters with well-defined structures to exert nanoscale control of actinides, to study new uranyl minerals with fascinating structures and compositions, to conduct calorimetric studies of actinide compounds extending into the transuranium elements, and to train graduate students in actinide chemistry.

Recent Progress

Two decades ago Burns *et al.* published a structural hierarchy of 180 inorganic uranyl compounds and minerals, as well as an evaluation of the polyhedral geometries and bond-valence parameters of U(VI). Subsequently, Burns published an updated and expanded hierarchy of 350 inorganic uranyl compounds, including minerals, in 2005. We (post-doctoral researcher Aaron Lussier, graduate student Rachel Lopez, and Burns) completed a massive redo of the hierarchy, which now includes more than 750 compounds. The published 105 page article includes color illustrations of all of the unique structural units, and elucidates relationships across vast ranges of structures.

Our studies of uranium mineralogy have been particularly fruitful, with publication of structures and descriptions of paddlewheelite, ewingite, gauthierite, and leószilárdite. Ewingite, $Mg_8Ca_8(UO_2)_{24}(CO_3)_{30}O_4(OH)_{12}(H_2O)_{138}$, was discovered in the classic Jáchymov locality in Czech Republic. It is interesting to note that the uranium ore that was studied by Marie Curie, that led to the discovery of radium and polonium, was from this locality. The structure of ewingite contains the only example of a nanoscale uranyl-based cage cluster found in Nature. The cage is constructed from trimers of uranyl polyhedra, as well as uranyl dicarbonate and uranyl tricarbonate units and Ca polyhedra (Fig. 1a). In all there are 24 uranyl polyhedra in the cluster, which is 2.3 nm in diameter. The novel combination of uranyl trimers and two types of uranyl carbonate units appears to constrain the pH of the parent solution to close to 8. According to the structure complexity concepts developed by Krivovichev, ewingite is the most complex mineral structure known. It was featured on the cover of *Geology* in December 2017.

Paddlewheelite, $MgCa_5Cu_2(UO_2)_4(CO_3)_{12}(H_2O)_{33}$, also from Jáchymov, contains a finite cluster consisting of four uranyl tricarbonate units connected through Cu^{2+} cations in square pyramidal coordination (Fig. 1b). Gauthierite, $KPb[(UO_2)_7O_5(OH)_7](H_2O)_8$, from Shinkolobwe, contains sheets of uranyl pentagonal bipyramids that are topologically unique and intermediate between those of fourmarierite and vandendriesscheite (Fig. 1c). Leószilárdite, $Na_6Mg(UO_2)_2(CO_3)_6(H_2O)_6$, is another example of a uranyl tricarbonate mineral and was found in Red Canyon (Utah).

We solved the crystal structure of swamboite, $Nd_{0.333}[(UO_2)(SiO_3OH)](H_2O)_{2.5}$, which is very complex because it is a (3+3) commensurately modulated structure. In collaboration with a

Canadian group, we studied natural uranium oxide nanoparticles and their role in mobilization of uranium.

Philip Smith's doctoral work resulted in three published papers concerning the synthesis, structures, and spectroscopy of novel neptunyl and uranyl compounds, with detailed analysis of the impact of structural unit charge density on the overall structures. Former post-doctoral fellows Zhang and Senchyk's work concerning porous uranium diphosphonates was also published. Finally, a novel bismuth phosphate that was encountered unexpectedly was characterized structurally and spectroscopically and published as a communication in *Inorganic Chemistry*.

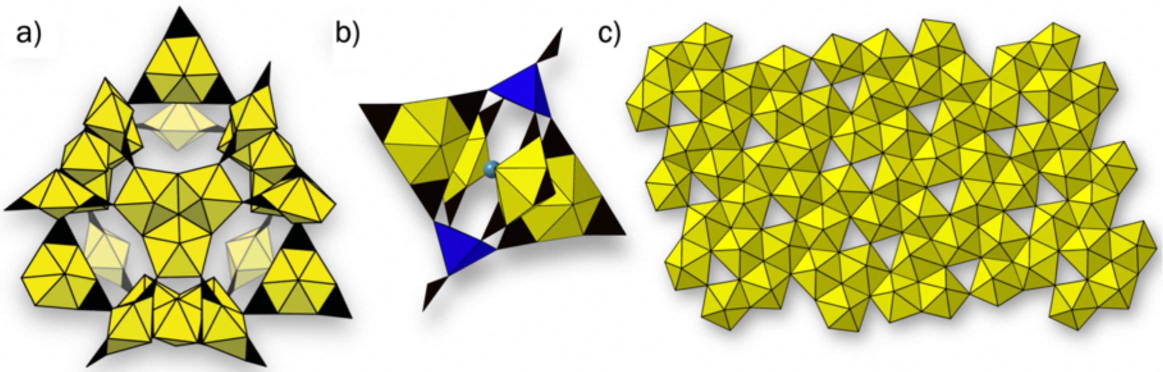

Fig. 1. Structural units in ewingite (a), paddlewheelite (b), and gauthierite (c). Uranyl, carbonate, and copper polyhedra are shown in yellow, black, and blue, respectively.

Future Plans

Following our success synthesizing a wheel-shaped uranyl vanadyl cluster containing 10 sulfate groups $\{U_{20}V_{20}\}$, we have been exploring syntheses using 3-ethyl-1-methylimidazolium with either diethyl phosphate or bistriflimide. The first of these approaches produced a series of very interesting clusters that include $\{U_8V_6\}$, $\{U_6V_3\}$ and $\{U_3V_6\}$ shown in Fig. 3. In each case the cluster consists of uranyl pentagonal bipyramids, vanadate square pyramids, and ethyl phosphate tetrahedra. Application of mild heat (80-100°C) resulted in assembly of the bowl-shaped $\{U_8V_6\}$ clusters into larger structural units, such as a helical chain. In our initial synthesis of $\{U_{20}V_{20}\}$, it is clear that the ethyl sulfate from the ionic liquid is an important constituent for its formation as it was the only sulfate source, although we later found that adding sulfate increased the reaction rate. Hydrolysis of the ethyl sulfate, followed by deprotonation, may occur either simultaneously or after bridging the uranyl centers, as the sulfate bridges three uranyl ions in $\{U_{20}V_{20}\}$. We expect a pH dependence of this reaction, as the presence of $EtOSO_3H$ rather than $EtSO_4^-$ would hinder complexation of the third oxygen to uranyl, and therefore the assembly of $\{U_{20}V_{20}\}$. When we used the ionic liquid [EMIM] $\{Et_2PO_4]$, the presence of two phosphate ester bonds appears to have prevented coordination to more than two uranyl ions, resulting in the smaller $\{U_8V_6\}$ and $\{V_6U_3\}$ clusters. We continue to optimize the synthesis of these compounds and complete their characterization and expect to submit manuscripts concerning these within the next several months.

We have completed calorimetry on a series of $M^{4+}(SO_4)_2(H_2O)_4$ compounds in which M^{4+} corresponds to Zr, Ce, and U. These $M^{4+}(SO_4)_2(H_2O)_4$ compounds crystallize in two structures that are closely related. In each the M^{4+} cation is coordinated by four monodentate sulfate groups and four H_2O groups in a square antiprism arrangement. These polyhedra are linked through the sulfate tetrahedra to form sheets that are either parallel to (001), in the α-form, or (100) in the β-form. The two structures differ in the local arrangement of sulfate and H_2O about the M^{4+} cation. We have drafted a manuscript reporting the results of this study and intend to submit it for consideration shortly.

Recent Publications Resulting from this Project

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Novel TRU materials via restricted $[AnO_2]^{2+}$(An=U, Np, Pu) speciation profiles and supramolecular assembly (DE-FG02-05ER15736)

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Drs. Jonathan Schwantes, Bruce McNamara, Robert Surbella, Kristi Pellegrini, Pacific Northwest National Lab
Dr. Andrew Kerridge, Department of Chemistry, Lancaster University, Lancaster, UK

Overall research goals: We aim to synthesize novel TRU bearing materials using supramolecular assembly techniques. We manipulate U and TRU species in aqueous, high-anion media to promote controlled speciation and oxidation state profiles. Molecular species (or 'tectons') are then assembled through 'synthons' such as halogen and hydrogen bonding interactions. This approach generates a library of compounds where we systematically probe: 1. Electrostatic surface potentials of $[AnO_2]^{2+}$ and $[AnCl_n(NO_3)_{6-n}]^{2-}$ species as a means of rationalizing assembly motifs; 2. Factors influencing 'yl' oxygen participation in non-covalent interactions; and 3. Factors influencing An-O_{yl} and An-ligand bond covalency.

Significant achievements during 2017-2019:

1. Promotion of halogen bonding interactions with uranyl oxo atoms

We have long been motivated by the desire to engage the nominally terminal uranyl oxygen atoms in bonding for the purpose of promoting structural diversity in molecular or coordination polymer assemblies. We have delineated criteria for doing so (reproducibly) by way of our 'cap-and-link strategy' wherein a chelating ligand such as phen or terpy occupies the equatorial region of the uranyl cation, and a second, halogenated ligand donates a non-covalent interaction to a neighboring O_{yl} (Figure 1). This has been a brute force study where some 60 crystal structures have been determined and analyzed for factors promoting halogen-O_{yl} interactions. In general, it is the combination of electron donation from the N-donor ligand and the polarizability of the halogen that drives such interactions, with the latter being more relevant.

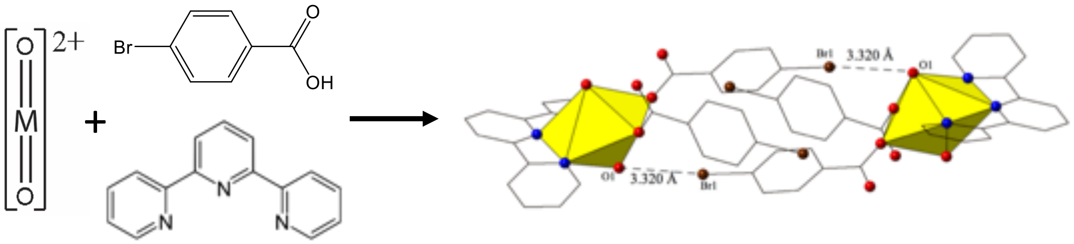

Figure 1. The structure of $[UO_2(tpy)(p\text{-}BrBA)_2]$ highlighting equatorial coordination by both terpyridine and p-bromobenzoic acid where the latter donates a halogen bond to the yl oxygen of a neighboring monomer.

2. Synthesis and bonding characteristics of four new plutonium chloride nitrato complexes

Four new $[Pu(IV)Cl_n(NO_3)_{6-n}]^{2-}$ (n = 0, 2, 3) and $[Pu(VI)O_2Cl_3(NO_3)]^{2-}$ containing materials were prepared from 6 M HCl via assembly with 4-iodopyridinium cations. This is of note owing to the presumption that all NO_3^- was destroyed in the process, leaving only trace amounts to compete with a several fold excess of Cl^-. Beyond this observation, these materials provided a platform for calculating electrostatic surface potentials to rationalize assembly motifs and perhaps inform future (for example) separations or other directed assembly effort. Moreover, the systematic variation in coordination sphere allowed for a computational probe of the Pu-NO_3, Pu-Cl and Pu=O_{yl} bonds using QTAIM (Quantum Theory of Atoms in Molecules) and NLMO (Natural Localized Molecular Orbital) analyses. In brief, the former reveal the Pu-NO_3 and Pu-Cl bonds are polar and largely ionic, whereas the Pu=O_{yl} is largely covalent in nature. NLMO indicates Pu-Cl and Pu-NO_3 bonds have Pu hybrid atomic orbitals of ~34% and ~39% f character, respectively.

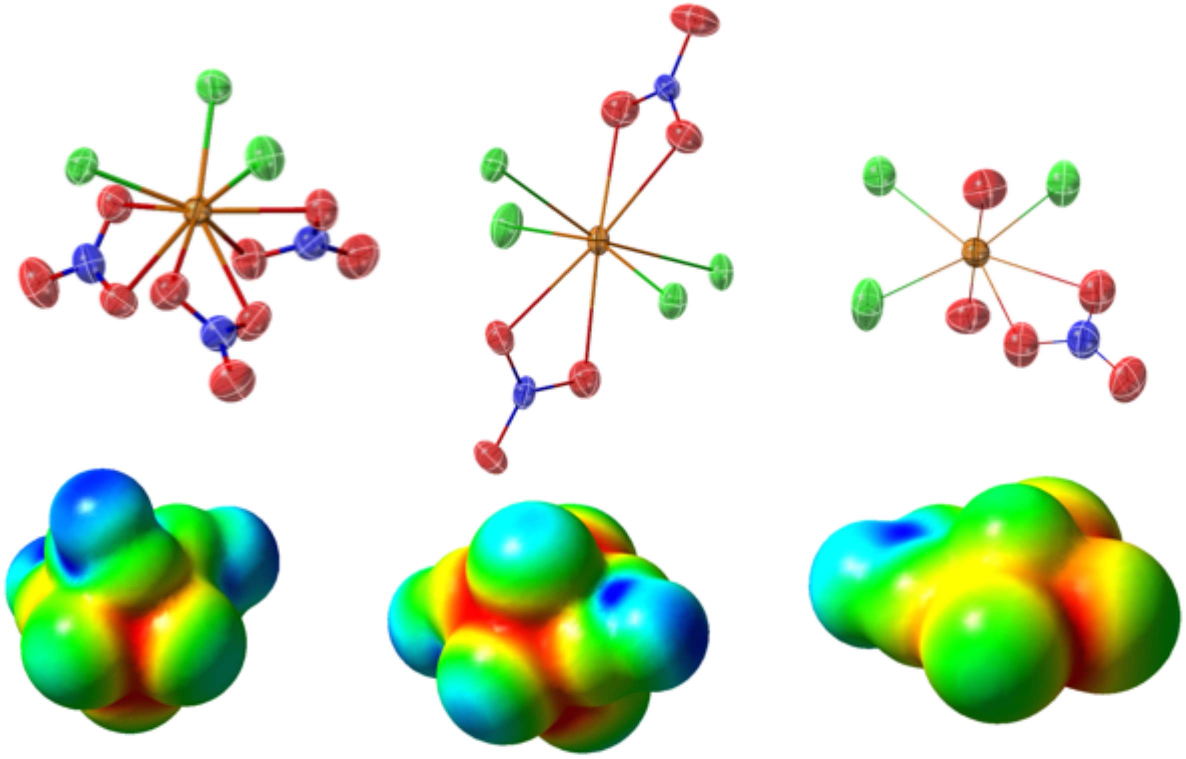

Figure 2. (L to R): Crystal structures of the $[PuCl_3(NO_3)_3]^{2-}$, $[PuCl_4(NO_3)_2]^{2-}$ and $[PuO_2Cl_3(NO_3)]^{2-}$ anions (top) and their corresponding electrostatic surface potentials (bottom).

Future Plans:

Future plans include a deeper commitment to TRU compounds owing to expanding engagement with Pacific Northwest national Lab, Moreover, recent publications and demonstration of our computational capacity (see publication list) have enabled us to consider probing of electronic structure and bonding more aggressively. Specifically, plans for the next three years include:

- Extend supramolecular assembly efforts to Pu(VI) and Am(III) chloride systems via continued engagement with PNNL. Continue to delineate assembly criteria via our combined crystallographic and computational approach.

- Revisit our extensive catalog of U and TRU compounds and use this as a platform for expanded computational efforts that probe covalency and f orbital participation An-X and An-O bonds.

- Systematically explore effect of non-covalent interactions at O_{yl} sites on Raman and luminescence spectra and expand modelling efforts therein to reconcile experimental observations. Efforts thus far have been qualitative in nature and an opportunity exists to decouple equatorial ligand donation from halogen polarizability with regard to promoting O_{yl} participation in bonding.

Publications from the last three calendar years

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(10) R. G. Surbella; L. C. Ducati; J. Autschbach; N. P. Deifel; C. L. Cahill (2018) "Thermochromic Uranyl Isothiocyanates: Influencing Charge Transfer Bands with Supramolecular Structure." *Inorg. Chem.* *57*, 2455. http://dx.doi.org/10.1021/acs.inorgchem.7b02702

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TITLE: Spectroscopic Investigation of Electronic Structure in the Actinide Elements

AWARD NUMBER: KC0302030-73200

PRINCIPAL INVESTIGATOR: Herman Cho

MAILING ADDRESS: Pacific Northwest National Laboratory, 902 Battelle Boulevard, P.O. Box 999, MSIN K2-57, Richland, Washington 99352

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OVERALL RESEARCH GOALS

In this project, we aim to map electron distributions around actinide centers in three structural series (Figure 1). The premise of this project is that a *systematic spectroscopic study of compounds of nearly identical structure, but with substitution of different metal centers* will unveil key aspects of the evolution in electron distributions from the light to heavy actinides. In particular, we will seek evidence that electronic sharing and correlation effects increase as *Z* decreases by measuring local magnetic and electric fields in these structure types for different metal substitutions.

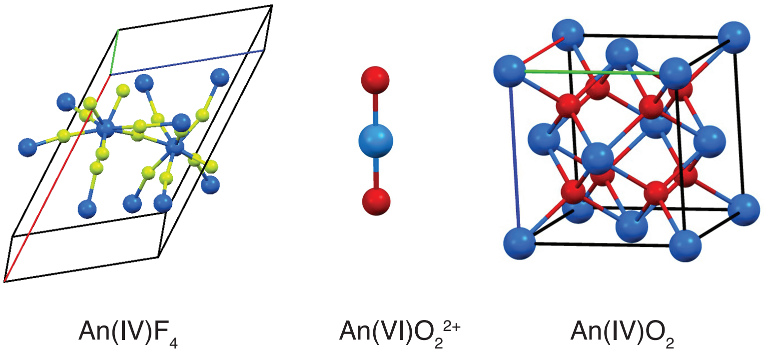

Figure 1: Three isostructural series of actinide compounds (blue = actinide; green = F; red = O). Tetrafluorides from Th to Am form with the same monoclinic unit cell; linear actinyls can be found with U to Am as the metal center; the dioxides crystallize in a fluorite lattice for Th to Cf. Lanthanide (4f) analogs also exist for the tetrafluoride and dioxide structures.

In the case of the actinide tetrafluorides (An(IV)F$_4$; An=Th, Pa, U, Np, and Pu), the magnetic field projected onto fluorine nuclei by surrounding metals is predicted to be proportional to the thermally averaged magnetic moment of the metal valence electrons; the shift and broadening of the ^{19}F nuclear magnetic resonance (NMR) lines thus provide a detailed view of the electronic state of the actinide.

In a similar fashion, the electric field gradients, magnetic shieldings, and hyperfine shifts of the ligand nuclei on actinyl salts (An(VI)O$_2^{2+}$) strongly depend on the electronic configuration of the metal. Measurement of these parameters, also by NMR spectroscopy, may be used to follow a progression from electron sharing to electron localization.

The dioxides (An(IV)O$_2$) present an intriguing contrast to the tetrafluorides, as noted by Dawson [1952] who discovered that Pu^{4+} exhibited a much larger atomic susceptibility in PuF$_4$ than in PuO$_2$. In part, the difference can be ascribed to lower symmetry of the metal site in the tetrafluorides; nevertheless, the evidence suggests the metal valence electrons are more delocalized (or “itinerant”) in the oxides. Determinations of field gradients and magnetic shieldings across the actinide series could provide a definitive explanation of the origin of this difference.

Experimental data will be compared with predictions obtained with a variety of methods. The simplest models are based on assumptions of uncorrelated electrons localized to the metal center, which allow calculation of field gradients and magnetic moments from point charge models with thermal averaging over electron spin states. More sophisticated predictions are available from relativistic *ab initio* computations.

RECENT PROGRESS

Tetrafluorides. In past work we have probed the microscopic magnetic fields produced by Pu(IV) centers at fluorine sites using ^{19}F NMR spectroscopy of polycrystalline PuF_4 [Capan et al. 2016]. Spectra of PuF_4 at fields of 2.35 and 7.05 T reveal a linearly scaled ^{19}F line shape, which we compared to theoretical models that treated the local magnetic field surrounding fluorine atoms as being due to dipolar couplings to Pu valence electrons approximated as point charges. Recently acquired spectra of UF_4 reveal a resonance of comparable shape and width, with slight but notable differences in the width and center.

Uranyls. Dicesium actinyl salts have been important models for understanding actinide-ligand interactions, and we have recently focused on one well known example, $Cs_2UO_2Cl_4$, as a promising system for a determination of electronic structure in an actinide centered molecular cluster. Because of the presence of several nuclei with $I \geq 1$ in $Cs_2UO_2Cl_4$, field gradient tensors can be measured at multiple sites around the metal to obtain an inclusive map of electronic distributions. The metal in $Cs_2UO_2Cl_4$ is coordinated by four crystallographically equivalent non-shared chlorine atoms arranged in an approximately square planar configuration, with the symmetric linear $U(VI)O_2^{2+}$ ion tilted slightly off the plane perpendicular. Determinations of ^{35}Cl and ^{37}Cl quadrupolar couplings thus provide field gradients at four points surrounding the uranium center. Experimental ^{35}Cl and ^{37}Cl spectra of $Cs_2UO_2Cl_4$ (Figure 2), when compared with spectra predicted from computed field gradients, provide a guide for developing accurate models of electron distributions [Cho et al., 2019].

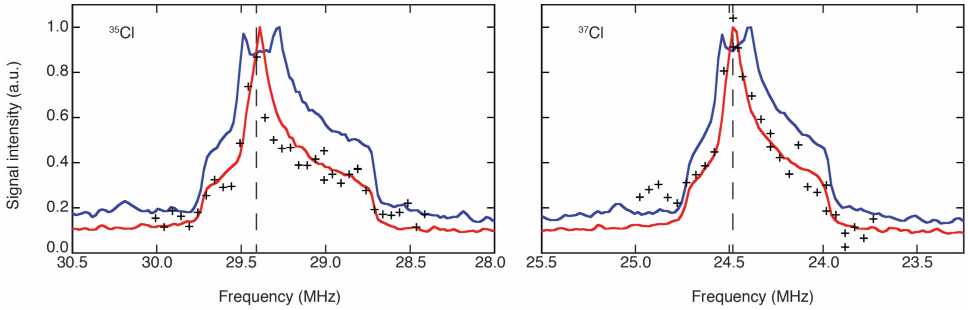

Figure 2: Chlorine-35 (top) and ^{37}Cl (bottom) NMR spectra of $Cs_2UO_2Cl_4$ in a 7.046 Tesla magnetic field. Blue and red spectra are simulations computed with EFG parameters from a SO-PBE0 calculation and a visual fit to the experimental data, respectively.

FUTURE PLANS

Tetrafluorides. We will examine the trends in electronic sharing and correlation effects in AnF_4 as a function of *Z*, and search for deviations in measured internal fields from models based on an assumption of localized, uncorrelated electrons on the metal center. Theoretical models for the

An(IV) magnetic moment lead to specific predictions of the dependence of shifts and broadenings of ^{19}F NMR lines on applied field and temperature. To fully test the validity of various models (and whether the "localized electron" picture applies to AnF_4), measurements at different temperatures and fields are planned. One key question, namely, the dependence of the broadening on the applied magnetic field, has already been answered as being linear for PuF_4.

Uranyls. Several anhydrous uranyl and bis-imido compounds are being prepared with isotope labeling to enable measurement of field gradients and shieldings at selected sites of the system, including the metal center, which we can enrich with isotopes (^{233}U and ^{235}U) having non-zero nuclear spin. Field gradients of uranium isotopes ^{233}U ($I = 5/2$) and ^{235}U ($I = 7/2$) are expected to be large enough to lead to detectable zero field nuclear quadrupole splittings in the 10^8 MHz range. After establishing a foundation for interpreting experimental data in terms of electronic distributions, we will progress to transuranic actinyl salts, namely, Np, Pu, and Am analogs. Paramagnetic shifts will be present in these compounds, but through strategies outlined for the tetrafluorides, we will have a firm basis for analyzing shifts of ligand nuclei and deducing electronic distributions.

