2023 Heavy Element Chemistry Principal Investigators' Meeting

Rockville, MD
April 24-26, 2023

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

2023 Heavy Element Chemistry Principal Investigators' Meeting

Rockville Hilton
1750 Rockville Pike
Rockville, Maryland
April 24-26, 2023

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

Cover photo: (Philip Wilk, 2023)

The research grants and contracts described in this document are, with the exception of the invited speakers, supported by the U.S. DOE Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division.

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Foreword

This abstract book provides a record of the twelfth U.S. Department of Energy Principal Investigators' meeting of the Heavy Element Chemistry program. 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 nearly seventy 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. 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 hope that this meeting enhanced research efforts and will nurture future collaborations. I would like to thank all the researchers whose dedication and innovation have advanced our research and made this meeting possible and productive.

Philip Wilk

Agenda

2023 Heavy Element Chemistry Principal Investigators' Meeting

Hilton Washington DC/Rockville Hotel & Executive Meeting Ctr
Monday, April 24 - Wednesday, April 26

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 23

	Arrival
7 -9 PM	Informal No-Host Meetup at "Olive's" Hilton Washington DC/Rockville Hotel & Executive Meeting Ctr

Monday, April 24

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

Philip Wilk
Program Manager
philip.wilk@science.doe.gov

Monday, April 24

8:00 - 9:00 Breakfast

9:00 Meeting Begins — Philip Wilk

Introduction, Agenda, Mini-Workshop Charge

9:15 Session 1a: Electronic structure and reactivity — Ben Stein

9:15	Michael Morse
	Electronic Structure, Spectroscopy, and Bond Dissociation Energies of Small Actinide Molecules
9:40	Michael Heaven
	Spectroscopic investigations of actinide bonding and electronic structure
10:05	Miles Beaux
	Resolving the f-electron challenge with scanning probe microscopy/spectroscopy
10:30	break

10:45 Session 1b: — Ben Stein

10:45	Thomas Persinger
	Spectroscopy and Electronic Structure of Actinide Molecules
11:10	Michael Servis
	Probing Phase Transitions and Mesoscale Aggregation in Liquid-Liquid Extraction
11:35	Robert (Gian) Surbella
	Spectroscopic Investigation of Electronic Structure in the Actinide Elements
12:00	Working Lunch for Collaboration (poster room will be open)

1:00 Session 2: Theory — Stosh Kozimor

1:00	Jochen Autschbach
	Computational studies of magnetism and spectra of actinide complexes
1:25	David Dixon
	Computational Studies of Structure, Thermodynamic Properties, and Reactivity Across the Actinide Row
1:50	Bess Vlaisavljevich
	CASPT2 Geometries, Spectra, and Relativistic Electronic Structures of Actinide Species
2:15	break
2:30	Enrique Batista
	Heavy Element Chemistry at Los Alamos National Laboratory
2:55	Laura Gagliardi
	Quantum Chemical Treatment of Strongly Correlated Systems Containing Heavy Elements
3:20	Ping Yang
	Debrief: 2nd International Workshop on Theory Frontiers in Actinide Science: Chemistry and Materials
3:35	Jenifer Shafer, ARPA-E
	Update: Advanced Research Projects Agency-Energy
3:50	break

4:10 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 25

8:00 - 9:00 Breakfast

9:00 Chemical Sciences, Geosciences and Biosciences Division Update — Philip Wilk

Gail McLean, acting Division Director

9:30 Session 3: — Sara Adelman

9:30 Justin Walensky
Small Molecule Reactivity with Actinide Complexes
9:55 Christopher Cahill
Novel TRU materials via restricted [AnO2]2+(An=U, Np, Pu) speciation profiles and supramolecular assembly
10:20 Omar Farha
Project: Low-Valent Actinide Complexes Featuring Tunable Carborane-based Ligands
10:45 break
11:00 Jackie Gates
Influence of Actinide and Transactinide Electronic Structure on Chemical Reactivity
11:25 Trevor Hayton
Measuring Covalency in An-N and An-C Bonds: A Combined Synthetic and Spectroscopic Investigation
11:50 Robin Rogers
Exploring the Nature of f-Element Soft Donor Interactions Using Electronically Tunable Azolate Ionic Liquids
12:15 Working Lunch for Collaboration (poster room will be open)

1:15 Session 4 — Srikanth Nayak

1:15 Rebecca Abergel
Explore New Coordination Modes in Actinide Molecules and Materials
1:40 Lou Messerle
Synthesis, Structural & Spectroscopic Characterization, and Theory of Complexes with Reactant-Accessible An-An Covalent Bonds
2:05 Christopher Dares
Modulating Actinide Redox Chemistry with Metal Oxide Electrodes
2:30 break
2:45 Andrew Gaunt
Heavy Element Chemistry at Los Alamos National Laboratory
3:10 Karah Knope
Tetravalent Actinide Specitation: Template Directed Assembly, Stabilization, and Reactivity
3:35 Ellen Matson
Understanding Photoluminescence in High- and Low-Valent Actinide Complexes

4:00 Heavy Element Chemistry program and Separation Science program updates

Philip Wilk, Program Manager
4:20 break

4:30 Poster Session #2

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

Wednesday, April 26

8:00 - 9:00	Breakfast	
9:00	**Session 5: Molecular & Electronic Interactions**	**Thomas Persinger**
9:00	Polly Arnold Influence of Actinide and Transactinide Electronic Structure on Chemical Reactivity	
9:25	Stefan Minasian Role of f Orbital Interactions in Determining Heavy Element Physical Properties	
9:50	Stosh Kozimor Heavy Element Chemistry at Los Alamos National Laboratory	
10:15	Rebecca Abergel Debrief: Basic Energy Sciences Roundtable - Foundational Science to Accelerate Nuclear Energy Innovation	
10:40	break	
10:55	**Mini-Workshop**	
12:00	Lunch on your own / dismissal	

Posters

P1	Thomas Albrecht-Schoenzart Isolation of a Californium(II) Crown Ether Complex
P2	Peter Armentrout Thermochemistry and Reactivity ofAtomic and Molecular Actinide Cations
P3	Suzanne Bart Investigating the Electronic Structure of Higher Order Actinide Imido Complexes
P4	James Blakemore Chemical and Electrochemical Studies ofUranium Redox Chemistry in Tailored Environments
P5	Kit Bowen Uranium-Containing and Thorium-Containing Anions Studied by Anion Photoelectron Spectroscopy
P6	Lan Cheng Novel Relativistic Electronic Structure Theories for Actinide-Containing Compounds
P7	Herman Cho Nuclear Quadrupole Resonance Spectroscopic Investigations of Uranium-Ligand Interactions in Uranyl Tetrahalides
P8	Scott Daly Exploratory Synthesis for Reactive f-Element Separations without Solvent
P9	John Despotopulos Chemistry at the Extreme Edges of the Periodic Table: Elucidating the Chemical Properties of the Superheavy Elements
P10	Bill Evans Exploring the Fundamental Chemistry of Actinide Metal Complexes
P11	Tori Forbes Impact of intermolecular interactions on the spectroscopic signals, energetics, and redox behavior of high valent 237Np
P12	Tori Forbes Direct air carbon dioxide separation using a uranyl superoxide catalyst
P13	Shane Galley Dipicolinic Acid Derivatization to Assess trans Plutonium Bonding Trends
P14	Henry La Pierre Redox chemistry and Spectroscopy of High-Valent, Non-Actinyl Mid-Actinide Complexes (U, Np, and Pu)
P15	Henry La Pierre The Application of FIRMS and INS in Determining Spin-Phonon Coupling in f-Element Qubits
P16	Xiaosong Li Recent Relativistic Electronic Structure Methods Developmentfor Heavy-Element Chemistry
P17	Evangelos Miliordos Quantum Chemical Calculations on Thorium Complexes with Diffuse Peripheral Electrons
P18	Srikanth Nayak Structure and Thermodynamics of Actinide Complexes in Aqueous and Organic Solutions
P19	Eric Schelter Expressing Tunable Emergent Quantum Phenomena in Molecular Systems with Strong Electron Correlations
P20	David Shuh Soft and Tender X-ray Spectromicroscopy Studies of Actinide Materials
P21	Ben Stein Photophysical Studies of f-Elements
P22	Eric Walter Magnetism and Electronic Structure of Actinide Tetrafluorides Probed by Variable Temperature 19F NMR Spectroscopy
P23	Richard Wilson Periodic Properties in Actinide Ligand Interactions
P24	Ping Yang Autonomous Discovery of Selective f-Elements Separation for Clean Energy

Abstracts from University Research Programs

Isolation of a Californium(II) Crown-Ether Complex

Thomas Albrecht-Schoenzart, Principal Investigator

Department of Chemistry and Nuclear Science & Engineering Center, Colorado School of Mines, Golden, Colorado 80401
Graduate Students: Todd N. Poe, Hannah B. Wineinger, Brian M. Rotermund, Jacob Brannon, Zhuanling Bai, Nicholas Beck, Brian N. Long
Collaborators: Harry Ramanantoanina (Karlsruhe), Joseph M. Sperling (Mines), Cristian Celis-Barros (Mines), Benjamin Scheibe (Mines)

Overall research goals: Our objective is to extend the boundaries of transuranium chemistry through the synthesis, isolation, and characterization of complexes containing actinide ions in unusually high or low-oxidation states (*e.g.* Cf(II) or Cf(IV)) and through the application of high pressures to these molecules. We seek to understand, and perhaps, gain control of the chemical bonding in these complexes in order to observe specific physio-chemical properties such as the change from 5*f*→5*f* transitions in An(III) complexes to 5*f*→6*d* transitions in An(II) complexes, or vibronic broadening of electronic transitions induced by increased hybridization at high pressures.

Significant achievements during 2021- 2023:

In addition to isolating the first Cf(II) complex, we prepared, characterized, and performed quantum mechanical studies on many other families of transuranium complexes including organometallic transplutonium compounds, high-pressure studies of many compounds containing actinides from Np to Cf, the synthesis of neptunium alkoxide clusters, and the investigation of the atomic structure of numerous isotopes of Cm, Cf, Es, and Fm via RIMS.

Science objectives for 2023- 2025:

The only Cf(II) complex ever isolated is the one described herein. Now that we know how to crystallize and isolate these compounds, we need to prepare more examples so that we can understand trends in the chemical and physical properties of Cf(II) molecules. We know that the spectroscopic properties should be highly sensitive to the coordination environment because the transitions are 5*f*→6*d* in nature. It should be anticipated that the physical properties will be symmetry dependent. We also have several viable routes to Cf(IV) and Cf(V) complexes as well. Again, these will be the first of their kind. Their properties are currently unknown.

Selected Publications supported by this project 2021-2023 (out of 29 total)

13. H. Zhang, A. Li, K. Li, Z. Wang, X. Xu, Y. Wang, M. V. Sheridan, H.-S. Hu, C. Xu, E. V. Alekseev, Z. Chai, T. E. Albrecht-Schönzart, S. Wang, "Ultrafiltration separation of nanoscale Am(VI)-polyoxometalate clusters from lanthanides," *Nature*, **2022**, *in press*. **DOI:** 10.1038/s41586-023-05840-z
12. T. N. Poe, H. Ramanantoanina, J. M. Sperling, H. B. Wineinger, B. M. Rotermund, J. Brannon, Z. Bai, B. Scheibe, N. Beck, B. N. Long, S. Justiniano, T. E. Albrecht-Schönzart, C. Celis-Barros, "Isolation of a Californium(II) Crown-Ether Complex," *Nature Chemistry*, **2023**, *in press*. **DOI:** 10.1038/s41557-023-01170-9
11. D. Grödler, J. M. Sperling, B. M. Rotermund, B. Scheibe, N. B. Beck, S. Mathur, T. E. Albrecht-Schönzart, "Neptunium Alkoxide Chemistry: Homo- and Bimetallic *Tert*-butoxides of Neptunium and Alkali Metals," *Inorganic Chemistry*, **2023**, *62*, 2513-2517. **DOI:** 10.1021/acs.inorgchem.2c04338
10. N. Beck, Z. Bai, J. Brannon, D. Gomez Martinez, D. Grödler, B. Long, T. Poe, B. Rotermund, T. Albrecht-Schönzart, J. Sperling, "Two Air-stable Neptunium(III) Mellitate

Coordination Polymers," *Inorganic Chemistry*, **2022**, *61*, 17730-17737. **DOI:** 10.1021/acs.inorgchem.2c02873

9. H. Arabzadeh, B. Walker, O. Acevedo, P. Ren, W. Yang, and Thomas Albrecht-Schönzart, "Molecular Dynamics and free energy calculations of dicyclohexano-18-crown-6 diastereoisomers with Sm^{2+}, Eu^{2+}, Dy^{2+}, Yb^{2+}, Cf^{2+} and three halide salts in THF and Acetonitrile using the AMOEBA Force Field," *Journal of Physical Chemistry B*, **2022**, *126*, 10721-10731. **DOI:** 10.1021/acs.jpcb.2c04613
8. Z. K. Huffman, J. M. Sperling, C. J. Windorff, B. N. Long, L. Cordova, C. Celis-Barros, T. E. Albrecht-Schönzart, "Synthesis and Characterization of a Bimetallic Americium(III) Pyrithionate Coordination Complex," *Chemical Communications*, **2022**, *58*. 11791-11794. **DOI:** 10.1039/D2CC03352F
7. F. Weber, T. E. Albrecht-Schönzart, M. Block, P. Chhetri, C. E. Düllmann, J. G. Ezold, V. Gadelshin, Alyssa N. Gaiser, F. Giacoppo, R. Heinke, T. Kieck, N. Kneip, M. Laatiaoui, C. Mokry, S. Nothhelfer, S. Raeder, J. Runke, F. Schneider, J. M. Sperling, D. Studer, P. Thörle-Pospiech, N. Trautmann, K. Wendt, "Atomic structure investigations of neutral einsteinium by laser resonance ionization," *Physical Review R*, **2022**, *4*, 043053. **DOI:** 10.1103/PhysRevResearch.4.043053
6. J. M. Sperling, N. Beck, B. Scheibe, Z. Bai, J. Brannon, D. Gomez-Martinez, D. Grödler, J. A. Johnson, X. Lin, B. Rotermund, T. E. Albrecht-Schönzart, "Synthesis, Characterization, and High-Pressure Studies of a 3D Berkelium(III) Carboxylate Framework Material," *Chemical Communications*, **2022**, *58*, 2200-2203. **DOI:** 10.1039/D1CC06958F
5. S. Nothhelfer, T. E. Albrecht-Schönzart, M. Block, P. Chhetri, Ch. E. Düllmann, K. Eberhardt, J. G. Ezold, V. Gadelshin, A. Gaiser, F. Giacoppo, R. Heinke, T. Kieck, N. Kneip, M. Laatiaoui, Ch. Mokry, S. Raeder, J. Runke, F. Schneider, J. Sperling, D. Studer, P. Thörle-Pospiech, N. Trautmann, F. Weber, K. Wendt, "Nuclear Structure Investigations of $^{253-255}$Es by Laser Spectroscopy," *Physical Review C*, **2022**, *105*, L021302. **DOI:** 10.1103/PhysRevC.105.L021302
4. B. N. Long, M. J. Beltrán-Leiva, C. Celis-Barros, J. M. Sperling, T. N. Poe, C. J. Windorff, T. E. Albrecht-Schönzart, "Structure, Spectroscopy, and Bonding in a Dinuclear Organometallic Americium Complex," *Nature Communications*, **2022**, *13*, 201-208. **DOI:** 10.1038/s41467-021-27821-4
3. C. J. Windorff, M. J. Beltran-Leiva, T. E. Albrecht-Schönzart, Z. Bai, C. Celis-Barros, C. A. P. Goodwin, Z. Huffman, N. C. McKinnon, J. M. Sperling, "Synthesis, Characterization, and Theoretical Analysis of Plutonyl Phosphine Oxide Complexes," *Dalton Transactions*, **2021**, *50*, 14537-14541. **DOI:** 10.1039/D1DT03041H
2. A. N. Gaiser, C. Celis-Barros, F. D. White, M. J. Beltran-Leiva, J. M. Sperling, S. R. Salpage, T. N. Poe, T. Jian, N. J. Wolford, N. J. Jones, A. J. Ritz, R. A. Lazenby, J. K. Gibson, R. E. Baumbach, D. Páez-Hernández, M. L. Neidig, T. E. Albrecht-Schönzart, "Creation of an Unexpected Plane of Enhanced Covalency in Cerium(III) and Berkelium(III) Terpyridyl Complexes," *Nature Communications*, **2021**, *12*, 7230. **DOI:** 10.1038/s41467-021-27576-y.
1. J. M. Sperling, E. J. Warzecha, B. E. Klamm, A. N. Gaiser, C. J. Windorff, M. A. Whitefoot, T. E. Albrecht-Schönzart, "Pronounced Pressure Dependence of Electronic Transitions for Americium Compared to Isomorphous Neodymium and Samarium Mellitates," *Inorganic Chemistry*, **2021**, *60*, 476-483. **DOI:** 10.1021/acs.inorgchem.0c03293

THERMOCHEMISTRY AND REACTIVITY OF ATOMIC AND MOLECULAR ACTINIDES

Peter B. Armentrout, Principal Investigator

Department of Chemistry, University of Utah, Salt Lake City, UT
Graduate Students: Arjun Kafle, Mandy Bubas, Sara Rockow, Postdoc: Wenjing Zhang
Collaborators: Kirk A. Peterson (Washington State U.), Bert de Jong (LBNL), Richard M. Cox (PNNL)

Overall research goals: The overall project objectives are to examine the thermochemistry and reactivity of actinide compounds of thorium and uranium using guided ion beam tandem mass spectrometry (GIBMS). In particular, we intend to experimentally determine bond dissociation energies (BDEs) that can act as benchmarks for theoretical explorations of the actinides. The experimental work will be accompanied by high-level ab initio calculations to determine mechanisms of reactions, structures of products, and to evaluate what levels of theory are needed to reproduce the experimental thermochemistry. Collaborations with Peterson and de Jong facilitate this latter goal.

Significant achievements during 2021-2023:

Collision-induced dissociation (CID) reactions of $Th^+(CO)_x$ (x = 1 – 6) with Xe were analyzed to determine thorium cation carbonyl bond dissociation energies (BDEs). The mono-carbonyl BDE of 0.94 ± 0.06 eV was replicated by the Feller-Peterson-Dixon (FPD) theoretical result of 0.94 ± 0.02 eV. For higher order carbonyls, the experimental results, which exhibit interesting non-monotonic behavior, are reproduced reasonably well by CCSD(T)/CBS calculations. Theory also indicates that thorium oxide ketenylidene carbonyl cations, $OTh^+CCO(CO)_y$, y = 1 – 4, are actually the most stable structures of $[Th,xC,xO]^+$, x = 2 – 6, although not observed experimentally because a barrier to C–C bond formation makes formation of $OTh^+CCO(CO)_y$ inaccessible kinetically under the experimental conditions.

Kinetic-energy dependent reactions of atomic U^+ with H_2, D_2, and HD were studied using GIBMS. Formation of UH^+ (UD^+) was observed in endothermic reactions which were modeled to yield $D_0(U^+–H) = 2.48 \pm 0.06$ eV, somewhat below previous determinations. This BDE was also explored by quantum chemical calculations, including high-level CASSCF-CASPT2-RASSI calculations of the spin-orbit corrections, which yields a BDE in good agreement with experiment. The experimental product branching ratio for reaction of U^+ with HD indicates that these reactions occur primarily via a direct reaction mechanism, despite the presence of a deep-well for UH_2^+ formation according to theory. Comparison of these results with those for transition and lanthanide metals suggest that the *5f* electrons on uranium are largely uninvolved in the reactive chemistry.

The kinetic energy dependences of the reactions of thorium and uranium cations with CF_4 and SF_6 were studied using GIBMS and yielded products including AnF_x^+ (An = Th or U, x = 1-5), CF_y^+ (y = 1-3), and SF_y^+ (y = 1-4). Although most reactions with CF_4 are exothermic according to literature thermochemistry, all cross sections display strong endothermic features indicating a restriction in the reactivity at low energies. In contrast, the reactivity of the actinide cations with SF_6 is efficient at thermal energies. Results for reaction of U^+ with SF_6 at thermal energies agree with previous results of Gibson, but new insight into this system is provided by examination of the kinetic energy dependences.

Reaction of atomic U^+ with CS_2 forms US^+ in an efficient exothermic reaction and UCS^+ in an inefficient endothermic process. The subsequent reaction of US^+ with CS_2 forms US_2^+ in low-energy endothermic process and UCS_2^+ and UCS^+ at much higher energies. Collision-induced dissociation of US^+ with Xe yields U^+ + S exclusively in an endothermic reaction. Analysis of the kinetic energy dependent cross sections of the endothermic processes yields 0 K BDEs for U^+-S, SU^+-S, U^+-CS, U^+-CS_2, SU^+-CS, and S-UCS^+. Theory is used to explore the structures and electron configurations of these species. The thermochemistry measured in this study was further compared to analogous values previously determined for select group 3 transition metals, lanthanides, and actinides.

GIBMS was used to examine the kinetic energy dependent reactions of U^+ with O_2 and CO. In the former reaction, the UO^+ product is formed in a barrierless and exothermic process. Formation of both UO^+ and

UC^+ in the reaction of U^+ with CO is endothermic and modelling these data provides 0 K BDEs of $D_0(U^+$-O) = 7.88 ± 0.09 eV and $D_0(U^+$-C) = 4.03 ± 0.13 eV. These values are within experimental uncertainty of previously reported experimental values. Additionally, the electronic states of UO^+ and UC^+ and the potential energy surfaces for the reactions were explored by quantum chemical calculations, including a full FPD composite approach with correlation contributions up to CCSDT(Q) for UO and UO^+, yielding D_0(U-O) = 7.82 eV and $D_0(U^+$-O) = 7.99 eV.

Reactions of CO_2 with U^+ were studied using GIBMS and with An^+ ($An^+ = Th^+$, U^+, Pu^+, and Am^+) using triple quadrupole inductively coupled plasma mass spectrometry (QQQ-ICP-MS). QQQ-ICP-MS reactions were studied at higher pressures where multiple collisions between An^+ and the neutral CO_2 occur, such that both AnO^+ and AnO_2^+ products were observed. Comparison of the periodic trends of the group 4 transition metal, lanthanide (Ln), and actinide atomic cations in reactions with CO_2 (a formally spin-forbidden reaction for most M^+ ground states), and O_2 (a spin unrestricted reaction) indicate that spin conservation plays a minor role, if any, for the heavier An^+ metals.

Finally, a review paper examined periodic trends in the oxidation and hydrogenation reactions and thermochemistry of lanthanides (AFOSR), 5d transition metals (NSF), and thorium (HEC/DOE).

Science objectives for 2023-2025:

Data has been collected for the reactions of U^+ with CO_2 and UO^+ with O_2 and CO. A paper on this work is in progress. Data has been acquired for reactions of U^+, UO^+, and US^+ with CS_2 and COS. The process of writing up these studies for publication has begun.

Selected publications supported by this project 2021-2023

Zhang, W.-J.; Demireva, M.; Kim, J.; de Jong, W. A.; Armentrout, P. B. "Reactions of U^+ with H_2, D_2, and HD Studied by Guided Ion Beam Tandem Mass Spectrometry and Theory" *J. Phys. Chem. A* **2021**, *125*, 36, 7825–7839. DOI: 10.1021/acs.jpca.1c05409

Bubas, A. R.; Owen, C. J.; Armentrout, P. B. "Reactions of Atomic Thorium and Uranium Cations with CF_4 Studied by Guided Ion Beam Tandem Mass Spectrometry" *Int. J. Mass Spectrom.* **2022**, *472*, 116778. DOI: 10.1016/j.ijms.2021.116778

Armentrout, P. B. "Periodic Trends in Gas-phase Oxidation and Hydrogenation Reactions of Lanthanides and 5d Transition Metal Cations" *Mass Spectrom. Rev.* **2022**, *41*, 606-626. DOI: 10.1002/mas.21703

Cox, R. M; Harouaka, K.; Citir, M.; Armentrout, P. B. "Activation of CO_2 by Actinide Cations (Th^+, U^+, Pu^+, and Am^+) as Studied by Guided Ion Beam and Triple Quadrupole Mass Spectrometry" *Inorg. Chem.* **2022**, *61*, 8168-8181. DOI: 10.1021/acs.inorgchem.2c00447

Bubas, A. R.; Iacovino, A. C.; Armentrout, P. B. "Reactions of Atomic Thorium and Uranium Cations with SF_6 Studied by Guided Ion Beam Tandem Mass Spectrometry" *J. Phys. Chem. A* **2022**, *20*, 3239-3246. DOI: 10.1021/acs.jpca.2c02090

Kafle, A.; Armentrout, P. B. "Sequential Bond Dissociation Energies of $Th^+(CO)_x$, x = 3 – 6: Guided Ion Beam Collision-Induced Dissociation and Quantum Computational Studies" *Inorg. Chem.* **2022**, *61*, 15936-15952. DOI: 10.1021/acs.inorgchem.2c02138

Rockow, S.; Bubas, A. R.; Krauel, S. P.; Stevenson, B. C.; Armentrout, P. B. "Thermochemistry of Uranium Sulfide Cations: Guided Ion Beam and Theoretical Studies of Reactions of U^+ and US^+ with CS_2 and Collision-induced Dissociation of US^+" *Molec. Phys.*, in press. DOI: 10.1080/00268976.2023.2175595

Zhang, W.; Hunt, A. R. E.; Kim, J.; Demireva, M.; Peterson, K. A.; Armentrout, P. B. Bond Energies of UO^+ and UC^+: Guided Ion Beam and Quantum Chemical Studies of the Reactions of Uranium Cation with O_2 and CO" *Isr. J. Chem.*, submitted for publication.

Computational studies of magnetism and spectra of actinide complexes

Jochen Autschbach, Principal Investigator

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Graduate students & Postdocs: Laura Motta, Xiaojuan Yu, Herbert Ludowieg, Ashima Bajaj
Collaborators: Stefan Minasian (Berkeley Lab), Herman Cho (PNNL), Trevor Hayton (UC Santa Barbara), R. Gian Surbella III (PNNL), Dumitru-Claudiu Sergentu (U. Rennes, France), Ning Chen (Soochow U., China), and others

Overall research goals: In this project, we investigate the electronic structures as well as spectroscopic and magnetic properties of chemical compounds with f-elements, i.e. actinides and lanthanides, by quantum theoretical calculations. The main objective is to learn how the observable magnetic, optical, 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 (EPR, NMR), magnetic susceptibilities, valence and core excitation spectra (UV-vis and X-ray spectroscopy), magnetic field-induced circular dichroism (MCD) and Mössbauer spectroscopic parameters. 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. Density functional theory (DFT) as well as multiconfiguration-wavefunction theory (WEFT) with relativistic Hamiltonians are used in this project.

Significant achievements during 2021- 2023: We continued our studies of X-ray near-edge structure (XANES) of f-element complexes, culminating in a Chem. Sci. article [1] showing with DFT and WFT calculations that old-fashioned molecular orbital theory with its interplay of atomic orbital overlap and energy matching fully explains the observed Cl K-edge XANES spectra of $[AnCl_6]^{2-}$, An^{IV} = Th, U, Np, Pu, complexes and their experimental assignment. There is no need to invoke an argument based on energy matching without overlap. We also published a short 'highlight' review of the capabilities developed within the project for ab-initio calculations of f-element X-ray spectra and the accompanying analysis of the relevant wavefunctions. [2]

Our collaboration with T. Hayton has continued full-steam, with five new publications since the last HEC meeting. We conducted joint experimental/theoretical studies of f-element complexes with Th, and U, typically with a focus on how metal-ligand covalent bonding impacts the ligand NMR chemical shifts via spin-orbit coupling, a relativistic effect. An example is ref. [3] reporting the first synthesis and characterization of actinide allenylidene complexes. Our lab has unique capabilities for analyzing NMR parameters obtained with relativistic DFT calculations in terms of bonding.

Postdoc Laura Motta performed a comprehensive theoretical study of ^{237}Np Mössbauer spectroscopic parameters [5-7]. This new project was prompted by plans among some of the HEC PIs to construct a new high-resolution Mössbauer instrument for ^{237}Np, decades after the instrument at Savannah River laboratory has been decommissioned. Our calculations assign and systematize nearly all ^{237}Np Mössbauer measurements reported in the literature. Important outcomes of these studies were (i) DFT with embedding models for crystal packing works well as long as the relativistic effects are treated properly. (ii) DFT fails for isomer shifts of multi-configurational systems. In those cases, the isomer shift can be calculated from CASPT2 WFT energy derivatives, for example, or from DMRG wavefunctions. (iii) We predict Np(II) isomer shifts to be in the same range as those for Np(III). (iv) The quadrupolar splitting can be modulated strongly by crystal packing effects.

Our on-going collaboration with Ning Chen has discovered new interesting new uranium and thorium bonding motifs that present themselves when actinide-containing small-molecule clusters are encapsulated inside fullerene cages. [8,9]

Science objectives for 2023- 2025: In Mössbauer spectroscopy, the three parameters obtained from the spectra are the isomer shift (IS), the quadrupole splitting (QS), and the hyperfine coupling (HC). Ref. [7] features the first calculations of QS for ^{237}Np, but more experience is needed with these extremely challenging calculations. Calculations of ^{237}Np HC have never been attempted in the Mössbauer context. We will explore QS and HC calculations based on the ca. 40 systems for which we explored the IS so far, to test the hypothesis formulated in ref. [7] that these parameters probe different aspects of the open 5f shell electronic structures. The X-ray absorption spectroscopy (XAS) project will continue. For example, we will probe further to what extent the appearance of the Ce L_3 edge is truly related to the multi-configurational character of the ground states. We will attempt XAS calculations for various actinide species as well. Our collaboration with S. Minasian [10] and others at Berkeley Lab on the topics of XAS and the electronic structure of f-element sandwich compounds will require extensive efforts; there are several studies in various stages of completion.

Publications supported by this project 2021-2023 (a selection)

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[3] Kent, G. T.; Yu, X.; Wu, G.; Autschbach, J.; Hayton, T. W., ‘Synthesis and Electronic Structure Analysis of the Actinide Allenylidenes, $[\{(NR_2)_3\}An(CCCPh_2)]^-$ (An = U, Th; R = $SiMe_3$)’, Chem. Sci. **2021**, 12, 14383–14388. https://doi.org/10.1039/D1SC04666G

[4] Kent, G. T.; Yu, X.; Wu, G.; Autschbach, J.; Hayton, T. W., ‘Ring-opening of a thorium cyclopropenyl complex generates a transient thorium-bound carbene’, Chem. Commun. **2022**, 58, 6805–6808. https://doi.org/10.1039/D2CC01780F

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[7] Motta, L. C.; Autschbach, J., ‘Theoretical Evaluation of Metal-Ligand Bonding in Neptunium Compounds in Relation to ^{237}Np Mössbauer spectroscopy’, Inorg. Chem. **2022**, 61, 13399–13412. https://doi.org/10.1021/acs.inorgchem.2c01516

[8] Shen, Y.; Yu, X.; Meng, Q.; Yao, Y.-R.; Autschbach, J.; Chen, N., ‘$ThC_2@C_{82}$ versus $Th@C_{84}$: Unexpected Formation of Triangular Thorium Carbide Cluster inside Fullerenes’, Chem. Sci. **2022**, 13, 12980–12986. Selected by the editors for journal front cover. https://doi.org/10.1039/D2SC04846A

[9] Meng, Q.; Abella, L.; Yao, Y.-R.; Sergentu, D.-C.; Yang, W.; Liu, X.; Zhuang, J.; Echegoyen, L.; Autschbach, J.; Chen, N., ‘$UN@C_{82}$: A U≡N Triple Bond Captured Inside Fullerene Cages’, Nat. Commun. **2022**, 13, 7192 (10 pages). https://doi.org/10.1038/s41467-022-34651-5

[10] Qiao, Y.; Ganguly, G.; Booth, C. H.; Branson, J. A.; Ditter, A. S.; Lussier, D. J.; Moreau, L. M.; Russo, D.; Sergentu, D.-C.; Shuh, D. K.; Sun, T.; Autschbach, J.; Minasian, S. G., ‘Enhanced 5f-δ bonding in $[U(C_7H_7)_2]^-$: Carbon K-Edge X-ray Spectroscopy, Magnetism and Electronic Structure Calculations’, Chem. Commun. **2021**, 57, 9562–9565. https://doi.org/10.1039/D1CC03414F

Synthetic, Spectroscopic, and Computational Studies of Uranium Complexes Supported by Redox-Active Ligands

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Prof. Laura Gagliardi, University of Minnesota, Minneapolis, MN
Dr. Stosh Kozimor, Los Alamos National Laboratory, Los Alamos, NM
Prof. Thomas Albrecht- Schönzart, Florida State University, Tallahassee, FL

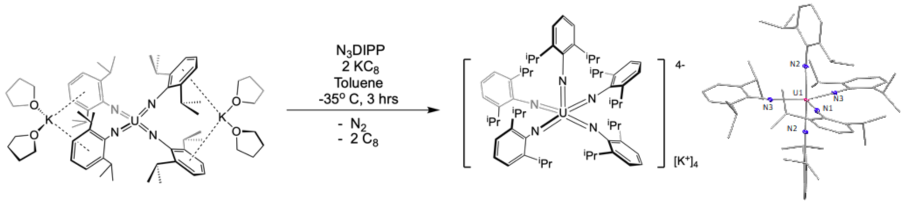
Overall research goals: A high level overview

Our project includes a broad study of lanthanide and actinide elements to explore redox chemistry, heavily loaded pi complexes, and transuranium coordination chemistry. These studies are complemented by in depth electronic structure studies. These species are fully characterized using ^{1}H NMR, infrared, electronic absorption, electronic paramagnetic resonance and X-ray absorption spectroscopies (Kozimor) as well as X-ray crystallography, electrochemistry, SQUID magnetization (Schelter), and computational methods (Gagliardi). Transuranic analogues, including Np (Bart), Pu, Am, and Cf (Albrecht-Schönzart), are studied to understand synthetic, reactivity, and bonding trends across the Periodic Table.

Significant achievements during 2021- 2023:

Our team focused on the generation of lanthanide and actinide complexes bearing a variety of ligand frameworks to understand how ligand-based electrons influence electronic structures. Concurrent with these studies was the synthesis of a pentakis(imido)uranate tetraanion, which showed that a uranium ion could support five multiply bound susbstituents. This is notable as no other metal on the periodic table has been demonstrated to support five multiple bonds. These advances were underpinned by full characterization using spectroscopic, magnetic, and computational studies. The methodology of using ligand electrons to manipulate electronic structure offers new opportunities in separations chemistry.

- Synthesis/full characterization of the first pentakis(imido)uranate tetraanion, including a full probe of the electronic structure of these species using computational methods.



- Formation of an unusual thorium-redox-active ligand series, with characterization of the first thorium complex with three independent ligand radicals.
- The first f-element terminal oxo complex synthesized from dioxygen in dry air is made from this system, forming $[O{=}Th(^{DIPP}isq)_2(^{DIPP}ap)][K(15\text{-}crown\text{-}5)_2]_2$.
- Two Np (III) halides, $NpI_3(THF)_4$ and $NpBr_3(THF)_4$, have been prepared and isolated in high yields.

