# 2021 Heavy Element Chemistry Principal Investigators' Meeting

Gaithersburg, MD
June 7–11, 2021

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*

# 2021 Heavy Element Chemistry Principal Investigators' Meeting

Virtual
June 7–11, 2021

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

Cover photo: Cicada (Philip Wilk, 2021)

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# Foreword

This abstract book provides a record of the eleventh U.S. Department of Energy Principal Investigators' meeting in heavy element chemistry. The Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences and its predecessors have sponsored research in heavy element chemistry for 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. 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. The virtual format was a departure from the traditional in-person meeting, which had included ample time for discussion and interactions by meeting attendees.

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*

## 2021 Heavy Element Chemistry Principal Investigators' Meeting | Final v20210611

Virtual
Monday,  June 7 - Friday, June 11

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

### Monday, June 07

**13:00** **Meeting Begins** **Philip Wilk**

Introduction, Agenda
Bruce Garrett: CSGB updates
Suzanne Bart, "Actinide Research Update: Bart Laboratory"
Wayne Lukens, "Exploring covalency in f2 octahedral complexes: UX62- and PrCl63"
John Arnold, "NewLigands Engender Novel Reactivity with Uranium"
Gaither.Town Q&A for Tuesday and Thursday

### Tuesday, June 08

**13:00** **Meeting Begins** **Philip Wilk**

James Blakemore, "Tuning the Redox Properties of the Uranyl Ion with Heterobimetallic Chemistry"
Kit Bowen, "Uranium-Containing and Thorium-Containing Anions Studied by Photoelectron Spectroscopy"
Lan Cheng, "Advances in relativistic quantum chemistry with applications to actinide spectroscopy"
Jeff Long, "Structural, Electrochemical, and Magnetic Properties of Radical-Bridged Diuranium Complexes"
David Shuh, "Soft X-ray Spectromicroscopy from Light Element Constituents of Actinide Materials"

**15:30** **Gaither.Town** **Herman Cho**

### Wednesday, June 09

**13:00** **Meeting Begins** **Philip Wilk**

Herman Cho, "Spectroscopic Investigation of Electronic Structure in the Actinide Elements"
William Evans, "Exploring the Fundamental Chemistry of Actinide Metal Complexes"
Peter Armentrout, "Thermochemistry and Reactivity of Atomic and Molecular Actinide Cations"
Tori Forbes, "Impacts of Systems Level Chemistry on Neptunyl Vibrational Spectra"
Richard Wilson, "Trivalent and Tetravalent f-Element Chemistry"

# 2021 Heavy Element Chemistry Principal Investigators' Meeting

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## Thursday, June 10

**13:00 Meeting Begins** — **Philip Wilk**

Amy Hixon, "Plutonium coordination and reduction in the presence of oxalate and U60Ox30"
Henry La Pierre, “Electron (De)Localization in f-Element Systems”
Xiaosong Li, "Challenges and Opportunities of Four-Component Relativistic Theory"
Benjamin Stein, “Excited State Dynamics of Lanthanide TTA Complexes”
Aaron Tondreau, "Promoting f-Orbital Interactions for Organometallic Chemistry"

**15:30 Gaither.Town** — **Herman Cho**

## Friday, June 11

**13:00 Meeting Begins** — **Philip Wilk**

Jenifer Shafer (ARPA-E)
Thomas Albrecht-Schoenzart, "Effects of High Pressures on the Structure and Spectroscopy of Cm and Cf Complexes"
Kirk Peterson, "Chemically accurate thermochemistry for actinide atoms, molecules, and complexes"
Eric Schelter (QIS project), "Towards Strongly Correlated f-Electron Materials from Molecular Precursors"
Ping Yang, "Quantum Molecular Dynamics for Actinide Chemistry"
Philip Wilk, brief HEC update

**Posters**

Justin Walensky, "Advancing Actinide Chemistry with Heavier Main Group Elements"
Michael Neidig, "Spectroscopic and Synthetic Studies in Molecular Actinide Chemistry"
Ellen Matson, "Electronic interactions and multielectron reactivity of actinide ions on metal-oxide surfaces"
Jochen Autschbach, "What's Hidden Under the Cerium XAS L3-edge Peaks"
Michael Heaven, "Spectroscopic investigations of Thorium(III) bonding and electronic structure: ThN and OThF"

# *Abstracts*

# Effects of High Pressures on the Structure and Spectroscopy of Curium and Californium Coordination Complexes

*Thomas E. Albrecht-Schoenzart, Principal Investigator*

Department of Chemistry & Biochemistry, Florida State University, Tallahassee, FL 32306
Graduate Students: Evan J. Warzecha, Bonnie E. Klamm, Alyssa N. Gaiser, Frankie D. White, Alexander T. Chemey, Brian N. Long, Todd N. Poe, Zach Huffman, Nick Beck
Post-docs: Cristian Celis-Barros, Cory J. Windorff, Maria J. Beltran-Leiva
Undergraduates: Megan A. Whitefoot
Research Professor: Joseph M. Sperling
Collaborators: Kenneth Hanson, Department of Chemistry & Biochemistry, Florida State University, Tallahassee, Florida 32306
Manfred Speldrich, Paul Kögerler, Institut für Anorganische Chemie, RWTH Aachen University, D-52074 Aachen, Germany
Jochen Autschbach, Ewa Zurek, Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14260
Ryan E. Baumbach, David Graf, National High Magnetic Field Laboratory, Tallahassee, Florida, 32310

*Overall research goals:* Our hypothesis is that pressurization of transuranium complexes and materials will compress An–L bonds and enhance the engagement of metal frontier orbitals in forming chemical bonds. This heightened metal character in the bonds will alteration in the physical properties and spectroscopic features of the compounds with respect to that observed under ambient conditions.

*Significant achievements during 2019-2021:*

Curium is unique in the actinide series because its half-filled $5f^7$ shell is lowered in energy through self-exchange, rendering it both redox inactive and resistant to engaging its $5f$ orbitals in forming chemical bonds. However, at high pressures metallic curium undergoes a transition from localized to itinerant $5f$ electrons that alters its structure and properties. Thus, the question arises whether the utilization of frontier metal orbitals and other aspects of curium-ligand interactions in molecules can also be modified by applying pressure using diamond-anvil techniques. In a recent *Nature* paper, we reported experimental and computational evidence for changes in the relative roles of the $5f/6d/7s$ orbitals in Cm–S bonds in $[Cm(pydtc)_4]^{1-}$ (pydtc = pyrrolidinedithiocarbamate) and increased ligand-field splitting associated with significant compression and molecular distortions at high pressures. We benchmarked these results using a $Cm^{III}$ mellitate that only possesses Cm–O bonds and $[Nd(pydtc)_4]^{1-}$ that show smaller or essentially nonexistent changes upon pressurization.

Similarly, studies of $Cf_2(mell)(H_2O)_{10}\cdot 4H_2O$ and its Gd(III) and Ho(III) analogs reveals that the average Cf–O bond distance is slightly longer than the average Gd–O bond, consistent with trends in effective ionic radii. UV-vis-NIR absorption spectra as a function of pressure were collected using diamond-anvil techniques for both $Cf_2(mell)(H_2O)_{10}\cdot 4H_2O$ and $Ho_2(mell)(H_2O)_{10}\cdot 4H_2O$. These experiments show that the Cf(III) $f \rightarrow f$ transitions have a stronger dependence on pressure than that of the holmium analog. In the former case the shift is nearly linear with applied pressure and averages 6.6 $cm^{-1}/GPa$, whereas in the latter it is $< 3\ cm^{-1}/GPa$.

*Science objectives for 2021-2023:*

Controlling the properties of heavy element complexes, such as those containing berkelium, is challenging because relativistic effects, spin-orbit and ligand-field splitting, and complex metal-ligand bonding, all dictate the final electronic states of the molecules. It is difficult to govern any of these factors. While the first two of these are currently beyond experimental control, covalent M–L interactions could theoretically be boosted through the employment of chelators with large polarizabilities that substantially shift the electron density in the molecules. To test this theory, a terpyridyl ligand that possesses this attribute, 4'-(4-nitrophenyl)-2,2':6',2"-terpyridine (terpy*), was synthesized, and $\mathrm{Bk(terpy^*)(NO_3)_3(H_2O)\cdot THF}$ was prepared and benchmarked with its closest electrochemical analog, $\mathrm{Ce(terpy^*)(NO_3)_3(H_2O)\cdot THF}$. Here, we show that not only was the goal of enhanced Bk–N interactions achieved, but rather polarization of the molecules by terpy* creates a plane wherein the M–L bonds trans to the terpy* ligand are shorter than anticipated. Moreover, these molecules are highly anisotropic and rhombic EPR spectra for the $\mathrm{Ce^{III}}$ complex were recorded.

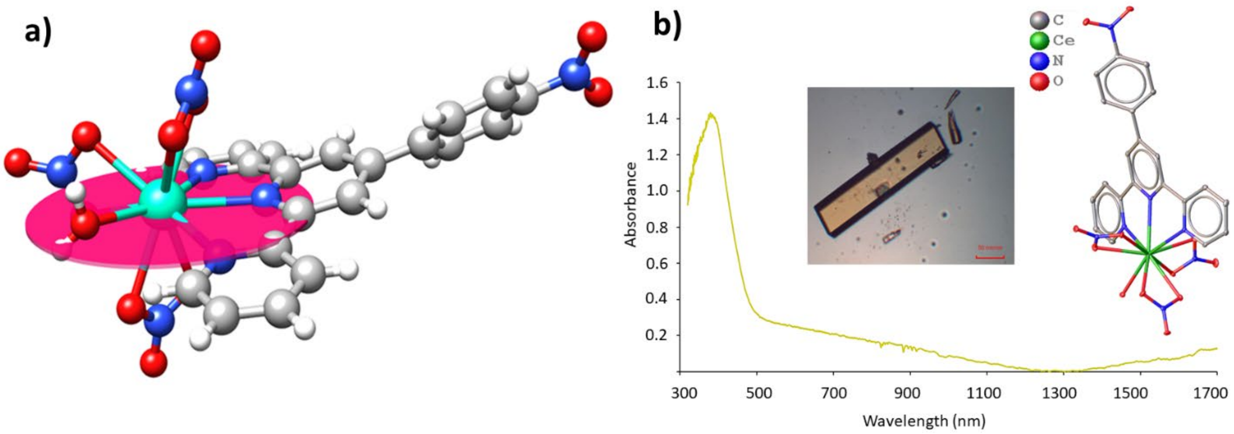

**Fig. 1 | Characterization of $\mathrm{Ce^{III}}$ and $\mathrm{Bk^{III}}$ terpyridine complexes**. Depiction of the plane defined by the terpyridine derivative, water molecule, and equatorial nitrate ligand (a). The optimization of the plane was performed using the coordinates of the terpyridine nitrogen atoms, metal center, and water oxygen atom. Absorption spectrum, crystal structure, and single crystal picture of **Ce1** (b).

*Selected publications supported by this project 2019-2021*

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
2. J. M. Sperling, E. J. Warzecha, C. Celis-Barros, D.-C. Sergentu, X. Wang, B. E. Klamm, C. J. Windorff, A. N. Gaiser, F. D. White, D. A. Beery, A. T. Chemey, M. A. Whitefoot, B. N. Long, K. Hanson, E. Zurek, J. Autschbach, T. E. Albrecht-Schönzart, "Compression of Curium Pyrrolidinedithiocarbamate Enhances Covalency," *Nature*, **2020**, *583*, 396-399. **DOI:** 10.1038/s41586-020-2479-2

# Trivalent and Tetravalent f-element Chemistry

*Richard E. Wilson, S. Skanthakumar, Principal Investigators*

Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 South Cass Ave.,
Argonne Illinois, 60439
Collaborators: L. Soderholm, Matthieu Autillo, Shanna Estes, Stephen Southworth, Gilles Doumi, Argonne National Laboratory. John K. Gibson, Lawrence Berkeley National Laboratory. Valerie Vallet, Florent Real, CNRS, University of Lille, France, David A. Dixon, University of Alabama.

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

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

Exploiting the periodic series of hexavalent actinides U(VI) to Pu(VI), we have investigated the formation of hydroxo-bridged dimers of these molecules in nitrate media, Figure 1. These synthetic and structural studies coupled with vibrational spectroscopy (FT-IR and Raman) have revealed systematic trends in the actinyl oxygen bonding, trends that are inspiring future work in understanding their underlying electronic structure. These synthetic campaigns have been extended to include an isostructural series of An(VI) nitrate mono-nuclear complexes as well as a series of homoleptic An(IV) nitrate complexes. We have used these series of actinide molecules as model systems for computational studies with our collaborators to understand the systematics of the role of the 5f electrons across the early actinide series.

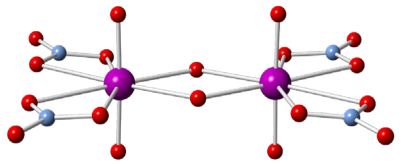

Figure 1. Representative structure of the isolated actinide hydroxide dimers for U(VI), Np(VI), and Pu(VI). $(Me_4N)_2AnO_2(OH)_2(NO_3)_4$.

More recently we have focused on complexes of the early actinides Th-Cm in their tri- and tetravalent oxidation states in both thiocyanate and nitrate solutions. In this portion of the actinide series, both the 5f and 6d electrons play roles in the chemistry of these elements with a periodic trend from principally d-character at Th to f-character beyond Pu. An initial study focused on the chemistry of the trivalent actinide and lanthanide thiocyanate complexes to investigate the differences in the metal-ligand interactions in these systems. Spectroscopic studies using Raman spectroscopy revealed principally electrostatic metal-thiocyanate interactions in both the lanthanides and the Am and Cm complexes studied.

Known periodic trends in the electronic structure of the actinides, notably the near degeneracy of the 5f and 6d orbitals at Pa suggest that further investigation of the tetravalent and trivalent oxidation states of Pa should further our understanding of the metal-ligand interactions of the actinide elements.

Experiments on the easily accessible tetravalent and trivalent oxidation states of the lanthanides and the transuranium elements lay the groundwork for the more ambitious experimental campaigns aimed at Pa. Our future goals are to extend this work to tetravalent and trivalent protactinium. Periodic trends in actinide electronic structure suggest that the interplay between both the 5f and 6d orbitals in the chemistry of these complexes should be greater than that for the transuranium elements.

*Science objectives for 2021-2023:*

- Study the chemistry of the tetravalent and trivalent actinides in simple ligand systems such as nitrate, halides and thiocyanate, and extend this chemistry to tetravalent and trivalent protactinium.
- Experiments to focus on the electrochemical behavior of tetravalent and trivalent protactinium along with the other early actinides Th-Am to understand the trends in their redox chemistry.
- 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 2019-2021

1. R. E. Wilson, S. Stegman, M. Tarlton. *Reactions of Neptunium(V) in Alkali Metal Hydroxides: A Structural Hierarchy. Inorganic Chemistry*. in press. 2020.

2. R. E. Wilson, T. J. Carter, M. Autillo, S. Stegman. *Thiocyanate Complexes of the lanthanides, Am and Cm. Chemical Communications* 2020, 56, 2622-2625. DOI: 10.1039/C9CC07612C

3. Evan L. Thomas, Samantha Stegman, R. E. Wilson. *Applications of Alkali Metal Hydroxide Hydrofluxes to the Synthesis of Single-Crystal Ternary Actinide Oxides. Chemistry –A European Journal*. 2020, 26, 1497-1500 (**HOT ARTICLE)** DOI: 10.1002/chem.201904677

4. Phuong D. Dau, Monica Valiliu, Richard E. Wilson, David A. Dixon, John K. Gibson. *Hydrolysis of Metal Dioxides Differentiates d-block from f-block Elements: Pa(V) as a 6d Transition Metal; Pr(V) as a 4f "Lanthanyl" The Journal of Physical Chemistry A.* 2020. 124, 44, 9272-9287. DOI: 10.1021/acs.jpca.0c08171.

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

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

# 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)

*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 2019-2021:*

Kinetic-energy dependent reactions of $Th^+$ with $N_2$ and NO were studied using GIBMS. Formation of $ThO^+$ in the reaction of $Th^+$ with NO is observed to be exothermic and barrierless. Formation of $ThN^+$ in the reactions of $Th^+$ with $N_2$ and NO is endothermic in both cases and modeling these data yields $D_0(Th^+–N) = 6.51 \pm 0.08$ eV, the first direct measurement of this bond dissociation energy (BDE). This BDE was also explored by quantum chemical calculations, including a full Feller-Peterson-Dixon (FPD) approach with correlation contributions up to CCSDTQ for ThN and $ThN^+$, yielding 6.49 eV, in excellent agreement with present experiment. Using ionization energies from Heaven's group, an experimental value for $D_0(Th-N) = 6.53 \pm 0.08$ eV was also derived, also in good agreement with the FPD value of 6.50 eV.

The kinetic energy dependence of the endothermic reaction, $ThO^+ + O_2 \rightarrow ThO_2^+ + O$, was studied using GIBMS. This cross section was modeled to determine $D_0(OTh^+-O) = 4.94 \pm 0.06$ eV. The FPD result (up to CCSDT(Q)) of 4.87 eV was in excellent agreement. A higher energy feature in the $ThO_2^+$ cross section suggested formation of an excited state of the product ion lying $3.1 \pm 0.2$ eV above the ground state. The $ThO_2^+$ BDE is larger than those of its transition metal congeners, $TiO_2^+$ and $ZrO_2^+$, which can be attributed partially to an actinide contraction, but also to contributions from the participation of *5f* orbitals on thorium that are unavailable to the transition metal systems, a conclusion supported by theory. The magnitude of the *5f* orbital contribution to the $OTh^+$-O BDE is relatively weak but significant, accounting for ~13% of the measured BDE. This result is one of the first experimental determinations of how much *5f* orbitals can contribute to covalent bonding.

The collision-induced dissociation reaction of $ThCO^+$ with Xe was analyzed to determine the thorium cation carbonyl BDE of $0.94 \pm 0.06$ eV, and was replicated by the FPD result of $0.94 \pm 0.02$ eV. Theoretical analysis shows that this carbonyl has a classic two-electron sigma donor ($CO \rightarrow Th$) and two-electron pi backdonation interaction ($Th \rightarrow CO$).

Hydration of thorium cations was examined in a series of three GIBMS studies. $Th^+$ reacts with water to form $ThO^+$ and $HThO^+$ efficiently at low energies, although the kinetic energy dependence shows that additional pathways for both products open at higher energies. Importantly, our synergistic theoretical work shows that quantitative interpretation of the experimental data requires that the PESs for these reactions include spin-orbit effects. $ThO^+$ and $ThO_2^+$ react with another molecule of water to form $OThOH^+$ in exothermic barrierless processes. CID of $OThOD^+$ (the deuterated variant) yielded $D_0(OTh^+-OD) = 6.00 \pm 0.17$ eV.

$OThOD^+$ reacts further with $D_2O$ to form the association complex $ThO_3D_3^+$, which is long-lived before dissociating back to the reactants. The kinetic-energy dependence of this association reaction was analyzed using a model that rigorously conserves angular momentum and yields $D_0(OThOD^+\text{-}OD_2) = 2.96 \pm 0.05$ eV. By comparison with theory, this BDE identifies the $ThO_3D_3^+$ species as thorium (IV) trihydroxide cation, $Th(OD)_3^+$. Complete potential energy pathways for all reactions were calculated theoretically to elucidate the mechanisms for all observed processes.

Reaction of the $Th(OH)_3^+$ core cation with additional water molecules generated $Th(OH)_3^+(H_2O)_n$ complexes for $n = 1 – 4$. These complexes were formed in our source and then subjected to CID with Xe as a function of kinetic energy using GIBMS. All these species are observed to sequentially lose water molecules until $OThOH^+$ is formed. Analysis of these CID cross sections yields hydration energies of 1.10 ± 0.06, 0.92 ± 0.06, 0.79 ± 0.04, and 0.53 ± 0.04 eV for $n = 1 – 4$, respectively. These values agree nicely with theoretical results both from our own work (done at four different levels) and the literature.

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

*Science objectives for 2021-2023:*

Data has been collected for the reactions of $U^+$ with $H_2$, HD, and $D_2$. A paper on this work has been written and is awaiting theoretical input from Bert de Jong. Data has been collected for reactions of $U^+$ and $UO^+$ with $O_2$, CO, and $CO_2$. A paper on this work is in progress. Data has been acquired for the collision-induced dissociation (CID) of $Th(CO)_x^+$ for x = 2 – 6 and will probably result in two or more papers. Data has been acquired for reactions of $U^+$ with $CS_2$ and COS, for $US^+$ with $CS_2$ and COS, and for CID of $US^+$ and $US_2^+$. The process of writing up these studies for publication has begun. Data has been acquired for reactions of $Th^+$ and $U^+$ with $CF_4$ and $SF_6$. A paper or two on these studies is in preparation.

*Publications supported by this project 2019-2021*

Kafle, A.; Armentrout, P. B. “Mechanism and Energetics of the Hydrolysis of $Th^+$ to Form $Th(OD)_3^+$: Guided Ion Beam and Theoretical Studies of $ThO^+$, $ThO_2^+$, and $OThOD^+$ Reacting with $D_2O$” *J. Phys. Chem. A* **2019**, *123*, 5893-5905. DOI: 10.1021/acs.jpca.9b03938

Cox, R. M; Armentrout, P. B. “Activation of Water by Thorium Cation: A Guided Ion Beam and Quantum Chemical Study” *J. Am. Soc. Mass Spectrom.* **2019**, *30*, 1835-1849. DOI: 10.1007/s13361-019-02162-1

Armentrout, P. B.; Peterson, K. A. “A Guided Ion Beam and Quantum Chemical Investigation of the Thermochemistry of Thorium Dioxide Cations: Thermodynamic Evidence for Participation of f Orbitals in Bonding” Armentrout, P. B.; Peterson, K. A. *Inorg. Chem.* **2020**, *59*, 3118-3131.
DOI: 10.1021/acs.inorgchem.9b03488

Kafle, A.; Nwokolo, C.; Sanchez, L.; Armentrout, P. B. “Threshold Collision-Induced Dissociation of Hydrated Thorium Trihydroxide Cation (IV): Experimental and Theoretical Investigation of the Binding Energies for $Th(OH)_3^+(H_2O)_n$ Complexes (n = 1 – 4)” *J. Phys. Chem. A* **2020**, *124*, 3090-3100.
DOI: 10.1021/acs.jpca.9b11516

Armentrout, P. B. “Periodic Trends in Gas-phase Oxidation and Hydrogenation Reactions of Lanthanides and 5d Transition Metal Cations” Armentrout, P. B. *Mass Spectrom. Rev.* **2021**, in press. DOI: 10.1002/mas.21703

# Computational studies of magnetism and spectra of actinide complexes

*Jochen Autschbach, Principal Investigator*

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Collaborators: Thomas Albrecht-Schönzart (Florida State U.), Herman Cho (PNNL), Trevor Hayton (UC Santa Barbara), Michael Neidig (U. Rochester), Eric Schelter (U. Penn.), 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 (electron paramagnetic resonance = EPR, nuclear magnetic resonance = NMR), magnetic susceptibilities, as well as valence and core excitation spectra (UV-vis spectroscopy & XAS), magnetic field-induced circular dichroism (MCD) and Mössbauer spectroscopic parameters (upcoming). 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.

