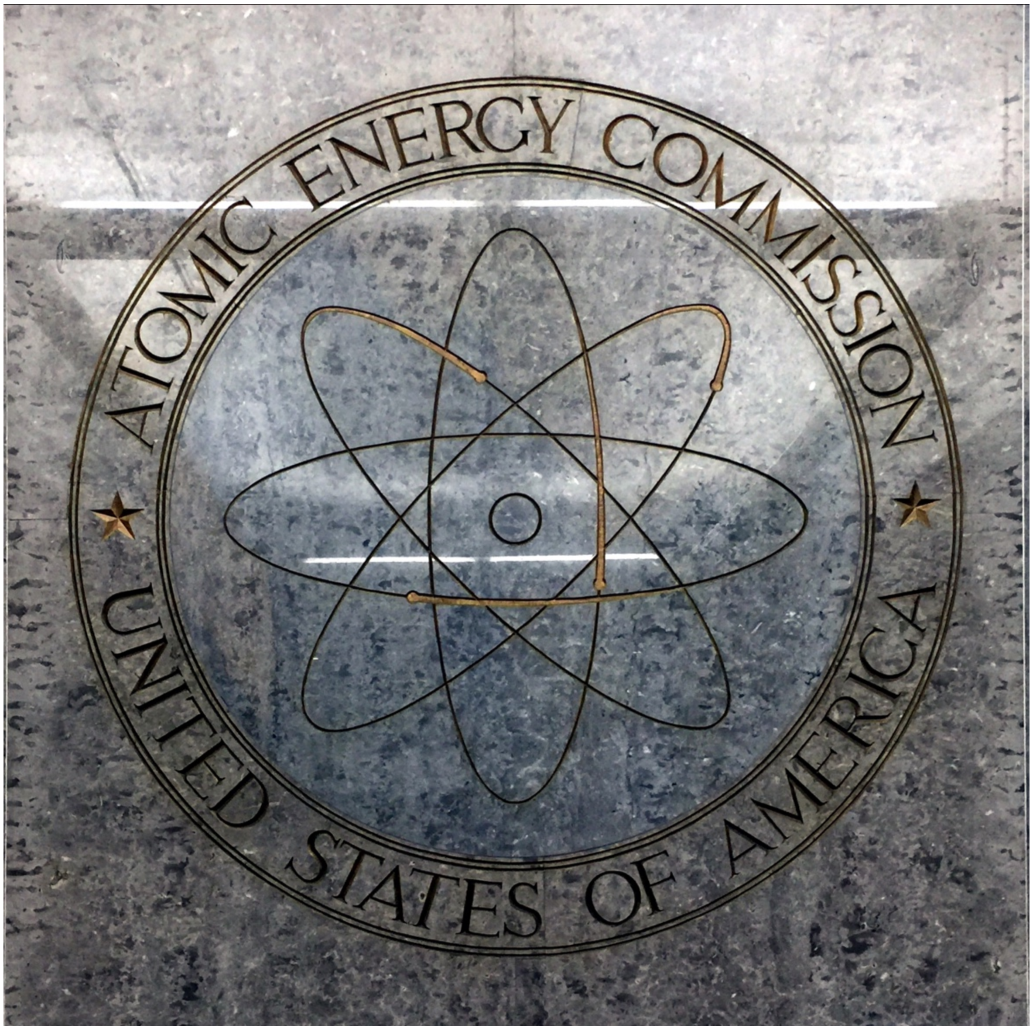
2017 Heavy Element Chemistry and Separation Science Principal Investigators' Meeting



Gaithersburg, MD
April 23–26, 2017

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

2017 Heavy Element Chemistry and Separation Science Principal Investigators' Meeting

Gaithersburg Marriott
Washingtonian Center
Gaithersburg, MD
April 23–26, 2017

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

Cover photo: Germantown DOE Headquarters Lobby (Philip Wilk, 19 January 2017).

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Foreword

This abstract booklet provides a record of the fourteenth U.S. Department of Energy contractors' meeting in separations sciences and the ninth 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 and separations sciences for over sixty years. This is the eighth joint meeting of these programs.

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

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

I would also like to thank Diane Marceau of the Chemical Sciences, Geosciences and Biosciences Division for her vital contributions to the administration of these programs.

Philip Wilk

Agenda

2017 Heavy Element Chemistry and Separation Science Principal Investigators' Meeting

Gaithersburg Marriott, Washingtonian Center
Sunday, April 23 - Wednesday, April 26

Meetings Notes:

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

Local Federal employees will need to pay ($16 breakfast, $17 lunch) for their meals.

Sunday, April 23

3:00-6:00	Check in and informal no-host meetup at "the Bench"	
7:00	Meeting Begins	
7:00-7:15	Philip Wilk introduction	
7:15-7:30	Questions and comments for Philip Wilk	
7:30-9:10	**Organometallics/Coordination Chemistry I**	Session Chair: Stosh Kozimor
7:30-7:55	Evans, William J.	UC Irvine
	Exploring the Fundamental Chemistry of Actinide Metal Complexes	
7:55-8:20	Wilson, Richard E.	ANL
	Chemical Periodicity in the Early Actinide Elements: The Interplay of the 5f and 6d electrons	
8:20-8:45	Gaunt, Andrew J.	LANL
	New Bonding Modes and Oxidation State Chemistry for Neptunium and Plutonium	
8:45-9:10	Albrecht-Schmitt, Thomas E.	FSU
	Transient Mixed-Valency in Berkelium(IV) Iodate	

Monday, April 24

7:30-8:30	**Breakfast**	
8:35-10:05	**Invited Speakers**	Session Chair: Tori Forbes
8:35-9:05	Garrett, Bruce	CSGB Division Director
	BES/CSGB Update and Outlook	
9:05-10:05	Arnold, Polly	Univ. of Edinbugh
	f-block organometallics; combining metal cations for new reaction chemistry and understanding	
10:05-10:30	**Break**	
10:30-12:05	**Separations/Soft Materials I**	Session Chair: Amar Flood
10:30-10:55	Schelter, Eric J.	Univ. of Penn.
	A Physicochemical Method for Separating Rare Earths: Addressing an Impending Shortfall	
10:55-11:20	Antonio, Mark R.	ANL
	Beyond Metallosurfactant Coordination Chemistry in Organic Phases for Heavy Element Separations	
11:20-11:45	Custelcean, Radu	ORNL
	Selective Crystallization of Anion-Water Clusters with Self-Assembled Guanidines	
11:45-12:05	He, Chuan	Univ. of Chicago
	Selective Recognition of Heavy Elements by Protein-Based Reagents	
12:10-1:30	**Working Lunch for Collaboration**	poster room will be open
1:30-2:45	**Theory I**	Session Chair: Gustavo Scuseria
1:30-1:55	Yang, Ping	LANL
	Theoretical Studies of Actinide-ligand Bonding Interactions and Spectroscopic Properties	
1:55-2:20	Peterson, Kirk A.	WSU
	Accurate ab Initio Thermochemistry and Spectroscopy of Molecules Containing f-block Elements	
2:20-2:45	Gagliardi, Laura	Univ. of Minnesota
	Modeling Actinide- and Transactinide-Systems with Multireference Quantum Chemical Methods	
2:45-3:05	**Poster Slam**	
	(Each poster presenter gets one minute and one slide, no questions)	
3:05-3:25	**Break**	
3:25-5:45	**Poster Session #1**	
	DINNER on your own and Collaborate	poster room will be open

Tuesday, April 25

7:30-8:30	**Breakfast**	
8:35-10:20	**Organometallics/Coordination Chemistry II**	Session Chair: Justin Walensky
8:35-9:00	Raymond, Kenneth N.	UC Berkeley
	The f Elements in Bondage: From Basics to Business	
9:00-9:25	Bart, Suzanne C.	Purdue Univ.
	Synthetic, Spectroscopic, and Computational Studies of Uranium Complexes Supported by Redox-Active Liga	
9:25-9:50	Boncella, James M.	LANL
	Probing Actinide Covalency Through Studies of Uranium Nitrogen Multiple Bonding and Reactivity	
9:50-10:20	Lukens, Wayne W.	LBNL
	Chemistry of Technetium, Americium, and Curium in Oxide Hosts	
10:20-10:40	**Break**	
10:40-12:15	**Thermodynamics, Thermochemistry**	Session Chair: S. Skanthakumar
10:40-11:05	Armentrout, Peter B.	Univ. of Utah
	Thermochemistry and Reactivity of Atomic and Molecular Actinides	
11:05-11:30	Rao, Linfeng	LBNL
	Actinide Solution Chemistry: Thermodynamics and Structure of Actinide Complexes in Solution	
11:30-11:55	Braley, Jenifer C.	Colorado School of Mines
	Heavy actinide-soft donor complexation thermodynamics	
11:55-12:20	Bryantsev, Vyacheslav S.	ORNL
	Structural and Thermodynamic Basis for Selective Liquid-Liquid Extraction and Crystallization from Molecula	
12:30-1:45	**Working Lunch for Collaboration**	poster room will be open
2:00-3:15	**Spectroscopy**	Session Chair: Michael Neidig
2:00-2:25	Shuh, David K.	LBNL
	Soft X-ray Synchrotron Radiation Spectroscopy of Actinide Materials	
2:25-2:50	Pinkerton, A. Alan	Univ. of Toledo
	Experimental Electron Density Distribution in Actinide Compounds – an Experimental Atoms in Molecules (A	
2:50-3:15	Booth, Corwin	LBNL
	Using actinide L3-edge resonant x-ray emission spectroscopy (RXES) to measure valence and delocalization e	
3:15-3:35	**Break**	
3:35-4:50	**Organometallics/Coordination Chemistry III**	Session Chair: Stefan Minasian
3:35-4:00	Forbes, Tori	Univ. of Iowa
	Assessing subtle variations in actinyl oxo reactivity through characterization of neptunyl complexes	
4:00-4:25	Arnold, John	LBNL
	New Reactivity in Actinide Chemistry Facilitated by Supporting Ligand Design	
4:25-4:50	Jin, Geng Bang	ANL
	Understanding the Influence of Counter Cations on the Formation of Actinide Compounds from Solution	
4:50-5:50	**Poster Session #2**	
	DINNER on your own and Collaborate	poster room will be open

Wednesday, April 26

7:30-8:30	**Breakfast**	
8:30-9:45	**Solutions/Separations/Interfaces**	Session Chair: Santa Jansome-Popova
8:30-8:55	Uysal, Ahmet	ANL
	Competitive Ion Adsorption at Interfaces in Highly Concentrated Solutions	
8:55-9:20	Moyer, Bruce	ORNL
	Selective Liquid-Liquid Extraction with Novel Anion Receptors	
9:20-9:45	Davis, Jeffery T.	Univ. of Maryland
	Self-Assembled Ionophores in Water: Supramolecular Hydrogels and Membrane Transporters	
9:45-10:05	**Break**	
10:05-12:00	**Summary, Discussion**	
12:00	**Lunch on your own / dismissal**	

Abstracts

Chelation, Stabilization, and Luminescence Sensitization of Trivalent and Tetravalent Actinides through Sequential Antennae and Conversion Processes

Rebecca J. Abergel, Principal Investigator
Peter Agbo, Postdoctoral Research Associate
Ilya Captain, Postdoctoral Research Associate
Gauthier Deblonde, Postdoctoral Research Associate

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Collaborators: Dr. Anthony D'Aléo, CNRS UMR 7325 CINaM, Marseille, France
Dr. Roland K. Strong, Fred Hutchinson Cancer Research Center, Seattle WA, USA
Dr. Ping Yang, Los Alamos National Laboratory, Los Alamos, NM, USA
Dr. Wibe de Jong, Lawrence Berkeley National Laboratory, Berkeley, CA, USA
Dr. John Gibson, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

Overall research goals: The objective of this work is to enable the selective stabilization and tuning of spectroscopic properties of specific actinide complexes through precision ligand design and molecular recognition. The actinide sensitization efficiency of selective synthetic and natural chromophore-containing ligands through the antenna effect is explored. Such study of the luminescence properties of actinide species is aimed at providing fundamental information on (i) the localization of the best accepting states, (ii) the energy transfer efficiency relative to the triplet excited state energy, and (iii) the effects of the coordination geometry on the resulting emission spectrum.

Significant achievements during 2015-2017:

1. The first americium and berkelium luminescence sensitization experiments were carried out using an established hydroxypyridinone-based ligand: 3,4,3-LI(1,2-HOPO) complexation of transplutonium elements Am, Cm, Bk, and Cf was probed in aqueous solution. Upon excitation of the ligand π-π* transitions, structured emission patterns were observed with Am and Bk, and were attributed to the Am(III) transition $^5D_0 \rightarrow {}^7F_1$ and the Bk(IV) transition $^6D_{7/2} \rightarrow {}^8S_{7/2}$. The relative bathochromic shift of the Bk(IV) emission upon complexation indicates a remarkable decrease in inter-electronic repulsion in comparison with the corresponding Am(III) and Cm(III) species. The much lower ligand-to-metal energy transfer efficiency observed with Bk(IV), when compared to Cm(III), is a result of the stronger Bk^{4+} spin-orbit coupling and metal-centered electronic energy levels closer to each other. In addition, these luminescence properties were used to determine complex formation constants, demonstrating higher stability for Am(III) complexes in comparison to the corresponding Eu(III) complexes, but lower stability than Cm(III) complexes. Mass spectrometry was also employed to confirm the unprecedented stabilization of Bk(IV) in solution.

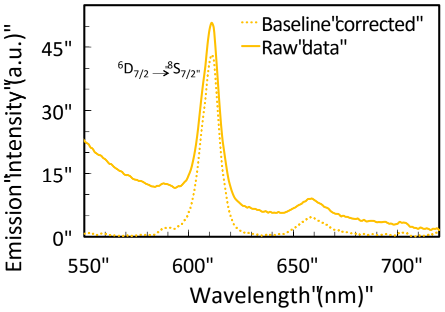

Figure 1. $[Bk^{IV}(3,4,3\text{-}LI(1,2\text{-}HOPO))]$ luminescence upon ligand excitation.

2. Based on the luminescence sensitization results obtained with Am(III), Cm(III), Bk(IV), we designed two series of new ligands to systematically map the electronic energy levels of these 5f elements and establish correlations with bonding and coordination features. The first series is based on the spermine ("3,4,3-LI") scaffold used in the octadentate 3,4,3-LI(1,2-HOPO) scaffold. It incorporates catecholamide (CAM) units that were also found to act as sensitizing chromophores in two different manners. The second series was prepared through a combinatorial approach using peptoid scaffolds, which allows for the sequential addition of chosen binding groups in a rigorously systematic manner. A total of 16 octadentate combinations were prepared and characterized for their

Eu(III) and Tb(III) luminescence sensitization properties. These last experiments demonstrated that extremely subtle differences in functional groups significantly affect the luminescence properties. We are now performing Cm(III) sensitization experiments with this new library of ligands.

3. To continue exploring the mapping of intermediate energy levels in 5f metal complexes, we chose to investigate the sensitization of Cm^{3+} ions once embedded in low symmetry nanocrystal hosts. We prepared and characterized $NaGd_{1-x}M_xF_4$ (M = Eu, Tb, Cm) nanoparticles featuring surface display of the ligand 3,4,3-LI(1,2-HOPO), the aromatic antenna functioning as the terminal light absorber in these systems. The results are ligand−nanocrystal hybrids that convert UV (250−360 nm) light into Eu(III), Tb(III), or Cm(III) luminescence with high external quantum yields. More importantly, spectroscopic features can now be employed to differentiate the sensitized molecular structures in solution from the nanocrystal assemblies and to determine the local metal environment.

Science objectives for 2017-2019:

- Use series of first identified Am(III) sensitizers to build functionalized ligand platforms with tuned actinide sensitization properties.
- Expand luminescence and thermodynamic investigations using peptoid-actinide complexes.
- Develop further multi-photon absorption and up/down-conversion experiments to systematically determine cross sections and energy transfer efficiency between ligands and f-block metals.

Publications supported by this project 2015-2017

1. Abergel, R. J., de Jong, W. A., Deblonde, G. J.-P., Dau, P. D., Captain, I., Eaton, T. M., Jian, J., van Stipdonk, M. J., Martens, J., Berden, G., Oomens, J., Gibson, J. K., “Formation of a Formal U^{6+} Chelate through Double Gas-Phase Activation of Uranyl with an Organic Catecholamide Ligand” *Submitted.*
2. Deblonde, G. J.-P., Sturzbecher-Hoehne, M., Rupert, P. B., An, D. D., Illy, M.-C., Ralston, C. Y., Brabec, J., de Jong, W. A., Strong, R. K., Abergel, R. J., “Chelation and Stabilization of Berkelium in Oxidation State +IV” *Nat. Chem.* **2017**, *In Press.*
3. Captain, I., Deblonde, G. J.-P., Rupert, P. B., An, D. D., Illy, M.-C., Rostan, E., Ralston, C. Y., Strong, R. K., Abergel, R. J., “Engineered Recognition of Tetravalent Zirconium and Thorium by Chelator-Protein Systems: Toward Flexible Radiotherapy and Imaging Platforms” *Inorg. Chem.* **2016**, *55*, 11930-11936.
4. Dau, P. D., Shuh, D. K., Sturzbecher-Hoehne, M., Abergel, R. J., Gibson, J. K., “Divalent and Trivalent Gas-Phase Coordination Complexes of Californium:Evaluating the Stability of Cf(II)” *Dalton Trans.* **2016**, *45*, 12338-12345.
5. Barasch, J., Hollmen, M., Deng, R., Hod, E. A., Rupert, P. B., Abergel, R. J., Allred, B. E., Xu, K., Darrah, S., Tekabe, Y., Perlstein, A., Bruck, E., Stauber, J., Corbin, K., Buchen, C., Slavkovich, V., Graziano, J., Spitalnik, S. L., Strong, R. K., Qiu, A., “Disposal of Iron by a Mutant form of Siderocalin – NGAL” *Nat. Comm.* **2016**, *7,* DOI:10.1038/ncomms12973.
6. Agbo, P., Abergel, R. J., “Ligand-Sensitized Lanthanide Nanocrystals: Merging Solid-State Photophysics and Molecular Solution Chemistry” *Inorg. Chem.* **2016**, *55*, 9973-9980 *(Invited Forum Article in Special Issue on New Trends and Applications for Lanthanides).*
7. Sturzbecher-Hoehne, M., Yang, P., D’Aleo, A., Abergel, R. J., “Intramolecular sensitization of americium luminescence in solution: shining light on short-lived forbidden 5f transitions” *Dalton Trans.* **2016**, *45*, 9912-9919. *(Invited for “New Talent: Americas” Themed Collection)*
8. Agbo, P., Xu, T., Sturzbecher-Hoehne, M., Abergel, R. J., “Enhanced Ultraviolet Photon Capture in Ligand-Sensitized Nanocrystals” *ACS Photon.* **2016**, *3*, 547-552.
9. Kamada, K., Namikawa, T., Senatore, S., Matthews, C., Lenne, P.-F., Maury, O., Andraud, C., Ponce-Vargas, M., Le Guennic, B., Jacquemin, D., Agbo, P., An, D. D., Gauny, S. S., Liu, X., Abergel, R. J., Fages, F., D’Aleo, A., “Borondifluoride curcuminoid fluorophores with enhanced two-photon excited fluorescence emission and versatile living-cell imaging properties” *Chem. Eur. J.* **2016**, *22*, 5219-5232.
10. Allred, B. E., Rupert, P. B., Gauny, S. S., An, D. D., Ralston, C. Y., Sturzbecher-Hoehne, M., Strong, R. K., Abergel, R. J., “Siderocalin-Mediated Recognition, Sensitization, and Cellular Uptake of Actinides” *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112*, 10342-10347.