- The first trivalent non-aqueous 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; q = quinone form) was prepared and fully characterized.
- Using DOPO^q, a family of tetravalent actinide (U, Th, Np, Pu) and Hf tris(ligand) coordination compounds were synthesized.
- Isolated first example of a Pu-ligand radical species and a rare example of magnetic data recorded for a homogeneous plutonium coordination complex.

Science objectives for 2023- 2025: This project aims to address fundamental questions in the chemistry of the actinides using a multiple imido framework on a variety of elements, including U, Th, and Np.

Project Objective 1: Synthesis and Characterization of High Order Actinide Imidos Generation of new Th, Np, and Pu derivatives featuring multiply bonded imido ligands analogous to our previous uranium chemistry. This will provide insight into the electronic structure of heavily loaded pi complexes in the actinide series, and facilitate further studies on covalency.

Project Objective 2: Further Characterization Uranium Imido Family and Reactivity of Pentakis(imido)uranate Tetranion Elucidation of the electronic structure of higher order uranium species *via* spectroelectrochemistry, X-ray Absorption Spectroscopy and reactivity studies.

Project Objective 3: Uranyl and Neptunyl Imidos Extension of our successful imido chemistry to activate strong uranium- and neptunium-oxygen bonds via heavy pi donation. This will also facilitate studies on understanding the electronic structure of actinides with 4 multiple bonds.

Publications supported by this project 2021-2023

1. Whitefoot, Megan A.; Perales, Diana; Zeller, Matthias; Bart, Suzanne C.* "Synthesis of Non-Aqueous Neptunium(III) Halide Solvates from NpO_2" *Chemistry: A European Journal* **2021***, 27,* 18054-18057.

2. Rupasinghe, D.M.Ramitha Y.P.; Gupta, Himanshu; Baxter, Makayla R.; Higgins, Robert F.; Zeller, Matthias; Schelter, Eric J.; Bart, Suzanne C.* "Elucidation of Thorium Redox-Active Ligand Complexes: Evidence for a Thorium-Tri(radical) Species" *Inorg. Chem.*, **2021**60, 14302-14309.

2. Galley, Shane S.; Pattenaude, Scott A.; Ray, Debmalya; Gaggioli, Carlo A.; Whitefoot, Megan A.; Qiao, Yusen; Higgins, Robert F.; Nelson, W.L.; Baumbach, Ryan; Sperling, Joseph M.; Zeller, Matthias; Collins, Tyler S.; Schelter, Eric J.; Gagliardi, Laura; Albrecht-Schönzart, Thomas E.; Bart, Suzanne C.* "Using Redox-Active Ligands to Generate Actinide Ligand Radical Species" *Inorganic Chemistry* **2021***, 60,* 15242-15252.

4. Rupasinghe, D. M. Ramitha Y. P.; Baxter, Makayla R.; Gupta, Himanshu; Poore, Andrew T.; Higgins, Robert F.; Zeller, Matthias; Tian, Shiliang; Schelter, Eric J.; Bart, Suzanne C.* "Actinide-Oxygen Multiple Bonds from Air: Synthesis and Characterization of a Thorium Oxo Supported by Redox-Active Ligands" *Journal of the American Chemical Society* **2022**, *144*, 17423-17431.

Uranyl Capture and Activation with Lewis Acids and Macrocyclic Hosts

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Collaborators: Tori Forbes (U. Iowa), Vanda Glezakou (ORNL), Michael Neidig (Rochester/Oxford), Henry La Pierre (Georgia Tech), and Richard Wilson (ANL)

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 in the uranyl ion (UO_2^{2+}). We are pursuing quantitative influence by elucidating the electrochemical properties of uranyl-containing compounds, plus related lanthanide complexes that are providing insight into strategies for tightly binding larger ions and modulating their electrochemical properties. Assembly of tailored molecular structures that bring the uranyl ion into close proximity of secondary metal ions is being pursued, a strategy inspired by metal cofactors in nature that engage in bond making and breaking with high efficiency. Electron- and group-transfer reactions are being studied with electrochemical methodologies, in order to map, and ultimately gain control over, the free energy relationships that govern U–O bond activation.

Significant achievements during 2021- 2023:

In the first area of investigation, we have developed a system for studying electrochemical activation of the uranyl ion. In this project, we have coupled chemical and electrochemical work in order to map the reaction mechanism involved in sequential reduction of uranium and electrophile attachment to the oxo ligands. This system relies on triphenylborane (BPh_3) as the electrophile, a relatively mild reagent that avoids reactivity issues that can be encountered when using tris(pentafluorophenyl)borane as the electrophile. Using electrochemical methods, we can generate a one-electron reduced form of our complex quite cleanly and then monitor reaction of this species with BPh_3. The resulting data provide thermodynamic and kinetic insights into the redox reactions involved in this reactivity manifold, offering a body of electroanalytical results that we are currently analyzing in detail. Collaborative work on this project includes electron paramagnetic resonance studies with Prof. Neidig's group as well as computational studies (ongoing) with Dr. Glezakou (ORNL). X-ray diffraction analysis has been used to understand the structures of the species involved in this chemistry, including the key mono- and bis-borylated species (see Figure 1). These species can be generated chemically or electrochemically, meaning they can be studied from multiple perspectives.

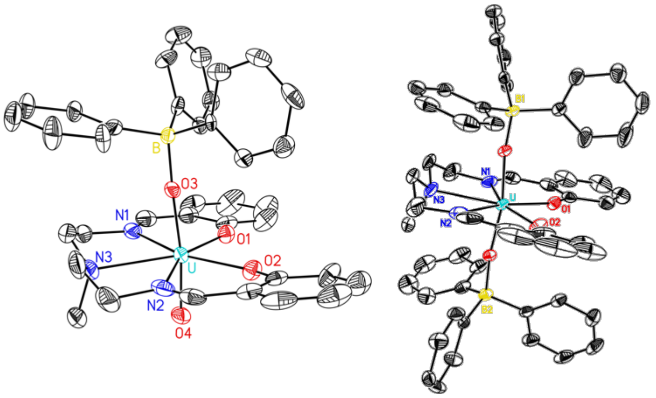

Figure 1. Solid state structures (XRD) of singly (left) and doubly (right) borylated complexes studied in this work. Displacement ellipsoids shown at the 50% probability level. Decamethylcobaltocenium counter-cations and all H atoms are omitted for clarity.

In a second area of investigation, we have continued our studies of heterobimetallic effects on the redox properties of uranium, along with other *f*-elements. We are using heteroditopic ligands in this work, in order to prepare heterobimetallic complexes of the uranyl ion, cerium, and europium. We have found that we can influence the supramolecular properties of the complexes (especially with regard to the binding of multiple metals) as well as tune their electrochemical properties by modulating the structure of our ligands. In collaboration with Prof. Forbes (U. Iowa), we have studied the vibrational spectroscopic properties of new uranyl species using this approach, in order to complement electrochemical work carried out in our laboratory. We continue to explore the observation that the identity of incorporated secondary metal cations modulates the kinetics of electron transfer to uranium. We have developed a new ligand framework capable of binding non-oxo-ligated *f*-elements, and applied this system for studying cerium(IV/III) and europium(III/II). In the former case, we have collaborated with Prof. La Pierre (Georgia Tech) to carry out X-ray absorption measurements that probe the influence of secondary metals on the cerium center.

In a third area of investigation, we have continued to develop new methods for directly measuring the Lewis acidity and solution-phase speciation of actinides. We are using a modification of the Gutmann-Beckett method for these measurements, but are applying appropriately tailored phosphorus-containing probe molecules and have made comprehensive measurements on rare earths and the uranyl ion for the first time. In one recently accepted paper, we showed how the identity of the phosphorus-containing probe molecule affects experimental outcomes, including compatibility for studies of actinides (UO_2^{2+}, Th^{4+}). With these findings as a technical foundation, we are now extending our full titration studies to selected salts of thorium(IV) and the uranyl ion; these studies are providing further quantitative measures of Lewis acidity and speciation in acetonitrile, findings of relevance to separations. We are also finding that speciation can be a key driver of tunable redox chemistry, making these measurements critical for further development of electrochemical tuning approaches like those we are studying elsewhere in our work.

In addition to the efforts described above, we have recently developed a reliable synthetic approach for incorporation of the uranyl ion into the 18-crown-6-like binding site of a macrocyclic ligand framework. The placement of the uranyl ion into this site has been confirmed by XRD analysis. The isolated compound can be used for detailed spectroscopic and electrochemical work; ongoing studies suggest that the unique coordination environment afforded by this species drives significant and useful changes in the properties of the uranyl ion. We anticipate that continued exploration of our new compound, and related examples under development, will be fruitful.

Science objectives for 2023- 2025:

We aim to pursue experiments that will elucidate how heterobimetallic effects and coordination environment can be used to systematically influence the redox chemistry, reactivity, and speciation of the uranyl ion, other actinyls, and other non-oxo actinide cations. In collaboration with Dr. Wilson, we plan to pursue work on preparation of neptunyl and plutonyl complexes for electrochemical studies via protonolysis reactivity, a route that has received less attention than it deserves and that will require development of suitable precursors. We are also developing complexes suitable for study of uranium redox cycling on electrode surfaces; these studies could help explain how surface confinement influences the properties of actinide elements.

Selected publications supported by this project 2021-2023:

Riddhi R. Golwankar, T. Davis Curry II, Cecilia J. Paranjothi, and James D. Blakemore, Molecular Influences on the Quantification of Lewis Acidity with Phosphine Oxide Probes, *Inorg. Chem.* **2023**, *Article ASAP*, doi: 10.1021/acs.inorgchem.3c00084.

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Uranium-Containing and Thorium-Containing Anions Studied by Photoelectron Spectroscopy

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Collaborators: Lan Cheng (Johns Hopkins U.), Kirk Peterson (Washington State U.), David Dixon (U. Alabama), Laura Gagliardi (U. Chicago), Bess Vlaisavljevich (U. South Dakota), Ping Yang (Los Alamos National Lab), and Puru Jena (Virginia Commonwealth U.)

Overall research goals: We report on our work studying uranium-containing and thorium-containing molecular anions using negative ion photoelectron spectroscopy. The information so obtained includes electron affinities and the electronic splittings of the anions' neutral counterparts. Our close collaborations with seven DOE-supported theorists both helps us to further interpret our photoelectron spectra and at the same time provides them with crucial benchmark data with which to test and improve their computational methods.

Significant achievements during 2021- 2023:

In addition to the results reported in the papers listed below, we also measured the anion photoelectron spectra of the following anions: UAu_n^- (3-8), U_xAuO^-, U_xPt^-, $UPtO_n^-$, $ThPtO_2^-$, $ThPtC^-$, $UOCl_2^-$, UCD_n^-, $U_nAr_m^-$, $Th(NH_3)_n^-$, $U(NH_3)_n^-$, $ThO_2^-(H_2O)_n$, and $(ThO_2)_n^-$.

Science objectives for 2023- 2025:

Our studies will focus on three broad themes: (1) uranium-containing and thorium-containing ***molecular*** anions, (2) ***metal-metal bonding*** in actinide metal-transition metal (***inter-metallic***) systems, and (3) ***ligated*** anionic molecular, metal-metal, and uranyl complexes.

Publications supported by this project 2021-2023

1. "ThH_5, An Actinide-Containing Superhalogen Cluster", M. Marshall, Z. Zhu, R. Harris, K. H. Bowen, W. Wang, J. Wang, C. Gong, X. Zhang, *ChemPhysChem* **22**, 5-8 (2021). DOI: 10.1002/cphc.202000918

2. "The Th_2O^-, Th_2Au^- and $Th_2AuO_{1,2}^-$ Anions: Photoelectron Spectroscopic and Computational Characterization of Energetics and Bonding", Z. Zhu, M. Marshall, R. Harris, K. Bowen, M. Vasiliu, D. Dixon, *J. Phys. Chem. A* **125**, 258-271, (2021).

3. "Photoelectron Spectroscopic and *Ab Initio* Computational Studies of the Anion, $HThO^-$", M. Marshall; Z. Zhu; J. Liu; L. Cheng; K. Bowen, *J. Phys. Chem. A* **125**, 1903-1905, (2021).

4. "The Electron Affinity of the Uranium Atom", S.Ciborowski, G. Liu, M. Blankenhorn, R, Harris, M. Marshall, Z. Zhu, K. Bowen, K. Peterson, *J. Chem. Phys.* , **154**, 224307 (2021). https://doi.org/10.1063/5.0046315.

5. "Anion Photoelectron Spectroscopic and Relativistic Coupled-Cluster Studies of Uranyl Dichloride Anion, $UO_2Cl_2^-$", M. Marshall, Z. Zhu, J. Liu, K. H. Bowen, L. Cheng, *Journal of Molecular Spectroscopy* , **379**, 111496, (2021). https://doi.org/10.1016/j.jms.2021.111496.

6. "Metal-Metal Bonding in Actinide Dimers: U_2 and U_2^-" S. M. Ciborowski, A. Mitra, R. M. Harris, G. Liu, P. Sharma, N. Khetrapal, M. Blankenhorn, L. Gagliardi, K. H. Bowen, *J. Am. Chem. Soc.*, **143**, 17023-17028, (2021), https://doi.org/10.1021/jacs.1c06417.

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8. "$ThAu_2^-$,$ThAu_2O^-$, and $ThAuOH^-$ anions: Photoelectric Spectroscopic and Theoretical Characterization", Z. Zhu, M. Marshall, K. Bowen, K. A. Peterson, *J. Chem. Phys.*, **156**, 054305, (2022), https://doi.org/10.1063/5.0079795.

9. "Molecular Properties of Thorium Hydrides: Electron Affinities and Thermochemistry", M. Vasiliu, M. Marshall, Z. Zhu, K. H. Bowen, D. Dixon, *J. Phys. Chem. A*, **126**, 15, 2388-2396, (2022), https://doi.org/10.1021/acs.jpca.2c01460.

10. "Experimental and Computational Description of the Interaction of H and H- with U", G. F. de Melo, M. Vasiliu, M. Marshall, Z. Zhu, B. Turfekci, S. Ciborowski, M. Blankenhorn, R. M. Harris, K. H. Bowen, D. A. Dixon, *J. Phys. Chem. A*, **126**, 27, 4432-4443, (2022), https://doi.org/10.1021/acs.jpca.2c03115.

11. "Au as a Surrogate for F: The case of UAu_6 vs UF_6", R. M. Harris, Z. Zhu, Deepika, B. A. Tufekci, K. Peterson, P. Jena, K. H. Bowen, *J. Am. Chem. Soc.*, **144**, 19685-19688, (2022), https://doi.org/10.1021/jacs.2c08231.

12. "Electronic Properties of UN and UN^- from Photoelectron Spectroscopy and Correlated Molecular Orbital Theory", G. d. Melo, M. Vasiliu, G. Liu, S. Ciborowski, Z. Zhu, M. Blankenhorn, R. Harris, C. Martinez-Martinez, M. Dipalo, K. Peterson, K. H. Bowen, D. Dixon *J. Phys. Chem. A*, **126**, 43, 7944-7953, (2022), https://doi.org/10.1021/acs.jpca.2c06012.

13. "A Theoretical and Experimental Study of the Spectroscopy and Thermochemistry of $UC^{+/0/-}$", G. d. Melo, M. Vasiliu, G. Liu, S. Ciborowski, Z. Zhu, M. Blankenhorn, R. Harris, C. Martinez-Martinez, M. Dipalo, K. Peterson, K. Bowen, D. Dixon *J. Phys. Chem. A*, **126**, 50, 9392-9407, (2022), https://doi.org/10.1021/acs.jpca.2c06978.

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

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Collaborators: Mark Schofield, Aaron Nicholas (GW); Gian Surbella, Herman Cho , Erik Walter (Pacific Northwest Nat’l Lab); Jochen Autschbach (Univ. Buffalo); Richard Wilson (ANL)

<u>Overall research goals:</u> We aim to synthesize novel TRU bearing materials using supramolecular assembly techniques. We control the formation of U and TRU species in aqueous, high-anion media to promote restricted speciation and oxidation state profiles. Molecular species (or ‘tectons’) are then assembled through non-covalent interactions (NCIs) such as halogen and hydrogen bonding, as well as cation-oxo interactions. What follows is a hybrid experimental and computational approach to probe: 1. Electrostatic surface potentials of $[AnO_2X_4]^{n+}$ (X = Cl, Br, NCS) species as a means of rationalizing assembly motifs; 2. Factors influencing ‘yl’ oxygen participation in non-covalent interactions; 3. Factors influencing An-O_{yl} and An-ligand bond covalency; 4. Platforms for studying charge transfer mechanisms to inform catalytic activity.

Significant achievements during 2021- 2023:

1. Promotion and probing of M^{n+}-oxo interactions

We have prepared 6 UO_2^{2+}/Pb^{2+} and 12 UO_2^{2+}/Ag^+ novel heterometallic compounds in which the M-oxo interactions were probed using structural, spectroscopic, and computational methods (*Inorg. Chem.* **2021**; *Dalton Trans.* **2022**) We show that close interaction between the oxo group and the metal cation can weaken the U=O bonds as evidenced by a red-shift in the Raman active UO_2^{2+} symmetric stretch peak and a decrease in the characteristic uranyl luminescence intensity. This observation was rationalized by Natural Bond Orbital computational analysis which indicated a depopulation of U=O bonding orbitals and a population of U=O anti-bonding orbitals as a result of strong interaction with orbitals on the metal (Figure 1). The stabilization energy associated with these interactions increases as the metal approaches the uranyl-oxo. Takeaways from this study are that the effect of the Ag^+ on the U=O bond is comparatively weaker than that of the Pb^{2+}, where only the two compounds with the closest metal-oxo interaction displayed a loss in luminescence. Additionally, interaction with the Ag^+ results in smaller Raman shifts and smaller stabilization energy values at similar metal-oxo interaction distances. Quantum Theory of Atoms in Molecules analysis indicates a loss of electron density in the U=O bonds where the oxo groups interact closely with the Pb^{2+} but did not indicate a similar loss with Ag^+.

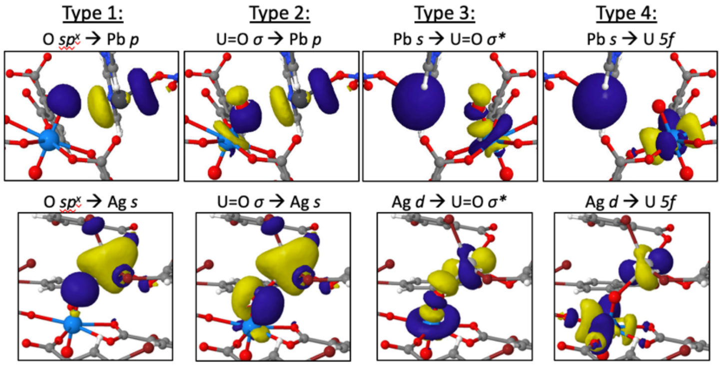

Figure 1. Isodensity renderings of representative orbitals involved in Pb– and Ag-oxo interactions.

2. Photoreactivity of viologen bearing uranyl tetrahalides

We have synthesized several novel uranyl tetrachloride-alkyl viologen compounds and observe atypical luminescence behavior (in the solid state) in that emission decreases after prolonged exposure to UV radiation (Figure 2). Preliminary studies suggest photoinduced electron transfer *from* the uranyl anion to the viologen could be responsible for the photoreactivity observed. Through collaboration with Pacific Northwest National Laboratory, we have obtained Electron Paramagnetic Resonance (EPR) spectroscopy that, in conjunction with kinetics and computation, further support the presence of radical species resulting from electron transfer.

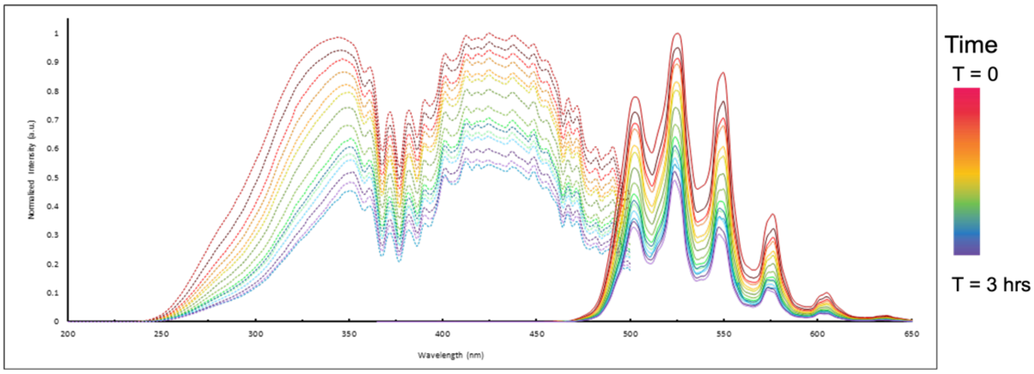

Figure 2. Time resolved loss of luminescence intensity in $(C_{12}H_{14}N_2)(UO_2Cl_4)$.

Science objectives for 2023- 2025:

1. Refine mechanism of solid state photoreactivity in viologen bearing compounds via computation, EPR and evaluation of more compounds with differing organic cations.
2. Prepare TRU analogs of uranyl-viologen compounds and probe photoreactivity in the solid state.
3. Expand catalog of M^{n+}-oxo compounds to include Cd^{2+} to probe effect of metal on U=O covalency
4. *Publications supported by this project 2021-2023*

1. Surbella, R. G., III*; Ducati, L. C.; Schofield, M. H.; McNamara, B. K.; Pellegrini, K. L.; Corbey, J. F.; Schwantes, J. M.; Autschbach, J.; Cahill, C. L.*, "*Plutonium Hybrid Materials: A Platform to Explore Assembly and Metal–Ligand Bonding*." *Inorganic Chemistry* **2022,** *61* (45), 17963-17971. http://dx.doi.org/10.1021/acs.inorgchem.2c02084.

2. Byrne, N. M.; Schofield, M. H.; Cahill, C. L.*, "*A novel symmetric pyrazine (pyz)-bridged uranyl dimer* $[UO_2Cl_3(H_2O)(Pyz)_{0.5}]_2^{2-}$*: synthesis, structure and computational analysis*." *Dalton Transactions* **2022,** *51* (29), 11013-11020. http://dx.doi.org/10.1039/D2DT01486F.

3. Brager, D. M.; Marwitz, A. C.; Cahill, C. L.*, "*A spectroscopic, structural, and computational study of Ag–oxo interactions in* $Ag+/UO_2^{2+}$ *complexes*." *Dalton Transactions* **2022,** *51* (26), 10095-10120. http://dx.doi.org/10.1039/D2DT01161A.

4. Brager, D. M.; Nicholas, A. D.; Schofield, M. H.; Cahill, C. L.*, "*Pb–Oxo Interactions in Uranyl Hybrid Materials: A Combined Experimental and Computational Analysis of Bonding and Spectroscopic Properties*." *Inorganic Chemistry* **2021,** *60* (22), 17186−17200. http://dx.doi.org/10.1021/acs.inorgchem.1c02518.

Novel Relativistic Electronic Structure Theories for Actinide-Containing Compounds

Lan Cheng, Principal Investigator

Department of Chemistry, The Johns Hopkins University, MD 21218
Graduate Student: Xuechen Zheng
Postdoc researcher: Junzi Liu

Overall research goals:

The present project is focused on the development of quantum-chemical methods for treating relativistic effects together with the application to heavy-element spectroscopy and chemistry. The work on relativistic exact two-component (X2C) approaches aims to provide accurate and efficient treatments of relativistic and spin-orbit effects. The development of relativistic coupled-cluster (CC) techniques aims to enhance the ability to treat electron correlation in heavy-atom containing molecules. The application work is focused on electronic structure of heavy-element containing molecules in collaboration with experimental and theoretical colleagues.

Significant achievements during 2021-2023:

We have developed analytic gradients for the spinor-based relativistic coupled-cluster singles doubles augmented with a non-iterative triples correction [CCSD(T)] method [1]. This enables efficient electron-correlation calculations of molecular structures with spin-orbit coupling rigorously included in the orbitals for heavy-atom-containing polyatomic molecules. We have also extended the atomic mean-field spin-orbit approach within the exact two-component theory (the X2CAMF scheme) to include the contributions from the Breit term [2]. Here we have developed an atomic Dirac-Coulomb-Breit (DCB) Hartree-Fock program with the exploitation of the spherical symmetry to efficiently evaluate the X2CAMF integrals, for which the computational time becomes negligible for molecular calculations. The DCB-based X2CAMF scheme [2] has been demonstrated to provide accurate treatments for relativistic effects on molecular properties, including those from the Breit term, while requiring only the non-relativistic molecular two-electron integrals. This new implementation and the inclusion of the Breit term greatly enhance the accuracy and the applicability of the X2CAMF scheme.

The molecular-application work has been focused on innovative use of the spin representation in computational studies of f-element containing atomic and molecular species [3-5], hereby exploiting the potential of the spinor representation in reducing the size the active spaces required in the calculations. We have demonstrated many important open-shell species containing f-elements to be single-reference systems in the spinor representation and/or using complex-valued wave functions [4]. We have carried out spinor-based relativistic CC calculations for the thermochemistry parameters for uranium-containing species and have systematically obtained accurate results. These techniques have also been employed to compute the electron affinity for the NdO molecule to high accuracy, in which both the neutral NdO molecule and the anion NdO^- have three open-shell 4f electrons [5]. The innovative use of the spinor representation also forms the basis for spinor-based relativistic CC studies of core- and valence-excited states for molecules containing f-elements.

Science objectives for 2023-2025:

One important next step in the method-development work is the development of analytic gradients for spinor-based equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) method to enable efficient electron-correlation calculations of molecular structures for electronically excited states of heavy-atom-containing molecules. This will significantly extend the ability to study electron spectroscopy for heavy-atom-containing molecules. The other near-term method-development work is to develop an efficient implementation of the core-valence separation condition for the X2CAMF-EOM-CCSD method to enable highly accurate calculations of core-level spectroscopy for molecules containing heavy atoms. After this, we plan to work on the assessment of the accuracy and efficiency for the pair natural orbital approach aiming to extend the applicability of the X2CAMF-CC methods to larger molecules.

The application work will be focused on the electronic structure and bonding properties in actinide-containing molecules using the methodologies that we have been/are developing. Ongoing efforts include spinor-based EOM-CC calculations of actinide M-edge spectroscopy to study the covalency of early actinides in collaboration with Ping Yang's group at Los Alamos National Laboratory, computational studies of the electronically excited states in the OThF molecule to facilitate the experimental study of Michael Heaven's group at Emory University, and the computational study of photoelectron spectra for $UOCl_2^-$ and $ThO_2^-(H_2O)_n$ to complement the experimental work of Kit Bowen's group at the Johns Hopkins University. Planned work also includes calculations of the infrared spectrum for PaO_2^+ in collaboration with Thomas Persinger and Richard Wilson at Argonne National Laboratory.

Publications supported by this project 2021-2023:

[1] Xuechen Zheng, Chaoqun Zhang, and Lan Cheng "Geometry Optimizations with Spinor-Based Relativistic Coupled-Cluster Theory." *J. Chem. Phys.* **2022***, 156,* 151101, doi.org/10.1063/5.0086281.

[2] Chaoqun Zhang and Lan Cheng "An Atomic Mean-Field Approach Within Exact Two-Component Theory Based on the Dirac-Coulomb-Breit Hamiltonian" *J. Phys. Chem. A* **2022***, 126,* 4537-4553, doi.org/10.1021/acs.jpca.2c02181.

[3] Lan Cheng "Relativistic Effects from Coupled-Cluster Theory", in *Comprehensive Computational Chemistry*, *in revision* (2023).

[4] Chaoqun Zhang and Lan Cheng "A Route to Chemical Accuracy for Computational Uranium Thermochemistry." *J. Chem. Theory Comput.* **2022**, *18*, 6732-6741, doi.org/10.1021/acs.jctc.2c00812.

[5] Mark C. Babin, Martin DeWitt, Jessalyn A. DeVine, David C. McDonald, Shaun G. Ard, Nicholas S Shuman, Albert A Viggiano, Lan Cheng, Daniel M. Neumark "Electronic Structure of NdO via Slow Photoelectron Velocity-Map Imaging Spectroscopy of NdO^-." *J. Chem. Phys.* **2021***, 155,* 114305, doi.org/10.1063/5.0063307.

[6] Junzi Liu, Devin A. Matthews, and Lan Cheng "Quadratic Unitary Coupled-Cluster Singles and Doubles Scheme: Efficient Implementation, Benchmark Calculations, and Formulation of an Extended Version." *J. Chem. Theory Comput.* **2022**, *18*, 2281-2291, doi.org/10.1021/acs.jctc.1c01210.

[7] Junzi Liu and Lan Cheng "Unitary Coupled-Cluster Based Self-Consistent Polarization Propagator Theory: A Quadratic Unitary Coupled-Cluster Singles and Doubles Scheme." *J. Chem. Phys.* **2021***, 155,* 174102, doi.org/10.1063/5.0062090.

Exploratory Synthesis for Reactive f-Element Separations without Solvent

Scott R. Daly, Principal Investigator; Gregory S. Girolami, Co-Principal Investigator

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Graduate Students: Nels T. Anderson, Anastasia V. Blake, Christopher M. Caroff, Taylor V. Fetrow, Rayford A. Harrison, Holly Huther, Jacob Schuely, Joseph C. Wright, Joshua Zgrabik
Undergraduate Students: Francesca D. Eckstrom, J. Peter Grabow, Zachary J. Theiler
Collaborators: Tatyana Elkin (LANL), Tori Forbes (UIowa), Andrew Gaunt (LANL), George Goff (LANL), Stosh Kozimor (LANL), Brian Scott (LANL), Bess Vlaisavljevich (South Dakota)

Overall research goals: The goal of this project is to develop lanthanide/actinide, lanthanide/lanthanide, and actinide/actinide separations by selective volatilization of f-element complexes. Our proposed separation strategy is aimed at using mechanochemistry and differences in the volatility of borohydride complexes to separate f-metals without using solvent. The principal advantage of this approach is that it avoids generating large volumes of contaminated solvent, a significant problem associated with conventional solvent extraction processes used for separating lanthanides and actinides (especially from spent nuclear fuel). A key objective of this work is to gain fundamental understanding of how new and known borohydride ligands give rise to f-element complexes with different volatility, especially with f-elements in the +3 oxidation state.

Significant achievements during 2021-2022:

1. We previously showed that mechanochemically-prepared $Ln(H_3BNMe_2BH_3)_3$ complexes with Ln = La – Nd sublime readily when heated under vacuum, but $U(H_3BNMe_2BH_3)_3$ does not. These aminodiboranate complexes have polymeric solid-state structures, and we proposed that differences in their volatility could be attributed to increased uranium-borohydride covalency that prevents depolymerization required for $U(H_3BNMe_2BH_3)_3$ to sublime. We have now identified evidence supporting this hypothesis in a class of related complexes called phosphinodiboranates. Dimeric $U_2(H_3BP^tBu_2BH_3)_6$ and $Ln_2(H_3BP^tBu_2BH_3)_6$ (Ln = La – Nd) deoligomerize to form equilibrium mixtures of dimers and monomers when dissolved, which allowed us to quantify the associated thermodynamic parameters using van't Hoff analysis. These studies revealed a small, but significant increase in ΔH of deoligomerization for the uranium complex compared to those with lanthanides ($\Delta\Delta H_{U/Ln} = 1.3(6)$ kcal·mol^{-1}) that correlated to bridging U-B distances that were 0.04 Å shorter than Ln-B distances (Fig. 1). The shorter U-B distances suggest the presence of increased metal-ligand covalency, which was corroborated by electronic structure calculations performed by the Vlaisavljevich Group at South Dakota.

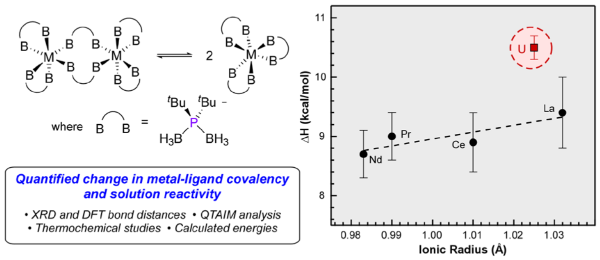

Fig. 1. Comparison of deoligomerization ΔH values for $M_2(H_3BP^tBu_2BH_3)_6$ complexes (M = U or Ln).

2. We completed numerous investigations into the synthesis, structures, and properties of chelating borohydride ligands with divalent and trivalent f-metals. We showed how $(H_3BNMe_2BH_3)^{1-}$ can form divalent complexes with Sm^{2+} and Tm^{2+}, thereby opening the door to redox facilitated lanthanide/lanthanide separations. We demonstrated the synthesis of $^{225}Ac(H_3BNMe_2BH_3)_3$ – a rare example of an Ac coordination complex – that can be sublimed using $Pr(H_3BNMe_2BH_3)_3$ as a carrier. We extended our efforts showing how f-metal phosphinodiboranate complexes can be prepared more reproducibly and isolated in higher yields using mechanochemical methods. These reactions permitted access to a wider range of $(H_3BPR_2BH_3)^{1-}$ complexes that showed how different substituents attached to phosphorus (R = ᵗBu, Ph, ⁱPr, Et, and Me) affect phosphinodiboranate metal

binding with lanthanides and uranium. We also reported new methods to prepare different aminodiboranate salts and important U(III) starting materials such as $UI_3(THF)_4$.

3. We successfully demonstrated the synthesis of uranium and lanthanide phosphinodiboranate complexes with <10 mg of metal starting material. These studies permitted the synthesis and first structural characterization of a Pu(III) borohydride complex on a separate collaborative project with Tanya Elkin, Andrew Gaunt, George Goff, and Brian Scott at Los Alamos National Laboratory. Similar studies with Np(III) are ongoing in collaboration with Tori Forbes at UIowa with theoretical support from Bess Vlaisavljevich at South Dakota.

4. We completed our first successful B K-edge X-ray absorption spectroscopy (XAS) studies of metal borohydride complexes at the Canadian Light Source in Saskatoon, Saskatchewan. These efforts are aimed at investigating the role of metal-ligand covalency on the differential volatility of f-metal borohydride complexes, but we first had to establish feasibility and work out practical aspects of sample preparation and air-free measurements with non-radioactive complexes. Moreover, the complexes used for these measurements cannot be volatile because the measurements are performed under ultra-high vacuum (10^{-9} Torr). We successfully collected B K-edge XAS data on $[Zr(H_3BR)_4]$ and $[Hf(H_3BR)_4]$ complexes where R = phenyl or benzyl, thereby setting the stage for similar studies with lanthanides, thorium, and uranium.