*Significant Achievements during 2019–2021:*

We continued our studies of XAS of f-element complexes during 2019–21. Early in 2020 we reported carbon K-edge and An N-edge XAS calculations for thorocene and uranocene. As in our initial work on actinide XAS, we found substantial orbital relaxation upon core excitation. This means there is a risk of misinterpretation of the spectra if only ground state orbitals are considered. The $L_3$ XAS edge of cerium is caused by excitations from the 2p shell of Ce to the 5d orbitals. Observed spectra generally feature a double peak with varying intensity ratios that have long been used to deduce 4f occupations and the extent of multi-configurational character of the ground state. However, the relation of the peak intensity ratios to the ground state 4f occupation and multi-configurational composition of the ground state has never been explained satisfactorily with the help of ab-initio calculations. We recently investigated the Ce $L_3$ edge XAS to remedy this situation. The study provided much insight into the electronic states that are responsible for the intensity in the $L_3$ edge, and we obtained excellent agreement between calculated and experimental spectra for cerocene and $CeO_2$.

In collaboration with T. Albrecht-Schönzart (Florida State U.) and his team, we studied the electronic structure and emission wavelengths of curium(III) pyrrolidinedithiocarbamate as a function of pressure. When the solid compound is put under pressure of up to 11 GPa, the wavelength of the Cm-centered orange emission changes appreciably. Our calculations showed that pressure enhances the covalent interactions between the ligands and the Cm 5f shell.

In 2017 we started to develop new theoretical methods that allow for the calculation of MCD from multi-reference wavefunctions with spin-orbit coupling (SOC). With collaborator M. Neidig (U. Rochester), we recently performed a first experimental/theoretical study of the MCD of 5f-5f transitions in $[UX_6]^-$ with X = F, Cl. These transitions are electric dipole-forbidden, and therefore we had to develop a treatment of vibronic and magnetic intensity for our MCD calculations. We published several other collaborative studies with Neidig during the 2019–21 period.

In collaboration with T. Hayton (UC Santa Barbara) we conducted several joint experimental/theoretical studies of f-element complexes with Th, U, and Ce. Two publications focused on the NMR chemical shift and the associated chemical shift tensor of nitrogens bound to Th, and the spin-orbit coupling (SOC) effects on the nitrogen chemical shift caused by the covalency of the Th-N bonds. There is typically a magnetic de-shielding of light ligand atoms bound to f-elements with empty f orbitals, which manifests itself in untypically large NMR chemical shifts. We also observed the SOC-driven de-shielding for the carbon bound to Ce in a covalent Ce(IV)-aryl complex that we studied recently in collaboration with E. Schelter (U. Penn.).

*Science Objectives for 2021–2023:*

XAS calculations will be extended to analogous Pu(IV) compounds such as $PuO_2$ and plutonocene. We will also attempt XAS calculations for Ce, Pr and Tb complexes. Calculations of vibrationally resolved electronic spectra require a more sophisticated treatment of the excited state structures and normal modes. Much of the effort during 2021–23 will be placed on developing improved theoretical methods for these calculations. We will also acquire expertise in calculations of $^{237}$Np Mössbauer spectroscopic parameters, in anticipation of an experimental/theorerical collaboration with Neidig and Albrecht-Schönzart who are constructing a new high-resolution Mössbauer instrument at Florida State U.

*Publications supported by this Project 2019–2021 (a selection):*

Sergentu, D.-C.; Booth, C. H.; Autschbach, J., 'Probing multiconfigurational states by spectroscopy: The cerium XAS L3-edge puzzle', Chem. Eur. J. **2021**, 27, 7239–7251. https://doi.org/10.1002/chem.202100145

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Ganguly, G.; Sergentu, D.-C.; Autschbach, J., 'Ab Initio Analysis of Metal-Ligand Bonding in An(COT)2, An = Th, U, in Their Ground- and Core-Excited States', Chem. Eur. J. **2020**, 26, 1776–1788. https://doi.org/10.1002/chem.201904166

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

*Suzanne C. Bart, Principal Investigator*

Tyler Collins, Ezra Coughlin - Graduate Students; Shane Galley - Postdoc
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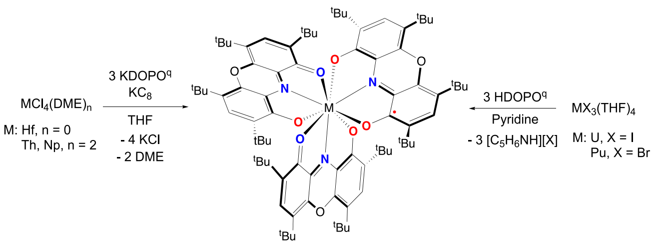
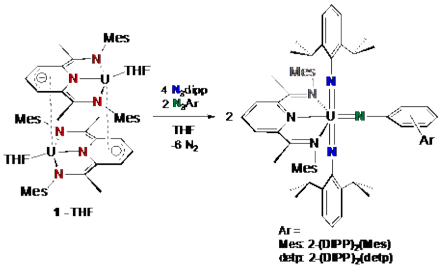
Collaborators: Prof. Eric Schelter, University of Pennsylvania, Philadelphia, PA
Prof. Laura Gagliardi, University of Minnesota, Minneapolis, MN
Dr. Stosh Kozimor, Los Alamos National Laboratory, Los Alamos, NM
Prof. Thomas Albrecht- Schönzart, Florida State University, Tallahassee, FL

*Overall research goals:* To explore Ln, Th, U, Np complexes bearing redox-active ligands, through synthesis, characterization, and reactivity 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), will be studied to understand synthetic, reactivity, and bonding trends across the Periodic Table.

*Significant achievements during 2019-2021:*

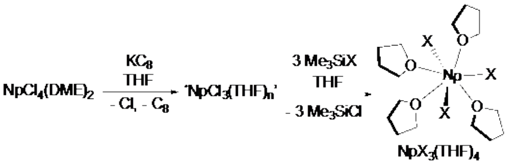
1. Synthesized a family of tetravalent transition metal and actinide derivatives of the dioxophenoxazine ligand of the form $M(DOPO^q)_2(DOPO^{sq})$ (M = Hf, U, Th, Np, Pu). Full characterization of these species showed one ligand contains a radical, and this was supported by computational studies. This is a rare example of SQUID measurements of a molecular plutonium-radical species.



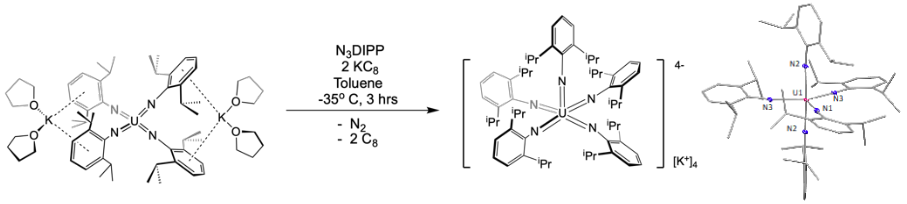


2. Uranium tris(imido) species have been synthesized using different imido groups in the axial and equatorial positions by treating $[(^{Mes}PDI^{Me})U(THF)]_2$ (**1-THF**), which is a uranium(IV) dimer that is supported by $^{Mes}PDI^{Me}$ tetraanions, with mixed organoazide solutions. The arrangement of the imido groups is determined by the reduction potentials of the organoazides.

3. Two Np (III) halides, $NpI_3(THF)_4$ and $NpBr_3(THF)_4$, were prepared and isolated in high yields. Starting with $NpO_2$, $NpCl_4(DME)_2$ was first generated in an updated, higher yielding synthesis than what was previously reported using HCl/HF. Reduction with $KC_8$, followed by subsequent ligand exchange generated $NpBr_3(THF)_4$ and $NpI_3(THF)_4$. Full characterization confirmed the molecular formulas and oxidation states.



4. A uranium(VI) pentakis(imido) tetraanion was recently synthesized and characterized in our laboratory. This is the first example of any metal with five multiple bonds to it. The structure was confirmed by spectroscopic and structural characterization, and the electronic structure was confirmed by computational methods. These U-N bonds are extremely activated compared to other imidos.



*Science objectives for 2019-2021:*

- Explore the reactivity of the newly synthesized pentakis(imido) species as well as our current uranium tetrakis(imido) examples.
- Study the formation and reactivity of thorium redox-active ligand compounds, as well as terminal oxo species.
- Continue our transuranic studies using our new neptunium setup that has been established over the past year. We plan to focus on neptunium starting materials, such are more halide complexes, as well as simple alkoxides, amides, and benzyls, as well as extend the chemistry to redox-active ligands.
- Generate U complexes bearing 3 multiply bonded species, including phosphinidenes and arsinidenes.
- Extend previous redox-active ligand neodymium work to americium through collaboration with Prof. Tom Albrecht-Schonzart's laboratory.

*Publications supported by this Project 2019–2021 (a selection):*

Raghavan, A.; Anderson, N.H.; Tatebe, C.J.; Stanley, D.A.; Zeller, M.; Bart, S.C.* "Insight into Geometric Preferences in Uranium(VI) Mixed Tris(Imido) Systems" *Chemical Communications* **2020**, *56*, 11138-11141.

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# Uranyl Capture and Activation with Lewis Acids and Macrocyclic Hosts

*James Blakemore, Principal Investigator*

Department of Chemistry, University of Kansas, 1567 Irving Hill Road, Lawrence, KS 66045
Graduate Students: Amit Kumar, Riddhi Golwankar, Shaun Kelsey, and Emily Mikeska
Collaborators: Tori Forbes (U. Iowa), Michael Neidig (Rochester), and Henry La Pierre (GA Tech)

*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 the energetic requirements and kinetics of U–O bond activation.

*Significant achievements during 2019-2021:*

In a first area of investigation, we are developing a small family of heteroditopic macrocyclic ligands and are using these to prepare heterobimetallic complexes of the uranyl ion. We have found that a monometallic uranyl-containing precursor complex that presents an open 18-crown-6-like moiety can be subjected to divergent metallation, affording access to a family of heterobimetallic compounds that pair a range of mono-, di-, and tri-valent redox-inactive Lewis acids with the uranyl ion. Figure 1 (below) shows some structures of these compounds as determined by single-crystal X-ray diffraction analysis. The Lewis acids are held in close proximity and at reasonably well-defined positions relative to the uranium center (< 4.0 Å) and thus exert a significant influence over the uranyl moiety. We have found that there is a quantitative relationship between Lewis acidity, as judged by the p$K_a$ values of the aqua ions of the incorporated Lewis acidic metals, and the reduction potential of the uranyl ion. In other words, we demonstrated that the poise of uranium(VI)/uranium(V) redox cycling can be modulated in heterobimetallic macrocyclic compounds.

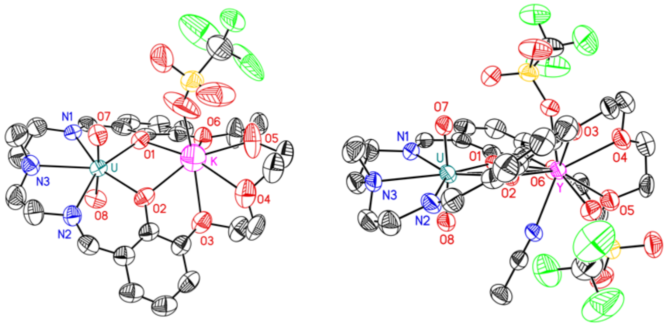

Figure 1. Solid-state structures (XRD) of heterobimetallic $UO_2^{2+}$ complexes

We have also found that the identity of the incorporated Lewis acid reliably modulates the kinetics of electron transfer to the uranyl ion. In particular, incorporation of strong Lewis acids slows electron transfer to the uranium centers. Stated another way, electron transfer to uranyl in a bimetallic construct containing potassium, a weak Lewis acid (p$K_a$ = 16.0), is significantly faster than electron transfer to the analogous complex containing calcium, a stronger Lewis acid (p$K_a$ = 12.6). Taken together with the thermodynamic tuning measured for the compounds, our results show that heterobimetallic chemistry, supported by appropriately tailored ligands, offers a powerful strategy for influencing and optimizing the reactivity properties of the uranyl ion.

Building on these results with uranyl redox cycling, we have also recently completed a comprehensive study of the ligand-centered redox chemistry of heterobimetallic complexes containing only redox-inactive metal ions. These studies represent a counterpoint to our work with heterobimetallic uranyl complexes, in that the chemistry of uranium-centered reductions in these compounds are significantly different from analogous ligand-centered reductions. We have been interested in comparing these two different types of processes, since little is known about how incorporation of redox-inactive metal ions into redox-active structures influences their redox chemistry, both in terms of thermodynamic potential shifts and electron transfer rates. Our new work shows that such processes display distinctive electrochemical signatures, but that redox-inactive metal ions can influence ligand-centered reduction processes similarly to how they can influence metal-centered redox chemistry. Our work used the classic redox-inactive metal ion zinc, and paired it either with itself in homobimetallic complexes or with other metal ions, including the strong Lewis acids yttrium(III) and neodymium(III) in heterobimetallic species.

And, finally, we have developed a new method for directly measuring the Lewis acidity of mono-, di-, and tri-valent redox-inactive metal ions. We are using a modification of the Gutmann-Beckett method for these measurements, but have applied the approach to a diverse array of metal ions for the first time, making comparisons and parametric work possible. We are using triphenyl- and triethylphosphine oxide as probe molecules and titrations of these probes with metal complexes of interest. We have uncovered influences of speciation chemistry and the formation of various adducts on Lewis acidity. Each metal ion's speciation chemistry can be understood with fitting to either curves for 1:1 stoichiometric binding, applicable to the more weakly acidic ions, or the Hill-Langmuir equation, a more general approach that enables comparisons across the full series of metal ions. These findings are important for work aimed at using secondary metal ions to tune the redox properties and reactivity of the uranyl ion, because our quantified Lewis acidity parameters can be used as activity descriptors for the influence of secondary metal ions. In prior work, p*K*a values for metal aqua ions have been used as the descriptor, leading to ambiguities since these values are measured in water but most work in the field is carried out in polar organic solvents.

*Science objectives for 2021-2023:*

In the coming months, we aim to deepen our understanding of the role of ligand structure in enabling formation and rational tuning of uranyl chemistry in heterobimetallic complexes. We are developing new ligands with different binding sites for the secondary metal ions to map these effects, and in collaboration with Profs. Forbes and Neidig, will leverage spectroscopies to gain new insights into the mechanistic origins of our observed tuning effects. We are also aiming to use electrochemical methods to initiate U–O bond activation processes and quantify their properties, wherein reduced forms of uranyl will react with exogenous electrophiles. Finally, we are also continuing development of our phosphine oxide probe-based methods for parametrizing Lewis acidity behaviors of diverse metal ions, particularly strong Lewis acids including trivalent ions as well as the uranyl ion itself.

*Publications supported by this project 2019-2021*

Amit Kumar, David Lionetti, Victor W. Day, and James D. Blakemore* "Redox-Inactive Metal Cations Modulate the Reduction Potential of the Uranyl Ion in Macrocyclic Complexes" *J. Am. Chem. Soc.*, **2020**, *142*, 3032-3041, doi: 10.1021/jacs.9b11903,

Amit Kumar and James D. Blakemore* "On the Use of Aqueous Metal-Aqua p$K_a$ Values as a Descriptor of Lewis Acidity" *Inorg. Chem.*, **2021**, *60*, 1107-1115 doi: 10.1021/acs.inorgchem.0c03239

Shaun R. Kelsey, Amit Kumar, Allen G. Oliver, Victor W. Day, and James D. Blakemore* "Promotion and Tuning of the Electrochemical Reduction of Hetero- and Homobimetallic Zinc Complexes" *ChemElectroChem*, **2021**, *Advance Article*, doi: 10.1002/celc.202100358

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

*Kit Bowen, Principal Investigator*

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Graduate Students: Mary Marshall, Zhaoguo Zhu, Sandy Ciborowski, Gaoxiang Liu, Rachel Harris, and Moritz Blankenhorn.
Collaborators: Lan Cheng (Johns Hopkins University), David Dixon (University of Alabama), Kirk Peterson (Washington State University), Laura Gagliardi (University of Chicago), and Xinxing Zhang (Nankai University).

*Overall research goals:* Our work focused on uranium-containing and thorium-containing anions studied by negative ion photoelectron spectroscopy in the gas phase with the objective of obtaining electronic structure information primarily about the mass-selected anions' neutral counterparts. This work was conducted in close partnership with several (mostly) DOE-funded theorists doing synergetic calculations. Our interactions with them served not only to supply benchmarks and validation for their calculations and to aid us in interpreting our spectra, but also to provide a powerful iterative and thus corrective mechanism for improving their theoretical methods. Given the extreme challenges encountered in carrying out meaningful calculations on actinide-containing molecules, the interactive nature of our theory-experiment partnership provided a means for identifying shortcomings in the computational methods being used. Their detection and subsequent correction in simple actinide-containing molecules is helping to build a firm foundation on which more complicated, real-world systems can be tackled. The net result is a deeper understanding of chemical bonding in actinide-containing molecules.

*Significant achievements during 2019-2021:*

Below, we list and briefly summarize the ***10*** completed experimental studies that we completed during this time period.

*$UN_2^-$* $UN_2$ is isoelectronic to $UO_2^{2+}$. Since the electronic absorption spectrum of free $UO_2^{2+}$ is unavailable for technical reasons, the electronic structure of $UN_2$ is particularly valuable. With our theoretical partner, Lan Cheng, we found that both electron attachment and electronic excitation significantly bent the $UN_2$ molecule and elongated its U≡N triple bond.

*$Th_2O^-$, $Th_2Au^-$, $Th_2AuO_{1,2}$* The anions and neutrals of these molecules exhibit both Th-Th and Th-Au metal-metal bonds. With our computational partner, David Dixon, we found the geometric structures of these species and explored ionic aspects of their bonding.

*$HThO^-$* With our theoretical partner, Lan Cheng, we found the atomic connectivity of this anion to be $HThO^-$ and not $ThOH^-$ with the thorium atom being inserted between the O and H atoms.

*$ThH_5^-$* $ThH_5$ was found to be a super-halogen. With our computational partner (also my former student), Xinxing (Colin) Zhang, we found $ThH_5^-$ ($C_{4v}$) to possess five Th-H single bonds and to exhibit the highest known H/M ratio among the actinide elements, M.

*$UO_2Cl_2^-$* With our theoretical partner, Lan Cheng, we found the photodetached electron from $UO_2Cl_2^-$ to be a 5f electron. Thus, the electron affinity, EA, of $UO_2Cl_2$ provides direct information about uranium 5f orbital energies.

*$U^-$* In this work, we measured the electron affinity of the uranium atom to be 0.309 eV, thereby filling-in its missing EA value in the periodic table. While the computational treatment of the uranium atom by our theoretical partner, Kirk Peterson, was at an unprecedentedly high level, it resulted in an EA value for uranium of 0.232 eV, rather than the

measured value, illustrating the extreme challenges faced by theory in dealing with even the atoms of the actinides.

$U_2^-$ Actinide metal-actinide metal bonds have long been of interest in chemistry. The simplest metal-metal bonds are found in their naked dimers. Working with our theoretical partner, Laura Gagliardi, we found the $U_2$ bond to exhibit a bond order of 5, and $U_2^-$ to display a bond order of 4. While we measured the EA of the uranium dimer to be 1.0 eV, Gagliardi's very high-level computational treatment found the EA of $U_2$ to be 0.71 eV, again illustrating the daunting challenges faced by theory in dealing with even the dimers of the actinides.

*$ThH^-$, $ThH_2$* Working with our computational partner, David Dixon, a surprisingly large number of close-lying thorium hydride states were found. While the experimental part of the work is complete, a few more calculations remain to be finished.

*$ThAu_2^-$, $ThAu_2O^-$, $ThAuOH^-$* The focus of this work with Kirk Peterson as our computational partner was on actinide-transition metal, (An-TM) bonding. These single thorium atom-containing molecules displayed strong ionic bonding character. The experimental part of this work is complete.

*$ThS_2^-$ and $ThSO^-$* Kirk Peterson was our computational partner on this work. Excellent agreement was found between the measured and computed EA and VDE values of $ThS_2$ and ThSO and $ThS_2^-$ and $ThSO^-$, respectively.

*Science objectives for 2021-2023:*

We anticipate studying the following three categories of systems. 1. New examples of uranium-containing and thorium-containing *molecular* anions, 2. *metal-metal bonding* in actinide-transition metal, hetero-dimeric anions, and 3. *ligated* anionic molecular, metal-metal, and *uranyl* complexes.

*Publications supported by this project 2019-2021*

G. Liu, C. Zhang, S. M. Ciborowski, A. Asthana, L. Cheng, K.H. Bowen, "*Mapping the Electronic Structure of the Uranium(VI) Dinitride Molecule, $UN_2$*", *J. Phys. Chem. A* **2020**, 124, 6486-6492. https://dx.doi.org/10.1021/acs.jpca.0c03735.

Z. Zhu, M. Marshall, R. Harris, K.H. Bowen, M. Vasiliu, D. Dixon, "*The $Th_2O^-$, $Th_2Au^-$ and $Th_2AuO_{1,2}^-$ Anions: Photoelectron Spectroscopic and Computational Characterization of Energetics and Bonding*", *J. Phys. Chem. A* ***2021***, 125, 258-271. https://dx.doi.org/10.1021/acs.jpca.0c09766

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M. Marshall, Z. Zhu, R. Harris, K.H. Bowen, W. Wang, J. Wang, C. Gong, X. Zhang, "*$ThH_5$, An Actinide-Containing Superhalogen Cluster*", *ChemPhysChem* **2021**, 22, 5-8. https://doi.org/10.1002/CPHC.202000918

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

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

## Neptunyl and Uranyl Peroxide Chemistry in Molten Salts, Uranyl Structures from Nature, and Thermodynamic Studies Extending into the Transuranium Elements

*Peter C. Burns, Principal Investigator*

Department of Civil and Environmental Engineering and Earth Sciences, Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN.
Graduate Students: Samuel Perry, Tsuyoshi Kohlgruber, Mengyu Xu, Travis Olds, Sara Gilson
Collaborators: Laura Gagliardi (University of Chicago)

*Overall research goals:* This project emphasizes synthesis of novel actinide compounds, discovery and characterization of natural uranium minerals, and nanoscale actinide oxide clusters, as well as detailed characterization of the structures and properties of these materials.