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Dawson, J. K., Magnetochemistry of the Heaviest Elements. Part VI. PuO_2-ThO_2 and PuF_4-ThF_4 Solid Solutions. *J. Chem. Soc.* **1952**, 1882-1886. DOI: http://dx.doi.org/10.1039/JR9520001882.

RECENT PUBLICATIONS (Project start date: 10/2018)

Müller, K.; Foerstendor, H.; Steudtner, R.; Tsushima, S.; Kumke, M. U.; Lefèvre, G.; Rothe, J.; Mason, H.; Szabó, Z.; Yang, P.; Adam, C.; André, R.; Brennenstuhl, K.; Chiorescu, I.; **Cho, H.**; Creff, G.; Coppin, F.; Dardenne, K.; Den Auwer, C.; Drobot, B.; Eidner, S.; Hess, N. J.; Kaden, P.; Kremleva, P.; Kretzschmar, J.; Krüger, S.; Platts, J. A.; Panak, P. J.; Polly, R.; Powell, B. A.; Rabung, T.; Redon, R.; Reiller, P. E., Rösch, N.; Rossberg, A.; Scheinost, A. C.; Schimmelpfennig, B.; Schreckenbach, G.; Skerencak-Frech, A.; Sladkov, V.; Solari, P.-L.; Wang, Z.; Washton, N. M.; Zhang, X. Interdisciplinary round-robin test on molecular spectroscopy of the U(VI) acetate system. *ACS Omega*. **In press**.

Farnan, I.; **Cho, H.**, Magic-Angle-Spinning Nuclear Magnetic Resonance of Plutonium Compounds. In *Plutonium Handbook, Second Edition*; American Nuclear Society: La Grange Park, IL, **2019 (in press).**

Cho, H.; Soderquist, C. Z.; Hall, G.; Gendron, F.; Autschbach, J., Experimental and Theoretical Study of Chlorine Electric Field Gradients in $Cs_2UO_2Cl_4$. **Submitted**.

Computational Studies of Hydrolysis of Actinides as Initial Steps in Aggregation and Attaining High Actinide Oxidation States
DE-SC0018921

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Prof. Kirk Peterson, Washington State University
Prof. Karl Christe, University of Southern California
Dr. Lynne Soderholm, Argonne National Laboratory
Dr. Richard Wilson, Argonne National Laboratory
Prof. Karah Knope, Georgetown University
Prof. Michael Duncan, University of Georgia

Overall research goals: The goal is to use computational electronic structure methods to reliably predict chemical properties of molecules and materials containing heavy elements with a focus on the actinides to help explain experimental results from different laboratories leading to an improved understanding of actinide chemistry. Predict potential energy surfaces for hydrolysis reactions for AnO_2^+ for the addition of up to 2 H_2O molecules. Predict energetics for ligand exchange reactions involving small actinide anions and cations for AnO_2+ and AnO_2^{2+}. Predict structures and properties of $(AnO_x)_n$ and mixed $(AnO_y(OH)_z)_n$ ultra-small nanoclusters and their hydrolysis and carbonation reactions. What is the role of the actinyl An=O bond? Predict the acidities in aqueous solution (pK_a's) of An^{n+} for the common oxidation states.

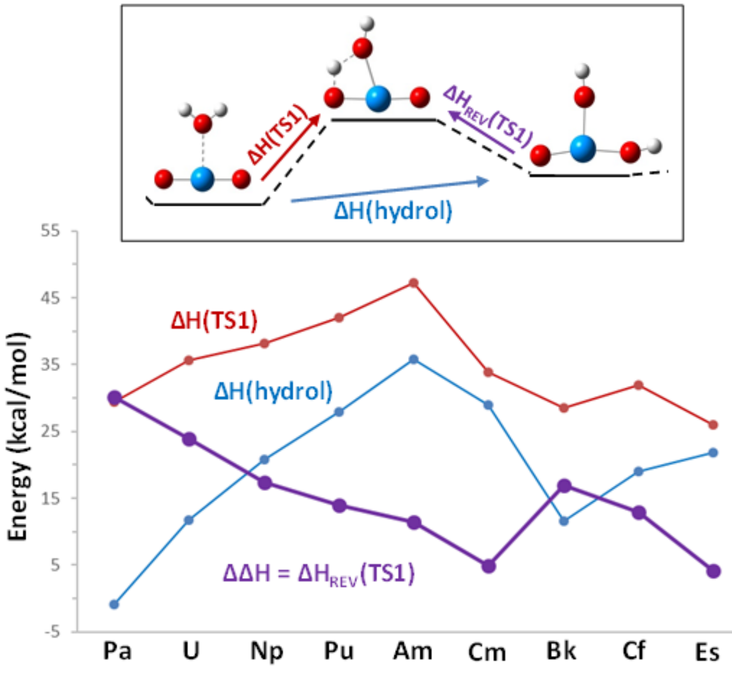

Figure 1. ΔH(hydrol) (red), ΔH(TS1) (blue), and the difference ΔΔH = ΔH(TS1) - ΔH(hydrol) = $\Delta H_{REV}(AnO(OH)_2^+ \rightarrow TS1)$ (purple).

Recent Progress 6/2018-3/2019

(1) The potential energy surfaces for adding H_2O to AnO_2^+ followed by a proton transfer, the first step in the hydrolysis of the AnO_2^+ were calculated at the CCSD(T) level with a large basis set including scalar relativistic effects (Figure 1). The computations predict that E(TS1) is below the reactant asymptote of $AnO_2^+ + H_2O$ for An =

Pa, U, Cm, Bk, Cf, and Es, and above it for Np, Pu, and Am. Although the An-OH_2 bond distances in the initial hydration complex do correlate with the expected actinide contraction, the initial hydration energies do not correlate with this trend showing that simple electrostatics is not the only effect. The computational results are in agreement with available experimental information, particularly those for gas-phase oxo-exchange of PaO_2^+ to PuO_2^+. The decrease in the ease of hydrolysis of AnO_2^+ is accordant with computed charges on the actinide centers in these species. Greater electron donation from oxo ligands to An results in a reduced charge and less effective bonding with ionic OH ligands, which should generally destabilize hydroxide products, as well as hydroxyl intermediates.

(2) The geometries and vibrational frequencies of $[AnO_2^{2+}(NO_3)_3]^-$ were calculated in support of the experimental efforts of Richard Wilson at ANL. The results are being analyzed in terms of the trends observed for the An-O stretches. A key result is that AmO_2^{2+} is a linear complex with $^3O_2$ bonded to Am^{2+} and Cm^{3+} is μ-bonded to $^2O_2^-$ showing the importance of the *5f*^{7} electron occupancy.

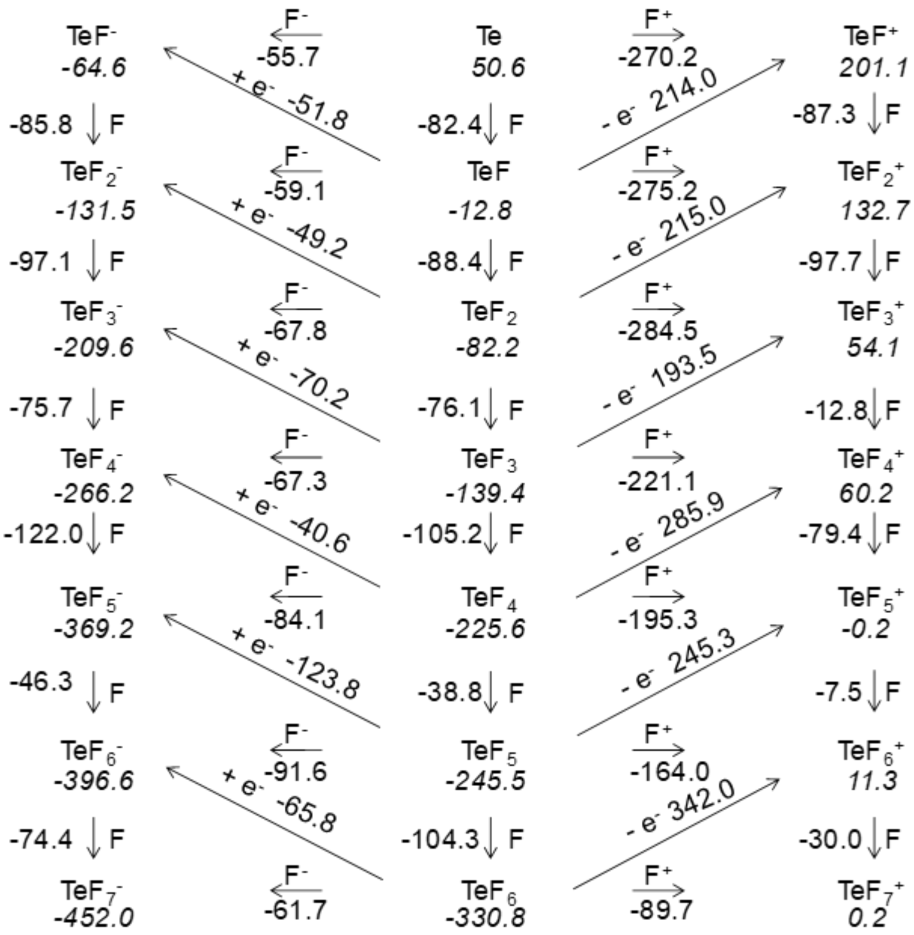

Figure 2. ΔH_f, BDE(+F), FA (+F^-), FCA(+F^+), IP (-e^-), and EA(+e^-) of TeF_n at 298 K in kcal/mol. ΔH_f are indicated below each species *in italics*. Vertical arrows correspond to the addition of F to TeF_n to form TeF_{n+1} in terms of the cation, neutral, and anion. Horizontal arrows to the left correspond to FAs. Horizontal arrows to the right correspond to FCAs. Diagonal arrows to the left correspond to the EA. Diagonal arrows to the right correspond to the IP.

(3) Tellurium is a fission product in nuclear reactor fuels (a radioactive decay product of uranium and its daughters, as well as from other nuclei) and will be formed in molten salt reactors The heats of formation (ΔH_f), bond dissociation energies (BDEs), fluoride affinities (FAs), fluorocation affinities (FCAs), electron affinities (EAs), and

ionization potentials (IPs) of TeF_n (n = 1 - 6) have been predicted using the Feller-Peterson-Dixon approach. Figure 2 summarizes the reaction enthalpies for the addition of an $F/F^+/F^-$ atom to $TeF_n^{0,\pm1}$ (n = 1 - 7) to form $TeF_{n+1}^{0,\pm1}$. The spin-orbit corrections make a significant contribution to the calculated heats of formation.

(4) The clustering of uranyl oxide neutral and cationic species are being calculated in support of the work of Mike Duncan at U. Georgia. The results show that DFT is not that accurate with the B3LYP functional. The energetics depend on the charge and the number of oxygen atoms. The PES for hydrolysis of UO_3 has been calculated to initiate further nanocluster hydrolysis studies.

Future Plans

- Add the second water of solvation to the PES's for $AnO_2^+ + H_2O$.
- Calculate the potential energy surfaces for the reactions of the nitrate anions with AnO_2^+ and AnO_2^{2+}.
- Study the following reactions of AnO^{2+} with NO_3^-, NO_2, and H_2O and AnO_2^+ with HNO_2.
- Model the formation of $(AnO_x)_n$ and mixed $(AnO_y(OH)_z)_n$ ultra-small nanoclusters and their reactions with H_2O and with CO_2.
- Calculate the thermodynamic properties of the actinide fluorides and oxyfluorides with higher computational levels than DFT.
- Calculate the acidities (pK_a's) of An^{n+}, AnO_2^+, and AnO_2^{2+} for the common oxidation states in aqueous solution with multiple solvent shells.
- Use results to explore formation of the actinyl bond.

Recent Publications Resulting from this Project (Project start date: 06/2018)

Gibson, J. K.; Vasiliu, M.; Dixon, D. A.; Peterson, K. A. Gas Phase Hydrolysis and Oxo-Exchange of Actinide Dioxide Cations: Elucidating Intrinsic Chemistry from Protactinium to Einsteinium. *Chem. Eur. J.*, WEB ASAP January, 2019, invited Concept paper, doi.org/10.1002/chem.201803932

Vasiliu, M.; Peterson, K. A.; Christe, K. O.; Dixon, D. A. Electronic Structure Predictions of the Energetic Properties of Tellurium Fluorides. *Inorg. Chem.* WEB ASAP, January, 2019, (July 2019 cover)DOI: 10.1021/acs.inorgchem.8b03235.

Exploring the Fundamental Chemistry of Actinide Metal Complexes

DE-SC0004739

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Undergraduate: Mary A. Angadol

Collaborators: At UC Irvine, Filipp Furche, Guo P. Chen, Alan K. Chan; at Los Alamos National Laboratory (LANL), Andrew J. Gaunt, Stosh A. Kozimor, Justin N. Cross, Michael T. Janicke, Brian L. Scott, Jing Su, Enrique R. Batista, Samantha K. Cary, Veronika Mocko, Benjamin W. Stein, Ping Yang; at Lawrence Berkeley Laboratory, Stefan Minasian; at Vanderbilt University, Timothy P. Hanusa

Overall Research Goals: The objective of this project is to explore new opportunities in actinide chemistry made possible by the discovery of the first crystallographically-characterizable molecular complexes of U(II) and Th(II) which have unusual $5f^3 6d^1$ and $6d^2$ electron configurations, respectively. This focus was chosen since it is so rare to identify new oxidation states in molecular species.

Significant Achievements Since the Last HEC Contractors Meeting: Highlights only are described with full details in the references on the fourth page.

A. Synthesis of the First Molecular Complex of Pu(II). At the time of the last contractor's meeting, the synthesis of the first isolable Pu(II) complex had been accomplished, but not yet published. This result is now published [6]. This new Pu chemistry was discovered in a collaboration with LANL which involved a graduate student from our lab, Cory J. Windorff, working at LANL for one year under the DOE SCGSR program. Previously, Windorff conducted a uranium study at UCI that proved to be crucial to the success of the Pu(II) chemistry [a] (alphabetical references are given after Section G). He synthesized U(II) complexes of the $C_5H_3(SiMe_3)_2$ (Cp″) ligand, namely $(Cp''_3U)^{1-}$, with four different countercations and found that these were more thermally stable than $[K(crypt)][Cp'_3U]$ ($Cp' = C_5H_4SiMe_3$; crypt = 2.2.2-cryptand), the first U(II) complex discovered in our lab. With that knowledge, the synthesis of Pu(II) was pursued with the Cp″ ligand rather than Cp′. The necessary precursor, Cp''_3Pu, was synthesized, structurally characterized, and reduced with potassium to generate $[K(crypt)][Cp''_3Pu]$. This study provided not only the first example of a complex of Pu(II), but also the first published X-ray crystal data on organometallic Pu complexes [6] (although more subsequently appeared in the literature [b]).

B. Synthesis of a Crystallographically-Characterizable Complex of Np(II). Once $(Cp''_3Pu)^{1-}$ was isolated, the synthesis of the Np analog was an obvious target. A heroic effort had been made with Cp′ to synthesize Np(II) as $(Cp'_3Np)^{1-}$ by Professor Polly Arnold and co-workers at the Institute for Transuranium Elements (ITU) in Karlsruhe, Germany [c], but the system was too thermally unstable to isolate. With our knowledge that Cp″ provided more stable An(II) species than Cp′ [a] and by agreement with Professor Arnold and co-workers, the synthesis of $(Cp''_3Np)^{1-}$ was pursued at LANL. A sequence similar to that used for Pu(II) was followed starting from the reaction of Np metal with I_2 to make "$NpI_3(Et_2O)_x$." This was treated with KCp'' to make a compound presumed to be Cp''_3Np. Reduction of this species produced $[K(crypt)][Cp''_3Np]$ which could be identified by X-ray crystallography [11]. Calculations indicated that the $5f^4 6d^1$ and $5f^5$ electron configurations in this complex were similar in energy, but calculations for the $5f^4 6d^1$ ground state best matched the structural and UV-vis data. The progression of electron configurations for $(Cp''_3An)^{1-}$ anions, i.e.

Th(II) as $6d^2$, U(II) as $5f^36d^1$, Np(II) with $5f^46d^1$ and $5f^5$ similar, and Pu(II) as $5f^6$, fits the trend expected from the literature for the relative change in 5f orbital energy versus 6d energy as a function of increasing atomic number across the actinide series [d].

C. Small Scale Lanthanide Reactions to Investigate Reaction Conditions for Transuranic Chemistry. An extensive amount of synthetic chemistry was developed at UCI with lanthanide complexes to support the Pu(II) and Np(II) discoveries in the collaboration with LANL described above. Reactions of large lanthanide ions similar in size to the actinides of interest were done on the small scale necessary for transuranic studies to determine optimum reaction conditions [8]. The goal was to minimize the number of transuranic reactions that would be needed to synthesize the target compounds and to minimize transuranic waste. The small scale lanthanide reactions started with the elemental metal to match the conditions at LANL with Pu and Np metal starting materials. The efficacy of synthesizing and isolating the iodide and cyclopentadienyl intermediates on a small scale was determined as a function of solvent and concentration. The results of these studies are broadly applicable to the actinides and can aid transuranic studies in laboratories around the world.

D. Cyclopentadienyl Thorium Metallocenes with Parallel Rings. The first metallocenes of thorium with parallel cyclopentadienyl rings have been synthesized and structurally characterized [10]. All previous bis(cyclopentadienyl)-thorium complexes had the two rings in a bent orientation. Complexes with parallel cyclopentadienyl rings had been observed for U [e], but never for thorium. This result showed that despite the difference in size and electron configurations of uranium and thorium, this unusual structural type was possible with both metals.

E. Uranium-in-Cryptand. The recent discoveries of the first molecular complexes of U(II), Th(II), Pu(II), and Np(II) as part of this project, have all involved the 2.2.2-cryptand (crypt) ligand to sequester the potassium countercation generated in the potassium graphite reductions. We now find that we can use the crypt ligand to encapsulate *uranium* to form crystallographically-characterizable complexes [12]. Uranium cryptand complexes were in the literature since 1976, but none had been crystallographically characterized. The synthesis was accomplished by a surprisingly simple reaction of UI_3 with crypt to form $[U(crypt)I_2]I$ [12]. This complex, as well as an aquo adduct, $[U(crypt)(OH_2)I][I]_2$, that is independently interesting as a rare example of a water stable U(III) complex, were fully defined by X-ray crystallography. Since cryptand ligands have been shown to stabilize Eu(II) with respect to oxidation, $[U(crypt)I_2]I$ could be a good starting material for new U(II) complexes.

F. A U(II) Complex Anion with a Chelate-Free Countercation. To expand the range of synthetic options for generating complexes of the actinide metals in the +2 oxidation state, reduction of Cp''_3U with lithium in the *absence* of either a crown ether or a cryptand chelate was explored. This provided crystallographically-characterizable $[Li(THF)_4][Cp''_3U]$ in good yield [13], *i.e.* chelating agents are not necessary to sequester the alkali metal countercation to form isolable crystalline U(II) products. This could provide a less complicated reaction protocol for the syntheses of transuranic An(II) complexes.

Reductions using cesium were also explored and X-ray crystallography revealed the formation of an oligomeric structure, $[Cp''U(\mu\text{-}Cp'')_2Cs(THF)_2]_n$, involving Cp″ ligands that bridge "$(Cp''U^{II})^{1+}$" moieties to "$[Cp''_2Cs(THF)_2]^{1-}$" units [13]. Formation of polymeric An(II) complexes may be beneficial in the case of highly reactive transuranic complexes, since the insolubility of the polymer may allow rapid precipitation of product that minimizes time in solution that could lead to decomposition.

G. Synthesis of U(II) Complexes with C_5Me_4H and $N(SiMe_3)_2$ Ligands. The initial discoveries of first complexes of +2 ions of Th, U, Pu, and Np, all involved cyclopentadienyl ligands with silyl groups that can reduce the donating ability of the ligand. It appeared that these new oxidation states would only be available with ligands that were not very electron donating. This generalization has been overturned with the synthesis and crystallographic characterization of [K(crypt)][$Cp^{tet}{}_3U$] (Cp^{tet} = C_5Me_4H) and [K(crypt)][$U(NR_2)_3$], (R = $SiMe_3$) [14]. This result has important implications in developing the reactivity of U(II) since the strongly donating C_5Me_4H and $N(SiMe_3)_2$ ligands are much better ancillary ligands for isolating crystalline actinide reaction products.

Alphabetical references for the text above:

a. "Expanding the Chemistry of Molecular U^{2+} Complexes: Synthesis, Characterization, and Reactivity of the $\{[C_5H_3(SiMe_3)_2]U\}^{1-}$ Anion" Windorff, C. J.; MacDonald, M. R.; Meihaus, K. R.; Ziller, J. W.; Long, J. R.; Evans, W. J. *Chem. Eur. J.* **2016**, *22*, 772-782. **DOI:** 10.1002/chem.201503583

b. (i) "A Structurally Characterized Organometallic Plutonium(IV) Complex" Apostolidis, C.; Walter, O.; Vogt, J.; Liebing, P.; Maron, L.; Edelmann, F. T. *Angew. Chem. Int. Ed.* **2017** *56*, 5066-5070. **DOI:** 10.1002/anie.201701858 (ii) "Solid-State Structure of Tris-Cyclopentadienide Uranium(III) and Plutonium(III)" Apostolidis, C.; Dutkiewicz, M. S.; Kovács, A.; Walter, *Chem. Eur. J.*, **2018**, *24*, 2841-2844. **DOI:** 10.1002/chem.201704845

c. (i) "Organometallic neptunium(III) complexes" Dutkiewicz, M. S.; Farnaby, J. H.; Apostilidis, C.; Colineau, E.; Walter, O.; Magnani, N.; Gardiner, M. G.; Love, J. B.; Kaltsoyannis, N.; Caciuffo, R.; Arnold, P. L. *Nat. Chem.* **2016**, *8*, 797-802. **DOI:** 10.1038/NCHEM.2520 (ii) "Reduction chemistry of neptunium cyclopentadienide complexes: from structure to understanding" Dutkiewicz, M. S.; Apostolidis, C.; Walter, O.; Arnold, P. L. *Chem. Sci.* **2017**, *8*, 2553-2561. **DOI:** 10.1039/C7SC00034K (iii) "Organometallic Neptunium Chemistry" Arnold, P. L.; Dutkiewicz, M. S.; Walter, O. *Chem. Rev.* **2017**, *117* (17), 11460-11475. **DOI:** 10.1021/acs.chemrev.7b00192

d. (i) "Density functional theory studies of the electronic structure of solid state actinide oxides" Wen, X.-D.; Martin, R. L.; Henderson, T. M.; Scuseria, G. E. *Chem. Rev.* **2013**, *113*,1063-1096. **DOI:** 10.1021/cr300374y (ii) "Does Covalency Increase or Decrease across the Actinide Series? Implications for Minor Actinide Partitioning" Kaltsoyannis, N. *Inorg. Chem.*, **2013**, *52*, 3407-3413. **DOI:** 10.1021/ic300602

e. (i) "An Unprecedented Type of Linear Metallocene with an f-Element" Maynadié, J.; Berthet, J.-C.; Thuéry, P.; Ephritikhine, M. *J. Am. Chem. Soc.* **2006,** *128*, 1082-1083. **DOI:** 10.1021/ja057226s (ii) "The Crucial Role of the f Electrons in the Bent or Linear Configuration of Uranium Cyanido Metallocenes" Maynadié, J.; Barros, N.; Berthet, J.-C.; Thuéry, P.; Maron, L.; Ephritikhine, M. *Angew. Chem. Int. Ed.* **2007,** *46*, 2010-2012. **DOI:** 10.1002/anie.200604114

Science Objectives for 2019-2021:

(a) We will explore the effects of the new ligand systems described above, i.e. Cp^{tet} and $N(SiMe_3)_2$, as well as the varying countercations, on the reactivity of the new U(II) and Th(II) ions. This could be a springboard to new actinide chemistry in general. We will also study the effects on their physical properties. (b) We will attempt the reduction of U(III)-in-crypt complexes and study reduction of An(II)-in-crypt complexes to synthesize the first An(I) compounds. (c) We will continue to do modeling studies for transuranic collaborations at LANL and Florida State University with emphasis on developing simple reactions that occur rapidly to give products that crystallize quickly in high yield. (d) We will explore the chemistry of the first square-planar complex of Th recently isolated in our lab.