Science objectives for 2023-2025:

- Complete the first structural and spectroscopic characterization of Np(III) borohydride complexes to determine how actinide borohydride bonding compares to U and Pu.
- Complete our first B K-edge XAS study of actinide and lanthanide borohydride complexes with trivalent and tetravalent f-metals.
- Prepare new, sterically bulky borohydride ligands that enable isolation of monomeric and highly symmetric borohydride complexes with trivalent f-metals.

Publications supported by this project 2021-2022 (a selection)

Taylor V. Fetrow; Joshua Zgrabik; Rina Bhowmick; Francesca D. Eckstrom; George Crull; Bess Vlaisavljevich; Scott R. Daly "Quantifying the Influence of Covalent Metal-Ligand Bonding on Differing Solution Reactivity of Trivalent Uranium and Lanthanide Complexes." *Angew. Chem., Int. Ed.* **2022**, *61*, e202211145, doi.org/10.1002/anie.202211145.

Christopher M. Caroff; Brian J. Bellott; Connor I. Daly; Scott R. Daly; Andrew C. Dunbar; Justin L. Mallek; Mark A. Nesbit; Gregory S. Girolami "Sodium Aminodiboranates $Na(H_3BNR_2BH_3)$: Structural and Spectroscopic Studies of Steric and Electronic Substituent Effects." *Inorg. Chem.* **2022**, *61*, 18412-18423. doi.org/10.1021/acs.inorgchem.2c01997

Scott R. Daly; Brian J. Bellott; Daniel R. McAlister; E. Philip Horwitz; Gregory S. Girolami "$Pr(H_3BNMe_2BH_3)_3$ and $Pr(thd)_3$ as Volatile Carriers for Actinium-225. The Deposition of Actinium-Doped Praseodymium Boride Thin Films for Potential Use in Brachytherapy." *Inorg. Chem.* **2022**, *61*, 7217-7221, doi.org/10.1021/acs.inorgchem.2c00442

Taylor V. Fetrow; Scott R. Daly "Mechanochemical Synthesis and Structural Analysis of Trivalent Lanthanide and Uranium Diphenylphosphinodiboranates." *Dalton Trans.* **2021**, 50, 11472-11484, doi.org/10.1039/D1DT01932E.

Nels T. Anderson; Joseph C. Wright; Gregory S. Girolami "Synthesis and Characterization of Divalent Samarium and Thulium *N,N*-Dimethylaminodiboranates." *Inorg. Chem.* **2021**, *60*, 11164-11176. doi.org/10.1021/acs.inorgchem.1c01139.

Taylor V. Fetrow; J. Peter Grabow; Johna Leddy; Scott R. Daly "Convenient Syntheses of Trivalent Uranium Starting Materials without Uranium Metal." *Inorg. Chem.* **2021**, 60, 7593-7601, doi.org/10.1021/acs.inorgchem.1c00598.

Modulating Actinide Redox Chemistry with Metal Oxide Electrodes

Christopher Dares, Principal Investigator

Department of Chemistry and Biochemistry, Florida International University, Miami, FL
Graduate Students: Jeffrey McLachlan, Xiangyang Hou, Gabriela Ortega, Evan Jones, Rhodney Pierre, Mariel Morales
Collaborators: Stosh Kozimor (LANL), Thomas Albrecht-Schoenzart (Mines)

Overall research goals: To generate, stabilize, and study actinides in unusual oxidation states using functionalized metal oxide electrodes.

Significant achievements during 2021- 2023:

An electrochemical separation of uranium from lanthanides was achieved in pH 4.8 acetate buffer (0.1 M) using an unfunctionalized indium tin-doped oxide (ITO) electrode. The Faradaic efficiency for this process is 70 % when reducing UO_2^{2+} to UO_2 at -0.5 V vs. the saturated calomel electrode (SCE). The ITO electrodes can be used repeatedly with no observable loss in activity. Little to no deposition of UO_2 is observed at pH 1. The presence of lanthanides results in cation-cation interaction species that are manifest in cyclic voltammograms and improve the stability of penta-valent uranium. In carbonate solutions, a chemical reversible and electrochemically quasi-reversible U(VI/V) couple is observed with UO_2^{2+} when using a bare ITO electrode. This is differs from the behavior observed with glassy carbon or planar ITO or FTO electrodes which are irreversible. Photoelectrochemical oxidation of Ce(III) can be performed using metal oxide electrodes including ITO and TiO_2. Depending upon the pH and material, the tetravalent cerium generated can be soluble or form an insoluble cerium oxide layer at the surface. The identity of this layer was confirmed using X-ray photoelectron spectroscopy. This oxide layer is present in in solutions with proton concentrations in excess of 0.1 M using ITO electrodes. The adsorbed Ce(IV) reduction is shifted ~0.7 V relative to the solution Ce(IV) couple, highlighting the stabilization that surface adsorption provides. In pH 4.7 acetate buffer, 0.2 V vs. SCE is sufficient when combined with a 100 mW/cm^2 white light source to adsorb cerium oxide. The combined used of light and electrochemical input (1.2 V) increases the amount of cerium adsorbed seven-fold compared to if just electrochemical input is used. The adsorbed cerium can be released from the surface by electrochemical stripping in a fresh solution at -0.6 V. This process is unaffected by the presence of other lanthanides, and can be repeated with no observable loss in electrode function. Radiolytic stability studies of unfunctionalized and surface-modified electrodes indicate that there is little damage to the metal oxide electrode. Ionizing radiation degrades the surface modification, but, even after 100 kGy, the $Ru(bpy)_3^{2+}$ dye used for diagnostic testing is still present.

Science objectives for 2023- 2025:

For 2023-2025, the focus will be on photoelectrochemical actinide oxidation (Np and Am) and reduction (U) studies with unfunctionalized ITO and TiO_2 electrodes. The effect of proton concentration, acid, electrochemical input, and the combination of electrochemical and photochemical input will be evaluated. There will also be an effort to identify any cation-cation interaction effects when using actinide solutions containing non-redox active lanthanides. In addition to these studies with unfunctionalized electrodes, studies with polyoxometalate and polyphosphate functionalized electrodes will be developed. This will include determining their mode(s) of binding with the surface, their electrochemical properties with actinides, and the synergistic effects of using both photochemical and electrochemical inputs. We intend on demonstrating the photoelectrochemical reduction of UO_2^{2+} at metal oxide electrodes, and our efforts to photoelectrochemically generate hexavalent Np and Am. Experiments with Np have been planned out, while experiment plans with Am are in development. Comparison of the behavior of our bare (unfunctionalized) electrodes to those modified with ligands will be completed with the working hypothesis that ligand modification will diminish the electrochemical input required.

Publications supported by this project 2021-2023

There are no publications supported by this work that have been published yet. There are papers in preparation or that have been rejected (to be resubmitted) that have been supported by this work. It is expected that these will be published by the next reporting period.

Xiangyang Hou, Jeffrey R. McLachlan, Christopher J. Dares "Electrochemical Redox Behavior of Uranium at a Metal Oxide Electrode in Acidic and Alkaline Conditions", *to be submitted.*

Johan R. Gonzalez-Moya, Xiangyang Hou, Christopher J. Dares "Photochemical Oxidation of Ce(III) to Ce(IV) at TiO_2 Electrodes", *to be submitted.*

Jeffrey R. McLachlan, Xiangyang Hou, Evan T. Jones, Christopher J. Dares "Electrochemical Behavior of Cerium at a Tin-Doped Indium Oxide (ITO) Electrode in Acidic Media", *to be submitted.*

Matthew V. Sheridan, Evan T. Jones, Jeffrey R. McLachlan, Felipe Pereiro, Christopher J. Dares "Electrochromic and Catalytically Active Carbon-Free Polyoxometalate Metal Oxide Electrodes", *in review at Langmuir.*

Further Program Manager notes:

Basically, this is brief update since the last PI meeting

2 pages total including publication list, bibliography, etc.

Publication list need not be exhaustive (a few is plenty) – indicate it's a selection if it is not exhaustive

Don't mess with the fonts, the abstract book should be all matchy matchy

Labs should include one abstract per theme/talk/poster depending, which will vary on the size of the program. It should NOT be one per PI.

Computational Studies of Structure, Thermodynamic Properties, and Reactivity Across the Actinide Row

David A. Dixon, Principal Investigator

Department of Chemistry & Biochemistry, The University of Alabama, Tuscaloosa, AL
Postdoctoral Fellow: Gabriel de Melo, Staff Scientist: Monica Valiliu
Collaborators: Kirk Peterson (WSU), Richard Wilson (ANL), John Gibson (LBNL), Kit Bowen (Johns Hopkins), Karh Knope (Georgetown)

Overall research goals: The overall goal is to use the most reliable computational chemistry tools available to make predictions to help explain and then to guide experimental results leading to an improved understanding of the actinides and their chemistry. A careful treatment of all important effects including multi-reference character, scalar relativistic effects, additional electron correlation, and spin-orbit coupling is required to obtain the accuracy needed to predict bond energies (BDEs) and heats of formation, ionization energies (IEs), electron affinities (adiabatic (AEA) and vertical (VDE)), redox properties, and Brønsted and Lewis acidities and basicities; these quantities help to control actinide molecular structures and reactivity.

Significant achievements during 2021-2023: Spectroscopic and thermodynamics properties including BDEs, AEAs and IEs have been predicted for AnH for An = Ac, Th, Pa, U, Np, and Pu using the Feller-Peterson-Dixon (FPD) composite approach based on CCSD(T)/CBS and SO-CAPT2 calculations. The AEAs and VDEs for ThH^- and UH^- were benchmarked by experiments from the Bowen group. There are a large number of excited states in the neutral that are accessible by anion photoelectron spectroscopy (PES). The An-H interaction has mainly ionic character with charges of similar magnitude across the actinide series (~ 0.70 e on the An). Ac and Th are more transition metal-like whereas Pa to Pu exhibit actinide-like behavior as the f orbitals are now occupied. The addition of an electron to AnH for An = Th to Pu to form AnH^- populates the 6d orbital. Formation of the cation AnH^+ from AnH is by removal of an electron from the 7s orbital. The σ bonding orbital is characterized by the interaction of the orbital An ($6d_{z2}$) with the H (1s). The study of H as a ligand binding to an actinide provides insights into the nature of the An-H bond as well as the properties of the atomic electronic configurations.

High-level FPD calculations have been made for the UX, UX^- and UX^+ molecules for X = N, C, and B. Anion PES for X = C and N by the Bowen group provided benchmarks of the computations. Again, there are a large number of excited states in the neutral molecules that are accessible from the PES measurements. The ground state electronic configurations of UX, UX^- and UX^+ differ in the 7s orbital occupations with $7s^1$, $7s^2$, and $7s^0$ configurations respectively, so that redox in these molecules is governed by the 7s orbital. The NBO analysis reveals three U-N bonding orbitals suggesting a triple U≡N bond for all three species. The NBO calculations show that the $UC^{0/+/-}$ molecules have a bond order of 2.5. NBO calculations for UB show that the U and B are connected by two one-electron π bonds and one one-electron σ bond with substantial ionic character and a bond order of 1.5, like that in B_2^-. There are 3 three unpaired electrons in the 5f on U. In contrast, WB has less ionic character than UB with a doubly occupied π bond and a singly occupied σ bond for a bond order of ~ 1.5. The borides retain fractional bonding character even for the heavy metals.

Science objectives for 2023-2025: We are continuing to study small systems as benchmarks, to interpret experimental data, and to provide insights into the atomic structures of the actinides, in collaboration with a range of experimental groups. We are completing work on $UO^{0/+/-}$ and $UF^{0/+/-}$ as well as for $PaC^{0/+/-}$ and $PaN^{0/+/-}$. We are completing a study of the structures of M_2O_5 for the Group 5 transition metal oxides and Pa. We are completing a study of the complete hydrolysis of the actinide oxide dimers for Th_2O_4, Pa_2O_5, U_2O_6, and Np_2O_6 to understand the nature of physisorption vs. chemisorption. We are completing our studies of the role of different anions such as NO_3^- with AnO_2^+ clusters with John Gibson. We will complete a study of the interaction of two and three F^- ligands with AnO_2^{2+} building on our AnO_2^{2+} work. A goal is to compare the oxide vs. fluoride 'walls' in terms of actinide complex stability as well as on structures, for example how do two fluoride ligands compare with one oxide ligand, MO_2F_2 vs MO_3. One interesting set of molecules to be studied is the structure of the actinides with one additional F atom beyond the highest oxidation state as done for the novel structure of ThF_5. We are making an extensive study of the redox potentials of the actinides in different oxidation states in aqueous solution.

Publications supported by this project 2021-2023

1. Vasiliu, M.; Peterson, K. A.; Dixon, D. A. Bond Dissociation Energies in Heavy Element Chalcogen and Halogen Small Molecules. *J. Phys. Chem. A*, **2021**, *125*, 1892-1902. DOI: 10.1021/acs.jpca.0c11393
2. Wacker, J. N.; Nicholas, A. D.; Vasiliu, M.; Marwitz, A. C.; Bertke, J. A.; Dixon, D. A.; Knope, K. E. Impact of Noncovalent Interactions on the Structural Chemistry of Thorium(IV)-Aquo-Chloro Complexes. *Inorg. Chem,* **2021**, *60*, 6375−6390. DOI: 10.1021/acs.inorgchem.1c00099
3. Lontchi, E. M.; Vasiliu, M.; Tatina, L. M.; Caccamo, A. C.; Gomez, A. N.; Gibson, J. K.; Dixon, D. A. Hydrolysis of Small Oxo/Hydroxo Molecules Containing High Oxidation State Actinides (Th, Pa, U, Np, Pu): A Computational Study. *J. Phys. Chem. A,* **2021**, *125*, 6158-6170 07/2021. DOI: 10.1021/acs.jpca.1c04048
4. Zhu, Z.; Marshall, M.; Harris, R. M.; Bowen, K. H.; Vasiliu, M.; Dixon, D. A. The Th_2O^-, Th_2Au^- and $Th_2AuO_{1,2}^-$ Anions: Photoelectron Spectroscopic and Computational Characterization. *J. Phys. Chem. A*, **2021**, *125*, 258–271, DOI: 10.1021/acs.jpca.0c09766
5. M. Vasiliu, K. A. Peterson, M. Marshall, Z. Zhu, B. A. Tufekci, K. H. Bowen, and D. A. Dixon, "Interaction of Th with $H^{0/-/+}$. Combined Experimental and Theoretical Thermodynamic Properties" *J. Phys. Chem. A,* **2022**, *126*, 198–210. DOI: 10.1021/acs.jpca.1c07598
6. Vasiliu, M.; Marshall, M.; Zhu, Z.; Bowen, K. H.; Dixon, D. A. Molecular Properties of Thorium Hydrides: Electron Affinities and Thermochemistry. *J. Phys. Chem. A*, **2022**, *126*, 2388–2396. DOI: 10.1021/acs.jpca.2c01460
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Exploring the Fundamental Chemistry of Actinide Metal Complexes

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Overall research goals: The goal of this project is to generate new fundamental knowledge on the chemistry of the actinide metals that will enhance the scientific basis for advancing nuclear energy systems and management of nuclear waste. A key aspect of this project is providing training to graduate students who will be the next generation of actinide scientists. This proposal is focused on expanding our understanding of the chemistry exhibited by uranium and thorium in the +2 and +3 oxidation states with the intention of extending this new chemistry to the transuranium elements through collaborations with Los Alamos National Laboratory (LANL).

Significant achievements during 2021- 2023:

We have collaborated with Los Alamos National Laboratory on several projects including the synthesis of a metallocene complex of californium (1), 2.2.2-cryptand complexes of Np and Pu (5), and trimethyltriazacyclohexane (Me$_3$tach) sandwich complexes of uranium, neptunium, and plutonium triiodides, (Me$_3$tach)$_2$AnI$_3$ (12).

We have discovered an unusual Th(III) to Th(II) and Th(IV) disproportionation reaction induced by a variety of anions including methyl anion, hydride, chloride, and azide that provides a new synthetic route to a Th(II) complex (7).

Attempts to make tris(cyclopentadienyl)alkyl Th(III) complexes by reduction of Th(IV) precursors have generated rare examples of Th(III) arene complexes even though the tris(cyclopentadienyl) Th(III) and Th(II) complexes are stable to arenes.

Attempts to make new examples of square planar 6d^1 Th(III) complexes of tri-substituted aryloxide ligands, (OC$_6$H$_2$R$_2$-2,6-R'-4)$^{1-}$, have demonstrated the importance of the tert-butyl substituents in the 2 and 6 positions.

We have synthesized and crystallographically characterized the first example of a tris(cyclopentadienyl) complex of Th(III) with a mono-silyl-substituted cyclopentadienyl ligand, Cp$^{TIPS}_3$Th^{III} [Cp^{TIPS} = C$_5$H$_4$(Si^{i}Pr$_3$)]. Previously, only di-silyl-substituted complexes like Cp$''_3$Th^{III} [Cp$''$ = C$_5$H$_3$(SiMe$_3$)$_2$] were known. Cp$^{TIPS}_3$Th^{III} was reduced to generate just the second example of a crystallographically characterizable Th(II) complex, [K(2.2.2-cryptand)][Cp$^{TIPS}_3$Th^{II}].

Science objectives for 2023- 2025:

We shall continue to examine the reactivity of U(II), Th(II), and Th(III) complexes to search for new actinide reaction chemistry and new classes of compounds. We shall correlate recent electrochemical results (3) with the chemically observed Th(III) to Th(II) and Th(IV) disproportionation chemistry (7) as well as with the new syntheses of Th(III) arene complexes. We hope to use the electrochemical results as predictors for appropriate Th(IV) and Th(III) precursors to reduce chemically.

Publications supported by this project 2021-2023:

(1) Conrad A. P. Goodwin, Jing Su, Lauren M. Stevens, Frankie D. White, John D. Auxier II, Thomas E. Albrecht-Schönzart, Enrique R. Batista, Sasha F. Briscoe, Justin N. Cross, William J. Evans, Alyssa

N. Gaiser, Andrew J. Gaunt, Michael R. James, Michael T. Janicke, Tener F. Jenkins, Zachary R. Jones, Stosh A. Kozimor, Iain May, Brian L. Scott, Joseph. M. Sperling, Cory J. Windorff, Ping Yang, and Joseph W. Ziller, "Isolation and Characterization of a Californium Metallocene" *Nature* **2021**, *599*, 421–424. DOI: 10.1038/s41586-021-04027-8

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Project: Low-Valent Actinide Complexes Featuring Tunable Carborane-based Ligands

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Collaborators: Wasielewski M. R. (Northwestern University), Gagliardi L. (University of Chicago)

Overall research goals: The overall goals of this research program include synthesizing and characterizing new low-valent actinide complexes featuring sterically and electronically tunable carborane-based ligands to elucidate the role and involvement of 5f-orbitals in metal-ligand bonding interactions. We will first investigate the fundamental properties of U(III) complexes and learn how to tune the electronic, physical, redox, and magnetic properties of these complexes via ligand functionalization, then extend our studies to probe the activity of these new complexes towards small molecule activation. After establishing an understanding of how these U(III) complexes behave, we will extend our studies to carborane-based low-valent transuranic analogues (e.g., Np(III), Pu(III), Am(III)) through collaborations at LANL. Through these combined studies, we hope to advance the fundamental understanding of the molecular properties of uranium and transuranium elements.

Significant achievements during 2021- 2023:

We established the project in 2021 and got it up and running within our laboratory. Specifically, we developed protocols to synthesize uranium(III) complexes with functionalized dicarbollide (**dc**)-based ligands, which can be thought of as three-dimensional analogues to cyclopentadienyl ligands. Importantly, our synthetic route should be amenable to functionalize **dc** ligands beyond what we reported here, which will likely draw broad interest from the low-valent actinide community.

We characterized these U(III) complexes using heteronuclear NMR, UV-vis-NIR absorption, and solution-state EPR spectroscopies, cyclic voltammetry, and density functional theory (DFT). Combined, these data confirm that changing the electronic nature of the functional group on the **dc** ligand affords changes in the electronic properties of the resulting U(III) complexes.

Science objectives for 2023- 2025:

Within the context of these U(III) complexes, we will explore their reactivity towards the activation of small molecules (e.g., N_2, CO, H_2, etc.). In addition, we will leverage emerging vertex-selective functionalization methods for carboranes to synthesize **dc** derivatives with functional groups installed at C- and other B-vertices, which will allow us to further explore how the electronic influence of the functional group varies as a function of its position on the **dc** ligand. Finally, we will work with our collaborators at LANL to synthesize analogous low-valent transuranium complexes (e.g., Np, Pu, and Am) using these functionalized **dc** ligands to gain insights into the metal-ligand bonding relationships for across the series of actinides.

Publications supported by this project 2021-2023

K. O. Kirlikovali, S. L. Hanna, F. A. Son and O. K. Farha, "Back to the Basics: Developing Advanced Metal–Organic Frameworks Using Fundamental Chemistry Concepts," *ACS Nanoscience Au*, **2023**, *3*, 37–45.

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Direct air carbon dioxide separation using a uranyl superoxide catalyst

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Overall research goals: Aqueous hydroxide absorbents (strong base process) have been studied for decades and are currently being evaluated for scalability for direct air carbon capture. This technique still faces some significant hurdles as the cost of use is prohibited due to the low thermodynamic efficiency of the CO_2 capture associated with liquid-phase kinetics and high temperatures needed for regeneration. Innovation in the strong base process is needed to create advanced solvents that allow chemistry to be readily available at the gas-liquid interface and develop reactivity that enhances the kinetics of CO_2 uptake. One means to improve the kinetics of this reaction is to introduce the superoxide radical ($O_2^{-\bullet}$) because it readily converts CO_2 to CO_3^{2-} under basic conditions and demonstrated improved kinetics within the strong base absorbent. The challenges with the $O_2^{-\bullet}$ are rapid decomposition with water, uncontrolled reactivity, and 9.5 M H_2O_2 needed for $O_2^{-\bullet}$ generation. We have discovered that U(VI) catalyzes the formation of $O_2^{-\bullet}$, stabilizes the radical in aqueous and non-aqueous solutions, and selectively converts to carbonate phases in presence of CO_2. Our initial results demonstrate the possibilities of a U(VI) superoxide catalyst to drive the CO_2 capture; however, there is a critical need to fully evaluate this system to improve the strong base process.

The goal of the current proposal is to optimize the uranyl superoxide catalyst (KUPS-1) for use in direct air CO_2 separation. Our overall hypothesis is that if the superoxide radical interacts with the U(VI) cation, then its reactivity in a strong base can be controlled to enhance CO_2 separation from air. This will lead to a carbon dioxide separation with significant improvement in atom economy and feasibility within the strong base absorbent process. This hypothesis will be tested through the following specific aims: (1) Delineate the decomposition process of the KUPS-1 catalyst in basic solutions to control reactivity; (2) Determine the reaction kinetics, uptake capacities, thermodynamics, and optimized conditions to drive rapid, selective carbonation of the KUPS-1 catalyst; (3) Identify regeneration processes that leads to the formation of the superoxide radical with minimal amount of chemical input. A range of spectroscopic techniques (Electron Paramagnetic Resonance (EPR), Raman, FTIR, and UV/Vis), elemental analysis, and Density Functional Theory (DFT) calculations will be utilized to achieve the research objectives.

Significant achievements during 2023:

Electron Paramagnetic Resonance (EPR) spectroscopy was utilized to evaluate the stability of the KUPS-1 catalyst in solution. When KUPS-1 and the DMPO spin trapping agent are dissolved in water, the DMPO-superoxide adduct is formed as evidenced by the standard splitting observed within the EPR spectrum. Typical lifetimes of the DMPO-superoxide adduct is one minute, but additional time dependent studies found no change in the signal even after four hours of analysis. Superoxide dismutase (SOD) was added to the aqueous solution containing KUPS-1 and DMPO to serve as a competitive scavenger of the superoxide radical. There was also no change in the EPR spectra over several hours, indicating that the stability of the KUPS-1 complex over SOD within that time frame. Results from the aqueous phase studies indicated that U(VI) complexation of the $O_2^{-\bullet}$ results in substantial stabilization of this radical species in water compared to the free ion (half-life of 1.8

milliseconds at pH 7). When KUPS-1 was added to water without the presence of DMPO, the resulting signal corresponded to a carbon-based radical. We hypothesize that the radical is associated with a $CO_2^{\bullet}$ or $CO_3^{\bullet -}$ species, but additional modeling is necessary to confirm the assignment. This result suggests that the KUPS-1 compound is highly reactive to dissolved CO_2 in the solution.

Initial efforts to evaluate the reaction kinetics and uptake capacities are focused on the solid KUPS-1 catalyst. We have built flow-through and batch reaction chambers to measure the uptake under a range of CO_2 and relative humidity values. For the initial experiments, KUPS-1 was placed in the flow-through apparatus and exposed to pure CO_2 for two hours at relative humidity (RH) values of 15, 45, and 70%. The solid product was evaluated using Raman Spectroscopy to monitor the carbonation reaction as this technique provides detailed information about chemical structure and bonding. Elemental analysis was utilized to provide quantitative information about the carbon content in the resulting material. Given the complexity of the spectral signals, we utilized Principal Component Analysis (PCA) to compare to the features from unreacted KUPS-1, reacted samples, and the expected product ($K_4[UO_2(CO_3)_2(O_2)](H_2O)$). Three principal components were identified that corresponded to 807, 767, and 1504 cm^{-1}. This analysis also enables us to determine that KUPS-1 exposed to RH values of 15% remained essentially unreacted during this period, whereas the product at 45% and 75% RH corresponded to a different intermediate species. After aging the sample exposed to 45% RH for an additional three days, PCA analysis indicated a strong correlation with the $K_4[UO_2(CO_3)_2(O_2)](H_2O)$ product. Elemental analysis indicated that the carbon content was 1.93, 4.84, and 4.63% for RH values of 15, 45, and 75% RH, respectively. The data for 45 and 70% RH is slightly higher than the expected value (4.02%) for $K_4[(UO_2)(CO_3)_2(O_2)](H_2O)$ at suggesting that there may be additional carbonate species present in the end product.

Science objectives for 2023-2025:

Research Objective 1: a) Finalize initial EPR measurements and model the C-based radical observed in the spectra; b) Utilize the DFT methodology to develop DMPO-KUPS-1 adduct models and further evaluate stability; c) Collect EPR spectroscopy on KUPS-1 under strong base conditions in degassed solutions to evaluate alternative degradation pathways.

Research Objective 2: a) Evaluate CO_2 uptake of KUPS-1 solid under conditions relevant for direct air capture (400 ppm CO_2, 15-80% RH). b) Determine kinetic rates of CO_2 uptake by KUPS under a range of CO_2 concentrations in both solid and strong base environments. c) Explore KUPS-1 reaction pathways in the presence of CO_2 using DFT to determine possible intermediate phases and overall energies.

Research Objective 3: a) Evaluate the use of radical initiators or gamma irradiation to regenerate the KUPS-1 catalyst; b) Explore pH swings and $CaCO_3$ precipitation to capture the pure carbon product; and c) Utilize molecular DFT to evaluate U(VI)-$O_2^{-\bullet}$ versus U(VI)-CO_3^{2-} binding energies and identify possible U(VI) complexes formed during the radical initiator process.

Publications supported by this project 2021-2023

Impact of intermolecular interactions on the spectroscopic signals, energetics, and redox behavior of high valent ^{237}Np

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Overall research goals: My long-term research goal is to identify the critical chemical components that influence the bonding of actinyl cations and provide a greater understanding of the observed chemical and physical properties of these species. The objective of this work is to apply a system level approach towards the understanding of neptunyl behavior in aqueous solution and solid-state phases to fully interpret vibrational spectra, understand the energy landscape, and control redox behavior. I hypothesize that intermolecular interactions (e.g. electrostatic, H bonding) controls the resulting spectroscopic signals, thermodynamic stability, and redox behavior of Np. More specifically, I hypothesize that large effects will occur with strong oxo interactions (with neighboring charge dense cations, cooperative hydrogen bonding networks, and diamond-type actinyl-actinyl interactions). Three research objectives have been delineated to test these hypotheses: 1) identify conditions that result in perturbations of the spectral features of the neptunyl cation and evaluate the changes in the electronic structure; 2) evaluate the energetic changes as a result of intermolecular interactions with the neptunyl oxo group, and 3) explore the impact of intermolecular interactions to influence the stability of Np(V), Np(VI), and Np(VII) in aqueous solutions.

Significant achievements during 2021-2023:

Activation of bands within vibrational spectroscopy can be linked to specific interactions between the Np(V) oxo group and neighboring species. For hydrogen bonding interactions, activation of the ν_3 asymmetric stretching band of the actinyl cation were noted within the Raman spectra for solid phases when the hydrogen bonding network impacted the uranyl or neptunyl oxo groups. While these spectral modes were readily apparent for solid-state compounds, we found that hydrogen bonding did not impact the spectral features within the solution phase. However, actinyl-actinyl (or cation-cation) interactions within $(Np(V)O_2)^+$ did result in the formation of novel modes for both solids and solution phases. Additional DFT calculations were performed that enabled us to identify specific modes for both T-shaped and diamond-shaped actinyl-actinyl dimers and related to oligomeric species observed in the experimental data. Theoretical results also indicated that the energy differences between the T-shaped and diamond-shaped actinyl-actinyl units were minimal and the choice in counter ion or ligand can influence the final coordination environment.

Novel methodology was developed to link hydrogen bonding networks to thermodynamic stability of actinyl coordination compounds. Calorimetric measurements of neptunium compounds are inherently challenging because of the small quantity of materials and limited capabilities to confirm purity, so we developed a DFT approach to evaluate the enthalpy of formation (ΔH_f) for coordination complexes with various actinyl-oxo interactions. This approach was classified as the "DFT+Thermodynamics" method and was benchmarked against experimental data for the U(VI) tetrachloro system. The absolute error between the experimental and theoretical values were less than 5%, which is far superior to other reported methodologies.T his data set also enabled us to explore descriptor that could be used for machine learning algorithms and indicated that the full, 3D hydrogen bonding network (delineated through the calculation of the total hydrogen bond energies, including C-H…A interactions) is a crucial to forming a chemical rationale of the stability of these phases.

Exploration of Np(VII) chemistry revealed importance of actinyl-cation interactions to stabilize rare oxidation state. By monitoring the behavior of Np(VI) in high ionic strength solutions, we noted that pentavalent neptunium undergoes disproportionation to Np(IV) and Np(VI) when $[Li(I)] \geq 8M$. The newly formed Np(VI) engages in actinyl-cation interactions as evidenced by the calculated shifts in the solution-phase Raman spectra. Interestingly, similar studies on the behavior of Np(VII) in high ionic strength solutions showed high redox stability of heptavalent neptunium, which had previously been suggested to be relatively unstable species. Our results indicated that Np(VII) can be formed after bubbling Np(V) in 2M LiOH for 5 minutes. The Np(VII) is stable in solution for months and we hypothesized that the Li(I) cation engages with the $Np(VII)O_4^-$ species through oxo interactions, preventing reduction to $Np(VI)O_2^{2+}$.

Science objectives for 2023:

Research Objective 2: a) Collect calorimetric data on Np(VI) tetrachloride with different H-bonding systems to identify the impacts on stability; b) Utilize the DFT methodology to provide predictive information and chemical descriptors for the stability of Np(V) and Np(VI) coordination compounds.

Research Objective 3: a) Develop relationship between lithium Np(VI) oxide phases and resulting Np(VII) species (collaboration with Richard Wilson, ANL); b) Comparison of Np(VII) stability in MOH (M = Li, Na, and K).

Publications supported by this project 2021-2023

Williams, J. M., M. M. Pyrch, D.K. Unruh, H. Lightfoot, and T. Z. Forbes "Influence of heterocyclic N-donors on the structural topologies and vibrational spectroscopy of uranyl selenate phases." *Journal of Solid-State Chemistry*, **2021**, 304, 122619.

Pyrch, M. M., L. J. Augustine, J. M. Williams, S.E. Mason and T. Z. Forbes "Use of vibrational spectroscopy to identify the formation of neptunyl-neptunyl interactions: A paired Density Functional Theory and Raman spectroscopy study." *Dalton Transactions* (invited article - listed as Hot Paper), **2022**, 51, 4772-4785.

Pyrch, M. M. F., J. Bjorklund, J. M. Williams, S.E. Mason, and T. Z. Forbes "Influence of charge and H-bonding on the activation of vibrational modes in uranyl compounds: Investigations with the cobalt hexamine uranyl carbonate system." *Inorganic Chemistry*, **2022** 61, 15023-15036.

Augustine, L. J., H. Rajapaksha, T. Z. Forbes*, and S. E. Mason* "Periodic Density Functional Theory Calculations of Uranyl Tetrachloride Compounds Engaged in Uranyl-Cation and Uranyl-Hydrogen Interactions: Electronic Structure, Vibrational, and Formation Energy Analysis." *Inorganic Chemistry*, Accepted

Augustine, L. J., M.M.F. Pyrch, D. V. Kravchuk, S.E. Mason, and T. Z. Forbes. "Density Functional Theory Guided Investigation of Ligand-Induced Neptunyl-Neptunyl Interactions." *European Journal of Inorganic Chemistry*, Accepted

Augustine, L. J., J. M. Kasper, T. Z. Forbes, S. E. Mason, E. R. Batista, P. Yang. "Influencing properties of the neptunyl (V, VI) cations with electron-donating and withdrawing Groups." *Inorganic Chemistry*, Accepted

Quantum Chemical Treatment of Strongly Correlated Systems Containing Heavy Elements

Award Number: DE-SC0002183
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Overall research goals: The goal of our project is to develop innovative quantum chemical methods for studying the chemistry of systems that contain actinides and transactinides, with a particular emphasis on actinide-based single molecule magnets (SMMs). These SMMs exhibit near-degeneracy electron correlation effects and are therefore inherently multiconfigurational systems. Due to this complexity, their electronic structure cannot be accurately represented by a single Slater determinant approach, such as density functional theory (DFT). To overcome this limitation, we develop and employ new methodologies that go beyond the current Kohn-Sham DFT. Our approach involves using powerful embedding methods to model inherently multireference magnetic systems that contain heavy elements. This enables us to calculate electron correlation energy for extended systems. As part of our efforts, we have studied various actinide-containing compounds and developed methodologies aimed at treating extended systems that contain heavy elements. A balanced quantum mechanical treatment of the electronic structure of these systems requires a multiconfiguration (MC) wave function as a starting point for adding dynamic electron correlation. Through our research, we aim to expand our understanding of the chemistry of actinide-based SMMs and contribute to the development of new methods for studying complex systems containing heavy elements.

Significant achievements during 2021- 2023:

Heavy Element Containing Systems

We used multireference methods to computationally explore the electronic structure and magnetic properties of a hypothetical Cf(III) complex that is isostructural to the experimentally synthesized Dy(dbm)3(bpy) complex (where bpy = 2,2′-bipyridine and dbm = dibenzoylmethanoate). We compared our results with those of the Dy(III) analogue. Our findings suggest that the Cf(III) complex can act as a single molecule magnet (SMM) and has a higher magnetic susceptibility than other early-actinide-based (U, Np, and Pu) magnetic complexes that have been studied both experimentally and computationally. Additionally, our study suggests that the ligand field is dominant in Cf(III), which helps to increase the magnetization blocking barrier by nearly three times that of its 4f congener. Overall, our computational exploration provides insights into the magnetic properties of early actinide-based complexes and highlights the importance of considering the effects of α-decay in designing and studying actinide-based molecular magnets.