*Significant achievements during 2019-2021:* Novel uranyl sulfates have been synthesized in ionothermal systems to probe the relationships between structural units and interstitial complexes.[1,2] Ionothermal synthesis also yielded two novel heteropolyoxometalates and demonstrated that they could be crystallized as isolated entities or linked into dimers and helical chains.[3] Mass spectroscopic data demonstrated that the clusters remain intact upon dissolution into a variety of solvents. These are rare examples of uranyl-bearing clusters that form in the absence of peroxide.

Functionalization of uranyl peroxide cage clusters was achieved by introduction of an aromatic ligand into a $U_{19}$ cage cluster that contains intra-molecular H-bonds.[4] Crystallization of these clusters yielded a supramolecular framework containing K-π and π-π interactions. Functionalization of uranyl peroxide cage clusters with organic ligands makes it possible to use supramolecular forces to direct arrangement of the clusters in three dimensions, and to modify the solubility of the cluster in different solutions. The functionalized cluster was unstable in aqueous solution upon heating, and was replaced by an organic-free $U_{24}$ cluster. We synthesized three uranyl peroxide cage clusters containing benzene-1,2-diphosphonic acid and determined the impact of addition of these ligands on cluster solubility in various solutions, and conversion of these clusters in water to the more stable $U_{24}$ cluster.[5]

We reported the enthalpies of formation, as measured by high temperature drop-solution calorimetry, of a series of Np(VI) phosphate compounds that are isostructural with autunite-group minerals,[6] thermochemical studies of a series of Zr, Ce and U sulfates,[7] and the synthesis and properties of two novel U(IV) compounds, one of which also contains uranyl ions.[8] We published several new compounds with novel structures.[9,10] We also completed studies focused on nanoscale uranyl-based cages containing phosphonate and proposed a general synthetic approach for designing uranyl coordination cages.[11,12] We reported various uranyl aqua sulfate compounds.[13]

We reported new uranyl minerals kroupaite[14] and seaborgite.[15] This is the outcome of continuing collaborations focused on the discovery and characterization of new uranium minerals. Kroupaite, $KPb_{0.5}[(UO_2)_8O_4(OH)_{10}]\cdot 10H_2O$, is a new member of the schoepite. As detailed in the recent book chapter in *Comprehensive Nuclear Materials 2nd edition*, hydrated uranium oxides are a highly complex and structurally varied group of compounds that are important in mineralogy and the nuclear fuel cycle.[16] Seaborgite, $LiNa_6K_2(UO_2)(SO_4)_5(SO_3OH)(H_2O)$, is the first uranyl mineral containing lithium and is an important addition to the complex family of uranyl sulfates found in the Red Canyon area of Utah.

We established a hierarchical arrangement of neptunium coordination chemistry for all oxidation states including illustrations of the structural units of 388 neptunium compounds.[17]

*Publications supported by this project 2019-2021:*

(1) Kohlgruber, T. A.; Mackley, S. A.; Dal Bo, F.; Aksenov, S. M.; Burns, P. C. The role of 1-ethyl-3-medlylimidazolium diethyl phosphate ionic liquid in uranyl phosphate compounds. *Journal of Solid State Chemistry* **2019**, *279*. 10.1016/j.jssc.2019.120938

(2) Kohlgruber, T. A.; Felton, D. E.; Perry, S. N.; Oliver, A. G.; Burns, P. C. Effect of Ionothermal Conditions on the Crystallization of Organically Templated Uranyl Sulfate Compounds. *Crystal Growth & Design* **2021**. 10.1021/acs.cgd.0c01198

(3) Kohlgruber, T. A.; Senchyk, G. A.; Rodriguez, V. G.; Mackley, S. A.; Dal Bo, F.; Aksenov, S. M.; Szymanowski, J. E. S.; Sigmon, G. E.; Oliver, A. G.; Burns, P. C. Ionothermal Synthesis of Uranyl Vanadate Nanoshell Heteropolyoxometalates. *Inorganic Chemistry* **2021**, *60*, 3355. 10.1021/acs.inorgchem.0c03765

(4) Xu, M. Y.; Traustason, H.; Dal Bo, F.; Hickam, S.; Chong, S.; Zhang, L.; Oliver, A. G.; Burns, P. C. Supramolecular Assembly of Geometrically Unstable Hybrid Organic-Inorganic Uranyl Peroxide Cage Clusters and Their Transformations. *Journal of the American Chemical Society* **2019**, *141*, 12780. 10.1021/jacs.9b05599

(5) Xu, M. Y.; Eckard, P.; Burns, P. C. Organic Functionalization of Uranyl Peroxide Clusters to Impact Solubility. *Inorganic Chemistry* **2020**, *59*, 9881. 10.1021/acs.inorgchem.0c01080

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

*Christopher L. Cahill, Principal Investigator*

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Graduate Students: Dominique Brager, Nicole Byrne, Jordan Herder, August Ridenour
Collaborators: Dr. Mark Schofield, Dr. Aaron Nicholas (GW); Jon Schwantes, Gian Surbella, Herman Cho (Pacific Northwest Nat'l Lab)

*Overall research goals:* 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 'synthons' such as 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 2019-2021:*

1. Formation of heterometallic $UO_2(NCS)_5]^{3-}/[M(NCS)_4]^{2-}$ compounds assembled through tunable S-S and S-Oyl interactions New compounds, assembly criteria and atypical Raman signatures.

The $UO_2(NCS)_5]^{3-}/[M(NCS)_4]^{2-}$ system allowed us to selectively promote S•••$O_{yl}$ interactions (Figure 1) upon introduction of a secondary $[Co(NCS)_4]^{2-}$ anion. Sterics and ligand polarization are at play to favor Oyl engagement (over S-S interactions) in herterometalic phases. An exemplary compound, $(C_4H_{12}N)_5[UO_2(NCS)_5][Co(NCS)_4]\cdot H_2O)$ displays atypical Raman behavior in that a distinct *blue* shift in the Raman active ($\nu_1$) stretch is observed. Second order perturbation theory (SOPT) results show -yl engagement occurs between heterometallic units primarily via donor S lone pairs and acceptor U=O $\pi^*$ orbitals. Pinpointing the participation of U=O antibonding orbitals as electron acceptors in S···$O_{yl}$ interactions provides strong evidence that this mode of -yl engagement proceeds exclusively as a destabilizing process, effectively *weakening* the uranyl bond, in contradiction to the Raman blue shift. Follow on frequency calculations revealed an energy and symmetry match of U=O and U-NCS stretching modes capable of allowing vibronic coupling and is in turn, the origin of the atypical blue shift by mixing U=O and U-NCS Raman stretch energies and intensities.

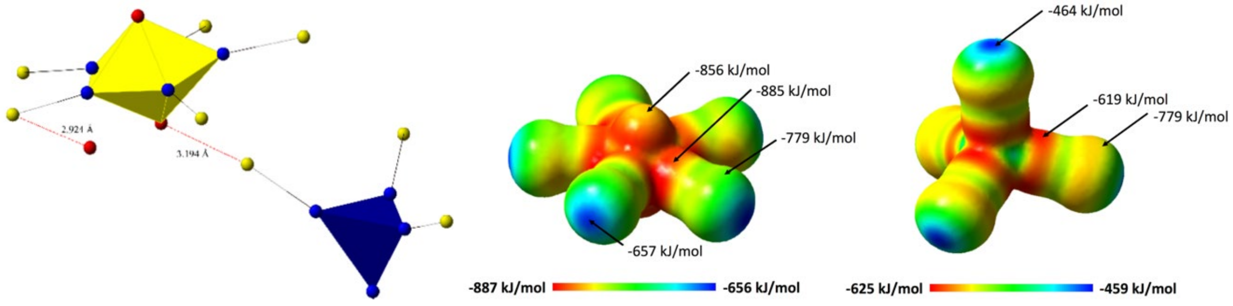

**Figure 1.** Left: The S•••$O_{yl}$ interaction in $(C_4H_{12}N)_5[UO_2(NCS)_5][Co(NCS)_4]\cdot H_2O$. Right: Electrostatic potential maps of the $[UO_2(NCS)_5]^{3-}$ and $[Co(NCS)_4]^{2-}$ anions showing relative 'acceptor' and 'donor' sites respectively.

*Science objectives for 2021-2023:*

1. Promote the formation of M-oxo interactions in TRU hybrid materials and evaluate their impact on luminescence and by extension, the nature of ‘yl’ bonding.
2. Probe criteria for H-bonding of substituted methyl pyridinium cations with oxo groups on $[AnO_2X_4]^{n-}$ anions (An = U, Np, Pu; X = Cl, Br)
3. Prepare families of $[UO_2X_4]^{2-}$ - viologen salts as a platform to probe charge transfer and inform photocatalytic reaction mechanisms in the solid state.
4. Expand the catalogue of heterometallic $[UO_2(NCS)_5]^{3-}/[M(NCS)_4]^{2-}$ compounds assembled through tunable S-S and S-Oyl interactions

*Publications supported by this project 2019-2021*

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## Novel Relativistic Electronic Structure Theories for Actinide-Containing Compounds

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Postdoc researcher: Junzi Liu

*Overall research goals:* The present project is focused on the development of quantum-mechanical methods for treating relativistic effects together with application to heavy-element spectroscopy and chemistry. The work on relativistic exact two-component (X2C) theory aims to provide accurate and efficient treatments of scalar-relativistic and spin-orbit effects. The development of X2C coupled-cluster (CC) techniques aims to enhance the capability to treat electron correlation in heavy-element containing molecules. The application work is focused on electronic and vibrational structures of heavy element containing molecules in collaboration with experimental colleagues.

*Significant achievements during 2019-2021:*

The method-development work has advanced the treatment of spin-orbit coupling within the exact two-component (X2C) theory and coupled-cluster methods [1-4]. We have recently developed an analytic scheme for the spin-orbit CC (SO-CC) calculations of first-order properties with spin-orbit coupling included at the orbital level [1]. In combination with efficient implementation of SO-CC methods [2], this first rigorous implementation of analytic first energy derivatives for SO-CC methods provides enhanced capability for calculations of molecular properties for heavy atom containing molecules. We have also developed an atomic mean-field (AMF) version of the mean-field spin-orbit approach within the exact two-component (X2C) framework for perturbative treatment of spin-orbit coupling [3, 4]. The perturbative treatment of spin-orbit coupling at the CC levels of theory has been shown to provide accurate treatment of spin-orbit coupling for heavy-element containing molecules, e.g., the prototypical $ThO^+$ molecule, for which the computed vibronic levels for low-lying electronically excited states are in excellent agreement with experimental measurement by Heaven group supported by the DOE Heavy Element Chemistry Program.

We have had a fruitful collaboration with the group of Kit Bowen supported by the DOE Heavy Element Chemistry Program [5-7] in joint anion photoelectron spectroscopy and relativistic coupled-cluster study of electronic structures of actinide-containing molecules. Computational studies have played interesting and indispensable roles in the interpretation of the sophisticated photodetachment spectra of $UN_2^-$ [5], $HThO^-$ [6], and $UO_2Cl_2^-$ [7]. The computations have found that electron attachment and certain electronic excitations significantly bend the $UN_2$ molecule and elongate its U≡N bond [5], which has interesting implications to the activation of $UN_2$. The calculations identified the atom connectivity of the observed $ThOH^-$ and ThOH to be $HThO^-$ and HThO [6]. Our joint experimental/computational study has also determined the adiabatic electron affinity ($EA_a$) and vertical detachment energy (VDE) for $UO_2Cl_2^-$ [7]. Relativistic CC calculations predict the photodetachment of $UO_2Cl_2^-$ to involve a U 5f electron and to be followed by significant geometry relaxation. Therefore, $EA_a$ of the uranyl dichloride neutral molecule, $UO_2Cl_2$, and VDE of its anion, $UO_2Cl_2^-$, provide valuable information about its uranium 5f orbital energies.

*Science objectives for 2021-2023:*

One next immediate step in method-development work is the implementation of analytic nuclear gradients for the spin-orbit coupled-cluster singles and doubles with a noniterative triples [SO-CCSD(T)] method, built upon the analytic scheme for the evaluation of first-order properties. This will enable efficient SO-CCSD(T) geometry optimization and frequency calculations for heavy element containing molecules, which is essential for chemical and spectroscopic applications of the SO-CCSD(T) method. Another short-term ongoing method-development work is the development of an atomic Dirac-Coulomb-Gaunt Hartree-Fock program with the exploitation of spherical symmetry for efficient implementation of the X2CAMF scheme. After this, we plan to work on extending the applicability of the X2CAMF CC methods to larger systems using Cholesky decomposition for two-electron integrals and pair natural orbital technique to compactify the correlation space.

Collaborative work with the group of Kit Bowen is planned to explore electronic and vibrational structures of uranium and thorium containing molecules. A particularly interesting direction is to investigate the effects of ligands and the metal formal oxidation state on the uranium 5f orbital energies.

*Publications supported by this project 2019-2021:*

Junzi Liu, Xuechen Zheng, Ayush Asthana, Chaoqun Zhang, and Lan Cheng "Analytic Evaluation of Energy First Derivatives for Spin-Orbit Coupled-Cluster Singles and Doubles Augmented with Noniterative Triples Method: General Formulation and An Implementation for First-Order Properties." *J. Chem. Phys.* **2021**, *154*, 064110, doi.org/10.1063/5.0038779.

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

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Undergraduate Students: Amber Gomez, Ashley Eberly, Lauren Tatina, Alyssa Caccamo
Collaborators: Dr. John Gibson Lawrence Berkeley National Laboratory; Prof. Kirk Peterson, Washington State University; Dr. Lynne Soderholm, Argonne National Laboratory; Dr. Richard Wilson, Argonne National Laboratory; Prof. Karah Knope, Georgetown University; Prof. Michael Duncan, University of Georgia; Prof. Kit Bowen, Johns Hopkins University; Prof. Robin Rogers, The University of Alabama

*Overall research goals*: The goal is to use computational electronic structure methods to reliably predict chemical properties of molecules and materials containing heavy elements with a focus on the actinides to help explain experimental results from different laboratories leading to an improved understanding of actinide chemistry. Predict potential energy surfaces for hydrolysis reactions for $AnO_2^+$ and $An_xO_y(OH)_z$. Predict energetics for ligand exchange reactions involving small actinide anions and cations for $AnO_2^+$ and $AnO_2^{2+}$. Predict structures and properties of $(AnO_x)_n$ and mixed $(AnO_y(OH)_z)_n$ ultra-small nanoclusters and their hydrolysis reactions.

*Selected Examples from Recent Progress*

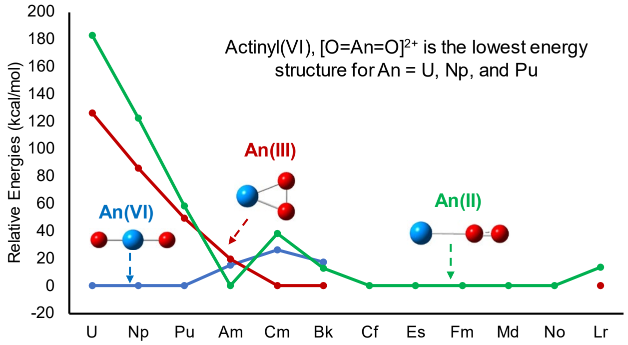

Figure 1. Relative energies for $AnO_2^{2+}$ structures.

High level electronic structure calculations of the isolated gas-phase actinide dioxide dications, $AnO_2^{2+}$ at the coupled cluster CCSD(T) level for the actinides in different oxidation states and geometries were used to assign the lowest energy structures of $AnO_2^{2+}$ for all actinides (An) beyond Pa (Figure 1) and to establish periodic trends. CASSCF calculations defined the orbital occupancies. Spin orbit effects were included in a number of cases and can be significant for these species. The early actinides form actinyls in the +VI oxidation state (OS), the middle members can be in the +II, +III, or +IV OS, and the later actinides are in the +II OS except for Lr at the end of the series in the +III OS. Whereas U-Pu form +VI actinyls, structures corresponding to An(II) and An(III) become more stable for Am and beyond. Spin orbit effects are important in determining stabilities of different OS of the middle actinides. Relative energies suggest that curyl(VI) and berkelyl(VI), like americyl(VI), might be stabilized by strong donor ligands. For Cf and beyond, the actinyl(VI) moieties will probably be elusive. The prevalence of +II and +III OS for transplutonium actinides reflects stabilization of the 5f orbitals. The results delineate the limited range of accessible high OS for actinides beyond Am, and suggest Cm(VI) and Bk(VI) as viable synthetic targets.

Gas-phase reactions of pentavalent metal dioxide cations $M^VO_2^+$ with an additional water molecule were studied experimentally by the Gibson group and computationally by us for M = V, Nb, Ta, Pr, Pa, U, Pu and Am. Addition of two $H_2O$ can occur by adsorption to yield a hydrate $(H_2O)_2M^VO_2^+$, or by hydrolysis to yield a hydroxide $M^V(OH)_4^+$. Displacement of $H_2O$ by acetone shows hydrate formation for $Pr^V$, $U^V$, $Pu^V$ and $Am^V$, whereas non-displacement indicates hydroxide formation for $Nb^V$, $Ta^V$ and $Pa^V$. Computed CCSD(T) reaction coordinate profiles agree with the experimental results. Structures and energies for several $M^V$, as well as $Th^{IV}$ and $U^{VI}$, indicate that hydrolysis is governed by involvement of valence f versus d orbitals in bonding. Linear f-element dioxides are more resistant to hydrolysis than bent d-element dioxides. For early actinides, hydrolysis of $Th^{IV}$ is characteristic of a 6d-block transition metal; hydration of $U^V$ and $U^{VI}$ are characteristic of 5f actinyls; and $Pa^V$ is intermediate between 6d and 5f.

*Selected Future Plans*

- Predict the photodetachment of electrons from small actinide anions including $ThH_x^-$, $UN^-$, $UC^-$, $UC_2^-$, and $UH^-$ to gain information about the neutrals and anions using CAS-PT2+SO.
- Predict the energetics for ligand exchange reactions involving small actinide anions and cations to support mass spectrometry experiments of J. Gibson (LBNL).
- Predict the structures and properties of $(AnO_x)_n$ and mixed $(AnO_y(OH)_z)_n$ ultra-small nanoclusters and examine the dependence of the actinyl An=O bond on the ligand.
- Predict the $pK_a$ and redox properties of charged An ions in aqueous solution and study the role of counterions, positive and negative, on the properties of aqueous ions and clusters

*Selected Recent Publications Resulting from this Project*

Gibson, J. K.; Vasiliu, M.; Dixon, D. A.; Peterson, K. A.: Gas Phase Hydrolysis and Oxo-Exchange of Actinide Dioxide Cations: Elucidating Intrinsic Chemistry from Protactinium to Einsteinium. *Chem. Eur. J.* **2019**, *25*, 4245-4254 doi.org/10.1002/chem.201803932

Jian, T.; Dau, P. D.; Shuh, D. K.; Vasiliu, M.; Dixon, D. A.; Peterson, K. A.; Gibson, J. K.: Activation of Water by Pentavalent Actinide Dioxide Cations: Characteristic Curium Revealed by a Reactivity Turn after Americium. *Inorg. Chem.* **2019**, *58*, 14005-14014. 10.1021/acs.inorgchem.9b01997

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## Exploring the Fundamental Chemistry of Actinide Metal Complexes

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*Collaborators:* Andrew J. Gaunt, Thomas E. Albrecht-Schönzart, Conrad A. P. Goodwin, Stosh A. Kozimor, David E. Hobart, Zhuanling Bai, Cory J. Windorff, Joseph M. Sperling, Alyssa N. Gaiser, Zachary K. Huffman, Bonnie E. Klamm, Todd N. Poe, Evan Warzecha, Filipp Furche, Samuel Bekoe, Jenny Y. Yang, Jeffrey M. Barlow.

*Overall research goals:* We seek to expand the fundamental understanding of the chemistry of the actinide (An) metals by exploring the new +2 oxidation states for uranium and thorium we discovered which have the unusual, previously unknown, $5f^36d^1$ and $6d^2$ electron configurations, respectively. The new U(II) and Th(II) chemistry developed at UCI will be transferred to Los Alamos National Laboratory (LANL) for extension to Np, Pu, Am, and Cf. The synthesis of new low valent actinide complexes will be pursued to enhance characterization and reactivity studies and to identify optimized targets for rapid small-scale synthesis of crystalline transuranic analogs. The reactivity of the new An(II) ions will be studied to discover new classes of actinide complexes and reaction pathways.

*Significant achievements during 2019-2021:* We have obtained excellent electrochemical data on a U(III)-in-(2.2.2-cryptand) system which demonstrates that this coordination environment can stabilize U(III) to water.

A comprehensive electrochemical study on the tris(cyclopentadienyl) uranium and thorium complexes that were critical to the discovery of the first crystallographically-characterizable molecular complexes of U(II) and Th(II) has been completed. The first electrochemistry on isolated Th(II) complexes was accomplished. In addition, spectroelectrochemical studies revealed new synthetic routes to Th(II) compounds directly from Th(IV) precursors without the need to isolate highly reactive Th(III) compounds.

A collaborative project with LANL has been completed that shows how much new information can be obtained from very small amounts of precious plutonium by judicious choice of a reaction. X-ray crystal structures of three Pu compounds were obtained from a single reaction of only 28 mg of an organoplutonium precursor.

C-H bond activation has been identified as a reactivity pathway when U(II) ions are generated.

*Science objectives for 2021-2023:* We will use the recently obtained electrochemical information to generate new Th(II) and Th(III) complexes. We will expand the actinide-in-(2.2.2-cryptand) chemistry to be applicable to Np and Pu in collaboration with LANL. We will seek analogs of the unusual square planar Th(III) complex discovered as part of this project.