Publications From DE-SC0004739 From the Past Three Years (W. J. Evans)

1. "Expanding Thorium Hydride Chemistry Through Th^{2+}, Including the Synthesis of a Mixed-Valent Th^{4+}/Th^{3+} Hydride Complex" Langeslay, R. R.; Fieser, M. E.; Ziller, J. W.; Furche, F.; Evans, W. J. *J. Am. Chem. Soc.* **2016**, *138*, 4036–4045. DOI: 10.1021/jacs.5b11508
2. "Synthetic Utility of Tetrabutylammonium Salts in Uranium Metallocene Chemistry" Webster, C. L.; Langeslay, R. R.; Ziller, J. W.; Evans, W. J. *Organometallics* **2016***, 35*, 520–527. DOI: 10.1021/acs.organomet.5b00942
3. "Tutorial on the Role of Cyclopentadienyl Ligands in the Discovery of Molecular Complexes of the Rare-Earth and Actinide Metals in New Oxidation States" Evans, W. J.; *Organometallics* **2016***, 35*, 3088-3100, ACS Authors Choice. DOI: 10.1021/acs.organomet.6b00466
4. "Expanding the +2 Oxidation State to the Rare-Earth Metals, Uranium, and Thorium in Molecular Complexes" Woen, D. H.; Evans, W. J. *Handbook on the Physics and Chemistry of the Rare Earths Including Actinides,* **2016**, *50*, Chapter 293, 337-394. DOI: 10.1016/bs.hpcre.2016.08.002
5. "Synthesis, Structure, and Reactivity of the Sterically Crowded Th^{3+} Complex $(C_5Me_5)_3Th$ Including Formation of the Thorium Carbonyl, $[(C_5Me_5)_3Th(CO)][BPh_4]$" Langeslay, R. R.; Chen, G. P.; Windorff, C. J.; Chan, A. K.; Ziller, J. W.; Furche, F.; Evans, W. J. *J. Am. Chem. Soc.* **2017**, *139*, 3387-3398. DOI: 10.1021/jacs.6b10826
6. "Identification of the Formal +2 Oxidation State of Plutonium: Synthesis and Characterization of $\{Pu^{II}[C_5H_3(SiMe_3)_2]_3\}^{1-}$" Windorff, C. J.; Chen, G. P.; Cross, J. N.; Evans, W. J.; Furche, F.; Gaunt, A. J.; Janicke, M. T.; Kozimor, S. A.; Scott, B. L. *J. Am. Chem. Soc.* **2017**, *139*, 3970-3973. DOI: 10.1021/jacs.7b00706
7. "Covalency in Americium(III) Hexachloride" Cross, J. N.; Su, J.; Batista, E. R.; Cary, S. K.; Evans, W. J.; Kozimor, S. A.; Mocko, V.; Scott, B. L.; Stein, B. W.; Windorff, C. J.; Yang, P. *J. Am. Chem. Soc.* **2017**, *139*, 8667–8677. DOI: 10.1021/jacs.7b03755
8. "Small-Scale Metal-Based Syntheses of Lanthanide Iodide, Amide, and Cyclopentadienyl Complexes as Analogs for Transuranic Reactions" Windorff, C. J.; Dumas, M. T.; Ziller, J. W.; Gaunt, A. J.; Kozimor, S. A.; Evans, W. J. *Inorg. Chem.* **2017**, *56*, 11981-11989. DOI: 10.1021/acs.inorgchem.7b01968,
9. "Trimethylsilylcyclopentadienyl (Cp′) Uranium Chemistry: Synthetic and Structural Studies of Cp'_4U and Cp'_3UX (X = Cl, I, Me)" Windorff, C. J.; MacDonald, M. R.; Ziller, J. W.; Evans, W. J. *Z. Anorg. Allg. Chem*. **2017**, *643*, 2011-2018. DOI: 10.1002/zaac.201700323
10. "Thorium Metallocene Cation Chemistry: Synthesis and Characterization of the Bent $[(C_5Me_5)_2Th(C_6H_5)(THF)][BPh_4]$ and the Parallel Ring $[(C_5Me_5)_2Th(NCR)_5][BPh_4]_2$ (R = Me, Ph) Complexes" Langeslay. R. R.; Windorff, C. J.; Dumas, M. T.; Ziller, J. W.; Evans, W. J. *Organometallics* **2018**, *37*, 454-458. DOI: 10.1021/acs.organomet.7b00855
11. "Identification of the Formal +2 Oxidation State of Neptunium: Synthesis and Structural Characterization of $\{Np^{II}[C_5H_3(SiMe_3)_2]_3\}^{1-}$" Su, J.; Windorff, C. J.; Batista, E. R.; Evans, W. J.; Gaunt, A. J.; Janicke, M. T.; Kozimor, S. A.; Scott, B. L.; Woen, D. H.; Yang, P. *J. Am. Chem. Soc.* **2018**, *140*, 7425–7428. DOI: 10.1021/jacs.8b03907
12. "Synthesis of uranium-in-cryptand complexes" Huh, D. N.; Windorff, C. J.; Ziller, J. W.; Evans, W. J. *Chemical Communications* **2018**, *54*, 10272-10275. DOI: 10.1039/C8CC05341C
13. "Chelate-Free Synthesis of the U(II) Complex, $[(C_5H_3(SiMe_3)_2)_3U]^{1-}$, Using Li and Cs Reductants and Comparative Studies of La(II) and Ce(II) Analogs" Huh, D. N.; Ziller, J. W.; Evans, W. J. *Inorg. Chem.* **2018**, *57*, 11809-11814. DOI: 10.1021/acs.inorgchem.8b01966
14. "Isolation of U(II) Compounds Using Strong Donor Ligands, C_5Me_4H and $N(SiMe_3)_2$, Including a Three-Coordinate U(II) Complex" Ryan, A. J.; Angadol, M. A.; Ziller, J. W.; Evans, W. J. *Chemical Communications* **2019**, 55, 2325-2327. DOI: 10.1039/c8cc08767a
15. *The Heaviest Metals: Science and Technology of the Actinides and Beyond* Evans, W. J.; Hanusa, T. P. Eds. In The Encyclopedia of Inorganic and Bioinorganic Chemistry (EIBC), Wiley, New York, **2019**. ISBN 978-1-11930409-8. Www.wileyonlinelibrary.com/ref/eibc

Assessing subtle variations in actinyl oxo reactivity through characterization of neptunyl complexes. (DE-SC0013980)

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Overall research goals: The objective of this project is to determine the chemical components that influence the intermolecular interactions occurring between actinyl ($[Np(V)O_2]^+$, $[Np(VI)O_2]^{2+}$, and $[U(VI)O_2]^{2+}$) cations and neighboring species. My overall hypothesis is that the intermolecular interactions that occurs between the actinyl oxo atoms and neighboring species (H atoms, low-valent cations, actinyl cations) is primarily controlled by the electronic properties of the actinyl cation, but can be further influenced by the electron donating properties of the equatorial ligands.

Recent Progress: Our neptunium lab was established in January 2016 and we have been exploring the effects of (1) actinyl-cation, (2) actinyl-hydrogen, and (3) actinyl-actinyl interactions within uranyl and neptunyl coordination complexes over the past three years. We are using single crystal X-ray diffraction and Raman spectroscopy to understand the impact of these interactions on the actinyl bond. In addition, we have begun pairing these experiments with DFT calculations performed with Professor Sara Mason (University of Iowa Department of Chemistry) and a co-advised graduate student, Jennifer Bjorklund.

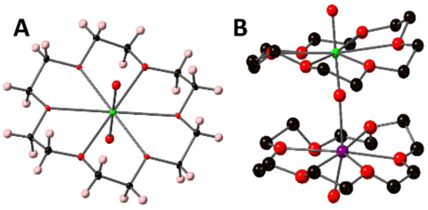

Figure 1. $[NpO_2(18\text{-crown-}6)]^+$ complexes could be synthesized as (a) isolated species or (b) with neptunyl-cation interactions.

1) **Actinyl-cation interactions**: The influence of actinyl-cation interactions was explored through crystallization and characterization of Np(V) and Np(VI) crown ether complexes. Within Np(V) solutions, the $[NpO_2(18\text{-crown-}6)]^+$ inclusion complex can be crystallized with and without actinyl-cation interactions. Raman spectroscopy indicates that direct interactions between a Na^+ cation and the neptunyl oxo results in a slight blue shift (5 cm^{-1}) for the neptunyl symmetric stretch (ν_1) compared to the isolated $[NpO_2(18\text{-crown-}6)]^+$ complex (Fig. 1). Additional solution studies indicated the inclusion complex is conserved and the ν_1 band is not impacted by the addition of K^+, Sr^{2+}, or Al^{3+} cation.

Np(VI) crown-ether experiments initially built upon previous investigations by Danis et al., 2001, which provided a systematic look at interactions between the uranyl oxo and alkali cations (Li+, Na+, and K+).[1] This previous study is cited as a rare example of direct actinyl-cation interaction between the oxo group in a uranyl tetrachloro complex and nearby Li^+ cations. Two $[A(18\text{-crown-}6)]_2[NpO_2Cl_4]$ A = Na^+, K^+ compounds were successfully crystallized, but we have yet to form the Li coordination compound. To further explore the Li^+ interaction in solution, Raman spectra were collected Np(VI) chloride solutions with increasing LiCl concentration (Fig. 2). At lower Li^+ concentration, a band at 857 cm^{-1} is observed in the spectra that corresponds to the $[NpO_2Cl_4]^{2-}$ complex. Addition of LiCl solid results in a red shift of this ν_1 mode (840 cm^{-1}) and the in-growth of a peak at 805 cm^{-1}. This band had been previously noted in a mixed Np(V)/Np(VI) solution containing $CaCl_2$, but was identified as the ν_3 band of the $Np(V)O_2$ cation.[2] This could not be the correct interpretation of our spectra because UV/Vis and Raman spectroscopy confirmed our solution was pure Np(VI). DFT calculations were performed on the $[NpO_2Cl_4]^{2-}$ complex and included Li^+ cations engaging with the molecules in four different configurations. In the absence of oxo interactions, the calculations predicted that the ν_1 band should be located at 860 cm^{-1} and the presence

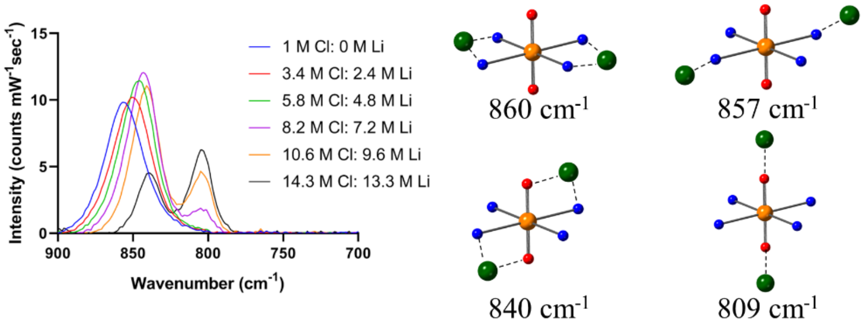

Figure 2. Raman spectra of Np(VI) stock (1 M HCl) with addition of LiCl. Increasing Li$^+$ in solution results in the ingrowth of a secondary band at 805 cm^{-1}. DFT calculations with different Li coordination (green spheres) indicate the formation of neptunyl-cation interactions.

of oxo interactions resulted in a significant red shift (840 and 809 cm^{-1}). Additional investigations of solutions containing Li+ and the $[UO_2Cl_4]^{2-}$ complex also indicates the presence of band at 840 cm^{-1} in the Raman spectra, which our DFT calculations predict (at 841 cm^{-1}) should be related to direct interactions between the Li$^+$ cation and the uranyl oxo. This study provides evidence of the influence of actinyl-cations interactions that are more pronounced in Np(VI) solutions than in the U(VI) system.

2) **Actinyl-hydrogen interactions**: We crystallized the $[NpO_2Cl_4]^{3-}$ complex in the presence of piperazinium cations, which was significant because it was the first Np(V) tetrachloride complex reported in the literature (Fig. 3a). In addition, there was direct actinyl-hydrogen interactions between the piperazinium cations and the neptunyl oxo that resulted in the formation of an asymmetric neptunyl bond (Np=O 1.859(3); 1.832(3) Å). Additional crystallization experiments were performed with morpholine, which resulted in the formation of a morpholinium neptunyl tetrachloride complex with a different hydrogen bonding network and symmetric neptunyl bond (Fig. 3b). Raman spectroscopy of the two compounds indicated that these subtle changes in the H-bonding network influenced the neptunyl bond and also resulted in additional activation of modes with the lower symmetry asymmetric neptunyl bond.

Piperazinium and morpholinium have not been reported to engage and perturb the U(VI)O_2 moiety, but we have observed activation of uranyl vibrational bands in the presence of cobalt (III) hexamine. Two compounds containing $[(UO2)(NO_3)_3]^-$ and $[Co(NH_3)6]^{3+}$ were crystallized with differing hydrogen bonding networks. Similar to the neptunyl chloride system, asymmetric uranyl bonds were observed with changes in the H-bonding network. This also led to distinct differences in the Raman spectra with the activation of several bands within the spectra. DFT calculations were again performed with similar H-bonding networks observed in the compound with the asymmetric uranyl bond. Surprisingly, the most intense band (exp.: 809 cm^{-1}; calc.: 806 cm^{-1}) in the spectral window of interest was not the symmetric stretch of the uranyl bond, but was associated with a nitrate bend. The symmetric stretch of the uranyl moiety was a concerted mode with the nitrate stretch, which was located at 752 cm^{-1} (calc.: 748 cm^{-1}). With the asymmetry bond, the ν_3 was also activated in the spectra at 951 cm^{-1} (calc.: 956 cm^{-1}).

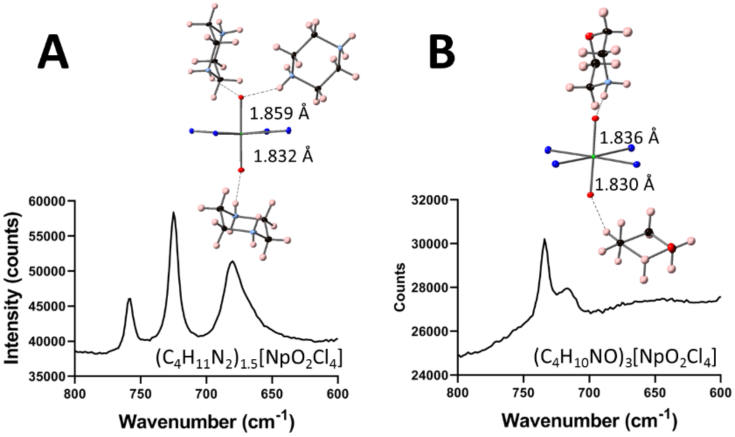

Figure 3. Structural features and Raman spectra of (a) $[C_4H_{11}N_2)_{1.5}[NpO_2Cl_4]$ and (b) $(C_4H_{10}NO)_3[NpO_2Cl_4]$.

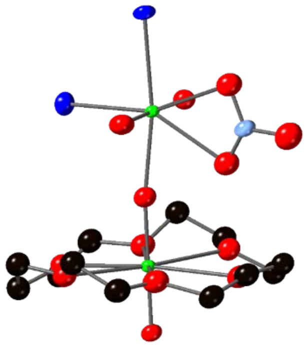

Figure 4. Neptunyl-neptunyl interaction within Np crown-ether system.

2) **Actinyl-actinyl interactions**: Within the neptunyl crown ether system, we were able to crystallize and characterize a complex with a neptunyl-neptunyl interaction (Fig. 4). In this compound, the Np(V) cation encapsulated by the 18-crown-6 molecule and bonded to the second Np(VI) atom through a neptunyl-neptunyl interaction to create the neutral molecule. Bonding to the neighboring neptunyl unit takes place through the equatorial plane and provides the "T-shaped" neptunyl-neptunyl interaction with a Np(1)-O(2)-Np(2) angle of 170(1)°. Neptunyl-neptunyl interactions within isolated molecular complexes have been previously reported, but contain either dimers with diamond interactions or tetrameric species with multiple T-type linkages.[3] Thus, the molecular complex within this compound represents the first report of an isolated complex that contains a simple T-shaped neptunyl-neptunyl interaction. While we have limited information regarding the stability of these two types of interactions in the neptunyl system, a computational assessment of uranyl-uranyl interaction chemistry was performed by Tecmer *et al.*[4] This investigation found that, in general, the T-shaped interactions are more than 20 kcal·mol^{-1} lower in energy than the diamond linkages. While the Raman spectra of this compound was complex, we assigned the band at 724 cm^{-1} to the Np(V)O_2^+ ν_1 symmetric mode and the 771 cm^{-1} signal to the activated Np(V)O_2^+ ν_3 asymmetric band.

Future Plans:

- Continued use of Raman spectroscopy to understand Np(V), Np(VI), and U(VI) solid-state and solution phases. This includes optimization of spectral fitting protocols to assess intensity, band widths, and peak shifts within the spectra that can be related to changes in the actinyl bond.
- Extend collaborations with Professor Mason to include Np(V) complexes. Initial calculation using TURBOMOLE, B3-LYP functionals, and def-SV(P) basis sets for U(VI) and Np(VI) complexes have good agreement with experimental results. We are not experiences the same level of agreement for Np(V), which suggests continued development on the pentavalent system would be a fruitful area of future investigations.
- Exploration of actinyl-cation interactions previously reported in Np(V) solutions by Guillaume et al.[5] Red shifts of the ν_1 band were observed with Np(V) in the presence of solutions containingTh^{4+} (-47 cm^{-1}), Bi^{3+} (-22 cm^{-1}), Pb^{2+} (-9 cm^{-1}), or Cu^{2+} (+16 cm^{-1}). Additional crystallization and spectroscopic analysis is necessary to understand the nature of these spectral shifts and the impact on bonding.
- Continued experimental and computational efforts to understand the impact of the H-bond on the actinyl bond. This includes using DFT to explore changes in the orbital energies and extend synthetic efforts to include other ligands that can result in distinct variations (e.g. two-centered bonds, three-centered bonds, bifurcation) in resulting H-bonding networks.
- Development of molecular models that contain different actinyl-actinyl motifs to determine the impact on the Raman signals. We have crystallized a coordination compound with a "T-shaped" neptunyl-neptunyl, but additional efforts are needed to create other motifs to elucidate the stability of these different arrangements, impacts on the actinyl bond, and changes in spectroscopic signals.

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Quantum Chemical Treatment of Strongly Correlated Magnetic Systems Based on Heavy Elements

Award Number: DE-SC0002183
Principal Investigator: Laura Gagliardi
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Overall research goals: The objective of this project, which has just started, is to develop and employ novel quantum chemical methods in order to study the chemistry of systems containing actinides, and transactinides, with special focus on actinide-based single molecule magnets.

We plan to model inherently multireference magnetic systems containing heavy elements with powerful embedding methods that will enable the calculation of electron correlation energy for extended systems. Commonly used magnetic materials that have potential applications in information storage, quantum information processing and spin electronics work thanks to the spin interactions between neighboring units in the bulk. Single molecule magnets (SMMs) can reduce the length scale of magnetic materials because they exhibit slow relaxation of the magnetization of purely molecular origin, and are thus able to retain their magnetization for a long time. The actinide and trans-actinide elements, because of their large spin-orbit coupling and the radial extension of the 5f orbitals, are promising for the design of both mononuclear and exchange-coupled molecules. Indeed, new actinide SMMs have emerged, and are already demonstrating encouraging properties.

Actinide based SMMs have near-degeneracy electron correlation effects and are thus inherently multiconfigurational systems. Their electronic structure cannot thus be accurately represented by a single Slater determinant approach, such as density functional theory (DFT). To overcome this limitation, we will develop and exploit new methodologies for extended systems that go beyond current Kohn-Sham DFT. A balanced quantum mechanical treatment of their electronic structure requires a multiconfiguration (MC) wave function as a starting point for adding dynamic electron correlation. We propose to do this by employing a recently developed multireference method, namely multiconfiguration pair-density functional theory, (MC-PDFT). We will extend this method from molecular systems to periodic systems within the framework of density matrix embedding theory (DMET).

We will apply these methods to SMMs by embedding the density matrix of a primary subsystem in that of the entire molecular crystal, thereby reducing the periodic problem to a primary-subsystem problem. We will explore mono-center and multiple-center SMMs, and their interaction with the environment vibrations, an effect that is crucial in quantum information processing where spin-phonon relaxation is the ultimate origin of decoherence of solid-state electron spin qubits at room temperature.

Recent Progress

In the previous funding period the grant had title "Modeling Actinide- and Transactinide-Systems with Multireference Quantum Chemical Methods" and under this umbrella we made progress in the following areas:

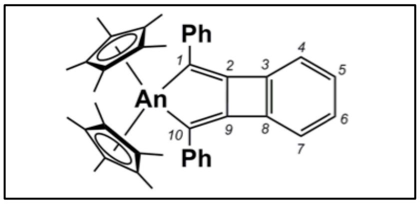

Figure **1**. Structure of the actinide metallabiphenylene complexes. An=Th, U.

- *Actinide Metallabiphenylene Complexes.* We computationally investigated some actinide metallabiphenylene complexes, namely $(C_5Me_5)_2An(2,5\text{-}Ph_2$ cyclopentadienyl[3,4]cyclobuta[1,2]benzene), synthesized in the group of Dr. Kiplinger (Fig. **1**). DFT and multireference calculations were performed to investigate the electronic structure of these species, the antiaromatic character of the cyclobutadiene ring and the aromatic character of the benzene ring. Spectroscopic evidence, molecular orbital compositions, and natural bond orbital calculations suggest significant covalency of the uranium f^2 electrons with the carbon-containing fragment.

- *Uranium(III)-Carbon Multiple Bonds Facilitated by Arene δ-Bonding in Mixed Valence Hexauranium Nanometre-Scale Wheels.* In collaboration with the group of Dr. Steve Liddle we explored some hexauranium methanediidenanometre-scale rings supported by arene bridges.[16] This combined experimental and computational study supports the presence of localized uranium(III) ions and the resulting polarised-covalent U=C bonds are facilitated by δ-bonded arene bridges. These arene bridges provide reservoirs that accommodate charge, thus avoiding inter-electronic repulsion that would destabilise these low oxidation state metal-ligand multiple bonds. This application of arene-binding could constitute a general synthetic strategy by which to circumvent f-element-ligand mismatches to access otherwise inherently unstable linkages. We performed multireference calculations based on species 2, 3, 4 (Fig. **2**) to analyze their electronic structure and explore the nature of the U=C bonds.