Transient Mixed-Valency in Berkelium(IV) Iodate

Thomas E. Albrecht-Schmitt, Principal Investigator
Mark A. Silver, Samantha K. Cary, Alejandro J. Garza, Alexandra A. Arico, Gregory A. Galmin, Kuan-Wen Chen, Jamie C. Wang, Alexander Chemey, Teresa M. Eaton, Matthew L. Marsh, T. Gannon Parker, Kevin Seidler,[1] Shane S. Galley, Graduate Students
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Collaborators: Jason A. Johnson & Ashley L. Gray, Environmental Health and Safety, Florida State University, Tallahassee, Florida 32306
Ronald J. Clark, David E. Hobart, Kenneth Hanson, Lambertus J. van de Burgt, Department of Chemistry & Biochemistry, Florida State University, Tallahassee, Florida 32306
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Ryan E. Baumbach, National High Magnetic Field Laboratory, Tallahassee, Florida, 32310, United States

Overall research goals: Electronic bistability is often exhibited by elements immediately adjacent to those with closed or half-filled electronic configurations. These elements on the cusp of stable states are troves for emergent electronic phenomena such as molecular Kondo effects, mixed- and intermediate-valency, and itineracy in general. Cerium exemplifies these qualities because of the facile and often ambiguous oxidation of Ce^{III} ($4f^1$) to Ce^{IV} ($4f^0$). Berkelium is one of the least explored elements that might be capable of exhibiting electronic bistability. The oxidation of Bk^{III} ($5f^8$) to Bk^{IV} ($5f^7$) occurs at a similar potential as that of Ce^{III} to Ce^{IV}. Cerium iodates have been shown to occur as Ce^{III}, Ce^{IV}, and mixed-valent $Ce^{III/IV}$ compounds, which leads one to wonder if similar chemistry is possible with berkelium. We have achieved these goals and found evidence for a transient, mixed-valent state that exists in $Bk(IO_3)_4$. We also performed a detailed experimental and computational examination of $Bk(IO_3)_3$.

Significant achievements during 2015-2017: We have prepared and characterized the first bulk samples of berkelium compounds including the first single crystal structures ever determined for berkelium compounds. We determined that the ground state of Bk(III) is multiconfigurational owing to spin-orbit coupling induced mixing of the ground state multiplet with the first excited state.

1. The synthesis, single crystal structure, detailed electronic spectroscopy, and quantum mechanical calculations of $Bk(IO_3)_3$ and $Bk(IO_3)_4$ were accomplished. The structure of $Bk(IO_3)_4$ is shown in Figure 1.

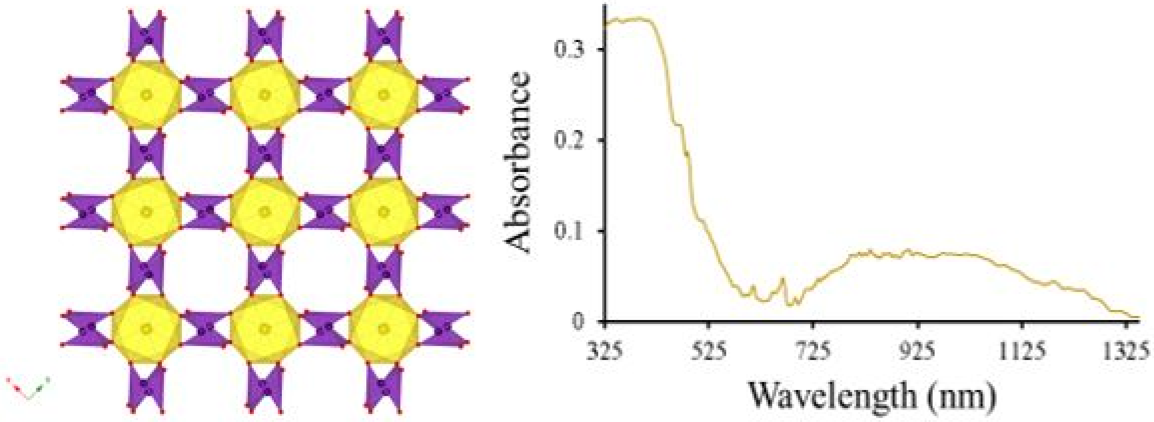

Figure 1. Left: View of a single layer in the structure of Bk(IO$_3$)$_4$, showing nearly perfect square antiprismatic coordination of Bk(IV) by iodate. Right: Absorption spectrum of a single crystal of Bk(IO$_3$)$_4$ showing a broad intervalence charge-transfer band owing to the presence of Bk(III) in the crystal.

Science objectives for 2017-2019:

- Prepare and characterize Bk(IV) coordination complexes.
- Synthesize and crystallize an Es(III) coordination complex. In particular, we are focused on collecting the low-temperature, photoluminescence spectrum from an Es(III) sample.
- Prepare Cf(II) coordination complexes with the primary goal of obtaining spectroelectrochemical measurements of these complexes in solution.

Selected publications supported by this project 2015-2017 (> 50 total)

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2. T. E. Albrecht-Schmitt, “A Fleeting Glimpse of an Elusive Element,” *Nature*, **2016**, *536*, 404-405. **DOI:** 10.1038/536404a
3. M. A. Silver, S. K. Cary, J. A. Johnson, R. E. Baumbach, A. A. Arico, M. Luckey, M. Urban, J. C. Wang, M. J. Polinski, A. Chemey, G. Liu, K.-W. Chen, S. M. Van Cleve, M. L. Marsh, T. M. Eaton, B. van de Burgt, A. L. Gray, D. E. Hobart, K. Hanson, L. Maron, J. Braley, T. E. Albrecht-Schmitt, “Characterization of berkelium(III) dipicolinate and borate compounds in solution and the solid state,” *Science*, **2016**, *353*, 888-894. **DOI:** 10.1126/science.aaf3762
4. M. A. Silver, S. K. Cary, J. T. Stritzinger, T. G. Parker, L. Maron, T. E. Albrecht-Schmitt. “Covalency-Driven Dimerization of Plutonium(IV) in a Hydroxamate Complex,” *Inorganic Chemistry*, **2016**, *55*, 5092–5094. **DOI:** 10.1021/acs.inorgchem.6b00340
5. S. K. Cary, M. G. Ferrier, R. E. Baumbach, M. A. Silver, J. Lezama-Pacheco, S. A. Kozimor, H. S. La Pierre, B. W. Stein, A. A. Arico, D. L. Gray, T. E. Albrecht-Schmitt, “Monomers, Dimers, and Helices: Complexities of Cerium and Plutonium Phenanthrolinecarboxylates,” *Inorganic Chemistry*, **2016**, *55*, 4373-4380. **DOI:** 10.1021/acs.inorgchem.6b00077
6. S. K. Cary, M. A. Silver, G. Liu, J. C. Wang, J. A. Bogart, J. T. Stritzinger, A. A. Arico, K. Hanson, E. J. Schelter, T. E. Albrecht-Schmitt, “Spontaneous Partitioning of Californium from Curium: Curious Cases from the Crystallization of Curium Coordination Complexes,” *Inorganic Chemistry*, **2015**, *54*, 11399-11404. **DOI:** 10.1021/acs.inorgchem.5b02052
7. S. K. Cary, M. Vasiliu, R. E. Baumbach, J. T. Stritzinger, T. D. Green, K. Diefenbach, J. N. Cross, K. L. Knappenberger, G. Liu, M. A. Silver, A. E. DePrince III, S. M. Van Cleve, J. H. House, N. Kikugawa, A. Gallagher, A. A. Arico, D. A. Dixon, T. E. Albrecht-Schmitt, “Emergence of Californium as the Second Transitional Element in the Actinide Series,” *Nature Communications*, **2015**, *6*, 6827-34. **DOI:** 10.1038/ncomms7827.

Beyond Metallosurfactant Coordination Chemistry in Organic Phases for Heavy Element Separations

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Collaborators: Drs. S. Skanthakumar, L. Soderholm, S. L. Estes, Chemical Sciences & Engineering Division, Argonne National Laboratory; Prof. M. Nilsson, Department of Chemical Engineering and Materials Science, University of California, Irvine, CA 92697

Overall research goals: At the most fundamental level, chemical separations of rare earth (*RE*) and actinide (*An*) ions embody all aspects of classical coordination chemistry. A key property of a practical extractant is its affinity to coordinate *RE* and *An* ions. Despite significant progress in extractant design, even today—nearly 65 years after the first kilogram-scale separation of gadolinium by solvent extraction (SX)—extractant behaviors are still not well understood. The traditional methods of metallosurfactant coordination chemistry are inadequate to fully describe bulk phase properties of extraction systems. This point is gaining recognition through contemporary synchrotron radiation research—like ours—showing that mesoscale phenomena, esp. multiscale structures and micellization, exhibit pronounced effects on separation factors, extraction efficiencies, and phase stabilities, to name three key parameters of SX. Our goal is to determine the organization of solutes—including multivalent *RE* and *An* ions—in organic solutions of relevance to SX chemistry. In this pursuit, fundamental knowledge about *RE* and *An* electrochemistry in bulk organic phases is enabling us to correlate extraction kinetics with extraction performance in manners not done before.

Significant achievements during 2015-2017: We have acquired insights into the phase behaviors as well as the speciation and electrochemistry of *RE* and *An* cations, hydrated protons $(H(OH_2)_n)^+$, and large oxoanions at liquid-vapor surfaces[4,9,11] and in aqueous[5,6,8] and organic[1-3,7,12,13] liquids of relevance to SX. As depicted in the Figure, we have obtained definitive evidence of the phenomenon of phase inversion in the Ce(IV)-HNO_3-TBP-*n*-$C_{12}H_{26}$ extraction system[1].

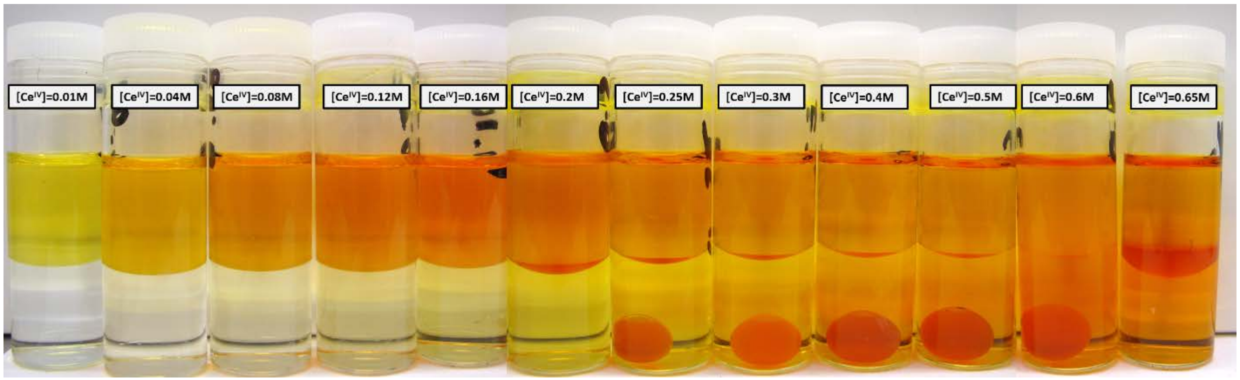

Figure. After SX of freshly-electrolyzed solutions of varying initial Ce(IV) concentrations (from 0.01 M on the left to 0.65 M on the right) in 3 M HNO_3 by 20% TBP (tri-*n*-butyl phosphate) in *n*-dodecane, the upper organic phase takes on the typical yellow-orange colors of tetravalent Ce. For five systems, $0.25\ M \le [Ce^{4+}] \le 0.60\ M$, third phases settle at the bottom of the vials as spherical red drops. These denser-than-water phases, which are referred to as "red oils", can be especially dangerous in industrial SX processes, like PUREX (Plutonium Uranium Reduction EXtraction), using TBP.

Science objectives for 2017-2019: Multiscale insights into organic phase solute architectures in liquid-liquid extraction systems are sought. Of particular interest is an understanding of electrochemical and structural phenomena, including the aggregation of extractant molecules with *An* and *RE* ions. Our objectives are to obtain knowledge about phase behaviors and speciation of *RE*- and *An*-ions that goes beyond the first, metallosurfactant coordination sphere. The results will impact the field of extractive hydrometallurgy, in general, and SX, in particular. In this research, we will exploit the use of purpose-built equipment for electroanalytical measurements, which have been developed in previous years' efforts, and develop new methods to probe the organization of solutes in organic phases by use of high-energy X-ray scattering (HEXS) studies to complement classical approaches by SAXS, EXAFS, and SX combined.

Publications supported by this project 2015-2017:

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Thermochemistry and Reactivity of Atomic and Molecular Actinides

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

Significant achievements during 2014-2017: The project has focused initially on the chemistry of thorium and reactions with H_2, D_2, HD, O_2, CO, and CH_4 have been characterized.

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

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

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

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

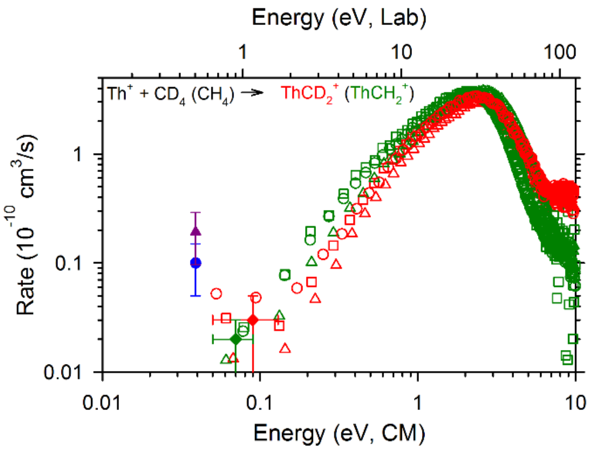

Fig. 1. Reaction rate for $Th^+ + CD_4$ (CH_4) → $ThCD_2^+$ ($ThCH_2^+$) + D_2 (H_2) plotted as a function of kinetic energy. Present work in red ($ThCD_2^+$) and green ($ThCH_2^+$). Average rates at 700 ± 300 K for $ThCD_2^+$ (red diamond) and 500 ± 150 K for $ThCH_2^+$ (green diamond). ICR-MS results from Gibson et al. (blue circle) and Marçalo et al. (purple triangle). Lab frame shown corresponds to the CD_4 reaction.

Science objectives for 2017-2020:

- Ongoing work includes studies of the reaction of Th^+ with D_2O, hydration energies of $Th(OH)_3^+$, and collision-induced dissociation of $Th^+(CO)_n$ where n = 1 – 6.
- Extensions to uranium chemistry are beginning.

Publications supported by this project 2014-2017

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New Reactivity in Actinide Chemistry Facilitated by Supporting Ligand Design

John Arnold, Principal Investigator

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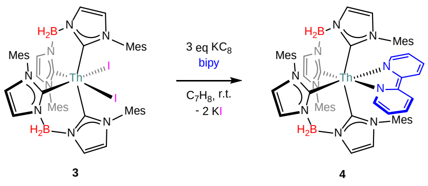
Graduate students: Alison Altman, Mary Garner, Nick Settineri, Michael Boreen
Collaborators: Dr Wayne Lukens, Dr David Shuh, Dr Stefan Minasian, Chemical Sciences Division, Lawrence Berkeley National Laboratory. Professor Laurent Maron, Université de Toulouse.

Overall research goals: The objective of this project is to explore concepts relating to metal-metal bonding in molecular complexes of the actinide and lanthanide elements. This will address some of the crucial issues surrounding nuclear fuel reprocessing and waste remediation by developing our insight into the fundamental bonding principles for *f*-elements. We focus on the synthesis of actinide and lanthanide coordination complexes with ligands containing metal or metalloid atoms. Our specific aims are to: develop new starting materials for the exploration of actinide chemistry in various coordination geometries and oxidation states; synthesize structurally related coordination complexes of actinide and lanthanide elements containing a direct, unsupported bond to another metal or metalloid atom; and examine bonding trends as a function of the 4*f* and 5*f* and 6*d* orbital energies, oxidation state, coordination number, and geometry of both participants in the M–M bond.

Significant achievements during 2014-2017

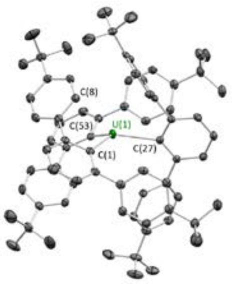
Molecular chemistry of the actinides is a burgeoning area of inorganic chemistry. The versatile coordination chemistry of the actinides and their ability to exist in various oxidation states make the actinide metals excellent candidates for the discovery of new structural types, reactivity, and physical and spectroscopic properties. Actinide metallocenes and related Cp species dominate this area but more examples of alternative supporting platforms have been reported recently. We have been active in this are over the last few years; some recent results are shown below.

NHCs as supporting ligands in actinide chemistry. We have demonstrated that careful ligand design not only affords reactive thorium-NHC compounds but also creates the steric and electronic environment necessary to stabilize unusual molecular and electronic structures. Indeed, the thorium-bis(NHC)borate complex (3) has been synthesized along with its reduced bpy (4) and terminal p-tolylimido (6) derivatives.



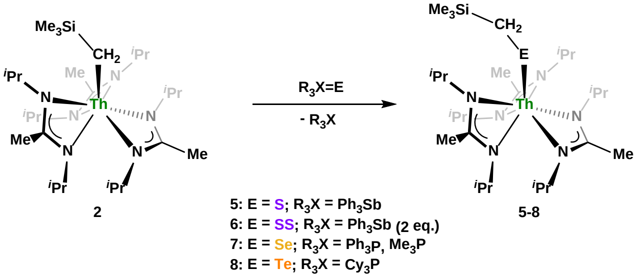
The new mesityl-substituted bis(NHC)borate scaffold has supported a reactive thorium complex through transformations with cabonylated substrates and p-tolylazide. Moreover, the steric environment afforded by this material was ideal to stabilize the first example of an unusual terminally-bound thorium-imido complex bearing a redox active ligand in its coordination sphere.

Contrasting those of previously reported actinide-bpy compounds, CASSCF calculations revealed the unusual multi-configurational open-shell singlet electronic ground state of **4**.

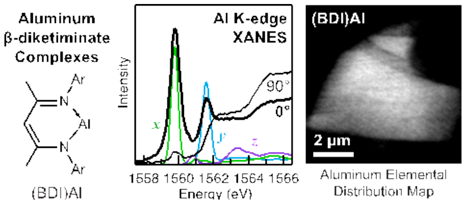


Homoleptic uranium aryls. We have isolated the homoleptic uranium(III) aryl, (Terph)3U (1), in high yield. Intramolecular proton abstraction is responsible for its thermal decomposition. In the presence of excess iPrN=C=NiPr, it is rapidly and cleanly converted to the double-insertion product, [TerphC(NiPr)2]2U(Terph) (2). The U–C bonds are also prone to protonolysis, yielding uranium(IV) tetrakis alkoxide and amide products. These results indicate the use of bulky ter-phenyl ligands in actinide chemistry is a fruitful endeavor that we aim to develop further in ongoing studies.