*Publications supported by this project 2019-2021*

"Electrochemical Studies of Tris(cyclopentadienyl) Thorium and Uranium Complexes in the +2, +3, and +4 Oxidation States" Justin C. Wedal, Jeffrey M. Barlow, Joseph W. Ziller,

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"A Single Small-Scale Plutonium Redox Reaction System Yields Three Crystallographically-Characterizable Organoplutonium Complexes" Cory J. Windorff, Joseph M. Sperling, Thomas E. Albrecht-Schönzart, Zhuanling Bai, William J. Evans, Alyssa N. Gaiser, Andrew J. Gaunt, Conrad A. P. Goodwin, David E. Hobart, Zachary K. Huffman, Daniel N. Huh, Bonnie E. Klamm, Todd N. Poe, and Evan Warzecha *Inorganic Chemistry* **2020**, *59*, 13301-13314. **DOI:** 10.1021/acs.inorgchem.0c01671

"C–H Bond Activation via U(II) in the Reduction of Heteroleptic Bis(trimethylsilyl)amide U(III) Complexes" Justin C. Wedal, Samuel Bekoe, Joseph W. Ziller, Filipp Furche, and William J. Evans *Organometallics* **2020**, *39*, 3425-3432. **DOI:** 10.1021/acs.organomet.0c00496

"Stabilization of U(III) to Oxidation and Hydrolysis by Encapsulation using 2.2.2-Cryptand" Daniel N. Huh, Jeffrey M. Barlow, Sierra R. Ciccone, Joseph W. Ziller, Jenny Y. Yang, and William J. Evans *Inorganic Chemistry* **2020**, *59*, 17077-17083 **DOI:** 10.1021/acs.inrogchem.0c02286

"Structural Variations in Cyclopentadienyl Uranium(III) Iodide Complexes" Justin C. Wedal, Cory J. Windorff, Daniel N. Huh, Austin J. Ryan, Joseph W. Ziller, and William J. Evans *Journal of Coordination Chemistry* **2020***, 74*, 74-91. **DOI:** 10.1080/00958972.2020.1856824

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# Impacts of systems level chemistry on neptunyl vibrational spectra

*Tori Forbes, Principal Investigator*

Department of Chemistry, University of Iowa, Iowa City, IA
Graduate Students: Mikaela Pyrch, Jennifer Bjorklund, Dmytro Kravchuk
Collaborators: Logan Augustine, Sara Mason (UI Chemistry)

*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 2019-2021:* Our previous work evaluated the impact of hydrogen bonding networks on the Raman spectroscopy of neptunyl chloride solids (Pyrch *et al.*, *Dalton Trans.* (2019) 49, 6854-6866) and suggested that the spectral signals were impacted by concerted motions. Therefore, we believe that the assumption that the neptunyl modes can be modeled using a simple $D_{\infty h}$ point group is likely not valid for spectral interpretation for solid state compounds. While the presence of asymmetric hydrogen bonding networks resulted in the activation of spectral features, we predict that the stronger interactions occurring between the neptunyl-neptunyl units change point-group symmetry for the molecular unit and lead to different features within the vibrational spectra.

We first evaluated stability of dimeric neptunyl-neptunyl models and predicted spectral signals using Density functional theory (DFT) analysis in collaboration with Prof. Sara Mason (UI Dept. Chemistry). We found that high spin states were most favorable for all dimeric models (both diamond and T-shaped) and that addition of explicit water molecules resulted in deviations in the lowest energy configuration and vibrational modes. With the inclusion of the explicit water molecules, the T-shaped Np(V)/Np(V) molecule displays a decrease in the Np-O=Np angle due to additional interactions with the ligated water molecule. The energetics are nearly equal between the T-shaped and diamond conformations, which suggests that the co-solutes present in the system could play a determining role the observable neptunyl-neptunyl conformation.

To explore the impact of these co-solutes, spectral signals from the DFT calculations were then paired with experimental Raman spectroscopy of simple neptunyl salt solutions. We initially evaluated perchlorate and nitrate systems because these ligands bind weakly to the $NpO_2^+$ cation. For the perchlorate system, five signals were observed within the spectral window of interest (500-900 $cm^{-1}$). The mode at 767 $cm^{-1}$ has previously been identified as a pentaaqua complex and two additional bands matched within 2 $cm^{-1}$ of the stretching bands of the T-shape neptunyl-neptunyl dimer that were predicted by DFT calculations. The remaining features were observed in the spectrum at lower energies and were not associated with predicted or previously identified vibrational modes. Similarly, we observed peaks in the nitrate system that were associated with the T-shaped complex and three additional bands that could not be fit with the dimeric model. Additional evaporation of the neptunyl nitrate solution resulted in the formation of a sodium neptunyl nitrate solid that contains a two-dimensional sheet topology built from an extension of the T-shape neptunyl-neptunyl interactions.

Given this final product, we hypothesize that the additional spectral signals within the Raman spectroscopy are associated with larger aggregates.

Only T-shaped neptunyl-neptunyl interactions were identified in the simple inorganic salt systems, so we explored the impact on carboxylate functional groups to induce the formation of diamond motifs. The benzoate system has previously been reported to form diamond-shaped dimers (Charushnikova et al. *Radiochimica Acta* (2007) 95, 495-499) and we utilized this system to explore the signals associated with this type of neptunyl-neptunyl interaction. We have tentatively identified four vibrational bands associated with the diamond-shaped neptunyl-neptunyl complex but additional DFT analysis is necessary to confirm these spectral assignments.

*Science objectives for 2021-2023:*

Research Objective 1: a) Identify neptunyl-neptunyl aggregates and their spectroscopic signals in solution. b) Identify the role of counterions in guiding the formation of T-shaped or diamond shaped neptunyl-neptunyl interactions. c) Further evaluate the role of charge density to activate vibrational modes in the vibrational spectra of neptunyl complexes.

Research Objective 2: a) Benchmark DFT calculations to accurately predict experimental enthalpies of formation in the actinyl tetrachloro system; b) Collect calorimetric data on Np(V) and Np(VI) tetrachloride with different H-bonding and alkali cations to identify the impacts on stability; c) Measure the enthalpy of formation for compounds with neptunyl-neptunyl interactions and compare to theoretical calculations.

Research Objective 3: a) Identify role of $Li^+$ in stabilization of Np(VII) species. b) Develop an understanding of the vibrational modes associated with the Np(VII) species. c) Evaluate the use of $Li^+$ cations to stabilize U(V) in solution.

*Publications supported by this project 2019-2021*

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

*Laura Gagliardi, Principal Investigator*

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Collaborators: Kit Bowen (Johns Hopkins), Suzanne C. Bart (Purdue), Kiplinger (LANL), Eric J. Schelter (University of Pennsylvania), Thomas E. Albrecht-Schönzart (Florida State)

*Overall research goals:*

The objective of this project is to develop and employ novel quantum chemical methods in order to study the chemistry of systems containing actinides, and transactinides, with special focus on actinide-based single molecule magnets.

*Significant achievements during 2019-2021:*

1) We computationally investigated some actinide metallabiphenylene complexes, namely ($C_5Me_5$)$_2$An(2,5-$Ph_2$ cyclopentadienyl[3,4]cyclobuta[1,2]benzene), synthesized in the group of Dr. Kiplinger. DFT and multireference calculations were performed to investigate the electronic structure of these species, the antiaromatic character of the cyclobutadiene ring and the aromatic character of the benzene ring. Spectroscopic evidence, molecular orbital compositions, and natural bond orbital calculations suggest significant covalency of the uranium $f^2$ electrons with the carbon-containing fragment.
2) In collaboration with several PIs in the HEC program, including Eric J. Schelter Thomas E. Albrecht-Schmitt, and Suzanne C. Bart, we investigated an isostructural family of *f*-element compounds (Ce, Nd, Sm, Gd; Am, Bk, Cf) of the redox-active dioxophenoxazine ligand ($DOPO^q$; DOPO = 2,4,6,8-tetra-*tert*-butyl-1-oxo-1*H*-phenoxazin-9-olate). We explored the electronic structure of this new family, by performing complete active space self-consistent field (CASSCF) calculations, which revealed these systems to be largely ionic in contrast to previous studies, where berkelium and californium typically have a small degree of covalent character. As part of this collaboration we have also explored Cf($DOPO^q$)$_2$(py)($NO_3$) (py = pyridine) where the nitrate anion is hypothesized to form via the alpha-radiolysis-induced reaction of pyridine with water. Computational analysis of the electronic structure of the complex reveals that the $Cf^{III}$–ligand interactions are largely ionic.
3) The electronic structures and magnetic anisotropies for compounds [An(COT)$_2$] (An = $U^{III}/U^{IV}$, $Np^{III}/Np^{IV}$ and $Pu^{III}/Pu^{IV}$, COT = cyclooctatetraene) were characterized using scalar relativistic density functional theory calculations and second-order perturbation theory based on a complete active space self-consistent field reference, including also spin-orbit coupling. The degree of participation of 5f orbitals in actinide-ligand bonding and the associated metal-ligand covalency is found to trend as U > Np $\geq$ Pu for both the tetra-positive and tri-positive An complexes. The weak SMM behavior in $[U(COT)_2]^-$ and [Np(COT)$_2$] is attributed to a subtle interplay between local symmetry and ligand-field splitting. Such a result suggests that magnetic anisotropy in $5f^3$ ions can be modulated in general by electrostatic ligand field design.

*Science objectives for 2021-2023:*

Actinide-ligand complexes frequently contain a large number of strongly-correlated electronic degrees of freedom in their wave functions, which renders traditional multiconfiguration self-consistent field (MCSCF) approaches like the CASSCF method problematic due to the factorial explosion of the computational cost of the latter with respect to the size of the active space. However, in many of these systems, the strongly correlated electronic degrees of freedom are centered around separable units, for example distant actinide nuclei or weakly-entangled monomers, and a low-scaling local correlation or fragmentation approach to the MCSCF framework may generate realistic chemical models.

Along these lines, we recently introduced the localized active space self-consistent field (LASSCF) method for strongly-correlated systems characterized by weakly-entangled subunits. LASSCF was originally conceived as a generalization of density matrix embedding theory (DMET), but unlike the latter, LASSCF generates a true wave function for the whole molecule and provides an upper bound to CASSCF and full configuration interaction (FCI) energies. LASSCF produces a localized active space (LAS) wave function, which is an approximation to a CASSCF wave function in which the active space is split into one or more non-overlapping, unentangled subspaces. This approximation to CASSCF eliminates the inherent factorial operation and storage cost explosion with increasing system size that is associated with handling a single configuration interaction (CI) vector spanning a direct-product basis of orbitals. Initial tests of LASSCF showed that it reproduces the results of comparable CASSCF calculations, as long as the strong electron correlation of the test system was localized and short-range. We will extend the LASSCF method to fully minimize the energy with respect to all orbital rotations, rendering it truly variational. This will hopefully improve the robustness and guess dependence of the LAS wave function. We are currently investigating some di-uranium species and exploring different ways of partitioning such systems in terms of active spaces. Magnetic susceptibilities and J coupling constants will be computed for these species.

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

*Shane Galley, Principal Investigator*

Department of Chemistry, Colorado School of Mines, Golden, CO
Graduate Students: Nathan Besson, Emma Archer, Felipe Periero, Erin Bertelsen, Eric Norfleet
Collaborators: Jenifer Shafer, Mark Antonio, Stosh Kozimor (LANL), Enrique Batista(LANL), Ping Yang (LANL), Colt Heathman (INL), Rebecca Abergel (LBNL), Corwin Booth (LBNL), and David Shuh (LBNL)

*Overall research goals:*

The major goal of this proposal is to couple thermodynamic complexation and electrochemical data of transuranic elements with computational and spectroscopic measures of covalency to understand how variables in ligand electronic structure impact the nature of ligand-actinide interactions and, consequentially, the strength of those interactions. By understanding the factors controlling metal-ligand interactions, a more robust framework for predicting actinide chemistry should be provided. A particular emphasis is placed on understanding chemistry of the trans-plutonium actinides.

*Significant achievements during 2019-2021:*

Actinide-Sulfur Project: Multiple publications have been published. A significant body of work now exists regarding the interactions of transplutonium actinides in solution-based systems regarding sulfur-ligand interactions.

Actinide-Nitrogen Project: Synthesis of dipicolinic acid derivatives is nearly complete. Synthesis of lanthanide and actinide terpy complexes has been executed, but a path for identifying a nitrogen-free synthesis path continues. By the end of the period of performance this year, preliminary data should have been completed on transplutonium partitioning studies with the dipicolinic acid dervatives. Preliminary calculations suggest some means of being able to predict separation and stability constant trends using the total binding energy. The electronic factors driving this will be assessed in the next year.

Sabbatical: While impacted by COVID, the sabbatical was crucial for developing a framework for continuing interactions with nearby LANL. Two students, Emma Archer and Felipe Periero, are already planning Seaborg Fellowships this summer and pathways for more consistent investigations with macroscopic actinides are now in place. The ability to participate in the sabbatical with one of my current students, Brian Arko, was also substantially beneficial and, furthermore, the publication of several papers during this past year was enabled by the sabbatical. On a per year basis, this was the highest publication year for this program to date.

*Science objectives for 2021-2023:*

Nitrogen-based project: During this next reporting period, k-edge spectroscopy will be continued and interpretation of lanthanide spectra will have initiated. It is not obvious at this time if computational interpretation of the spectra will be something that can be completed by then. Synthesis of extractants will continue and distribution studies with heavy actinides and lanthanide stability constant measurements will also initiate. Electrochemical studies will also be executed.

*Publications supported by this project 2019-2021*

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

*Trevor W. Hayton, Principal Investigator*

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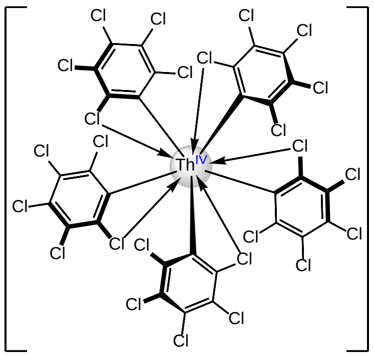
Collaborators: Jochen Autschbach, Dumitru-Claudiu Sergentu, and Xiaojuan Yu, Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY 14260; Herman Cho, Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, USA; Andrew J. Gaunt and Aaron M. Tondreau, Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

*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. My research group has been developing the use of NMR spectroscopy to quantify this covalency. Thus far, we have measured An-L covalency for a variety of ligand types, including chalcogenides, carbenes, alkyls, amides, and nitrides, and for a variety of isotopes, including $^{13}$C, $^{15}$N, $^{77}$Se, and $^{125}$Te. In the case of actinide organometallic complexes, specifically, the $^{13}$C NMR chemical shifts for the actinide-bound carbon environments are strongly affected by spin-orbit (SO) coupling, a consequence of 5f (and to a lesser extent, 6d) orbital participation in the An-C σ-bond. In 5f$^0$ systems with low-lying, empty 5f or 6d orbitals, this SO coupling causes $^{13}$C deshielding when the An-C σ-bond has sizable C 2s character. This SO deshielding correlates to the 5f (and 6d) participation in the An-C bond.



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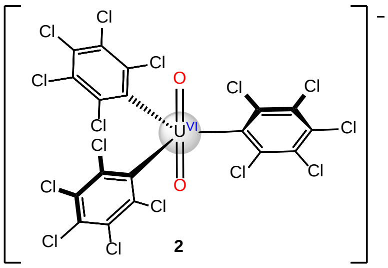
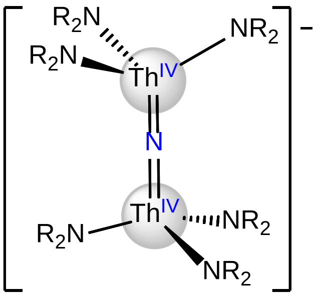


2

*Significant achievements during 2019-2021:* During the 2019-2021 reporting period, we synthesized and characterized a large series of perchlorophenyl complexes of thorium and uranium, including $[Th(C_6Cl_5)_5]^-$ (**1**) and $[UO_2(C_6Cl_5)_3]^-$ (**2**). These complexes feature surprisingly good thermal stability, which we ascribe to the *ortho*-Cl substitution of the $[C_6Cl_5]^-$ ligand. Importantly, this enhanced thermal stability facilitates their spectroscopic characterization. For example, the $^{13}$C{$^1$H} NMR spectrum of **1** features a resonance at 198.78 ppm, attributable to the *ipso* carbon of the pentachlorophenyl ligand. The calculated $C_{ipso}$ chemical shift for this complex (203 ppm) is in good agreement with experiment and includes 27 ppm deshielding due to SO coupling. In contrast, significantly larger SO deshielding (68 ppm) is observed for **2**, due to a combination of large U weight (20% overall) and 5f contribution (43% of the U weight) in its U-C bonds. This difference reflects both the change in element and the higher oxidation state in the uranyl example.

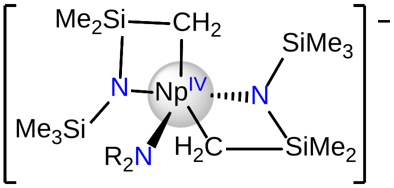


**3**

Building on this work, we recorded the solid-state $^{15}$N NMR powder spectrum of the thorium nitride complex, $[(R_2N)_3Th(\mu\text{-}^{15}N)(Th(NR_2)_3]^-$ (**3**). The experimentally measured tensor span of **3**

($\Omega$ = 847 ppm) is comparable to those measured for transition metal nitrides. In addition, relativistic DFT calculations nicely reproduce the experimental chemical shift and tensor span. Moreover, NLMO shielding analysis confirms that the large tensor span in **3** is principally a consequence of the 5f orbital involvement in the two $\sigma$(N-Th) bonds. Importantly, this result unambiguously confirms the contribution of the 5f valence orbitals to the Th-N$_{\text{nitride}}$ interactions, and suggests that solid-state NMR spectroscopy should be more broadly applied toward the analysis of actinide-ligand bonding. This work was performed in collaboration with Herman Cho at PNNL and Jochen Autschbach at U. Buffalo.

Finally, we synthesized a series of Np silylamide complexes, including $[Np(NR_2)_3Cl]$, $[Np(NR_2)_3Cl]^-$, and $[Np\{\mathit{N}(R)(SiMe_2\mathit{C}H_2)\}_2(NR_2)]^-$ (**4**), greatly expanding the scope of anhydrous Np coordination chemistry. Notably, complex **4** is an exceptionally rare example of a structurally-characterized neptunium hydrocarbyl. These transuranic materials can be easily synthesized in good yields and should greatly help advance non-aqueous neptunium coordination chemistry, which lags markedly behind that of uranium and thorium. Going forward, we plan to employ complex **4** as a precursor to Np oxo, imido, and nitrido complexes. This work was performed in collaboration with Andy Gaunt and Aaron Tondreau at LANL.



**4**

*Science objectives for 2021-2023:*

For the 2021-2023 reporting period, we plan to expand our use of NMR spectroscopy to evaluate An-L bonding, especially with respect to An-C and An=C bonds multiple bonds. In this regard, we exploring the syntheses of Th and U parent acetylide complexes in an effort to evaluate the covalency of their An-C bonds using $^{13}$C NMR spectroscopy and DFT calculations. These complexes are intriguing targets, both because of the insights they could give into actinide electronic structure, but also because of the potential for enhanced reactivity relative to alkyl- or aryl-substituted acetylide complexes. However, the synthetic chemistry to access actinide parent acetylides is not well established. This work is being done in collaboration with Jochen Autschbach at U. Buffalo.

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## Spectroscopic investigations of actinide bonding and electronic structure

*Michael C. Heaven, Principal Investigator*

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Collaborators: Timothy C. Steimle (Arizona State University), Anh Le (Georgia Institute of Technology), Kirk A. Peterson (Washington State University). Alexey L. Kaledin (Emory University) Leonid A. Kaledin, (Argonnide, Fl)

*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. There is a critical need for such data as the results obtained from condensed phase measurements are complicated by solvent-solute or lattice interactions. The ongoing studies are focused on the characterization of the ground and low-lying electronic states of prototypical actinide compounds. These are the states that determine both the physical and chemical properties of the molecules, and they are also the most amenable for detailed theoretical investigations. We are also exploring the limitations imposed on optical spectroscopy by the electronic complexity (density of vibronic states) of open-shell polyatomic actinide species.

*Significant achievements in 2019-2021:*

*The Electronic Structure of the Actinide Oxides and Their Cations.*

Predictive ligand field theory (LFT) calculations of energy levels were performed for the neutral actinide mono-oxides (AnO) and their singly and doubly ionized cations ($AnO^+$ and $AnO^{2+}$). The molecular electronic states were treated as $An^{m+}$ free-ion energy levels perturbed by the electric field of $O^{2-}$ or $O^-$ (where An is Th through Lr and m=1, 2, 3, or 4). LFT parameters obtained from fits to the energy levels of ThO, $ThO^+$, UO, and $UO^+$ were used to compute molecular energy levels for the lowest energy 5f-core states of $An^{4+}$, $An^{3+}$, $An^{2+}$, and $An^+$ for the majority of the $An^{4+}O^{2-}$, $An^{3+}O^-$, $An^{3+}O^{2-}$, $An^{2+}O^-$, $An^{2+}O^2$, and $An^+O^-$ electronic configurations. Simple linear relationships enabled predictions of the dissociation energies for AnO, $AnO^+$ and $AnO^{2+}$ (where An is Bk through Lr) and ionization energies for AnO and $AnO^+$ (where An is Bk through Lr), mainly based on recent accurate experimental data for the ionization energies of An atoms (where An is Fm, Md, No, and Lr) and correlations with the energetics of the atoms and ions.

*Spectroscopy and electronic structure of the low-energy states of ThN*

The electronic spectrum of ThN over the range 19600 – 21200 $cm^{-1}$ is remarkably congested, showing at least twenty vibronic bands originating from the ground state zero-point level. Rotationally resolved spectra for eleven of these bands have been examined to probe the underlying reasons for the dense manifold of states. Dispersed fluorescence spectra and fluorescence decay lifetimes were also measured to provide addition insights. The experimental measurements were complemented by electronic structure calculations for the low-energy doublet and quartet states. The ab initio calculations yielded a density of excited states that was consistent with the congested spectrum. These states were derived from the formal configurations $Th^{3+}(6d)N^{3-}$, $Th^{2+}(7s^2)N^{2-}(2p^5)$ and $Th^{2+}(7s6d)N^{2-}(2p^5)$. The calculations indicated that the rotational and vibrational constants would be characteristic of the electronic configurations. This prediction was not borne out by the experimental data, suggesting that the full range of inter-configurational state interactions were not captured by the computational model. Further studies of this problem are in progress.

*Equipment Transfer*

Equipment from Prof. Timothy Steimle's laboratory at ASU is being used to establish a facility for recording high resolution electronic and microwave spectra at Emory. The equipment, transferred in December 2020, includes two complete molecular beam vacuum systems. One is configured for high-resolution laser induced fluorescence and microwave-optical double resonance (MODR) measurements, the other for two-dimensional spectroscopy (excitation and dispersed fluorescence).

*Science objectives for 2021-2023:*

We have recently obtained the first spectroscopic data for OThF. This molecule has a bent equilibrium structure and intense vibronic band systems at wavelengths near 490 nm. Further studies of OThF and $OThF^+$ will be carried out using fluorescence excitation and multi-photon ionization techniques. Electronic structure calculations will be carried out in support of the experimental measurements. The goal will be to investigate the role of the 5f electrons in the bonding. In parallel, the ASU high-resolution system will be reassembled and calibrated. The recording of rotationally resolved data for $UO_2$ will be the first objective for the high-resolution system.