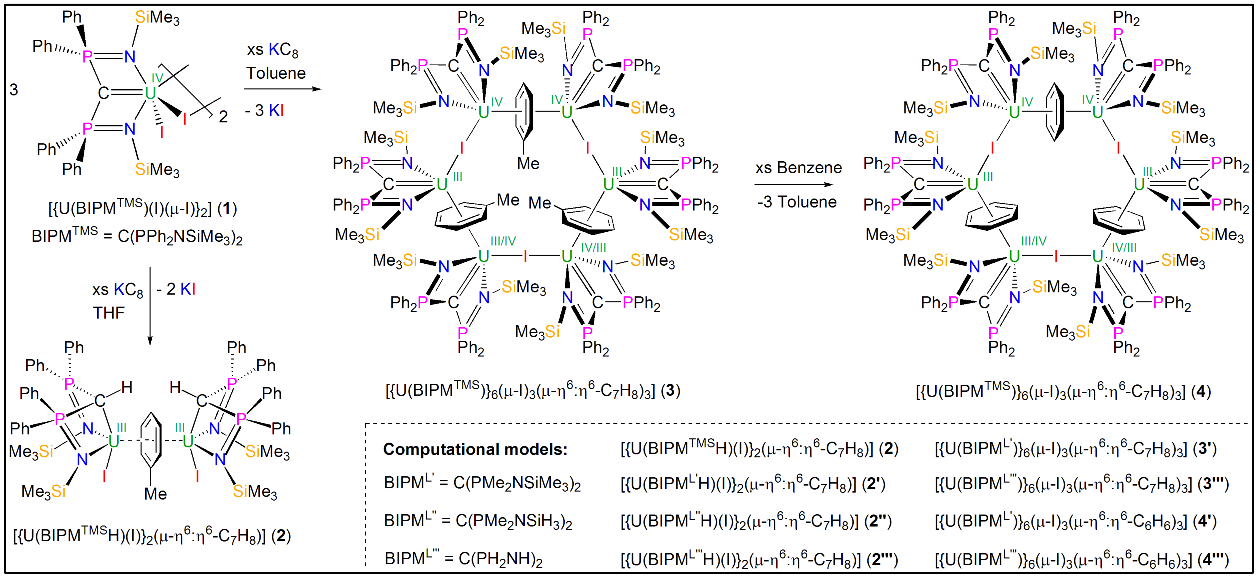

Figure **2.** Synthesis of complexes **2**, **3**, and **4** along with definitions of computational models used in this study.

- We have analyzed theoretically the electronic and magnetic properties of a Pu based SMM ($PuTp_3$, Tp^- = hydrotris(pyrazolyl)borate) (Fig. **3** system **1**) which was recently synthesized and showed a slow magnetization relaxation, with a measured effective anisotropy barrier about 5 times larger than the isostructural uranium based SMM. We have also considered some variants of this system

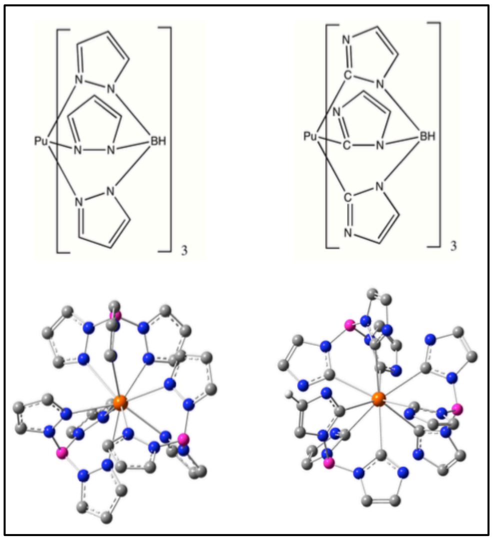

Figure **3.** Schematic representation of the complexes studied. Left: System **1,** $PuTp_3$. Right: System **2** Pu complex with modified ligand (carbene).

with different ligands (Fig. **3** system **2**). We employed CASSCF and CASPT2 calculations to elucidate the electronic structure of different spin states and we computed the magnetic susceptibilities with the SINGLE-ANISO code, which requires as input energies (ε) and magnetic moments (μ) of the spin-orbit states obtained from the RASSI calculation, and uses them in an equation based on the van-Vleck formalism.

- In collaboration with several PIs in this program, including Eric J. Schelter Thomas E. Albrecht-Schmitt, and Suzanne C. Bart, we have investigated an isostructural family of *f*-element compounds (Ce, Nd, Sm, Gd; Am, Bk, Cf) of the redox-active dioxophenoxazine ligand ($DOPO^q$; DOPO = 2,4,6,8-tetra-*tert*-butyl-1-oxo-1*H*-phenoxazin-9-olate). We explored the electronic structure of this new family, by performing CASSCF calculations, which revealed these systems to be largely ionic in contrast to previous studies, where berkelium and californium typically have a small degree of covalent character.

Future Plans:

Future work will be divided as follows:

1) Development of quantum chemical methods for strongly correlated systems

2) Development of embedding methods to describe strong and weak correlation in extended systems

3) Modeling the properties of actinide- and trans-actinide single molecule magnets

We have already made some progress in terms of 1) and 2). We have recently developed a new methods called LASSCF (localized active space SCF) aimed at studying extended systems with multiple metal centers. We will test the method on actinide containing systems with multiple actinides that can be used as SMMs. Currently we are exploring some Np-based SMMs.

In collaboration with Dawn Shaughnessy and John Despotopulos at LLNL we are also exploring some compounds of Hg^{2+} and Pb^{2+} and their superheavy analogues Cn^{2+} and Fl^{2+} containing some thiacrowns, and we computationally study the affinity of these crowns for the different cations.

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Tailoring Redox Active Ligands for Probing the Reactivity of Actinides

Award Number: DE-SC0019177

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Collaborators: Byron Farnum, Auburn University
John D. Gorden, Auburn University
Michael McKee, Auburn University

Overall research goals:

Figure 1. Chemical structures of new ligands(*t*-bu)phen-BIAN (**1**) and dpp-BIAN (**2**).

Redox-active and redox non-innocent ligands have been used widely in transition metal chemistry, but uranium complexes with redox-active ligands are surprisingly rare. The primary goal of this program is to synthesize and characterize ligands featuring soft-donor atoms to probe the differences between the 4f and 5f elements based on our understanding of the properties of bonding in f element compounds. We have developed a new series of redox-active ligands nicknamed "phen-BIAN" ligands (for example: N,N'-bis(iminophenol)acenaphthene, **1**, *Figure 1)*, for investigations of the electronic behavior of uranium and other actinides. This ligand framework borrows features from two classes of Schiff base ligands—the tetradentate O-N-N-O binding pocket from salens, and the redox-active α-diimine unit and backbone from Ar-BIANs (N,N'-bis[(aryl)imino]acenaphthenes, which can accept up to four electrons upon reduction. With these, in addition to other thiol or functionalized analogs, we hope to prepare actinide metal complexes that can be used to electrochemically prepare lower-oxidation state or non-oxo uranium complex, to better characterize the influence of substituent groups on the redox activity, coordination geometry, and covalent interactions. Systems in which the U(VI)/U(V) redox couple can be more fully characterized are relevant to understanding the impacts equatorial ligands have on the reduction of uranyl and stabilization of U(V) species, as pentavalent uranyl intermediates have been found to be critical in bioremediation.[2] Key

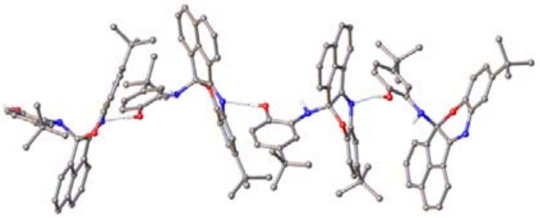
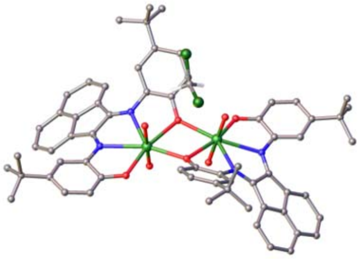


Figure 2. (above) Molecular structure demonstrating the hydrogen-bonding contacts in extended structure of **1** (N,N'-bis(iminophenol)acenaphthene). (below) The molecular structure of the uranyl complex of **1** as a oxo-bridged dimer [UO$_2$(phen-BIAN)]$_2$.[1]



project goals include extensive preparation, structural and spectroscopic characterization and will allow us to address probative questions about the nature of actinide bonding, the degree of covalency, the validity of lanthanides as models for the actinides, hard-soft interactions, interactions between metals in bimetallic complexes and what combination of electronic and steric affects affect the selectivity of a ligand.

Recent Progress:

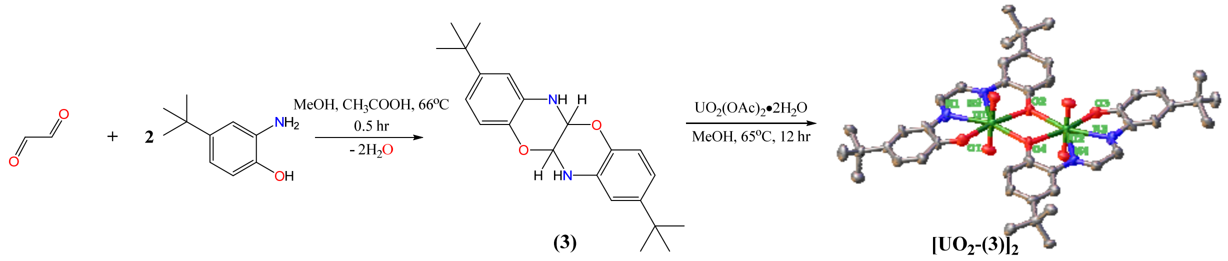
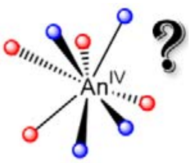


Figure 3..Synthesis of tbu-gbha **(3)**. Yield 69%. Crystals of **(3)**. were grown from a saturated MeOH solution. Crystals of the corresponding uranyl dimer $[UO_2\text{-}(\mathbf{3})]_2$ were grown from acetone//pentane.

An analogous simple Schiff base glyoxal bis(2-hydroxyanil) (gbha) ligand (**3**) lacking the extended conjugation of the phen-BIAN species has been recently synthesized, and its uranyl complex studied structurally and electrochemically (Figure 3). Both complexes are aryloxide bridged dimers with each U(VI) center coordinating the tetradentate pocket. Comparison with the phen-BIAN complex (as the oxo- bridged dimer $[UO_2(\text{phen-BIAN})]_2$, see Figure 2.) electrochemical profile and the observed shift in the ligand reduction potential usually observed only with more specialized redox-active ligands allows for a more detailed characterization of the phen-BIAN electrochemical behavior. In the electrochemistry of $[UO_2(\text{phen-BIAN})]_2$, the more extended π conjugated system demonstrates multiple accessible oxidation states through the formation of U(VI)/U(V) and U(V)/U(IV) mixed-valence complexes that are not observed in the characterization of the gbha complex. The lack of observed oxo-interactions and the significantly less complex electrochemical profiles of the glyoxal species indicate that extended conjugation in the ligand backbone plays a large role in determining the electronic properties of uranyl complexes.

Future Plans:

- Given the deficit of characterized An(IV) complexes (relative to those of UO_2^{2+}), phen-BIAN complexes of U(IV) and Th(IV) will be prepared and characterized.
- Electrochemical studies and experiments will employ chemical reduction to probe the lower oxidation state complex behavior and the redox effects of the redox ligands.



- A family of phen-BIAN ligands with varying phenolic substituents and donor atoms will be prepared to compare the effect of ligand electron donation/withdrawing, steric demands, and donor atom hardness on actinide coordination spheres.
- Analysis of selectivity for actinides and characterization of the stability of the complexes will also be investigated through model extraction studies and metal complex formation with new ligands prepared from modifications to the phenolic framework of the ligand.

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Recent Publications Resulting from this Project (Project start date: 09/2018)

Not Applicable

Coupling Synthesis to Calculation: Expanding our Understanding of Covalency and 5f Orbital Involvement in Actinide-Ligand Bonding

PI: Trevor W. Hayton, Award #: DE-SC0001861

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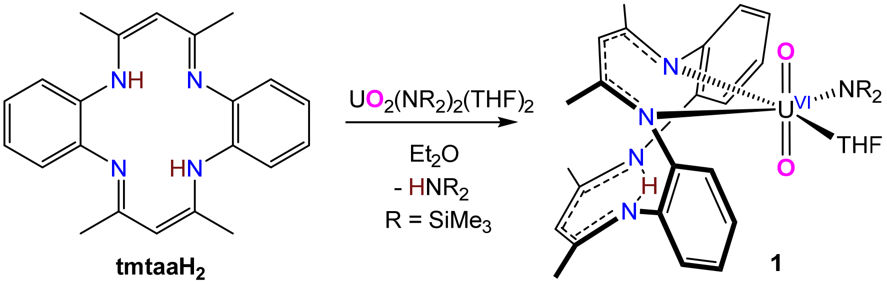
Overall research goals: Our long term goal is to answer fundamental questions about *d* and *f* orbital participation in actinide-ligand bonding. For the current funding period, we seek to answer these questions by exploring three distinct, but synergistic topics: (1) measuring covalency in octahedral 5f^1 systems; (2) synthesis of actinide complexes with An=C and An=N bonds; and (3) development of new strategies for the perturbation of the uranyl ion.

Recent Progress: We have begun to explore the reactivity of uranyl with small macrocycles,[1] in an effort to effect an unprecedented *trans* to *cis* isomerization within the UO_2^{2+} fragment. In particular, we explored the reactivity of the 14-membered tetra(aza)macrocycle, $(tmtaa)^{2-}$ ($tmtaaH_2$ = dibenzotetramethyltetraaza[14]annulene) with the uranyl ion in an effort to form *cis*-$[UO_2(tmtaa)]$. Surprisingly, reaction of $tmtaaH_2$ with $[UO_2(N(SiMe_3)_2)_2(THF)_2]$ results in formation of $[UO_2(tmtaaH)(N(SiMe_3)_2)(THF)]$ (**1**) (Scheme 1).[2] Complex **1** is the result of partial protonation of $[UO_2(N(SiMe_3)_2)_2(THF)_2]$, as it still contains one silylamide ligand and one β-diketimine moiety. This observation demonstrates that elimination of $HN(SiMe_3)_2$ does not provide the required driving force to effect the desired *trans*/*cis* oxo isomerization. The isolation of complex **1** also highlights several other major challenges that need to be overcome in the effort to successfully isolate a *cis*-uranyl complex, such as ligand flexibility, along with unwanted ligand binding modes, which can result in unanticipated reaction products.

Scheme 1. Synthesis of $[UO_2(tmtaaH)(N(SiMe_3)_2)(THF)]$ (**1**)

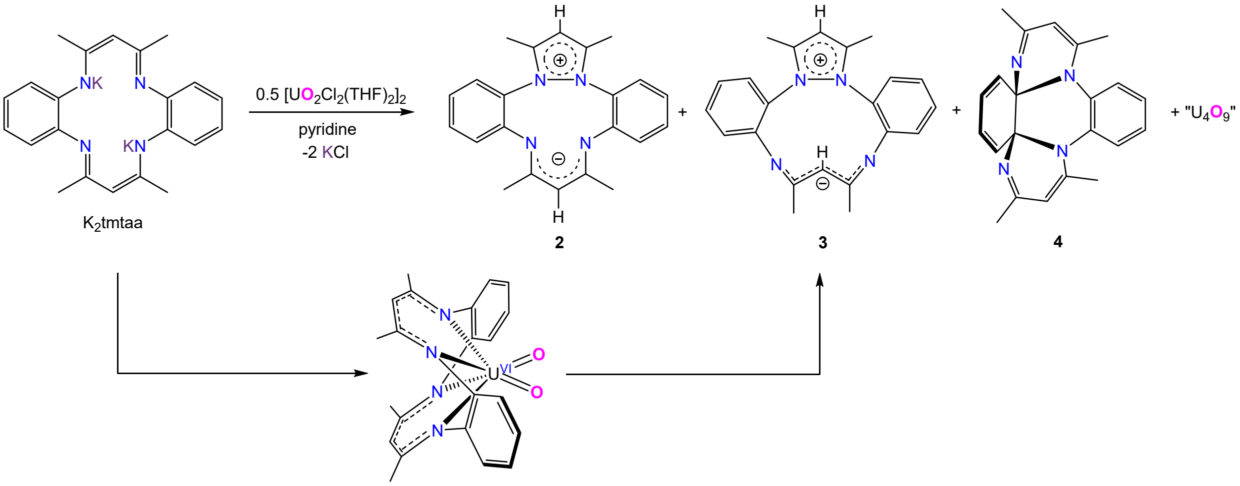


In a subsequent attempt to form a *cis*-uranyl complex, we turned our attention to the potassium salt of $tmtaaH_2$, $K_2(tmtaa)$, on the assumption that KCl elimination would offer sufficient thermodynamic driving force to promote *cis*-$[UO_2(tmtaa)]$ formation. Thus, reaction of $[UO_2Cl_2(THF)_2]_2$ with $K_2(tmtaa)$ in pyridine results in formation of a dark brown solution, from which three isomers of $C_{22}H_{22}N_4$ (compounds **2**, **3**, and **4**) were isolated as a mixture of orange crystalline solids in 41% combined yield (Scheme 2).[3] The identities of **2**, **3**, and **4** were confirmed by X-ray diffraction and each is the product of the two electron oxidation of the $\{tmtaa\}^{2-}$ dianion. Also formed in the reaction is a brown powder, which we tentatively identified as the mixed-valent uranium oxide, U_4O_9, by XPS.

To account for these observations, we hypothesize that reaction of $K_2(tmtaa)$ with $[UO_2Cl_2(THF)_2]_2$ generates *cis*-$[UO_2(tmtaa)]$ (Scheme 2), which is unstable and rapidly decomposes via intramolecular electron transfer to form the 2e$^-$ oxidation products, **2**, **3**, and **4**, along with uranium oxide. Overall, these results further buttress the premise that the putative *cis*-

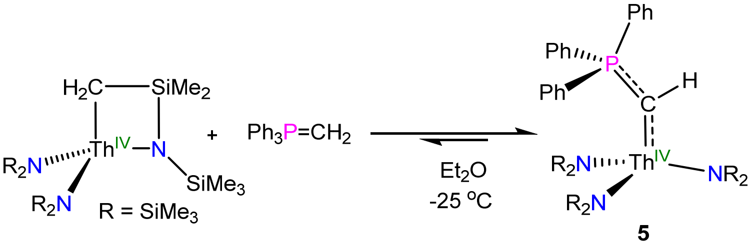
uranyl ion is a strong oxidant, likely on account of diminished *d* and *f* orbital participation within its U-O bonding framework.

Scheme 2. Reaction of K_2(tmtaa) with $[UO_2Cl_2(THF)_2]_2$



We have also continued to explore the synthesis and spectroscopic characterization of actinide carbenes. Most recently, we synthesized a rare example of a thorium carbene, $[Th(CHPPh_3)(NR_2)_3]$ (**5**) (Scheme 3).[4] X-ray diffraction studies, together with NMR spectroscopic data and DFT calculations, provide clear evidence for the presence of an actinide-carbon multiple bond in this complex. Additionally, the large downfield chemical shift of the methine carbon in its ^{13}C NMR spectrum (ca. 117 ppm) was found to be a consequence of the large degree of covalency within the Th=C bond, further demonstrating that ^{13}C NMR spectroscopy is a useful tool for probing An-C bond covalency for actinide organometallics. This work was performed in collaboration with Dr. Peter Hrobárik at Comenius University.

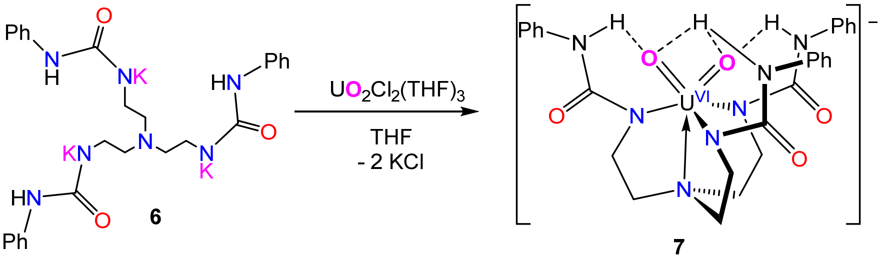
Scheme 3. Synthesis of the thorium carbene, $[Th(CHPPh_3)(NR_2)_3]$ (**5**)



Future plans:

New Strategies for Uranyl (UO_2^{2+}) Perturbation. We propose to ligate the known ureate-substituted TREN ligand $[K]_3[H_3buea]$ (**6**) ($H_3buea = N(CH_2CH_2NC(O)NHPh)_3$)[5] to the uranyl fragment, generating the *cis*-uranyl complex, $[K][cis\text{-}UO_2(H_3buea)]$ (**7**) (Scheme 4). The H_3buea ligand was designed specifically to stabilize highly reactive oxo linkages

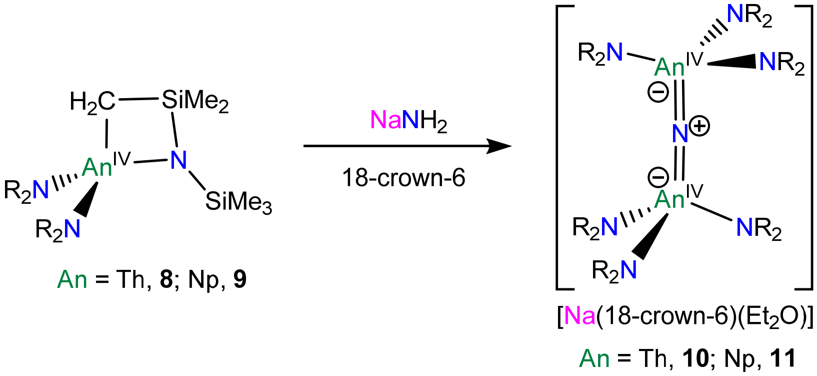
Scheme 4. Synthesis of $[K][cis\text{-}UO_2(H_3buea)]$ (**7**)



via a network of hydrogen bonding interactions. For example, this ligand was used to isolate the first terminal Fe(III) oxo complex, $[FeO(H_3buea)]^{2-}$. Thus, we hypothesize that **6** will temper the reactivity of the *cis*-uranyl fragment via hydrogen bonding interactions with the two oxo ligands in uranyl, facilitating its isolation and characterization. We anticipate that **7** will feature weakened U-O bonding, which we will probe via X-ray crystallography, IR spectroscopy, and DFT calculations.

Generation of An=N Multiple Bonds. Very recently, my group discovered that sodium amide ($NaNH_2$) could be used as a nitride source with thorium. Specifically, reaction of the Th(IV) metallacycle, Th{*N*(R)$SiMe_2$*C*H_2}$(NR_2)_2$ (R = $SiMe_3$) (**8**), with $NaNH_2$ and 18-crown-6 resulted in the formation of $[Na(18\text{-c-}6)][(R_2N)_3Th(\mu\text{-}N)(Th(NR_2)_3]$ (**10**) (Scheme 5) in good yields. This complex was characterized by NMR, IR, EA, and X-ray crystallography. Complex **10** is the first nitrido complex known for thorium. Building on this work, we plan to extend this nitride chemistry to Np. Specifically, we propose that reaction of the Np(IV) metallacycle, Np{*N*(R)$SiMe_2$*C*H_2}$(NR_2)_2$ (**9**), with $NaNH_2$ should afford $[Na(18\text{-c-}6)][(R_2N)_3Np(\mu\text{-}N)Np(NR_2)_3]$ (**11**), the first Np nitride complex (Scheme 5). Complex **11** will be characterized by a wide variety of techniques, including DFT calculations and X-ray crystallography. In addition, we will make the ^{15}N labelled nitride complex, **11-^{15}N**, which we will characterize by IR and Raman spectroscopies. This vibration data will allow us to benchmark our DFT calculations, giving our bonding analysis further veracity. For this work, test reactions to install the label in Th analogue **10** will be absolutely critical as it will allow us to optimize ^{15}N incorporation without the need to waste valuable Np starting materials. This work will be performed in collaboration with Dr. Andrew Gaunt at LANL.