Actinide chemistry with amidinate and guanidinate ligands. A new thorium mono-alkyl complex supported by a tris-amidinate framework undergoes insertion of chalcogen atoms resulting in alkoxide, thiolate, disulfide, selenolate, and tellurolate complexes. Insertion was achieved by balancing the thermodynamic driving force of chalcogenolate formation versus the BDE of the pnictogen-chalcogen bond in the transfer reagent. Utilizing oxygen atom transfer reagents bearing adjacent C-H bonds in-stead led to activation and SiMe4 extrusion rather than oxygen atom insertion.



Group 13 derivatives of actinides. We have been using X-Ray absorption spectroscopy (XAS) to probe the electronic structure of Group 13 compounds, with a focus on Al. This research will provide a baseline for comparison of complexes containing Al-An bonds and allow for better understanding of their electronic structure. The results of more recent studies in which we explore actinide chemistry with these species as ligands will be presented.



Publications supported by this project

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f-block organometallics; combining metal cations for new reaction chemistry and understanding

THE UNIVERSITY *of* EDINBURGH

Polly L Arnold, Keynote Lecture

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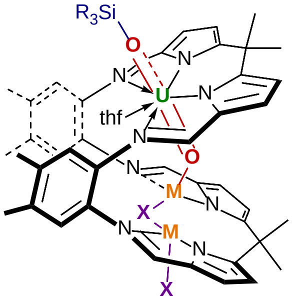
The subtleties of structure and bonding in compounds of uranium, the heaviest naturally occurring element, and its neighbours in the f-block are still poorly-understood. A fundamental understanding is needed to develop environmentally cleaner ways to extract technology-critical rare earth metals, and for the safe, long-term handling of our nuclear waste legacies.

Drawing on our research to target exotic new f-block complexes, this lecture will explore what organometallic chemistry can teach us about these complicated but important metals.

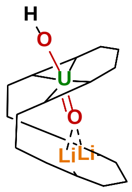
Two organometallic approaches will be discussed, with focus first on the U^{VI} uranyl ion and then on low oxidation state actinide chemistry:

The most common motif in uranium chemistry is the d^0f^0 uranyl ion $[UO_2]^{2+}$ in which the oxo groups are rigorously linear and inert. The strong, covalent U=O bonds render the oxo groups poorly Lewis basic, which explains the dominance of this ion in the laboratory and its persistence as an environmental contaminant, but also makes it a poor model for the more radioactive heavier actinyl ions which are prone to unwanted clustering in nuclear waste separations. Using a Schiff-base polypyrrolic macrocycle, a 'Pacman' scaffold (Fig.1), we have probed the fundamental chemistry of the d^0f^0 uranyl ion $[UO_2]^{2+}$ oxo groups.[1] It is possible to isolate robust complexes of the aqueous-unstable $[U^{V}O_2]^{+}$ by judicious control of metallation or p-block elementation of one or both groups.[2] We will show how we have learnt to control this, with elements from across the periodic table, from H to Np and Pu.[3] But we will also discuss how we still do not understand the processes that lead to oxo-group rearrangement in our systems, or the fact that some unusual U^{V} oxo-bridged dimers, including the first air-stable $U^{V}_2O_4$ 'butterfly' motif do not disproportionate to U^{IV} and uranyl.[4]

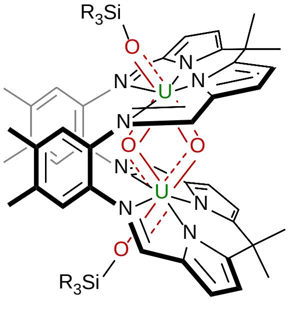
first covalent bond formed to a uranyl oxo group



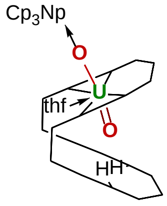
first thermal C-H bond activation by the uranyl ion



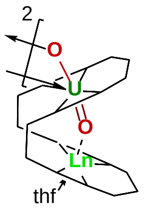
oxo migration to *cis*-



exo oxo binding: first uranyl-Np coupling



endo oxo binding rare uranyl-Ln coupling



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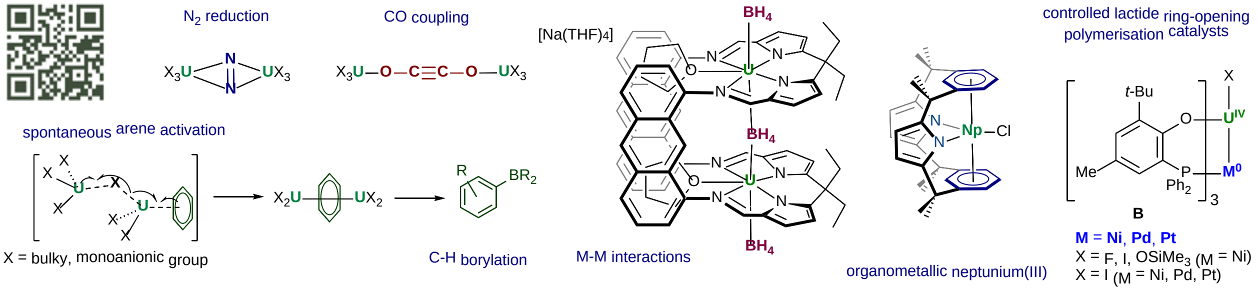
The activation of small, traditionally inert molecules by f-block metal complexes contributes to our fundamental understanding of metal-ligand bonding and can open up new areas of catalysis.[5] The rare earths, whose salts are as common as iodine and ten times less toxic than those of iron, offer great potential as Lewis acids for the catalytic conversions of simple inert molecules needed for our future, renewable-based chemical industry, In anaerobic conditions, all the oxidation states down to formal U^{II} have now been reported, and we and others have shown many U^{III} complexes that are powerful reductants for small molecules;[6] we note that depleted uranium (DU) is a widely untapped resource, with approximately 1.3 million tonnes stored globally in 2008. The study of interactions electron-rich π-systems such as arenes has also provided important contributions to the understanding of covalency.[7]

By using ligands with macrocyclic and/or polydentate structures we have been able to make the first structurally characterised molecules containing two U^{III} or two Np^{III} centres. These electron-rich compounds are magnetically complex and pre-organised for multi-electron reductions of small molecules,[8] but here we will focus on their electronic structures, and on their reduction to target new low formal oxidation states, with a focus on Np(II).[9] Analyses showed significant covalency differences between 4f- and 5f- analogues, proving that fundamental Np organometallic chemistry can provide new insight in f-element bonding theory.



Finally, the most recent addition to our studies in f-block M-M' bonding explores the metallic bonding, strength, and covalency in the first full set of comparable U-M compounds, by varying both M (Ni, Pd, Pt, Rh) and the trans-ligand (F, I, $OSiMe_3$).[10] We will present contrasting catalytic reactivity for pairs of U and Ce complexes and discuss whether this can be attributed to the *Inverse Trans Influence (ITI*).[11]

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Computational studies of magnetic properties of open-shell f-element complexes

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Overall research goals: We investigate the electronic structure and magnetic properties of compounds of 5f-elements, i.e. actinides, by using quantum chemical calculations. The main objective is to learn how observable magnetic properties are related to the geometrical structure, chemical bonding, and the nature of the ground and excited electronic states. We develop and apply state-of-the-art relativistic theoretical methods, for example for computing of magnetic resonance parameters (electron paramagnetic resonance = EPR, nuclear magnetic resonance = NMR), magnetic susceptibilities, and chemical bonding of actinide complexes. The project goals include developments of new relativistic quantum chemical methods in the NWChem and Molcas quantum chemistry packages, along with stand-alone new software.

Significant achievements during 2015-2017:

Theoretical studies were carried out for numerous U, Np, Pu, A, Cm, Cf, and Bk compounds with unpaired electrons, and a few lanthanide systems, mainly using multi-reference (CAS-based) wavefunctions including effects from spin-orbit (SO) coupling. For example, CAS calculations on a cluster model for PuO_2 explain a 50-year old puzzle, namely why the magnetic susceptibility of PuO2 is temperature-independent up to 1000 K.

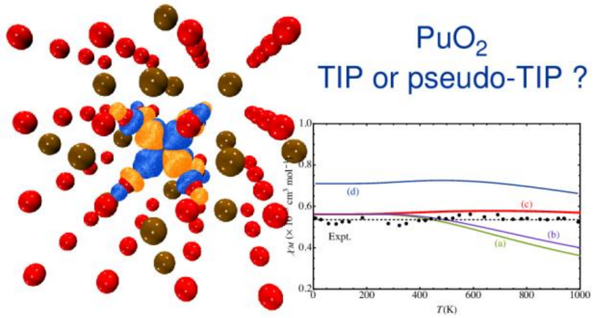

Figure 1: Temperature-dependent contributions in the magnetic susceptibility of PuO_2 appear above 300 K, but they cancel almost perfectly

Following the development of a new code for EPR hyperfine coupling in 2015, a module for calculating the ligand NMR shift effects due to the actinide's paramagnetism (pNMR) was developed. With this new code, we performed the first-ever fully ab-initio relativistic calculations of pNMR shifts, specifically for actinyl carbonate complexes and Cp_3U-CH_3. Furthermore, we extended the EPR, pNMR, and bonding analysis modules in the Molcas package to be able to use matrix product states (MPSs) from density matrix renormalization group (DMRG) calculations, and to calculate SO matrix elements between MPSs with non-orthogonal orbital bases. Going forward, these calculations will allow us to interpret complicated nuclear magnetic resonance spectra of f-element complexes, analyse their bonding, and determine their magnetic properties using comparatively large active spaces. Several new collaborations within the group of PIs funded by the HEC program were initiated, with several publications either already in print or in late stages of preparation. We just started to investigate magnetic circular dichroism of actinide complexes by calculations. The development of eXact 2-Component (X2C) relativistic methods is continuing.

Science objectives for 2017-2019:

- Apply the new MPS relativistic quantum chemical methods for magnetic properties of open-shell f-element complexes to multi-nuclear actinide complexes and systems where many ligand orbitals need to be part of the active space.

- Investigate the importance of solvent effects or the surrounding of a complex in crystals on the magnetic properties of actinide complexes.

- Develop an improved treatment of spin polarization in CAS and MPS calculations

- Predict quadrupolar resonance parameters of actinide nuclei and ligand nuclei in actinide complexes.

- Continue and extend collaborations with experimental groups

Selected Publications supported by this project 2015-2017:

Gendron, F.; Autschbach, J., 'Puzzling lack of temperature dependence of the PuO2 magnetic susceptibility explained according to ab-intio wavefunction calculations', J. Phys. Chem. Lett. 2017, 8, 673–678. http://dx.doi.org/10.1021/acs.jpclett.6b02968

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

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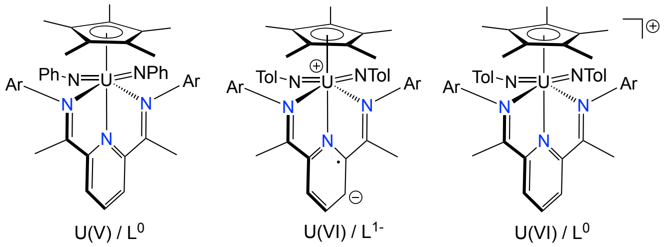
Prof. Thomas Albrecht-Schmitt, Florida State University, Tallahassee, FL
Prof. Justin Walensky, University of Missouri, Columbia, MO

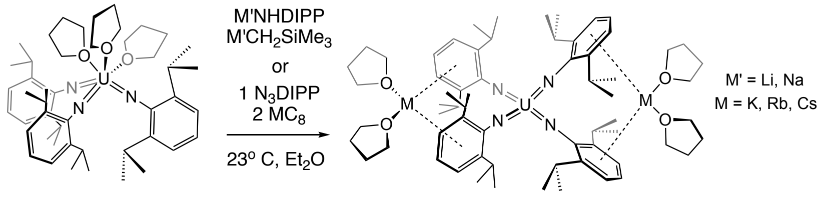
Overall research goals: To explore lanthanide and uranium complexes bearing redox-active ligands, through synthesis, characterization and reactivity studies. These species will be fully characterized using ^{1}H NMR, infrared, electronic absorption, electronic paramagnetic resonance and X-ray absorption spectroscopies (Kozimor) as well as X-ray crystallography, electrochemistry, SQUID magnetization (Schelter), and computational methods (Gagliardi). Transuranic analogues, including Np (Walensky), Pu, Am, and Cf (Albrecht-Schmitt), will be studied to understand synthetic, reactivity, and bonding trends across the Periodic Table.

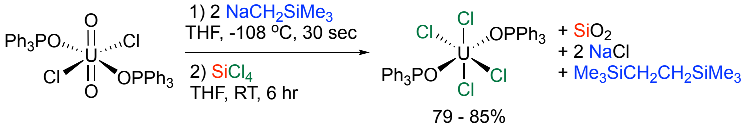
Significant achievements during 2015-2017:

1. Synthesized and characterized three different uranium bis(imido) species via multi-electron transfer from Cp*U(^{Mes}PDI^{Me})(THF), which contains a trianionic pyridine(diimine) ligand. Each bis(imido) species was assigned as having a unique electronic structure, pointing to the effects of ancillary ligand variation. The mechanism of N=N bond cleavage by uranium was also elucidated.



2. Generated a family of pseudo-see saw uranium tetrakis(imido) dianions, $[M]_2[U(NDIPP)_4]$ (M = Li, Na, K, Rb, Cs), and accomplished full characterization and computational analysis to determine geometric preferences. Cation sequestration led to the isolation of the tetrahedral imido, $[(2.2.2\text{-Crypt-K})]_2[U(NDIPP)]_4$.





3. Synthesized a uranyl complex with a new electronic structure, supported by a pyridine(diimine) ligand radical, and demonstrated facile reductive silylation. This work was extended to show that this process could 1) be accelerated using Lewis bases, and 2) be accomplished readily using commercially available reagents to convert ***any*** uranyl salt to uranium(IV) chloride.

Science objectives for 2017-2019:

- Explore the synthesis and reactivity of higher order uranium imido species, including a uranium pentakis(imido) species. Our current uranium tetrakis(imido) examples provide excellent starting points, and multiple synthetic pathways are underway.
- Continue our uranium and transuranic studies using the dioxophenoxazine ligand framework in collaboration with Prof. Albrecht-Schmitt, focusing on additional characterization of our transuranic derivatives for publication.
- Expand the family of known uranium tris(imido) complexes via ligand substitution reactions. Computational studies were used to elucidate geometric preferences. Explore reactivity trends for uranium tris(imido) species, including generation of mixed imido species.
- Exploration of neptunium and lanthanide complexes bearing redox-active ligands, including the pyridine(diimine) and iminoquinone ligands, for bonding and reactivity comparisons to uranium analogues. The transuranic work is done in collaboration with Prof. Justin Walensky.

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Covalency in Americium(III) Hexachloride

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Overall research goals: The overarching goal of the program at Los Alamos is the study of the nature of chemical bonds between actinide elements and their ligands in a variety of coordination environments.

In this poster, we present one recent study of Am-Cl bonds which contains experimental and theoretical aspects aimed working together to describe the nature of the chemical interactions in this system. The importance of the study of orbital mixing as addressing the nature of the chemical bond, which is the cornerstone of chemistry. For example, covalence occupies a central role in directing chemical and physical properties for almost any given compound or material. Hence, improving understanding of covalency has potential to lead to broad and substantial advances, ranging from biological applications to condensed matter physics. Given the importance of understanding orbital mixing combined with the difficultly of measuring the degree of covalency of a given bond, estimating or inferring covalency often leads to a fiery debate. Consider the 60-year controversy sparked by SEABORG and coworkers (1954) when it was proposed that covalency from 5*f*-orbitals contributed to the unique behavior of americium. Herein, we describe the use of ligand K-edge X-ray absorption spectroscopy (XAS) and ground state electronic structure calculations to quantify the extent of covalent bonding in – arguably – one of the most difficult systems to study, the Am–Cl interaction within $AmCl_6^{3-}$. We observed both 5*f*- and 6*d*-orbital mixing with the Cl-3*p* orbitals; however, contributions from the 6*d*-orbitals were more substantial. Comparisons with the isoelectronic $EuCl_6^{3-}$ indicate similar bonding for the Am^{III} 6*d*- and Eu^{III} 5*d*-orbitals. Meanwhile, the results confirmed SEABORG'S 1954 hypothesis that Am^{III} 5*f*-orbital covalency was more substantial that 4*f*-orbital mixing for Eu^{III}.

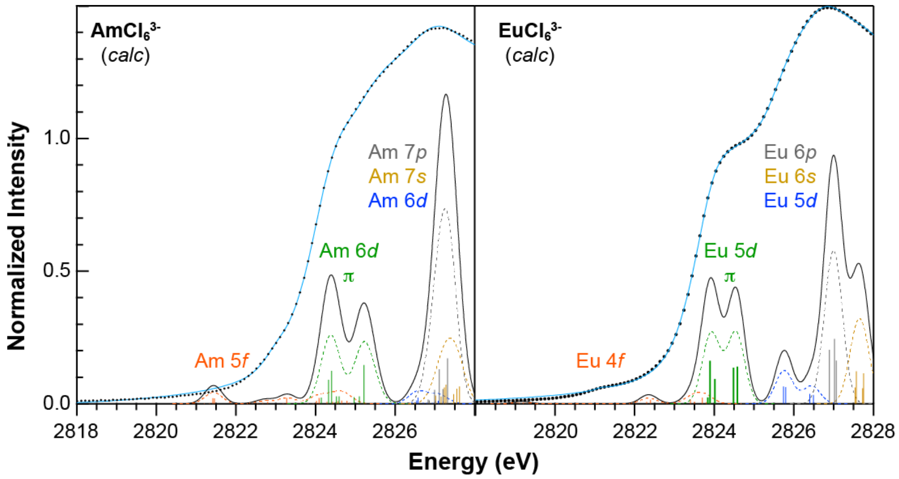

Figure 1: The experimental data (●) and the curve fitted model (blue trace) for the Cl K-edge XAS spectrum from $(PPh_4)_3AmCl_6$ and $(PPh_4)_3EuCl_6$. Comparison between the experimental Cl K-edge XAS spectrum and DFT calculations predicted intensities (black trace). The orange, green, purple, and grey bars and dashed traces represent the energy and oscillator strength for the calculated transitions involve Am 5f, 6d, 7s, 7p-final states and Eu 4f, 5d, 6s, 6p-final states, respectively.