*Publications supported by this project 2019-2021*

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

*Amy E. Hixon, Principal Investigator*

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Collaborators: Laura Gagliardi (U Chicago)

*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.

*Significant achievements during 2019-2021:*

We completed our study investigating the interactions between hafnium(IV) and the uranyl peroxide nanocluster $U_{24}Pp_{12}$ ($[(UO_2)_{24}(P_2O_7)_{12}]^{48-}$). Electrospray ionization mass spectrometry and Raman spectroscopy were used to probe the stability of clusters in solution as a function of hafnium concentration. Dynamic light scattering and ultra-small-angle X-ray scattering were used to measure the hydrodynamic radius and radius of gyration, respectively, of solutions containing $U_{24}Pp_{12}$ and hafnium to determine if aggregation occurred. Finally, ultrafiltration and inductively-coupled plasma optical emission spectroscopy were used to quantify the amount of hafnium associated with the clusters.

Experimental results indicated that the $U_{24}Pp_{12}$ cluster remained intact regardless of hafnium concentration. Hafnium readily associated with $U_{24}Pp_{12}$ even at low ratios (e.g., 10:1 $U_{24}Pp_{12}$:Hf), but aggregation did not occur, whereas equimolar concentrations of $U_{24}pp_{12}$ and hafnium resulted in the formation of polydisperse blackberry-type aggregates (**Figure 1**).

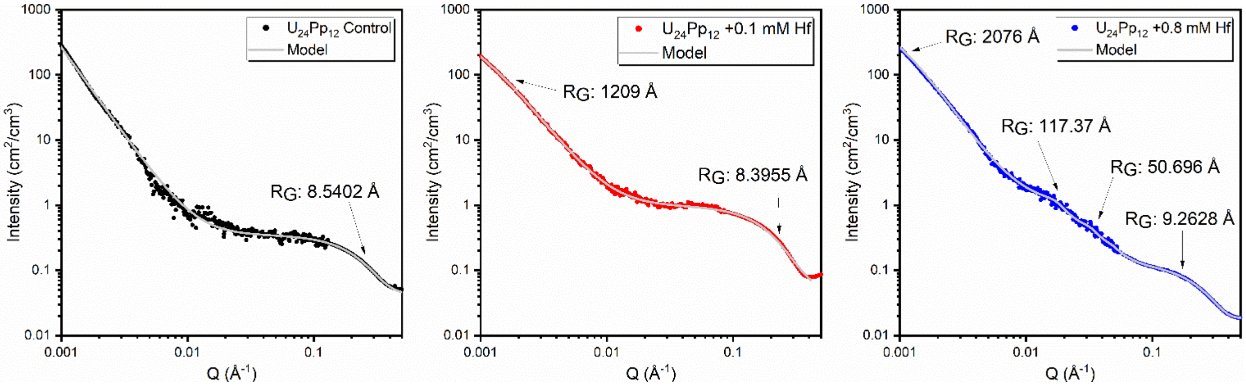

**Figure 1.** Ultra-small angle X-ray and small angle X-ray scattering patterns for solutions containing 10 mg mL$^{-1}$ $U_{24}Pp_{12}$ (left), 10 mg mL$^{-1}$ $U_{24}Pp_{12}$ + 0.1 mM Hf (center), and 10 mg mL$^{-1}$ $U_{24}Pp_{12}$ + 0.8 mM Hf (right). Guinier regions on each pattern are labelled with the radius of gyration ($R_G$) obtained from the model fit.

Extending similar studies to Pu(IV) has been challenging due to the hydrolysis and polymerization of plutonium given that the uranyl peroxide nanoclusters are typically stable in solution under alkaline conditions. Instead, we have shifted our focus to studies containing Np(V) or Pu(VI). The rate and extent of aggregate formation increased with decreasing $U_{24}pp_{12}$ concentration at constant Np(V) concentration, but recrystallization efforts suggested that neptunium and $U_{24}Pp_{12}$ recrystallize separately instead of in the form of a blackberry at the lowest $U_{24}Pp_{12}$ concentration.

Our Pu(VI) suggests that plutonium undergoes reduction in the presence of $U_{24}Pp_{12}$ and $U_{60}Ox_{30}$ ($[UO_2(O_2)(OH)]_{60}^{60-}$) and that this reduction happens over the course of a few hours. Overlap between the uranyl and plutonyl stretches using Raman spectroscopy have made initial interpretation of the results difficult, prompting us to focus on the binary Pu(VI)-oxalate system, since information is lacking in the literature. We used UV-vis-NIR spectroscopy, Raman spectroscopy, and liquid scintillation counting to study the effect of pH, ligand:metal ratio, and time on the Pu(VI)-oxalate system. The UV-vis-NIR results show the stepwise addition of oxalate as well as pH effects. Reduction of Pu(VI) to Pu(IV) occurred regardless of pH, resulting in several unique Pu(IV)-oxalate crystals and precipitates. A plutonium oxalate chain, $Na_{12}Pu_4(C_2O_4)_8 \cdot 22H_2O$, crystallized from a 1:5 ratio of plutonium:oxalate at pH 3 and a plutonium oxalate sheet, $Pu(C_2O_4)_2 \cdot 4H_2O$, crystallized from a 1:3 ratio of plutonium:oxalate at pH 1 (**Figure 2**).

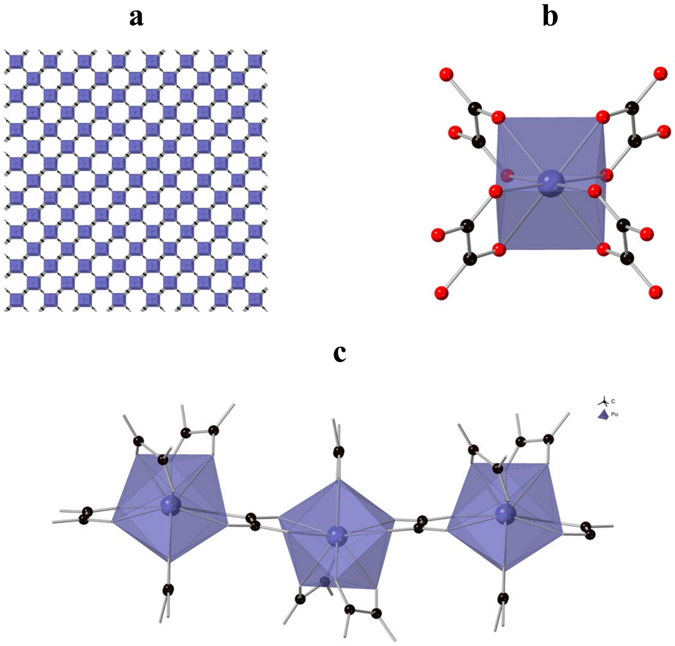

**Figure 2.** Crystal structures of $Pu(C_2O_4)_4 \cdot 4H_2O$ (a-b) and $Na_{12}Pu_4(C_2O_4)_8 \cdot 22H_2O$ (c). Purple = Pu, red = oxygen, black = carbon.

*Science objectives for 2021-2023:*

- Use ultra-small angle X-ray scattering, small angle X-ray scattering, and wide angle X-ray scattering to study the aggregation of UPOMs in the presence of neptunium and plutonium as a function of UPOM concentration.
- Use time-resolved laser fluorescence spectroscopy to study the speciation of neptunium- and plutonium-UPOM complexes (i.e., at UPOM concentrations that do not trigger aggregation).
- Use UV-vis-NIR spectroscopy, Raman spectroscopy, and LSC to study the Pu(VI)-pyrophosphate system as a function of pH, metal:ligand ratio, and time.

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

*Karah E. Knope, Principal Investigator*

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Collaborators: Rebecca Abergel (Lawrence Berkeley National Laboratory); David A. Dixon, Monica Vasiliu, (University of Alabama); Stosh A. Kozimor (Los Alamos National Laboratory); May Nyman (Oregon State University); Eric Schelter (University of Pennsylvania), Sarah Stoll (Georgetown University); Robert Gian Surbella III (Pacific Northwest National Laboratory)

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

*Significant achievements during 2019-2021:*
1. We have demonstrated that outer coordination sphere interactions may be tuned to stabilize various An-$H_2O$-Cl complexes, with the identity of the complex showing dependence on the counter-cation. Further, we have paired our experimental investigations with computational studies that provide insight into the relative energetics that underpin species formation and stabilization. For example, evaporation of acidic aqueous chloride solutions containing Th and protonated N-heterocycles yielded a series of seven distinct thorium complexes of the general formula $[Th(H_2O)_xCl_{8-x}]^{x-4}$ ($x = 2, 4$) and $[Th\text{-}(H_2O)_xCl_{9-x}]^{x-5}$ ($x = 5-7$). The complexes ranged from chloride-deficient $[Th(H_2O)_7Cl_2]^{2+}$ to chloride-rich $[Th(H_2O)_2Cl_6]^{2-}$ species, and provided a foundation from which theory could be used to understand the relative energies that separate complexes via the stepwise chloride addition to an aquated Th cation. Electronic structure theory predicted the reaction energies of chloride addition and release of water and generally highlighted an energetic driving force for chloride complexation. The role of the counterion in the stabilization of the complexes was examined using electrostatic potential (ESP) surfaces. Importantly, the ESP surfaces indicated a dependence of the chloride distribution about the Th metal center on the pKa of the countercation, providing evidence for the directing effects of noncovalent interactions (e.g., H bonding) on Th speciation.

This work has since been extended to Pu(III) systems, in collaboration with Stosh Kozimor (LANL), and preliminary results likewise point to a dependence of the composition and charge of the Pu(III)-$H_2O$-Cl complexes isolated on the identity of the counter-cation.

2. We have harnessed non-covalent interactions to isolate large Ce-oxo clusters. Changes in the XANES and UV-vis-absorption spectra of a chloride decorated $Ce_{38}$ cluster were observed over time and remarkably, reactivity at the cluster surface was captured in the solid state via a single-crystal-to-single-crystal transformation using X-ray diffraction. Overall, a loss of chloride and water molecules and the formation of new $\mu_2$–OH sites at the cluster surface were apparent. The observed single-crystal-to-single-crystal transformation provides an exceedingly rare example of cluster surface lability and reactivity, and also affords important insight with which the behavior of ceria nanoparticles and other, related (actinide) metal-oxo clusters, may be understood.

***Science objectives for 2021-2023:*** Worked supported by this award has shown that outer coordination sphere interactions may be capitalized on towards the stabilization and crystallization of novel An(IV) and Ce structural units as highlighted by the examples above. Future efforts will expand this work in two ways. First, we will examine other monoanionic ligand systems; previous work has largely focused on chloride systems. Second, we will continue to push our synthetic efforts into Np and Pu systems.

Prior work out of our lab has shown that $An_6$ clusters can serve as single source precursors for $AnO_2$ nanoparticles. Yet the effects of the identity of the capping ligand on the reactivity and size of the resulting nanoparticles are not well developed. We have already assembled a catalog of $An_6$ clusters capped by various ligands and future work will focus on examining the solution thermolysis of these $An_6$ clusters with an eye towards understanding the effects that ligand binding strength and sterics have on the reactivity of An(IV) structural units.

Finally, we will extend our efforts aimed at understanding template directed assembly to include 2D surfaces. Preliminary work shows that we can deposit $An_6$ clusters on carboxylate terminated self-assembled monolayers; the phases show preferred orientation consistent with template directed assembly. Future efforts will focus on characterizing the deposited phases and understanding the effects of surface functionalization on phase formation.

*Publications supported by this project 2019-2021*

Wacker JN; Nicholas AD; Vasiliu M; Marwitz AC; Bertke JA; Dixon DA; **Knope KE**.* 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.

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## Resolving the *f*-electron Challenge with Scanning Probe Microscopy/Spectroscopy

*Miles Beaux, Principal Investigator*

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Graduate Students: TBD
Collaborators: Paul Tobash, Ping Yang, Stosh Kozimor, Andy Gaunt (LANL), Brian Powell, Shanna Estes (Clemson University)

*Overall research goals:* The ability to predict the chemical and physical properties of a material is directly related to the structure and interactions of its electrons. For materials comprised of *f*-block elements (the lanthanides and actinides found in the last two rows of the periodic table), the complexity of electronic structure has presented great difficulty in understanding, modelling, and predicting material properties. For this reason, resolving the *f*-electron challenge was identified by the Department of Energy's Basic Energy Sciences program as one of three Grand Challenges to be overcome in order to transform the scientific field. The objectives of this project are to probe the electronic structures of a series of single-crystal actinide (An) carbide, nitride, oxide, and intermetallic samples using scanning tunneling spectroscopy (STS) techniques. Specifically, neptunium (Np), plutonium (Pu), and americium (Am) are targeted due to their unique location in the actinide series of elements, which straddle a transition from itinerant bonding behavior, and localized non-bonding behavior. 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, a seamless mapping of both the occupied and unoccupied electronic structures of these materials can be obtained using a local probe, providing a means by which their complex chemical and physical properties can be understood. The results thus obtained will be compared to mapping of the electronic structures in these materials obtained by other methods, such as photoemission, X-ray absorption, and X-ray emission spectroscopies. Computational modelling of the electronic structures of these materials will be used to correlate the surface electronic states measured by STS, to bulk electronic states and bonding modes of molecular complexes with analogous bonds relevant to Heavy Element Chemistry (HEC) research.

*Significant achievements during 2019-2021:*

N/A: ECRP was recently awarded and has yet to begin.

*Science objectives for 2021-2023:*

-To probe (via STS techniques) and model the electronic structures of the following actinide compounds:

PuSb, $PuSb_2$, $PuIn_3$, $PuPt_3$, $PuCoIn_5$, $PuRhIn_5$, $PuCoGa_5$, $PuRhGa_5$, $PuGa_3$, $Pu_3Ga$, PuTe, $PuIrIn_5$, $PuRu_2Si_2$, $PuO_2$, NpSb, and $NpSb_2$

-To compare the actinide bonding of the listed compounds to analogous bonds in molecular complexes relevant to HEC research.

*Publications supported by this project 2019-2021*

N/A: No publications yet as the project has yet to begin

# Actinide Electronic Structure, Bonding, Coordination Chemistry, and the Dynamics

*Benjamin W. Stein, Aaron M. Tondreau, Ping Yang*

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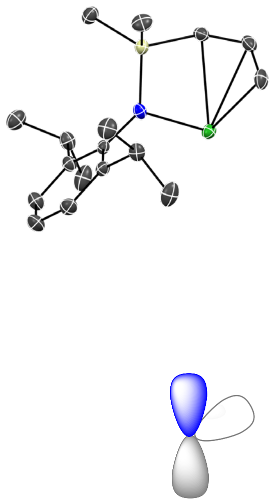
Collaborators: Rebecca J. Abergel (LBNL), Thomas Albrecht-Schmitt (FSU), Jochen Autschbach (University at Buffalo), Enrique R. Batista (LANL), James M. Boncella (LANL), William Evans (UCI), Marc J Cawkwell (LANL), Andrew J. Gaunt (LANL), Kenneth Hanson (FSU), Steven Hill (FSU/NHMFL), Jennifer A. Hollingsworth (LANL), Nik Kaltsoyannis (University of College London), Karah Knope (Georgetown), Andrew Keridge (Lankaster Univeristy), Martin L. Kirk (UNM), Stosh A. Kozimor (LANL), Laura M. Lilley (LANL), Ellen M. Matson (Rochester), Stefan Minasian (LBNL), Michael Neidig (Rochester), Danny Perez (LANL), Jeff J. Rack (University of New Mexico), Eric Schelter (University of Pennsylvania), Gerald T. Seidler (University of Washington), David K. Shuh (LBNL), Robert G. Surbella (PNNL), Vivien Zapf (LANL)

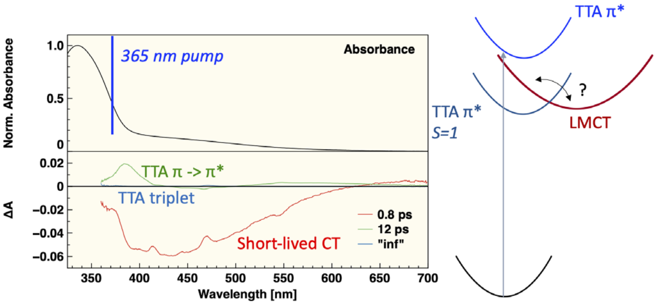
*Overall Research Goals:* The central goal of the Los Alamos Heavy Element Chemistry program is to advance understanding of how unusual electronic structures associated with 5*f*-elements impact the chemistry and physics of actinide containing compounds. Objectives include advancing fundamental understanding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

Promoting interactions of *f*-orbitals and π* orbitals.



*Significant Achievements, 2019-2021:* Actinides occupy central roles in many areas that are important for our quality of life. These range from developing targeted alpha therapy in treating cancer to processing spent nuclear fuel. Hence, there is need to advance fundamental understanding of actinide coordination chemistry. Numerous efforts that have advanced understanding of actinide chemistry revealed that the actinides are able to adopt new structure types that are inaccessible to the main group and the *d*-block transition element series. Understanding the bonding and reactivity within these novel structure types is critical for developing more sophisticated descriptions for the 5*f*-elements, as is further exploring what other unexpected and unprecedented structure types can be accessed by actinide elements. Toward this end, we are investigating the electronic structures of novel actinide complexes and are characterizing the involvement of the *f*-orbitals in the bonding interactions. This presentation describes our efforts to tether arene rings and allyl groups to amido ligands. Constraints associated with this ligand construct holds the organic substituents in bonding distance of the actinide center upon amido complexation by the actinide. As a result, actinide–arene and actinide–allyl sandwich complexes form and can be studied. Within this framework, we reproducibly generated uranium allyl bonds, generated a formally U(+1) complex, and generated a neutral Pu(2+) compound. The resulting molecules were studied using a suite of spectroscopic and computational methods; NMR, UV/Vis, and EPR spectroscopy, and DFT. In addition to defining the actinide–arene and actinide–allyl electronic structures, preliminary reactivity studies have been carried out. Collectively, these results suggest that the arene and allyl fragments interact with the actinide elements through different *f*-orbitals, either $\delta$-type for arene coordination or $\phi$-type for allyl coordination. We found that the formal U(+1) complex represents an example where the formal oxidation state and the number of valence electrons localized on the metal do not agree. For instance, this compound is best described as having a $5f^3$ electronic configuration (like $U^{3+}$) and that the arene is di-anionic (not neutral). In contrast, the Pu(2+) arene sandwich complex has a non-magnetic ($J = 0$) ground state and provides an example where the formal oxidation state and the Pu electronic configuration are in agreement.

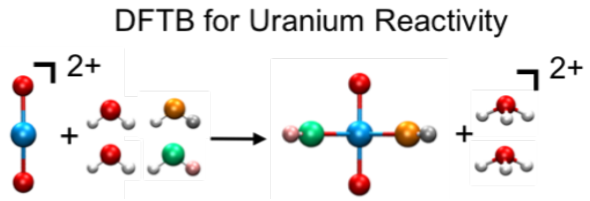
In our continued effort to identify new spectroscopic methods that provide insight into characterizing actinide electronic structure and bonding, we have embarked on an effort to characterize actinide photophysical properties. This campaign could have substantial impact, especially when characterizing electronic properties from actinide compounds in unusual oxidation states, like those described above. In addition, selective control of *f*-element photochemical transformations could open up new areas of separations, unprecedented chemistry, access to new oxidations states, among others. Meeting this challenge requires understanding the photophysics of these systems to a much higher-level of detail than currently exists, which leads to the fundamental question: what happens after a quanta of light is absorbed by an actinide element? To demonstrate "proof-of-principle," we have applied ultrafast (femtoseconds-nanoseconds) transient absorption spectroscopy to a series of early lanthanide (M = $Ce^{III}$, $Ce^{IV}$, $La^{III}$) thenoyltrifluoroacetone (TTA) complexes. These compounds were chosen because of they are known to have rich photochemistry. In addition, the complexing ligands are easily derivatized, which enables actinide electronic structure and photophysical response to be characterized as one meticulously and methodically modifies the ligand's structure and electronic properties. Transient absorption spectroscopy allowed us to deconvolute the states that arise from direct excitation of the ligand as well as those arising from charge transfer excitations. This work has clearly demonstrated that in the appropriate chemical environment – and with judicious choice of wavelength – we can *selectively excite* states of fundamentally different electronic character and avoid their interconversion



Ultra-fast transient absorption spectroscopy of $Ce(TTA)_4$ demonstrating the convolution of ligand centered and charge-transfer states. Selective excitation allows for selection of the LMCT state directly, giving the potential for *state-specific photochemistry*.

despite, drastic differences in lifetimes. Overall, we are excited at the opportunity to further study the electronic structure of photoaccessible actinide excited states and at the opportunity to use these transient species to access unique actinide reactivity.

Critical for the characterization of the compounds described above and for understanding the actinide photophysical chemistry in complex chemical environments is the development more advanced computational methodologies, particularly those that describe more accurately actinide behavior in a time-resolved manner. Unfortunately, it is a challenging task. The limitations stem from the large number of atoms needed for a realistic model and from the large number of simulation steps needed to reach solutions. There is a pressing need to develop accurate molecular dynamics methods that can (*1*) describe their quantum mechanical behavior, such as bond breaking and forming, (*2*) simulate large enough systems, e.g., that includes the second or third coordination shells, and (*3*) achieve long enough timescales to observe processes such as, diffusion in solution or over activation barriers, changes in coordination environments, and chemical reactions. High level wavefunction methods are not suited for molecular dynamics. The fastest current electronic-structure molecular dynamic methods, based on DFT, can only reach to tens of picoseconds for systems containing up to ~200 atoms, while classical force fields cannot accurately handle the charge transfer processes involved in bond breaking and forming. To achieve this goal, we developed the first set of density functional theory tight-binding (DFTB) parameters for actinide chemistry, which will be instrumental in understanding actinide speciation, reaction mechanisms, and kinetics. In this talk, we demonstrate the transferability of our DFTB model using prediction of structural parameters of various molecular clusters and the calculation of variety of chemical reaction free energies. This model has enabled the first microsecond quantum molecular dynamic simulations of actinide nanoparticle systems.