Scheme 5. Synthesis of nitride complexes of Th and Np



References:

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(2) Pedrick, E. A.; Assefa, M. K.; Wakefield, M. E.; Wu, G.; Hayton, T. W. Uranyl Coordination by the 14-Membered Macrocycle Dibenzotetramethyltetraaza[14]annulene. *Inorg. Chem.* **2017**, *56*, 6638-6644.

(3) Assefa, M. K.; Pedrick, E. A.; Wakefield, M. E.; Wu, G.; Hayton, T. W. Oxidation of the 14-Membered Macrocycle Dibenzotetramethyltetraaza[14]annulene upon Ligation to the Uranyl Ion. *Inorg. Chem.* **2018**, *57*, 8317-8324.

(4) Smiles, D. E.; Wu, G.; Hrobárik, P.; Hayton, T. W. Synthesis, Thermochemistry, Bonding, and ^{13}C NMR Chemical Shift Analysis of a Phosphorano-Stabilized Carbene of Thorium. *Organometallics* **2017**, *36*, 4519–4524.

(5) Shirin, Z.; Hammes, B. S.; Young, V. G.; Borovik, A. S. Hydrogen Bonding in Metal Oxo Complexes: Synthesis and Structure of a Monomeric Manganese(III)−Oxo Complex and Its Hydroxo Analogue. *J. Am. Chem. Soc.* **2000**, *122*, 1836-1837.

Recent Publications Resulting from this Project

1. Assefa, M. K.; Hayton, T. W.* Bis(1,2-dimethoxyethane)tetra(chloride)uranium(IV), $UCl_4(DME)_2$. *Inorg. Synth.* **2019**, *In Press.*

2. Assefa M. K., Pedrick E. A., Wakefield M. E., Wu G., Hayton T. W.* Oxidation of the 14-Membered Macrocycle Dibenzotetramethyltetraaza[14]annulene upon Ligation to the Uranyl Ion. *Inorg. Chem.* **2018**, *57*, 8317–8324. DOI: 10.1021/acs.inorgchem.8b00966

3. Hayton, T. W.* Understanding the origins of O_{yl}–U–O_{yl} bending in the uranyl (UO_2^{2+}) ion. *Dalton Trans.*, **2018**, 47, 1003-1009. DOI: 10.1039/C7DT04123C

4. Seaman, L. A.; Pedrick, E. A.; Wu, G.; Hayton T. W.* Promoting Oxo Functionalization in the Uranyl Ion by Ligation to Ketimides. *J. Organomet. Chem.* **2018**, *857*, 34-37. DOI: 10.1016/j.jorganchem.2017.08.007

5. Hayton, T. W.*; Kaltsoyannis, N.* Organometallic Actinide Complexes with Novel Oxidation States and Ligand Types. In: *Experimental and Theoretical Approaches to Actinide Chemistry*. Eds. de Jong, W.; Gibson, J., Wiley; New York, **2018**, pp. 181-236. DOI: 10.1002/9781119115557.ch4

6. Smiles, D. E.; Wu, G.; Hrobárik, P.*; Hayton, T.W.* Synthesis, Thermochemistry, Bonding, and ^{13}C NMR Chemical Shift Analysis of a Phosphorano-Stabilized Carbene of Thorium. *Organometallics* **2017**, *36*, 4519-4524. DOI: 10.1021/acs.organomet.7b00202

7. Pedrick, E. A.; Assefa, M. K.; Wakefield, M. E.; Wu, G.; Hayton T. W.* Uranyl Coordination by the 14-Membered Macrocycle Dibenzotetramethyltetraaza[14]annulene. *Inorg. Chem*. **2017**, *56*, 6638-6644. DOI: 10.1021/acs.inorgchem.7b00700

Probing Actinide Bonding by Electronic and Photoelectron Spectroscopy

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Overall research goals

The primary goal of this program is to investigate the bonding and electronic structure of simple actinide compounds using high-resolution spectroscopic techniques in the gas phase. The intention is to advance our understanding of the roles that the 5f electrons play in actinide bonding, and to evaluate the computational electronic structure methods that are used to predict and interpret actinide chemistry. Gas phase spectra are particularly valuable as they yield definitive electronic state assignments and structural information. These results can be used in the direct assessment of theoretical predictions for the isolated molecule. This avoids the ambiguities in experimental spectral assignments and the theoretical approximations that must be invoked when dealing with condensed phase samples.

Recent Progress

(i) Development of a configuration interaction – ligand field theory model for the electronic states of ThO

We have developed configuration interaction – ligand field theory (CI LFT) models as a means to predict and interpret the electronically excited states of ionically bound actinide compounds. Initially, we have focused on ThO as this is the species that has the most extensive experimental database for electronically excited states. A CI LFT Hamiltonian matrix was constructed with the goal of providing configurational assignments for observed states of ThO in the range 0-5 eV. The model, validated against states with known atomic ion configurational assignments, was used to establish configurations for the unassigned experimental data listed in the Vatican Atlas (A. Gatterer *et al.* Molecular Spectra of Metallic Oxides Specola Vaticana (1957)). The model included all states arising from the Th^{2+} $6d^2$, $6d7s$, $6d7p$, $5f7s$, $7s7p$, $7p^2$, and $7s^2$ configurations. We did not include two manifolds of charge-transfer states from $Th^+(6d7s^2)O^-(2p^5)$ and $Th^+(6d^27s)O^-(2p^5)$ whose lowest energy states are predicted to lie at 44,100 cm^{-1} and 50,900 cm^{-1}, respectively.

Twenty-nine experimentally characterized ThO v=0 energy levels and the energy difference between the v=0 levels of the *Y* and *W* states were available for fitting the CI LFT model parameters (all states with $\Omega\leq3$). The results from the optimized model were then used to propose assignments for previously unidentified ThO molecular bands that are listed in the Vatican Atlas. As a result, term values for 30 electronic states have been determined based on these assignments. Subsequently, the CI LFT model was refined by fitting to the full set of 59 electronic term energies. Predictions from these calculations were used to provide assignments for 171 out of 250 ThO band heads listed by Gatterer et al. Term energies for 30 electronic states have been determined.

(ii) Electronic spectroscopy of jet-cooled ThO

A systematic study of the laser induced fluorescence (LIF) spectrum of jet-cooled ThO was carried out over the energy range from 16700 to 23000 cm^{-1}. There were two motivations for this effort. The first was to extend the characterization of the electronically excited states that fall in this energy range. The second was to facilitate our ongoing efforts to characterize Th-containing species by means of LIF techniques. We routinely use pulsed laser ablation as the means to generate gas phase samples of refractory Th compounds. The oxide is always present in the ablation plumes. Consequently, a map of the ThO spectrum, generated under jet-cooled conditions, facilitates the recognition of these bands in spectral searches for other target molecules.

For the energy range examined we observed 22 previously unreported bands at the level of rotational resolution. Least squares analyses of these data were used to obtain rotational constants, vibronic term energies and excited state term symbols. The bands were assigned to new vibronic levels of the D, E, F and I states. Although the rotational temperature of the bands was relatively low (typically near 80K), vibrationally excited levels of the ground state up to v=4 were populated and observed via hot bands. Using these data we have been able to significantly improve the vibrational constants. Combining this information with the data from a previous study of the pure rotational spectrum we have generated an accurate RKR potential energy curve for ThO(X) (a new benchmark for the evaluation of quantum chemistry calculations). Vibrational intervals for the electronically excited states exhibited irregularities due to local perturbations. This work has been submitted for publication in the Journal of Molecular Spectroscopy.

(iii) The Electronic Structure of the Actinide Oxides and Their Singly Charged Cations: A Ligand Field Approach

The primary objective of this sub-task is to develop LFT models for all of the neutral and singly charged actinide monoxides and to determine the density distributions of bound electronic states. This density-of-states model for electronic structure together with estimated molecular parameters can be used to calculate partition functions and thermodynamic properties for the AnO and AnO^{+} series (where $An \in$ Th through Lr).

Ligand field theory calculations of energy levels have been carried out for the neutral actinide monooxides and their singly charged cations by treating the molecular electronic states as An^{m+} free-ion levels perturbed by the O^{2-} ligand. LFT parameters obtained from analyses of ThO, ThO^{+}, UO, and UO^{+} energy levels were used to compute molecular energy levels with the lowest (maximum S_c, maximum L_c) 5*f*-core of An^{3+}, An^{2+}, and An^{+} atomic multiplet state for the majority of the $An^{3+}O^{2-}$, $An^{2+}O^{-}$, $An^{2+}O^{2-}$, and $An^{+}O^{-}$ configurations.

Simple linear relationships enable prediction of the dissociation energies for AnO^{+} and the ionization energies for AnO and AnO^{+} (where $An \in$ Bk through Lr), mainly based on recent experimental data for the ionization energies of An atoms (where $An \in$ Fm, Md, No, and Lr) and correlations with the energetics of the atoms and ions.

(iv) Microwave spectroscopy of ThN(X)

The microwave spectrum of ThN($X^2\Sigma^+$) was examined in a collaborative effort with Prof. T. Steimle of Arizona State University (ASU). Microwave-optical double resonance data were obtained during M. Heavens' visit to ASU in July 2018. The ΔN=1 transitions (where N is the quantum number for rotational angular momentum) exhibited splittings due to spin-rotation and hyperfine interactions. The latter were associated with the nuclear spin of the nitrogen atom. Two spin-rotation and three hyperfine coupling constants were determined from the lines of the N”=0

→N'=1, 2→3 and 3→4 transitions. Accurate values for the B and D rotational constants were also obtained.

The dominant hyperfine term arises from the Fermi contact interaction, which is dependent on the spin density of the ground state electronic wavefunction at the N atom nucleus. A relativistic density functional calculation yielded a Fermi contact term of 0.000460 cm^{-1}, in respectable agreement with the experimentally determined value of 0.0004665 cm^{-1}.

(v) Pulsed field ionization – zero kinetic energy photoelectron spectroscopy of UN^+

The UN^+ ion provides a diatomic example where U is formally in the +4 oxidation state. From the perspective of the metal ion, it may be usefully compared with UO_2. Prior to our study, there were no reported spectroscopic data for UN^+. The first gas phase electronic spectrum for neutral UN was recorded by Matthew and Morse (JCP, **138**, 184303 (2013)). As this molecule is isoelectronic with UO^+ it might be expected to have the same ground state (i.e., $U^{3+}(5f^3\ {}^4I_{9/2})N^{3-}$, $\Omega=4.5$). However, the spectra clearly show that the ground state is $\Omega=3.5$, most probably arising from the configuration $U^{3+}(5f^27s\ {}^4H_{7/2})N^{3-}$. It appears that the shorter bond length of UN, combined with the greater charge on the ligand, pushes $5f^3$ above $5f^27s$ (the latter being less strongly destabilized by the ligand owing to the polarizability of the 7s orbital). Turning to the ion, the low energy states UN^+ will be derived from the metal ion 5f7s and $5f^2$ configurations.

We have characterized low energy vibrational states of UN^+ using a two-color pulsed field ionization - zero kinetic energy (PFI-ZEKE) photoelectron spectroscopy technique. The first task for this measurement was to determine the ionization energy (IE) of UN by means of two-color photo-ionization efficiency (PIE) measurements. For the neutral molecule excitation step we used a transition centered at 18635 cm^{-1} that yielded strong ionization signals when the energy of the second photon was chosen to be well above the IE. A tunable dye laser was then used to scan the energy of the second photon over the total energy ($h\nu_1+h\nu_2$) range where the IE was expected. The onset of ionization was located at 50802±30 cm^{-1}. This value was refined by performing PFI-ZEKE measurements. Rotationally resolved data were obtained, yielding an IE for UN of 50802±5 cm^{-1}. The rotational structure for the ion was consistent with an $\Omega=4$ ground state, as expected for the $U^{4+}(5f^2)N^{3-}$ configuration. Scanning to higher energy revealed the v=1 and v=2 vibrational levels. These were located 1072±5 and 2134±5 cm^{-1} above the zero-point level. We expect to find levels from electronically excited states as we push our measurements to higher energies. Relativistic quantum chemical calculations (CASSCF/MRCI-SO) for UN and UN^+ have been carried out in parallel with the experimental efforts. These calculations confirm the $5f^27s$, $\Omega=3.5$ and $5f^2$, $\Omega=4$ ground state configurations for UN and UN^+, and demonstrate that the orderings of low-energy electronic states are consistent with the expectations of ligand field theory.

Future plans

The next targets for our REMPI and PFI-ZEKE spectroscopy techniques will be tri-atomic actinide species of increasing complexity. One objective will be to delineate the factors that control the resolution achievable in studies of polyatomic actinide species by means of electronic spectroscopy. The species to be studied include the linear molecules OThF, $OThF^+$, NUN and NUO^+. The uranium species are of particular interest as they are isoelectronic with the uranyl ion. In a collaboration with Dr. Ping Yang (LANL) we will examine a range of mass-selected thorium oxide clusters using slow electron velocity map imaging spectroscopy.

Recent Publications Resulting from this Project

M. C. Heaven and K. A. Peterson in "Experimental and Theoretical Approaches to Actinide Chemistry". Editors, J. K. Gibson and W. De Jong. Pages 1-52, Wiley, 2018 (https://www.wiley.com/en-gb/Experimental+and+Theoretical+Approaches+to+Actinide+Chemistry-p-9781119115526)

"Chapter 1: Probing actinide bonds in the gas phase: theory and spectroscopy" R. A. VanGundy, J. H. Bartlett, M. C. Heaven, S. R. Battey and K. A. Peterson, J. Chem. Phys., 146, 054307 (2017) http://dx.doi.org/10.1063/1.4975070

"Spectroscopic and theoretical studies of ThCl and ThCl$^+$"

L. A. Kaledin, A. L. Kaledin and M. C. Heaven, J. Comp. Chem., 40, 430-446 (2019) https://doi.org/10.1002/jcc.25710

"The electronic structure of thorium monoxide: ligand field assignment of states in the range 0–5 eV"

J. R. Schmitz, L. A. Kaledin and M. C. Heaven, J. Mol. Spectrosc. Submitted, March 2019

"Laser induced fluorescence spectroscopy of jet-cooled ThO"

A. T. Le, S. Nakhate, T. Nguyen, T. C. Steimle and M. C. Heaven, J. Phys. Chem., Revision submitted, March 2019

"Characterization of Gas-Phase Thorium Nitride"

UNDERSTANDING THE CHEMICAL COMPLEXITY OF MULTI-COMPONENT SYSTEMS: URANIUM POLYOXOMETALATES AS NANOSORBENTS

Award Number: DOE-SC-0018231

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Overall Research Goals

The overarching objective of this project is to develop a molecular-scale understanding of chemical interactions of the transuranic elements with uranyl-based polyoxometalate nanoclusters. This project was inspired by the PI's arrival at the University of Notre Dame, where uranyl polyoxometalate clusters were discovered, and represents a natural synergy between the wealth of expertise and knowledge at Notre Dame surrounding their synthesis and characterization while building upon the PI's prior work investigating the mechanisms and kinetics of processes which control the behavior of plutonium at the solid-water interface. The relatively recent discovery of uranyl polyoxometalate clusters offers the opportunity to better understand the evolution of the uranyl ion in solution, which is the foundation of uranium chemistry.

The focus of this research is to investigate the interactions of neptunium, plutonium, and americium with various uranyl polyoxometalates and to compare their behavior to others on the periodic table in order to understand trends and relationships between *s*-, *d*-, and *f*-block elements. Currently, the three possible mechanisms governing such reactions are believed to be sorption, encapsulation, and aggregation. The later causes clusters to assemble in solution as large hollow aggregates colloquially called blackberries. Once the chemical conditions have been tuned to optimize neptunium, plutonium, or americium association with the clusters, they can be recovered via filtration. This would allow for cleaner fuel reprocessing techniques than what is currently available.

Recent Progress

Current efforts are focused on U_{60} ($[(UO_2)(O_2)(OH)]_{60}^{60-}$) and $U_{24}Pp_{12}$ ($\{[(UO_2)(O_2)]_{24}(P_2O_7)_{12}\}^{48-}$) as model clusters because their aqueous-phase behavior is relatively well-understood and they can be synthesized as pure phases in gram quantities. Initial studies have focused on non-radioactive tetravalent metals (e.g., Hf^{4+}) and lower-valent cations (e.g., alkali and alkaline earth elements), which allows us to probe a larger experimental space while training students to work safely with the transuranic elements.

Experiments with U_{60}

We are working on creating full trends with monovalent (Na^+, K^+, Rb^+, and Cs^+), divalent (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}), trivalent (Ce^{3+}, Eu^{3+}), and tetravalent (Hf^{4+}) cations using dynamic light scattering (DLS) and small angle X-ray scattering (SAXS). These techniques allow us to determine the hydrodynamic radius (R_h) and the radius of gyration (R_g), respectively, of species in solution and determine if U_{60} aggregates or blackberries form upon addition of these cations. We are complementing these analyses with centrifugal filtration to determine the extent to which each cation associates with U_{60}. Our initial results indicate that U_{60} coexists with these cations in solution without degradation of the clusters and that aggregates are retained by the filters. As the cation valence increases, the concentration needed to induce U_{60} aggregation decreases; the R_h of U_{60} aggregates decreases down the Group 1 and 2 elements (see Figure 1).

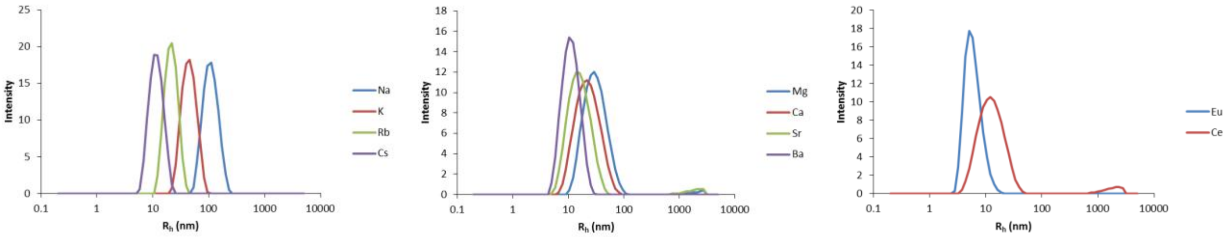

Figure 1. R_h measurements of solutions containing U_{60} and monovalent cations (left), divalent cations (middle), or trivalent cations (right). The R_h of U_{60} in the absence of additional cations is ~1nm.

Experiments with $U_{24}Pp_{12}$

Pilot experiments were performed on $U_{24}Pp_{12}$ solutions where the R_h was monitored as a function of time and hafnium concentration (0.05 – 5 mM). Regardless of hafnium concentration, the R_h initially increased from ~1 nm to 50-200 nm, suggesting the formation of $U_{24}Pp_{12}$ aggregates in solution. In samples where the hafnium concentration was greater than ~0.5 mM, hafnium precipitated as a hydroxide after several days. A sample containing $U_{24}Pp_{12}$ and 0.1 mM Hf was allowed to recrystallize. Initial unit cell determinations match those of $U_{24}Pp_{12}$ and we are in the process of fully refining the structure.

Our current Pu(IV) stock solution is prepared in 2 M HCl. We expect this acid concentration to be problematic since the U_{60} and $U_{24}Pp_{12}$ are stable under alkaline conditions. Preliminary experiments using a hafnium stock solution of similar acid concentration show that a 1:10 dilution will be required to prevent conversion of $U_{24}Pp_{12}$ to studtite or an unidentified yellow precipitate. A two mole equivalent of LiOH will also be added to the $U_{24}Pp_{12}$ working solution before the addition of plutonium in order to prevent the pH of the solution from dropping below the range of $U_{24}Pp_{12}$ stability.

As mentioned above, it is necessary to keep the hafnium concentration less than 0.5 nM in order to prevent the precipitation of hafnium hydroxide. Thus, the difference in uranium concentration and hafnium concentration in our samples spans several orders of magnitude. This makes it difficult, and sometimes impossible, to measure the concentration of hafnium via inductively coupled plasma optical emission spectroscopy (ICP-OES) due to matrix effects. We are developing a method to quantify lithium, sodium, phosphate, uranium, and hafnium via ICP-OES that is based on initial separation of hafnium and uranium using UTEVA resin. When the resin is conditioned and washed with 3 M nitric acid, hafnium should elute from the column and uranium should be retained by the column. A preliminary separation performed on a solution containing discrete uranium and hafnium demonstrated that this separation was possible. However, when the separation was performed on a cluster sample doped with 0.125 mM Hf, the analysis was unsuccessful. The hafnium could not be quantified and uranium breakthrough was observed on the ICP-OES. We suspect that this breakthrough is attributed to the presence of pyrophosphate. In acidic solutions, the pyrophosphate can breakdown into phosphoric acid, which can affect the retention of uranium on the resin.

Future Plans

We are in the final stages of approving our in-house SAXS and electrospray ionization mass spectrometry (ESI-MS) instruments for use with transuranic materials. One final approval is received, we will start studies investigating Np(V) and Pu(IV) interactions with $U_{24}Pp_{12}$. The UTEVA method that we develop should be applicable to Pu/$U_{24}Pp_{12}$ systems, but adjustments will likely be needed for the Np/$U_{24}Pp_{12}$ systems. The full suite of analysis – DLS, SAXS, ESI-MS, and ICP-OES – should provide a robust picture of neptunium and plutonium interactions with $U_{24}Pp_{12}$, which will be the basis of a user proposal to the Advanced Photon Source for X-ray absorption spectroscopy experiments. We also plan to expand the U_{60} work to investigate the effect of temperature on cation-induced aggregation by using a stepwise approach on the DLS for each of the cations.

Title: Tetravalent Actinide Speciation: Template Directed Assembly, Stabilization, and Reactivity
Award Number: DE-SC0019190
Principal Investigator: Karah E. Knope
Address: Department of Chemistry, Georgetown University, Washington, DC 20057
Email: kek44@georgetown.edu

Overall research goals: We aim to elucidate the impact of inner and outer coordination sphere interactions, broadly defined as template effects, on actinide speciation and reactivity. Our experimental efforts focus on the molecular level structural characterization of Ce and Th-Pu solution and solid state phases and address the effects of (1) complexing ligands, (2) non-bonding interactions, and (3) functionalized surfaces on actinide complex formation, stabilization, crystallization, and reactivity.

Recent Progress: 1. We have demonstrated that under acidic aqueous conditions, noncovalent interactions such as hydrogen bonding may be used to stabilize and crystallize elusive tetravalent metal ion (Th, U, Pu) complexes. 2. We have further demonstrated that these outer coordination sphere interactions coupled with solution conditions may be harnessed towards the isolation of novel polynuclear complexes of the tetravalent metal ions including Ce, Th, and U, with the nuclearity of the complexes showing a degree of counter-cation dependence.

1. Evaporation of acidic aqueous chloride solutions containing Th, U, or Pu and protonated N-heterocycles led to the isolation of a series of fifteen An(IV) chloride complexes. Th and U complexes were prepared at Georgetown University and the Pu compounds were prepared at Pacific Northwest National Laboratory. Figure 1 shows the solid state structural units observed for each metal ion and highlights both the utility of H-bond donors in isolating elusive structural units such as U-aquo-chloro complexes as well as trends in chemical periodicity that are observed from Th-Pu.