We investigated the potential of the unsaturated hexathia-18-crown-6 (UHT18C6) molecule for the extraction of Hg(II) in both HCl and HNO3 media, and compared it to the recently studied saturated hexathia-18-crown-6 (HT18C6) extractant. The default conformation of the S lone pairs in UHT18C6 is endodentate, where the pocket of the charge density is oriented toward the center of the ring according to the crystal structures, which should allow for better extraction of Hg(II) compared to the exodentate HT18C6. To delineate a plausible extraction mechanism, we conducted speciation studies. Density functional theory calculations that included relativistic effects were performed on both Hg(II)-encapsulated HT18C6 and UHT18C6 complexes to shed light on the binding strength and the nature of bonding. Our calculations offer insights into the extraction mechanism. Additionally, we performed calculations on the hypothetical divalent Cn(II) ion and found that both HT18C6 and UHT18C6 can extract Cn(II). Finally, we explored the extraction kinetics to assess whether this crown can extract the short-lived Cn(II) species in a future online experiment.

A breakthrough has been achieved by the group of Kit Bowen who reported, for the first time, the anion photoelectron spectrum of U_2^-. The lowest electron binding energy (EBE) spectral band threshold occurs at 1.0 eV, which corresponds to the electron affinity (EA) of U_2. Additionally, the vertical detachment energy of U_2- is found at EBE ~ 1.2 eV. We conducted electronic structure calculations on U_2 and U_2^- using state-of-the-art theoretical methods. The computed values of EA(U_2) and EA(U) and the difference between the computed dissociation energies of U_2 and U_2- are found to be internally consistent and consistent with the experiment. Analysis of the bonds in U2 and U_2- reveals that, while U_2 has a formal quintuple bond, U_2- has a quadruple bond, with the effective bond orders differing by only 0.5 units instead of one unit. This experimental-computational synergy offers insights into the nature of metal-metal bonding in U_2 and U_2-.

Science objectives for 2023- 2025:

We will continue developing methodologies for strongly correlated systems and apply them to study compounds containing heavy elements.

Selected publications supported by this project 2021-2023

1 Abhishek Mitra, Matthew Hermes, Laura Gagliardi “Density Matrix Embedding Using Multiconfiguration Pair-Density Functional Theory” **2023**, https://chemrxiv.org/engage/chemrxiv/article-details/6409fdf7cc600523a3ecb75c

2 D. Ray, M. Oakley, A. Sarkar, X. Bai, Xiaojing, L. Gagliardi “Theoretical Investigation of Single-Molecule Magnet Behavior in Mononuclear Dysprosium and Californium Complexes”, *Inorg. Chem.* **2023**, 62, 1649–1658 DOI: 10.1021/acs.inorgchem.2c04013

3 M. Otten, M. R. Hermes, R. Pandharkar, Y. Alexeev, S. K. Gray, and L. Gagliardi, “Localized Quantum Chemistry on Quantum Computers”, *J. Chem. Theory Comput.*, **2022**, 18, 12, 7205–7217 DOI: 10.1021/acs.jctc.2c00388

4 Ferrier, Maryline G.; Valdez, Carlos A.; Singh, Saurabh Kumar; Hok, Saphon; Ray, Debmalya; Gagliardi, Laura; Despotopulos, John D., “Unsaturated Sulfur Crown Ethers Can Extract Mercury(II) and Show Promise for Future Copernicium(II) Studies: A Combined Experimental and Computational Study”, *Inorg. Chem.*, **2022**, 61, 807-817 DOI: 10.1021/acs.inorgchem.1c01869

5 Mitra, Abhishek; Pham, Hung Q.; Pandharkar, Riddhish; Hermes, Matthew R.; Gagliardi, Laura, “Excited States of Crystalline Point Defects with Multireference Density Matrix Embedding Theory”, *J. Phys. Chem. Lett.*, **2021**, 12, 11688-11694. DOI: 10.1021/acs.jpclett.1c03229

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7 Galley, Shane S.; Pattenaude, Scott A.; Ray, Debmalya; Gaggioli, Carlo Alberto; Whitefoot, Megan A.; Qiao, Yusen; Higgins, Robert F.; Nelson, W. L.; Baumbach, Ryan; Sperling, Joseph M.; Zeller, Matthias; Collins, Tyler S.; Schelter, Eric J.; Gagliardi, Laura; Albrecht-Schonzart, Thomas E.; Bart, Suzanne C., “Using Redox-Active Ligands to Generate Actinide Ligand Radical Species”, *Inorg. Chem.*, **2021**, 60, 15242-15252. DOI: 10.1021/acs.inorgchem.1c01766

Manipulation of ligand electronic structure to control *f*-element covalency

Shane S. Galley, Principal Investigator

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Collaborators: Prof. David Shuh, University of California, Berkeley, Berkeley, CA
Dr. Stosh Kozimor, Dr. Ping Yang, Dr. Enrique Baptista, Los Alamos National Laboratory, Los Alamos, NM

Overall research goals: A high level overview

Our project includes a broad study of lanthanide and actinide elements to explore the bonding with respect to separations by exploring the rich coordination chemistry. These studies are complemented by in depth electronic structure studies. These species are fully characterized using ^{1}H NMR, infrared, electronic absorption, electrochemistry, radioanalytical techniques, and X-ray absorption spectroscopies (Shuh), and computational methods (Yang, Enrique) actinides analogues, including Np, Pu, Am, and Cf (Kozimor), are studied to understand synthetic, stability constants and bonding trends across the Periodic Table.

Significant achievements during 2021- 2023:

Our team focused on the generation of new dipicolinic acid (DPA) derivatives to understand how electronics of donating and withdrawing groups affect the bonding, oxidation state stability, and separation factors. Synthetic routes for extractants were reexplored to provide better pathways for facile synthesis Americium holdback extractions with DPA and derivatives provided trends in stability constants based on electronics of extractants. Electrochemical studies and X-ray experiments have been implemented to establish bonding and oxidation state stability.

- Synthesis/full characterization of DPA derivatives for extraction and electrochemistry studies.
- Holdback extractions studies with DPA and extractants of Am(III) in agreement the modelling. Provides validation to the stability constants obtained.
- Electrochemical studies revealed DPA derivatives with more electron donating groups stabilize Ce(IV).
- Preliminary X-ray studies on $[K(crypt)]UO_2(DPAx)_2$ systems were established to probe covalent bonding in the DPA system.
- Facile synthesis of lanthanide and Americium terpyridine complexes.
- Preliminary X-ray absorption studies showing shifts in energy in the N K-edge of lanthanide complexes due to antibonding orbital bonding with a lanthanide.

Science objectives for 2023- 2025: This project aims to address the effects of ligand electronics with respect to stability constants and bonding for separations.

Project Objective 1: Stability constant assessment with dipicolinic acid and relevant derivatives. Synthesis of DPA derivatives for extraction studies of transplutonium elements. This will provide insight into the electronic structure and lead into further studies on covalency.

Project Objective 2: Electrochemical assessments with dipicolinic acid and relevant derivatives Elucidation of the electronic structure of unusual oxidation states of lanthanides and actinides to understand new forms of chemical separations.

Project Objective 3: N-Donor ligands for probing covalency in f-elements Synthesis of terpyridine lanthanide and Americium complexes studying the metal to ligand bonding through X-ray absorption spectroscopy.

Publications supported by this project 2021-2023

1. Brian T. Arko, David Dan, Sara L. Adelman,* David B. Kimball,* Stosh A. Kozimor,* Jenifer C. Shafer,* Benjamin W. Stein. "Electron Transfer Between Neptunium and Sodium Chlorite in Acidic Chloride Media" *Inorg. Chem.*, Submitted.
2. Brian T. Arko, David Dan, Sara L. Adelman*, David B. Kimball*, Stosh A. Kozimor*, Marki M. Martinez, Tara Mastren, Daniel L. Huber, Veronika Mocko, Jung Rim, Jenifer C. Shafer *, Benjamin W. Stein, E. Miller Wylie II, "Exploring how exposure to radiolysis and harsh chemical reagents impact americium-241 extraction chromatography" *Mater. Adv.,* **2023**, *4*, 265-283.
3. Xiaobin Zhang, Sara L. Adelman, Brian T. Arko, B. Channa De Silva, Jing Su, Stosh A. Kozimor*, Veronika Mocko, Jenifer C. Shafer, Benjamin W. Stein, Georg Schreckenbach, Enrique Batista*, Ping Yang, * "Advancing 241-Am Extractant Design through the Interplay among Planarity, Preorganization and Substitution Effects" *Inorg. Chem*. **2022**, 61, 11556-11570.
4. Brian T. Arko, David Dan, Sara L. Adelman, Daniel L. Huber, David B. Kimball*, Stosh A. Kozimor*, Mila N. Lam, Veronika Mocko, Jenifer C. Shafer*, Benjamin W. Stein, and Sara L. Thiemann, "Characterizing Extraction Chromatography for Large-Scale Americium-241 processing" *Ind. Eng. Chem. Res*., **2021**, *60*, 14282-14296.
5. Nathan P. Bessen, Ivan A. Popov, Colt R. Heathman, Travis S. Grimes, Peter R. Zalupski, Liane M. Moreau, Kurt F. Smith, Corwin H. Booth, Rebecca J. Abergel, Enrique Batista, Ping Yang, and Jenifer C. Shafer*, "Complexation of Lanthanides and Heavy Actinides with Aqueous Sulfur-Donating Ligands" *Inorg. Chem*., **2021**, 60, 6125-6134

Studying *f*-Electron Contributions in Thorium- and Uranium-Containing Molecules

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Stephen Cooke, Co-Principal Investigator

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Graduate Students: Joshua Isert
Collaborators: Kirk Peterson (Washington State University)

Overall research goals: We will study small molecules and complexes containing U or Th with a particular interest in quantifying *f*-electron contributions to chemical bonding using advanced techniques in pure rotational spectroscopy in the lower microwave regions of the electromagnetic spectrum. Target compounds will be produced using laser ablation of U or Th rods in the presence of a variety of precursor gases. Once formed the target compounds will undergo cooling through adiabatic expansion and will then be interrogated with microwaves with frequencies between 2 GHz and 26 GHz. Line widths as narrow as 10 kHz ($3.3\text{x}10^{-7}$ cm^{-1}) can be achieved. The resolution of the technique is such that fine and hyperfine splittings due to various couplings of unpaired electrons and/or nuclear spins with end-over-end molecular rotation will be measurable. Resulting fine and hyperfine parameters provide both direct and computationally tractable information on the bonding within the molecule and its potential energy surface.

Significant achievements during 2021- 2023:

A new laser ablation nozzle has been constructed. We began this process using carbonyl sulfide, OCS, a well-known calibrant in microwave spectroscopy, and adjusting the laser pulse such that it removes most of the OCS J = 1-0 signal. Following this, testing is underway using a silver rod with chlorine gas as a precursor. The reason for this is twofold. Firstly, silver (I) chloride forms easily in a laser ablation nozzle and is known to have very strong rotational spectra. Hence, silver metal with chlorine gas is a good choice for tuning up a laser ablation nozzle assembly and ensuring timings, i.e. gas pulse, laser pulse, microwave pulse, are all optimized. Secondly, uranium (I) chloride or thorium (I) chloride are to be our first target compounds and so we simply have to switch out the silver rod for either a uranium or thorium rod.

In February of 2023 the Co-PI's laser ablation equipped, chirped pulse Fourier transform microwave spectrometer was relocated from Wesleyan University to the lead PI's lab at Missouri University of Science and Technology. This spectrometer was used to study the first ever recorded pure rotational spectra of an actinide-containing compound, namely thorium (II) oxide. Transitions, yet unidentified, but requiring the laser ablation of a uranium rod have also been recorded on this instrument. The instrument is currently being "plumbed" into its new location.

Lastly, over the winter break, the vacuum chamber for the new chirped pulse Fourier transform microwave spectrometer was completed and delivered. This chamber is now being incorporated into a vacuum system and the electronics added for completion of a new, hopefully more sensitive, instrument that will be used in this research.

Science objectives for 2023- 2025:

The most pressing issue for the beginning of this next stage in the project is, of course, bringing all of the needed spectrometers online, or back online. It is our objective to do this quickly. We then hope to begin recording microwave spectra for the uranium monohalides and thorium monohalides. We will then begin experiments with other precursor gases.

Measuring Covalency in An-N and An-C Bonds: A Combined Synthetic and Spectroscopic Investigation

Trevor W. Hayton, Principal Investigator

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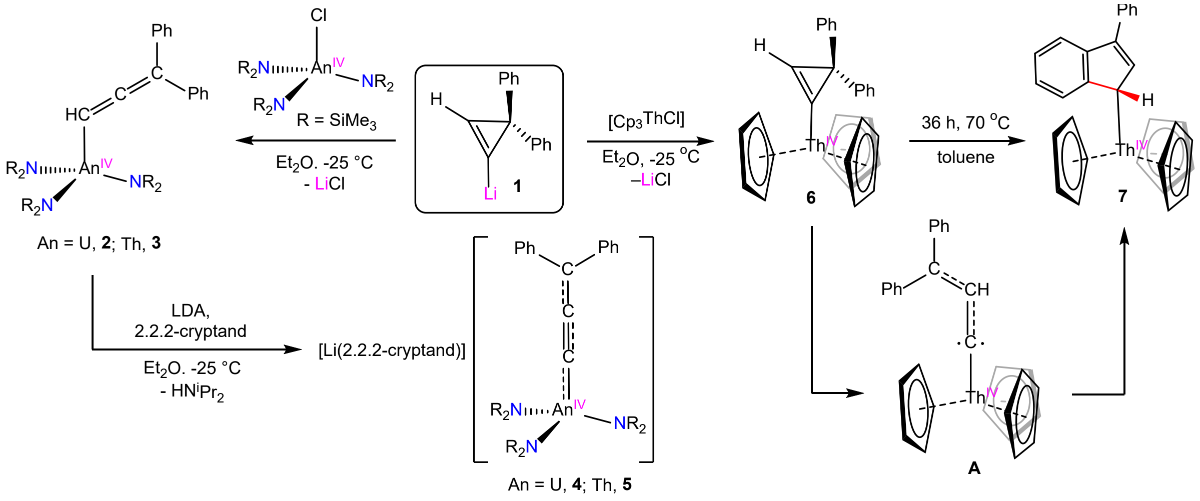
Undergraduate students: Megan Schuerlein
Collaborators: Jochen Autschbach and Xiaojuan Yu, Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY 14260; Herman Cho, Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, USA; Andrew J. Gaunt and Aaron M. Tondreau, Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA; Wayne L. Lukens, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, 94720, USA.

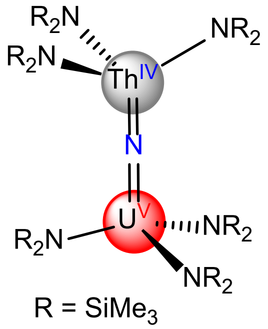
Overall research goals: The study of actinide-ligand covalency is at the heart of efforts to create of a robust, safe, and sustainable nuclear fuel cycle. We seek to interrogate actinide-ligand covalency using a multi-pronged approach that combines synthesis, spectroscopy, and computation. In particular, we propose to generate actinide complexes featuring An-C, An=C, and An≡C bonds, which we analyze using solution and solid-state ^{13}C NMR spectroscopy and DFT calculations. These data allow us to quantify the degree of 5f and 6d orbital involvement within these bonds with an unprecedented degree of confidence.

Significant achievements during 2021-2023: During the 2021-2023 reporting period, we dedicated considerable effort toward the synthesis of An-C multiple bonds, and in 2021, we reported the synthesis of the first actinide allenylidene complexes, $[\{(NR_2)_3\}An(CCCPh_2)]^-$ (An = U, **4**; Th, **5**; R = $SiMe_3$), which represent the first non-heteroatom-supported carbene complexes of the actinides. Complexes **4** and **5** were synthesized by deprotonation of the actinide allenyl complexes, $[\{(NR_2)_3\}An(CH{=}C{=}CPh_2)]$ (An = U, **2**; Th, **3**), which themselves were made from the ring-opening reaction between 1-lithium-3,3-diphenylcyclopropene (**1**) and $[AnCl(NR_2)_3]$. A combined DFT and ^{13}C NMR spectroscopic analysis reveals considerable π-character in the An-C interaction. Additionally, the C_α chemical shift in complex **5** exhibits SOC-induced deshielding due to 5f orbital participation in its Th=C bond, as expected given the large 5f-2s overlap in this interaction. This work was performed in collaboration with Jochen Autschbach at U. Buffalo.



Building on this work, we attempted to synthesize a Cp-supported thorium allenyl complex by reaction of $[Cp_3ThCl]$ with 1-lithium-3,3-diphenylcyclopropene (**1**). Surprisingly, this reaction did not result in formation of an allenyl, but instead resulted in the formation of [Cp$_3$Th(3,3-diphenylcyclopropenyl)] (**6**). Thermolysis of **6**, in an attempt to make the allenyl complex, resulted in isomerization to the ring-opened product, [Cp$_3$Th(3-phenyl-1*H*-inden-1-yl)] (**7**) *via* a transient triplet carbene intermediate **A**. This transformation represents a new mode of reactivity of 3,3-diphenylcyclopropene with the actinides, improving our ability to use this reagent as a carbene source.

Finally, we synthesized the first heterobimetallic actinide nitride, $[(NR_2)_3U^{V}(\mu\text{-}N)Th^{IV}(NR_2)_3]$ (**8**), which we characterized by EPR spectroscopy, SQUID magnetometry, and NIR-visible spectroscopy. A crystal field analysis of **8** reveals that the ground state is predominantly $m_J = 5/2$ with a small admixture of the $m_J = -1/2$ state. Additionally, the highest energy 5f excited state is primarily 5f-N$_{\text{nitride}}$ σ-antibonding in character. Both findings are in accord with the strong σ and π bonding expected for the nitride ligand. This work was performed in collaboration with Wayne Lukens at LBNL.



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Science objectives for 2023-2025: For the 2023-2025 reporting period, we will continue to pursue the synthesis and characterization of actinide carbene and carbyne complexes. In particular, we have identified a number of non-standard carbene and carbyne sources that could provide access to complexes with formal An=C and An≡C bonds. Among our proposed synthetic targets are butenylidenes, cyclopropylidenes, and cyclobutylidenes, which, on account of their unique electronic and geometric properties, should exhibit greater thermodynamic and kinetic stability than prototypical Schrock-type alkylidenes. This increased stability will allow us to study their An=C and An≡C bonds in unprecedented detail, using ^{13}C NMR spectroscopy and DFT calculations, among other techniques. This work is being done in collaboration with Jochen Autschbach at U. Buffalo.

Publications supported by this project 2021-2023:

1. Staun, S. L.; Kent, G. T.; Gomez-Torres, A.; Wu, G.; Fortier, S. Hayton, T. W.* Reductive Coupling of Xylyl Isocyanide Mediated by Low-Valent Uranium. *Organometallics* **2021**, *40*, 2934–2938. DOI: 10.1021/acs.organomet.1c00365

2. Kent, G. T.; Yu X.; Pauly, C.; Wu G.; Autschbach J.;* Hayton T. W.* Synthesis of Parent Acetylide and Dicarbide Complexes of Thorium and Uranium and an Examination of Their Electronic Structures. *Inorg. Chem.* **2021**, *60*, 15413–15420. DOI: 10.1021/acs.inorgchem.1c02064

3. Kent, G. T.; Yu X.; Wu G.; Autschbach J.;* Hayton T. W.* Synthesis and electronic structure analysis of the actinide allenylidenes, $[\{(NR_2)_3\}An(CCCPh_2)]^-$ (An = U, Th; R = SiMe$_3$). *Chem. Sci.*, **2021**, *12*, 14383-14388. DOI: 10.1039/D1SC04666G

4. Staun, S. L.; Wu, G.; Lukens, W. W.;* Hayton, T. W.* Synthesis of a heterobimetallic actinide nitride and an analysis of its bonding. *Chem. Sci.*, **2021**, *12*, 15519-15527. DOI: 10.1039/D1SC05072A

5. Kent, G. T.; Yu X.; Wu G.; Autschbach J.;* Hayton T. W.* Ring-opening of a Thorium Cyclopropenyl Complex Generates a Transient Thorium-bound Carbene. *Chem. Commun.* **2022**, *58*, 6805-6808. DOI: 10.1039/D2CC01780F

6. Keener, M.; Mattejat, M.; Zheng, S.-L.; Wu, G.; Hayton, T. W.; Ménard, G.* Selective electrochemical capture and release of uranyl from aqueous alkali, lanthanide, and actinide mixtures using redox-switchable carboranes. *Chem. Sci.*, **2022**, *13*, 3369-3374. DOI: 10.1039/D1SC07070C

7. Ordoñez O.; Yu X.; Wu G.; Autschbach J.;* Hayton T. W.* Assessing the 4f Orbital Participation in the Ln–C Bonds of $[Li(THF)_4][Ln(C_6Cl_5)_4]$ (Ln = La, Ce). *Inorg. Chem.*, **2022**, *61*, 15138–15143. DOI: 10.1021/acs.inorgchem.2c02304

Spectroscopic investigations of actinide bonding and electronic structure

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Graduate Students; Thomas D. Persinger, Arianna Rodriguez
Collaborators: Timothy C. Steimle (Arizona State University), Anh T. Le (Georgia Institute of Technology).

Overall research goals: The role of the 5f electrons in actinide bond formation is one of the central issues of actinide chemistry. This question is being investigated using a combination of strategic experimental measurements and state-of-the-art theoretical calculations. The primary objective for this program is to obtain high-resolution spectroscopic data for prototypical actinide molecules in the gas phase. In many cases the transitions being observed can be uniquely assigned, without the need for guidance from theoretical calculations. Due to this independence, the results define rigorous benchmarks for the testing and development of relativistic quantum chemistry models of actinide bonding.

Significant achievements during 2021- 2023:

(i) Electronic Configuration Assignments for UO from Electric Dipole Moment Measurements

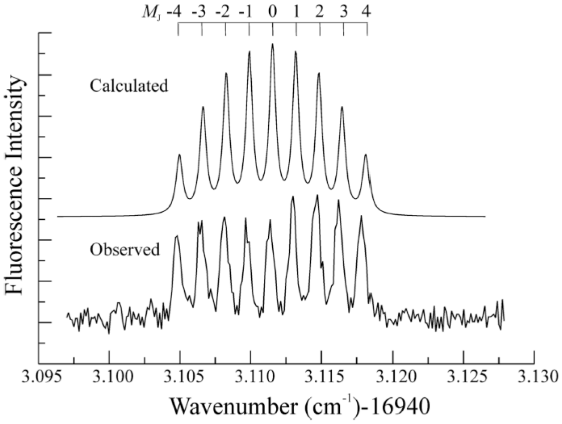

Figure 1. Stark splitting of the [16940]5-X(1)4 R(4) line. This trace was recorded with an applied electric field of 2551 V cm^{-1}.

Diatomic UO has more than 48 bound states within 10000 cm^{-1} of the ground state. This electronic state congestion has been attributed to interleaved states from the electronic configurations $U^{2+}(5f^37s)O^{2-}$ and $U^{2+}(5f^27s^2)O^{2-}$. Ligand field theory predicts that each electronic configuration will exhibit states with distinguishable, characteristic vibrational and rotational constants. However, vibronic state mixing modifies the observed vibration-rotation constants, leading to uncertainty in the configurational assignments. The permanent electric dipole moment (μ_e) of an electronic state should also manifest a value that is characteristic of the parent electronic configuration. μ_e and other electrostatic and magnetostatic properties should be less influenced by vibronic state mixing, providing more robust indicators for configurational assignments. As a test of this reasoning, we measured the permanent dipole moment of the (2)4 state of UO, which lies just 294 cm^{-1} above the ground state, and is known to be influenced by vibronic mixing. The dipole was determined from Stark level splittings that were measured in the presence of an applied electric field, as shown in Fig. 1. The dipole moment obtained for the (2)4 state (2.154 D) was considerably smaller than the value previously determined for the X(1)4 ground state (3.363 D). The smaller dipole moment of the (2)4 state is a direct consequence of the transfer of a 4f electron to the more polarizable 7s orbital. While the vibronic constants for the X(1)4 and (2)4 states are closely similar, the dipole moment measurements clearly demonstrate that the X(1)4 and (2)4 states are derived from the $U^{2+}(5f^37s^1)O^{2-}$and $U^{2+}(5f^27s^2)O^{2-}$ configurations, respectively.

(ii) Electronic spectroscopy of OThF

One objective of the present program is to extend our gas-phase spectroscopic techniques to polyatomic actinide species. We had previously found that we could not achieve rotational resolution in a spectroscopic study of UO_2, and identified the high density of electronically excited states as a possible limitation on the resolution. A study of OThF was initiated as this molecule has a lower electronic complexity. The ground state has only one unpaired electron in a metal-centered valence orbital (formally $O^{2-}Th^{3+}(7s^1)F^-$), and the visible-range electronic spectrum is dominated by transitions that promote the 7s electron. Prominent vibronic bands were observed in the range 27700-28900 cm^{-1}. An additional intense band was observed at 22430 cm^{-1}. Electronic structure calculations (time-dependent DFT) indicate that OThF is a bent molecule in the ground and low-lying excited states, with ground state vibrational frequencies of 861 (O-Th stretch), 532 (Th-F stretch) and 127 (bend) cm^{-1}. Dispersed fluorescence spectra obtained using 22430 cm^{-1} excitation indicate a Th-F stretch fundamental of 546 cm^{-1} and a bending fundamental of 136 cm^{-1}. The Th-O stretch mode does not appear to be active. Rotational resolution has not yet been achieved in these measurements, but rotational band contour fitting gives results that are consistent with the predicted bent structure for both the ground and excited states.

(iii) Spectroscopic investigations of YbOH/D and $YbOCH_3$

Studies of YbOH/D and $YbOCH_3$, prototypical polyatomic lanthanide species, were carried to assist research groups who are attempting to laser cool these molecules and to shed light on problems with the bond energy determination for YbOH that were discussed by John Gibson (PCCP **23**, 11314 (2021)). YbOH and $YbOCH_3$ have been recognized as being of potential value for spectroscopic experiments that explore charge-parity and time reversal symmetry violation effects. These measurements require high precision, which, in turn, necessitates that the molecules be manipulated at ultra-cold temperatures. Both YbOH and $YbOCH_3$ have A-X electronic transitions that appear suitable for laser cooling, but the available spectroscopic data was not sufficient to assign many of the vibronic bands, or determine the extent to which population leaks may compromise the optical cooling processes. In our recent study we have recorded spectra for the A-X transition of jet-cooled YbOD to facilitate vibronic assignment. Spectra for the B-X transition of YbOH were recorded, establishing the origin band at 20473.8 cm^{-1}. Two-photon ionization spectroscopy yielded accurate ionization energies of IE(YbOH)=45788(10) and IE($YbOCH_3$)= 45283(10) cm^{-1}. The IE for YbOH is relevant to problems encountered in previous attempts to determine the bond dissociation energy of $YbOH^+$.

Science objectives for 2023- 2025:

We will carry out high-resolution studies of the molecules $U^{17}O$, UF, UP, ThP, OThF, ThC_2 and NUN These measurements will yield physical properties (dipole moments, g-factors, hyperfine coupling constants and bond lengths) that report on the bonding and atomic orbital composition of the ground and low energy valence states.

Publications supported by this project 2021-2023

Jiande Han, Anh T. Le, Timothy C. Steimle and Michael C. Heaven, "Electronic Configuration Assignments for UO from Electric Dipole Moment Measurements" *J. Phys. Chem. Lett,* **2022**, 13, 10799, 10.1021/acs.jpclett.2c03150

Thomas D. Persinger, Jiande Han, Anh T. Le, Timothy C. Steimle and Michael C. Heaven, "Electronic spectroscopy and ionization potentials for YbOH and $YbOCH_3$" *Phys. Rev. A*, **2023**, 107, 032810, 10.1103/PhysRevA.107.032810

Understanding the Chemical Complexity of Multi-Component Systems: Uranium Polyoxometalates as Nanosorbents

Amy E. Hixon, Principal Investigator

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Collaborators: Jan Ilavsky (APS), Sara Isbill (ORNL), Allen G. Oliver and Peter C. Burns (UND)

Overall research goals:

The overarching objective of this project is to develop a molecular-scale understanding of chemical interactions of the transuranic elements (TRU) with uranyl-based polyoxometalate nanoclusters (UPOMs). The specific goals that support this overarching objective are to:

- quantify TRU interactions with UPOMs as a function of TRU, carbonate, and UPOM concentration, pH, and temperature;
- examine the molecular-scale bonding environment of TRU-UPOM complexes; and
- develop a rate expression capable of describing the sorption and reduction of TRU by UPOMs.

The published literature suggests several potential interactions can occur in TRU-UPOM systems: (i) encapsulation of TRU and coordination with the internal '-yl' oxygens of the UPOM, (ii) coordination of TRU with the external '-yl' oxygens of the UPOM, and (iii) coordination of TRU with the bridging ligands (e.g., peroxo, hydroxo, oxalate) of the UPOM. The latter two may induce aggregation of the UPOMs. The concept of encapsulation is demonstrated by the X-ray diffraction structure of crystallized U_{20}, which reveals a Na^+ cation under each pentagonal face (Sigmon et al., 2009). Computational modeling shows that, while the negative charge of U_{20} is spread among all the oxygen atoms, the internal '-yl' oxygens host the most negative charge (Miro and Bo, 2012). This negative charge is reduced through the complexation of the templating sodium ions in the interior of the UPOM. Furthermore, Nyman et al. (2011) shows that cesium can exit through the pentagonal window of U_{28} in the aqueous phase, suggesting that the TRU elements, which are smaller than cesium, may be capable of entering a UPOM through these windows in an exchange reaction.

Significant achievements during 2021- 2023:

We completed our studies investigating the interactions between Np^V and the uranyl peroxide nanocluster $U_{60}Ox_{30}$ using ultra-small and small angle X-ray scattering ((U)SAXS), dynamic light scattering (DLS), and X-ray diffraction. Two different interaction mechanisms were observed depending upon neptunium concentration. When the neptunium concentration was less than or equal to 10 mM, neptunium induced $U_{60}Ox_{30}$ aggregation, and the size of the aggregates increased with increasing neptunium concentration above a critical salt concentration of 1.5 mM. When the neptunium concentration was greater than or equal to 15 mM, neptunium preferentially coordinated with oxalate and crystallized as a neptunyl oxalate hexahydrate ($(NpO_2)_2C_2O_4{\cdot}6H_2O(cr)$). Smaller uranyl peroxide species that initially form in solution ultimately precipitate as studtite ($(UO_2)(O_2)(H_2O)_2{\cdot}2H_2O(s)$).

We also completed our studied investigating interactions between Pu^{VI} and the uranyl peroxide nanoclusters U_{60} and $U_{60}Ox_{30}$ using UV-vis-NIR spectroscopy, (U)SAXS, and DLS. Plutonium added as > 95% Pu(VI) reduced to Pu(V) in the presence of U_{60} and to a mixture of Pu(IV) and Pu(V) in the presence of $U_{60}Ox_{30}$ over the course of two weeks. Pu(V) subsequently promoted U_{60} aggregation in the form of blackberries (i.e., hollow aggregates of hollow macro-ions) and U_{60} macro-aggregation in the form of newly identified U_{60} blackberry brambles (i.e., haollow macro-aggregates of hollow aggregates). In the $U_{60}Ox_{30}$ system, Pu(IV/V) promoted aggregation in the form of large mass fractals. U_{60} blackberries and $U_{60}Ox_{30}$ aggregates became more compact with increasing plutonium concentration, suggesting encapsulation of plutonium within U_{60} and $U_{60}Ox_{30}$.

Finally, we have continued our work investigating Pu^{VI}-oxalate binary systems. We used Raman and absorption spectroscopies to probe solutions as a function of pH (1, 3, >6) and metal-to-ligand ratio (M/L; 10:1 – 1:10). Peak changes in the UV-vis-NIR spectra were associated with the formation of multiple Pu(VI)-oxalate complexes with increasing M/L, such as $PuO_2(C_2O_4)(aq)$ and $PuO_2(C_2O_4)_2^{2}$, $PuO_2(C_2O_4)_3^{4-}$, or $(PuO_2)_2(C_2O_4)_3^{2-}$. These observations were used to determine the formation constant for $PuO_2(C_2O_4)(aq)$ ($\log K° = 4.64 \pm 0.06$). In related work, we determined the first crystal structures for $Pu^{IV}(C_2O_4)_2{\cdot}6H_2O(s)$ and $Th^{IV}(C_2O_4)_2\ 6H_2O(s)$. This data, along with new characterization of $U^{IV}(C_2O_4)_2{\cdot}6H_2O(s)$ and $Np^{IV}(C_2O_4)_2{\cdot}6H_2O(s)$, resulted in the full determination of the structures and resolution of the disorder. Specifically, we identified the coordination of two water molecules with each metal center, which necessitates a change in oxalate coordination mode from axial to equatorial that has not been reported in the literature.

Science objectives for 2023- 2025:

This project has reached the end of its funding cycle.

Select publications supported by this project 2021-2023

Kyson R. Smith, Jan Ilavsky, Amy E. Hixon, "Crystallization of a Neptunyl Oxalate Hydrate from Solutions Containing Np^{V} and the Uranyl Peroxide Nanocluster $U_{60}Ox_{30}$" *Chem – Eur J.*, **2023**, doi.org/10.1002/chem.202203814.

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Ginger E. Sigmon, Jie Ling, Daniel K. Unruh, Laura Moore-Shay, Matthew Ward, Brittany Weaver, Peter C. Burns, "Uranyl-Peroxide Interactions Favor Nanocluster Self-Assembly" *J. Am. Chem. Soc.* **2009**, *131*, 16648-16649.

Pere Miro, Carles Bo, "Uranyl-Peroxide Nanocapsules: Electronic Structure and Cation Complexation in $[(UO_2)_{20}(\mu\text{-}O_2)_{30}]^{20-}$" *Inorg. Chem.* **2012**, *51*, 3840-3845.

May Nyman, Mark A. Rodriguez, Todd M. Alam, "The U_{28} Nanosphere: What's Inside?" *Eur. J. Inorg. Chem.* **2011**, *2011*, 2197-2205.

Tetravalent Actinide Speciation: Template Directed Assembly, Stabilization, and Reactivity

Karah E. Knope, Principal Investigator

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Overall research goals: The goals of this work are to broadly understand the effects of inner- and outer- coordination sphere interactions on actinide speciation and reactivity. Our experimental efforts have focused on the molecular level structural characterization of Ce, Th, U, and Pu solution and solid-state phases in an effort to elucidate how ligand-, counter-ion, and metal-ion identity impact actinide complex formation, stabilization, crystallization, and reactivity.