Publications:

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Probing Actinide Covalency Through Studies of Uranium Nitrogen Multiple Bonding and Reactivity

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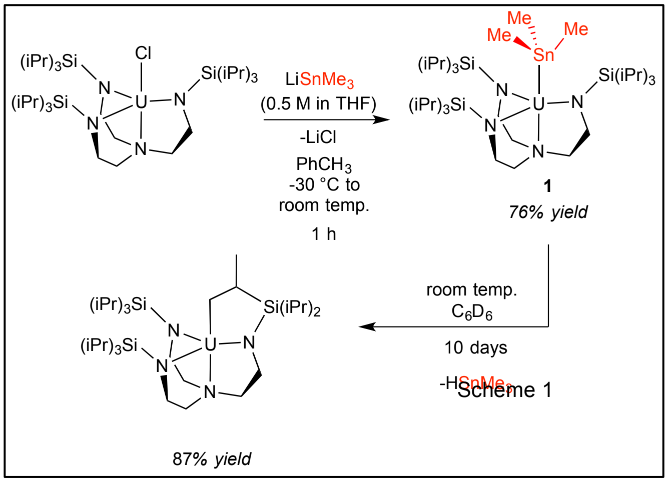
Current Collaborators: E. R. Batista, P. Yang, A.J. Gaunt, S. A. Kozimor (LANL), M. Neidig, (U. of Rochester)

Overall research goals: Understanding the role covalency in M-L bonding in actinide complexes by investigating the chemistry of compounds containing U-N multiple bonds. Understanding the redox reactions of uranium compounds in non-aqueous media. The synthesis of compounds having unusual U-element bonds. This synthetic chemistry is also valuable as a guide to viable synthetic routes to unprecedented transuranic compounds.

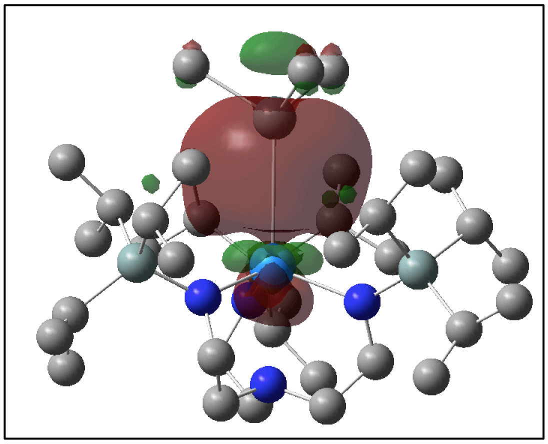
Significant achievements during 2015-2017:

1.) Using the original synthesis of U(V) and U(IV) bis- and mono-imido complexes from UCl_4 as a guide, the synthesis of Np(V) bis-imido complexes from $NpCl_4$ was described.[1] Treatment of the Np(IV) precursor with the parent amido, in the presence of a supporting bipyridine co-ligand, resulted in oxidation of Np(IV) to Np(V) and generation of a bis-imido analogue of neptunyl(V). It is the first example of a transuranic metal-ligand multiple bond.

2.) The synthesis and structural characterization of a uranium stannyl complex, **1**, was accomplished as shown in scheme 1.[2] Analysis of the U-Sn σ bond in **1** (NBO analysis) demonstrated significant covalency in the U-Sn interaction, with 25% contribution from U and 75% from Sn. The polarity in this bond is demonstrated by the spontaneous elimination of Me_3Sn-H as shown in Scheme 1.

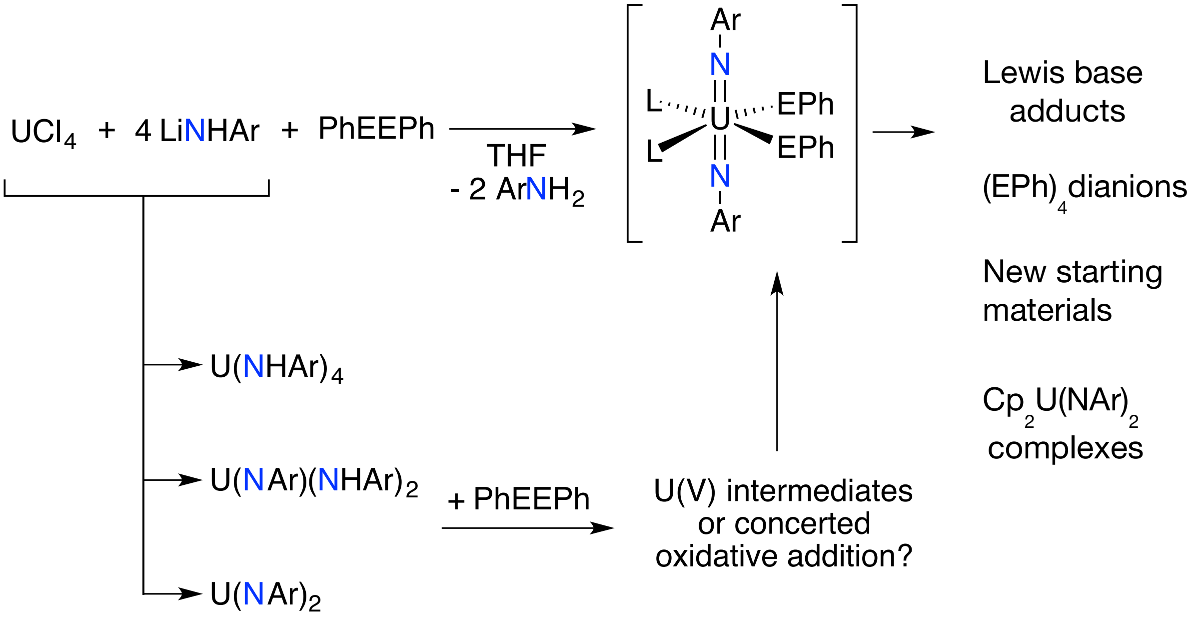


Scheme 1



3.) An improved synthetic route to U bis-imido complexes from $UCl_4(L)_x$ precursors has resulted in the synthesis of the tetrachalcogenide complexes, $[U(=NR)_2(EPh)_4]^{2-}$ (E=S, Se, Te). These complexes are of interest for XAS studies of their bonding because they allow a direct comparison with the tetrachloride analogues. The synthetic route for their synthesis is shown in Scheme 2.

Investigation of this reaction sequence has demonstrated that reaction of UCl_4 with 4 equivalents of the amide anion $[RNH]^-$ gives an equilibrium mixture of U(IV) tetra amide, imido/bis(amide), bis(imido) and RNH_2. Addition of the oxidant, in this case, PhE-EPh, gives the U(VI) product. The observation that a new paramagnetic intermediate is formed (likely U(V)), which subsequently decays, giving the final diamagnetic U(VI) product suggests that the oxidation proceeds via a one electron process rather than a concerted oxidative addition pathway.



SCHEME 2

Science objectives for 2017-2019:

- Explore/develop novel methods for U-element multiple bond formation including atom abstraction with one electron oxidation.
- Develop new methods for the reduction of U(IV) to U(III) and investigate their utility as methods for the synthesis of lower valent Np and Pu complexes.
- Investigate bonding in chalcogenolate and stannyl complexes using XAS.

Publications supported by this project 2015-2017

1. J. L. Brown, E. R. Batista, J. M. Boncella, A. J. Gaunt, S. D. Reilly, B. L. Scott, and N. C. Tomson *A Linear trans-Bis(imido) Neptunium(V) Actinyl Analogue: $Np^V(NDipp)_2(^tBu_2bipy)_2Cl$ (Dipp = $2,6\text{-}^iPr_2C_6H_3$)*, *J. Am. Chem. Soc.* **2015**, 137, 9583-86. **DOI:** 10.1021/jacs.5b06667
2. M. S. Winston, E. R. Batista, P. Yang, A. M. Tondreau, J. M. Boncella *Extending Stannyl Anion Chemistry to the Actinides: Synthesis and Characterization of a Uranium-Tin Bond Inorg. Chem.* **2016**, 55, 5534-39. **DOI:** 10.1021/acs.inorgchem.6b00543
3. M. S. Winston, E. R. Batista, A. M. Tondreau, J. M. Boncella *Coordinatively Versatile Tripodal Tris(pyrrolide) Ligands for Uranium(IV)*, Submitted.
4. N. C. Tomson, N. H. Anderson, A. M. Tondreu, B. L. Scott, J. M. Boncella *Mechanistic Insight into the Formation of Bis(imido)U(VI) Compounds from U(IV) Precursors.* In preparation.
5. A. M. Tondreau, P. Yang, B. Stein, J. M. Boncella *Synthesis, Structure and Bonding of Tetrakis(amido)U(V) Cations* In preparation.

Using actinide L_3-edge resonant x-ray emission spectroscopy (RXES) to measure valence and delocalization effects in intermetallics

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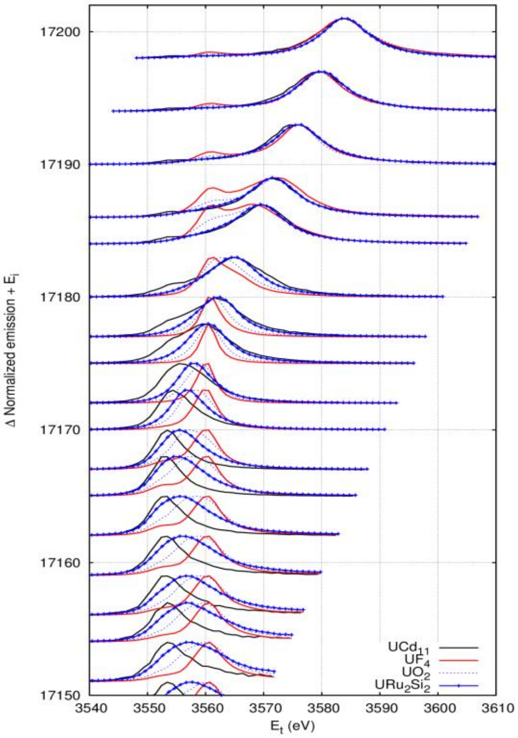
Overall research goals: The objective of this project is to determine 5f orbital occupancy and the degree of delocalization in actinide materials using advanced hard x-ray spectroscopic methods.

Significant achievements during 2014-2016:

1. An improved fitting methodology allowed for quantifying delocalization and occupancy effects in resonant x-ray emission spectroscopy (RXES) data. This methodology was employed to a range of Pu intermetallic compounds, especially $PuSb_2$, $PuCoGa_5$ and $PuCoIn_5$, with implications for superconductivity in the latter two compounds, and was also applied to α- and δ-Pu [1].

2. In collaboration with researchers at the University of Nevada, Las Vegas, we obtained high-resolution partial fluorescence yield data on a strongly-localized uranium intermetallic, UCd_{11}, demonstrating strong changes to the U L_3/L_α spectra with applied pressure up to nearly 30 GPa. This result is significant because it establishes how changes in 5f occupancy and delocalization affect such spectra (Fig. 1) [12].

3. These techniques have been applied to the so-called "hidden order" system, URu_2Si_2, in an effort to limit applicable theories of hidden order to those that have certain occupancy and delocalization characteristics. The use of UCd_{11} and UF_4 as localized $5f^3$ and $5f^2$ spectroscopic standards was critical in determining a mixed valent ground state with a nearly $5f^3$ character that is nevertheless strongly delocalized (Fig. 1) [16].



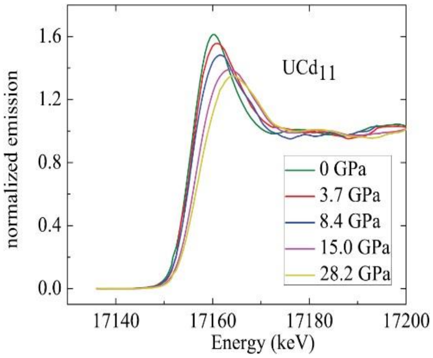


Fig. 1: Uranium $L_3/L_{\alpha 1}$ resonant x-ray emission spectra: (left) Spectra are a function of incident energy (E_I), transfer energy (E_T) plane. Comparison to model compounds is crucial, with UF_4 representing a localized f^2 compound and UCd_{11} a localized f^3 compound. (top) Partial fluorescence yield data for UCd_{11} demonstrate that pressure can delocalize the system to a predominantly f^2 configuration.

Science objectives for 2017-2019:

- Further develop technique by exploring other materials as potential standards, especially UPd_3.
- Work toward more materials under applied pressure.
- Expand hard x-ray studies into transplutonium compounds.

Publications supported by this project 2014-2016

1. C. H. Booth et al., “Delocalization and occupancy effects of 5f orbitals in plutonium intermetallics using L_3-edge resonant X-ray emission spectroscopy.” J. Elect. Spec. Rel. Phen. **194**, 57 (2014). doi: 10.1016/j.elspec.2014.03.004
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3. G. Nocton et al., “Reversible sigma C-C bond formation between phenanthroline ligands activated by $(C_5Me_5)_2Yb$.” J. Am. Chem. Soc. **136**, 8626 (2014). doi: 10.1021/ja502271q
4. G. Nocton, C. H. Booth, L. Maron, L. Ricard, R. A. Andersen, “Carbon-hydrogen bond breaking and making in the open-shell singlet molecule $Cp^*_2Yb(4,7\text{-}Me_2phen)$.” Organometallics **33**, 6819 (2014). doi: 10.1021/om500843z
5. J. A. Bogart et al., “A ligand field series for the 4f-block from experimental and DFT computed Ce(IV/III) electrochemical potentials.” Inorg. Chem. **54**, 2830 (2015). doi: 10.1021/ic503000z
6. A. Durand et al., “The effects of Co_3O_4 on the structure and unusual magnetism of $LaCoO_3$.” J. Phys.: Condens. Matter, **27**, 126001 (2015). doi: 10.1088/0953-8984/27/12/126001
7. A. Durand et al., “The unusual magnetism of nanoparticle $LaCoO_3$.” J. Phys.: Condens. Matter **27**, 176003 (2015). doi:10.1088/0953-8984/27/17/176003
8. J. G. Tobin, C. H. Booth, W. Siekhaus, D. K. Shuh, “EXAFS investigation of UF_4.” J. Vac. Sci. Technol. A, **33**, 033001 (2015). doi: 10.1116/1.4915893
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11. J. A. Bogart, C. A. Lippencott, P. J. Carroll, C. H. Booth, and E. J. Schelter, “Controlled redox chemistry at cerium within a tripodal nitroxide ligand framework.” Chem.-Eur. J. **21**, 17850 (2015). doi: 10.1002/chem.201502952
12. F. Nasreen et al., “High pressure effects on U L_3 x-ray absorption in partial fluorescence yield mode and single crystal x-ray diffraction in the heavy fermion compound UCd_{11}.” J. Phys. Condens. Matt. **28**, 105601 (2016). doi: 10.1088/0953-8984/28/10/105601
13. P. Soderlind et al., “On the valence fluctuation in the early actinide metals.” J. Elect. Spec. Rel. Phen. **207**, 14 (2016). doi: 10.1016/j.elspec.2015.11.014
14. N. P. Butch et al., “Pressure-resistant intermediate valence in Kondo insulator SmB_6.” Phys. Rev. Lett. **116**, 156401 (2016). doi: 10.1103/PhysRevLett.116.156401
15. T. A. Pham et al., “A macrocycle chelator that selectively binds Ln^{4+} over Ln^{3+} by a factor of 10^{29}.” Inorg. Chem. **55**, 9989 (2016). doi: http://dx.doi.org/10.1021/acs.inorgchem.6b00684
16. C. H. Booth et al., “Probing 5f-state configurations in URu_2Si_2 with U LIII-edge resonant x-ray emission spectroscopy.” Phys. Rev. B **94**, 045121 (2016)Phys. Rev. B, **94**, 045121 (2016). doi: http://dx.doi.org/10.1021/acs.inorgchem.6b00684

Heavy actinide-soft donor complexation thermodynamics

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Overall research goals: The objective of this project is to understand how covalency impacts the thermodynamics of heavy actinide complexation. The complexation thermodynamics of actinide-aminopolycarboxylates are currently being considered.

Significant achievements during 2015-2017: Project was expedited significantly with the acquisition of berkelium and californium and additional hires of graduate students Nathan Bessan and Matthew Urban. To date, the complexation thermodynamics (ΔG, ΔH and ΔS) of Am, Cm, Bk and Cf have been assessed with dipicolinic acid. The complexation thermodynamics have also been assessed for Bk with several aliphatic aminopolycarboxylates. Two significant results have emerged:

1. The stability constants for the heavy actinides seem to be split into two groups, with Am and Cm forming weaker 1:3 metal:dipicolinate complexes and Bk and Cf forming stronger 1:3 complexes. The enthalpic binding constants describing the stability constants show less exothermic interactions in the californium:dipicolinate complexes relative to the earlier actinides.

Table 1 Complexation thermodynamics for select trivalent actinides with dipicolinic acid in 1 M $HClO_4$. Overall stability constants are reported for 25 °C, whereas ΔH (kcal mol^{-1}) and ΔS (cal mol^{-1} K^{-1}) terms are assessed over a temperature range.

	Am^{3+}	**Cm^{3+}**	**Bk^{3+}**	**Cf^{3+}**
β_{101}	9.14 ± 0.07	9.13 ± 0.03	9.07 ± 0.07	9.1 ± 0.1
ΔH	-5.2 ± 0.7	-4.8 ± 0.5	-4.5 ± 0.2	-3.8 ± 0.5
ΔS	24.1 ± 0.7	26 ± 2	26 ± 1	28 ± 2
β_{102}	16.4 ± 0.1	16.5 ± 0.1	17.23 ± 0.2	17.33 ± 0.4
ΔH	-10.0 ± 0.2	-11.0 ± 0.7	-8.6 ± 0.2	-8.6 ± 0.2
ΔS	41.1 ± 0.5	38 ± 2	50.0 ± 0.7	50.4 ± 0.7
β_{103}	22.65 ± 0.1	22.67 ± 0.5	23.14 ± 0.01	23.29 ± 0.03
ΔH	-15.0 ± 0.2	-15.77 ± 0.48	-15.3 ± 0.72	-12.67 ± 0.48
ΔS	52.8 ± 0.7	51 ± 2	55 ± 2	64 ± 1

2. The linear free energy relationships for berkelium suggest more preferential interactions for aminopolycarboxylates with berkelium relative to samarium, the comparably sized lanthanide, than previously thought. Information regarding other aminopolycarboxylate-berkelium interactions, such as CDTA and DTPA, are being interpreted currently and will be included in the presentation.

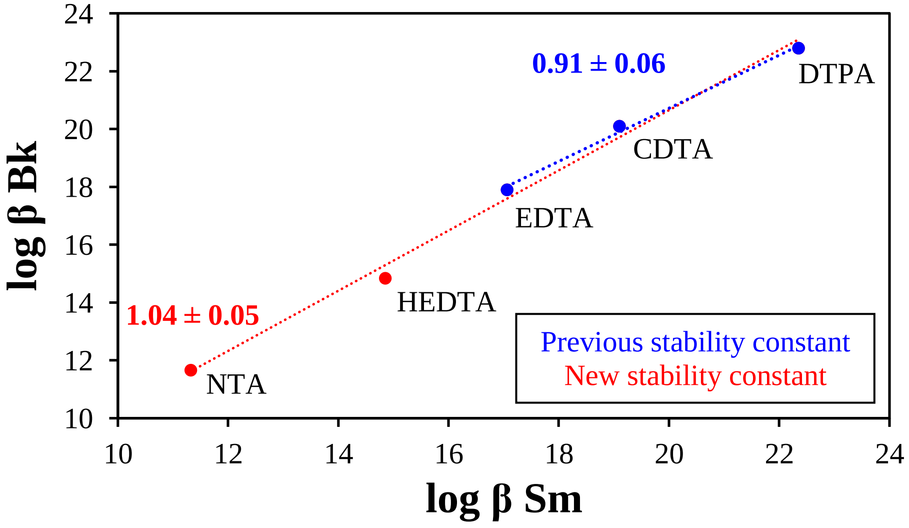

Figure 2. Linear free energy relationship between berkelium and samarium using various aminopolycarboxylates. All compared stability constants are at the same ionic strength.