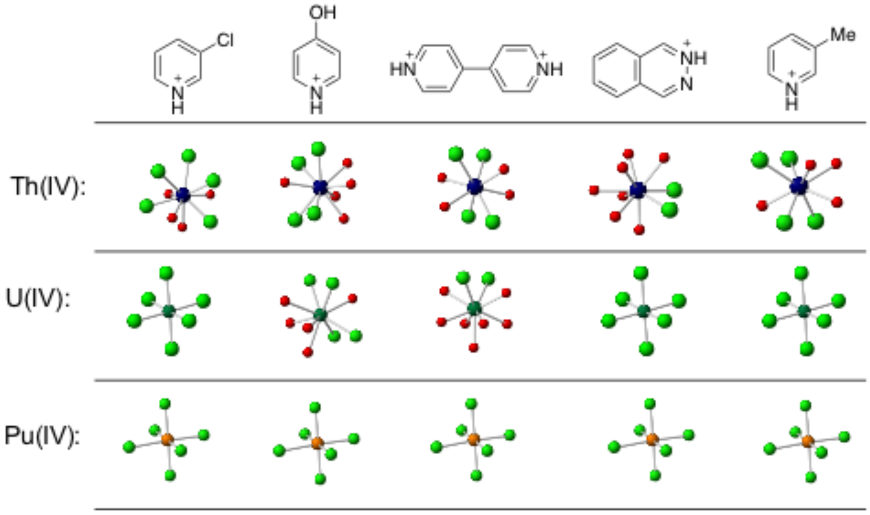

Figure 1. Actinide chloride complexes isolated from acidic aqueous chloride solutions in the presence of protonated N-heterocycles.

2. The presence of counter-cations coupled with the judicious tuning of solution conditions have led to the isolation of Ce, Th, and U complexes that range in nuclearity from mononuclear units to large polynuclear clusters. Preliminary work has shown that the nuclearity of the complexes is governed by both solution conditions as well as the identity of the countercation. Figure 2 highlights representative examples of Ce complexes and clusters recently synthesized in our lab. Isolation of the Ce_{52} cluster, the largest known for the tetravalent metal ions, is dependent on the identity of the counter ion.

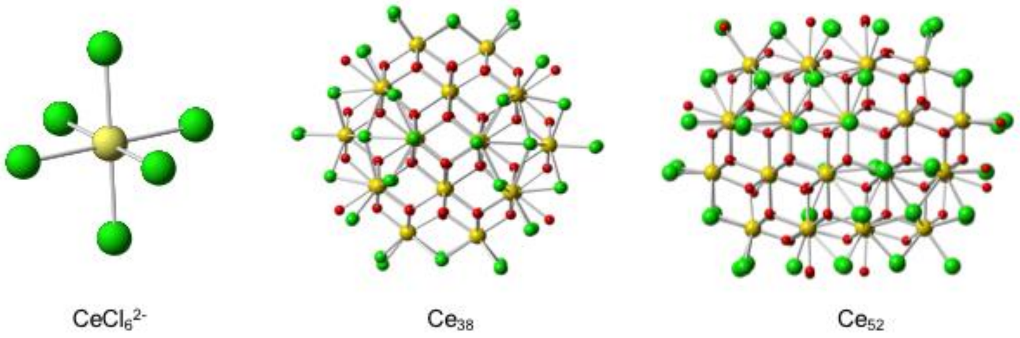

Figure 2. Representation of the mononuclear $CeCl_6^{2-}$ complex and polynuclear Ce_{38}- and Ce_{52}-oxo clusters isolated from aqueous chloride media.

Future Plans:

- We have recently synthesized and stabilized polynuclear Ce-oxo clusters including Ce_{38} and Ce_{52} as described above; however, the oxidation state assignment in these polynuclear species is unclear. The oxidation state of the Ce sites will be determined using EXAFS and complementary spectroscopic techniques.
- Examine how the identity of complexing ligands affects the reactivity of An_6 structural units.
- Examine the effects of redox chemistry on the formation and stability of polynuclear An(IV) species.
- Extend Ce, Th, and U efforts into Np and Pu systems
- Extend template directed assembly efforts to include 2D surfaces such as self-assembled monolayers (e.g. gold-thiols, siloxanes) and functionalized nanoparticles (e.g. polystyrene beads).

Recent Publications Resulting from this Project: Project Start Date 09/2018

Molecular Approaches to the Electronic Structure of Actinide Materials
DE-SC0019385

Henry S. La Pierre, Principal Investigator
Graduate Students: Natalie T. Rice, Thaige P. Gompa, Brandon J. Yik, Luis M. Aquirre-Quintana; Postdoc: Kai Wang
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Collaborators: Ivan A. Popov, Ping Yang, and Enrique R. Batista, Theoretical Division, Los Alamos National Laboratory; Joshua Telser; Department of Biological, Chemical and Physical Sciences, Roosevelt University; Lukas Palatinus; Institute of Physics, Czech Academy of Sciences; John Bacsa, School of Chemistry and Biochemistry, Georgia Institute of Technology.

Overall Research Goals: The principal goal of the proposed synthetic and X-ray absorption spectroscopic (XAS) studies is to disentangle the complex electronic structure of actinide materials. Three problems of electron (de)localization in actinide materials will be addressed in this study. We intend to focus on the synthesis of actinide complexes that enforce ground state electronic structures that include mixed valence metal ions (*i.e.* mixed *f/d* occupancy by the valence electrons in a monometallic complex), multi-configurational electronic structures, and magnetic superexchange (*i.e.* exchange coupled systems). Mono- and multimetallic complexes that present these electronic phenomena are designed to be evaluated by multi-edge XAS studies and thermodynamic probes such as magnetometry and heat capacitance in order to establish a clear correspondence between spectroscopic signature, electronic structure, and physical properties.

Recent Progress Fall 2018–2019:
The project was initiated in September 2018 focusing on developing the synthetic chemistry and spectroscopy of low-valent, bimetallic lanthanide imidophosphorane complexes and early actinides (Th and U) imidophosphorane complexes. Synthetic studies of organic ligands designed to stabilize multi-configurational actinide complexes were also initiated. To-date, two significant results have been identified:

1) Our laboratory has developed synthetic methodologies to access homoleptic imidophosphorane complexes of the trivalent lanthanides based on *tris*-dialkylamino-imidophosphorane ligands. These complexes form dimers with short intermetallic distances (3.4126(6) Å in the case of ytterbium). These bimetallic complexes with Ln^{3+}/Ln^{3+} cores can be reduced by several methods to form mixed-valent complexes with formally Ln^{2+}/Ln^{3+} cores. In the case of ytterbium, the resultant mixed-valent complex has a contracted intermetallic distance of 3.008(3) Å. The combination of structural analysis, UV/Vis/NIR spectroscopy, and Yb L_3-edge XANES suggest that the Yb ions are strongly electronically coupled and that the complex has competing valence electronic structures near room temperature. In particular, the observed thermo- and solvatochromatic behavior indicate that the complex is at the transition between Class II and Class II – III behavior on the Robin-Day classification scheme. The analogous Sm and Eu complexes in under investigation to provide comparison to the transuranic (Np and Pu) complexes in development in the group.

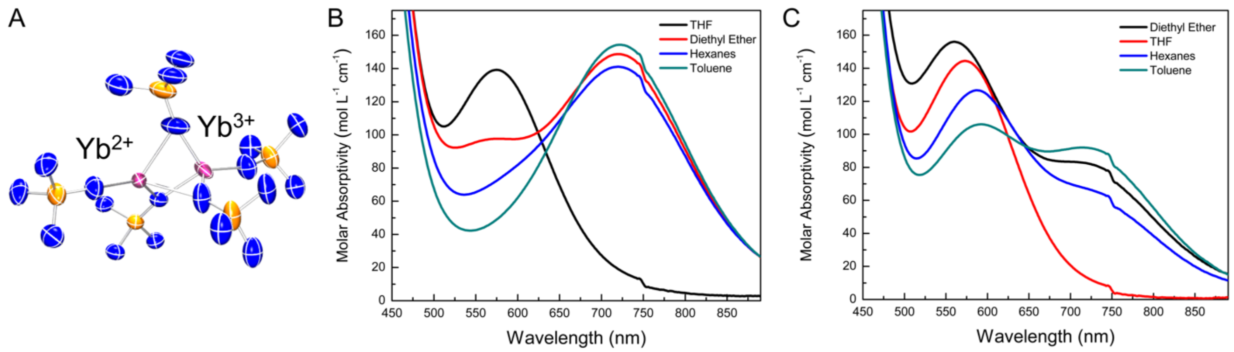

Figure 1: A) Structure of [$Yb_2(NP(Pip)_3)_5$]; B) Vis/NIR spectra of [$Yb_2(NP(Pip)_3)_5$] at 25 ºC; C) Vis/NIR spectra of [$Yb_2(NP(Pip)_3)_5$] at –3 ºC.

2) In developing the early actinide, imidophosphorane coordination chemistry, the tetrahomoleptic complex U^{4+} complex, [$U(NP(Pip)_3)_4$], was prepared. This complex is a strong, two electron reductant and undergoes oxidative atom transfer reactions. Two-electron chemistry of uranium is dominated by the U$^{3+/5+}$ couple and transformations from U^{4+}/U^{6+} are rare. With mesityl azide, the U^{6+} complex, [$U(NMes)(NP(Pip)_3)_4$], is formed. This 5-coordinate complex is a square-base pyramid in the solid-state with metal-ligand bond lying in the equatorial plane, rather than axially in a trigonal bipyramid.

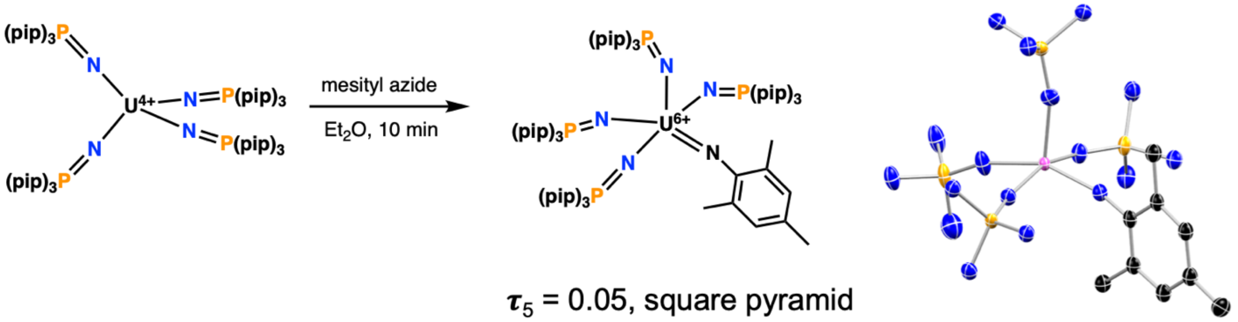

Figure 2: Structure and reaction chemistry of [$U(NP(Pip)_3)_4$] and [$U(NMes)(NP(Pip)_3)_4$].

Future Plans for 2019–2021:

- Extend mixed-valent coordination chemistry from lanthanides and early actinides to mid-actinides (Np and Pu) with the completion of transuranic synthetic facilities.
- Continued development of XAS studies of low-valent, bimetallic lanthanide and actinide complexes.
- Expand synthetic and spectroscopic studies of multiconfigurational actinide complexes.

Publications Supported by this Project 09/2018–2019:

1. Thaige P. Gompa, Brandon J. Yik, John Bacsa, Ping Yang, Enrique R. Batista, and Henry S. La Pierre, "Intervalence Charge Transfer in a Mixed-Oxidation State, Homobimetallic, Ytterbium Complex," *in preparation*.
2. Natalie T. Rice, John Bacsa, Lukas Palatinus, Ping Yang, Enrique R. Batista, and Henry S. La Pierre, "Two-Electron Oxidative Atom Transfer to Tetravalent Uranium," *in preparation.*

Structure, Bonding and Mechanism in f-Element Chemistry

Award Number DE-SC0016002

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Overall research goals

The objective of this project is to develop insight into electronic structure, bonding and reactivity in f-element chemistry through the development of *C*-term magnetic circular dichroism spectroscopy combined with additional freeze-trapped spectroscopic methods and low-temperature synthetic studies to evaluate the nature of transient f-element complexes and their reactivities. Development and application of Np-237 Mössbauer spectroscopic capabilities in the U.S.

Recent Progress

C-term MCD Spectroscopy of UCl_6^- in the Charge-Transfer Region. Our initial work on *C*-term magnetic circular dichroism (MCD) spectroscopy for evaluation of f-element electronic structure focused on a combined *ab initio* theoretical and experimental study of the MCD spectrum of the octahedral UCl_6^- complex ion in the UV-Vis spectral region. The ground state in this system is an orbitally non-degenerate doublet $E_{5/2u}$ and the MCD is a *C*-term spectrum caused by spin–orbit coupling. Calculations of the electronic spectrum at various levels of theory indicate that differential dynamic electron correlation has a strong influence on the energies of the dipole-allowed transitions and the envelope of the MCD spectrum. The experimentally observed bands are assigned to dipole-allowed ligand-to-metal charge transfer into the 5f shell, and 5f to 6d transitions. Charge transfer excitations into the U 6d shell appear at much higher energies. The MCD-allowed transitions can be assigned *via* their signs of the *C*-terms: Under O_h double group symmetry, $E_{5/2u} \rightarrow E_{5/2g}$ transitions have negative *C*-terms whereas $E_{5/2u} \rightarrow F_{3/2g}$ transitions have positive *C*-terms if the ground state *g*-factor is negative, as it is the case for UCl_6^-.

Theoretical and Experimental MCD Studies of Ln(II) Complexes. While there have been significant advancements in the synthesis of organometallic complexes featuring f-block elements, analysis of their electronic structure and bonding remains underdeveloped compared to their d-block analogs. One recent development in synthetic lanthanide chemistry that presents challenges in spectroscopic and computational analysis involves the discovery that 2.2-cryptand)][LnCp'$_3$] (Ln = Y, La, Pr, Eu, Gd; Cp' =$C_5H_4SiMe_3$), which contain ions in the formal +2 oxidation state. These complexes were chosen to evaluate the $4f^n5d^1$ electron configuration assignments of the recently discovered La(II), Pr(II), and Gd(II) ions versus the traditional 4f $^{n+1}$ configuration of the long-known Eu(II) ion. The $4d^1$ Y(II) complex provided another benchmark complex in the MCD study. Transitions with f-orbital character were observed in the NIR MCD spectra of the $4f^25d^1$ complex $[PrCp'_3]^-$. These signals are much broader than would be predicted for pure f-f transitions, suggesting significant 4f/5d orbital mixing as predicted by restricted active-space RAS calculations. For further insight into the electronic structure of these $[LnCp'_3]^-$ complexes, experimental UV-vis MCD spectroscopy was coupled to calculated spectra allowing for the assignment

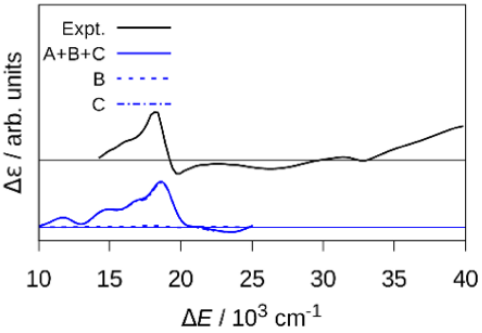

Figure 1. Calculated and experimental MCD spectrum of $[Pr(C_5H_4SiMe_3)_3]^-$.

of transitions in the UV-Vis spectral region. Importantly, this study extended our combined experimental and computational MCD methodology to lower symmetry complexes with multiple f-electrons, proving MCD spectroscopy is a powerful, high resolution method to evaluate electronic structure in f-electron molecular chemistry.

Synthesis and Electronic Structure Studies of U(aryl)$_6^{2-}$ Complexes. Previous work in our group isolating thermally unstable homoleptic iron-aryl species utilizing low temperature synthetic techniques motivated us to re-explore the longstanding synthetic challenge in of accessing homoleptic organouranium species with simple aryl substituents, with the goal of developin useful series of molecules for detailed electronic structure studies using MCD. The addition of 6 equiv. of phenyllithium to a slurry of $[UCl_4(1,4\text{-dioxane})]_2$ in THF/Et_2O at -80 °C resulted in an immediate color change from yellow to red. After filtering through celite and addition of hexane, storage at -80 °C resulted in the formation of red needle crystals identified as $[Li(THF)_4][(THF)LiUPh_6]$•1.5THF (**1**) (Fig. 1). This complex was found to be air and temperature sensitive, decomposing readily above -80 °C. With a successful method identified for isolation of **1**, the substituents of the *p*-position of the aryl group were varied to further explore the electronic contribution of the aryl ring on the nature of the U-C bond. Following similar synthetic procedures but using *p*-tolyllithium and *p*-Cl-phenyllithium, the analogous six coordinate uranium species were isolated, $[(THF)_3LiXLi(THF)_3][(THF)LiU(p\text{-tolyl})_6]\cdot Et_2O\cdot 0.62THF$ (**2**) and $[Li(THF)_4]_2[U(p\text{-ClPh})_6]$ (**3**). It was interesting to note that complex **3** does not contain the inner sphere lithium counterion which both complexes **1** and **2** have. Complex **3** was also found to be much more thermally stable, withstanding temperatures of 0 °C for up to 12 hours. MCD spectroscopy combined with theoretical calculations was utilized to further explore the electronic effects of these complexes, including direct insight into ligand variation effects, providing unique insight insight into the electronic effects of aryl ligand character on the nature of U-C bonding in sterically unencumbered uranium(IV)-aryl species.

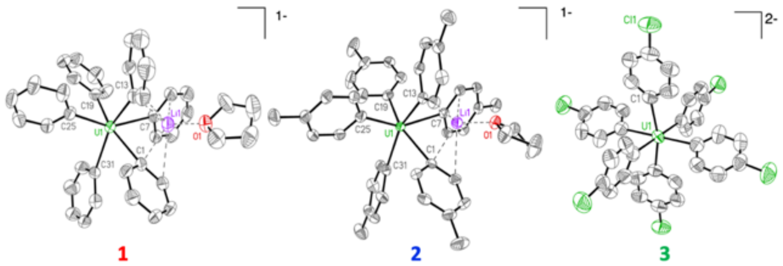

Figure 2. X-ray crystal structures of complexes **1**, **2**, and **3**.

Unusual Uranium-Methyl Complexes in Reactions of UCl_4 and MeLi: Accessing Unusual Molecules for Electronic Structure Insight. The isolation and characterization of homoleptic uranium-alkyl have remained underexplored in the literature, in part due to their significant thermal instability which has led to the observed rapid thermal decomposition pathways and instead the detection of organic products has been utilized as indirect evidence for *in situ* generated species. These organic product distributions also imply the possible presence of uranium alkyl species in low oxidation states as well as possible multimeric uranium reaction pathways. Due to our interest in understanding the electronic structure and bonding through connectively simple models, these homoleptic uranium-alkyl and -aryl species, were targeted as surrogates to access the low oxidation state uranium-alkyl species which may be present through controlled warming and cooling experiments. The simplest homoleptic uranium-alkyl species, previously demonstrated by Hayton and coworkers in 2009 using TMEDA as a reaction additive, $[Li(THF)_4][Li(THF)_2UMe_6]$, could be accessed and isolated in the absence of TMEDA utilizing low temperature synthesis. The low temperature (-80 °C) generation of **1** in situ followed by transfer to a cold plate at 0 °C and subsequent stirring as a function of time then rapid cooling to -80 °C has led to the generation of several multimeric uranium-alkyl species including an unprecedented uranium-methyl dimer, $[[Li(THF)_4]_2[Me_4U(\mu\text{-}Me)_3UMe_3]$. If the reaction mixture warmed for prolonged periods (excess of 30 minutes), a tetrameric uranium complex containing μ_3-oxo bridging atoms and ring-opened THF ligands is formed. These studies demonstrated the ability of low temperature synthesis protocols for the identification and isolation of unstable complexes which can provide unique insight into electronic structure, bonding and reaction pathways with simple sigma donor ligands. This work has been submitted for publication.

Extension of *C*-Term MCD Spectroscopy for Evaluation of Ligand Effects on Electronic Structure in Uranium Coordination Complexes. Since this experiment is underdeveloped, studying ideal complexes is required to build a strong basis of understanding that can be built upon. With that in mind, octahedral U(V) complexes, effectively eliminating geometry and *f*-electron repulsion effects, are being studied to understand the affect that ligands have on electronic structure. For this study hexahalides and complexes previously reported by the Hayton group are being investigated: $[UCl_6]^-$, $[UF_6]^-$, $[U(NC_5H_{10})_6]^-$, $[U(NC(^tBu)(Ph))_6]^-$, $[U(MeTMS)_6]^-$, and $[U(OC_6F_5)]^-$. Similar features appear in each complex demonstrating how the character of the ligand affects only the relative energies of orbitals in high symmetry complexes. In addition, in collaboration with the Baker group at Trinity College Dublin, the effects of varying a complex's geometry on its electronic structure is also under investigation. By changing the cation of U(IV) thiocynate complexes, $[X]_4[U(NCS)_8]$ ($X = Cs, Me_4N, Et_4N$, and $^nPr_4N$), the crystal packing structure of these complexes is affected and this is reflected in the NIR MCD spectra of these complexes.

Future Plans

Extending MCD Spectroscopy to Probe Electronic Structure in Lower Symmetries, Oxidation States and Coordination Number Complexes. An extension of our MCD Studies is to explore the electronic structure of lower symmetry complexes, namely the D_{4h} complexes $[U(MeTMS)_4(O^tBu)_2]^-$ and $[U(Cl)_4(O^tBu)_2]^-$. By systematically lowering the symmetry being studied, effects of geometry and ligand character on electronic structure can be further understood. In addition, an extensive new collaboration with Polly Arnold (Edinburgh) will extend our MCD development to low coordinate U(III) and U(IV) complex with varying ligand sets. Additional studies will include expansion of our Ln(II) MCD studies to complexes beyond Cp' ligands.

Spectroscopic Studies of Transient Actinide Intermediates in Reaction Pathways. Ongoing collaborations will continue to explore the nature of transient intermediates in reactions pathways of uranium complexes. Using electronic paramagnetic resonance (EPR) spectroscopy in conjunction with NMR and crystallographic studies, we will identify key uranium reaction intermediates in transformation of organic substrates and small molecules that will broaden our understanding of fundamental correlations between uranium electronic structure/bonding and reactivity. For example, studies will include identification of intermediates in multinuclear uranium complex catalyzed N_2 reductions. This insight into electronic structure and bonding in intermediates in these transformations will continue to expand our understanding of bonding effects on reactivity in actinide chemistry.

Np-237 Mössbauer Spectroscopy. Following our recent completed design of a Np-237 Mössbauer spectrometer, we will continue our efforts towards the construction, testing and development of this critical capability in the U.S.

Recent Publications Resulting from this Project (Project Start Date: 07/2016)

Gendron, F.; Fleischauer, V. E.; Duignan, T. J.; Scott, B. L.; Löble, M. W.; Cary, S. K.; Kozimor, S. A.; Bolvin, H.; Neidig, M. L.*; Autschbach, J.*, "Magnetic circular dichroism of UCl_6^- in the ligand-to-metal charge-transfer spectral region," *Phys. Chem. Chem. Phys.* **2017**, *19*, 17300-17313. DOI: 10.1039/C7CP02572F

Tondreau, A. M.; Duignan, T. J.; Stein, B. W.; Fleischauer, V. E.; Autschbach, J.; Batista, E. R.; Boncella, J. M.; Ferrier, M. G.; Kozimor, S. A.; Mocko, V.; Neidig, M. L.; Cary, S. K.; Yang, P., "A pseudotetrahedral uranium(V) complex," *Inorg. Chem.* **2018**, *57*, 8106-8115.
DOI: 10.1021/acs.inorgchem.7b03139

Accurate ab Initio Thermochemistry and Spectroscopy of Molecules Containing *f*-block Elements

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Award Number: DE-SC0008501

Overall research goals: Develop and apply a systematic quantum chemistry methodology that will be capable of providing chemically accurate thermochemistry (within 1-3 kcal/mol) and accurate spectroscopic properties (bond lengths to a few mÅ and vibrational frequencies better than 10 cm^{-1}) for molecules involving *f*-block elements, i.e., the lanthanides and actinides. This includes the development of systematically convergent Gaussian basis sets, as well as determining accurate methods for the recovery of relativistic effects, particularly spin-orbit coupling.