Significant achievements during 2021- 2023:

Previous work out of our laboratory examined the structural chemistry of tetravalent actinides (Th, U, and Pu) in chloride ligand systems. We showed that outer coordination sphere interactions (e.g. H-bonding interactions) could be used to isolate a series of mononuclear Th complexes that ranged from chloride -deficient $[Th(H_2O)_7Cl_2]^{2+}$ to chloride-rich $[Th(H_2O)_2Cl_6]^{2-}$ species. Related aquo-chloro units were isolated for U; however, U showed a greater tendency to form the UCl_6^{2-} dianionic unit. Furthermore, Pu(IV) exclusively formed $PuCl_6^{2-}$ irrespective of the N-H donor present in the reaction solution. Building on this work, we have sought to further understand An(IV) speciation in other monoanionic ligand systems (e.g. Br^- and NO_3^-). From acidic, aqueous bromide solution, we isolated the previously reported $[Th(H_2O)_{10}]Br_4$ structural unit, but upon pyridinium inclusion into the reaction solution observed $Th(H_2O)_4Br_4$. To the best of our knowledge, this is a rare example of an An(IV) complex isolated from aqueous solution that exhibits Th-Br binding; this work highlights the utility of noncovalent interactions in isolating elusive An structural units. From nitrate solutions, we have also isolated and characterized a series of fifteen Th-nitrate complexes using a range of -NH hydrogen bond donors, Unlike the chloride system, we observed much more limited speciation, with only two distinct structural units precipitating from solution. Despite nitrate also forming relatively weak An-L complexes which should permit the competition of H_2O and nitrate, this limited structural chemistry is likely attributed to the bidentate coordination mode of the ion. Interestingly, these results taken together with previous literature reports show that introduction of cations (i.e. outer coordination sphere interactions) drives the formation of anionic units including the penta- and hexa-nitrato units. The energetics of nitrate complexation were also examined computationally in collaboration with David Dixon.

By adjusting reaction conditions we have shown that we can synthesize polynuclear species for Th and U. In an effort to extend this work to Pu, we examined Ce/HCl solutions in the presence of various counterions. We previously reported the isolation of a Ce_{38} cluster (using K^+) that showed a single-crystal-to-single-crystal transformation, wherein the solid-state reactivity of the cluster surface could be observed. In an effort to further explore the stabilization of this and related cluster-types by outer sphere interactions, we examined reaction of Ce/HCl in the presence of HPy^+. Interestingly, HPy^+ yields a Ce_{52}-oxo cluster, which represents the largest chloride capped cluster reported to date. However, efforts to extend this work to Pu have thus far been unsuccessful, likely due to the low yield which we attribute to Ce redox chemistry, lability of the surface ligands, and sensitivity of crystallization to the reaction conditions. With this in mind, we have begun to pivot away from acidic, aqueous solutions towards both solvent and ligand systems that afford a greater degree of control over Ce and An cluster formation and precipitation.

Science objectives for 2023- 2025:

As noted previously, our group has started examining An cluster formation in solvent- and ligand-systems that afford a greater degree of control over hydrolysis and condensation. We have preliminary data that suggests that betadiketonates together with solvent identity are useful handles for controlling cluster nuclearity and precipitation. Moreover, these reactions are high yielding and amenable to solution- and solid-state interrogation. One of our primary objectives for 2023-2025 is to translate this work to Th-Pu.

Notably absent from much of the work that we have reported thus far is Np(IV). Over the past year, we have worked with our RSO and Georgetown University to equip a lab for Np synthetic chemistry. Our lab is expected to be operational in August 2023, at which point we will examine the effects of outer sphere interaction on Np(IV) speciation.

Publications supported by this project 2021-2023

Anamar Blanes-Diaz A; Orlando Stewart Jr; Monica Vasiliu; Aaron D. Nicholas; Aphra V. Murray, Madeline C. Shore; David A. Dixon; Karah E. Knope.* Th(IV) Bromide Complexes: Homoleptic Aqua Ion and a Novel $Th(H_2O)_4Br_4$ Structural Unit., *Crystal Growth & Design,* **2022.**

Jennifer N. Wacker, Alexander S. Ditter, Samantha K. Cary, Aphra V. Murray, Jeffery Bertke, GT Seidler, Stosh A. Kozimor, Karah E. Knope**.*** Reactivity of a Chloride Decorated, Mixed Valent $Ce^{III/IV}{}_{38}$-Oxo Cluster. *Inorganic Chemistry.* **2022**, 61(1), 193-205. DOI: 10.1021/acs.inorgchem.1c02705.

Jennifer Wacker; Aaron D. Nicholas; Monica Vasiliu; Alexander Marwitz; Jeffery Bertke; David A. Dixon; Karah E. Knope**.*** Impact of Noncovalent Interactions on the Structural Chemistry of Thorium(IV)–Aquo–Chloro Complexes. *Inorganic Chemistry*, **2021**, 60, 9, 6375-6390. DOI: 10.1021/acs.inorgchem.1c00099.

Aphra V. Murray, Jennifer N. Wacker, Jeffery Bertke, Karah E. Knope.* Synthesis, Characterization, and Solid-State Structural Chemistry of Uranium(IV) Aliphatic Dicarboxylates. *Crystal Growth & Design*, **2021**, 21, 4, 2429-2444. DOI: 10.1021/acs.cgd.1c00042.

Collaborative publications citing this award; corresponding authors are noted:

Jones Z; Livshits M; White F; Dalodiere E; Kerlin (Ferrier), M; Lilley L; Knope KE; Kozimor SA;* Mocko V; Stein B; Wacker JN; Woen DH. Advancing Understanding of Actinide(III) (Ac, Am, Cm) Aqueous Complexation Chemistry. *Chemical Science*, **2021**, 12, 5638-5654. DOI: 10.1039/D1SC00233C.

M. MacInnes, Z. Jones, N. Anderson,* E. Batista,* IM DiMucci, C. Eiroa-Lledo, KE Knope, M. Livshits, SA Kozimor,* V Mocko, KA Pace, FR Rocha, B. Stein,* JN Wacker. Using Molten Salts to Probe Outer-Coordination Sphere Effects on Lanthanide(III)/(II) Electron Transfer Reactions. *Dalton Transactions* **2021**, 50, 15696-15710. DOI: 10.1039/D1DT02708E.

Carter KP, Shield KM, Smith KF, Jones ZR, Wacker JN, Arnedo-Sanchez L, Mattox TM, Moreau LM, Knope KE, Kozimor SA*, Booth CH***,** Abergel RJ***.** Structural and spectroscopic characterization of an einsteinium complex. *Nature* **2021,** *590* (7844), 85-88. DOI: 10.1038/s41586-020-03179-3.

Molecular Approaches to the Electronic Structure of Actinide Materials

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Overall research goals: The understanding and control of the electronic structure in actinide materials is essential to the US-DOE mission. Key materials for national security and energy production such as plutonium metal and plutonium nitride remain challenging from an electronic structure perspective. This proposal develops a systematic molecular and spectroscopic approach to understanding the electronic structure and properties of plutonium and other mid-actinide materials. This research program pairs synthetic actinide (Th, U, Np, and Pu) studies with synchrotron spectroscopies and physical property studies to break down the challenge of understanding the electronic structure of f-element systems. Our efforts to-date have focused on the synthesis and analysis of systems governed by one of three phenomena: magnetic super-exchange (i.e. exchange coupled systems), multi-configurational electronic structures (ground state degeneracy including hybridization with ligand/band states), and mixed-valence metal ions (i.e. mixed f/d occupancy and mixed-oxidation states). Understanding and controlling the manifestation of these phenomena is crucial for understanding the physics underpinning topological insulators such as PuB_6, superconductors such as $PuCoGa_5$, and multiconfigurational insulators such as CmO_2.

The principal goal of the proposed synthetic, physical, and spectroscopic studies is to disentangle the complex electronic structure of actinide materials. Definitive spectroscopic and thermodynamic signatures of electronic structure phenomena unique to transuranic materials are underdeveloped. In particular, the process of establishing clear correspondence between spectroscopic signature, electronic structure, and physical properties is complicated by competition between multiple electronic phenomena on similar energy scales.

Significant achievements during 2021-2023:

- December 2021: Renovations/repairs to transuranic lab completed and synthetic studies with Np and Pu commence
- Initial synthetic, crystallographic, electrochemical, and spectroscopic studies with Np imidophosphorane complexes lead to identification of unique cathodically shifted potentials and accessibility of unusual high-valent complexes (see ref. 5 and subsequent studies in preparation)
- Ligand development to lead to low-disorder, high-resolution structures on small scale reactions of actinide isotopes (ref. 4).
- Early actinide studies lead isolation and magnetic and spectroscopic characterization of rigorously isotypic series of trigonal bipyramidal pentavalent uranium complexes leading to quantitative analysis SOC/CF competition across spectrochemical series.
- Development of a library of oxidative atom transfer reactions (and uranium products) to guide mid-actinide studies (ref 3 and 2).
- Development and application of spectroscopic probes (on lanthanide systems) including RIXS (at APS) and EPR and FIRMS (at NHMFL, Ref. 1)

Science objectives for 2023-2025:

- Extend synthetic studies and complete characterization of high-valent Np complexes
- Establish high-valent Pu chemistries based on established imidophosphorane complexes of U and Np
- Build libraries of unique heteroleptic, imidophosphorane complexes with high-valent ions and reactive ligands
- Extend spectroscopic tools to mid-actinide analytes

Publications supported by this project 2021-2023

5. Kaitlyn S. Otte, Julie E. Niklas, Chad M. Studvick, Andrew C. Boggiano, John Bacsa, Ivan A. Popov,* and Henry S. La Pierre,* "Divergent Stabilities of Tetravalent Cerium, Uranium, and Neptunium Imidophosphorane Complexes," **In Revision**, *Journal of the American Chemical Society*.

4. Julie E. Niklas, Chad M. Studvick, John Bacsa, Ivan A. Popov,* and Henry S. La Pierre* "Ligand Control of Oxidation and Crystallographic Disorder in the Isolation of Hexavalent, Uranium Mono-oxo Complexes," *Inorganic Chemistry*, **2023**, 62(5), 2304-2316 DOI: 10.1021/acs.inorgchem.2c04056.

3. Luis M. Aguirre Quintana, Julie E. Niklas, Ningxin Jiang, John Bacsa, Laurent Maron, and Henry S. La Pierre,* "Elemental Chalcogen Reactions of a Tetravalent Uranium Imidophosphorane Complex: Cleavage of Dioxgen," *Chemical Communications*, **2022**, 58 (95), 13242-13245. DOI: 10.1039/D2CC05066H.

2. Fabrizio Ortu, Simon Randall, David J. Moulding, Adam Woodward, Andrew Kerridge, Karsten Meyer, Henry S. La Pierre,* and Louise Natrajan,* "Photoluminescence of Pentavalent Uranyl Amide Complexes," *Journal of the American Chemical Society*, **2021**, 143, *33*, 13184–13194. DOI: 10.1021/jacs.1c05184

1. Thaige P. Gompa, Samuel M. Greer, Natalie T. Rice, Ningxin Jiang, Joshua Telser, Benjamin W. Stein, and Henry S. La Pierre,* "High-Frequency and -Field EPR Spectroscopic Analysis of Metal-Ligand Covalency in a $4f^7$ Valence Series (Eu^{2+}, Gd^{3+}, Tb^{4+})," *Inorganic Chemistry*, **2021**, *60*, 9064-9073. DOI: 10.1021/acs.inorgchem.1c01062

Defining Coordination Chemistry Design Principles for f-Element Molecular Spin Qubits

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Overall research goals: This project will elucidate the mechanisms of magnetic relaxation and decoherence (relaxation pathways and associated processes) driven by spin-phonon coupling in *f*-element molecular nanomagnets (MNMs) – including both single-molecule magnets (SMMs) and molecular spin qubits (MSQs) – through cross examination of single-ion properties and intra- and intermolecular molecule/ligand effects. The research will leverage synthetic, spectroscopic (synchrotron, neutron scattering, electron-paramagnetic resonance (EPR), magneto-infrared (IR), and magneto-Raman spectroscopies), magnetometric, and theoretical techniques to generate cohesive and predictive models of spin-phonon relaxation processes – impacting both (1) the design of MSQ technologies for spin-based quantum information systems, and (2) design of SMM technologies.

Significant achievements during 2021- 2023:

- Funded 9/27/2022

Science objectives for 2023-2025:

In order to "overcome the tyranny of low temperatures" in the application of MNMs in quantum information processing, further development must contend with the mechanistic details of spin-phonon relaxation between magnetic molecules and molecular/lattice vibrations (optical/acoustic phonons). This understanding is the principal objective of the synthetic, physical, spectroscopic, and theoretical studies proposed here and will require addressing three specific aims:

Aim 1: Investigate how single-ion properties, including SOC and CF, determine the dynamic magnetic properties of MNMs. This aim will be achieved by expanding the chemical space of MNMs considered for MSQs to lanthanides and actinides and for SMMs across the early actinide elements (Th, U, Np, and Pu). Complex design will focus on coordination chemistry to address how changes in symmetry, metal charge and valence, and metal-ligand covalency govern the observed dynamic magnetic properties of MNMs, in particular how spin-phonon coupling leads to demagnetization and decoherence. Ligand architectures that allow for direct modification of metal-ligand bond strength and vibrational structure via the substitution of isoelectronic ligands (such as halides and pseudohalides) will facilitate the development of design principles to mitigate spin-phonon coupling mediated decoherence and demagnetization in MNMs.

Aim 2: Develop multi-modal spectroscopic tools to correlate changes in local structure and dynamic magnetic properties with changes in the vibrational spectrum and in spin-phonon coupling. In order to define the magneto-structural correlations governing spin-phonon coupling in f-element MNMs, a suite of X-ray, neutron, and magneto-vibrational spectroscopies will be paired with advanced pulsed EPR employed to measure changes in structure, vibrational spectrum, and spin-phonon coupling.

Aim 3: Develop and apply first principles simulations, effective models (e.g., crystal field theory and spin Hamiltonian formalism), and semi-analytical approaches to simulate experimental results. These theoretical models will rationalize the effect of spin-phonon coupling on spin relaxation.

From Accurate Variational Relativistic Electronic Structure Theory to Practical Applications in Heavy-Element Chemistry

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Overall research goals:

The proposed work aims to produce a hierarchical set of relativistic electronic structure methods that are designed to accurately predict heavy-element properties from molecular orbitals to many-body excited states, from atomic electronic structures to molecular complexes with multiple heavy-element centers. We will steer away from perturbative approximations in favor of a truly variational multi-reference method that integrates reusable and interoperable software components into a predictive computational platform. This work will support future joint theory and experimental research efforts in the domain of heavy-element chemistry. Specifically, we propose two method developments with increasing theoretical complexity, including variational relativistic two- and four-component multi-reference configuration interaction methods with the Dirac-Coulomb-Breit Hamiltonian and relativistic embedding theory.

Significant achievements during 2021-2023:

During this funding period, we have published 12 peer-reviewed articles and released a new version of the open-source software package that includes new algorithms and methods developed under the support of this grant. We made several methodological breakthroughs that enable low-cost calculations of relativistic electronic structure methods for heavy-element research, including:

(1) development of a fully spin-separated four-component Dirac-Coulomb-Breit Hamiltonian using the Pauli quaternion representation that achieves the theoretical limit of the computational cost of the Dirac-Hartre-Fock method;

(2) development of fully correlated Dirac-Coulomb-Breit many-body methods within the complete active space approach for molecular calculations.

Science objectives for 2023-2025:

There are three specific plans:

(1) We will develop four-component Dirac-Coulomb-Breit multireference configurational interaction (MRCI) methods with the new multi-spin-physics concept.

(2) We will collaborate with experimentalists to simulate M-edge spectroscopies of heavy-element complexes and to provide theoretical insights into their electronic characteristics.

(3) We will apply the relativistic multi-spin-physics Dirac-Coulomb-Breit multi-reference method to study chemical bonding in triatomic uranium species, including NUN or CUO, in a new collaboration with Prof. Bess Vlaisavljevich.

Publications supported by this project 2021-2023

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2. C. E. Hoyer, H. Hu, L. Lu, S. Knecht and X. Li, “Relativistic Kramers-Unrestricted Exact-Two-Component Density Matrix Renormalization Group”, Journal of Physical Chemistry A, **2022**, 126, 5011–5020.
3. S. Sun, J. N. Ehrman, Q. Sun and X. Li, “Efficient Evaluation of the Breit Operator in the Pauli Spinor Basis”, Journal of Chemical Physics, **2022**, 157, 064112.
4. L. Lu, H. Hu, A. J. Jenkins and X. Li, “Exact-Two-Component Relativistic Multireference Second-Order Perturbation Theory”, Journal of Chemical Theory and Computation, **2022**, 18, 2983–2992.
5. A. Grofe and X. Li, “Relativistic Nonorthogonal Configuration Interaction: Application to $L_{2,3}$-edge X-ray Spectroscopy”, Physical Chemistry Chemical Physics, **2022**, 24, 10745–10756.
6. J. M. Kasper, X. Li, S. A. Kozimor, E. R. Batista and P. Yang, “Relativistic Effects in Modeling the Ligand K-Edge X-ray Absorption Near-Edge Structure of Uranium Complexes”, Journal of Chemical Theory and Computation, **2022**, 18, 2171–2179.
7. T. F. Stetina, A. Ciavarella, X. Li and N. Wiebe, “Simulating Effective QED on Quantum Computers”, Quantum, **2022**, 6, 622.
8. S. Sun, T. F. Stetina, T. Zhang, H. Hu, E. F. Valeev, Q. Sun and X. Li, “Efficient Four-Component Dirac–Coulomb–Gaunt Hartree–Fock in the Pauli Spinor Representation”, Journal of Chemical Theory and Computation, **2021**, 17, 3388–3402.
9. S. Sun, T. F. Stetina, T. Zhang and X. Li, In Rare Earth Elements and Actinides: Progress in Computational Science Applications; D. A. Penchoff, T. L. Windus and P. C. C. Ed.; American Chemical Society: **2021**, Chapter 10 - On the Finite Nuclear Effect and Gaussian Basis Set for Four-Component Dirac Hartree-Fock Calculations., 207–218.
10. J. J. Goings, H. Hu, C. Yang and X. Li, “Reinforcement Learning Configuration Interaction”, Journal of Chemical Theory and Computation, **2021**, 17, 5482–5491.
11. A. Grofe, J. Gao and X. Li, “Exact-Two-Component Block-Localized Wave Function: A Simple Scheme for the Automatic Computation of Relativistic ΔSCF”, Journal of Chemical Physics, **2021**, 155, 014103.
12. T. Zhang, X. Liu, E. F. Valeev and X. Li, “Toward the Minimal Floating Operation Count Cholesky Decomposition of Electron Repulsion Integrals”, Journal of Physical Chemistry A, **2021**, 125, 4258–4265.

Understanding Photoluminescence in High- and Low-Valent Actinide Complexes

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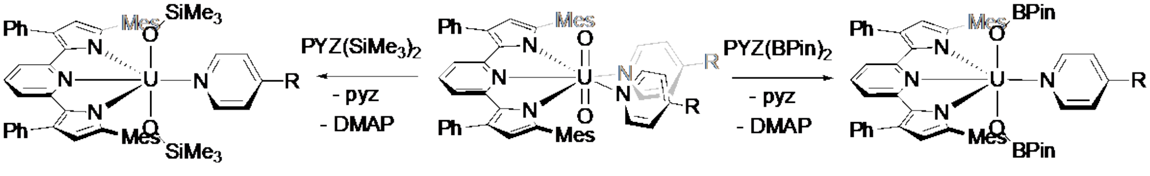
Overall research goals:

Our research project focuses on the investigation of the photoluminescence of uranium and thorium complexes to understand the role 5f-orbitals and electrons play in these processes. Molecules investigated range simple, previously reported uranium alkoxide and uranyl complexes, as well as novel actinide compounds supported by pyridine dipyrrolide ligands. All compounds are routinely characterized by ^{1}H NMR and electronic absorption spectroscopies and single crystal X-ray diffraction. We also leverage our expertise in electrochemical analysis (cyclic voltammetry) under rigorously anhydrous conditions to understand the redox properties of all actinide complexes prepared. excited state electronic structure of complexes is probed through photoluminescence spectroscopy and time-correlated single photon counting. Computation methods performed by our collaborator (Vlaisavljevich) provide insight into the electronic structure of ground and excited states, providing opportunities to interrogate the role actinide-ligand covalency plays in emissive processes observed in these species.

Significant achievements during 2021- 2023:

Since the previous PI meeting, our research has continued our work in the attempted synthesis of actinide substituted polyoxovanadate and polyoxotungstate clusters. Both sets of complexes have proven difficult to isolate. This has prompted interest in the study of other ligands as electronically non-innocent supports for uranium and thorium. Specifically, we have been studying the synthesis of actinide complexes coordinated to pyridine dipyrrolide (^{Ph}PDP^{Ar}; Ar = Ph, Mes, Cl$_2$Ph) ligands. The ability of the ^{Ph}PDP^{Ar} ligands to participate in ligand to metal charge transfer processes proved exciting, as transient reduction of the actinide center could prove relevant for promoting activation of otherwise inert species. Accomplishments during the past project period include isolation of uranyl complexes supported by the ^{Ph}PDP^{Ar} ligand, (^{Ph}PDP^{Ar})UO$_2$(L) (Ar = Mes, Cl$_2$Ph; L = THF, DMAP) and investigation of their electronic structure via cyclic voltammetry and electronic absorption spectroscopy (*Inorg. Chem.*, 2022). Subsequent work probing the activation of the uranyl fragment of these compounds was published; while not specific to ^{Ph}PDP^{Ar}-supported complexes, our group showed that the concerted transfer of silylium ions and electrons via addition of Mashima's reagent to UO$_2^{2+}$ species results in quantitative conversion to U(IV) siloxide species (*Chem. Comm.*, 2022).



$(^{Mes}PDP^{Ph})U(OSiMe_3)_2(DMAP)_2$ $(^{Mes}PDP^{Ph})UO_2(DMAP)_2$ $(^{Mes}PDP^{Ph})U(OBPin)_2(DMAP)_2$

A serendipitous discovery by a graduate student during standard characterization of uranium precursors. We observed that the uranium(IV) alkoxide compound is strongly emitting when irradiated with visible light. Emission in low-valent uranium complexes in nonaqueous solvent has been scarcely reported in the literature. As such, our group has pivoted to understand these emissive properties observed across the series of U(IV), U(V) and U(VI) alkoxide complexes. We note that this work is currently unpublished; we are planning submission of a manuscript in collaboration with Bess Vlaisavlievich's research group at USD over the summer.

Science objectives for 2023- 2025:

During the next project period, our work of relevance to the Heavy Element Program will be organized around the following Project Objectives:

Project 1: Photoluminesence of homoleptic actinide complexes. The majority of our efforts over the next two years will focus on expanding our understanding of the photoluminescence of homoleptic uranium complexes across a range of oxidation states and ligand-types. Homoleptic uranium amide, alkyl, and sulfide complexes have been reported by Hayton and coworkers across a range of oxidation states. We plan to generate these complexes and interrogate their photoluminescence and electrochemical properties to understand the role ligands play in tuning the excited state electronic structure of high- and mid-valent uranium compounds.

We also have preliminary results that suggest that the dimeric versions of uranium alkoxide complexes, $[U_2(O^tBu)_9]^{1-}$ and $U_2(O^tBu)_9$ possess strikingly different photoluminescence. Further investigation of these multimetallic assemblies will allow for understanding how electronic communication between the two uranium ions influences excited state properties of the compounds.

Project 2: Photoluminesence of transactinide alkoxide complexes. Our current work have primarily focused on emission of previously reported uranium alkoxide complexes. In an attempt to expand this chemistry to transuranic elements in collaboration with Suzanne Bart (Purdue University), we are developing synthetic methodology for the isolation of crystalline samples of these alkoxide complexes from reactions run on milligram scales. The graduate student working on this project also plans to apply for an SCSGR fellowship to continue this work at a national lab, where they will have access to additional transuranic elements.

Project 3: Synthesis of uranium and thorium complexes supported by redox-active metalloligands. Our initial studies focused on the formation of actinide substituted polyoxovanadate clusters have proven difficult. What's more, the field of polyoxometalates as ligands for transactinide elements has exploded during the past three years, with an emphasis on the use of these heavy clusters in separations and for the crystallization of novel complexes containing transuranic elements (e.g. $^{243}Am^{3+}$, $^{248}Cm^{3+}$). As such, my team will pivot and probe a complementary set of redox-active metalloligands derived from molybdenum and tungsten sulfide hemicubane clusters (e.g. $(Cp^*M)_3S_4$; M = Mo, W). We anticipate the use of soft, sulfur ligands and donors will provide orthogonal reactivity and electronic structures to the harder polyoxometalate ligands. To date, we have synthesized these ligands and obtained a crystal structure of our first actinide compound, $(Cp^*Mo)_3S_4UI_3$.

Publications supported by this project 2021-2023

1. Thomas Auvray, Olaf Nachtigall, William W. Brennessel, William D. Jones, Ellen. M. Matson. "Development of sterically hindered siloxide-functionalized poloxotungstates for the complexation of 5d-metals" *Dalton Transactions*, **2021**, *50*, 4300-43100 (DOI: 10.1039/D1DT00256B).
2. Brett D. Hakey, Dylan C. Leary, Lauren Lopez, Leyla R. Valerio, William W. Brennessel, Carsten Milsmann, Ellen M. Matson. "Synthesis and characterization of pyridine dipyrrolide uranyl complexes" *Inorganic Chemistry* **2022**, *61*, 6182-6192 (DOI: 10.1021/acs.inorgchem.2c00348).
3. Leyla R. Valerio, Brett D. Hakey, William W. Brennessel, Ellen M. Matson. "Quantitative U=O bond activation via silyl radical transfer" *Chemical Communications* **2022**, *58*, 11244-11247 (DOI: 10.1039/D2CC04424B; selected by Editor as a "Hot Article").

Synthesis, Structural and Spectroscopic Characterization, Theory, and Small-Molecule Reactivity of Complexes with Reactant-Accessible Actinide–Actinide Covalent Bonds

Lou Messerle, Principal Investigator

Departments of Chemistry and Radiology (secondary appointment), University of Iowa, Iowa City IA
Graduate Students: Grant Forsythe, James Earl
Undergraduate Students: Michael Rodriguez (senior), Jillian Druzgalla and Julianne Green (juniors)
Collaborators: Profs. Michael Neidig (University of Rochester: physical inorganic spectroscopies), David Dixon (University of Alabama: theory), Scott Daly (University of Iowa: extension to Np), Amanda Haes (University of Iowa: Raman spectroscopy of An–An stretching frequencies)

Overall research goals:

1) Employ dinucleating ligands in order to support the first discrete mid-valent early diactinide and organodiactinide U-U, Th-Th, and Np-Np compounds with covalent An-An bonding;
2) Study new diactinide compounds, in collaboration, via physical inorganic spectroscopies and high-level theoretical studies, to contribute to understanding the *f*-orbital challenge;
3) Examine the small-molecule solution reactivity of new diactinide, organodiactinide, and polyactinide cluster compounds;
4) In collaboration, extend these studies to mid-valent dineptunium organodimetallic and dinuclear coordination chemistries.

Significant achievements during late Summer 2022 - Spring 2023: (Project start July 15, 2022):

Prepared Th and U chloride and bromide precursors, dipyridylamide (dpa) and hexahydropyrimidopyrimidinate (hpp) trimethylsilyl reagents for metathesis with U and Th halides. One example was synthesis, solid-state structure, and spectroscopic characterization of the new compound Th(hpp)Br_3. New compounds were reduced with conventional non-amalgam inorganic reductants (e.g., KC_8) and novel organic-soluble, salt-free reductants based on aza-trimethylsilylated antiaromatic 4,4'-bipyridines, diazapyrenes, and diazaheterocycles bearing substituents that preclude actinide coordination of the resultant aromatic heterocycle by-products. This constitutes a reductive approach from higher-valent, harder actinide halides to lower-valent, softer ligand-coordinated diactinide halides.

Explored the complementary approach, oxidative addition to known but little-studied known Rieke U(0) and Th(0) suspensions (presumably nanoparticles) of (peralkylcyclopentadienyl) halides (Br, I) in presence and absence of dinucleating ligands.

Undergraduate researchers synthesized new bulky peralkylcyclopentadienes and their peralkylcyclopentadienyl reagents, previously unexplored in actinide organometallic chemistry, for future syntheses of $(h\text{-}C_5R_5)_2An_2Cl_n$ (n = 3, 4) with An–An covalent bonds.

In an expansion of our proposed studies and based on our published, facile reductive syntheses of discrete hexatantalum, hexatungsten, and tritungsten halide cluster compounds with metal-metal bonding, examined solid-state, tube-furnace reaction of UCl_4 and UBr_3 with nonconventional main-group Sb, Bi and Ga_2Cl_4 reductants, with and without added alkali metal halides in order to break up extended structures, for targeted triactinide and higher-nuclearity actinide clusters.

Science objectives for 2023- 2025:

Further development of reductive and oxidative addition synthetic approaches to mid- and lower-valent diactinide and polyactinide molecular compounds with dinucleating ligands, including softer disulfide and diphosphine ligands, for lower-valent actinide, diactinide, and organodiactinide complexes, followed by solid-state X-rqy diffractometric and solution structural studies, collaborative physical inorganic spectroscopic, and collaborative theoretical studies.

Publications supported by this project mid-Summer 2022 - Spring 2023: none

Quantum chemical calculations on thorium complexes with diffuse peripheral electrons: Towards thorium liquid metals and electrides for redox chemistry applications

Evangelos Miliordos, Principal Investigator

Department of chemistry and biochemistry, Auburn University, Auburn, AL
Graduate Students: Benjamin Jackson, Isuru Ariyarathna
Undergraduate Students: Zhongyuan Lu, Jared Stinson
Collaborators: Anne Gorden (Texas Tech University)

Overall research goals: The relatively low ionization energies of f-block metals enable the formation of coordination complexes that can host more than one solvated/diffuse electrons. Focusing on thorium, we show that crown-ethers, cyclams, and ammonia can form up to tenfold coordination complexes hosting up to four diffuse peripheral electrons. Such complexes are the building units for novel electrides and liquid metals with excess diffuse electrons which can be used for multi-electron reduction reactions.

Significant achievements during 2021- 2023:

We have shown that similarly to alkali, alkaline earth, and transition metals,[1-3] the studied thorium complexes can host outer diffuse electrons populating hydrogenic-type orbitals with an identical Aufbau principle to alkali and alkaline earth metals regarding the lowest energy orbitals (1s, 1p, 1d, 2s).[4] Th(12-crown-4) and Th(15-crown-5) crown ethers and cyclams retain one or two valence electrons in 6d orbitals, but in $Th(NH_3)_{10}$ all four valence electrons are displaced to the periphery of the complex with a $1s^21p^2$ electronic configuration. This implies that the formation of thorium-ammonia liquid metals will lead to a thoroughly difference electronic band structure and more reducing materials compared to the experimentally observed $Li(NH_3)_4$ liquid metals.[5]

Science objectives for 2023- 2025:

Although our future objectives will not be supported financially by this grant (expired), we are planning to study reactions of $Th(NH_3)_{10}$ with O_2 or CO_2 (in presence of H_2) to see if the assumed multi-electron reduction reactions with four solvated/diffuse electrons are possible. We showed recently that $Li(NH_3)_4$ can reduce CO_2 to CO_2^-, which is radical and reactive towards lactones or methanol.[6]

Publications supported by this project 2021-2023

B. Jackson, Z. Lu, J. Stinson, E. Miliordos, "Electronic structure of thorium coordination complexes with crown ethers, cyclams, and ammonia ligands, and implications for proposed thorium electrides and liquid metals" *(manuscript in preparation).*

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Electronic Structure, Spectroscopy, and Bond Dissociation Energies of Small Actinide Molecules

Michael D. Morse, Principal Investigator

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Graduate Students: Dakota Merriles, Kim Tomchak, Joshua Ewigleben, Tommy Kawagoe

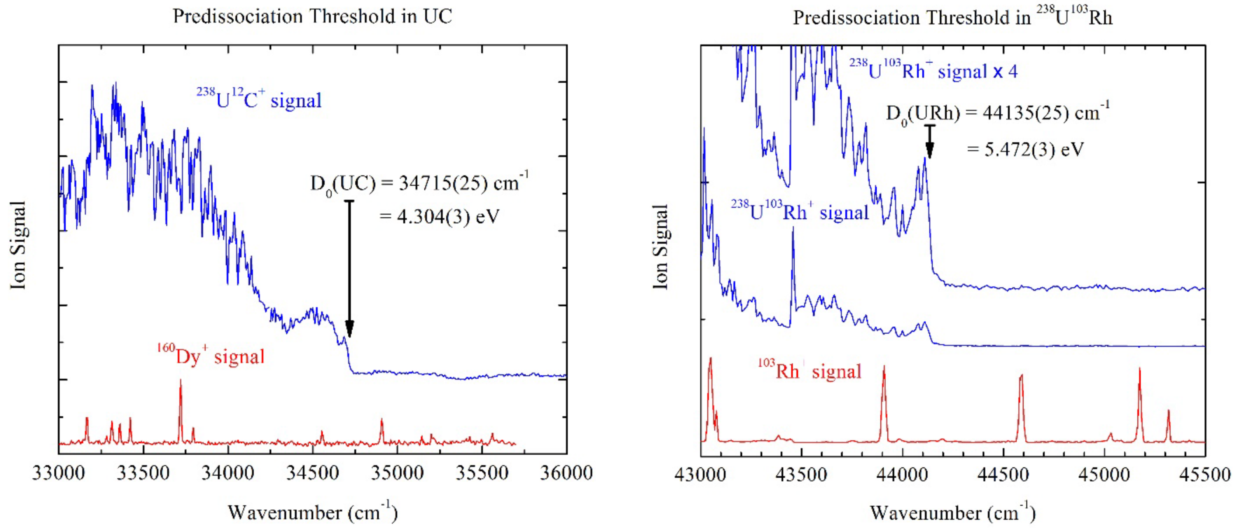
Overall research goals: This work is focused on obtaining detailed, precise information concerning the electronic structure, spectroscopy, and bond dissociation energies of small thorium and uranium molecules, with the goal of providing precise data that can be used to assess the approximations employed in quantum chemical calculations on these species. Ultimately, it is our hope that the precise data we obtain will be useful in benchmarking quantum computational methods for the 5*f* elements, allowing efficient and accurate methods to be developed for application to the transuranic elements.

Significant achievements during 2021- 2023:

In recent years, the Morse group has established that an effective means of precisely measuring bond dissociation energies (BDEs) in small open shell *d*- and *f*-block molecules is through the measurement of sharp predissociation thresholds in a congested, quasicontinuous vibronic spectrum.[1] For these types of molecules, the extremely large density of electronic states present at the ground separated atom limit causes rapid predissociation to set in as soon as the bond dissociation energy is exceeded. In our resonant two-photon ionization (R2PI) spectroscopic studies, the predissociation threshold is readily identified by a sharp drop in ion signal to baseline as the BDE is exceeded.