Previous examinations of berkelium stability constants with DTPA did not account for formation of a protonated species, which has been shown to form for Am, Cm, and Cf. Californium stability constant measurements are pending. Dipicolinic acid is not included in this linear free energy relationship as work with a variety of americium dipicolinate derivatives has suggested aromatic amines impart more selectivity relative to aliphatic amines.

Science objectives for 2017-2019:

- Complete examination of aliphatic aminopolycarboxylate thermodynamic information with Am, Cm, and Cf. Work with Am and Cm is already initiated and constants are under review.
- Collaborate with Drs. Yang and Batista with theoretical calculations that will expand interpretation of aliphatic aminopolycarboxylate – actinide interactions
- Expand to alternative systems, such as derivatized pyridine dipicolinates or sulfur donors

Publications supported by this project 2015-2017

1. Drader, J.A.; Luckey, M.A.; **Braley, J.C**. “Thermodynamic considerations of covalency in trivalent actinide-(poly)aminopolycarboxylate interactions.” Solv. Extr. Ion Exchange, 2016, 32 (2), 114-125. http://dx.doi.org/10.1080/07366299.2016.1140436
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3. Kelley, M.; Urban, M.; Luckey, M.; Yang, P.; **Braley, J.C.**, On the origin of covalent bonding in heavy actinides. Submitted
4. Urban, M.; **Braley, J.C.** Heavy actinide complexation thermodynamics with aliphatic aminopolycarboxylates. In Preparation.

Structural and Thermodynamic Basis for Selective Liquid-Liquid Extraction and Crystallization from Molecular Simulations

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Overall research goals: Our overarching research goal is to develop a rational basis for the design of molecular structure with desired functionalities for anion recognition. The important step in this process is to develop a computational framework for predictive modeling of complexation behavior of target ions in the gas phase, solution, and solid state. Fundamental understanding of structural and thermodynamic factors governing the complexation behavior of ions provides the basis for the design of more efficient and selective ligands for liquid-liquid extraction and crystallization.

Significant achievements during 2016–2017:

The role of solvent in molecular recognition systems is often ignored, especially when the solvent is nonpolar and aprotic. The crystal structure for the complex of interest is often the only source of structural information. However, the solution structure might be significantly different from the crystal structure where packing forces along with long-range electrostatics can play a major role. We used a combination of extended X-ray absorption spectroscopy (EXAFS), density functional theory (DFT), and classical molecular dynamics (MD) simulations to probe the solution structure and outer-sphere counterion coordination in lanthanide(III) complexes with diglycolamide (DGA) ligands (Figure 1). We investigated the homoleptic 3:1 ligand–metal $[Ln(DGA)_3]^{3+}$ complexes in solution with outer-sphere coordination of counterions, Cl^- and NO_3^-. Both EXAFS and theoretical calculations suggest the formation of homoleptic 3:1 ligand–metal $[Ln(DGA)_3]^{3+}$ complexes in nonpolar organic solutions, with anions located in the clefts formed between the tree coordinating DGA ligands. This knowledge can elucidate new strategies for controlling the assembly of outer-sphere ion clusters, extraction strength and selectivity.

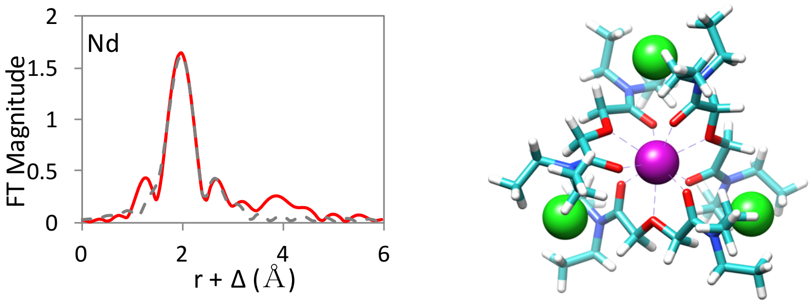

Figure 1. FT-EXAFS data for the Nd-DGA complex in hydrocarbon diluent and model fitting (left panel). DFT optimized structure of $Nd(DGA)_3]Cl_3$ (right panel).

In another study, DFT calculations were performed to explain how the addition of the alkyl chain to the meso-carbon of the calix[4]pyrrole affects the structure of the ligand and modulates anion binding affinity. Analysis of the relative stabilities of various isomers allowed us to assess the role of steric hindrance and hydrophobic interaction in stabilizing conformations observed in the solid state. A more realistic model of interaction of calix[4]pyrrole and anions in nonpolar solvents should invoke the formation of an ion-pair complex, where the cation is encapsulated into the anion-induced calix[4]pyrrole cup. The experimental EXAFS measurements and theoretical calculations were used to understand the coordination environment around cesium(I) coordinated to calix[4]pyrrole in toluene solution. Unlike in crystal structures, where the encapsulated Cs^+ cation forms a contact ion pair with an anion, we find that the open face of Cs^+ interacts with aromatic solvent molecules through additional cation-π interactions. The EXAFS analysis suggesting a very high coordination number for Cs-C and Cs-N interactions (27±2.5) is fully corroborated by DFT and classical MD simulations.

To elucidate the origin of binding and selectivity in crystallization of oxoanions by a family of bis(iminoguanidinium) ligands, we performed DFT calculations on a series of crystal structures determined by Dr. Custelcean and co-workers. Several DFT methods were evaluated with respect to their ability to predict lattice constants and geometric parameters of hydrogen-bonded complexes. Thermodynamic calculations were used to investigate the mechanism of CO_2 release from 2,6-pyridine-bis(iminoguanidinium) carbonate.

Science objectives for 2017–2019:

- Understand the solvation and complexation behavior of ions in solution. A specific example includes a relative partitioning of Fr^+ versus Cs^+ in extractive systems.
- Investigate various guanidinium-based scaffolds, rank them with respect to proton acidity and binding affinity, and validate the trends against the experimental data for the competitive extraction of oxoanions against chlorides.
- Develop and apply computational methods to predict thermodynamic properties that control selective crystallization.
- Synthesize the target receptors and characterize their structural and thermodynamic properties in binding and separating anions.

Publications supported by this project 2016–2017:

1. Williams, N. J.; Bryantsev, V. S.; Custelcean, R.; Seipp, C. A.; Moyer, B. A. $\alpha,\alpha',\alpha'',\alpha'''$-meso-tetramethyl-calix[4]pyrrole: an easy-to-prepare, isomerically pure anion extractant with enhanced solubility in organic solvents. *Supramol. Chem.* **2016**, *28*, 176-187.
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Neptunyl and Uranyl Oxide Clusters, Uranyl Structures from Nature, and Thermodynamic Studies Extending into the Transuranium Elements

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

Significant achievements during 2015-2016:

1. We have synthesized and characterized a novel wheel-shaped uranyl vanadyl oxide cluster (Fig. 1).[1] This cluster contains 20 uranyl pentagonal bipyramids and 20 vanadyl square pyramids, as well as ten sulfate tetrahedra. It was crystallized by first dissolving uranyl nitrate into ionic liquid 3-ethyl-1-methylimidazolium ethyl sulfate (EMIM- EtSO$_4$), followed by adding an aqueous solution containing sodium vanadate. The outer surface of the cluster is stabilized by "yl" oxygens of uranyl and vanadyl, and the inner surface by those of uranyl ions.

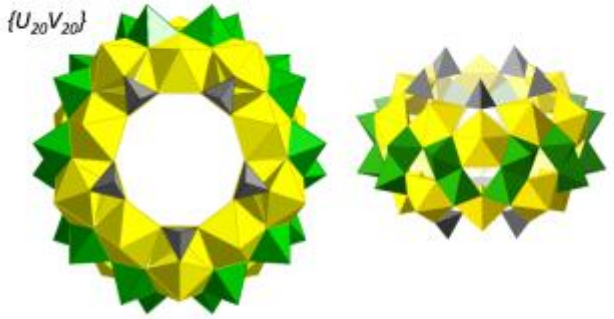

Figure 1. The wheel-shaped $\{U_{20}V_{20}\}$ uranyl (yellow) vanadate (green) cluster with sulfate tetrahedra (grey) crystallized from an ionic liquid – water mixture.

The $\{U_{20}V_{20}\}$ cluster, as well as a smaller cluster, are very distinct from the extensive family of uranyl peroxide cage clusters in the lack of peroxide, the occurrence of uranyl pentagonal bipyramids (rather than hexagonal bipyramids), and the arrangement of polyhedra to form a novel topology. In the case of topology, $\{U_{20}V_{20}\}$ consists of two ten-membered rings of uranyl pentagonal bipyramids that are linked through the vanadyl square pyramids. In contrast, the topologies of almost all uranyl peroxide clusters consist of combinations of squares, pentagons, and hexagons.

2. We synthetically prepared a series of uranyl tungstate framework compounds containing U(VI) cation-cation interactions, and characterized the exchange capacity of these materials relative to interstitial constitudents.[2]

3. We have massively reworked the structural hierarchy of uranyl inorganic compounds, including minerals.[3] In this work we examine 727 structures. Topological analysis tools were used to identify structural relationships across this large range of compounds.

4. We discovered and described the new uranyl mineral gauthierite, which is a potassium-lead uranyl oxyhydrate that presents a novel sheet of uranyl polyhedra.[4] We have also completed the descriptions of several other new uranyl minerals, some of which have very recently been formally approved as new species by the International Mineralogical Association. Manuscripts describing three of these have been submitted to journals for consideration.

Science objectives for 2017-2018:

- Further develop the ionic liquid based synthesis of uranyl vanadyl clusters and extend this work into Np(V) and Np(VI) systems.
- Complete synthesis of a series of lanthanide and actinide sulfates and measure their heats of formation using drop-solution calorimetry.
- Complete characterization and description of several new uranyl minerals, and develop synthetic approaches aimed at producing some of these.

Publications supported by this project 2015-2016

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2. Balboni, E. & Burns, P.C. (2015): Hydrothermal syntheses and characterization of uranyl tungstates with electro-neutral structural units. *Zeitschrift fur Krisallographie* 230, 499-505. 10.1515/zkri-2014-1799
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4. Olds, T.A., Plasil, J., Kampf, A.R., Skoda, R., Burns, P.C., Cejka, J., Bourgoin, V. & Boulliard, J-C. (2016): Gauthierite, $KPb[(UO_2)_7O_5(OH)_7].8H_2O$, a new uranyl-oxide hydrate mineral from Shinkolobwe with a novel uranyl-anion sheet-topology. *European Journal of Mineralogy* 10.1127/ejm/2017/0029-2586.
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Novel TRU bearing materials prepared via restricted actinyl speciation profiles and supramolecular assembly.

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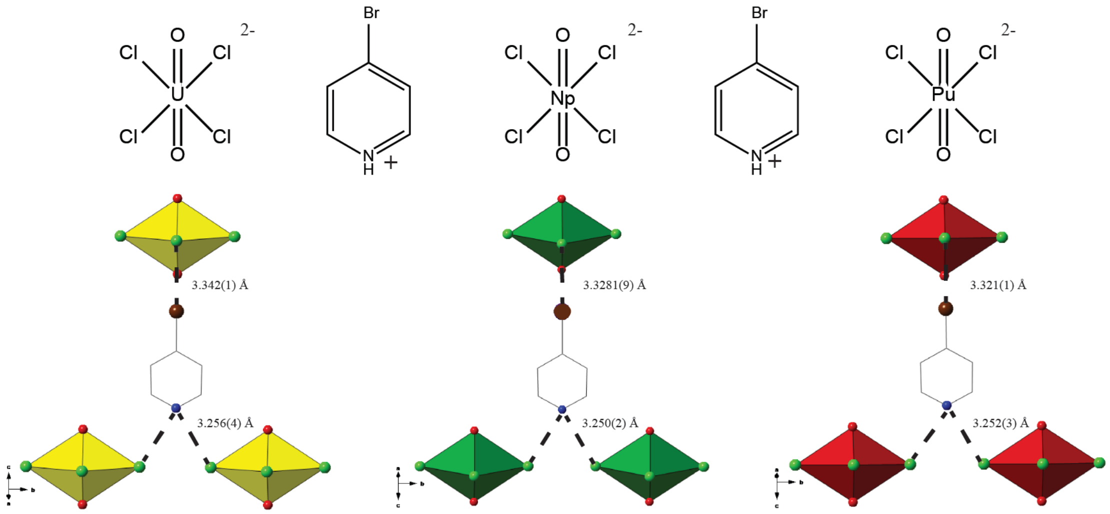
Overall research goals: We aim to synthesize novel TRU bearing materials using supramolecular assembly techniques. We manipulate U and TRU species in aqueous, high-anion media to promote controlled speciation and oxidation state profiles. Molecular 'tectons' are then assembled through 'synthons' such as halogen and hydrogen bonding interactions.

Significant achievements during 2015-2017: 1.We have synthesized three isomorphous series of uranyl, neptunyl and plutonyl tetrachlorides assembled via halopyridinium cations. 2. We have calculated electrostatic surface potential maps of the tetrachloride anions, as well as strengths of the various non-covalent interactions using DFT (counterpoise methods with BSSE corrections).

1. Three isomorphous series of $[AnO_2Cl_4]^{2-}$ (An = U(VI), Np(VI) and Pu(VI)) bearing materials charge balanced with halopyridinium cations (halogen – Cl, Br, I) have been prepared via room temperature, self-assembly methods. Uranyl compounds were prepared at GW, whereas TRU materials were prepared in collaboration with PNNL. Figure 1 shows the crystal structures of the bromopyridinium series and highlights the common synthons of bifurcated hydrogen bonding and halogen-halogen interactions.



$(C_5H_5NBr)_2[UO_2Cl_4]$ $(C_5H_5NBr)_2[NpO_2Cl_4]$ $(C_5H_5NBr)_2[PuO_2Cl_4]$

Figure 1. A schematic representation of the molecular $[AnO_2Cl_4]^{2-}$ and 4-BrPyH tectons (top), which assemble into extended structures via hydrogen and halogen bonding interactions (bottom).

2. We have calculated the electrostatic potential at the molecular surface (using Gaussview 09 rev. D.01) of both the actinyl tetrachloride anions and halopyridinium cations with the goal of reconciling crystallographically observed acceptor-donor pairings (the presence of C-Br···Cl halogen bonds, for example) with the potentials of each participant (Figure 2). As a result, we have determined that the potential on the chloro ligands (the non-covalent interaction *acceptor* sites) of the actinyl units are relatively constant across the TRU series. Moreover, the electrostatic potential at the O_{yl} sites is smaller (less negative) than the equatorial chloro ligands, which likely explains why the C-Br···Cl and N-H···Cl halogen and hydrogen bonds form in the *equatorial* plane and are preferred over coordination with the axial oxo groups. The relatively constant potential values at the chloro sites likely also explains the high degree of isomorphism in the structures in this family and suggests that structural variation (and indeed *strengths* of interactions) will likely be dictated by choice of organic cation.

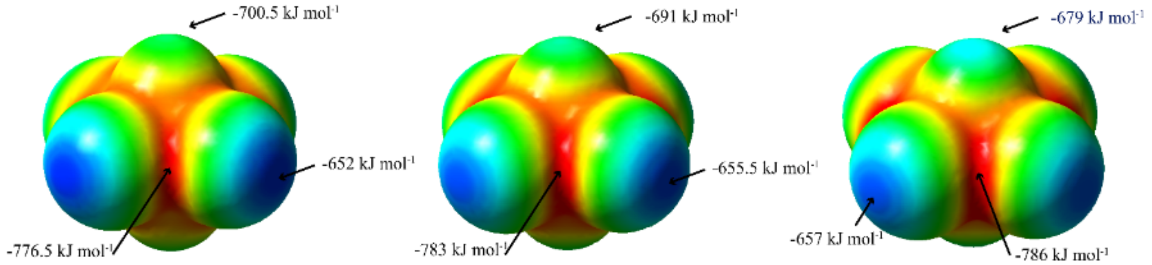


Figure 2. The molecular surface (0.001 au) electrostatic potential maps of the $[AnO_2Cl_4]^{2-}$ (An = U, Np, Pu ; left-to-right) building units with several regions of interest highlighted. The color scale ranges from dark blue to red, which represent a potential of -652 kJ mol^{-1} and -786 kJ mol^{-1}, respectively.

Science Objectives for 2017-2019:

- Extend supramolecular assembly efforts to Pu(III), Pu(IV) and Am(III) chloride systems as we have established methods for control of oxidation state.

- Systematically explore effect of non-covalent interactions at O_{yl} sites on Raman and luminescence spectra.

- Continue computational efforts to reconcile spectroscopic and crystallographic observations; move towards predictive modeling.

Partial list of publications supported by this project 2015-2017:

(1) K. P. Carter; M. Kalaj; C. L. Cahill (2017) "Harnessing uranyl oxo atoms via halogen bonding interactions in molecular uranyl materials featuring 2,5-diiodobenzoic acid and N-donor capping ligands." *Inorganic Chemistry Frontiers 4*, 65. http://dx.doi.org/10.1039/C6QI00352D

(2) R. G. Surbella III; M. B. Andrews; C. L. Cahill (2016) "Self-assembly of $UO_2X_4^{(2-)}$ (X=Cl, Br) dianions with gamma substituted pyridinium cations: Structural systematics and fluorescence properties." *J. Solid State Chem. 236*, 257. http://dx.doi.org/10.1016/j.jssc.2015.09.011

(3) K. P. Carter; M. Kalaj; C. L. Cahill (2016) "Probing the Influence of N-Donor Capping Ligands on Supramolecular Assembly in Molecular Uranyl Materials." *Eur. J. Inorg. Chem.*, 126. http://dx.doi.org/10.1002/ejic.201501118

Investigations of Internuclear Interactions in Plutonium Tetrafluoride by Solid-State NMR Spectroscopy

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We have measured local magnetic fields at the fluorine sites of PuF_4 by ^{19}F NMR spectroscopy to elucidate the electronic structure of the Pu^{4+} centers and the degree of interaction of the valence electrons with F^-. The broadening and shift of the ^{19}F resonance scale linearly with the applied field, indicating that F atoms interact with their two nearest neighbor Pu^{4+} centers primarily through the dipolar fields of the metal's four magnetized valence electrons.

The ^{19}F NMR linebroadening and shifts were analyzed by treating the valence electrons in PuF_4 and UF_4 as being in localized non-interacting atomic orbitals with thermally averaged polarizations. Models that assume purely localized $5f^4$ (for PuF_4) and $5f^2$ (for UF_4) electronic configurations for the metal centers systematically underestimate the magnitudes, shifts, and anisotropy of the hyperfine field, suggesting that the magnetic moments are larger than states with only 5f valence electrons. Larger moments may be obtained with mixed valence states such as $5f^4 6d^1$ for PuF_4, but the best agreement with experimental data is found with admixtures of states such as $5f^4$ and $5f^4 6d^1$.