Recent Progress:

1. In a joint experimental-theory study,[1] the stability of gas phase actinide dioxide cations were assessed – with BkO_2^+ and CfO_2^+ synthesized for the first time via experiment and PaO_2^+ through LrO_2^+ calculated from high level quantum chemistry calculations. For PaO_2^+ through AmO_2^+ , linear actinyl structures with two short An=O bonds are clearly the most stable. In contrast, the lowest energy structure of CmO_2^+ is a highly bent peroxide η^2-structure in which the oxidation state is $5f^7$ Cm^{III}. For BkO_2^+ and CfO_2^+ the actinyl(V) structures are somewhat more stable than the An^{III} peroxides, and for EsO_2^+ the Es^V structure is slightly more stable than the Es^{II} superoxide. Beginning with FmO_2^+ the An^{II} superoxides become more stable, with the trivalent peroxide the most stable in the case of Lr due to the stability of closed-shell $5f^{14}$ Lr^{III}.

2. The Active Thermochemical Tables (ATcT) methodology was applied for the first time[2] to the complex and challenging chemical environment of key uranium oxides and fluorides both in crystalline and gaseous phases. In addition to critically compiling known, experimental results, this study utilized new gas phase quantum chemistry calculations for the determination of more reliable thermal functions, as well as using our FPD composite methodology for accurate determinations of reaction enthalpies (including new calculations of UO_3, UO_2, UO_2^+, and UO_2^{2+}). Ultimately, ATcT provided improved results over previous thermochemical compilations even for the most well characterized molecules, and in the case of gas phase species the improvement borders on an order of magnitude.

3. The lowest 8 ionization potentials of the Pu atom have been accurately computed using an all-electron, relativistic composite FPD approach using both multireference configuration interaction and coupled cluster theory.[3] Contrary to the currently accepted values on NIST, the 6th-8th IPs clearly involve removal of the remaining 5f electrons with no explicit involvement of the 6p subshell.

4. Gas phase actinyl cation-cation interactions (CCIs) were studied by an accurate composite coupled cluster thermochemical approach for the first time.[4] A number of CCI dimers were constructed from the monomers UO_2^{2+}, UO_2^+, NpO_2^{2+}, NpO_2^+, PuO_2^+, and AmO_2^+. All CCI dimers studied were calculated to be thermodynamically unstable, but in most cases kinetic stability was indicated by calculated local minima with well depths as large as ~15 kcal/mol. For both mixed-valent An(VI)/An(V) and mono-valent An(V) dimers, the stability decreased

in the donor series U(V)>Np(V)>Pu(V)>Am(V). These trends correlate well with experimental trends in condensed phase CCIs. CCIs are the direct result of a competition between charge transfer stabilization, which was calculated to be as much as 0.11e or 30.7 kcal/mol at equilibrium, and Coulombic repulsive destabilization.

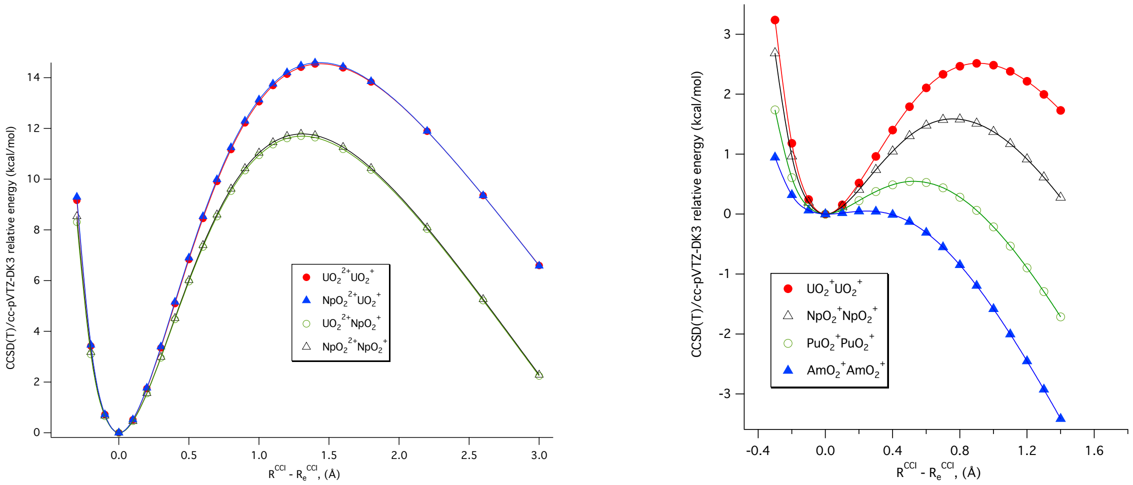

Figure 1: Calculated 1-D potential energy curves at the CCSD(T)/VTZ-DK3 level of theory for the T-shaped heterodimers (left) and An(V) homodimers (right).

5. Motivated by the previous density functional calculations of Van Stipdonk and co-workers[5] where a novel 2-electron, 3-centered η^2 uranyl(V)-O_2 compound was predicted, accurate CCSD(T)-based FPD calculations were carried out for the interactions of AnO_2^+ with O_2, NO, CO, and N_2.[6] Our high-level coupled cluster calculations confirmed the previous conclusions for the O_2 complex with UO_2^+ and found that the open-shell electron of NO can also form side-on bonding interactions. In the case of the interactions of closed-shell molecules, however, neither CO or N_2 form stable side-on complexes with either UO_2^+ or NpO_2^+, only more conventional T-shaped compounds.
6. New all-electron (DK3 and X2C) and pseudopotential-based correlation consistent basis sets were developed for the heavy alkali and alkaline earth metals from K to Ra.[7] Since 2017 when they were published, these basis sets have already been cited (and presumably used) in 14 different computational studies.

Future Plans:

- Complete the last few details of a comprehensive computational FPD study of the structures and thermochemistry of AnX_n molecules where An=U, Np, and Pu; X = F, Cl, and Br; with n=4-6.
- Update and correct the NIST atomic ionization potential database by accurately computing the (high energy) ionization potentials of the transuranic elements like what we have recently done for Pu.
- Initial tests on UO_3 and UF_6 using explicitly correlated CCSD(T)-F12 methods with just double-zeta (DZ) quality basis sets demonstrate that the resulting structures are of quadruple-zeta (QZ) quality and the vibrational frequencies are better than triple-zeta (TZ) quality. Since PP-basis sets are currently compatible with Molpro's F12 methods, we will develop -PP-F12 basis sets (including auxiliary fitting sets) at the DZ level for Th, Pa, and U. The experience gained there, including their performance in molecular benchmark calculations, will carry over to the all-electron case when the adaptation of F12 to DK3 and X2C is finished (this is

currently underway by Markus Reiher's group). Extending the sets to TZ quality still requires higher angular momentum functions in Molpro for the fitting sets, and we hope this will finally be accomplished in the coming year.

- Finish a nearly complete coupled cluster FPD study involving the substitution of Pt for O in actinide dioxide molecules, AnO_2, AnO_2^+, and AnO_2^{2+} where An = U, Np, and Pu.
- Based on our initial preliminary all-electron X2C correlation consistent basis sets developed for Oganesson (Z=118), analogous sets are being developed for the other members of the 7p block.
- In support of recent experimental results by the Armentrout group, we are finishing up a study that involves accurately computing the bond dissociation energies and ionization potentials of the first few carbonyls involving thorium, i.e., $Th(CO)_n$ and $Th(CO)_n^+$ with n=1-4, with the FPD methodology.
- Determine the spectroscopic properties of the UP/UP^+ (nearly finished), FUO/FUO^+, and NUN using either SO-CASPT2 or IH-FS-CCSD in collaboration with the experimental work of Heaven.
- In collaboration with the Ruscic group at ANL, begin to add thorium and plutonium species to the new actinide ATcT thermochemical network.

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1. P. D. Dau, M. Vasiliu, K. A. Peterson, D. A. Dixon, and J. K. Gibson, Remarkably high stability of late actinide dioxide cations: Extending chemistry to pentavalent berkelium and californium, *Chem. Eur. J.* **260**, 1753-1711 (2017).
2. S. R. Battey, D. H. Bross, B. Ruscic, and K. A. Peterson, Active Thermochemical Tables: Revisions to “key” enthalpies of formation for uranium oxides and fluorides, in preparation (2019).
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2. R. M. Cox, M. Citir, P. B. Armentrout, S. R. Battey, and K. A. Peterson, Bond energies of ThO(+) and ThC(+): A guided ion beam and quantum chemical investigation of the reactions of thorium cation with O_2 and CO, *J. Chem. Phys.* **144**, 184309 (2016). DOI: 10.1063/1.4948812
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8. Z. Fang, M. Vasiliu, K. A. Peterson, and D. A. Dixon, Prediction of bond dissociation energies/heats of formation for diatomic transition metal compounds: CCSD(T) works., *J. Chem. Theory Comp.* **13**, 1057-1066 (2017). DOI: 10.1021/acs.jctc.6b00971
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10. Feng, Vasiliu, Peterson, and Dixon, Acidity of M(VI)$O_2(OH)_2$ for M = Group 6, 16, and U as central atoms., *J. Phys. Chem. A* **121**, 1041-1050 (2017). DOI: 10.1021/acs.jpca.6b11889
11. Hill and Peterson, Gaussian basis sets for use in correlated molecular calculations. XI. Pseudopotential-based and all-electron relativistic basis sets for alkali metal (K–Fr) and alkaline earth (Ca–Ra) elements, *JCP* **147**, 244106-244113 (2017). DOI: 10.1063/1.5010587
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Project Title: *Exploring the Nature of f-Element Soft Donor Interactions Using Electronically Tunable Azolate Ionic Liquids*
Award Number: DE-SC0019220
Principal Investigator: Robin D. Rogers
Mailing Address: Box 870336, The University of Alabama, Tuscaloosa, AL 35487
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Overall Research Goals

The goal of this work is to develop azolium azolate ionic liquid (IL) platforms as highly coordinating, exclusively N-donor functionalized liquids with unprecedented electronic tunability for the isolation of f-element N-donor complexes in order to understand the fundamental differences between actinide and lanthanide interactions with moderately soft donor ligands. The keys to our approach include:

- The use of ILs effectively allows soft donor ligand to be used as the solvent without any interfering O-donor solvents – creating a “sea” of N-donors where dissolution of a metal salt absolutely requires metal N-donor interactions.
- Nearly any amphoteric azole is potentially accessible to a solventless strategy and ILs made from them can be tuned in a similar way to molecular solvents in order to control crystallization with no need to add additional molecules.
- The azolium azolate IL platform allows tunable basicity to explore the nature of metal-nitrogen interactions as a function of ligand electron donor character linking observed behavior unambiguously to the electronics of the unidentate ligands.
- The nature of individual metal-nitrogen bonds can be investigated independently of the effects of molecular geometry.
- The reactions are simple, often one-pot procedures that allow the isolation of f-element complexes from readily available starting materials, which is a major potential advantage for extending to transuranics.

Recent Progress

We are developing experimental and IL design criteria based on the study and understanding of thermodynamic conditions, electronic, steric and charge environment of azoles to govern f-element chemistry. In our current IL design the IL contains coordinating nitrogen functional groups such as amino, imino, or cyano on the anion and the cation; we avoid any hard donor atoms such as oxygen; the IL is liquid at room temperature or below to facilitate the stabilization of possibly weak metal complexes; the IL is non-volatile and thermally stable to beyond 100 ^{o}C; and we add (if necessary) neutral N-heterocycles to expand the liquid range and adjust concentrations to optimize conditions for crystal growth. We describe below the results for one of our first papers being drafted.

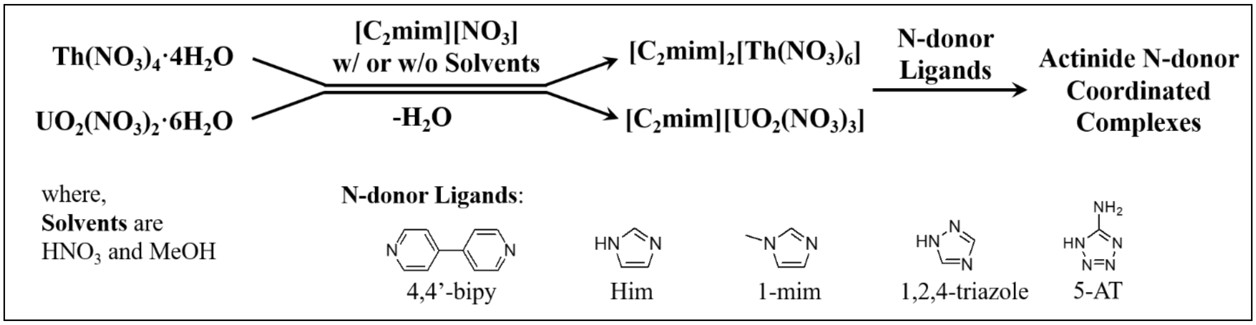
Dehydrating Actinide Salt Hydrates with Nitrate Ionic Liquids and Using Anhydrous Nitrate Complexes as Labile Intermediates for Bench top N-Donor Chemistry

We report a unique strategy to readily prepare crystalline N-donor actinide coordination complexes from readily available hydrated actinide salts by first dehydrating them with an ionic liquid containing a common anion and then reacting the anhydrous complexes with N-heterocyclic ligands. The hydrated actinide salts, $Th(NO_3)_4\cdot 4H_2O$ *and* $UO_2(NO_3)_2\cdot 6H_2O$*, were dissolved in 1-*

ethyl-3-methylimidazolium nitrate ($[C_2mim][NO_3]$) to prepare anhydrous $[C_2mim]_2[Th(NO_3)_6]$ and $[C_2mim][UO_2(NO_3)_3]$. Reaction of these anhydrous salts with N-donor heterocycles yielded several new actinide N-donor coordinated complexes, $[H(1\text{-}mim)_2][Th(NO_3)_5(1\text{-}mim)_2]$), $[C_2mim]_2[(UO_2(NO_3)_3)_2(4,4'\text{-}bipy)]\cdot 2\{UO_2(NO_3)_2(4,4'\text{-}bipy)\}$, ($UO_2(NO_3)_2(1\text{-}mim)_2$, and $UO_2(NO_3)_2(H\text{-}im)_2$ (1-mim = 1-methylimidazole; H-im = imidazole). These results challenge the concept that f-elements prefer O-donors over N-donors, suggesting it is the acidic hydrogen atoms from water which compete with the f-elements for access to the N-donor that impedes access to the more elusive N-donor coordination complexes.

We chose the two most abundant actinides, thorium-232 and uranium-238, in their most stable oxidation states, U(VI) and Th(IV), which are strongly acidic and prone to polymerization through hydrolysis.[1] Thorium(IV) Lewis base adducts have been made from thorium tetrahalides, but these require strictly anhydrous conditions.[2] It has been known that $Th(NO_3)_4\cdot 4H_2O$ reacts with N-heterocycles to form ammonium salts of $[Th(NO_3)_6]^{2-}$.[3,4] Weakly ligated uranyl ($[UO_2]^{2+}$) complexes such as triflate salts[5] or $UO_2Cl_2(THF)_3$,[6] can be used to make Lewis base adducts, but these typically must be isolated as intermediates and purified. We sought instead to dehydrate the hydrated nitrate salts of these elements with a nitrate IL on the benchtop, and react the resulting anhydrous compounds or solutions with N-heterocyclic ligands, again on the benchtop with no special precautions to exclude air.

In our general strategy (**Scheme 1**), we started with $Th(NO_3)_4\cdot 4H_2O$ and $UO_2(NO_3)_2\cdot 6H_2O$, and dissolved them in 1-ethyl-3-methylimidazolium nitrate ($[C_2mim][NO_3]$) with and without solvent. Volatilization of the water and solvents (if present) led to the anhydrous salts $[C_2mim]_2[Th(NO_3)_6]$ (**Figure 1**) and $[C_2mim][UO_2(NO_3)_3]$ (a liquid, **Figure 2**) which were obtained quantitatively and in large scale. Subsequent reactions of these anhydrous salts with imidazole (H-im), 1-methylimidazole (1-mim), 5-aminotetrazole (5-AT), 1,2,4-triazole (1,2,4-Triaz), and 4,4'-bipyridyl (4,4'-bipy) led easily to several N-donor complexes (**Figures 1** and **2**).



Scheme 1. Dehydration and complexation strategy.

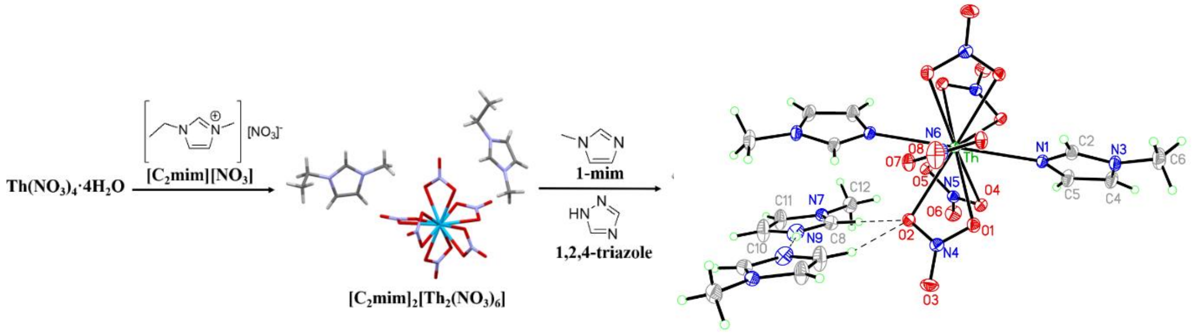


Figure 1. Preparation of $[H(1\text{-}mim)_2][Th(NO_3)_5(1\text{-}mim)_2]$ from $[C_2mim]_2[Th(NO_3)_6]$.

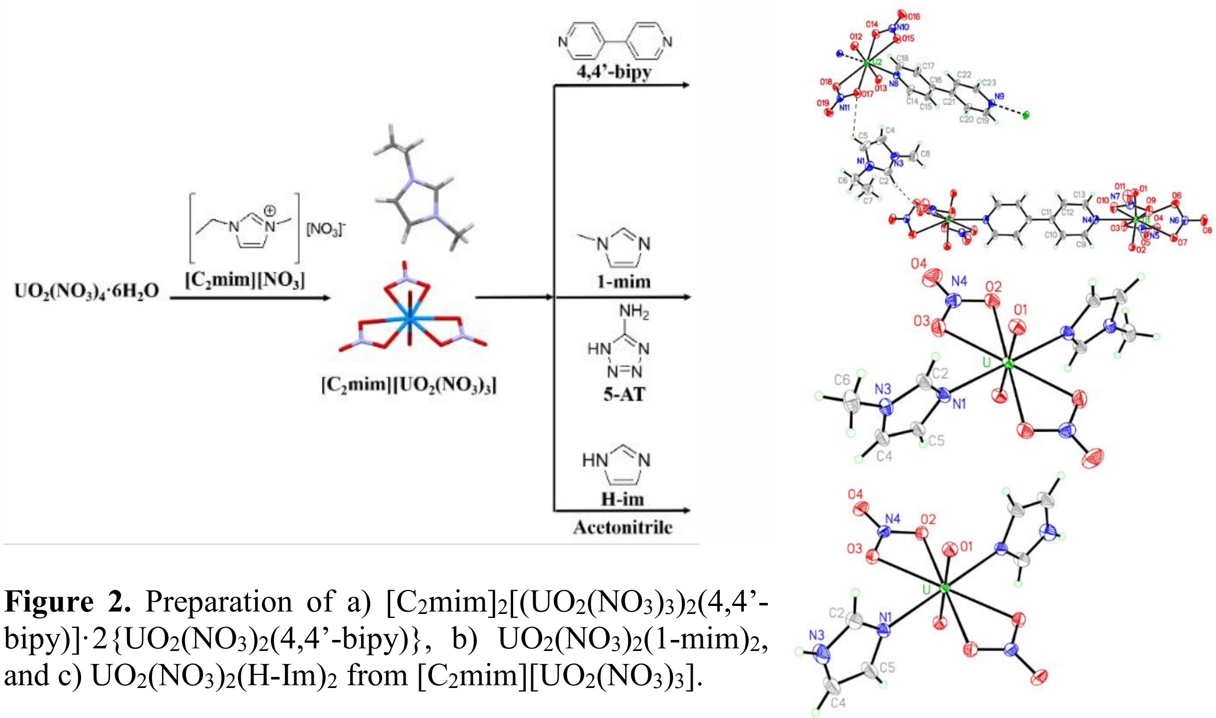


Figure 2. Preparation of a) $[C_2mim]_2[(UO_2(NO_3)_3)_2(4,4'\text{-}bipy)]\cdot 2\{UO_2(NO_3)_2(4,4'\text{-}bipy)\}$, b) $UO_2(NO_3)_2(1\text{-}mim)_2$, and c) $UO_2(NO_3)_2(H\text{-}Im)_2$ from $[C_2mim][UO_2(NO_3)_3]$.

$Th(NO_3)_4\cdot 4H_2O$ and $UO_2(NO_3)_2\cdot 6H_2O$ can thus, be readily dehydrated by the IL $[C_2mim][NO_3]$ to give anhydrous nitrate complexes, and the resulting anhydrous complexes can be used as intermediates in the preparation of complexes with N-heterocyclic ligands. Non-aqueous chemistry on nitrate complexes of these elements has been limited by their poor solubility in hydrophobic solvents and hydrolytic instability in hydrophilic solvents. The ability to isolate and use $[C_2mim][UO_2(NO_3)_3]$ as a liquid affords it particular flexibility as a reagent in non-aqueous synthesis. The $[NO_3]^-$ counterion was also found to be more sensitive to the effects of N-heterocycle coordination than more strongly coordinating anions typically used in the literature, leading to observable effects on metal-ligand bond distances and multiple coordination geometries.

Future Plans

When successful methods for isolating N-donor complexes have been achieved, we will extend our work to ^{227}Ac, ^{231}Pa, ^{237,239}Np, ^{236,237,239,242}, Pu, ^{241,243}Am, ^{248}Cm, and/or ^{249}Cf. Alternatives other than 1-methylimidazole will also be employed to force complexation of the azolate donors.

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Recent Publications Resulting from this Project (Project start date: 07/2018)

There have been no publications yet resulting from this new project.

Novel Wavefunction Approaches for Studying Actinides and Other Heavy Elements

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Overall research goals

The major goal of this project is the methodological development and computational implementation of quantum chemistry methods for the accurate calculation of electronic structure and properties of molecules, solids, and surfaces containing actinides and other heavy elements.

Recent Progress

The model reported during the first year of this grant, which combines singlet-paired coupled cluster theory (CCD0) for dealing with static correlation with density functionals (DFT) for dynamic correlation, has continued to be applied to actinide molecules. Previous work assessed the accuracy of CCD0 and CCD0+DFT compared to well-established quantum chemical methods for describing ground-state properties of singlet actinide molecules. The f^0 actinyl series (UO_2^{2+}, NpO_2^{3+}, PuO_2^{4+}), the isoelectronic NUN, and thorium (ThO, ThO^{2+}) and nobelium (NoO, NoO_2) oxides were studied. We are now in the process of extending these ideas to open-shell cases. In general, restricted single-reference coupled cluster theory truncated to single and double excitations accurately describes weakly correlated systems, but often breaks down in the presence of static or strong correlation. Good quality coupled cluster energies in the presence of degeneracies can be obtained by using a broken-symmetry reference, such as unrestricted Hartree-Fock, but at the cost of good quantum numbers, which is far from ideal. A large body of work has shown that modifying the coupled cluster ansatz allows for the treatment of strong correlation within a single-reference symmetry-adapted framework. Our CCD0 method is one such model, which recovers correct behaviour for strong correlation without requiring symmetry breaking in the reference. In work supported by this grant, we have continued working on the extension of CCD0 for application to open shell molecules via restricted open-shell singlet-paired coupled cluster singles and doubles (ROCCSD0). The ROCCSD0 approach retains the benefits of standard coupled cluster theory and recovers correct behaviour for strongly correlated, open-shell molecules using a spin-preserving ROHF reference. In singlet-paired coupled cluster, eliminating the triplet-pairing channel recovers reasonable qualitative behaviour for strong correlation at the cost of a decreased description of dynamical correlation in weakly correlated situations. This behaviour seems to hold for both closed- and open-shell systems.