Table 1. Bond dissociation energies measured by the onset of predissociation

Molecule	BDE (eV)	Status	Molecule	BDE (eV)	Status
ThSe	5.484(12)	Preliminary	USe	4.609(9)	Finalized
UC	4.304(3)	Finalized	URh	5.472(3)	Finalized
US	5.25(5)	Preliminary	UIr	5.647(13)	Preliminary
SU-S	4.96(2)	Preliminary			



Figs 1 and 2. Sharp predissociation thresholds in the R2PI spectra of UC and URh provide precise values of their bond dissociation energies, as reported in Table 1 above.

In other work, we have collaborated with Prof. Tim Steimle to study ThC. He has used the locations of the ThC vibronic bands that we have measured in low resolution to obtain high resolution LIF and dispersed fluorescence spectra. The rotational analysis is ongoing, but the ThC $X^3\Sigma^+$ ground state vibrational interval, $\Delta G_{1/2}$, has been measured as 798 cm^{-1}.

We are also completing the construction of a cryo-cooled ion photodissociation instrument that will allow us to extend these BDE measurements to mass-selected cations. During the 2021-2023 period, we have designed, modeled, and assembled the laser ablation source region of this instrument. This includes the laser ablation ion source itself, an ion funnel to collect the cations, a hexapole preliminary trap that can be used to ligate the cooled ions with stable molecules, and an octupole ion guide to transport the ions to a quadrupole mass filter for mass selection. The remainder of the instrument was built prior to this period and employs a quadrupole bender, a cryo-cooled linear quadrupole ion trap, a second quadrupole mass filter set to the mass of the expected fragment, and a conversion dynode for counting fragment ions. The cryo-cooled linear quadrupole trap is constructed so that two collimated laser beams can be sent through the cell from opposite directions, allowing photodissociation-based probes of the trapped ions. At this point in time, construction is complete but we are still working to obtain the rf power supplies that are needed to operate the ion funnel, hexapole trap, and octopole ion guide. When those are in hand, the system will be complete.

Science objectives for 2023- 2025:

During the next two years, we plan to finalize the preliminary BDEs listed above and measure BDEs of additional small neutral molecules such as UB, U-B_2, UN, ThB, Th-B_2, ThN, and ThS. We will also measure the BDEs of additional actinide-metal molecules such as URu, UPt, ThRu, ThRh, ThIr, and ThPt. We will collaborate with computational chemists to understand the electronic structure of these species. We will also measure the BDEs of the actinide dimers Th_2 and U_2. A precise BDE for U_2 will be particularly useful as a benchmark for quantum chemical calculations. We will complete the rotational analysis of ThC and work to collect rotationally resolved spectra of UC to measure its bond length and identify its ground electronic state experimentally. We also plan to record vibrationally resolved spectra of UO_2 and other species in the near-infrared region using an R2PI scheme employing two tunable OPO lasers. One will scan in the near-infrared region while the second is used to provide a fixed wavelength ionization source. This method will provide very useful means of investigating the calculated low-energy electronic states of UO_2. Once successfully demonstrated on UO_2, I anticipate using this method for other actinide species as well, fleshing out our knowledge of their electronic states in the near infrared region.

The nearly-completed cryo-cooled ion photodissociation spectrometer will be used to provide precise BDEs of UF^+, UO^+, and UO_2^+ using a resonant two-photon dissociation scheme. In NSF-funded work, a similar method has been quite successful in measuring ionization energies of neutral molecules like RuB, RhB, OsB, IrB, and PtB.[2] The BDEs of multiply-ligated cations will be more readily measured than for the corresponding neutrals, allowing BDEs of a series of species such as UF_2^+, UF_3^+, UF_4^+, *etc.* to be measured.

Publications supported by this project 2021-2023

None as of yet.

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

Kirk Peterson, Principal Investigator

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Overall research goals: Develop and apply a systematic quantum chemistry methodology (FPD) that will be capable of providing chemically accurate thermochemistry (within 1-3 kcal/mol) and accurate spectroscopic properties 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.

Significant achievements during 2021- 2023: We have successfully applied the composite FPD approach based on CCSD(T) calculations, including relativistic 4-component CCSD(T), to accurately predict electron affinities, bond dissociation energies, and atomization energies for a wide range of actinide-containing molecules, most in collaboration with HEC-supported experimental groups. In addition to the papers below, we have made progress in F12-based basis sets for uranium and initiated new collaborations with the groups of Titov and Mosyagin to incorporate their accurate relativistic ECPs for heavy elements into our methodology (requires new basis sets from us), as well as Morales and Zhang at the Flatiron Institute to apply AFQMC to relativistic calculations on actinides.

Science objectives for 2023- 2025: In addition to applying FPD to interesting metalloactinyls (An-TM) as well as small actinide-containing molecules containing S, Se, and Te, we will focus on methodological improvements for heavy element chemistry: (a) new systematically convergent Gaussian basis sets using the new GRECPs of Titov, Mosyagin, and co-workers, (b) Gaussian basis sets for explicit correlation (F12), and (c) investigating the performance of auxiliary field quantum Monte Carlo (AFQMC) for strong correlation problems in heavy element chemistry.

Publications supported by this project 2021-2023

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Exploring the Nature of f-Element Soft Donor Interactions Using Electronically Tunable Azolate Ionic Liquids

Robin D. Rogers, Principal Investigator

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Postdoctoral Associates: Ethan A. Hiti, Gabriela Gurau
Collaborators: Thomas Albrecht-Schönzart (Colorado School of Mines), David A Dixon (The University of Alabama), Anja Verna-Mudring (Aarhus University)

Overall research goals: The overall goal of this research is to advance the understanding of how f-elements interact with moderately soft donors (including during hydrolysis reactions), a heavily investigated yet inconclusive area of study which is of prime importance in spent nuclear fuel processing, f-element environmental mobility, and fundamental inorganic chemistry.

Significant achievements during 2021- 2023: This abstract will focus on one aspect of our recent work. Using Ce(III) and Nd(III) as both representative lanthanides and actinide analogs, the ability of mixtures of acidic and basic azoles to allow direct access to homoleptic N-donor f-element complexes in one pot reactions from hydrated salts as starting materials was examined by reacting mixtures of 4-amino-1,2,4-triazole (4-NH_2-1,2,4-Triaz), 5-amino-tetrazole (5-NH_2-HTetaz), and 1,2,3-triazole (1,2,3-HTriaz) in 1:1 and 1:3 ratios with $CeCl_3$•$7H_2O$, $[C_2mim]_3[CeCl_6]$ ($[C_2mim]^+$ = 2-ethyl-1-methylimidazolium), and $Ln(NO_3)_3$•$6H_2O$ (Ln = Ce, Nd). Although unsuccessful in our goal, single crystal X-ray diffraction revealed that neutral 4-NH_2-1,2,4-Triaz is structure directing via $\eta^2\mu_2\kappa^2$ bridging, with the formation of the dinuclear complexes $[Ce_2Cl_2(\mu_2$-4-NH_2-1,2,4-$Triaz)_4(H_2O)_8]Cl_4$•$4H_2O$, $[Ce_2(\mu_2$-4-NH_2-1,2,4-$Triaz)_4$(4-NH_2-1,2,4-$Triaz)_2(Cl)_6]$, and [4-NH_2-1,2,4-HTriaz]$[Ln_2(\mu_2$-4-NH_2-1,2,4-$Triaz)_2(\mu_2$-$NO_3)(NO_3)_6(H_2O)_2]$ (Ln = Ce, Nd) . When the synthetic conditions favored hydrolysis, the hexanuclear Ln(III) complexes $[Ce_6(\mu_3$-$O)_4(\mu_3$-$OH)_2(\mu_3$-$Cl)_2(Cl)_6(\mu_2$-4-NH_2-1,2,4-$Triaz)_{12}]$•$7H_2O$ and $[Nd_6(\mu_3$-$OH)_8(Cl)_6(\mu_2$-4-NH_2-1,2,4-$Triaz)_{12}][Cl_4]$•$2H_2O$ were isolated (**Figure 1**). These hydrolysis products represent the first examples of a high nuclearity lanthanide complex where all Ln atoms are pairwise connected through 12 N-donor ligands or 12 neutral bridging ligands of any type, a rare example of incorporation of non-oxo coordinating anions in the M_6X_8 core, and the first reported Ce(III) hexanuclear complex.

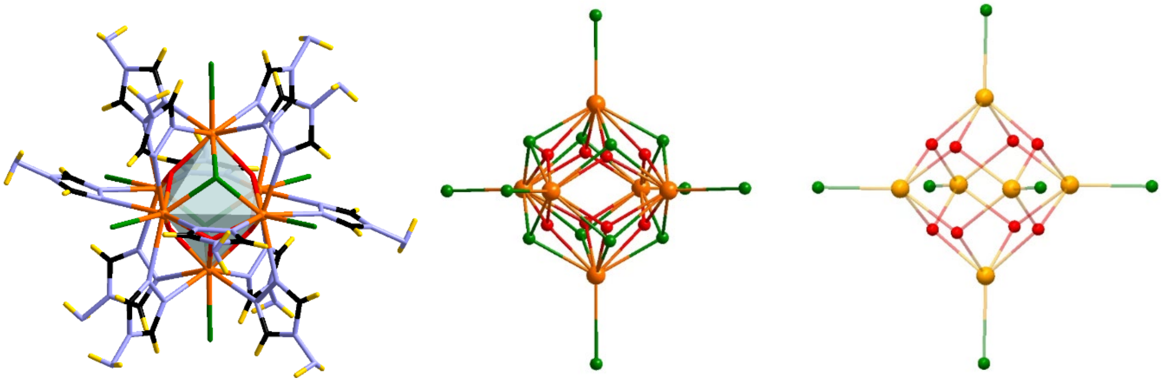

Figure 1. An ordered model of the primary coordination sphere (**left**) and the locations of the statistical mixture of 50% O^{2-}, 25% OH^-, and 25% Cl^- μ_3-bridges (**middle**) in $[Ce_6(\mu_3$-$O)_4(\mu_3$-$OH)_2(\mu_3$-$Cl)_2(Cl)_6(\mu_2$-4-NH_2-1,2,4-$Triaz)_{12}]$•$7H_2O$, and the ordered core in $[Nd_6(\mu_3$-$OH)_8(\mu_2$-4-NH_2-1,2,4-$Triaz)_{12}(Cl)_6][Cl_4]$•$2H_2O$ (**right**).

Science objectives for 2023- 2025: Our major objectives for this renewal period include a) using azolium azolate IL chemistry to overcome *f*-element hydrolysis problems that prohibit the isolation of the *f*-elements soft donor complexes, in order to build a library of *f*-element N-donor complexes as a means to understand the fundamental differences between actinide and lanthanide interactions with moderately soft donor ligands and b) to transfer this chemistry from 4*f* elements to transuranic elements, particularly in the study of hydrolysis of Pu(III). In this grant period, we will also spend significant effort to understand the serendipitous discovery that certain azoles seem capable of trapping *f*-element hydrolysis products in reproducible solid-state M_6O_8 motifs and transfer this chemistry to Pu(III).

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Expressing Tuneable Emergent Quantum Phenomena in Molecular Systems with Strong Electron Correlations

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Co-PIs/Collaborators: Stefan Minasian (LBNL), Corwin Booth (LBNL), Jochen Autschbach (Buffalo)

Overall research goals: The overall goal of this project is to synthesize molecular materials whose properties can be tuned systematically using local structure design principles and ultimately, to achieve emergent, heavy electron behavior in such molecular materials. A major aspect of the ongoing research is to use redox active lanthanide-based molecular precursors with strong electron correlations and magnetic moments for the understanding of emergent quantum phenomena. Other aspects include discovery of new multi-configurational f-element complexes and studies of their electronic structures using spectroscopy and theory. And application of such compounds into molecular materials with new properties.

Selected Significant achievements during 2021-2023:

- A study on the role of 5d orbitals in the bonding, electronic and magnetic structure of Ce imido and oxo complexes was completed (Figure 1). XAS measurements revealed that the imido and oxo materials exhibit features in the Ce L_{III} absorption of partial f-orbital occupancy that are relatively constant for all measured compounds. Magnetism studies revealed enhanced levels of TIP. In contrast to established multiconfigurational systems, no clear correlation between the level of TIP and f-orbital occupancy was found. CASSCF calculations defy a conventional van Vleck explanation of the TIP, indicating a single-reference ground state with no low-lying triplet excited state, despite accurately predicting the measured values of f-orbital occupancy. The calculations do, however, predict strong 4f/5d hybridization. In fact, within these complexes, despite having similar f-orbital occupancies and therefore levels of 4f/5d hybridization, the d-state distributions vary depending on the bonding motif (Ce=O vs. Ce=N) of the complex.

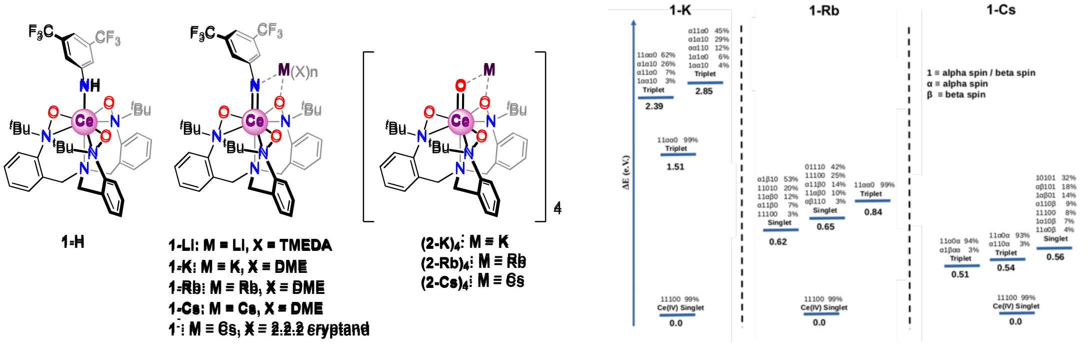

Figure 1. Structures of the Ce(IV) anilide **1-H**, imido **1-M,** and oxo **$(2\text{-M})_4$** compounds (left). Energy levels and configurations of **1-K** (left), **1-Rb** (center) and **1-Cs** (right) complexes obtained at the CASSCF(6,5) level. 0, α or β and 1 are used for depicting when the occupation of the MO is zero, one or two, respectively. All ground states represent closed-shell singlets (right).

- A set of organolanthanide(III) complexes featuring Ce(III)−C_{aryl} σ-bonds were synthesized and characterized. The syntheses follow salt metathesis reactions of the salts with the corresponding metallocene precursors. Electrochemical studies were performed for the organolanthanide(III) complexes. Reversible Ce(III)/Ce(IV) redox couples were observed for $(C_5Me_5)_2Ce$(*κ2-ortho*-oxa) (**3-Ce**) and $[Li(DME)_3][(C_5Me_5)_2Ce(biphen)]$ (**5-Ce**) complexes (Figure 2). DFT-bonding analysis suggested strong bond polarization in the complexes (**3-Ce** and **5-Ce**) with weights of 7-8% from Ce in the donation-bond orbitals.

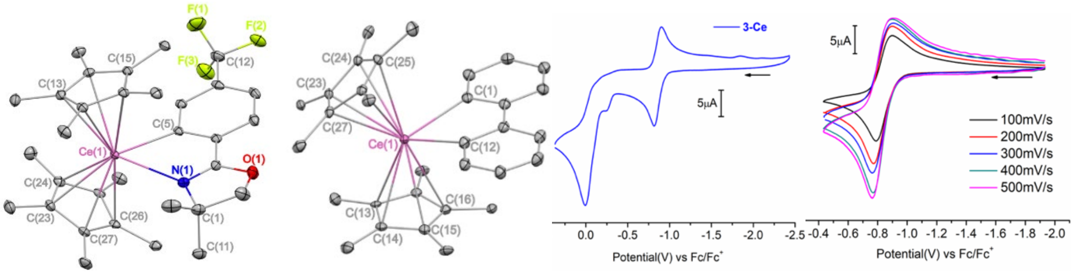

Figure 2. Thermal ellipsoid plots of **3-Ce** (far left) and **5-Ce** (second from left) at the 30% probability level. Full scan cyclic voltammogram from –2.5 to +0.5 V for **3-Ce** (second from right) and scan rate dependence (far right) for **3-Ce** with $E_{1/2} = -0.86$ V versus Fc/Fc^+.

Selected Science objectives for 2023-2025:

- Molecular materials that exhibit properties tunable through external phenomena, especially comprising f-elements, are rare. The team recently discovered new classes of materials where f-electron magnetic and conducting interactions can be tuned, as evidence in magnetism and EPR studies. The team will continue to characterize these materials, especially their electronic transport properties, to understand how molecular f-element materials can be altered using external stimuli.
- The team will pursue studies of new organocerium compounds with multiconfigurational (MC) effects. Previous work by the team in computations of Ce L_{III} edges (*Chem. Eur. J.* **2021**, *27*, 7239) indicated that MC effects are rare and limited to a few examples of organo-Ce/Yb compounds. Recently, new discoveries by the team have identified a new family of MC compounds in new geometries. We plan to expand on this discovery and to create materials based on this motif.

Publications supported by this project 2021-2023

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CASPT2 Geometries, Spectra, and Relativistic Electronic Structures of Actinide Species

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Overall research goals: This project will contribute to the improved understanding of the behavior of *f*-electrons by using methods based on a multireference complete active space approach to 1) compute structural properties, 2) predict spectra, and 3) and characterize the electronic structure by using methods that account for strong correlation and spin–orbit coupling self-consistently. DFT is well-known to fail for multiconfigurational electronic structures across the periodic table, but these challenges are compounded in complexes involving actinides where the proper treatment of relativistic effects is required. While many studies optimize geometries with DFT and, when necessary, characterize the electronic structure with a higher-level method, our group has shown the utility of performing full CASPT2 geometry optimizations and subsequent partial (or full) vibrational analysis for transition metal complexes with up to ~100 atoms. Then, upon a structure that is a minimum for the multiconfigurational ground state, subsequent electronic structure studies can be performed. When feasible, this highest level of theory will be based on four-component Dirac–CASSCF computations, that recover strong correlation and spin–orbit effects simultaneously. Our goal is to extend the use of these methods to new systems and provide insight into the role of spin-orbit effects in spectroscopic transitions, bonding, and magnetic properties. Additionally, the size of the so-called state-truncation error in state-interaction methods (*e.g*, SO-CASPT2) can be evaluated by making comparisons with such computations. Non-dynamical correlation will also be included (Dirac-CASPT2 or Dirac-NEVPT2) when appropriate.

Significant achievements during 2021- 2023: The project is in its first year of support and began in July 2023. We have selected systems ranging from three atoms to coordination complexes of actinides. We have begun performing calculations in the following five areas: 1) A series of linear AnL_2 complexes (where An = U, Np, Pu, and Am), 2) a study of linear triatomic molecules (with Li), 3) a family of homoleptic uranium-arenide complexes (with Fortier) and uranium-arene complexes (with Goodwin), 4) a series of Np^{V} and Np^{IV} complexes (with LaPiere and Popov), 5) a series of uranium alkoxide complexes (with Matson), and 5) a thorium complex with a surprisingly long Th-O bond (with Bart).

Science objectives for 2023- 2025: Our work will focus on three objectives: 1) Predict molecular structures for challenging cases by employing CASPT2 geometry optimizations, 2) elucidate the role of the 5*f*, 6*d*, and 6*p* orbitals in bonding using four-component relativistic mutireference methods, and 3) evaluate the electronic structure, spectroscopic properties, and magnetic parameters of actinide complexes. In addition to completing the initial projects, we plan to continue to establish strong collaborations to ensure that the computations we perform can be compared with state-of-the-art experimental results.

Publications supported by this project 2021-2023. None to report.

Small Molecule Reactivity with Actinide Complexes

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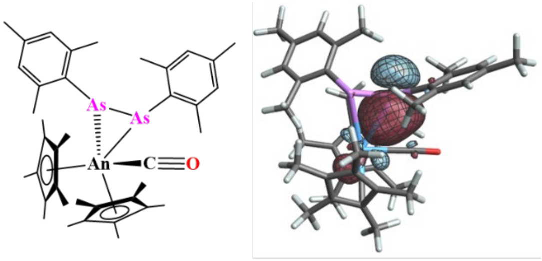
Overall research goals: Exploiting the size and electropositive nature of the actinides towards small molecule reactivity is well established within the community. However, this is typically done with uranium(III) due to the reducing nature of this oxidation state, and typically insertion reactivity is observed mainly with Th(IV) and U(IV) complexes. Our overall goal is to investigate the reactivity of actinide complexes towards small molecules that will afford intermediates that are not known or poorly characterized with respect to industrially interesting processes. These examples can lead to a better understanding of these catalytic processes, for example Fischer-Tropsch or Haber-Bosch chemistry, and potentially lead to enhanced catalysts.

Significant achievements during 2021- 2023:

Ligand design plays a significant role in small molecule activation. Our group has used uranium(III) complexes to reduce small molecules such as CO, CO_2, and CS_2, but we have also used soft donor ligands to do transformations. For example, we learned that a diarsenido complex of both thorium(IV) and uranium(IV) was able to form CO complexes that showed significant backbonding (see below). In this case, the electronic properties of the diarsenido ligand are responsible for the backbonding.



An = Th, ν(CO): 1979 cm^{-1}
U, ν(CO): 1939 cm^{-1}

σ (Th-As)
Donor NBO

Another example we have demonstrated is that the steric properties of the ligand can lead to coordination of CO or reductive coupling. The uranium(III) complex, $(C_5Me_5)_2(2,6\text{-}^tBu_2\text{-}4\text{-}MeC_6H_2O)U$ only coordinates CO, while $(C_5Me_5)_2(2,4,6\text{-}Me_3C_6H_2O)U(THF)$ reacts with CO to form an ethyne diolate moiety. This ethyne diolate can react with other electrophiles such as more CO, diphenylketene, and SO_2 to form unusual species that are derived directly from CO. The reductive chemistry of these heteroleptic metallocene aryloxide ligand framework with other small molecules such as azides, CE_2 (E = O, S), and diazoalkanes.

Science objectives for 2023- 2025:

While we have observed cooperative chemistry between the metal center, ligand, and small molecule, we have primarily focused on CO, and will look at other small molecules such as H_2. We will also investigate the reactivity of uranium hydride complexes that can be made with our metallocene aryloxide complexes. For example, we have been able to isolate and structurally characterize, $[(C_5Me_5)_2(2,4,6\text{-}Me_3C_6H_2O)U(CH_2CH_3)]$, which can be hydrogenated to form the corresponding hydride. We believe this complex is a monomer/dimer equilibrium, which we are currently studying. In addition, we have different ligand platforms to examine. For example, our collaboration with Prof. Viktoria Däschlein-Gessner's laboratory is forming f element yldiide complexes and investigating their reactivity. Most importantly, our Np-237 laboratory has been out of commission for the past nearly 2 years but should be coming online in the next month. We have many results to finish and have outlined a plan moving forward with respect to our Np chemistry.

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Abstracts from National Laboratory Research Programs

Spectroscopy and Electronic Structure of Actinide Molecules

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Overall research goals: The aim of this program is to understand the fundamental electronic properties of actinide molecules using optical spectroscopy as a probe of their electronic structure, in particular the 5*f* electrons. Specifically, we aim to study the electronic properties of actinide molecules collected from gas phase reactions either directly, or by collection of these molecules in noble gas matrices. Gas phase and matrix isolation studies allow for the study of small molecule actinide species unaffected by external forces such as crystal fields or solvent effects. Studying these simple molecules with limited external forces will provide a detailed view on how ligands perturb the electronic structure of actinide ions and the extent to which the 5*f* electrons play a role in bonding between actinide and ligand. These results will provide valuable data that when coupled with computational studies, will provide more accurate descriptions of the roles of the 5*f* electrons in driving both the structure and reactivity of heavy element species.

Significant achievements during 2021- 2023: This is a new effort started at ANL in the Fall of 2022. In anticipation of building the spectroscopic capabilities to accomplish our scientific goals, this program has focused on the spectroscopic study of rare-earth and actinide hybrid double perovskites. Solid-state Raman and photoluminescence spectroscopy have been employed to probe both the structural phase transitions in these materials, and to elucidate the effects of the crystal matrix on the f-element ions in these solids. The relationship between the phase transition temperature and metal centers were examined in hybrid double perovskites ($A_2B'BX_6$, B'=Na-Rb, B=La-Gd) using variable temperature Raman (VTR) and photoluminescence (VTPL). In Figure 1 the VTPL spectra shows how changing the alkali metal in the perovskite effected its structural properties. For example, the Na- series exhibited the greatest crystal field splitting, indicating a greater departure in structure from cubic phase, and a greater perturbed crystal field around Eu that caused the splitting of spin-orbit states. A trend was also observed wherein lanthanides later in the series formed cubic phases at decreasing temperatures. A more comprehensive spectroscopic study on heavy element complexes such as these is a major aim for this program going forward.

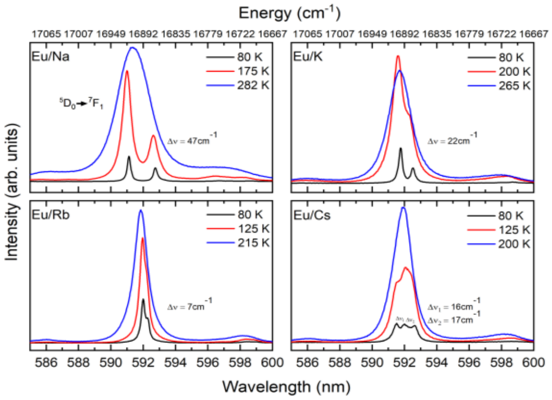

Figure 1. VTPL spectra of the $^5D_1 \leftarrow {}^7F_0$ transition in Eu^{3+}. $[(Me_4N)_2MEu(NO_3)_6]$, M= Na-Rb.

Science objectives for 2023- 2025: Matrix isolation experiments will be conducted to isolate small actinide complexes, in particular Pa and the trans-U actinides, that are not made easily through alternative methods and to study their structure and reactivity. A major focus of this project will be the observation of changes in bonding behavior between actinide atomic ions and ligands across the first half of the series. This work is being conducted in collaboration with Michael Heaven at Emory University.

Of particular interest in this project is Pa, an element in a transitional position in the periodic table between transition metal and actinide bonding behavior, where Pa is the first metal to have a valence f-orbital electron. With Th the 6*d* orbital is lower in energy than the 5*f* and the Th bonds similarly to *d*-block transition metals, but with U and the rest of the actinides the orbital energy levels are flipped. Pa stands at a crossroads among the actinides, where the 6*d* and 5*f* orbitals are very close in energy, making it a useful element to study ligand effects on the bonding characteristics in actinides and the interplay between the 5*f* and 6*d*-orbitals. Dixon et. al have predicted that in the case of PaO_2 the 5*f* orbitals are involved in bonding, giving it a linear geometric structure like uranyl, but in contrast to ThO_2 which is bent because of 5*f*-6*d* hybridization. This project will isolate PaO_2 in noble gas matrices, minimizing external influences on its electronic structure and provide experimental studies of its bonding properties. Additional studies on Pa-containing molecules with various ligand species are aimed at understanding the effects of the ligands in perturbing the electronic structure of Pa such that energy level ordering between 5*f* and 6*d* orbitals can be manipulated.

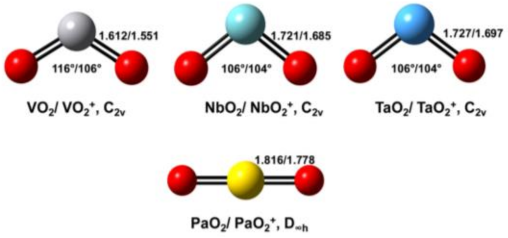

Figure 2. Optimized geometries for MO_2 and MO_2^+ (M = V, Nb, Ta, Pa). "Prediction of the structures and heats of formation of MO_2, MO_2, and M_2O_5 by Dixon et al.

Comparable species of ligands and transuranic -yl ions will be studied using matrix isolation techniques providing important spectroscopic information on the trends that develop in both their electronic structure and reactivity across the actinide series. The diverse range of oxidation states and presence of 5*f* electrons in the early transuranic elements (Np-Cm) means they are more likely to participate in more diverse bonding with ligands. Actinide oxyhalide (AnO_xCl_y) species will be investigated to study trends in bonding behavior between halide ligands and actinyl ions. Fundamental properties such as the preferred bonding structure with ligands, along with the formation and reactivity of these complexes will be investigated using matrix isolation techniques. Correlating this work to efforts in separation sciences will help in the discovery of new mechanisms for actinide separation in nuclear waste.

Publications supported by this project 2021-2023

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2. Michael L. Tarlton, Suntharalingam Skanthakumar, Danielle Hutchison, Alexander J. Gremillion, Allen G. Oliver and Richard E. Wilson, "Synthesis of an Isostructural Series of 12-Coordinate Lanthanide Nitrate Hybrid Double Perovskites with Cubic Symmetry" *Inorganic Chemistry*, **2022**, *17101-17108*, DOI: 10.1021/acs.inorgchem.2c02546
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Probing Phase Transitions and Mesoscale Aggregation in Liquid-Liquid Extraction

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Collaborators: Brian Stephenson, Subramanian Sankaranarayanan, Maria Chan, Srikanth Nayak (ANL)

Overall research goals:

Understanding the molecular-scale origins of structure and phase transitions in multicomponent, hierarchically structured liquid phases is a fundamental challenge. One important application affected by these phenomena is liquid-liquid extraction, a predominant low-energy separations technique. This technique is a go-to process for metal ion separations, including recovery and recycling of f-elements. The complex solutions encountered in these applications are widely known to feature structure at the nanoscale, typically attributed to reverse micellization. Further, a fundamental limitation to liquid-liquid extraction is the undesirable liquid-liquid phase transition, third phase formation, that occurs upon sufficient loading of metal ions into extractant-containing organic phases. In this research, we show how this solution nanostructuring and phase transition are fundamentally connected by a different aggregation mechanism: critical fluctuations.

By combining small angle X- ray scattering with molecular dynamics simulations, we demonstrate how organic phase structure over a wide range of process-relevant compositions is dominated by critical concentration fluctuations. Scaling relations provided by critical point theory provide a quantitative connection between aggregation and phase behavior, deepening our understanding of both and enabling the design of more efficient separations processes. This research is also working to close the gap between experiment and simulation. Advances in coherent synchrotron x-ray flux and detector design are enabling measurements at smaller and shorter lengthscales and timescales. Meanwhile, we are developing machine-learning-based coarse grained models to simulate mesoscopic structure for larger systems and at longer timescales without sacrificing model accuracy. Therefore, this research is poised to capitalize on two significant developments at Argonne, the APS upgrade and implementation of a new exascale computing system.

Significant achievements during 2021- 2023:

Structure in organic phases over a wide range of compositions and extractant types and molecular structures was a primary focus leading up to the APS shutdown. Recent development of a robotic liquid handing system at the beamline enabled us to collect data for ~2,000 organic phases under a wide range of conditions. While previous studies were limited by manually loading and cleaning the sample cell, this advancement has allowed us to collect SAXS patterns for over one order of magnitude more samples per beamtime. This has been essential to obtain a more universal perspective on solution structure across the phase diagram and in response to many compositional variables.

We collected temperature-dependent static and dynamic measurements near critical points to measure critical scaling laws. These are complex measurements to make at the synchrotron, where the dynamic x-ray photon correlation spectroscopy takes about an hour to collect data per temperature per sample. These measurements also require precise, custom sample chamber and temperature control equipment.

We developed a coarse-grained molecular dynamics model for a representative extractant molecule. By training the data with DFT energies and using a Tersoff formalism for the intermolecular potentials, we achieved significantly larger simulation length scales than are accessible to atomistic models. This enabled us to calculate scattering patterns from simulation trajectories and compare to experimental data over a wide q-range, validating the simulations' mesoscopic structuring and dependence on organic phase composition.

Science objectives for 2023- 2025:

Our wide range of scattering data will enable us to demonstrate the extent of critical fluctuations across the phase diagram. By breaking down system complexity and systematically studying the role of adding each component to the organic phase---water, acid, metal ions and different combinations of these---we can isolate the role of each. Additionally, through scaling laws, we can map compositional variables onto temperature and composition dimensions. This dimensional reduction, enabled by the unique universality of critical phenomenon, will allow us to predict phase behavior and design better extraction systems. Ongoing efforts include sample characterization---how much water, acid and metal are extracted in a sample---to relate the compositions to an effective reduced temperature. This will help us answer important questions that we have identified related to the unique characteristics of different f-element, such as why light lanthanides increase the critical temperature more, on a per-molecule basis, than heavy lanthanides.

Expanding the coarse-grained MD models to include aqueous solutes is a primary objective for the next year. We implemented a flexible formalism for nonbonded interactions, so we expect that through DFT fitting and use of generic mixing rules that we can expand the complexity of simulated systems. We have collected expansive scattering data to validate structure and phase behavior of simulations. We also demonstrated the ability to calculate dynamic "speckle" patterns from simulation, analogous to single-pixel events in x-ray photon correlation spectroscopy measurements, enabling correlations of dynamic behavior across length scales.

Lastly, we are also developing thermodynamic models to predict phase equilibria and calculate phase diagrams. By virtue of the experimental data that we have collected, we can readily validate such models. These models will provide insight into the molecular-scale behavior of separation systems by comparing, e.g., predicted phase equilibria for a given set of species to our experimentally measured composition data. Ultimately, by tying thermodynamic predictions of phase behavior to observed critical fluctuations, we can generate readily-validated predictions for phase boundaries and learn how each component in the separation system, such as f-element identity, broadly affects structure and phase transitions.

Publications supported by this project 2021-2023

Servis, Michael J., Nayak, Srikanth, & Seifert, Soenke. "The pervasive impact of critical fluctuations in liquid–liquid extraction organic phases." *The Journal of Chemical Physics,* **2021**, 155 (24), 244506, doi.org/10.1063/5.0074995.

Sheyfer, Dina and Servis, Michael J and Zhang, Qingteng and Lal, Jyotsana and Loeffler, Troy and Dufresne, Eric and Sandy, AR and Narayanan, Suresh and Sankaranarayanan, Subramanian and Szczygiel, R and Maj, P and Soderholm, L and Antonio, Mark and Stephenson, G. Brian. "Advancing chemical separations: Unraveling the structure and dynamics of phase-splitting in liquid-liquid extraction." *The Journal of Physical Chemistry B,* **2022**, 126 (12), 2420–2429, doi.org/10.1021/acs.jpcb.1c09996.