Supramolecular Organization Within Electrolyte Solutions and the Importance of Molecular Hydrophobicity to Successful Actinide Solvent Extraction

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Collaborators: Ken Nash, Washington State University
Sue Clark, Washington State University
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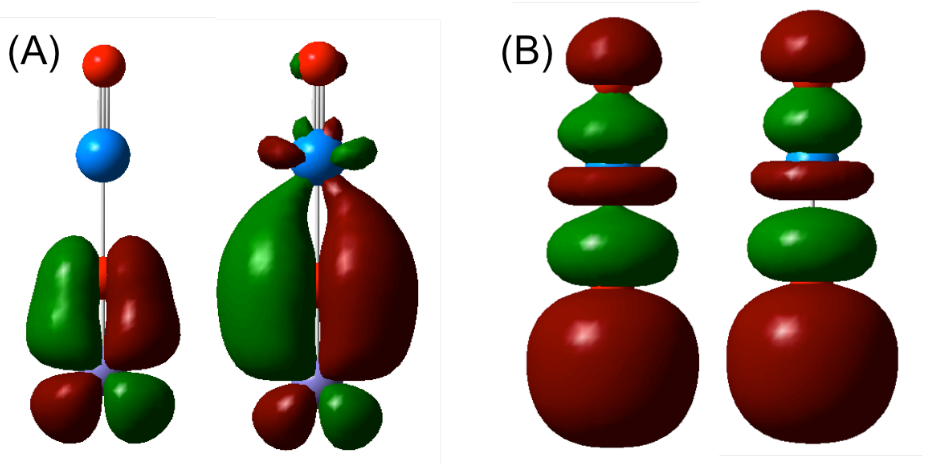
Overall research goals: The goal of the current work is twofold. First, to provide an improved understanding of how perturbations to the H-bonding network and dynamics of water influence actinide complexation reactions and transport across aqueous:organic phase boundaries. Second, to understand changes to speciation that are important during transport of actinide complexes across a liquid:liquid interface.

Significant achievements during 2015-2017: (9 publications) Several significant results have been reported and may be classified as those that focus upon: 1) ion speciation, and 2) those that focus upon interfacial behavior. A representative example from #1 is below.

1. Formation of cation-cation complexes under high-ionic strength aqueous conditions. While successful at segregation of UO_2^{2+} and Pu^{4+} from the remainder of the fuel, the PUREX process leaves the minor actinides (Np, Am, Cm) and other used fuel constituents together. This remaining fuel component is typically high in ionic strength, and has been shown to support the formation of cation-cation complexes. In a combined experimental and computational study, the stability (or equilibrium) constants have been determined for neptunyl-cation formation with Fe^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, Al^{3+} using spectrophotometry as a function of the transition metal concentration, and under similar solution chemistry conditions as prior reports. A detailed analysis of the bonding interactions has complemented the experimental work using density functional theory. These data indicate that the NpO_2^+ dioxocation acts as a π-donor with transition metal cations and a sigma donor with Group 13 cations. The small changes in electron donating ability is modulated by the overlap with the coordinating metal ion's valence atomic orbitals (Figure 1).



α(*d*-*p* π) β(*d*-*p* π) α(*s*-*p* σ) β(*s*-*p* σ)

Figure 1. (A) The alpha and beta *d-p* π molecular orbitals in implicitly solvated $[NpO_2\bullet Fe]_{aq}^{4+}$, and (B) the alpha and beta *s-p* σ molecular orbitals in implicitly solvated $[NpO_2\bullet Ga]_{aq}^{4+}$.

Science objectives for 2017-2019:

- Explore mechanisms of phase separation for water:organic mixtures as a function of different solution phase conditions (using molecular dynamics).
- Map the free energy landscape of metal-ligand transport across water:organic interfaces under a large range of interfacial conditions so as to determine the fundamental drivers for thermodynamic versus kinetically controlled transport processes.

Publications supported by this project 2015-2017

1. Kelley, M.; Yang, P.; Clark, A E. Competitive Interactions Within Trivalent Ion Solvation in Binary Water/Methanol Solutions. *Inorganic Chemistry*, **2017**, *submitted.*
2. Zhou, T.; McCue, A.; Ghadar, Y.; Bako, I.; Clark, A. E. On the Behavior of Capillary Wave Fronts and Their Role in Defining Interfacial Regions of Water. *Journal of Chemical Physic*s, **2017**, *submitted*.
3. Freiderich, J.; Burn, A.; Leigh, M.; Nash, K.; Clark, A. E. A Combined Density Functional Theory and Spectrophotometry Study of the Bonding Interactions of $[NpO_2 \bullet M]^{4+}$ Cation-Cation Complexes. *Inorganic Chemistry*, **2017**, DOI: 10.1021/acs.inorgchem.6b02369.
4. Kelley, M. P., Yang, P.; Clark, S. B.; Clark, A. E. Structural and Thermodynamics Properties of the Curium(III) Ion Solvated by Water and Methanol. *Inorganic Chemistry*, **2016**, 55, 4992-4999.
5. Ghadar, Y.; Christiansen, S. L.; Clark, A. E. Influence of Aqueous Ionic Strength Upon Liquid:Liquid Interfacial Structure and Dynamics. *Fluid Phase Equilibria*, **2016**, 407, 126-134. Invited article – special issue Aqueous Solutions: Bulk Fluids and Interfaces.
6. . Kelley, M.; Donley, A.; Clark, S.; Clark, A. E. Structure and Dynamics of NaCl Ion Pairing in Solutions of Water and Methanol. *Journal of Physical Chemistry B* **2015**, 119, 15652-15661.
7. Clark, A. E.; Samuels, A.; Wisuri, K.; Landstrom, S.; Saul, T. Sensitivity of Solvation Environment to Oxidation State and Position in the Early Actinide Period. *Inorganic Chemistry*, **2015**, 54, 6216-6225.
8. Ghadar, Y.; Parmar, P.; Samuels, A.; Clark, A. E. Solutes at the Liquid:Liquid Phase Boundary – Solubility and Solvent Conformational Response Alter Interfacial Microsolvation Reactions, *Journal of Chemical Physics*, **2015**, 142 , 104707.
9. Parmar, P.; Samuels, A.; Clark, A. E. Applications of Polarizable Continuum Models to Determine Accurate Solution-phase Thermochemical Values Across a Broad Range of Cation Charge – The Case of U(III-VI), *Journal of Chemical Theory and Computation*, **2015**, 11, 55-63.

Selective Crystallization of Anion-Water Clusters with Self-Assembled Guanidines

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Collaborators: Vyacheslav Bryantsev, Charles Seipp (grad student), Neil Williams (grad student), Alexander Ivanov (postdoc), Oak Ridge National Laboratory

Overall research goals: We seek to understand how self-assembly of simple molecular units, ions, and water of hydration, can lead to effective anion separation from aqueous solutions via crystallization. Our approach combines structural and thermodynamic analyses, electronic-structure calculations, and structure-solubility relationships studies to identify the factors controlling the anion selectivity and separation efficacy in competitive aqueous crystallizations. Ultimately, this research may lead to solutions to real-world problems related to energy and the environment such as sulfate separation from seawater for scale prevention, or atmospheric CO_2 capture by carbonate crystallization for climate change mitigation.

Significant achievements during 2015-2017: We have discovered a new approach to aqueous anion separation based on selective crystallization of anion-water clusters with bis-guanidinium ligands self-assembled *in situ* by condensation of aminoguanidinium salts with simple dialdehydes such as glyoxal or terephthaldehyde. The resulting bis-iminoguanidinium (BIG) cations form extremely insoluble salts with tetrahedral oxoanions like sulfate, thus providing a simple and effective separation approach for this class of anions via crystallization. Single-crystal X-ray diffraction analyses showed the sulfate anions crystallized as extended $[SO_4(H_2O)_5{}^{2-}]_n$ or discrete $[(SO_4)_2(H_2O)_4]^{4-}$ sulfate-water clusters, (Figure 1). The exceptionally low aqueous solubilities of these sulfate salts, comparable to $SrSO_4$ or $BaSO_4$, were rationalized based on the favorable stacking of the rigid and planar BIG cations, and the reduced dehydration penalty of the sulfate-water clusters compared to the naked sulfate anion. Another important factor appears to be the entropically favorable release of solvent water molecules from the strongly hydrated sulfate anions, and from the planar and hydrophobic BIG cations. The real-world utility of this crystallization-based approach to sulfate separation was demonstrated by removing more than 99% of sulfate from seawater in a single step, which has the potential to mitigate scale problems in oil field operations.

Another ligand from the BIG class, obtained by imine condensation of 2,6-pyridinedialdehyde with aminoguanidinium, was found to capture atmospheric CO_2 as a crystalline carbonate salt of very low aqueous solubility. Single-crystal X-ray and neutron diffraction analyses revealed the presence of extended $[CO_3(H_2O)_4{}^{2-}]_n$ clusters hydrogen-bonded tightly inside the crystal by the guanidinium groups (Figure 2). The bound CO_2 can be released by relatively mild heating of the crystals at 80-120 °C, which regenerates the BIG ligand quantitatively. Thus, this crystallization-based approach offers the prospect for effective and economical carbon capture technologies.

Science objectives for 2017-2019:

- Understand the factors controlling the structures, solubilities, and anion selectivities of the bis(iminoguanidinium) crystals.
- Investigate the structural, thermodynamic, and kinetic factors controlling the CO_2 capture and release by the bis(iminoguanidinium) ligands.

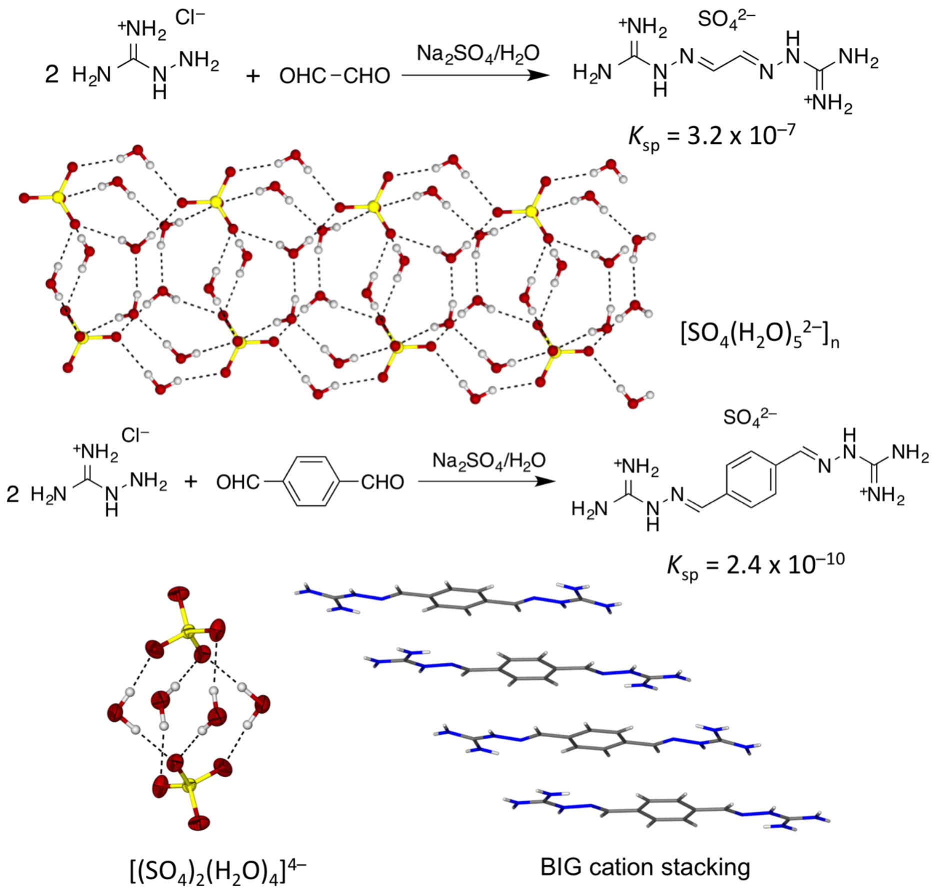

Figure 1. Selective crystallization of sulfate-water clusters with BIG ligands.

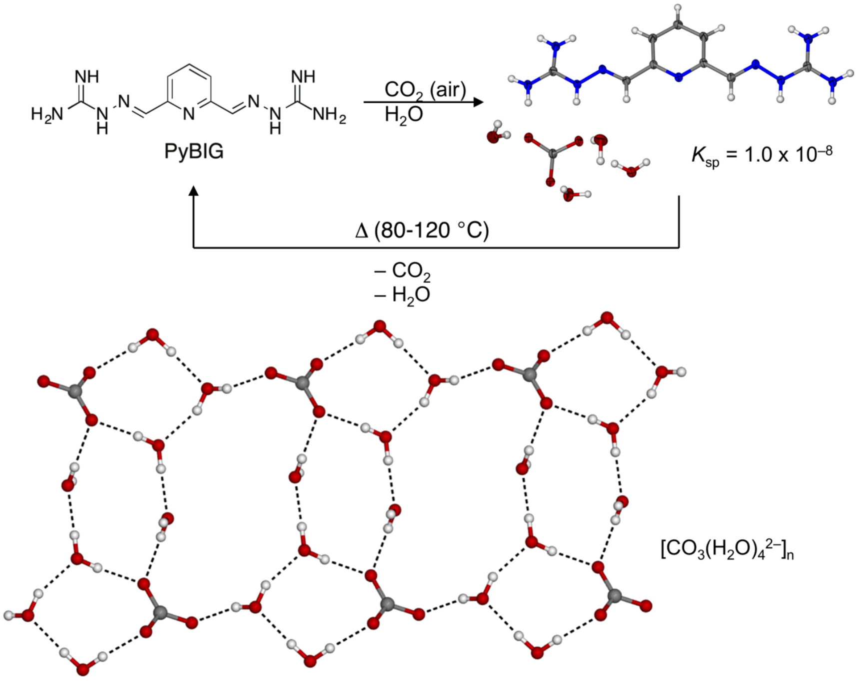

Figure 2. CO_2 capture from ambient air by carbonate crystallization with a BIG ligand.

Self-Assembled Ionophores in Water: Supramolecular Hydrogels and Membrane Transporters

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Overall research goals: This project's two major aims are: **Aim 1**) to synthesize supramolecular hydrogels from nucleoside derivatives that have new properties and functions. In particular, we seek to develop self-assembled hydrogels that can be used for the selective separations of cations (such as Pb(II), Ba(II), Cs(I)) and also for the selective separation of small organic molecules, such as dyes and reactive aldehydes; Aim **2**) to develop new ways to transport ions and small molecules such as nucleosides and nucleotides across lipid membranes.

Significant achievements during 2014-2016: **Achievement 1)** The synthesis of supramolecular hydrogels from is a completely new area for us. The first key finding is that guanosine and potassium borate form a transparent and stable hydrogel, based on guanosine-borate (GB) linkages. This supramolecular GB hydrogel is formed by a hierarchical self-assembly process that involves formation of borate diesters, K^+ templated formation of hydrogen bonded G_4-quartets, stacking of these G_4-quartets to give nanofibers, and bundling of the nanofibers to give the hydrogel (**Fig. 1**).

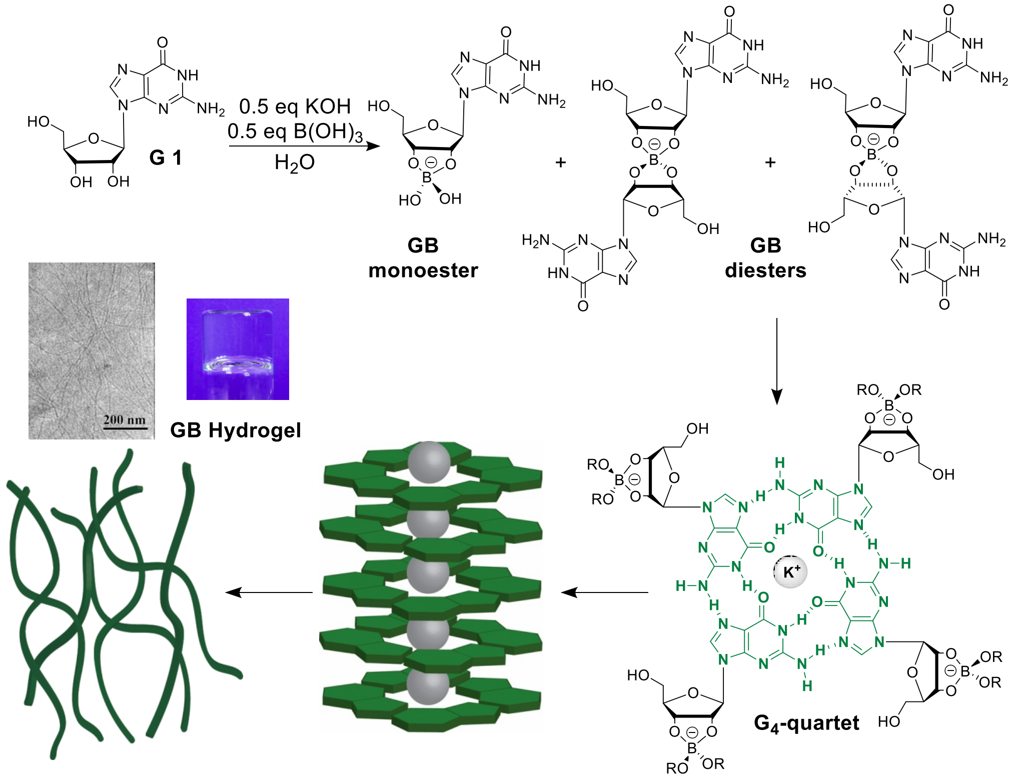

Fig. 1. Depiction of hierarchical self-assembly process that leads to formation of stable guanosine-borate (GB) hydrogels.

Achievement 2) *Cationic Dyes as Molecular Chaperones for GB gelation.* One major finding was that absorption of cationic dyes, such as thioflavin T (ThT), increased the strength of the anionic GB hydrogels. When sub-stoichiometric amounts of ThT (1 % mol to **G 1**) were added to a shear-thinning hydrogel, such as Li^+ GB hydrogel, we observed a ~10 fold increase in gel strength, as determined by rheology. We found similar increases in gel strength for other cationic dyes. In contrast, non-planar or anionic dyes did not affect hydrogel strength. In addition to increasing gel strength, these cationic dyes also increased the rate of hydrogelation by **G 1** and improved the gel's ability to reform after mechanical stress. We hypothesized that the cationic dyes act as molecular chaperones by templating and stabilizing smaller G_4-quartet fragments necessary for fiber formation and hydrogelation. The implications of this study, published in *J. Am. Chem. Soc.*, are significant. First, we provide fundamental insight into the nucleation-growth mechanism of these materials. Second, for environmental remediation, these GB hydrogels can selectively separate cationic dyes from anionic dyes. Finally, these GB materials can be used to screen molecules that bind DNA G_4-quartets, which may identify new diagnostics.