On a separate project, we have finished a very important milestone: spin-projected unrestricted coupled cluster theory. This theory is very accurate and versatile. See Reference 5 below. The combination of symmetry projection for strong correlation and coupled cluster theory for weak correlation offers tantalizing promise to account for both on an equal footing. In order to do so, however, the coupled cluster portion of the wave function must be optimized in the presence of the symmetry projection. This paper discusses how this may be accomplished, and shows the importance of doing so for both the Hubbard model Hamiltonian and the molecular Hamiltonian, all with a computational scaling comparable to that of traditional coupled cluster theory.

Future Plans

We are currently implementing a production level code for molecules of the spin-projected coupled cluster theory. When finished, this program will allow us to use it for both open-shell and closed-shell actinide molecules. We expect to accomplish this major goal during 2019, which is the last year of this grant.

Publications supported by this project 2016-present

1. Using full configuration interaction quantum Monte Carlo in a seniority zero space to investigate the correlation energy equivalence of pair coupled cluster doubles and doubly occupied configuration interaction, J. J. Shepherd, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys*. **144**, 094112 (2016). http://dx.doi.org/10.1063/1.4942770

2. Singlet-paired Coupled Cluster theory for open shells, J. A. Gomez, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys*. **144**, 244117 (2016).
http://scitation.aip.org/content/aip/journal/jcp/144/24/10.1063/1.4954891

3. Recoupling the singlet- and triplet-pairing channels in single-reference Coupled Cluster theory, J. A. Gomez, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys*. **145**, 134103 (2016).
http://dx.doi.org/10.1063/1.4963870

4. Electronic Structure and Properties of Berkelium Iodates, M. A. Silver, S. K. Cary, A. J. Garza, R. E. Baumbach, A. A. Arico, G. A. Galmin, K.-W. Chen, J. A. Johnson, J. C. Wang, R. J. Clark, A. Chemey, T. M. Eaton, M. L. Marsh, K. Seidler, S. S. Galley, L. van de Burgt, A. L. Gray, D. E. Hobart, K. Hanson, S. M. Van Cleve, F. Gendron, J. Autschbach, G. E. Scuseria, L. Maron, M. Speldrich, P. Kögerler, C. Celis-Barros, D. Páez-Hernández, R. Arratia-Pérez, M. Ruf, T. E. Albrecht-Schmitt, *J. Am. Chem. Soc*. **139**, 13361-13375 (2017).
http://pubs.acs.org/doi/abs/10.1021/jacs.7b05569

5. Projected Coupled Cluster Theory: Optimization of cluster amplitudes in the presence of symmetry projection, Y. Qiu, J. Zhao, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys*. **149**, 164108 (2018).
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6. Assessing Combinations of Singlet-Paired Coupled Cluster and Density Functional Theory For Treating Electron Correlation in Closed and Open Shells, J. A. Gomez, M. Molla, A. J. Garza, T. M. Henderson, and G. E. Scuseria, *Mol. Phys*. submitted.

Characterization of Gas-phase Uranium and Thorium Containing Molecules via Optical Stark, Zeeman, and Microwave Spectroscopy

Award number: DE- SC0018241

Principal Investigator: Timothy C. Steimle,
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Overall Research Goals:

The primary goal of this laboratory-based project is to precisely determine fundamental properties of small neutral uranium and thorium gas-phase molecules using an orchestra of medium and high-resolution optical spectroscopic techniques as well as microwave spectroscopy. All measurements, including microwave transition frequencies involving rotational levels in the ground electronic state, exploit the sensitivity of laser induced florescence detection. The small U- and Th-ligand gas-phase molecules studied here provide the most direct method for elucidating actinide chemistry, which is needed for identifying new procedures for treating, transmuting, and storage of spent nuclear fuel. The determined molecular properties include electronic state energies, bond lengths and angles, vibrational frequencies, permanent electric dipole moments, $\vec{\mu}_{el}$, magnetic dipole moments, $\vec{\mu}_{m}$, magnetic and nuclear electric quadrupole hyperfine interactions, florescence branching ratios, radiative lifetimes, and oscillator strengths. These properties probe the nature of the chemically relevant valence electrons and provides insight into *f*-and *d*-orbital participation in bonding. Although small gas-phase actinide containing molecules are the simplest molecules in terms of the number of nuclei involved and geometry, they are not necessarily the simplest in terms of electronic structure because, in general, they are not fully ligated. As a result, the non-bonding electrons produce a multitude of low-lying interacting electronic states, which are difficult to model. The quantitative data produced in this research provides a rigorous means of assessing emerging computational methodologies.

Recent Progress:

i. *Development of a two-dimensional (2D) optical spectrometer for sensitive detection of transient actinide containing molecules.*

A medium spectral resolution ($\Delta\nu \cong$ 1GHz), time resolved ($\Delta t \cong$ 1ns), two dimensional (2D) (excitation/dispersed fluorescence (DF)) spectrometer has been constructed and brought "on-line" as a means of efficiently detecting here-to-fore unknown Th and U containing gas-phase molecules. The 2D spectra are created by stepping the pulsed dye laser wavelength and capturing a 75 nm wide spectral region of the dispersed laser induced fluorescence as viewed through a 2/3 m, low *f*-number, monochromator. The center wavelength of the monochromator is tracked with the pulsed laser wavelength and the signal is detected using a cooled, gated, intensified CCD attached to the monochromator. An internally cold (T^{rot} < 10K) sample of these ephemeral molecules is generated in a laser ablation/supersonic expansion. The 2D spectra are subsequently processed to produce excitation spectra (for electronic state energy determinations, E^{el}), DF spectra (for vibrational spacing determinations, ΔE^{vib}), and fluorescence decay curves (for radiative lifetimes, τ). The combination of E^{el}, ΔE^{vib} and τ, along with chemical synthesis routes, is usually sufficient information to unambiguously identify the molecule responsible for the observed optical signature from the multitude of species generated in the laser ablation plasma. Recording and analyzing 2D spectra is an essential prelude to recording high-resolution ($\Delta\nu \cong$ 10 MHz) field-free, Stark, Zeeman and microwave spectra.

ii. A comparative study of the bonding in thorium halides: ThF and ThCl.

Experimentally and theoretically determined magnetic and electric dipole moments, bond distances and vibrational spacings were used for a comparative study of the bonding in ThF and ThCl. This project was greatly aided by the previous combined experimental and theoretical studies by the Heaven group on the ThF/ThF$^+$ system (Barker, B. J.; Antonov, I. O.; Heaven, M. C.; Peterson, K. A. *J. Chem. Phys.* **2012,** *136* (10), 104305) and more recently on the ThCl/ThCl$^+$ system (VanGundy, R. A.; Bartlett, J. H.; Heaven, M. C.; Battey, S. R.; Peterson, K. A. *J. Chem. Phys.* **2017,** *146* (5), 054307). A particular goal of this study was to determine if the observed properties of ThF and ThCl can be qualitatively understood via a ligand-field interactions description and Cl *vs* F dependence and to evaluate the performance of newly developed relativistic predictions. There are subtle differences in ThCl and ThF bonding due to the more dispersed charge on the larger Cl$^-$ anion as compared to the smaller F$^-$ anion. In addition, the longer bond distance of ThCl results in a weaker electrostatic repulsion causing less of a bifurcation of the states arising from the Th$^+$($7s^2 6d^1$) and Th$^+$($7s^1 6d^2$) configuration. The observed $X^2\Delta_{3/2}$ state is the $|\Omega| = 3/2$ component of the $^2\Delta_r$ state (i.e. $X^2\Delta_{3/2}$) arising from the Th$^+$($7s^2 6d^1$) configuration.

Numerous bands in the visible electronic spectra between 16400 -18800 cm^{-1} of supersonically cooled molecular beam samples were detected using medium resolution ($\Delta\nu \approx 0.1\text{cm}^{-1}$), two dimensional (2D) spectroscopy. Subsequently, high resolution ($\Delta\nu < 20$ MHz) field-free, Stark, and Zeeman spectroscopy of the detected [18.6] Ω=3/2 – $X^2\Delta_{3/2}$ band of ThF near 538.4 nm and the [18.2] Ω=3/2 – $X^2\Delta_{3/2}$ band of ThCl near 551.0 nm were recorded and analyzed. Stark shifts and splitting were analyzed to produce $|\vec{\mu}_{el}|$ values of 1.426(18) D and 0.586(30) D, for the $X^2\Delta_{3/2}$ and [18.6]Ω=3/2 states of ThF, respectively, and 2.022(35) D and 3.020(55) D, for the $X^2\Delta_{3/2}$ and [18.2]Ω=3/2 states of ThCl. Zeeman splittings and shifts were analyzed to produce g_e values of 1.038(4) and 1.079(4) for the $X^2\Delta_{3/2}$ and [18.6]Ω=3/2 states of ThF and 1.130(4) and 1.638(4) for the $X^2\Delta_{3/2}$and [18.2]Ω=3/2 states of ThCl. Analysis of g_e values demonstrated that the $X^2\Delta_{3/2}$ and [18.6]Ω=3/2 states of ThF and the $X^2\Delta_{3/2}$ state of ThCl are predominately $^2\Delta_{3/2}$ spin-orbit components, whereas the [18.2] Ω=3/2 state of ThCl is an admixture of $^2\Delta_{3/2}$ and $^2\Pi_{3/2}$ spin-orbit components. A molecular orbital description of the ground states was used to rationalize the observed $|\vec{\mu}_{el}|$ values for the ThX(X=F,Cl,O and S) series, and garner insight into the bonding mechanism.

Relativistic coupled-cluster calculations were performed (by Prof. Lan Cheng, Johns Hopkins University) in order to obtain accurate predictions for the ground-state dipole-moment values. Excited state properties were not reliably predicted. For the ground states, the CCSD(T) method together with the exact two-component Hamiltonian using atomic mean-field spin-orbit integrals (the X2CAMF Hamiltonian) was used to obtain consistent treatments of scalar-relativistic, spin-orbit (SO), and electron-correlation effects. It was demonstrated that the systematic inclusion of electron-correlation contributions play an essential role in obtaining accurate predictions for the dipole-moment values in ThF and ThCl. The experimentally determined $X^2\Delta_{3/2}$ $|\vec{\mu}_{el}|$ values of 1.426(18) D and 2.022(35) D for the $X^2\Delta_{3/2}$ states of ThF and ThCl, respectively, are much less than the approximate 6D expected for a Th^{+1} F^{-1} or Th^{+1} Cl^{-1} charge distribution due to the induced dipole of the back polarized non-bonding 7*s* electrons. The induced dipole moment associated with polarization of the Th-metal centered electrons opposes that of the primary moment. At the Hartree-Fock level of prediction the μ_{el} values for ThF and ThCl are -0.018D and 0.645D with the negative sign indicating an unexpected $Th^{\delta-}F^{\delta+}$ charge distribution. Upon inclusion of electron correlation the predicted μ_{el} changes sign in the case of ThF and values for both ThF and ThCl increase in magnitude. Electron correlation accounts for the contribution from the $Th^{+}(7s^{1}6d^{2})$ configuration to the description of the $X^{2}\Delta_{3/2}$ states. The 6*d* orbital of this configuration is more contracted and less back-polarized than the 7*s* orbital reducing the induced dipole moment.

iii. Characterization of thorium nitride: ThN.

Properties of gas-phase thorium nitride, ThN, were experimentally determined from a combined optical and microwave spectroscopic study. This project was done in collaboration with Prof. Michael Heaven (Emory University) and was assisted by Heaven's previous study (Heaven, M. C., Barker, B. J. & Antonov, I. O. *J. Phys. Chem. A* **118**, 10867–10881 (2014)). An intense band near 555 nm was identified using 2D spectroscopy. Based upon subsequent high resolution optical Stark and Zeeman spectra, this band was assigned as the [18.0]1.5 -$X^{2}\Sigma^{+}$ (0,0) transition. The observed optical Stark shifts were analyzed to determine permanent electric dipole moments, $\vec{\mu}_{el}$ for the [18.0]1.5 and $X^{2}\Sigma^{+}$ states of 4.38±0.02D and 5.11±0.09D, respectively. Zeeman shifts were used to determine the magnetic g-factors. The pure rotational spectrum was recorded using a separated field optical pump/probe microwave repopulation scheme and analyzed to determine the ground state bond length and ^{14}N magnetic hyperfine and nuclear electric quadrupole parameters. A molecular orbital correlation diagram and ligand field electronic structure models are used to provide a qualitative interpretation of the electronic state ordering, magneto- and electro-static properties and hyperfine interactions. Electronic structure calculations for the $X^{2}\Sigma^{+}$ state were performed and results compared with observations. It was demonstrated that a relativistic density functional calculation yielded a Fermi contact term in reasonable agreement with observation, but exhibited a strong dependence on the choice of basis set and functional.

The ordering of reduced dipole moments $\mu_{el}^{Red.}\left(\equiv \mu_{el}/R_{e}\right)$ is ThN>ThS>ThO>ThCl>ThF whereas the electronegativity differences have the ordering ThF> ThO>ThCl>ThN> ThS. This apparent inconsistency can be understood by considering the dominant configurations and polarization of the Th-metal centered electrons. ThS, ThO, ThCl and ThF all have two electrons in the 7*s* orbital which readily hybridizes to shift the electron density away from the negatively charged ligand. This polarization reduces the dipole moment. ThN has only one electron in the 7*s* orbital, so the reduction in the dipole resulting from polarization is less. Predicting this polarization is very sensitive to the computational methodology.

Future Plans:

In the course of our studies of Th reaction products, we have recorded 2D spectra for what we believe to be ThC, ThC_2 and $ThNH_2$. The immediate plan is to follow-up the 2D measurements with high-resolution spectroscopic techniques. In parallel we will begin investigations of uranium ablation reaction products. The target molecules include UO_2, $UOCH_3$, UCH_3, UNH_2, UNH, UCS, and UC_2 generated in reaction of ablation uranium with CH_4, CH_3OH, O_2, NH_3, CS_2 and H_2. These studies will be aided by the experiments being initiated in Prof. Bowen's laboratory (Johns Hopkins University). His photoelectron spectroscopic studies of anions maps out the electronic state distribution of the neutrals. Those experiments use mass-spectroscopic detection methods, which complement our fluorescent detection methods. The availability of a measured electronic state distribution will greatly reduce the time required to record 2D spectra. Furthermore, our groups use common laser ablation/reaction schemes for molecular production and our shared experience will facilitate establishing the optimum chemical synthesis.

Recent Publications Resulting from this Project
Project start date: 08/2017

1. Nguyen, D.-T., Steimle, T., Linton, C. & Cheng, L. Optical Stark and Zeeman Spectroscopy of Thorium Fluoride (ThF) and Thorium Chloride (ThCl). *J. Phys. Chem. A* **123**, 1423–1433 (2019). https://pubs.acs.org/doi/10.1021/acs.jpca.8b11853
2. Le, A.T. Nakhate, S.,Nguyen,T.,Steimle,T.C.,& Heaven M.C., *J. Chem. Phys.* Revision submitted March 2019

Exploring Covalency in the Actinides Using Soft Donor-Based Ligands and Metal-Ligand Multiple Bonding

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Overall Research Goals

The fundamental coordination chemistry and reactivity of the actinides comprise one of the last frontiers of the periodic table. They represent the cornerstone of the nuclear energy industry, but their chemistry is significantly underdeveloped compared to that of the transition metals. One of the most interesting and debated properties of the actinides is a paradox that exists within the context of actinide-ligand bonding. As one traverses the series, the 5f orbitals decrease in energy to a point where they become degenerate with the ligand-based orbitals. Hence, the actinide-ligand bonds are observed, at least computationally, to have greater covalency than those of the middle actinides (Pu-Cf). This also occurs when moving down a group, which has been shown for example, by examining series of isostructural complexes bearing O, S, Se, and Te donor atoms. However, this increasing covalency does not necessarily indicate a stronger bond with the actinide, which has implications in separations applications. To explore this concept in greater depth, our group's main focus is the coordination chemistry, spectroscopy, and reactivity of thorium, uranium, and neptunium complexes with soft donor-based ligands. Donor atoms of primary interest to us are sulfur, selenium, phosphorus, arsenic, and carbon, i.e., elements that have relatively low electronegativity compared to the highly electropositive actinide. Furthermore, we have investigated actinide-ligand multiple bonding that necessitates a covalent interaction.

Therefore our research goals are: 1) To investigate actinide-ligand bonding with soft-donor ligands with respect to their structure, bonding, spectroscopy, and reactivity; 2) Examine actinide-ligand multiple bonding.

Recent Research Progress

Sulfur and selenium. Initial studies were conducted with sulfur and selenium using dithio- and diselenophosphonate ligands and subsequently examined dithio- and diselenophosphinates. Thorium- and uranium-selenium bonds were observed to have greater covalent character than their sulfur analogs. Since the thorium complexes are amenable to characterization via ^{77}Se NMR spectroscopy we synthesized other selenium-based ligands such as a selenium bis(phenolate) which was subsequently coordinated to Ti, Zr, Hf, Th, U, and Np. A similar series of dithiocarbamate ligands was utilized in an effort to compare bonding in transition metal and actinide complexes, which revealed an unusual trend that demonstrated the covalency in the metal-sulfur bond following the order of: $\mathrm{Hf} < \mathrm{Zr} < \mathrm{Th} < \mathrm{Ti} < \mathrm{U} \approx \mathrm{Np}$. A similar trend was recently shown with the use of aryloxide ligands (*Dalton Trans.* **2019**, *48*, 2939). Neither study elucidated the origin of this trend, leaving an exciting opportunity for further research.

Phosphorus and arsenic. Very few actinide complexes with phosphorus and arsenic were known when we initially started this work. As such, we have worked mostly with primary phosphido and arsenide ligands, $[\mathrm{EH(Mes)}]^{1-}$ and $[\mathrm{EH(Tipp)}]^{1-}$, E = P, As; Mes = 2,4,6-$\mathrm{Me_3C_6H_2}$; Tipp = 2,4,6-$^{i}\mathrm{Pr_3C_6H_2}$. The objective was to develop a ligand framework that would sterically satisfy the actinide, but due to the weaker donor properties of P and As, leave their electronic demands unmet. Not only does phosphorus have an NMR-active nuclei (^{31}P), it is a soft donor atom so small that the metal-phosphido bond should be highly reactive. The remaining proton on the phosphorus-donor can be deprotonated, providing the basis for our second objective of forming actinide-ligand multiple bonds. Indeed, $(C_5Me_5)_2Th[PH(Mes)]_2$ reacts with small molecules in relatively simple ways such as insertion-type reaction with benzophenone and CO_2, and replacement with ^tBuNC to form the parent phosphine, as well as proton migration in the cases of substrates like CO and ^tBuCN. We have also synthesized complexes containing thorium-phosphorus and thorium-arsenic multiple bonds by removing the remaining proton from the phosphido or arsenido ligands. We are currently collaborating with Peter Hrobárik (Comenius University, Slovakia) in an effort to use NMR spectroscopy for correlating the ^{31}P NMR resonances ~~to~~ with the molecular and electronic structures of our phosphido complexes.

Carbon. We have also examined the tetral series (initially focusing on carbon), as silicon has been known to primarily form highly unstable An-Si bonds. A series of dimethylbenzylamine (DMBA) complexes with Th(IV), U(III), and Np(III) have been synthesized. While the reactivity of U(III) typically produces U(IV) products, the Np starting material ($Np(DMBA)_3$) can be used for facile access to Np(III) compounds without the need for an external reductant. For example, reaction of $Np(DMBA)_3$ with three equivalents of $HE(2,6\text{-Mes-}C_6H_3)$, E = O, S, forms $Np[E(2,6\text{-Mes-}C_6H_3)]_3$.

Further, we have made a series of phosphorano-stabilized carbene complexes that feature short thorium- and uranium-carbon bonds. These complexes of the form $(C_5Me_5)_2An(CHPPh_3)(X)$ can be synthesized directly from $(C_5Me_5)_2An(CH_3)(X)$, X = Cl, Br, I, with an ylide, $H_2C{=}PPh_3$. We were also able to correlate the ^{13}C NMR resonances with the metal-carbon bond distances, showing that the associated resonance shifts downfield as they decrease.

Future Plans

Chalcogens. Although our focus has shifted from studies involving sulfur and selenium-based ligands, we continue to use chalcogen-donors with sterically encumbering terphenyl-derived substituents of the form, $[E(2,6\text{-Mes-}C_6H_3)]^{1-}$, to support low-valent actinide metal centers. Most of our neptunium work features neptunium aryloxides, and will be prominent in our continuing efforts.

Pnictogens. We have also started to mix substituent sets on An-centers, namely in the case of phosphorus and carbon to produce mixed-ligand complexes such as $(C_5Me_5)_2An[P(SiMe_3)(R)](CH_3)$, R = Mes, Ph, in which two reactive sites are present. In addition, the nitrogen analogs, i.e. primary amido complexes, have not been studied in detail so we have begun to examine the differences in reactivity between amido, phosphido, and arsenido actinide complexes. Further work that ambitiously expands upon this is the synthesis of thorium and uranium-phosphinidene and -arsinidene complexes which are rare, but represent an ideal framework to study metal-ligand multiple bonding.

Tetrals. Our work on phosphorano-stabilized carbenes is also continuing with a focus on the chemistry of different ylides (varying both substituents on the pnictogen, and the pnictogen itself) to examine the effect on their donor ability. For example, changing phosphorus for another pnictogen like arsenic or antimony to form ylides of the type $H_2C{=}EPPh_3$ (E = As, Sb). We also intend to explore the chemistry of the phosphorano-stabilized carbenes to probe the actinide-ligand multiple bonding with substrates like acetylenes.

Given the poor donor ability of the tetrals, we will endeavor to use chelating ligands with Si, Ge, and Sn to stabilize the metal centers. All of these elements have NMR active nuclei which will assist with correlating covalency in actinide-tetral bonds.

Neptunium and Plutonium. As our work with neptunium progresses, we would like to extend our efforts to plutonium, as Pu(DMBA)$_3$ is a viable synthetic target. The redox chemistry of Np(III) and Pu(III) will be explored with respect to creating Np(IV) complexes for use as single-molecule magnets as well attempts to prepare non-neptunyl Np(V) compounds.

Recent Publications Resulting from Project

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6. Vilanova, S. P.; Alayoglu, P.; Heidarian, M.; Huang, P.; Walensky, J. R. Metal-Ligand Multiple Bonding in Thorium-Phosphorus and –Arsenic Complexes, *Chem. Eur. J.* **2017**, *23*, 16748.
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10. Rungthanaphatsophon, P.; Duignan, T. J.; Myers, A. J.; Vilanova, S. P.; Barnes, C. L.; Autschbach, J.; Batista, E. R.; Yang, P.; Walensky, J. R. Influence of Substituents on the Electronic Structure of Mono- and Bis(Phosphido) Thorium(IV) Complexes, *Inorg. Chem.* **2018**, *57*, 7270.
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12. Myers, A. J.; Rungthanaphatsophon, P.; Behrle, A. C.; Vilanova, S. P.; Kelley, S. P.; Lukens, W. W.; Walensky, J. R. Structure and Properties of $[(4,6\text{-}^tBu_2C_6H_2O)_2Se]_2An(THF)_2$, An = U, Np, and Their Reaction with *p*-Benzoquinone, *Chem. Commun.* **2018**, *54*, 10435.
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