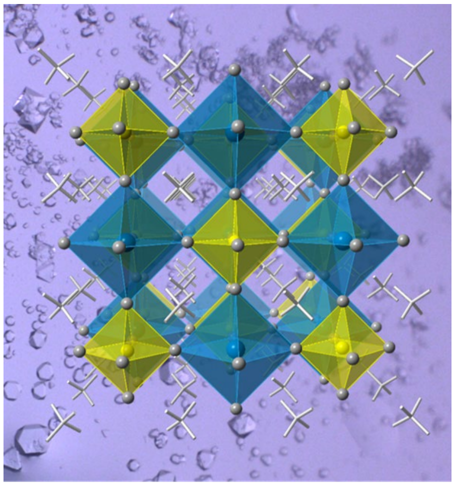
Periodic Properties in Actinide-Ligand Interactions

Richard E. Wilson

Chemical Sciences and Engineering Division, Argonne National Laboratory
Collaborators: Srikanth Nayak, Thomas Persinger, S. Skanthakumar, Lynda Soderholm, Michael Tarlton, Nicole Byrne, Danielle Hutchison, Andrey Yakovenko Argonne National Laboratory. Valerie Vallet, Hanna Oher, Andre Severio-Gomes, CNRS, University of Lille, France, David A. Dixon, University of Alabama, Suzanne Bart, Purdue University, Justin Walensky, University of Missouri, Christopher Cahill, George Washington University, James Blakemore, University of Kansas, Tori Forbes, University of Iowa.

Overall research goals: This research program is aimed at understanding the periodic trends in the chemistry, reactivity and speciation of actinide ions and molecules with the goal of understanding the fundamental properties of actinide f-electrons and their influence on their chemistry. We use a multifaceted approach combining chemical synthesis, structural characterization in solids and liquids, along with spectroscopic and computational studies to realize these goals.

Significant Achievements during 2021-2023: In our efforts to assemble and study periodic series of actinide molecules and compounds we have focused on leveraging chemical synthesis of actinide, lanthanide, and transition molecules containing simple inorganic anions. These synthesized materials provide a launching point for studying f-element electronic structure and chemical properties and serve as benchmarking compounds for study of their structure and reactivity in solutions. In particular we investigated the structural chemistry of trivalent f-element ions with nitrate ligands, developing a complete periodic series of Am, Cm, and rare earth nitrate complexes with quaternary amines as the counter-cations. These studies have resulted in the identification of effects of the size of the quaternary amines on the nitrate coordination to the f-ions as well as a new class of centrosymmetric f-element nitrato perovskite phases that are centrosymmetric, thus providing a direct entry to studying the electronic structure of the actinides where the d- and f-orbitals are prohibited from mixing by symmetry. These trivalent complexes with nitrate complement our earlier studies on trans-U thiocyanate complexes.



Crystals of the $Am(NO_3)_6^{3-}$ complexes and their crystallographic packing. The Am and Cm complexes reported represent the first homoleptic nitrate and thiocyanate complexes of the trivalent actinides.

We have investigated the chemistry of actinyl nitrate and actinyl coordination complexes in the solid state using single crystal diffraction and vibrational spectroscopy extending our studies of periodic series of actinide ions to the hexavalent ions. These studies focused on the structure and bonding properties of the actinyl ions, U, Np, and Pu, as probed by vibrational spectroscopy and computational studies of their electronic structures. These solid state studies are being followed on by studies of actinyl complexation in solution and the effects of ion-pairing interactions on their speciation, reactivity, and thermodynamic properties as revealed through spectroscopic and electroanalytical studies of these ions in solution.

Science objectives for 2023-2025:

- Study the chemistry of the tetravalent and trivalent protactinium in ligand systems such as nitrate, halides and thiocyanate to understand the effects of ligand coordination on the interplay of the d- and f-electrons at Pa.
- Experiments to focus on the spectroscopic properties of tetravalent and trivalent protactinium along with the other early actinides Th-Am to understand the progression of f-electron behavior across the actinide series.
- Study, and correlate the solution speciation of actinide complexes in non-aqueous solvents using high-energy X-ray scattering techniques and other synchrotron based techniques.
- Correlate these studies with other ongoing efforts in separations sciences and our understanding of the energy partitioning that drives separations processes.

Publications supported by this project 2021-2023

1. Hanna Oher, Andre Severo Gomes, Richard E. Wilson, David D. Schnaars, Valerie Vallet. “Does the bending of uranyl influence its spectroscopy and luminescence?” chemRxiv 2023. 10.26434/chemrxiv-2023-m3spw

2. Michael L. Tarlton, S. Skanthakumar, D. Hutchison, A. Gremillion, A. G. Oliver, Richard E. Wilson. “Synthesis of an Isostructural Series of 12-Coordinate Lanthanide Nitrate Hybrid Double Perovskites with Cubic Symmetry.” *Inorganic Chemistry*. 61(43), 17101-17108. 2022

3. Michael L. Tarlton, S. Skanthakumar, V. Vallet, Richard E. Wilson. “Hexanitrato complexes and hybrid double perovskites of Am 3+ and Cm 3+” *Chemical Communications*. 58(85), 11997-12000. 2022.

4. Michael L. Tarlton, Richard E Wilson. “Synthesis and Characterization of Homoleptic Rare Earth Nitrato Complexes with the Quaternary Ammonium Cations Et4N+ and nPr4N+.” *European Journal of Inorganic Chemistry.* 35, e202200506. 2022.

5. C. Tamain, M. Autillo, D. Guillaumont, L. Guerin, R. E. Wilson, C. Berthon. “Structural and Bonding Analysis in Monomeric Actinide(IV) Oxalate from Th(IV) to Pu(IV): Comparison with the An (IV) Nitrate Series.” *Inorganic Chemistry*. 61(31), 12337-12348. 2022.

6. Richard E. Wilson, Samantha Stegman, Michael Tarlton, S. Skanthakumar. “Reactions of Np(V) in Alkali-Metal Hydroxides.” *Inorganic Chemistry*. 60(23), 17480-17486. 2021.

Autonomous Discovery of Selective Separation of f-Elements for Clean Energy

Ping Yang, [1] *Principal Investigator (PI); Joshua Schrier,*[2] *(Co-PI); Stosh A Kozimor,*[3]*(Co-PI); Sara L Adelman,*[3] *Enrique R Batista,*[1] *Marc J Cawkwell,*[1] *Nicholas E Lubbers,*[4] *Danny Perez* [1]

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Graduate Students: Jiyoung Lee (University of Texas Austin), Logan Augustine (University of Iowa)
Collaborators: Tori M Forbes (University of Iowa), Graeme Henkelman (University of Texas Austin)

Overall research goals:

A grand challenge in chemical separations currently stands in the way of the development of abundant, affordable, and reliable forms of clean energy. Critical 4*f* rare earths and minor 5*f* actinides are all +3 *f*-elements with similar chemistries, but often very different applications. Separating these elements from one another in high purity and in high yield is essential to the success of the DOE Clean Energy Initiative, but separation is extremely difficult given their nearly indistinguishable chemical characteristics. Addressing this challenge would advance extraction, recovery, and recycling of critical rare earth materials used, e.g., in permanent magnets for wind turbines and electric vehicles. It would also enable a next generation of nuclear reactors compatible with advanced spent fuel recycling methods. The successful deployment of decarbonizing techniques in the US is at risk unless a reliable supply of these critical materials can be secured. Concerningly, their supply heavily relies on imports, often from a single foreign supplier, making the importance of developing new efficient separation processes even more critical. Despite extensive community efforts in the last seven decades, the solution to the +3 *f*-element separation problem remains elusive, largely because of the large number of factors that contribute to successful separations, e.g. extractant, solvent, aqueous and organic matrix identity, binding kinetics, hold-back agent, temperature, counter-ions, process conditions, etc. The lack of predictive models for 4*f*/4*f* and 4*f*/5*f* separations has made innovation slow, incremental, and labor intensive, resulting in only fragmentary exploration of the vast chemical space. Our central scientific mission is to accelerate *f*-element separation science design using an integrated data-driven autonomous discovery loop that explores the vast space of separation chemistries with minimal human bias, in a way that provides fundamental molecular-level understanding of the separation process. Toward this end, this proposal concentrates on separation of critical rare earth materials from one another and from actinides relevant to nuclear energy generation.

Significant achievements during 10/2022- 2023:

High-throughput Advanced Simulations

We introduce *Architector*, a high-throughput in-silico synthesis code for s-, p-, d-, and f-block mononuclear organometallic complexes capable of capturing nearly the full diversity of the known experimental chemical space. Beyond known chemical space, *Architector* performs *in-silico* design of new complexes including any chemically accessible metal-ligand combinations. *Architector* leverages metal-center symmetry, interatomic force fields, and tight binding methods to build many possible 3D conformers from minimal 2D inputs including metal oxidation and spin state. Over a set of more than 6,000 x-ray diffraction (XRD)-determined complexes spanning the periodic table, we demonstrate quantitative agreement between Architector-predicted and experimentally observed structures. Further, we demonstrate out-of-the box conformer generation and energetic rankings of non-minimum energy conformers produced from *Architector*, which are critical for exploring potential energy surfaces and training force fields. Overall, Architector represents a transformative step towards cross-periodic table computational design of metal complex chemistry.

High-throughput Experimental Separation Process

Over the last year, we have begun to utilize the LANL Super Separator to explore the large experimental space that defines this project. The LANL Super Separator is a combinatorial separations instrument that can be used for *f*-element containing samples. The SUPER SEPARATOR was designed for handling solutions comprised of organic solvents as well as corrosive mineral acids. It was also designed to automate nearly every manipulation associated with general chemical reactions, such as dispensing organic and aqueous solvents (10 uL - 10 mL with accuracy and precision of ± 5-10%), solid dispensing (1 mg - 25 g with accuracy and precision of ± 5-10%), heated and timed vortexing for controlling contact time and temperature, and filtering. Using specialized software to combine these individual tasks into experimental workflows, the SUPER SEPARATOR can automate the liquid/liquid extractions that will benchmark our computational models. We have been working to establish an integrated workflow that characterizes the distribution ratios of *f*-elements in solvent extraction experiments with systematic variations in the parameters that describe a separation, i.e. extractant identity, hold-back agent identity, acid identity, acid concentration, ionic strength, mixing rate, temperature, contact time, and phase transfer agent concentration. With this automated workflow in place, we will begin to explore the vast experimental space that defines this project.

Science objectives for 2023- 2025:

Our goal is to directly address the core challenge for +3 *f*-element separation by overcoming the sheer size of the chemical space and the limited extent to which it has been explored. We will take an unbiased look at this chemical space by using high-throughput experiments and calculations integrated together using modern autonomous discovery techniques. Our team aim to develop efficient simulation methods, machine learning (ML) approaches for improving extractant design and separation processes.

Publications supported by this project 10/2022-2023

- Michael G Taylor, Daniel J Burrill, Jan Janssen, Enrique R Batista, Danny Perez, Ping Yang; "Architector: high-throughput cross-periodic table 3D complex builder", *Nature Communications,* **2023**, *In Press*.
- Logan J Augustine, Joseph M Kasper, Tori Z. Forbes, Sara E Mason, Enrique R Batista, Ping Yang; "Influencing Bonding Interactions of the Neptunyl(V, VI) Cations with Electron-Donating and -Withdrawing Groups", *Inorganic Chemistry,* **2023**, *In Press.*

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- Logan J Augustine, Joseph M Kasper, Tori Z. Forbes, Sara E Mason, Enrique R Batista, Ping Yang; "Influencing Bonding Interactions of the Neptunyl(V, VI) Cations with Electron-Donating and -Withdrawing Groups", *Inorganic Chemistry,* **2023**, *In Press.*

Heavy Element Chemistry at Los Alamos National Laboratory

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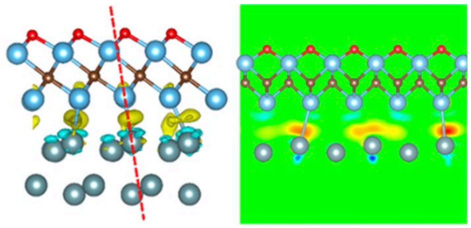
Collaborators: Thomas Albrecht-Schönzart (Colorado School of Mines), Nickolas Anderson (LANL), David Emslie (McMaster), William Evans (UC – Irvine), Skye Fortier (UT – El Paso), Trevor Hayton (UC – Santa Barbara), Stephen Liddle (Manchester), Nikolas Kaltsoyannis (Manchester), Karah Knope (Georgetown), Veronika Mocko (LANL), Francisca Rocha (LANL)

Overall Research Goals: A ubiquitous challenge with plutonium (Pu) and the other actinides exists that is obstructing the Department of Energy's (DOE) missions in energy, environment, and national security. The issue stems from insufficient understanding about fundamental 5*f*-element chemistry. This knowledge gap impedes innovation for: (*1*) designing next generation nuclear reactors, those that are compatible with spent fuel recycling, (*2*) resolving environmental issues that linger from nuclear activities, and (*3*) ensuring the safety, security, and effectiveness of the U.S. nuclear stockpile. Talks presented at the 2023 Heavy Element Chemistry PI meeting will describe LANL's efforts to address this shortfall and advance understanding of actinide electronic structure to the point that 5*f*-element chemistry is easier to predict and control.

Significant Achievements, 2021-2023: Numerous efforts have advanced understanding of actinide chemistry and revealed that the actinides are able to adopt new structure types that are inaccessible to main group and *d*-block transition elements. Understanding the bonding and reactivity within these novel structure types is critical for developing more sophisticated descriptions of 5*f*-element chemistry. Toward this end, we demonstrated that aqueous acidic stock solutions can be used to prepare $AnCl_4(DME)_2$ compounds. These starting materials can be used to support the synthesis of air- and moisture-sensitive compounds for a wide range of actinide metals, e.g. Th, U, Np, Pu, Am, Cm, and Cf. With this synthetic technology in hand, we have begun defining trends in electronic structure and reactivity as a function of actinide (An) vs lanthanide (Ln) metal identity. For example, using the Cp^{tet} anion ($C_5Me_4H^{1-}$), we began mapping energy shifts in the 6*d*-5*f* transitions across the $AnCp^{tet}{}_3$ series. Another example included the more electron donating Cp* anion ($C_5Me_5{}^{1-}$). These reactivity studies showed that within the $Cp^*{}_2An(I)(THF)$ framework complexation of *N*-heterocyclic carbenes generated An–C bond distances that were shorter than analogous Ln–C distances, particularly for the Am/Nd comparison pair. We have also carried out studies that deploy chalcogen (S, Se) containing ligands. This platform was used to assess covalency trends for An's vs Ln's. Finally, we have been examining how covalency in metal-ligand bonding interactions varies as a function of metal identity. These studies suggested that molecules containing formal An=C bonding were more covalent than Ln=C bonding.

Another way in which we have been attempting to fill important knowledge gaps in heavy element chemistry is by using molten salt matrixes to correlate electronic structure and bonding with chemical reactivity and physical properties. We believe developing methods to define actinide speciation and reactivity in molten salts will enable us to (*1*) characterize how the inner vs. outer coordination spheres influence 5*f*-orbital mixing and (*2*) correlate those electronic effects with observable actinide redox chemistry. If successful – and the probability for success seems high – we will directly address the longstanding and important hypothesis in actinide chemistry that 5*f*-orbital participation in bonding substantially contributes to actinide chemistry and physics.



Side view of UO_2 coated with a 2D layer of Ti_2CO_2. The density plot shows accumulation (yellow) and depletion (blue) of charge respect to the un-coated surface.

The development of advanced computational methodologies is critical for the characterization of actinide compounds and the reactivity of actinides in the complex chemical environments described above. As a representative example of our efforts on this front, we began using a synergistic combination of density functional theory (DFT) and multi-configurational wavefunction methodologies, in conjunction with relativistic Hamiltonians. This approach provides accurate analysis and prediction of actinide electronic structure, bonding, and spectroscopic properties. One recent study focused on the theoretical analysis of organoneptunium systems – $(({}^{t}\mathrm{Bu}_2\mathrm{P})\mathrm{ONO})\mathrm{NpCl}_2(\mathrm{dtbpy})$ and $(\mathrm{indenide})(({}^{t}\mathrm{Bu}_2\mathrm{P})\mathrm{ONO})\mathrm{NpCl}$ – and their uranium analogues. Whereas differences in chemical bonding (bond lengths and bond orders) indicated that the indenide ligand conferred more stability to the An-ONO core, the differences between U(IV) and Np(IV) compounds were more subtle. Another research example focused on surface chemistry and corrosion processes for actinide metals. Along these lines, six representative 2D nanomaterials were selected from the 2D material library. Calculations were then carried out to characterize binding abilities of these materials to the surface of uranium and to determine which material had the highest probability of preventing uranium metal corrosion. Ti_2C-based MXenes (Ti_2CO_2 and Ti_2CO) had binding energies that were quite high, larger than -2.0 J/m^2 than the other test candidates. The binding strength was traced back to charge transfer at the interface, which also lead to the quenching of surface magnetic moments. It was found that the binding strength was not sensitive to the phase and surface orientation of uranium metal. Among all the studied 2D nanomaterials, Ti_2C-based MXenes were the most suitable coatings for uranium metal and may find use in technologies that prevent metal corrosion.

Scientific Objectives for 2023-2025: The proposed research supports HEC's mission to "*resolve the f-electron challenge and master the chemistry and physics of actinides*." It is also in the spirit of how the U.S. historically leveraged fundamental actinide research to identify creative solutions for technical problems facing the nation. Our research aim will continue arming the DOE with adequate acumen for "Controlling Matter and Energy at the Electronic, Atomic, and Molecular Level" and providing a foundation for researchers and engineers to develop innovative solutions for important applied actinide related problems that society faces today.

Publications supported by this project 2021-2023

Goodwin, C. A. P.; Su, J.; Stevens, L. M.; White, F. D.; Anderson, N. H.; Auxier II, J. D.; Albrecht-Schönzart, T. E.; Batista, E. R.; Briscoe, S. F.; Cross, J. N.; Evans, W. J.; Gaiser, A. N.; Gaunt, A. J.; James, M. R.; Janicke, M. T.; Jenkins, T. F.; Jones, Z. R.; Kozimor, S. A.; Scott, B. L.; Sperling, J. M.; Windorff, C. J.; Yang, P. Ziller, J., "Isolation and Characterization of a Californium Metallocene" *Nature*, **2021**, *599*, 421. DOI: 10.1038/s41586-021-04027-8

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Resolving the *f*-electron challenge with scanning probe microscopy/spectroscopy

Miles F. Beaux II, Principal Investigator

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Graduate Students: Benjamin Heiner (ND)
Postdoc Researchers: Aparna Subramanyam, Greta Chappell, Natalie Rice (LANL)
Collaborators: Stosh Kozimor, Ping Yang, Paul Tobash (LANL), Ryan Baumbach (FSU), Thomas Albrecht-Schoenzart (CSM), Krzysztof Gofryk (INL), James Tobin (UWOSH), Shanna Estes (CU)

Overall research goals: The objectives of this project are to probe the electronic structures of a series of molecular crystal and bulk single-crystal actinide (An) carbide, nitride, oxide, and intermetallic samples using scanning tunneling spectroscopy (STS) techniques. Specifically, the neptunium (Np), plutonium (Pu), and americium (Am) series of actinide elements are targeted to investigate instabilities existing within the itinerant to localized crossover. The instabilities in electronic structure that occur near this transition are thought to be responsible for the complexity of material behaviors observed for derivative compounds of these actinide elements. By performing scanning tunneling spectroscopy (STS) on a range of bulk single crystal actinide intermetallic compounds and molecular crystals, a seamless mapping of both the occupied and unoccupied electronic structures for these materials can be obtained using a local probe, providing a means by which their complex chemical and physical properties can be understood.

Significant achievements during 2021- 2023:

- Sample Preparation
  - The facility for production of actinide samples has been approved as a hazard category 3 nuclear facility.
  - Authorization to begin working with plutonium materials has been granted.
  - Bulk single crystals of $PuCoGa_5$ have been grown and mounted for transport and measurement in the STM/STS instrument. These are the first Pu crystals produced in the new RLUOB facility since cessation of activities in the CMR facility.
  - Molecular crystals are being prepared on standards to test the feasibility of direct STM/STS probing of molecular samples for HEC integration.
  - Plan to obtain Np metal source material from INL is being pursued for Np sample growth.
- STM/STS System and Measurements
  - An updated control system for the STM/STS instrument has been set up and tested.
  - Cryogenic cooling components have been ordered.
  - A method for mounting the actinide samples has been developed specifically for this work, and tested with surrogate material (i.e., non-radiological)
  - STM and STS probing of small plutonium boride crystals has been conducted.
  - Authorization has been obtained for the addition of Np and Am operations to the already existing plutonium operations.
- Theory and Modelling
  - A non-integer orbital occupancy representation for multiconfigurational ground states resulting from superposition mixing between near-energy degenerate occupancy configurations has been formalized.
  - By considering the occupancy configurations as statistical mechanics macrostates, and the possible permutations of electrons as microstates within those microstates, an

  over-approximation of entropy for elemental ground state electronic structures has been worked out.
  - Pu-Sb structure stabilities were calculated to predict stable stoichiometries. Previously grown PuSb and $PuSb_2$ were identified, as well as other potentially stable stoichiometries with Pu_4Sb_3 predicted to be the most stable.

- Presentations and Posters
  - **(Poster)** Beaux, M.F. "From Combinatorics to an Over-Approximation of Entropy in Elemental Multiconfigurational Ground State Electronic Structures", *2nd International Workshop on Theory Frontiers in Actinide Science: Chemistry & Materials*, Feb. 2023, Santa Fe, NM.
  - **(Invited Talk)** Beaux, M.F. "A Thermodynamics-Like Interpretation of Multiconfigurational Ground State Electronic Structures", *Idaho National Laboratory* (recorded), Feb. 2023, Idaho Falls, ID.
  - **(Invited Talk)** Beaux, M.F. "The Non-Integer Occupancy Ground State Hypothesis", *AVS 68th International Symposium & Exhibition*, Nov. 2022, Pittsburgh, PA.

Science objectives for 2023- 2025:

- Additional bulk single crystal An intermetallic samples [AnX (X= Sb, Te), AnX_2 (X= Sb), AnX_3 (X= In, Pt, Ga), An_3Ga, $AnMX_5$ (M= Co, Rh, Ir; X= In, Ga), $AnRu_2Si_2$, and $AnPt_2In_7$] will primarily be produced via the molten-metal flux growth technique, mounted for STM/STS, and transported to the system. Growth of Pu_4Sb_3 will be attempted to test its stability prediction.

- Cryogenic cooling components will be installed and authorized, and low temperature electronic structure mapping via STS will be performed for the listed compounds.

- In addition to these crystalline materials, processes are being developed to introduce actinide containing molecular crystals into the STM/STS system for direct measurement.

- Theoretical methods will be developed for determining the contributing occupancy configuration macrostates as a function of temperature based on the non-integer occupancy hypothesis.

- A methodology for the theoretical modelling of the electronic structures will be developed. Specifically, a methodology for Density Functional Tight Binding (DFTB) parameters for interfaces will be developed, and then applied to model the electronic structures of the planned materials and molecular samples. Comparison of the experimental results and the modelling will be an ongoing effort throughout this FWP.

Publications supported by this project 2021-2023

- Miles F. Beaux II, "An Over-Approximation of Entropy for Elemental Multiconfigurational Ground State Electronic Structures" Submitted to *AVS Quantum Science* (Under Review)

- Aparna Subramanyam and Ping Yang "Exploring structural and electronic properties of Pu-Sb intermetallic compounds" (tentative title, paper in preparation)

Influence of Actinide and Transactinide Electronic Structure on Chemical Reactivity

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Collaborators: David Britt (UC Davis), David Dixon (U Alabama), Nikolas Kaltsoyannis (U Manchester), Laurent Maron (U Toulouse)

Overall research goals: This research 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.

Significant achievements during 2021- 2023:

Masked U(I) reactivity in a U(II) arene complex. Our previous investigations into U amidates led to the synthesis of the anionic bis(arene) U^{I} synthon $[U(TDA)_2][K[2.2.2]cryptand]$ (TDA = N-(2,6-di-iso-propylphenyl)pivalamido) (**Fig. 1**). Electron paramagnetic resonance (EPR) spectroscopy, magnetic susceptibility measurements, and density functional theory (DFT) calculations all provide strong evidence that the electronic structure of this compound is best described as a U^{II} center bound to a mono-reduced arene. As with nearly all other published examples of U^{II}, the complex is supported by δ-bonding interactions with U frontier orbitals. We intend to extend this ligand framework to Np and Pu to yield low-valent, bound-arene $An(TDA)_2$ species. These compounds will be used to explore the extent of and subtle differences in δ-bonding in these TRU actinides.

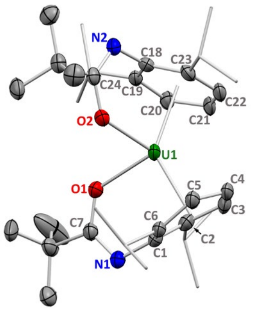

Fig. 1. Molecular structure of $[U(TDA)_2]^{1-}$. A $[K[2.2.2]cryptand]^{+}$ molecule is omitted.

Development of new supporting ligands to control electronic structure and reactivity. There are still relatively few ligands in f-block organometallic chemistry that bind to the f-block metal cations using only carbon atoms, despite the field now being more than fifty years old. Carbocyclic ligands are unique in the f-block for supporting both high valent and low valent complexes. Current work is providing new architectures for TRU complexes to better prove the effect of symmetry on orbital covalency, as well as contributing to the stabilization of highly reactive species. N-heterocyclic carbenes (NHCs) have seen application as σ-donating ligands to metals across the periodic table, and are highly tunable. We have made a family of f-block complexes of tris(NHC)chelates [**C3**], to provide a new, strongly electron donating ligand field for f-block metal cations. Scale-down chemistry of early and late Ln and early An has been successful (**Fig. 2**).

In unpublished work, we have developed complexes with highly polarized An-C bonds allowing for rapid protonolysis reactivity, in order to provide access to new bonding motifs that are otherwise inaccessible for short-lived, rare isotopes. Such polarized bonds are of additional interest as small changes in covalency can have outsized impacts on the observed reactivity, allowing for further investigation of the subtle changes in electronic structure across the An series.

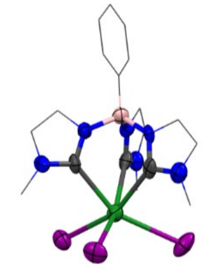

Fig. 2. Solid-state structure of **$U(C3)I_3$.**

Understanding and Controlling Actinide Reactivity in the Gas Phase. Reactivity of oxo bonds in actinyl(V) dioxo cations, AnO_2^+, was assessed by conversion of An=O to $An(OH)_2$, either as the product of H_2O chemisorption or as an intermediate in oxo-exchange with $H_2{}^{18}O$. Oxo-exchange for PaO_2^+ to CmO_2^+ shows activation of the strong bonds in PaO_2^+,whereas the weaker AmO_2^+ bonds are inert. After AmO_2^+ a reactivity turn appears for CmO_2^+, which exhibits oxo-exchange. Computations suggest efficient oxo-exchange reflects dominant 6d bonding in the likes of ThO_2 and PaO_2^+, whereas lower reactivity reveals 5f bonding in PuO_2^+ and AmO_2^+. PrO_2^+ was identified as the first 4f "lanthanyl" analogous to the 5f actinyls. Coordination dimers having uranyl (V) and (VI) moieties linked by dicarboxylates, $^-OOC\text{-}(CH_2)_n\text{-}COO^-$, allow control of structures and bonding by varying the length n. For short linkers, $n = 1$ or 2, the two uranyl are constrained to non-interacting quasi-parallel orientations, while long flexible linkers, $n \geq 3$, facilitate $U^V\text{-}U^{VI}$ "cation-cation interactions". In other work, actinyl(V) coordinated by sulfonate, $An^VO_2(RSO_2)_2^-$, exhibited controllable reactivity. Dissociation of benzenesulfonates ($R = C_6H_5$) induced hydrolytic replacement of an RSO_2^- by OH^- to yield $An^VO_2(RSO_2)(OH)^-$, whereas the weaker C-S bond in methanesulfonates ($R = CH_3$) cleaved to yield $An^VO_2(CH_3SO_2)(SO_2)^-$. Replacement of the SO_2^- ligand in the latter by O_2 formed $AnO_2(CH_3SO_2)(O_2)$, which is a U^{VI} peroxide whereas Np^V and Pu^V superoxides. Characterization of $[(UO_3)(NO_3^-)]^-$ and $[(UO_3^+)(NO_3^-)_2]^-$ by reactivity and IRMPD spectroscopy confirmed better donor ligand character for the equatorial oxo in neutral UO_3—i.e. "uranyl oxido" $(UO_2^{2+})(O_{eq}^{2-})$—compared with oxyl in cationic UO_3^+—i.e. $(UO_2^{2+})(O_{eq}^-)$. Short $U{=}O_{ax}$ and long $U{=}O_{eq}$ bonds in UO_3 epitomize the inverse-trans effect that results in *trans* bonds stronger than *cis*. Bond dissociation energies of Ln halides and hydroxides, LnX and LnX^+ (X = F, Cl, OH) suggest remarkably similar hydroxide and fluoride bonding, which led to an assessment of An halide BDEs towards characterizing their bonding as ionic, covalent or intermediate. Ln complexes containing a terminal Ln=O oxo bond were found to exhibit unexpectedly higher stability of tetravalent Pr *vs.* Tb.

Science objectives for 2023- 2025:

- Future gas-phase chemistry efforts will focus on atom-at-a-time studies of reactivity of the late An elements Md, No and Lr, and the transAn Rf, Db, Sg and beyond. This work will explore fundamental superheavy element chemistry in collaboration with PIs Gates and Pore.
- We will further develop the use of all-carbon donor ligand sets to support transPu reactivity studies, and to manipulate redox.
- Additional work will focus on controlling oxo-group reactivity of the actinyl ions.

Publications supported by this project 2021-2023:

Tian Jian, Monica Vasiliu, Zachary R. Lee, Zhicheng Zhang, David A. Dixon and John K. Gibson, "Dinuclear Complexes of Uranyl, Neptunyl, and Plutonyl: Structures and Oxidation States Revealed by Experiment and Theory," *J. Phys. Chem. A*, **2022**, *126*, 7695–7708, DOI: 10.1021/acs.jpca.2c06121.

Ziad Shafi and John K. Gibson "Lanthanide Complexes Containing a Terminal Ln=O Oxo Bond: Revealing Higher Stability of Tetravalent Praseodymium versus Terbium,", *Inorg. Chem.*, **2022**, *61*, 7075-7087, DOI: 10.1021/acs.inorgchem.2c00525.

John K. Gibson, "Bond Dissociation Energies Reveal Participation of d-Electrons in f-Element Halide Bonding," *J. Phys. Chem. A*, **2022**, *126*, 272-285, DOI: 10.1021/acs.jpca.1c09090.

Jeffrey T. Kwarsick, Jennifer L. Pore, Jacklyn M. Gates, Kenneth E. Gregorich, John K. Gibson, Jiwen Jian, Gregory K. Pang and David K. Shuh, "Assessment of the Second-Ionization Potential of Lawrencium: Investigating the End of the Actinide Series with One-Atom-at-a-Time Gas-Phase Ion Chemistry Technique," *J. Phys. Chem. A.*, **2021**, *125*, 6818-6828, DOI: 10.1021/acs.jpca.1c01961.

Mark D. Straub, Erik T. Ouellette, Michael A. Boreen, R. David Britt, Khetpakorn Chakarawet, Iskander Douair, Colin A. Gould, Laurent Maron, Iker Del Rosal, David Villarreal, Stefan G. Minasian,* and John Arnold*, "A Uranium(II) Arene Complex That Acts as a Uranium(I) Synthon", *J. Am. Chem. Soc.* **2021**, *143*, 19748–19760. DOI: 10.1021/jacs.1c07854.

Role of f Orbital Interactions in Determining Heavy Element Physical Properties

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Stefan G. Minasian,[1] *David K. Shuh*[1]

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Collaborators: Jochen Autschbach (SUNY Buffalo), Sergei Butorin (Uppsala U), Herman Cho (PNNL), Claude Degueldre (U Lancaster), William Evans (UCI), Shane Galley (CS Mines), Trevor Hayton (UCSB), Lingfeng He (NCSU), Joseph Kasper (LANL), Kristina Kvashnina (FZDR), Stosh Kozimor (LANL), Michael Neidig (U Rochester), Taoxiang Sun (Tsinghua U), Justin Walensky (U Missouri), Ping Yang (LANL)

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. New techniques, methods, and instrumentation are being developed to enable and improve our capability to determine the physical properties of the An, with an emphasis on the transuranics. Efforts primarily focus on synchrotron radiation- and transmission electron microscope (TEM)-based approaches.

Significant achievements during 2021- 2023:

Carbon K-edge XAS of Actinide Organometallics. Previously, the amount of f-orbital mixing in the δ-bonding orbitals of e_{2u} symmetry was found to be nearly equivalent for $(C_8H_8)_2Ce$ (24% C 2p, 76% Ce 4f) and $(C_8H_8)_2U$ (28% C 2p, 71% U 5f). However, differences in the amount of orbital overlap result in a much greater increase in stability due to covalent bonding for $(C_8H_8)_2U$. To explore the limits of this behavior we conducted C K-edge XAS measurements on $[(C_7H_7)_2U]^{1-}$, which is the only example of a pentavalent An metallocene. Because $[(C_7H_7)_2U]^{1-}$ is known to have a multiconfigurational ground state, *ab initio* calculations by Autschbach were necessary to accurately simulate the spectra (**Fig. 1**). Enhanced 5f-δ mixing was also observed for $[(C_7H_7)_2U]^{1-}$ in comparison with tetravalent $(C_8H_8)_2U$, as a possible consequence of lower energy 5f orbitals for the U^{5+} vs. U^{4+} metals.

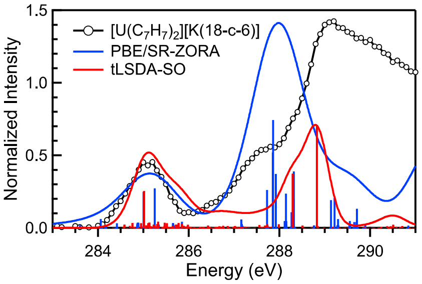

Fig 1. Experimental C K-edge XAS for $[U(C_7H_7)_2]^{1-}$ and calculated spectra using scalar-relativistic TDDFT (blue) and *ab initio* calculations with spin-orbit coupling (red). Both calculations show the similar low-energy features, higher energy transitions are best reproduced with *ab initio* methods.

Quantifying Overlap in Actinide Hexahalides. Many trends in An covalency can be rationalized by accounting for changes in 5f orbital energies, and without invoking overlap. Quantifying orbital overlap is important for efforts to harness covalency to control An stability. Because values for the F and Cl valence orbital ionization potentials are known precisely, we hypothesized that comparing orbital mixing in MF_6^{2-} and MCl_6^{2-} would provide an opportunity to control for changes in orbital energy and quantify the effect of orbital overlap. Previous Cl K-edge XAS studies on $AnCl_6^{n-}$ (An = Th, U, Np, Pu, Am; n = 1-3) set the stage for these experiments. The analogous octahedral hexafluorides, AnF_6^{n-}, were carefully selected for this study because results from F K-edge XAS can be compared directly to findings from the earlier Cl K-edge XAS studies. The highly symmetric octahedral ligand environment is also preferable for interpretation of the XAS and DFT calculations. During the previous period, high-yield, high-purity syntheses were developed for $(Ph_4P)_2MF_6$ salts, where M = Ti, Zr, Hf, Ce, U, Np, Pu (**Fig. 2**). High quality F K-edge spectra and DFT calculations (with LANL) were also obtained for $(Ph_4P)_2MF_6$, where M = Ti, Zr, Hf, setting the stage for ongoing work with actinide systems.