*Scientific Objectives for 2021-2023:* The LANL Heavy Element Chemistry program leverages over 70+ years of LANL's excellence in Pu science to transform uncharted waters of HEC into well-characterized phenomena that can be used to support DOE missions and the national nuclear agenda. Future goals for this project are to continue efforts in advancing understanding of actinide electronic structure, covalent bonding, and reactivity. Particular effort will be placed on evaluating transuranic elements. These efforts are closely aligned with the DOE HEC mission, namely "*Resolving the f-electron challenge to master the chemistry and physics of actinides and actinide bearing materials*." The effort tightly integrates expertise in theory, spectroscopy, and synthesis. Success will identifying the next frontiers in actinide science and has potential for far reaching impact within the DOE's mission space.

Publications Supported by this Project:

- "A. M., Diastereoselective Template Synthesis on Iron and Uranium." Carpenter, S. H.; Billow, B. S.; Tondreau, *Organometallics*, **2021**, accepted.

- "Advancing Understanding of Actinide(III) (Ac, Am, Cm) Aqueous Complexation Chemistry." Jones, Z. R.; Livshits, M. Y.; White, F. D.; Dalodire, E.; Ferrier, M. G.; Lilley, L. M.; Knope, K. E.; Kozimor, S. A.; Mocko, V.; Scott, B. L.; Stein, B. W.; Wacker, J. N.; Woen, D. H. *Chem. Sci.* 2021, 12, 5638. doi:10.1039/D1SC00233C.
- "Structural and Spectroscopic Comparison of Soft-Se vs Hard-O Donor Bonding in Trivalent Americium/Neodymium Moledules." Goodwin, C. A. P.; Schlimgen, A. W.; Albrecht-Schonzart, T. E.; Batista, E. R, Gaunt, A. J.; Janicke, M. T.; Kozimor, S. A.; Scott, B. L.; Stevens, L. M.; Whitte, F. D.; Yang, P. *Angew Chem Int. Ed*. **2021**, 60, 9459-9466. doi.org/10.1002/anie.202017186
- "Complexation of Lanthanides and Heavy Actinides with Aqueous Sulfur-Donating Ligands." Bessen N. P.; Popov I. A.; Heathman, C. R. R.; Grimes, T. S.; Zalupski, P. R.; Moreau, L. M.; Smith, K. F.; Booth, C. H.; Abergel, R. J.; Batista, E. R.; Yang, P.; Shafer, J. C. *Inorg Chem,* **2021**, 60, 6125-6134. doi.org/10.1021/acs.inorgchem.1c00257
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# Molecular Approaches to the Electronic Structure of Actinide Materials

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*Overall research goals:* The goal of this proposal is to develop a systematic molecular and spectroscopic approach to understanding the electronic structure and properties of plutonium and other mid-actinide materials. Molecular complexes of plutonium can provide definitive relationships between electronic structure and spectroscopic features that are not obtainable in measurements of extended solid materials due intrinsic experimental problems (such as self-irradiation and heating) and complex spectroscopic features arising from multiple competing electronic phenomena on similar energy scales. 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. Particularly in solid-state systems, the *f*-elements present unique valence electronic structures due to the near degeneracies engendered in these systems and strong electron correlation. 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 $CmO_2$. This proposal will expand on research during the last funding period to understand these three key phenomena in plutonium material electronic structure.

*Significant achievements during 2019-2021:*

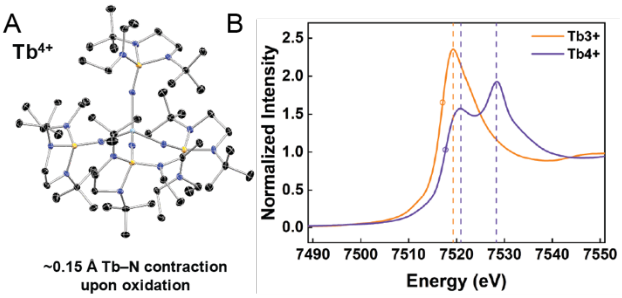

**Fig. 1:** A) SC-XRD molecular structure of **$[Tb^{4+}(NP^*)_4]$** (hydrogen atoms removed); B) Background subtracted and normalized Tb $L_3$-edge XANES spectra of **$[Tb^{4+}(NP^*)_4]$** (indigo) and **$K[Tb^{3+}(NP^*)_4]$** (orange).

We have acknowledged support of the HEC program in eight publications during this funding period. Our work during the last funding period was focused on two areas: multiconfigurational and mixed-valence behavior in monometallic and bimetallic complexes. The efforts relied on the development of several new ligands and the application of Ln and An $L_3$-XANES and magnetometry, in conjunction with electrochemical analysis and reactivity studies, to expand multiconfigurational and mixed-valent low- and high-valent complexes of the lanthanides and actinides. These studies include reporting the synthesis and physical characterization of an $S_4$ symmetric, four-coordinate tetravalent terbium complex, $[Tb^{4+}(NP^*)_4]$, (Fig. 1). The significant stability of the exceptionally rare tetravalent terbium complex enables its thorough characterization. The group has also completed initial synthetic studies for the isolation of high-valent and potentially multiconfigurational mid-actinide complexes. These studies include the isolation of a tetrahomoleptic, tetravalent uranium complex, $[U(NP)_4]$, which is readily undergoes two-electron oxidative atom/group transfer reactions with nitrous oxide and mesityl azide to give the hexavalent products $[U^{6+}(O)(NP)_4]$ and $[U^{6+}(NMes)(NP)_4]$, respectively. Most importantly, the accessibility of the $U^{4+/6+}$ couple in a homoleptic imidophosphorane ligand field will facilitate the formation of MLMB complexes of Np and Pu since low-valent actinide ions become less reducing with increasing Z.

*Science objectives for 2021-2023:*

Three problems of electron (de)localization in plutonium materials will be addressed in this study. In this project period, we intend to focus on the synthesis of neptunium and plutonium complexes that enforce ground state electronic structures that include multiconfigurational electronic structures, mixed-valence metal ions (*i.e.* mixed *f/d* occupancy by the valence electrons), and exchange coupled systems (*i.e.* magnetic superexchange). Mono-, bi-, tri- or tetrametallic complexes that present these electronic phenomena are designed to be evaluated spectroscopically by multi-edge XAS (including high energy resolution fluorescence detected, HERFD), resonant inelastic X-ray scattering (RIXS), and electron paramagnetic and nuclear magnetic resonance (EPR and NMR), as well as by magnetometry, in order to establish clear correspondence between spectroscopic signature, electronic structure, and physical properties.

*Publications supported by this project 2019-2021*

Rice, N. T.; McCabe, K.; Bacsa, J.; Maron, L.; La Pierre, H. S., "Two-Electron Oxidative Atom Transfer at a Homoleptic, Tetravalent Uranium Complex." *Journal of the American Chemical Society* **2020,** *142* (16), 7368-7373. [DOI].

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

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Postdoctoral Researchers: Dr. Stephan Hohloch, Dr. Tian Jian, Dr. Mariah Parker

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

*Recent Progress*

*Development of New Supporting Ligands to Control Electronic Structure and Reactivity.* The first An–heavy tetrylene bonding interactions have been realized in the form of uranium–silylene complexes through reaction of a U(III) complex with base-stabilized Si(II) precursors. The resulting complexes feature dative U–Si bonding interactions. Density functional theory calculations reveal polarization to the U–Si bonds, yet with high bond orders and therefore substantial covalent character. Using a bulky cyclopentadienyl ligand, mononuclear metallocene U(III) and U(IV) dihalides were isolated for F through I for the first time; the 'base free' metallocenium salt was also prepared. The unique electronic properties of F, versus the other halides, as a ligand to U was demonstrated, especially by electrochemistry and UV-visible spectroscopy. The magnetic properties of the base-free metallocenium cation and the monoiodide complex advanced our understanding of An single-molecule magnets. Functionalization of a U(III) $\beta$-diketiminate (BDI) complex with aryloxide ligands was employed to form new heteroleptic U(III) complexes: a dinuclear iodo-aryloxide and a mononuclear bis(aryloxide). The latter compound exhibits a rare (for U(III)) tetrahedral geometry, and displays single-molecule magnet behavior. While uranium azides have attracted considerable attention for their ability to generate uranium nitrides, the isoelectronic isocyanate ligand ($NCO^-$) has been the subject of comparatively few studies. Nearly identical structures, but subtle differences in electronic properties, were observed in U(IV) metallocene diazide and diisocyanate complexes. Computational studies helped elucidate energetic preferences for linkage isomers and the effect of borane coordination on bonding in these species.

*Understanding and Controlling Actinide Reactivity at the Molecular Level in Gas Phase.* The gas-phase projects span three interrelated themes: (1) reactivity of An-ligand bonds; (2) modification of An reactivity by coordination; and (3) An in extreme oxidation states. Experimental studies of variations in bonding and reactivity across the An series from Th to Es elucidate underlying effects and provide testable hypotheses. Some recent highlights are summarized, with others described in the cited publications. A focus is reactivity of oxo bonds in actinyl(V) dioxo cations, $AnO_2^+$, as assessed by conversion of An=O to $An(OH)_2$ either as a product of $H_2O$ chemisorption or as an intermediate in oxo-exchange with $H_2{}^{18}O$ to ultimately yield An=$^{18}$O. We examined this reactivity experimentally for An = Th-Cm, in parallel with computations by collaborators. Coordination dimers in which a uranyl(V) and uranyl(VI) are linked by dicarboxylates provide control of structures and bonding through adjustment of linker length $n$. For $n = 3$ or 4, the uranyl moieties are constrained to non-interacting nearly parallel orientations, whereas greater flexibility of longer linkers, $n \geq 5$, enables $U^{V}$-$U^{VI}$ "cation-cation interactions". Such rational control of structure and resultant reactivity will be extended to neptunyl and plutonyl dimers, with a goal of providing guidance towards new condensed phase chemistry. Actinyl(V) ions coordinated by sulfonates, $An^{V}O_2(RSO_2)_2^-$, exhibit reactivity that depends on the specific actinyl and sulfonate. The results suggest unexpected similarity between bonding in hydroxides and fluorides, which led to an ongoing assessment of actinide halides to understand the nature of the bonding, specifically whether it is predominantly ionic or covalent.

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

*Selected Publications supported by this project 2019-2021*

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4. Vallet, V.; Gong, Y.; Saab, M.; Réal, F.; Gibson, J. K. Carbon-Sulfur Bond Strength in Methanesulfinate and Benzenesulfinate Ligands Directs Decomposition of Np(V) and Pu(V) Coordination Complexes. *Dalton Trans.* **2020**, *49*, 3293-3303. DOI: 10.1039/d0dt00125b.
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# Role of f Orbital Interactions in Determining Heavy Element Physical Properties
## FWP CH030203 – Thrust 2

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*Overall Research Goals:* A central issue in coordination chemistry is the effect of orbital interactions on electronic structure, which in turn affects complex stability, ionic radii, magnetic behavior, reactivity, and luminescence. In the actinide (An) series, the effective nuclear charge of a given oxidation state increases from Th through Lr, which leads to both stabilization and contraction of the 5f orbitals. These changes have profound and contradictory effects on An-ligand interactions. New techniques, methods, and instrumentation are also being developed enable and improve the capability to determine the physical properties of the An, with an emphasis on the transuranics. The efforts primarily focus on on synchrotron radiation- and transmission electron microscope (TEM)-based facility approaches.

*Significant achievements during 2019-2021:*

*Hard X-Ray Spectroscopy.* We have developed methods for routine EXAFS measurements of the local structures of transPu solutions and ng-scale solids (with Kozimor, LANL), using hydroxypyridinone/catecholamide multidentate chelators as model structures. Changes in An-O bond lengths in model complexes formed with ligand 3,4,3-LI(1,2-HOPO) are evidenced as one passes through Cf to Es in the An series (Fig. 1). *Soft X-ray Spectroscopy.* The first soft x-ray experiments with focused ion beam (FIB) sections of $UO_2$-based spent nuclear fuel have been conducted (with He, INL) utilizing the scanning transmission X-ray microscope (STXM) at the Advanced Light Source (ALS) Beamline 11.0.2. Results from oxygen K-edge spectro-microscopy electronic structure analysis show that the fuel is oxidized near defects such as voids and intergranular cracks as shown in Fig. 2. This establishes the viability and utility of soft X-ray STXM combined with FIB lamellae for determining electronic structure and chemical differences from radioactive materials at a scale of tens of nanometers. The electronic structure of UN (an advanced fuel) and $UN_2$, have been investigated at the nitrogen K-edge using the same methodology. During the analysis, a modification to non-negative matrix factorization methods for STXM data developed for this project could have wide spread application for STXM experiments. Covalency was measured at the C K-edge for f-element metallocenes, showing that covalent orbital mixing in the δ-antibonding orbitals of $e_{2u}$ symmetry was similar for $Ce(C_8H_8)_2$ and $U(C_8H_8)_2$ (Fig. 3). However, the more diffuse 5f orbitals resulted in better metal-ligand overlap a greater covalent contribution to stability for $U(C_8H_8)_2$ and greater reactivity for $Ce(C_8H_8)_2$. With the aid of DFT calculations (Batista, Yang, LANL), an intuitive model was developed which suggested that this counterintuitive relationship between covalency and stability may be more common as the 5f orbitals contract later in the actinide series.

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

*Science objectives for 2021-2023:*

The main experimental model for the electronic structures of lanthanide (Ln) and An complexes is crystal field theory (CFT), which works very well for trivalent Ln's and An's but less well for complexes in higher oxidation states. On potential reason that CFT may work less well is that it assumes that the effects of orbital overlap are isotropic – they affect all f-orbitals equally. In higher oxidation state complexes, the An orbitals are stabilized relative to $An^{3+}$ complexes resulting in smaller $\Delta E_{An-L}$, and greater $\lambda$. We developed a new version of CFT that allows for anisotropic overlap yet uses the same number of parameters as conventional CFT. The model was applied to $5f^2$ complexes ($UX_6^{2-}$, X = F, Cl, Br, I) and a $4f^2$ complex, ($PrCl_6^{2-}$). Relative to conventional CFT, the new model more precisely fit spectra of $UX_6^{2-}$ and less precisely fit the spectrum of $PrCl_6^{2-}$, which is consistent with the increased $\lambda$ for 5f orbitals relative to 4f (Fig. 5).

*Selected Publications supported by this project 2019-2021*

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# Designing New Structural Platforms for Heavy Element Chemistry
## FWP CH030203 – Thrust 3

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### *Overall Research Goals:*

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

### *Research Progress*

*Nature-Inspired Ligands for An Coordination Chemistry.* Liquid-liquid extraction methods were developed to determine conditional stability constants for complexes formed between 3,4,3-LI(1,2-HOPO) and the heavier actinide ions $Am^{3+}$, $Cm^{3+}$, $Bk^{4+}$, $Cf^{3+}$, and $Es^{3+}$, with minute amounts of ligand and tracer levels of the metal ions. We are now able to derive conditional stability trends along the Ln and An series, which will inform us of the potential of these ligands for element separation based on metal identity and oxidation state. We prepared series of ligands through a combinatorial approach using polyamine and peptoid bioplymer scaffolds as well as macrocyclic architectures, which allows for the sequential addition of chosen binding groups in a systematic manner. New ligands were characterized for their Cm(III) luminescence sensitization properties, drastically enhancing the effects of different functional groups on luminescence properties that were previously observed with Eu(III) and Tb(III). Metal coordination was probed by EXAFS for all metal complexes formed with elements from U to Cf. Combined with spectro-electrochemical data and Raman measurements, these studies highlighted the reduction power of hydroxypyridinone ligands, which stabilize earlier actinide centers in the +IV oxidation state (reduction of uranyl and neptunyl compounds). Charge-based separation strategies are now being devised, taking advantage of the facile tuning of these oxidation states.

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

*Bridging Understanding of Actinide Chemistry Across Length Scales.* We developed syntheses for new single-source molecular precursors for An solids, including syntheses of four homoleptic thorium(IV) amidate complexes. Each can be sublimed at atmospheric pressure, with the substituents on the amidate ligands significantly impacting their volatility and thermal stability. The complexes decompose via alkene elimination to give $ThO_2$ without need for a secondary oxygen source. A detailed characterization study including X-ray spectromicroscopy at the ALS showed that $ThO_2$ samples formed from pyrolysis of C-alkyl amidates were found to have higher purity and crystallinity than $ThO_2$ samples formed from C-aryl amidates. In addition, we synthesized U(III) and U(IV) amidinate compounds as precursors for uranium nitrides. By varying the ligand substituents and azide source, we were able to control the composition and nuclearity of multinuclear uranium nitride products. We reported the structural properties of ultra-small $ThO_2$ and $UO_2$ nanoparticles (NPs), which were synthesized from molecular precursors by employing a covalent organic framework (COF-5) as an inert template.

*Light Conversion in f-Element Nanoparticles.* Non-linear optics and up- and downconversion mechanisms form another set of properties that remain unexplored in An materials. High upconversion (uc) efficiencies are known for lanthanide-doped solids. While a large number of suitable hosts doped with lanthanides or transition-metal ions (3*d*, 4*d*, 5*d*) have been reported to show anti-Stokes luminescence, scarce reports of this phenomenon have been made for An ions. We investigated the spectroscopic properties of rare-earth, core-shell nanoparticles decorated with 3,4,3-LI(1,2-HOPO). Evidence of photon downconversion is corroborated through detailed power dependence measurements, with emission being dominated by normal, Stokes' shifted fluorescence. Specifically, ultraviolet ligand photosensitization of $Nd^{3+}$ ions in a $NaGdF_4$ host shell results in energy transfer to a $Nd^{3+}/Yb^{3+}$-doped $NaGdF_4$ nanoparticle core. Emphasis is placed on the generality of this material architecture for realizing ligand-pumped, multi-photon downconversion, with the $Nd^{3+}/Yb^{3+}$ system functioning as a working prototype for a design principle that may be readily extended to other Ln and An pairs.

*Selected Publications supported by this project 2019-2021*

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5. Pallares, R. M.; An, D. D.; Deblonde, G. J. P.; Kullgren, B.; Gauny, S. S.; Jarvis, E. E.; Abergel, R. J. Efficient discrimination of transplutonium actinides by in vivo models. *Chem. Sci.* **2021**, *12* (14), 5295-5301. DOI: 10.1039/D0SC06610A.
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# From Accurate Variational Relativistic Electronic Structure Theory to Practical Applications in Heavy-Element Chemistry

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Collaborators: Ping Yang (LANL), Enrique R. Batista (LANL), Stefan Minasian (LBNL)

*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 2020-2021:*

During this funding period, we have published 4 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 an efficient four-component Dirac-Coulomb-Gaunt Hartree-Fock method using the Pauli spinor representation that achieves the theoretical limit of the computational cost of the Dirac-Hartre-Fock method;

(2) development of the minimal floating-point operation count Cholesky decomposition to greatly reduce the storage requirement of two-electron repulsion integrals.

*Science objectives for 2021-2023:*

There are three specific plans:

(1) We will develop four-component configurational interaction in the Pauli spinor basis. In this framework, we expect to develop four-component complete active space self-consistent-field (CASSCF) and multireference configurational interaction (MRCI) methods.

(2) We will develop the fast Cholesky-ERI enabled four-component Dirac Hartree-Fock method to support CASSCF and MRCI applications for large scale heavy-element complexes.

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

*Publications supported by this project 2019-2021*

1. Shichao Sun, Torin F. Stetina, Tianyuan Zhang, Hang Hu, Edward F. Valeev, Qiming Sun, Xiaosong Li, “Efficient Four-Component Dirac-Coulomb-Gaunt Hartree-Fock in the Pauli Spinor Representation” *J. Chem. Theory Comput.,* **2021**, *17*, 388-3402, DOI: 10.1021/acs.jctc.1c00137.
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3. Joseph M. Kasper, Torin F. Stetina, Andrew J. Jenkins, Xiaosong Li, “Ab Initio Methods for L-edge X-ray Absorption Spectroscopy”, *Chem. Phys. Rev.*, **2020**, 1, 011304, DOI: 10.1063/5.0029725.
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# Probing Electronic Interactions of Actinides with Metal-Oxide Surfaces using Actinide-functionalized Polyoxometalates

*Ellen M. Matson, Principal Investigator*

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*Overall Project Goals:* The goal of this project is to explore the synthesis, electronic structure and reactivity of low-valent actinide-functionalized metal oxide clusters (polyoxotungstates and polyoxovanadates). It is our hypothesis that the delocalized electronic structure of the metal-oxide "metalloligand" will support electronic communication between cluster and the electronic-rich actinide ion, effectively mimicking the surface-heteroion electronic interactions operative in atomically disperse actinide-functionalized metal oxide materials. This research will address critical scientific challenges in the field of fundamental actinide research, including the role of 5*f* electrons in bonding and reactivity.

*Recent Progress:*

*Synthesis of actinide-functionalized polyoxovanadate clusters.* Toward the primary objective of this proposal, the reactivity of low- and high-valent actinide and vanadyl precursors have been explored. The results of these findings have shown that actinide centers bearing chloride ligands serve to halogenate the vanadium center, resulting in the formation of monometallic ion pairs as opposed to clusters containing both vanadium and a given actinide. Current work is focused on alternative An(IV) alkoxide adducts as precursors for the desired mixed-metal oxide assemblies. We have also investigated the addition of high-valent uranyl moieties to reduced polyoxovanadate cluster precursors to generate mixed-valent uranium/vanadium oxide clusters. Exposure of $[^nBu_4N]_4[V^V{}_8V^{IV}{}_2O_{26}]$ to an equivalent of uranyl nitrate results in the formation of a novel uranium-vanadate cluster, $[^nBu_4N][U_4V_{20}O_{60}]$. Our team is currently exploring improved synthetic routes and characterization of this low-valent mixed metal oxide assembly.

*Synthesis of actinide-functionalized polyoxotungstate clusters.* The challenges associated with isolating low-valent derivatives of polyoxovanadate clusters that arise as a result of the *in situ* reduction of the vanadate salts by $U^{IV}$ precursors have reinvigorated our interest in the development of organofunctionalized polyoxotungsate clusters as redox-active metalloligands for low-valent actinide ions. Indeed, the organofunctionalized polyoxotungstates targeted in these investigations have been reported to possess cluster-derived reduction potentials of -1.54 and -2.39 V vs. $Fc^{+/0}$, values substantially shifted from the reduction potential of the dodecavanadate clusters described above ($E_{1/2}$ = -0.74 V vs. $Fc^{+/0}$). Further justification for exploring these systems in tandem with the polyoxovanadates described above rests in the well-defined metalation strategies for these organofunctionalized polyoxotungstate ions: in contrast to self-assembly routes proposed for actinide-functionalized polyoxovanadates, the well-defined coordination pocket of the polyoxotungstate clusters affords facile synthesis of heterometal functionalized polyoxotungstates. Our progress, to date, has been rooted in the synthesis of new derivatives of organofunctionalized polyoxotungstates, namely clusters featuring bulky organic moieties to better protect the large actinide ion. We have successfully synthesized and characterized three new derivatives of the siloxide-functionalized trilacunary Keggin ions, $[PW_9O_{34}(RSiOH)_3]^{3-}$ (R = Ph, $^tBu_2$-Ph, PhPh). Metalation of all three clusters, in addition to the originally reported cluster, $[PW_9O_{34}(^tBuSiOH)_3]^3$, with hafnium(IV) ($Hf(O^tBu)_4$) has been accomplished. Current investigations are focused on extending these studies to the coordination of tetravalent actinides ($Th^{IV}$, $U^{IV}$) to the siloxide-functionalized polyoxotungstate clusters.