Achievement 3) *G_4-Hydrogels for Separation and Remediation of Heavy Metals, Anionic Dyes and Reactive Aldehydes.* We discovered a new hydrogel made from KCl and the analog, 8-amino-guanosine (**8-AmG 2**), without the need for the borate salt. These **8-AmG** hydrogels are cationic, rather than anionic like the parent GB hydrogels made from guanosine **G 1** and borate. This charge difference is crucial for reversing the selectivity in separations of ionic dyes. Thus, hydrogels made from **8-AmG 2** extract and bind tightly to anionic dyes, such as napthol blue black (NBB), a pollutant produced by the textile industry. Since we no longer need to use borate anion, which forms insoluble precipitates with divalent ions, we find that hydrogels made from into the gel matrix. It is likely that the Pb^{2+} and Ba^{2+} cations replace K^+ cations initially bound inside this G_4-quartet hydrogel. We will soon submit a manuscript *"Supramolecular Hydrogels for Environmental Remediation: G-Quartet Gels that Selectively Absorb Pb(II) and Diazo Dyes,"* to *J. Am. Chem. Soc.* That describes these unique hydrogels

Science objectives for 2017-2019

We will continue to focus on the synthesis, characterization and application of supramolecular hydrogels. Our immediate goal in the first part of the next reporting period will be to finish up the projects on the Pb (II), anionic dye and aldehyde remediation applications. These studies should result in 2-3 papers in 2017. We will also initiate some new studies on the catalysis of the hydrogelation process. Thus, we will undertake a project that seeks to answer the following questions: 1) Can the gelation of water by guanosine **G 1** be catalyzed by conformationally biased G analogs? 2) Do hydrogelation rates by G **1** and these analogs correlate with rates of G_4-quartet formation in solution? 3) How do the thermodynamic and molecular recognition properties of these new binary hydrogels, especially those formed quickly at lower temperature, compare to hydrogels made from G **1** itself? To accomplish these goals she will synthesize a group of conformationally constrained analogs and then measure gelation rates using a battery of spectroscopic techniques. Finally, as always, we will be on the lookout for applications of any new hydrogels in separations and analysis of toxic metal ions and organic dyes.

Exploring the Fundamental Chemistry of Actinide Metal Complexes

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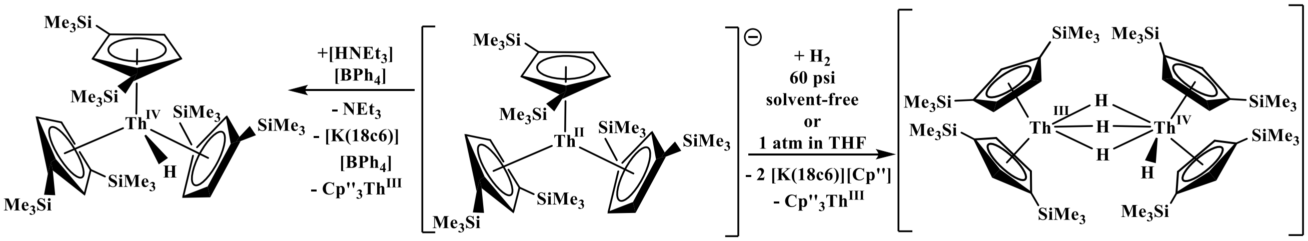
Collaborators: At UC–Irvine, Professor Filipp Furche, Guo P. Chen, Alan K. Chan; at UC–Berkeley, Professor Jeffrey R. Long, Katie R. Meihaus; at Los Alamos National Laboratory (LANL), Dr. Andrew J. Gaunt, Dr. Stosh A. Kozimor, Dr. Justin N. Cross, Dr. Michael T. Janicke, Dr. Brian L. Scott

Overall Research Goals: The objective of this project is to explore new opportunities in actinide chemistry made possible by the discovery of the first crystallographically-characterizable molecular complexes of U^{2+} and Th^{2+} which have unusual $5f^36d^1$ and $6d^2$ electron configurations, respectively. This focus was chosen since it is so rare to identify new oxidation states in molecular species.

Significant Achievements Since the Last HEC Contractors Meeting: (Highlights only are described with full details in the references below.)

A. Following the discovery of the first molecular complexes of U^{2+} and Th^{2+}, $[K(crypt)][Cp'_3U]$ and $[K(crypt)][Cp''_3Th]$ ($Cp' = C_5H_4SiMe_3$; $Cp'' = C_5H_3(SiMe_3)_2$; crypt = 2.2.2-cryptand) under this grant, by reduction of Cp'_3U and Cp''_3Th, respectively, the reduction of Cp''_3U was explored in efforts to generate a pair of An^{2+} complexes with the same ligand system. $(Cp''_3U)^{1-}$ was isolated with four different countercations (1) and this provided U^{2+} complexes more amenable to physical and chemical characterization since they had greater thermal stability than $[K(crypt)][Cp'_3U]$. Knowledge of the enhanced stability of $(Cp''_3U)^{1-}$ vs $(Cp'_3U)^{1-}$ proved crucial in defining the first molecular example of Pu^{2+} described in section E.

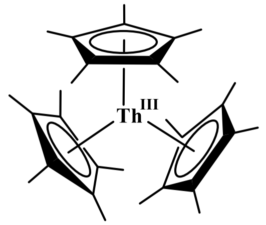
B. Investigation of the reactivity of the Th^{2+} complex $[K(18\text{-crown-}6)(THF)_2][Cp''_3Th]$, **1**, provided new classes of thorium hydride compounds (2), including Cp''_3ThH, **2**, and $[K(18\text{-crown-}6)(Et_2O)][Cp''_2ThH_2]_2$, **3**. Complex **3**, which is the first mixed valence Th^{4+}/Th^{3+} complex and the first Th^{3+} hydride complex, can be made by a solvent-free solid/gas reaction.



2 **1** **3**

C. The progression of advances that led to the discovery of the first molecular complexes of the rare earth metals, thorium, and uranium in the +2 oxidation state has been compiled and analyzed with the goal of identifying new directions for developing the low oxidation state chemistry with these metals further in the future (3, 4).

D. A new crystallographically-characterizable Th^{3+} complex, Cp*$_3$Th (Cp* = C$_5$Me$_5$), was synthesized (5). This was surprising because Th^{3+} complexes are rare and Cp*$_3$M complexes are sterically crowded and tend to be highly reactive. They are difficult to isolate and typically display unusual Cp*-based reactivity to relieve the strain and to form less crowded Cp*$_2$MX products. Cp*$_3$Th is further unusual in that it reacts to make *more* sterically crowded complexes, Cp*$_3$ThX where X = H, Cl, Me, and I. This defies all previously identified trends of transition metals, rare earth metals, and uranium. This indicates that thorium can display unique chemistry. The Th^{4+} precursor to Cp*$_3$Th provided [Cp*$_3$Th(CO)][BPh$_4$], the first isolable molecular thorium carbonyl and the first An^{4+} carbonyl complex.



E. In a joint collaboration with LANL involving a graduate student from our lab who worked at LANL for one year under the DOE SCGSR program, the synthesis of a Cp″ complex of Pu^{2+} was pursued using the knowledge obtained previously for Th^{2+} and U^{2+}. This led to the synthesis and structural characterization of the precursor, Cp″$_3$Pu, which provided the first X-ray data on an organometallic complex of Pu, and [K(crypt)][Cp″$_3$Pu], which is the first example of a new oxidation state for plutonium in a molecular complex, namely Pu^{2+} (6).

Science Objectives for 2017-2019:

(a) We will explore the synthesis of the new complexes of U^{2+} and Th^{2+} to evaluate the chemical and physical properties as a function of ligand field and electron configuration. (b) We will examine the reactivity of these An^{2+} complexes including reduction to An^{1+} species. (c) We will develop An^{3+} chemistry using the new complexes provided by the An^{2+} compounds and by pursuing the synthesis of An^{3+} complexes of new ligand systems.

Publications From DE-SC0004739 Since the Last HEC Contractors Meeting:

1. Windorff, C. J.; MacDonald, M. R.; Meihaus, K. R.; Ziller, J. W.; Long, J. R.; Evans, W. J "Expanding the Chemistry of Molecular U^{2+} Complexes: Synthesis, Characterization, and Reactivity of the $\{[C_5H_3(SiMe_3)_2]U\}^{1-}$ Anion" *Chemistry, A European Journal* **2016**, *22*, 772-778. DOI: 10.1002/chem.201503583
2. Langeslay, R. R.; Fieser, M. E.; Ziller, J. W.; Furche, F.; Evans, W. J. "Expanding Thorium Hydride Chemistry Through Th^{2+}, Including the Synthesis of a Mixed-Valent Th^{4+}/Th^{3+} Hydride Complex" *J. Am. Chem. Soc.* **2016**, *138*, 4036-4045. DOI: 10.1021/jacs.5b11508
3. Evans, W. J. "Tutorial on the Role of Cyclopentadienyl Ligands in the Discovery of Molecular Complexes of the Rare-Earth and Actinide Metals in New Oxidation States" *Organometallics* **2016**, *35*, 3088-3100, ACS Authors Choice. **DOI**: 10.1021/acs.organomet.6b00466
4. Woen, D. H.; Evans, W. J. "Expanding the +2 Oxidation State to the Rare-Earth Metals, Uranium, and Thorium in Molecular Complexes" In *Handbook on the Physics and Chemistry of the Rare Earths Including Actinides*; Bünzli, J, -C. G.; Pecharsky, V. K., Eds.; Elsevier Science: Amsterdam, 2016; Vol. 50; pp 337-394. **DOI**: 10.1016/bs.hpcre.2016.08.002
5. Langeslay, R. R.; Chen, G. P.; Windorff, C. J.; Chan, A. K.; Ziller, J. W.; Furche, F.; Evans, W. J. " Synthesis, Structure, and Reactivity of the Sterically Crowded Th^{3+} Complex (C$_5$Me$_5$)$_3$Th Including Formation of the Thorium Carbonyl, [(C$_5$Me$_5$)$_3$Th(CO)][BPh$_4$]" *J. Am. Chem. Soc.* **2017**, *139*, 3387-3398. **DOI**: 10.1021/jacs.6b10826
6. Windorff, C. J.; Chen, G. P.; Cross, J. N.; Evans, W. J.; Furche, F.; Gaunt, A. J.; Janicke, M. T.; Kozimor, S. A.; Scott, B. L. "Identification of the Formal +2 Oxidation State of Plutonium: Synthesis and Characterization of $[\mathrm{Pu^{II}}\{C_5H_3(SiMe_3)_2\}_3]^{1-}$" *J. Am. Chem. Soc.* **2017**, *accepted*. **DOI**: 10.1021/jacs.7b00706

Binding Anions Selectively with Modular Triazolophanes and Releasing them with Light

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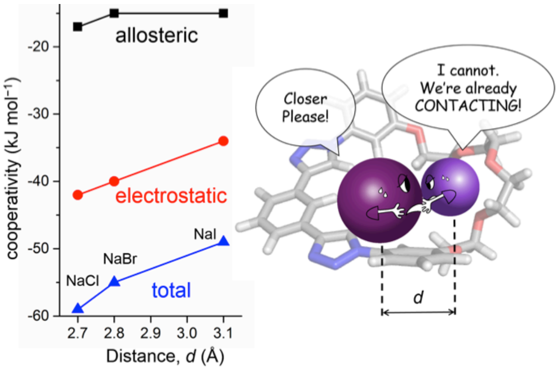
Collaborators: Professor Krishnan Raghavachari, Department of Chemistry, Indiana University, Bloomington, IN 47405.

Overall research goals: Synthesize macrocycles and foldamers for binding oxyanions and to release them using light-based stimuli; such receptors could confer selectivity in ion separations for future use in the nuclear fuel cycle.

Significant achievements during 2015-2017: Developed the first full explanation of the cooperativity in ion-pair binding with the aid of computations, and the first *ab initio* explanation with experiment and theory of solvent effects in ion recognition – two priority outcomes:

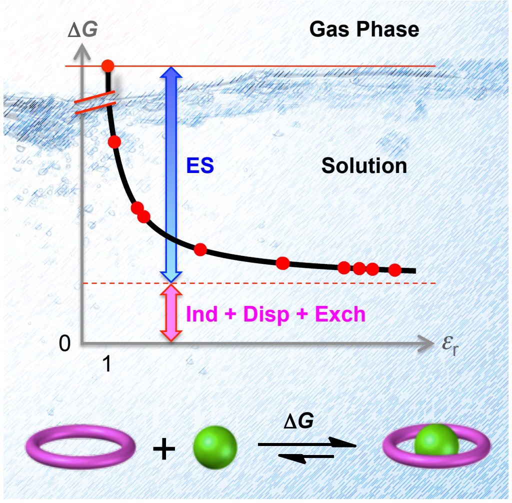
1. Electrostatic and Allosteric Cooperativity in Ion-pair Binding: A Quantitative and Coupled Experiment-Theory Study with Aryl-Triazole-Ether Macrocycles

Cooperative binding of ion pairs to receptors is crucial for the manipulation of salts but a comprehensive understanding of cooperativity has been elusive. To this end, we combine experiment and theory to quantify ion-pair binding and to separate allostery from electrostatics to understand their relative contributions. We designed aryl-triazole-ether macrocycles (**MC**) to be semi-flexible, which allows ion pairs (NaX; X = anion) to make contact, and to be monocyclic to simplify analyses. A multi-equilibrium model allows us to quantify, for the first time, the experimental cooperativity (α) for the equilibrium, $\mathbf{MC}\bullet\mathrm{Na}^+ + \mathbf{MC}\bullet\mathrm{X}^- \rightleftharpoons \mathbf{MC}\bullet\mathrm{NaX} + \mathbf{MC}$, associated with contact ion-pair binding of NaI ($\alpha = 1300$, $\Delta G_\alpha = -18$ kJ mol^{-1}) and $\mathrm{NaClO_4}$ ($\alpha = 400$, $\Delta G_\alpha = -15$ kJ mol^{-1}) in 4:1 dichloromethane-acetonitrile. We used accurate energies from density functional theory to deconvolute how the electrostatic effects and the allosteric changes in receptor geometry individually contribute to cooperativity. Computations, using a continuum solvation model (dichloromethane), show that allostery contributes ~30% to overall positive cooperativity. The calculated trend of electrostatic cooperativity using pairs of spherical ions (NaCl > NaBr > NaI) correlates to experimental observations (NaI > $\mathrm{NaClO_4}$). We show that intrinsic ionic size, which dictates charge separation distance in contact ion pairs, controls electrostatic cooperativity. This finding supports the design principle that semi-flexible receptors can facilitate optimal electrostatic cooperativity. While Coulomb's law predicts the size-dependent trend, it overestimates electrostatic cooperativity; we suggest that binding of the individual anion and cation to their respective binding sites dilutes their effective charge. This comprehensive understanding is critical for rational designs of ion-pair receptors for the manipulation of salts.



2. *Anion Binding in Solution is Not Dominated by Electrostatics*

A fundamental understanding of anion binding is essential for designing receptors to control concentrations of anions intimately related to the sustainable development of modern society. However, designing receptors to operate in solution is inhibited by a persistent blind spot in our understanding; we do not know how solvent impacts recognition. One idea is that anion binding depends on solvent polarity; but this idea stands untested. We experimentally discovered an underlying $1 / \varepsilon_r$ dependence on solvent dielectric constant (ε_r). We found this relationship by exploiting the rigidity of a macrocyclic triazolophane that resists shape changes to significantly simplify analysis and interpretation. We accurately determined the triazolophane's chloride affinities across the widest range of organic solvents and aqueous mixtures to date: ε_r ranging from 5 to 60. The $1 / \varepsilon_r$ dependence is consistent with the never tested but long held idea that anion binding is dominated by electrostatics in the gas phase. Intriguingly, the very same dependence necessitates that the electrostatic contribution to binding in solution is largely diminished in solvents of just moderate polarity, like acetone. This new and surprising understanding was confirmed with density functional theory, which shows a close match to experiment with high accuracy (<1.0 kcal mol^{-1}). Our theory-backed model accurately predicts Cl^- affinity in 1,2-dichloroethane and nitrobenzene, which are widely used surrogates for liquid-liquid extractions in the nuclear fuel cycle. This binding model offers a general foundation for other anion receptors and electrostatically driven complexation.



Science objectives for 2017-2019:

- Develop 3D cages as high-affinity receptors for ion and ion pair extraction from aqueous solutions
- Develop understanding of how to compute increasingly large receptor structures.
- Establish the synthesis and function of photoactive foldamers

Publications supported by this project 2015-2017

1. Flood, A. H., Creating molecular macrocycles for anion recognition, *Beilstein J. Org. Chem.* **2016**, *12*, 611-627. http://dx.doi.org/10.3762/bjoc.12.60
2. Qiao, B.; Sengupta, A.; Liu, Y.; McDonald, K. P.; Pink, M.; Anderson, J.; Raghavachari, K.; Flood, A. H., Electrostatic and Allosteric Cooperativity in Ion-pair Binding: A Quantitative and Coupled Experiment-Theory Study with Aryl-Triazole-Ether Macrocycles, *J. Am. Chem. Soc.* **2015**, *137*, 9746–9757. http://dx.doi.org/10.1021/jacs.5b05839

Assessing subtle variations in actinyl oxo reactivity through characterization of neptunyl complexes.

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

Significant achievements during 2015-2017: Our neptunium lab was established in January 2016 and we have been exploring both charge assisted hydrogen bonding within extended uranyl topologies and uranyl and neptunyl coordination complexes within the crown ether and cucurbit[5]uril systems.

Three significant results have emerged:

1. Exploration of the uranyl glycine system has revealed significant interactions between the uranyl oxo and the positively charged amine group on the glycine ligand through charge-assisted hydrogen bonding (Figure 1). A linear relationship was observed when the average donor to acceptor distance was plotted against the average uranyl oxo bond valence sum. In addition, the calculated force constants (k_1) for uranyl glycine compound within this system are 6.47 and 6.55 mdyn/Å, which fall on the low end of the reported range (6.45 to 7.92 mdyn/Å) for uranyl compounds.

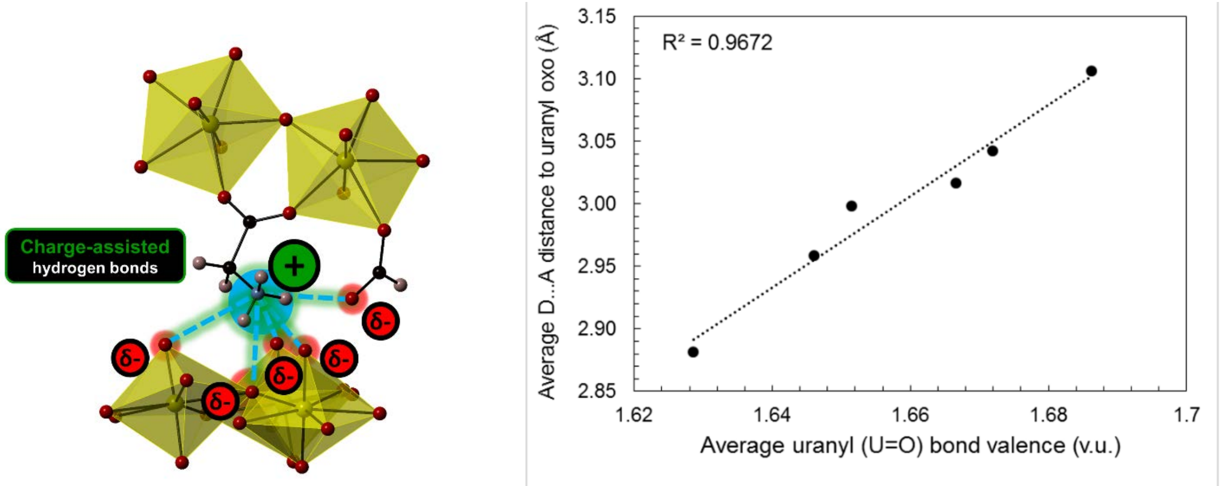

Figure 1. **Left**: Charge assisted hydrogen bonding with the uranyl glycine system. **Right**: A linear relationship is observed between the average donor (amine) to acceptor (uranyl oxo) distance and the average bond valence for the uranyl oxo.