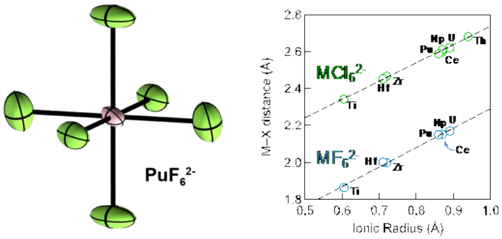

Fig. 2. *Left*, crystal structure of $(Ph_4P)_2PuF_6$ (Ph_4P^{1+} cations omitted for clarity). *Right*, plot showing a linear correlation between M ionic radius and M–X distance for MX_6^{2-} molecules, indicating that there is no structural evidence for covalent bonding.

Variable high-pressure single crystal XRD studies. Electronic structure manipulation through geometry for f-block complexes is an emergent field, with potential applications in molecular- and quantum-scale sensing and computing applications. By monitoring structural changes in simple An aryloxide, and related complexes (An = Th, U) we demonstrate the extent to which covalency can be manipulated by externally-applied conditions, and understand the reasons for unanticipated geometric preferences in the f-block. Single-crystal diffraction was carried out on crystals of $An(OAr)_4$ (An = Th, U), at pressures up to 4.3 GPa. DFT studies using QTAIM and NBO analysis of the natural localized molecular orbitals show that differences in the metal involvement in bonding is primarily the result of the periodic increase in f-orbital involvement (Th < U , **Fig. 3**).

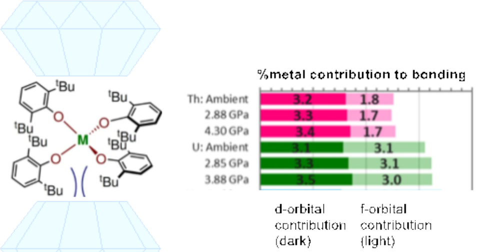

Fig. 3. % Metal contribution to bonding in $An(Oar)_4$ determined by computational analysis of high-pressure XRD data.

Science objectives for 2023- 2025:

- Using the newly-installed inert atmosphere gloveboxes in the Heavy Element Research Laboratory, we seek to isolate transU organometallic complexes of interest for physical characterization studies.
- We will further develop the use of ligand K-edge XAS, STXM, and theory to characterize the nature of the chemical bonding in An oxide, boride, carbide, nitride, and fluoride compounds.
- The tender X-ray spectromicroscopy developmental effort will be maintained to ensure that the flagship beamline at the ALS-U will be suited for An studies when the ALS-Upgrade is completed.

Publications supported by this project 2021-2023:

Staun, Selena L.; Wu, Guang; Lukens, Wayne W.; Hayton, Trevor W. "Synthesis of a heterobimetallic actinide nitride and an analysis of its bonding" *Chem. Sci.* **2021**, *12*, 15519-15527. DOI: 10.1039/D1SC05072A.

Ditter, A. S.; Smiles, D. E.; Lussier, D.; Altman, A. B.; Bachhav, M.; He, L.; Mara, M. W.; Degueldre, C.; Minasian, S. G.; Shuh, D. K.; "Chemical and Elemental Mapping of Spent Nuclear Fuel Sections by Soft X-ray Spectromicroscopy" *J. Synch. Rad.,* **2022**, *29*, 67-79. DOI: 10.1107/S1600577521012315.

Amidani, L.; Dumas, T.; Shuh, D. K.; Butorin, S.; Sahle, C.; Longo, A.; Kvashnina, K. O.; "The O K Edge of ThO_2 and CeO_2: Experiment, Interpretation and Effects of Structural Parameters" J. Phys. Chem. C, **2023**, 127, 3077-3084. DOI: 10.1021/acs.jpcc.2c07771.

Amy N. Price, Victoria Berryman, Tatsumi Ochiai, Jacob J. Shephard, Simon Parsons, Nikolas Kaltsoyannis, Polly L. Arnold. "Contrasting behaviour under pressure reveals the reasons for pyramidalization in tris(amido)uranium(III) and tris(arylthiolate) uranium(III) molecules." *Nature Commun.* **2022**, *13*, 3931. DOI: 10.1038/s41467-022-31550-7.

Yusen Qiao, Gaurab Ganguly, Corwin H. Booth, Jacob A. Branson, Alexander S. Ditter, Daniel J. Lussier, Liane M. Moreau, Dominic Russo, Dumitru-Claudiu Sergentu, David K. Shuh, Taoxiang Sun, Jochen Autschbach, Stefan G. Minasian, "Enhanced 5f-δ bonding in $[U(C_7H_7)_2]^-$: Carbon K-Edge X-ray Spectroscopy, Magnetism and Electronic Structure Calculations", *Chem. Comm.* **2021**, *57*, 9562-9565. DOI: 10.1039/D1CC03414F.

Explore New Coordination Modes in Actinide Molecules and Materials

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Collaborators: Jochen Autschbach (SUNY Buffalo), Kristina Kvashnina (ESRF & HZDR), Andrew Minor (LBNL), Liane Moreau (WSU), Arne Skerra (TU Munich)

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.

Significant achievements during 2021- 2023:

Isolation of TransU Organometallics. Development of Bk organometallic chemistry poses several unique scientific and technical challenges owing to the scarcity and high radioactivity of its longest-lived isotope, ^{249}Bk ($t_{1/2}$ = 330 days). The chlorotriphenylmethane oxidant and both the unsubstituted COT and hdcCOT ligands (hdcCOT = hexahydrodicyclopenta[8]annulene) were selected for Bk experiments because they consistently provided crystalline products during mmol-scale test reactions with Ce. Ultimately, $(hdcCOT)_2Bk$ was isolated via a reaction of $BkCl_3$ and $K_2(hdcCOT)$ followed by *in situ* oxidation with chlorotriphenylmethane, ultimately yielding crystals of $(hdcCOT)_2Bk$ (**Fig. 1**). The solid-state crystal structure shows that the complex is stabilized in the tetravalent oxidation state by two substituted cyclooctatetraene ligands, and contains the first crystallographically characterized Bk–C bond. $(hdcCOT)_2Bk$ adopts a staggered conformation that is different from what was observed in subsequent structural analyses for other $(hdcCOT)_2M$ complexes we also isolated (M = Ce, Th, U, Np, Pu). The complex exhibits luminescence behavior that is consistent with a formal tetravalent oxidation state. Ab-initio wavefunction and density functional calculations indicate that the electronic structure for $hdcCOT)_2Bk$ is distinct from its Ce analog, $(hdcCOT)_2Ce$, and more similar to that observed for other tetravalent actinocenes, e.g. COT_2U.

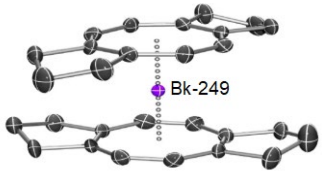

Fig. 1. Molecular structure of $(hdcCOT)_2Bk$, the first structurally authenticated Bk organometallic complex.

Encapsulation and Confinement of An in Hierarchical Structures. Our work has focused on the use of multidentate strong-donor chelating molecules to investigate An coordination chemistry. Based on the selected chelator, we have demonstrated the ability to control the oxidation state of Np and U and the speed of in situ actinyl reduction concurrent with oxo group activation. Similarly, we have observed the chelation-driven oxidation of trivalent Ce and Bk to stable +IV species, and subsequent in situ reduction when exposed to synchrotron light. Tuning the oxidation state of these metal ions in solution affords unprecedented separations strategies based mostly on different charges. We have used macromolecular crystallography to study the binding of early and late actinide small molecule complexes by proteins, recently leading to the structural characterization of an actinium complex, while also offering new, qualitative information on metal-ligand covalency as protein recognition changes the electrostatic character of bonds in the actinide small molecule complexes.

Single-Source Precursors for Actinide Oxide Materials. Precise, reproducible studies of physical behavior in the An are entirely dependent on access to high quality An materials. Single-source precursors (SSPs) contain all the necessary elements to form the desired material, and have the capacity to decompose cleanly without additional reactants that can generate undesired impurities. A library of Th and U amidate molecules was prepared to explore how varying metal characteristics and ligand substituents impacted precursor thermal stability, volatility, and decomposition pathways. Thermal decomposition studies showed that the complexes can all undergo an alkene elimination mechanism to yield ThO_2 or UO_2 without the need for an external oxygen source (**Fig. 2A**). The amidate complexes also possess adequate thermal stability and volatility, enabling deposition of phase-pure metal oxide films through gas-phase methods such as chemical vapor deposition (CVD) and atomic layer deposition (ALD), as shown through collaborative work with Mathur (Cologne). The alkyl-substituted amidates provided oxides with better crystallinity and compositional purity, as shown through powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), as well as O K-edge and Th or U $N_{5,4}$-edge STXM-XAS (**Fig. 2B**).

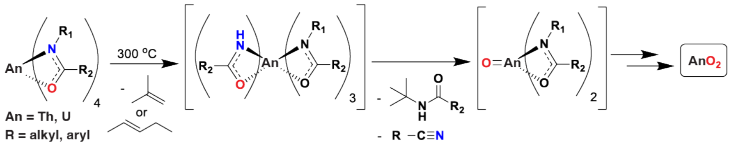

Fig. 2A. Proposed decomposition mechanism of tetravalent actinide amidates leading to formation of AnO_2. Alkene, amide, and nitrile byproducts were observed directly by ^{1}H NMR spectroscopy. Intermediate products shown in brackets are postulated.

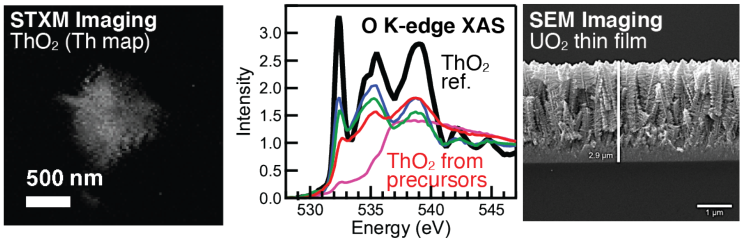

Fig. 2B. Representative plots showing characterization of AnO_2 products formed via decomposition of actinide amidates.

Science objectives for 2023- 2025:

- We will further develop amidates and thioamidates as SSPs for transU oxides and sulfides.
- We will establish new colloidal synthetic methodologies to rationally prepare transU nanoparticles that can be used to evaluate changes physical properties across the An series.
- We will continue manipulating macromolecular systems to characterize An coordination chemistry.

Publications supported by this project 2021-2023:

Shinhyo Bang, Dominic R. Russo, Ashley D. Knapp, Mark D. Straub, Kurt F. Smith, Corwin H. Booth, Stefan G. Minasian, and Liane M. Moreau, “Modeling Heterogeneity in UO_2 Nanoparticles Using X-ray Absorption Spectroscopy” *Eur. J. Inorg. Chem.* **2022**, *26*, e202200417. DOI: 10.1002/ejic.202200417.

MD Straub, ET Ouellette, MA Boreen, JA Branson, A Ditter, ALD Kilcoyne, TD Lohrey, MA Marcus, M Paley, J Ramirez, DK Shuh, SG Minasian, J Arnold, "Thorium amidates function as single-source molecular precursors for thorium dioxide” *Chem. Comm.* **2021**, 57, 4954-4957. DOI: 10.1039/D1CC00867F.

MD Straub, LM Moreau, Y Qiao, ET Ouellette, MA Boreen, TD Lohrey, NS Settineri, S Holoch, CH Booth, SG Minasian, J Arnold, “Amidinate Supporting Ligands Influence Molecularity in Formation of Uranium Nitrides”, *Inorg. Chem.* **2021**, *60*, 6672–6679. DOI: 10.1021/acs.inorgchem.1c00471.

KP Carter, JN Wacker, KF Smith, GJP Deblonde, LM Moreau, JA Rees, CH Booth, RJ Abergel “In Situ Beam Reduction of Pu^{IV} and Bk^{IV} as a Route to Trivalent TransU Coordination Complexes with Hydroxy-pyridinone Chelators” *J. Synchr. Radiat.* **2022**, *29* (2), 315-322. DOI: 10.1107/S1600577522000200.

Molecular f-Element Qubits with Controllable Quantum Coherence and Entanglement

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Postdocs: Alexia Cosby, Bahman Golesorkhi, Olivia Gunther, Rachel Meyer, Appie Peterson, Luis Quintana, Patrick Smith, Jennifer Wacker
Collaborators: Jochen Autschbach (University of Buffalo).

Overall research goals: Advancing quantum technology will require tuning the chemical environment of qubits to create and control coherence in scalable quantum systems. The central hypothesis of this proposal is that the simultaneous and synergistic optimization of coherence times and optical initialization/read-out can be achieved with molecular complexes of the lanthanides (Ln) and actinides (An), both at the level of single qubits and in entangled assemblies. To test this hypothesis, we will use chemical design to create new molecular qubits with long coherence lifetimes, and highly efficient optical control of initialization and read-out. Synthetic chemistry will be used to map the established physics of solid-state color centers and trapped ions onto molecular architectures, thereby effectively replacing solid-state matrices and ion traps with highly tunable, atomically precise ligand shells.

Significant achievements during 2021- 2023:

Identification of a 9.9 GHz Clock Transition Enabled by a $4f^25d^1$ Configuration. Molecular qubits offer an attractive basis for quantum processing, however their inherent strong coupling to the environment often leads to very short relaxation times and, consequently, diminished performance. Qubits based on avoided energy-level crossings, often termed "clock transitions" due to their use in atomic clocks, offer a method to improve T_2 in molecular qubits. At these avoided crossings the dependence of the transition frequency on the magnetic field vanishes, and as such T_2 is much less sensitive to magnetic noise. We propose a general strategy for identifying molecules with high-frequency clock transitions based on systems wherein a d-electron is coupled to the crystal-field singlet state of an f-configuration, resulting in a minimally anisotropic ground state with strong hyperfine coupling. Using this approach, EPR spectroscopy (Figure 1) was used to identify a 9.9 GHz clock transition was identified in a molecular Pr complex,

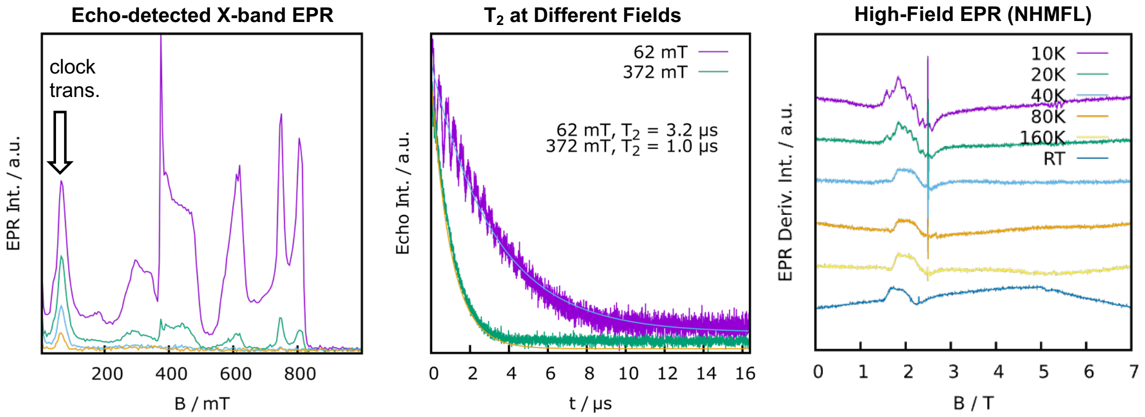

Figure 1. EPR spectra obtained from [K(crypt)]{Cp'_3Pr^{II}}. The X-band data were modelled with $4f^25d^1$ $^4H_{7/2}$ (LS coupled): $g_\perp = 2.57$, $g_\parallel = 0.91$, $A_\perp = 4.5$ GHz, $A_\parallel = 0.9$ GHz

[K(crypt)]{Cp′$_3$Pr^{II}], where T_2 is enhanced ca. threefold relative to other transitions in the spectrum. This system displays massive hyperfine coupling ($A_\perp$ = 4.5 GHz) and minimal magnetic anisotropy. In addition to these favorable T_2 relaxation properties, the T_1 relaxation of this molecule appears to be substantially less temperature sensitive than typical open-shell lanthanide systems. While further examples are necessary to demonstrate the generality of this phenomenon, *this result tests and validates a key hypothesis of our project and indicates the promise of using our design for further development of lanthanide and actinide systems for quantum information applications*.

Externally Induced Entanglement with STM-ESR. Our new STM has both low temperature (2 K) and high magnetic field (10 T) capabilities, and now has the capability of performing STM-ESR measurements of quantum coherent behavior for single magnetic molecules. In STM-ESR microwave signals are sent to the STM tip, thus causing resonant spin-flip transitions in the tunnel junction region and enabling the quantum coherent properties of surface moments to be controlled and measured at the single spin level. Figure 2 shows recent data taken with our instrument on Tb-based single-molecule magnets (SMMs) synthesized by the J. Long group. These SMMs are promising candidates for future molecule-based qubits and the ability to perform STM-ESR on them is important for optimizing their performance and characterizing their suitability for quantum information applications.

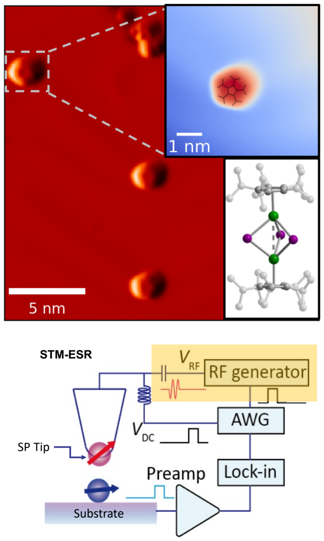

Figure 2. *Top*, STM image of mixed-valence M_J = 15/2 Tb nanomagnets on Au(111) taken with a 2 K, 10 T cryogenic STM. A close-up of the molecule shows its 5-fold symmetry from above (inset). *Bottom*, schematic for CW and pulsed STM-ESR coherent manipulation of coupled spins.

Science objectives for 2023- 2025:

- Test for the presence of clock transitions in Th(III) organometallics based on the rare isotope Th-229, which has a non-integer nuclear spin $I = {}^5/_2$ (the more abundant Th-232 has $I = 0$.
- Explore the effect of ligand substitution on decoherence mechanisms in other Pr(II) qubit analogs based on alkoxide, amide, and other organometallic ligand frameworks.
- Couple the individual qubits discovered recently with organic linkers that impart magnetic exchange coupling functionality.
- Use STM-ESR to demonstrate entaglement between a molecule attached to the STM tip and another molecule on the surface.
- Investigate the ensemble spin relaxation dynamics (T_1) of shallow NV centers with a layer of molecular qubits deposited on the surface of diamond.

Publications supported by this project 2021-2023:

1. Randall, Joseph; Bradley, Conor E.; van der Gronden, F. V.; Galicia, Asier.; Abobeih, Mohamed H.; Markham, Matthew; Twitchen, Daniel J.; Machado, Francisco.; Yao, Norman Y.; Taminiau, Tim H., Many-Body–Localized Discrete Time Crystal with a Programmable Spin-Based Quantum Simulator. *Science* **2021**, 374, 1474-1478. DOI: 10.1126/science.abk0603.
2. Lam, Francis Y.; Wells, Jordann A.; Ochiai, Tatsumi; Halliday, Connor J.; McCabe, Karl N.; Maron, Laurent; Arnold, Polly L., A Combined Experimental and Theoretical Investigation of Arene-Supported Actinide and Ytterbium Tetraphenolate Complexes. *Inorg. Chem.* **2022,** *61* (11), 4581-4591. DOI: 10.1021/acs.inorgchem.1c03365.

Magnetism and Electronic Structure of Actinide Tetrafluorides Probed by Variable Temperature ^{19}F NMR Spectroscopy

Herman Cho, Principal Investigator

Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA
Project Team: Eric Walter, Robert G. Surbella
Postdoctoral Fellows: Sejun Park

Overall research goals: The objective of this project is to map the evolution of electronic structure and chemical bonding from light to heavy actinide elements. The radiofrequency and optical spectroscopic methods implemented in this effort will provide new ways of acquiring information on electronic distributions for researchers who seek to predict and control actinide chemistry and physics.

Significant achievements during 2021-2023: Fluorine-19 magnetic shielding tensors have been measured in a series of actinide tetrafluorides (AnF_4) by solid state nuclear magnetic resonance (NMR) spectroscopy. Tetravalent actinide centers with 0 to 8 valence electrons can form tetrafluorides with the same monoclinic structure type, making these compounds an attractive choice for a systematic study of the variation in electronic structure across the 5f row of the periodic table. Pronounced deviations from predictions based on localized valence electron models have been detected by these experiments, which suggests that this approach can be a quantitative probe of electronic correlations.

Early NMR experiments were performed at room temperature, which exhibited the expected linear field dependence of the shifts and widths of the resonance. Since then, we have developed the capability to perform cryogenic measurements with a versatile cryogenic sample holder (Figure 1). Preliminary results with a closed cycle cryostat down to 15 K reveal a pronounced deviation from conventional Curie-Weiss behavior in the uranium, neptunium, and plutonium tetrafluorides, which indicates the existence of electron correlations at low temperature not evident at ambient temperatures.

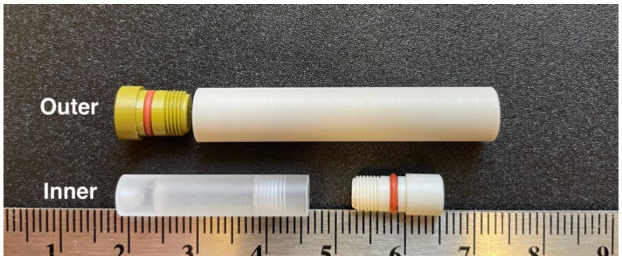

Figure 1: Double containment capsule for cryogenic NMR and NQR experiments.

Science objectives for 2023- 2025:

This project aims to obtain spectroscopic data from complexes containing elements on both sides of $Z = 94$ (Pu), for the purpose of determining electronic distributions around the metal. Special attention will be given to structure types that can form with multiple actinides, such as the monoclinic tetrafluorides and the cubic dioxides. The main experimental techniques are nuclear magnetic resonance and nuclear quadrupole resonance spectroscopy, and for Am and heavier actinides, luminescence spectroscopy. The systems we will study and the information we seek are summarized below:

Systems	Experimental data	Information
An(IV)F_4 and An doped Th(IV)F_4	Fluorine hyperfine shift; hyperfine interaction; Fermi contact coupling	Electronic configuration of metal center; exchange interactions; evidence of electron sharing and correlation; through space and through bond couplings
Uranyl, bis-imido, nitrides	EFG and shielding tensor (NMR of ligands; ^{233,235}U NQR)	Electron distributions throughout complex; evidence of electron sharing
Pu(IV)O_2	^{239}Pu magnetic shielding	Electronic configuration of metal center; exchange interaction; evidence of electron sharing and correlations
An doped Th(IV)O_2	Hyperfine interaction; Fermi contact term	Exchange interactions; through space and through bond couplings; evidence of electron sharing
An(III)-molecular complexes	Splitting between ground and excited electronic states	Electronic state energy level diagrams and metal–ligand bond character

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Robert G. Surbella, III,* Lucas C. Ducati, Mark H. Schofield, Bruce K. McNamara, Kristi L. Pellegrini, Jordan F. Corbey, Jon M. Schwantes, Jochen Autschbach, and Christopher L. Cahill*, "Plutonium Hybrid Materials: A Platform to Explore Assembly and Metal-Ligand Bonding" *Inorganic Chemistry*, **2022**, *61*, 17963–17971, https://doi.org/10.1021/acs.inorgchem.2c02084.

Trent R. Graham*, Joel Castillo, Sergey Sinkov, Artem V. Gelis*, Gregg J. Lumetta*, and Herman Cho*, "Multiplicity of Th(IV) and U(VI) HEH[EHP] Chelates at Low Temperatures from Concentrated Nitric Acid Extractions" *Inorganic Chemistry*, **2023**, *62*, 792-801, https://doi.org/10.1021/acs.inorgchem.2c03307.

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Gabriel B. Hall, Emily L. Campbell, Nathan P. Bessen, Trent R. Graham, Herman Cho, Matthew Risenhuber, Forrest D. Heller, and Gregg J. Lumetta*, "Extraction of Nitric Acid and Uranium with DEHiBA Under High Loading Conditions" *Inorganic Chemistry*, in press.

Nuclear Quadrupole Resonance Spectroscopic Investigations of Uranium-Ligand Interactions in Uranyl Tetrahalides

Herman Cho, Principal Investigator

Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA
Project Team: Eric Walter, Robert G. Surbella
Postdoctoral Fellows: Sejun Park
Collaborators: Jochen Autschbach (University of Buffalo)

Overall research goals: The objective of this project is to map the evolution of electronic structure and chemical bonding from light to heavy actinide elements. The radiofrequency and optical spectroscopic methods implemented in this effort will provide new ways of acquiring information on electronic distributions for researchers who seek to predict and control actinide chemistry and physics.

Significant achievements during 2021-2023: We have previously demonstrated experiments on uranyl clusters that directly probe electronic structure in the plane perpendicular to the O-U-O axis through measurements of electric field gradient (EFG) tensors at equatorial ligands. The experimental data have been compared with values computed by relativistic Kohn-Sham methods with and without environment embedding for $Cs_2UO_2Cl_4$ and $Cs_2UO_2Br_4$. The directions and relative magnitudes of the field gradient principal axes are found to be sensitive to the σ and π electron donation from the ligands and the model of the environment.

In an extension of this work, we are performing variable temperature nuclear quadrupole resonance (NQR) measurements of the EFG and relaxation times. This work is motivated by the proposal by Yosida and Moriya (*J. Phys. Soc. Jpn.* **11**, 33 (1956)) that the temperature dependence of these parameters is a sensitive indicator of the degree of electron sharing between a metal and its ligands. In their treatment, fluctuations in electron distributions arising from a second order (Raman) coupling to thermally activated phonon modes lead to a temperature dependent modulation of the EFG tensor of halide ligands. We have applied this method to predict variations of ^{35}Cl NQR frequencies and spin-lattice relaxation times in ^{235}U-depleted $Cs_2UO_2Cl_4$ as a function of temperature; this approach also allows an estimate of the Debye temperature to be derived (Figure 1). From an examination of experimental trends, an enhanced picture of theoretical descriptions of covalent interactions can be derived.

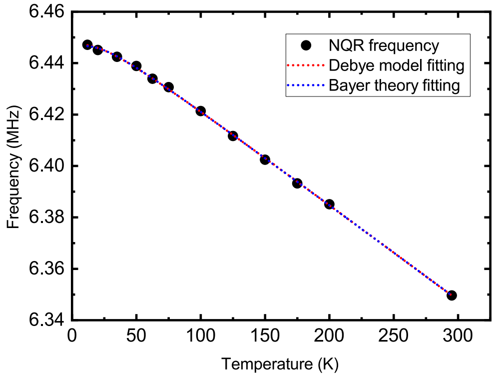

Figure 1: Temperature dependence of the ^{35}Cl NQR transition frequency for $Cs_2UO_2Cl_4$. Black dots represent experimental data, and dashed lines are fits to theoretical models.

Science objectives for 2023- 2025:

This project aims to obtain spectroscopic data from complexes containing elements on both sides of $Z = 94$ (Pu), for the purpose of determining electronic distributions around the metal. Special attention will be given to structure types that can form with multiple actinides, such as the monoclinic tetrafluorides and the cubic dioxides. The main experimental techniques are nuclear magnetic resonance and nuclear quadrupole resonance spectroscopy, and for Am and heavier actinides, luminescence spectroscopy. The systems we will study and the information we seek are summarized below:

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Spectroscopic Investigation of Electronic Structure in the Actinide Elements

R. Gian Surbella III, Principal Investigator

National Security Directorate, Pacific Northwest National Laboratory, Richland, WA
Project Team: R. Herman Cho, Eric Walter, Aaron Nicholas, and Ana Arteaga.
Collaborators: Jochen Autschbach (UB), Lucas Ducati (USP)

Overall research goals: We aim to map the evolution of electronic structure and chemical bonding from the light to heavy actinide elements. A key approach of our efforts is the use optical spectroscopy to explore electronic structure changes in Am^{3+} containing complexes that are caused by bond formation. To do so, we prepare and study crystalline Am^{3+} bearing small–molecules and metal–organic frameworks and identify the key structural parameters affecting absorbance and photoluminescence spectra. The crystalline constructs are characterized by X-ray diffraction to characterize the metal coordination environment and symmetry while a complementary computational approach is used to uncover the underlying bond mechanics.

Significant achievements during 2021-2023:

- Prepared and crystallographically characterized a series of new Am^{3+} containing compounds, including coordination polymers and metal–organic frameworks (MOFs), that provided a platform to identify key material characteristics that are important for interpreting the optical data.

Americium formate, $Am(CHO_2)_3$, is arguably the simplest MOF and adopts a non-porous three-dimensional structure. This compound was prepared and for the first time, crystallographically and spectroscopically characterized. The Eu^{3+} and Nd^{3+} analogs were also studied and used to rationalize the $Nd^{3+}–O < Eu^{3+}–O < Am^{3+}–O$ bond strengths and elucidate the mechanism—infrared spectroscopy and the quantum theory of atoms in molecules and the natural localized molecular orbital approaches were invaluable in this regard. Importantly, the Am^{3+}-valence orbital participation in bonding was notably small, which was consistent with our interpretation of the absorbance and luminescence data. Similar observations were made when investigating a novel Am^{3+}-oxalate coordination polymer, $Am(C_2O_4)(H_2O)_3Cl$, using the same crystallographic, spectroscopic, and computational protocol. Collectively, these systems provided the necessary context for applying our methodologies to a more complex Am^{3+} bearing metal-organic framework—the results of which are still being interpreted. Overall, we are actively developing a workflow to explore photophysics as a tool for interpreting changes in electronic structure and bonding.

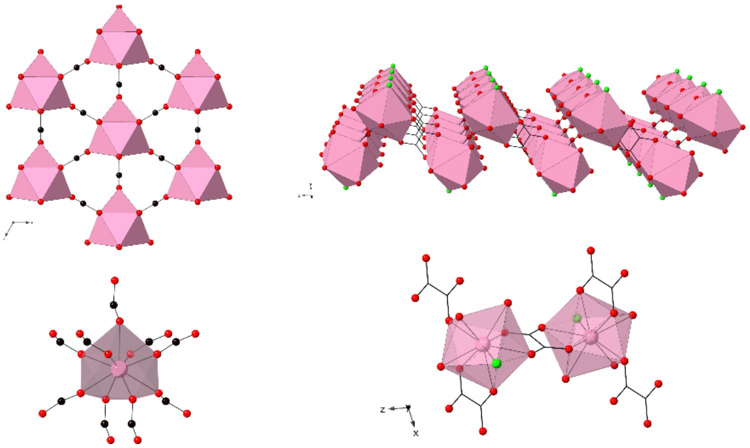

Figure 1. The crystal structures of $Am(CHO_2)_3$ (left) and $Am(C_2O_4)(H_2O)_3Cl$ (right). The extended structures are shown on the top and the local coordination environment on bottom.

Science objectives for 2023- 2025:

1. Prepare a family of isostructural Am^{3+}-small molecule complexes that feature ligands with subtle changes in hard/soft donor character. This will permit systematical changes in ligand bond strength, bond mechanism, and electron donating properties to be identified. The optical properties will be explored in tandem and their utility for elucidating these structural and electronic structure changes evaluated.

2. Prepare and explore additional Am^{3+}-MOF platforms that are based on existing lanthanide analogs. Themes of enhanced luminescence intensity, ligand bond strength, and the influence thereof on Am^{3+} photophysics will be explored while differences in 4f and 5f element behavior are delineated.

3. Incorporate other trivalent actinides (e.g., Np^{3+}, Pu^{3+}) into our crystalline constructs to explore electron paramagnetic resonance spectroscopy experiments with Drs. Herman Cho and Eric Walter for obtaining electronic structure information.

Publications supported by this project 2021-2023

*Corresponding author(s)

Ana Arteaga, Aaron D. Nicholas, Lucas C. Ducati, Jochen Autschbach, and Robert G. Surbella III*, Americium Oxalate: An Experimental and Computational Investigation of Metal–Ligand Bonding. *Inorganic Chemistry,* **2023**, pre-print, https://doi.org/10.1021/acs.inorgchem.2c03976

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Chemistry at the Extreme Edges of the Periodic Table: Elucidating the Chemical Properties of the Superheavy Elements

John Despotopulos, Principal Investigator

Nuclear and Chemical Sciences Division, Lawrence Livermore National Laboratory, Livermore, CA
Collaborators: Ken Gregorich, Dawn Shaughnessy, Kelly Kmak, Roger Henderson, Carlos Valdez, William Kerlin, Jackie Gates (LBNL), Laura Gagliardi (U. Chicago)

Overall research goals:

The periodic table is a working document that arranges elements into groups (columns) and periods (rows) based on their fundamental chemical properties. The position of elements on the periodic table corresponds to trends in chemical behaviour, atomic size, and electronic configurations. In particular, elements within the same group, homologs, have similar chemical properties. The correct placement of newly discovered elements is vital to preserving the periodic table in its current form as a graphical description of chemical properties. However, when a new transactinide element (atomic number > 103) is discovered, it has traditionally been placed in the periodic table solely based off its atomic number, Z, the number of protons in the nucleus. Due to relativistic effects, which increase with Z^2, this placement may not be correct as these superheavy elements may not behave similarly to the direct homologs in the same group. Only through studying the chemical properties of these elements can their correct position on the periodic table be confirmed.

The goal of this proposed research is to perform the first aqueous-phase chemical studies of Cn and Fl. This will incorporate both experiments to elucidate the chemical properties and theoretical descriptions, through collaborations with the University of Chicago, to fully understand and interpret the experimental results. Using the results from these ground-breaking experiments, further experiments can be fielded to explore the heaviest elements on the periodic table in novel ways integrating both theory and experiments through a first-of-its-kind US-based program.

Significant achievements during 2021- 2023:

This is a new project which was started at the beginning of FY23. Thus far a position and energy sensitive flow-through liquid scintillation detector has been built and is undergoing testing for integration to a microfluidic chemistry system for on-line studies of the transactinides. Synthesis of thiacrown ethers, molecules of interest for Cn and Fl chemistry, in gram quantities for on-line experiments has been accomplished.

Science objectives for 2023- 2025:

In the coming year we plan to test the liquid chemistry system and detector off-line with homologs of Cn and Fl. A recoil transfer chamber for collecting produced transactinides and delivering them to the chemistry apparatus will be designed and built with collaboration at LBNL. In future years integrating the chemistry and detection system with the BGS at the 88-inch cyclotron at LBNL will be accomplished and the system tested with on-line produced homologs of Cn and Fl prior to an experiment with the transactinides themselves.