*Synthesis and optical properties of pyridine dipyrrolide adducts of low- and high-valent actinide centers.* Complementary to our An-POV studies, we have also initiated a collaboration with Carsten Milsmann and coworkers at West Virginia University, studying LMCT reactions of low- and high-valent actinide complexes supported by pyridine dipyrrolide (PDP) ligands. To date, we have successfully isolated $U(^{Ph}PDP^{Ph})_2$ from the reaction of in situ generated $Li_2{}^{Ph}PDP^{Ph}$ with $ThCl_4(dme)$ and $UCl_4$. Characterization of the dark-red, paramagnetic U(IV) complex has been performed by $^1H$ NMR and cyclic voltammetry (CV), with its molecular structure has been confirmed by single crystal X-ray diffraction. Additional work has probed the reactivity of $[UO_2]^{2+}$ within the planar, tridentate PDP ligand. Previously, researchers have demonstrated that uranyl complexes carrying pyrrolide-type ligands exhibit diverse chemical applications spanning from luminescent complexes to complexes where reductive functionalization of the uranyl moiety is possible. To date, we have characterized a novel uranyl complex, namely $(^{Mes}PDP^{Ph})UO_2(thf)$, sourced from reaction of $Li_2{}^{Mes}PDP^{Ph}$ and the uranyl dimer $[UO_2Cl_2thf_2]_2$. Structural characterization of $(^{Mes}PDP^{Ph})UO_2(thf)$ reveals the compound features a slightly activated $UO_2$ fragment, evidenced by a O-U-O angle of 173.94(9)°. Preliminary electrochemical characterization has demonstrated a reversible reduction event ($E_{1/2} = 1.51$ V vs. $Fc^{+/0}$), suggesting that reduction of $(^{Mes}PDP^{Ph})U^{VI}O_2(thf)$ to $(^{Mes}PDP^{Ph})U^{V}O_2(thf)$ may be feasible.

*Future Plans:*

We are extremely excited about the opportunities for the development of controlled syntheses of low-valent actinide complexes supported by siloxide-functionalized polyoxotungstate clusters. Current efforts to extend the reported chemistry for coordination of Hf(IV) alkoxide compounds to Th(IV) and U(IV) have been met with challenges, but we believe this is due to our selection of starting materials. Ongoing investigations are probing the reactivity of U(IV) and Th(IV) alkoxide and aryl-oxide precursors that we believe will be more productive for metalation to the pocket of the trisiloxide-functionalized assemblies. We also plan to study a series of disiloxide functionalized polyoxotungstates that we hypothesize will be better suited for coordination of the uranyl ion and subsequent investigations related to U=O bond activation at the surface of redox-active metal oxides.

While molecular synthesis is a major priority for all the projects described in this progress report, we are optimistic that in the next funding period we will be able to move beyond the generation and isolation of actinide complexes supported by metal oxide ligands and our investigations probing the electronic structure of these multimetallic assemblies. We are particularly excited about investigating reduced variants of the actinide-functionalized polyoxometalate clusters described above, as we anticipate charge transfer between f- and d-orbitals may be operative upon excitation of electron density in the intervalence charge transfer bands of these compounds. The major focus of these studies will rest in developing an understanding of electron dynamics within the excited states of these molecules.

*Recent Publications Resulting from this Award:*

Auvray, T.*; Matson, E. M.* "Polyoxometalate-based complexes as platforms for the study of actinide chemistry" *Dalton Trans.* **2020**, *49*, 13917-13927 (selected by editor as "Hot Article"). DOI: 10.1039/D0D102755C

Auvray, T.; Nachtigall, O.; Brennessel, W. W.; Jones, W. D.; Matson, E. M.* "Development of sterically hindered siloxide-functionalized polyoxotungstates for the complexation of 5d-metals" *Dalton Trans.*, **2021**, *50*, 4300-4310. DOI: 10.1039/D1DT00256B.

# Tailoring Redox Active Ligands for Probing the Reactivity of Actinides

*Evangelos Miliordos, Principal Investigator*

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Graduate Students: Isuru Ariyarantha, John Ducilon, Emily Hardy, Ethan Hiti, Julie Niklas
Undergraduate Students: Madeleine Forbes, Katherine Hunter, Jacob Mayhugh, Grant Wilkinson
Collaborators: Anne E. V. Gorden, John D. Gorden, Ana de Bettencourt-Dias, Jorge Monteiro

*Overall research goals:* Redox-active and redox non-innocent ligands have been used to compare electrochemical behavior in transition metal chemistry, but uranium complexes with redox-active ligands are rare. Previously, we developed a new redox-active ligand, "phen-BIAN" (N,N'-bis(iminophenol)acenaphthene) (Figure 1), for investigations of the electronic behavior of uranium and other actinides. The work proposed here entails extensive preparation, structural and spectroscopic characterization of actinide and lanthanide complexes with this and related Schiff based ligands. This will allow us to address probative questions about the nature of the 4f -and 5f – elements including actinide bonding, the degree of covalency, the validity of lanthanides as models for actinides, hard-soft interactions, and what electronic and steric affects affect the ligand selectivity.

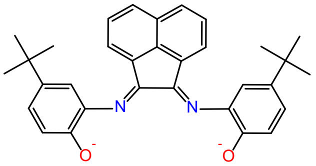
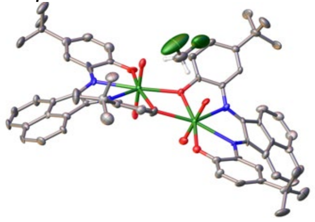


**FIGURE 1: (Top)** *Structure of **1**.* N,N'-bis(iminophenol)acenaphthene **(Bottom)** *Molecular structure of the dimeric uranyl ($UO_2^{2+}$) complex of **1**.*



*Significant achievements during 2019-2021:*

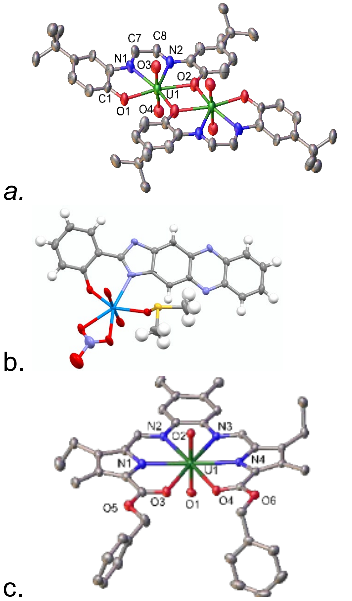


**FIGURE 2:** *Molecular structures from X-ray diffraction data of **a.** $UO_2$-Methoxy- α-diimine glyoxal bis(2-hydroxyanil complex **b.*** $UO_2$*-2-(1H-imidazo[4,5-b]phenazin-2-yl)phenol complex **c.*** $UO_2$-pyrrophen complex

- A series of uranyl complexes with substituted α-diimine ligands (gbha and phen-BIAN – see figure 1, figure 2a) have been characterized to compare the effects of aryl group substitution as well as extended π-systems on the behavior of the axial oxo moieties. These species can form rare μ-phenolato bridged dimers. The non-innocence of the systems can be observed in multiple redox-processes and allows significant reduction of the complexes. This has allowed the comparison of the U(VI)-U(VI) complexes with the lower oxidation species through electrochemical reduction. This work was described in a paper published in *Inorganic Chemistry.*

- Pyrrophen, a sal-porphyrin analogue and the dimethyl derivative have been prepared and characterized as the uranyl complexes both in the solid state and in solution(see figure 2c). This ligand is unique in that it forms 1:1 complexes readily with uranyl and dimetallic helicate species with transition metals and it makes a very symmetrical complex with U(VI). The ligand is also somewhat selective for uranyl, with uranyl displacing other 2+ metals to form complexes.

- Uranyl complexes of the new imidazole backboned ligand 2-(1H-imidazo[4,5-b]phenazin-2-yl)phenol (nicknamed "salimidizine") have been prepared and characterized. This ligand was found to be highly fluorescent and the emission was observed to increase with the addition of uranyl and decrease with the addition of copper. This ligand charge metal transfer was uranyl was distinct and we used TD-DFT to identify the state with the highest oscillator strength in the region of the absorption frequency used. Based on these results, For copper, the electron transition is clearly a ligand-to-ligand transition. For uranyl, the same ligand to ligand transition has substantial involvement of the uranium f-orbital. This work has been submitted for publication.

- Three 2:3 M:L Ln(III) complexes with a cyano-naphthylsalophen ligand metal sandwich structure have been prepared (See figure 2c). Complexes containing a mixture of Er(III) and Yb(III), or Er(III), Yb(III), and Y(III ), or Er(III) display Er-centred red and green emission upon excitation with a 980 nm laser at low power densities, indicative of two photon up-conversion, making these rare examples of upconverting LnIII-based molecules.

*Science objectives for 2021-2023:*

In continuing this work, we will probe the electronics of uranyl and thorium complexes with the pyrazine ligands both with and without peroxides, and explore the preparation of lower-oxidation state and non-oxo uranium complexes. Additional members of the phen-BIAN family will be synthesized, including naphthalene and pyridine derivatives, and the influences of these substituted groups on the redox activity, coordination sphere, and covalent interactions of the metal center will be evaluated structurally and electrochemically. New emphasis will be placed on the isolation and detailed study of low-oxidation state uranium complexes and their properties. The latter will assist greatly in providing a benchmark against which to compare and evaluate the distinct behaviors exhibited by 5f-element complexes.

*Publications supported by this project 2019-2021*

Julie E. Niklas, Katherine M. Hunter, Anne E. V. Gorden, "Bonding Interactions in Uranyl α-Diimine Complexes: A Spectroscopic and Electrochemical Study of the Impacts of Ligand Electronics and Extended Conjugation" *Inorganic Chemistry* **2019**, 58, 22, 15088-15100. (https://doi.org/10.1021/acs.inorgchem.9b01695)

Jacob T. Mayhugh, Julie E. Niklas, Madeleine G. Forbes, John D. Gorden, Anne E. V. Gorden, "Pyrrophens: Pyrrole-Based Hexadentate Ligands Tailor-Made for Uranyl Coordination and Molecular Recognition," *Inorganic Chemistry* **2020**, 59, 14, 9560–9568. (https://doi.org/10.1021/acs.inorgchem.0c00439)

Jorge S. K. Monteiro, Ethan A. Hiti, Emily E. Hardy, Grant R. Wilkinson, John D. Gorden, Anne E. V. Gorden, Ana de Bettencourt-Dias "New up-conversion luminescence in molecular cyano-substituted naphthylsalophen lanthanide (iii) complexes" *Chemical Communications* **2021**, *57*, 2551-2554. (https://doi.org/10.1039/D0CC08128K )

Ethan A. Hiti, Grant R. Wilkinson, Isuru R. Ariyarathna, Charmaine D. Tutson, Emily E. Hardy, Branson A. Maynard, Evangelos Miliordos, Anne E. V. Gorden, “Comparing Coordination Uranyl (VI) Complexes with 2-(1H-imidazo[4,5-b]phenazin-2-yl)phenol and Derivatives ,” **2021** *submitted to Dalton Transactions*

# Structure, Bonding and Mechanism in f-Element Chemistry

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Collaborators: Jochen Autschbach, Department of Chemistry, University at Buffalo; Thomas Albrecht-Schönzart, Department of Chemistry and Biochemistry, Florida State University; Stosh A. Kozimor and Aaron Tondreau, Chemistry Division, Los Alamos National Laboratory; William J. Evans, Department of Chemistry, University of California, Irvine; Stefan Minasian, Chemical Sciences Division, LBNL; Robert Baker, School of Chemistry, Trinity College Dublin; Suzanne Bart, Department of Chemistry, Purdue University

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

*Significant Achievements during 2019-2021:*

(1) *Development and Application of C-term Magnetic Circular Dichroism Spectroscopy in f-Element Systems.* We have continued to expand our development and application of C-term MCD spectroscopy for applications to studies of electronic structure and bonding in f-element chemistry. We recently reported on experimental studies and theoretical method development for the simulation of f-element C-term MCD spectra in the f-f transition region. The experimental NIR MCD studies were further extended to $[U(OC_6F_5)_6]^-$, $[U(CH_2SiMe_3)_6]^-$, and $[U(NC(^tBu)(Ph))_6]^-$ to evaluate the effects of ligand-type on the f-f MCD fine features. In collaboration with the Autschbach group (U. at Buffalo), theoretical calculations were conducted to calculate the Laporte forbidden f-f transitions and their MCD intensity experimentally observed in the NIR spectra of the U(V) hexahalide complexes, via the inclusion of vibronic coupling, to better understand the underlying spectral fine structure features for these complexes. Additional studies have extended the application of *C*-term MCD spectroscopy to obtain insight into the electronic structure of formal lanthanide(II) complexes using MCD spectroscopy and to evaluate ligand effects on electronic structure and bonding in U(III) coordination complexes. Additional recent applications of *C*-term MCD include studies of a series of homoleptic U(IV)-aryl complexes and a collaboration with the Baker group at Trinity College Dublin using near-IR MCD to evaluate the effects of geometric perturbations on electronic structure and bonding in a series of U(IV) thiocyanate complexes.

(2) *Studies of Unstable and Transient f-Element Complexes.* We have applied advanced low temperature synthetic method combined with freeze-trapped EPR and MCD spectroscopies to develop into transient uranium complexes in order to further our understanding of electronic structure, bonding and reactivity in actinide chemistry. Our work focused specifically on long-standing challenges in organouranium chemistry and provided access to both novel and long sought after homoleptic alkyl and aryl complexes. This work provides both opportunities to further studies bonding and reduction pathways in such species as well as a fundamental infrastructure in low temperature and freeze-trapped methods that can be applied to reactive actinide chemistry. In addition to prior publication of homoleptic uranium aryl complexes, we have recently reported investigations into the exceptional diversity of homoleptic uranium-

methyl complexes. Utilizing cryogenic synthesis and handling techniques, we were able to circumvent the need for additives and reported the isolation of several homoleptic uranium-methyl complexes, including the first example of a homoleptic uranium-alkyl dimer, $[Li(THF)_4]_2[U_2Me_{10}]$. Additionally, the analog to the TMEDA stabilized monomeric complex was successfully synthesized, $[(Li(THF)_4][Li(THF)_2UMe_6]$. Additional compounds identified included the 7-coordinate U(IV)-methyl complex, $\{Li(OEt_2)Li(OEt_2)_2UMe_7Li\}_n$, and a homoleptic uranium(V)-methyl complex was also isolated from this reaction medium. Further characterization and electronic structure descriptions of these complexes using NMR, EPR, and computational analysis provided insight into structure and bonding in organouranium chemistry.

(3) *Development and Application of $^{237}$Np Mössbauer Spectroscopy.* To bring a $^{237}$Np Mossbauer capability back to the United States actinide research community, we have worked over the past few years to design and develop a $^{237}$Np Mössbauer spectrometer, which is currently under development at Florida State University in collaboration with Thomas Albrecht-Schönzart. In addition to the instrumentation, works continues to the development of additional $^{241}$Am source materials that might yield improved instrument performance moving forward.

*Science objectives for 2021-2023:*

- We will expand our studies to transient molecular actinide chemistry in order to define intermediates, reaction pathways and electronic structure contributions to reactivity in molecular actinide chemistry, focusing on reactive uranyl chemistry.
- We will continue synthetic efforts in organouranium chemistry to broadly define electronic structure and bonding in novel uranium complexes, including oxidized and reduced analogs of our homoleptic uranium-aryl and -alkyl compounds and uranium complexes containing C(sp)-hybridized substituents (i.e. alkynes).
- We will continue our work on $^{237}$Np Mössbauer spectroscopy. Once the instrument is finalized and testing is complete, we will use this technique for studies including further exploration and development of new $^{241}$Am sources to further optimize instrument performance as well as substantial focus on the application of $^{237}$Np Mössbauer spectroscopy to evaluate electronic structure and covalency in molecular Np chemistry.

*Publications supported by this project 2019-2021*

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

*Kirk A. Peterson, Principal Investigator*

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Collaborators: Peter Armentrout (Utah), Kit Bowen (Johns Hopkins), Slava Bryantsev (ORNL), David Dixon (Alabama), John Gibson (LBNL), Eric Glendening (Indiana St.), Michael Heaven (Emory)

*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 2019-2021:*

- Developed new all-electron, relativistic, correlation consistent basis sets for Pt and Au and used these in composite FPD thermochemistry calculations of metalloactinyls involving U through Pu. In particular, the Pt atom was indeed found to behave very similarly to the oxygen atom, while Au had similar behavior as a halogen, as predicted previously in the literature.
- Applied our accurate relativistic FPD method to interpret the experimental anion photodetachment spectra of $Th^-$, $U^-$, and several diatomic and triatomic anions involving Th with O, Pt, and Au.
- By comparison with accurate experimental measurements, the relativistic FPD method was shown to yield accuracies of 1-2 kcal/mol for bond dissociation energies and ionization energies of small molecules involving Th and U. An accurate treatment of spin-orbit coupling was essential, while high order electron correlation corrections beyond CCSD(T) were required to obtain sub-2 kcal/mol accuracy.
- FPD calculations of the ionization energies and electron affinities of the heavy p-block atoms demonstrated sub-kcal/mol accuracy in nearly all cases by combining accurate scalar relativistic results with correlated 4-component treatments of spin-orbit coupling.
- Using our FPD approach, it was found that strong complexes were formed between $N_2$ and CO with $AnO_2^{n+}$ where An=U, Np, and Pu (n=0-2). A particularly strong interaction was predicted between $O_2$ and $UO_2$.

*Science objectives for 2021-2023:*

- Finish study of the high ionization potentials of the actinide atoms Np through Cm that investigates when and if the 6p shell ionizes before the 5f electrons are completely removed. Accurately determine the electron affinities for transuranic atoms.
- Develop explicitly correlated F12 basis sets matched to relativistic ECPs for Ac – Lr.
- Determine the efficacy of the Brueckner coupled cluster method for accurate thermochemistry
- Accurately predict the thermochemistry of chalcogen-substituted actinyls and compare to the analogous dioxo species.
- Continue to support current experimental efforts on fundamental studies of small molecules involving early actinides.

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# Spectroscopic Investigation of Electronic Structure in the Actinide Elements

*Herman Cho, Principal Investigator*

Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA
Project Team: Eric Walter, Gian Surbella
Postdoctoral Fellows: Elizabeth Flowers, Trent Graham, Sejun Park

*Overall research goals:* The objective of this project is to map the evolution of electronic structure and chemical bonding from the 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 2019-2021:*

*Electronic structure in actinide tetrafluorides.* Fluorine-19 magnetic shielding tensors have been measured in a series of actinide tetrafluorides by solid state nuclear magnetic resonance spectroscopy (NMR) (Fig. 1). Tetravalent actinide centers with 0 to 8 valence electrons can form tetrafluorides with the same monoclinic structure type, which provides the unique opportunity for a systematic survey of variations 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, and indicate the presence of electronic correlations even for the lower *Z* actinides.

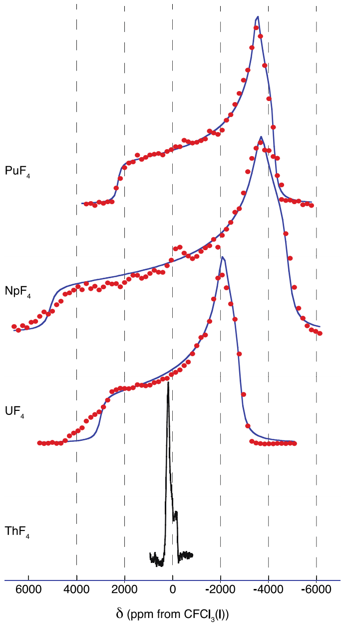

**Figure 1**: Room-temperature $^{19}$F NMR spectra of AnF$_4$ powders recorded in an applied field of 7.05 T. Red dots are amplitudes of a spectrum acquired at the indicated frequency, and solid lines are fits of the data to an anisotropic lineshape function.

<u>Electronic structure in the equatorial plane of actinyl ions</u>. Electric field gradient tensors in the equatorial plane of the UO$_2^{2+}$ ion have been measured by NMR (Fig. 2) and nuclear quadrupole resonance (NQR) experiments and computed by relativistic Kohn-Sham methods with and without environment embedding for Cs$_2$UO$_2$Cl$_4$ and Cs$_2$UO$_2$Br$_4$. 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. This approach expands the possibilities for probing electronic structure in uranyl complexes beyond the strongly covalent U–O bonds.

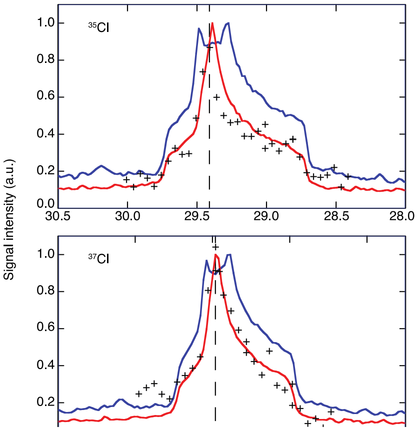

**Figure 2**: Chlorine-35 (top) and $^{37}$Cl (bottom) NMR spectra of Cs$_2$UO$_2$Cl$_4$ in a 7.046 Tesla magnetic field. Blue and red spectra are simulations computed with EFG parameters from a SO-PBE0 calculation and a visual fit to the experimental data, respectively. The chemical shift 0 ppm position is indicated by the dashed line.

*Upgrade of experimental capabilities.* A major renovation of the Radiological Magnetic Resonance Facility at the Pacific Northwest National Laboratory was undertaken in 2020. Four new state of the art NMR and NQR spectrometers were installed (Fig. 3), with capabilities for analyzing both solution and solid samples. A closed cycle cryostat was also procured, which will allow analysis of nuclear materials down to 4 K.

**Figure 3:** Panorama view of the Radiochemical Processing Laboratory (RPL) NMR facility after completion of renovations and equipment installation. The three main new instruments are identified by yellow labels.

### *Science objectives for 2021-2023:*

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, 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 (direct $^{239}$Pu NMR detection) | 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 |

### *Publications supported by this project 2019-2021*

Ian Farnan and Herman Cho, “Magic Angle Spinning Nuclear Magnetic Resonance of Plutonium Compounds,” in *Plutonium Handbook, 2<sup>nd</sup> Ed.*, D. L. Clark, D. A. Geeson, and R. J. Hanrahan, Jr., Eds., **2019**, Chapter 42.

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

*Robin D. Rogers, Principal Investigator*

Department of Chemistry & Biochemistry, The University of Alabama, Tuscaloosa, AL
Undergraduate Students: Hannah Wineinger; Post-Doctoral Researchers: Amrita Nayak, Gabriela Gurau
Collaborators: Volodymyr Smetana, Anja Mudring (Stockholm University), David A. Dixon

*Overall research goals:* We seek to study f-element interactions with moderately soft donors by achieving N-donor coordination to f-elements in easy one-step, one-pot reactions using ionic liquids to provide a "sea" of surrounding N-donors and moderate heat to drive off volatiles, with the ultimate goal of scaling down for transuranic reactions.

*Significant achievements during 2019-2021:* We have explored saturating hydrated lanthanide salts in N-donor containing ILs and have achieved a variety of (an)hydrous complexes and polymers incorporating dicyanamide or tricyanomethanide, resulting in the publication "Forcing Dicyanamide Coordination to f-Elements by Dissolution in Dicyanamide-Based Ionic Liquids". Our work with tricyanomethanide ($[C(CN)_3]^-$) ionic liquids has resulted in the synthesis of the first 1D (**Figure 1a, b**) and 2D (**Figure 2c, d**) polymers exhibiting f-element tricyanomethanide coordination and is currently being written for publication.

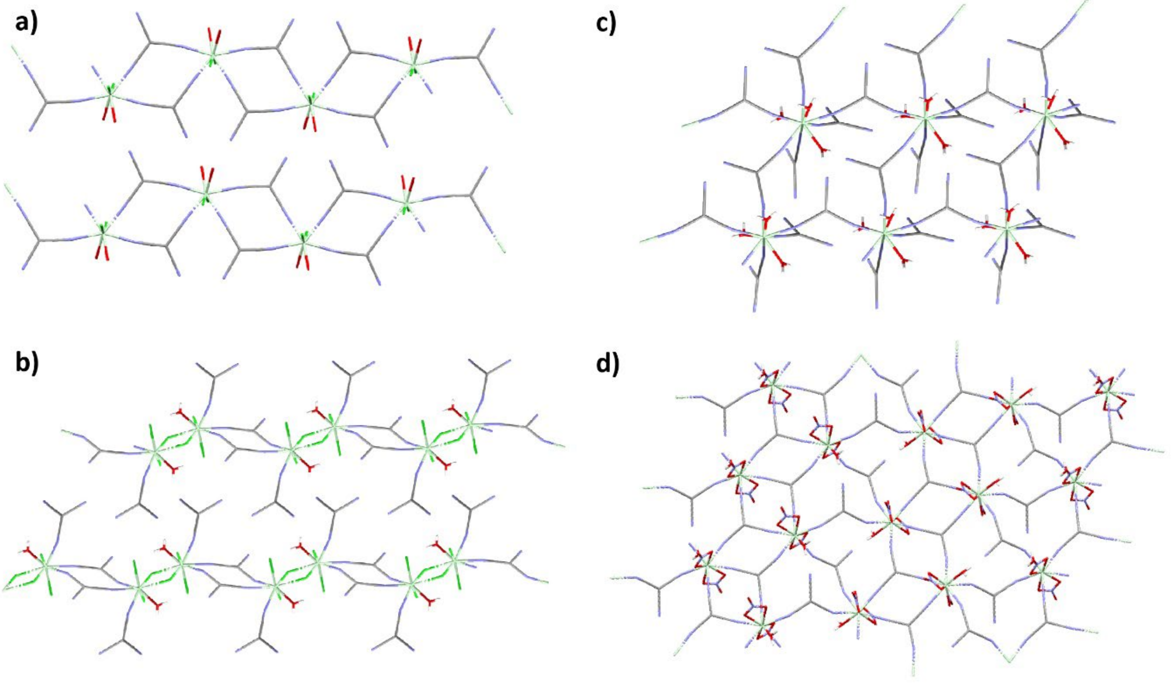

**Figure 1**. Polymers exhibiting Nd(III)/$[C(CN)_3]^-$ coordination

In addition to our work with ionic liquids, we have also employed the use of mixtures of acidic and basic azoles to form tunable ionic liquid-like mediums through which to achieve coordination. Through mixtures of 4-amino-1,2,4-triazole with 5-aminotetrazole or 1,2,3-triazole with $CeCl_3•7H_2O$ or $CeBr_3•1H_2O$, we synthesized multiphasic solid/liquid mixtures with single crystals, later resolved by SCXRD analysis to be $[Ce_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_2(\mu_3\text{-}Cl)_2(Cl)_6(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-}Triaz)_{12}]•7H_2O$ and a very disordered structure exhibiting a similar motif, herewith termed **2**. Both structures exhibit the very first examples of hexanuclear octahedron Ce(III) hydrolysis products with 12 $\mu_2$ coordinating azoles and 9-coordinate (capped square antiprismic) Ce(III). The vast majority of previously published 8-coordinate (square antiprismic) Ce(IV) hexanuclear pseudo-clusters are pairwise bridged by 12 carboxylate substituted ligands (Ce – O = C = O – Ce); however, the pairwise bridging observed in our new structures is exclusively by 12 neutral monocyclic N-donors (12 neutral 4-amino-1,2,4-triazole ligands; Ce – N = N – Ce), where charge balance of the cationic cluster-like molecules is achieved via a combination of terminally Ce-coordinated halides and counter anions. The most similar analogue to our cluster appears to be a 9-coordinate Pu(IV) structure with a similar $[Pu_6(O)_4(OH)_4]^{12+}$ octahedron (hydr)oxo anion core, with 12 coordinating zwitterionic neutral glycine ligands (DOI: 10.1021/ic4007185). This motif was further extended when we isolated a Nd(III) hexanuclear hydrolysis product $[Nd_6(\mu_3\text{-}OH)_8(Cl)_6]^{4+}$ from a mixture of $NdCl_3 \cdot 6H_2O$ in an aqueous solution of 4-amino-1,2,4-triazole (see **Figure 2**, right).

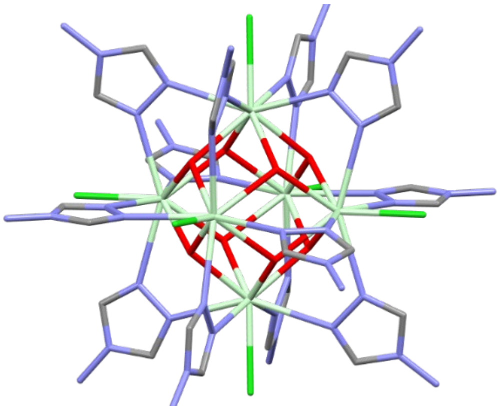

**Figure 2**

*Science objectives for 2021-2023:* We will focus our attention on robust synthetic strategies to obtain the hexanuclear clusters first for Nd(III) and Ce(III-IV) and then to Am(III) and Pu(III-IV). The similarities of the isolated products suggest that our Ce(III) hydrolysis products have the potential to unlock new aspects of Pu(III) hydrolysis chemistry, of which a hexanuclear hydrolysis product has not been previously isolated. Additionally, because these cerium products are trivalent, there is potential to extending this motif to other trivalent lanthanides and, by extension, their actinide analogues. Despite our initial goals of seeking homoleptic N-donor complexes, our surprising hydrolysis products have turned our attention to the use of N-donors, specifically 4-amino-1,2,4-triazole, as a method of controlling the degree of hydrolysis and limiting the formation of insoluble high nuclearity precipitates and colloidal solids which plague cerium and plutonium chemistry.

*Selected publications supported by this project 2019-2021:*

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7. Miscellaneous: (Ionic Liquids) DOI: 10.1073/pnas.2008379117, DOI: 10.1021/acs.cgd.9b01454; DOI: 10.1080/00958972.2021.1876851; (Actinide/Lanthanide) DOI: 10.1021/acs.inorgchem.9b03077.

# Towards Strongly Correlated f-Electron Materials from Molecular Precursors

*Eric J. Schelter, Principal Investigator*

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Graduate Students: Himanshu Gupta, Henry Wilson, Ekaterina Lapsheva
Collaborators: Corwin Booth (LBNL), Jochen Autschbach (Buffalo)

## *Overall research goals:*

- The overall goal of this project is to synthesize heavy electron coordination polymers and/or molecular solids for the first time whose properties can be tuned systematically using molecular design principles, and ultimately, to achieve superconductivity in such molecular materials. The major aspect of the ongoing research is to use redox active lanthanides based molecular precursors with strong electron correlation and magnetic moment for the understanding of emergent quantum phenomena. The research is mainly focused on to identify develop and modulate the strong local interaction due to multiconfigurational effects and strong electron correlation in molecular materials.

## *Significant achievements during 2019-2021:*

- To achieve the overall goal of the project, we have been developing suitable lanthanide based molecular precursors that can be used for the synthesis of the molecular materials. In this regard molecular design principles and studies of structure-property relationship is essential. An important contribution was realized in our recent work, where we have demonstrated that the judicious choice of ligands around the Ce(IV) complexes provides notable physical and electronic properties.[1] The effect of sterically hindered guanidinate ligands into Ce(IV) complexes leads to intense charge transfer bands. The associated low-lying excited states were hypothesized as important for the observation of multi-configurational ground states. Detailed computational studies, augmented with spectroscopic characterization, revealed the key role of guanidinate ligands on LMCT transitions, 4f and 5d covalency, and stabilization of the Ce(IV) oxidation states (Figure 1).

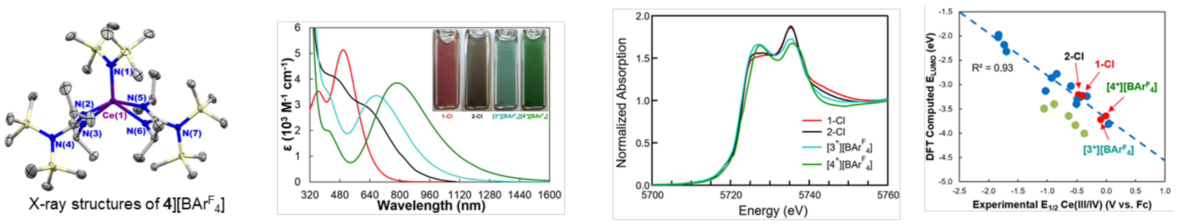

**Figure 1.** Structure-property relationships for the Ce(IV) guanidinate-amide complexes: Compounds with more guanidinate ligands tend to show lower energy absorption bands (left), larger $n_f$ values (middle), and more positive $Ce^{III/IV}$ reduction potentials (right).

- In work primarily supported by DE-SC0001136 (Autschbach), Ce $L_3$ edge XAS spectra of $CeO_2$ and cerocene $[Ce(C_8H_8)_2]$ were calculated with relativistic ab-initio multireference wavefunction approaches capable of reproducing the observed spectra accurately.[2] The study aimed to resolve the decades-long puzzle regarding the relationship between the number and relative intensities of the XAS peaks and the 4f electron occupation in the ground state versus the core-excited states. he pattern therefore reveals excited states that can be interpreted in terms of Ce IV and III oxidation numbers, as long assumed, with Ce II states additionally appearing in the cerocene spectrum. Booth provided expertise on spectroscopy work and interpretation on multiconfigurational ground states in Ce systems. These results are being developed further in the next project year.

- Co-PI Jochen Autschbach (JA) and postdoc Rulin Feng, in addition to the research carried out jointly with the experimental teams, have developed new capabilities for characterizing the local electronic structure around a lanthanide, by developing a relativistic multi-reference wavefunction method for calculating electron-nucleus hyperfine coupling. The article reporting the development features several f-element examples and demonstrates that excellent agreement with experiments can be achieved.[3]

*Science objectives for 2021-2023:*

- To discover new strong f-electron correlation phenomena, multi-metallic species and coordination polymers exhibiting these effects must be synthesized and studied. For the next project year, this will include the synthesis of molecular materials with donor-acceptor properties and studies of their magnetic and conducting properties. Redox active organocerium complexes with acceptor molecule (like fullerenes TCNQ and TCNE) is being carried out. The team is currently studying two new Cp based organocerium compounds with $C_{60}$, i.e. $[(CpMe4)_3Ce]_2[C_{60}]$ and $[Cp^*_2(Oxa\text{-}Lig)]_3[C_{60}]$ (figure 3). Detailed studies on it's donor-acceptor properties are currently being carried out. The compounds have been characterized by X-ray FT-IR Raman spectroscopy and SQUID magnetometry. Calculations on the same system for charge transfer are also being carried out. Based on the preliminary results, further tuning of organocerium complexes will be required to enhance the reducing power of organocerium complexes leading to the ultimate goal of charge transfer and conductivity by such molecular materials.

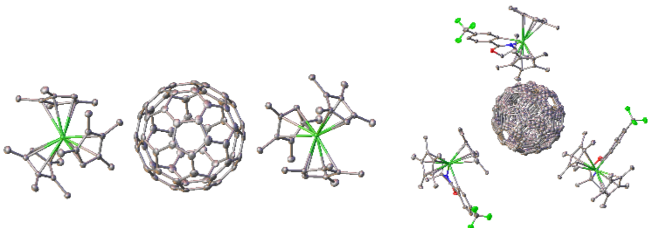

**Figure 3.** X-ray structute of $[(CpMe_4)_3Ce]_2[C_{60}]$ and $[Cp^*_2(Oxa\text{-}Lig)]_3[C_{60}]$.

- In addition to above mention work a method to calculate natural transition orbitals (NTOs) from multi-reference wavefunctions that include spin-orbit (SO) coupling is under active development by our Co-PI Jochen Autschbach. The SO-NTO program will be used to assign the transitions in the Ce L3-edge X-ray absorption spectrum of cerium complexes synthesized and characterized by the experimental teams, and other types of electronic spectra. As dewcribed above, the utility of NTOs in the context of Ce L3-edge spectra has been showcased recently by JA and his team, but so far the calculations were restricted to wavefunctions that do not include SO coupling.[3]

*Publications supported by this project 2019-2021*

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

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Collaborators: Michael Heaven (Emory University), Lan Cheng (Johns Hopkins University)

*Overall Research Goals:* The primary goal is to precisely determine fundamental properties of small neutral uranium and thorium gas-phase molecules using an orchestra of medium and high-resolution optical and microwave spectroscopic techniques. All measurements, including microwave transition frequencies, exploit the sensitivity of laser induced florescence detection. The determined molecular properties include electronic state energies, bond lengths and angles, vibrational frequencies, permanent electric dipole moments, $\vec{\mu}_{el}$, magnetic dipole moments, $\vec{\mu}_{m}$, magnetic and nuclear electric quadrupole hyperfine interactions, florescence branching ratios, radiative lifetimes, and oscillator strengths. These properties probe the nature of the chemically relevant valence electrons and provides insight into *f*-and *d*-orbital participation in bonding elucidating actinide chemistry. Although these small gas-phase actinide containing molecules are the simplest molecules in terms of the number of nuclei involved and geometry they are not full ligated resulting in a multitude of low-lying interacting electronic states, which are difficult to model. The quantitative data produced in this research provides a rigorous means of assessing emerging computational methodologies being developed for predicting actinide chemistry.

*Significant Achievements 2019-2021*

i. *Characterization of thorium nitride, ThN, analysis of optical and microwave spectra.*

The visible spectrum of ThN was recorded using two-dimensional(2D) (laser excitation and dispersed fluorescence) spectroscopy and analyzed to identify electron states and determine associated vibrational frequencies. Subsequently, the intense electronic transitions were studied a high spectral resolution. The observed optical Stark shifts were analyzed to determine permanent electric dipole moments, $\mu_{el}$, for the [18.0]1.5 and $X^2\Sigma^+$ states of 4.38 ± 0.02D and 5.11 ± 0.09D, respectively. Zeeman shifts were used to determine the magnetic g-factors. The pure rotational spectrum was recorded using a separated field optical pump/probe microwave repopulation scheme and analyzed to determine the bond length and $^{14}$N magnetic hyperfine and nuclear electric quadrupole parameters. A molecular orbital correlation diagram and ligand field electronic structure models were used to provide a qualitative interpretation of the electronic state ordering, magneto- and electro-static properties, and hyperfine interactions. Electronic structure calculations for the $X^2\Sigma^+$ state were performed, and results were compared with observations. Observed trends in $\mu_{el}$ for the ThX (X = N, S, O, F, and Cl) series were discussed.

ii. *Magneto- and electro-static properties of Uranium nitride, UN.*

Electronic transitions of UN that exhibit intense laser induced fluorescence (LIF) signals were identified using 2D spectroscopy. The [18.35]4.5 - $X^2\Sigma^+$ and [18.64]4.5 - $X^2\Sigma^+$ bands, which had been previously identified in the mass-selected two photon ionization spectra (Matthew and Morse,

J. Chem. Phys. **138**, 184303 (2013); Battey, et al. J. Chem. Phys. 152, 094302 (2020)) were selected for high-resolution optical Stark and Zeeman studies. The derived spectroscopic parameters are presented in Table 1. Relativistic coupled-cluster calculations are being performed (by Prof. Lan Cheng, Johns Hopkins University) to aid in the interpretation.

Table 1: Fine parameters *($cm^{-1}$)* for the $X^2\Sigma^+$ (v=0), [18.35]4.5 and [18.64]3.5 states of UN

| Parameter | X | [18.35]4.5 | [18.64]3.5 |
|---|---|---|---|
| $B''$ | 0.40948(9) | 0.3766(1) | 0.38864(8) |
| $10^7D''$ | 10(7) | 69(9) | 17(6) |
| $\left\lvert\vec{\mu}_{el}\right\rvert$ (Debye) | 4.30(2) | 4.05(3) | 4.32(2) |
| *g-factor* | 2.160(9) | 3.93(1) | 3.599(9) |
| $T_0$ | 0 | 18349.289(3) | 18630.064(1) |

## iii. Searching for new U-containing molecules

The 2D spectra of the supersonic expansion reaction products of ablated uranium in the presence of numerous reagents ($NH_3$, $N_2O$, $CH_4$, $CH_3CN$, $H_2$ etc.) have been recorded in the 750-480 nm range. In all cases the spectra are highly congested and overlapped by bands of UO. In an attempt to deconvolute the optical spectra with aim of identifying spectral features associate with small polyatomic molecules (e.g. $UN_2$, $UO_2$, and UCN), a data processing algorithm that simultaneously correlates the laser excitation, dispersed fluorescence and radiative lifetimes (i.e. adding a third dimension) is being developed.

## *Science objectives for 2021-2023:*

The low and high-resolution molecular beam spectrometers have been transferred to Prof. Michael Heaven's labs at Emory University. We will integrate mass-spectroscopic detection methods available in the Heaven lab, which complement our fluorescent detection methods, into the reconstructed instruments.

## *Publications supported by this project 2019-2021*

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# Advancing the Chemistry of the Actinides with Heavier Main Group Elements

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Collaborators: Laurent Maron (Toulouse, France), Andrew Kerridge (Lancaster, UK), Jochen Autschbach (SUNY Buffalo)

*Overall research goals:* The overall goal for this project is to gain an understanding of the interplay between the energy-driven-covalency concept and when the metal and ligand-based orbitals become more degenerate using heavier main group elements such as those found in the 3p, 4p, and 5p rows. We will do this by combining synthetic and spectroscopic techniques, as well as examining the unique reactivity of these bonds. In addition, we will extend the coordination and organometallic chemistry of the actinides by working with $^{237}$Np. Our objectives for achieving this goal are:

*Project Objectives:*

1) *Investigation of actinide-ligand bonds with soft donors: synthesis, characterization, and reactivity*

This aim will be accomplished by analyzing the structure, bonding, and reactivity of thorium and uranium complexes with ligands in 3p (Si, P, S), 4p (Ge, As, Se) and 5p (Sn) series. Here, we are interested in actinide-ligand single bonds to provide a baseline and establish benchmarks for what is expected in terms of the thorium(IV) or uranium(VI)-ligand bond distance, NMR chemical shift of the NMR-active nuclei ($^{29}$Si, $^{31}$P, $^{77}$Se, and $^{119}$Sn), and delocalization index of an actinide-ligand single bond. This will then be compared to actinide-ligand multiple bonds which can also include atoms with carbon (phosphorano-stabilized carbenes) and nitrogen (imidos), where $^{13}$C and $^{15}$N NMR spectroscopy, respectively, is possible.

2) *Exploring low-valent neptunium chemistry*

This aim will be accomplished by the synthesis and characterization of neptunium(III) and neptunium(IV) complexes using non-cyclopentadienyl ligands. Since little is known about these oxidation states, we will focus on making comparisons to Th(IV), U(IV), and U(III), with respect to the energy-driven-covalency concept, as well as examining the reductive and substitution chemistry.

## *Significant achievements during 2019-2021:*

In the past two years, we have been examining the structure, bonding, and reactivity of thorium and uranium complexes with phosphorus and arsenic ligands. We have created many thorium and uranium complexes with one or two phosphido or arsenido ligands. The reactivity of these complexes has been studied with small molecules such as CO, $CO_2$, $^t$BuNC, $^t$BuCN, and benzophenone. Our hypothesis that the mismatch in soft ligand (P, As) versus hard Lewis acid (Th, U) would create highly reactive complexes seems to be mostly correct. In all cases, the incoming substrate inserts into the An-E bond, but, to our surprise, when a primary pnictido is used, proton transfer occurs leading to unusual functionalizations.

With respect to neptunium chemistry, we reported the first structurally characterized Np(III) hydrocarbyl compound and showed the utility of this complex in making other Np(III) species. We have recently been examining the coordination and reductive chemistry of Np(III) compounds. This is work that will be submitted for publication soon.

## *Science objectives for 2021-2023:*

With respect to thorium and uranium chemistry, our objective for the next two years is to start to examine the reactivity of our phosphinidiide and arsinidiide complexes. These complexes have some multiple bond character, but tend to react slowly, leading to products that are readily isolable. Comparisons will be made with single An-E bonds versus An-E bonds with slightly more than single bond character to observe differences in reactivity based on the amount of covalent bonding character.

Our other aim is expanding Np(III) chemistry with different ligand sets. We have found that our current ligand framework lead to ligand redistribution, so a change in ligand is in order. We will continue to focus on our hydrocarbyl ligand since it is only solvent-free starting material that has been created to date, thus making it attract for making complexes in hydrocarbon solvents without coordinating solvents.

*Publications supported by this project 2019-2021*

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