2. To explore the influence of monovalent cations on the actinyl oxo group, we have synthesized a series of Np(V) and Np(VI) crown ether complexes. This work initially built upon previous investigations by Danis et al., 2001 which indicated limited interaction between the oxo group in uranyl tetrachloro complexes and nearby alkali metals. Np(VI) shows similar interactions, but the Np(V) tetrachloro species were not readily crystalized (Figure 2). Instead, crown ether inclusion complexes were formed with significant interactions to neighboring cations. In addition, reduction to Np(IV) led to the formation of novel sandwich complexes with 12-crown-4 and 15-crown-5.

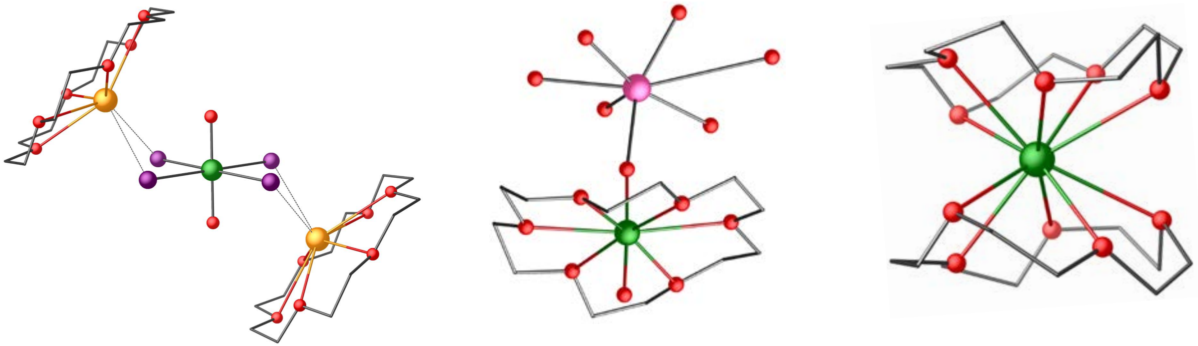

Figure 2. **Left**: the $[Np(VI)O_2Cl_4]^{3-}$ anion interacting with K^+ 18-crown-6. **Middle**: Np(V) 18-crown-6 complex displays oxo interactions with sodium cation (pink sphere). **Right**: Np(IV) sandwich complex with 15-crown-5.

3. The formation of the Np(V) crown ether inclusion complexes inspired additional work investigating the U(VI) and Np(V) cucurbit[5]uril system (Figure 3). The identity of the metals in the cucurbituril inclusion complexes can be tuned to investigate specific interactions to the neptunyl oxo. In addition, encapsulation of metals and molecules inside these macrocycles can lead unique redox properties and greater control over chemical reactivity.

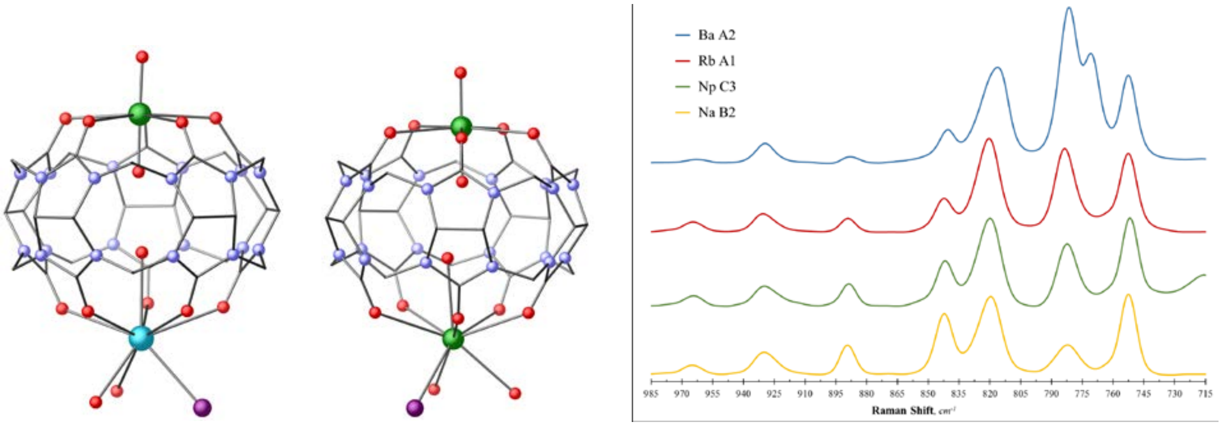

Figure 3. Neptunyl cucurbit[5]uril complexes with (Left) Np(V) (green sphere) and Ba(II) (blue sphere), (Middle) Np(V) and Np(IV), and (Right) solid state Raman spectra of the neptunyl cucurbituril complexes.

Science objectives for 2017-2019:

- Assessment of the influence of charge assisted hydrogen bonding for Np(V) by synthesis and characterization of neptunyl glycine complexes.
- Explore properties of Np(IV, V, VI) crown ether and cucurbituril complexes in both the solid and solution phases
- Expand efforts towards understanding actinyl (U(VI) and Np(V/VI)) oxo reactivity under confinement.

Publications supported by this project 2015-2017

1. de Groot, J, Cassell, B. A., Basile, M., Fetrow, T., and Forbes, T.Z. "Charge assisted hydrogen bonding and crystallization effects in U(VI) glycine and formate compounds." Accepted European Journal of Inorganic Chemistry. **DOI: 10.1002/ejic.201700024**
2. Basile, M., Cole, E. and Forbes, T.Z., "Charcterization of neptunyl complexation in the presence 18-crown-6 and 15-crown-5." In prep for Inorganic Chemistry.

Modeling Actinide- and Transactinide-Systems with Multireference Quantum Chemical Methods

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Overall research goals: The objective of this project is to develop and employ quantum chemical methods in order to study the chemistry of systems containing actinides, and transactinides in the gas phase, and in condensed phase.

Significant achievements during 2015-2017: We have made progress in the following areas:

1. We performed multiconfigurational electronic structure theory calculations including spin−orbit coupling effects on four uranium-based single-molecule-magnets. Several quartet and doublet states were computed and the energy gaps between spin−orbit states were then used to determine magnetic susceptibility curves. Trends in experimental magnetic susceptibility curves were well reproduced by the calculations, and key factors affecting performance were identified.

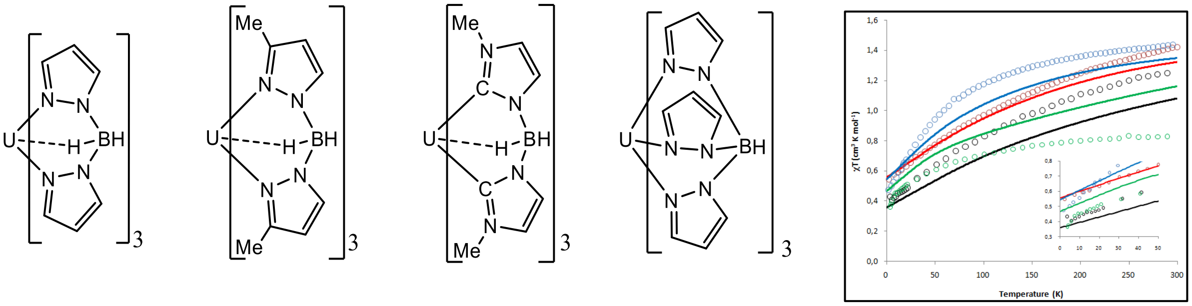

Figure 1. Compounds 1, 2, 3 and 4 from left to right. On the right panel magnetic susceptibility plot for compounds 1 (green), 2 (red), 3 (blue) and 4 (black). Experiment (circles) and SO-CASSCF(3,7) (lines). Inset shows the low temperature region.

2. We computationally investigated a family of uranium(VI) dianions bearing four U-N multiple bonds, $[M]_2[U(NR)_4]$ (M = Li, Na, K, Rb, Cs) (Fig. 2), synthesized in the group of Professor Bart. DFT calculations of **2-Li** – **2-Cs**, using the molecular formula $[M]_2[U(NDIPP)_4]$, were performed.

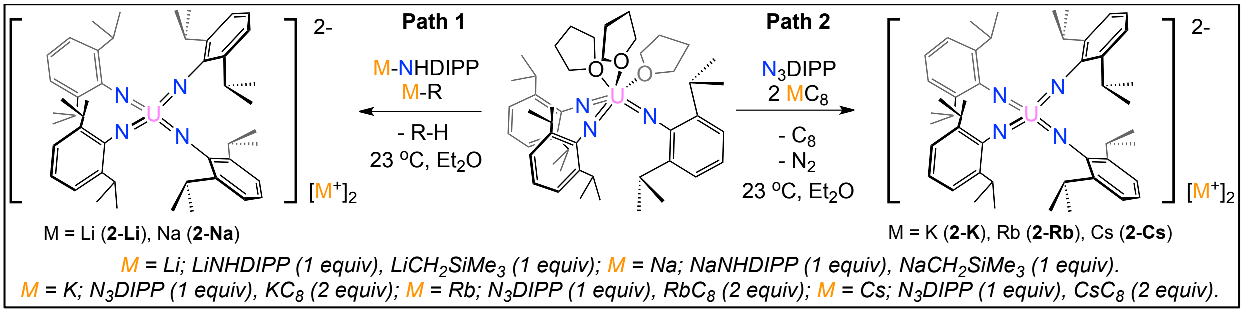

Figure 2. Synthesis of **2-Li** – **2-Cs**.

Geometry optimized structures are consistent with the experimentally determined structures. The U-N bonds in **2-Li** – **2-Cs** are composed of two covalent bonds of predominantly U 5*f*, U 6*d*, and N

2*p* orbitals, with strong competition for the limited number of uranium-based orbitals due to the sharing among all four strongly π-donating imido ligands. The uranium-nitrogen bond orders for **2-Li** – **2-Cs** were found to range from 2.00 to 1.98, indicating double bond character. Thus, this analysis supports that the near-linear nature of the U-N-C angles in **2-Na**, **2-Rb**, and **2-Cs** is not reflective of enhanced π-bonding that would contribute to triple bond formation.

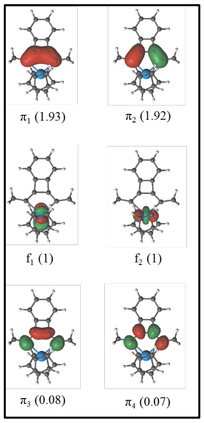

Figure 4. The U compound CASSCF molecular orbitals.

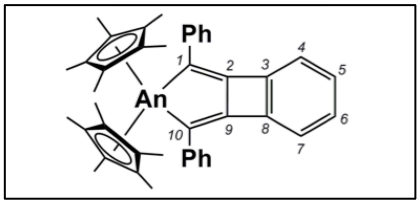

Figure 3. Structure of the actinide metallabiphenylene complexes. An=Th, U.

3. We computationally investigated some actinide metallabiphenylene complexes synthesized in the group of Dr. Kiplinger, namely $(C_5Me_5)_2An(2,5\text{-}Ph_2$ cyclopentadienyl[3,4]cyclobuta[1,2]benzene). (Fig. 3) 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.

Science objectives for 2017-2019:

- Explore the magnetic properties of single molecule magnets containing transuranium atoms, namely Np and Pu. Use different multireference methods to compute magnetic susceptibility curves and establish a protocol to be used in these calculations.
- Test the newly developed multiconfiguration pair-density functional theory for electronic properties of heavy elements beyond uranium.
- Investigate the electronic structure of metal-actinide multiply bonded systems synthesized in the group of Professor Connie Lu at the university of Minnesota.

Publications supported by this project 2015-2017

1. A. Kovacs, R. J. M. Konings, J. K. Gibson, I. Infante, and L. Gagliardi, “Quantum Chemical Calculations and Experimental Investigations of Molecular Actinide Oxides”, Chem. Rev., 115, 1725-1759 (2015) DOI: 10.1021/cr500426s
2. N. H. Anderson, S. O. Odoh, U. J. Williams, A. J. Lewis, G. L. Wagner, J. L. Pacheco, S. A. Kozimor, L. Gagliardi, E. J. Schelter, and S. C. Bart, “Investigation of the Electronic Ground States for a Reduced Pyridine(diimine) Uranium Series: Evidence for a Ligand Tetraanion Stabilized by a Uranium Dimer”, J. Am. Chem. Soc. 137, 4690–4700 (2015) DOI: 10.1021/ja511867a
3. M. Spivak, K. D. Vogiatzis, C. J. Cramer, C. de Graaf, and L. Gagliardi, “Quantum Chemical Characterization of Single Molecule Magnets Based on Uranium”, J. Phys. Chem. A, 121 1726–1733 (2017) DOI: 10.1021/acs.jpca.6b10933
4. N. H. Anderson, J. Xie, D. Ray, M. Zeller, L. Gagliardi, S. C. Bart “Elucidating Bonding Preferences in Tetrakis(imido)uranate(VI) Dianions”, Nature Chemistry, in press (2017)
5. J. K. Pagano, K. A. Erickson, J. Xie, D. E. Morris, B. L. Scott, R. Wu, R. Waterman, L. Gagliardi, and J. L. Kiplinger, “Synthesis and characterization of actinide metallabiphenylene complexes: Tuning aromaticity with actinides” in preparation (2017)

New Bonding Modes and Oxidation State Chemistry for Neptunium and Plutonium

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Overall research goals: To advance knowledge regarding transuranic coordination chemistry, reactivity, bonding and electronic structure. A central goal revolves around targeting molecules that contain metal-ligand multiply bonded motifs, allowing assessment of trends in covalent contributions and orbital mixing across the 5f series. Additionally, studies of new reactivity and redox chemistry organometallic plutonium molecules can offer breakthroughs in terms of characterizing new bonding types in plutonium molecules and developing access to unusually low-valent species.

Significant achievements (2015–2017):

1. Targeting of transuranic molecules containing metal-ligand multiple bonds. Establishment of the new $NpCl_4(DME)_2$ precursor in the previous cycle (2013-2015), facilitated a viable reactivity pathway towards the generation of an Np(V) bis-imido analog of actinyl cations. Treatment of the Np(IV) precursor with the parent amido, in the presence of a supporting bipyridine co-ligand, resulted in oxidation of Np(IV) to Np(V) and generation of a bis-imido analogue of neptunyl(V). The molecule has been structurally and spectroscopically characterized (Figure 1).[1] It is the first example of a transuranic metal-ligand multiple bond. Follow-on studies have focused on attempts to better understand the reaction mechanism in order to increase the product yield and allow more in-depth spectroscopic analysis of the electronic structure. This research has included examining different ligand scaffolds able to support other Np-imido species, and targeting a Np(VI) tris-imido species (which also uncovered an alternative synthetic pathway to generate the Np(V) bis-imido product). Also explored, were pathways to generate terminal oxo, nitride, sulfido, and selenido moieties – preliminary reactions appear promising.

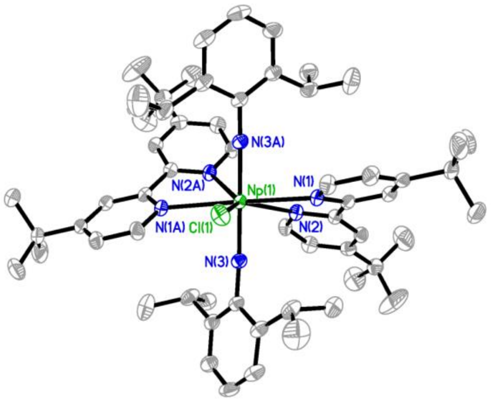

Figure 1. Solid-state structure of the Np(V) bis-imido molecule, $[Np^{V}(=NDipp)_2(\mathit{t}Bu_2\text{-bipy})_2Cl]$, the first example of a transuranic non-dioxo metal-ligand multiple bond.

2. Synthesis, isolation and characterization of a molecular compound containing plutonium in the formal +2 oxidation state. The range of accessible oxidation states for a given element of the periodic table is one of the most fundamental properties that heavily influences and dictates reactivity, coordination preferences and electronic structure. As such, this area has been heavily studied for each element for many decades and it is generally presumed that all accessible oxidation states in molecular form have been identified. Therefore, any new findings that break this view are extremely rare and significant. Nonetheless, reduction of $\mathrm{Pu^{III}Cp''_3}$ [$\mathrm{Cp'' = C_5H_3(SiMe_3)_2}$] (itself the first reported full single-crystal structural determination of a Pu–C bond) with $\mathrm{KC_8}$ in the presence of 2.2.2.-cryptand (crypt) generates the $\mathrm{Pu^{2+}}$-containing salt $\mathrm{[K(crypt)][Pu^{II}Cp''_3]}$. The molecular compound has been structurally verified (Figure 2), spectroscopically characterized, and analyzed by Density Functional Theory, The initial results indicate the plutonium represents an intriguing crossover case between $5f^n6d^1$ and $5f^{n+1}d^0$ as the favored electronic configuration.

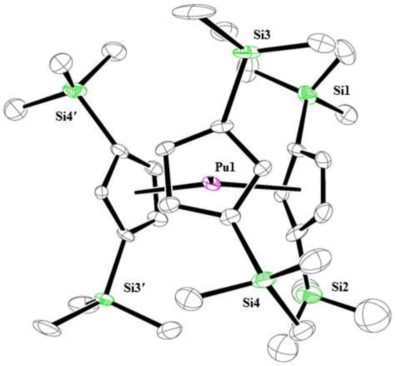

Figure 2. Solid-state structure of the anion in $\mathrm{[K(crypt)][Pu^{II}Cp''_3]}$, which formally contains Pu in the +2 oxidation state.

Science objectives for 2017-2019:

- Focus on the pursuit and characterization of transuranic molecules containing new metal-ligand multiple-bonds. Reaching this objective will require significant effort in developing synthetic pathways, reactivity, and redox studies across a range of different supporting scaffolds and preparative routes. Several collaborations will be continued at LANL and academia to help extend the work of others in the program from lanthanides and U/Th into the transuranic realm.
- Through collaborations, extensively probe the electronic structure by computational and theoretical analysis of the molecular compounds that are isolated. This will facilitate systematic elucidation of bonding and covalency trends across the actinide series.

Selected publications receiving support (full or partial) in the period 2015-2017

1. J. L. Brown, E. R. Batista, J. M. Boncella, A. J. Gaunt, S. D. Reilly B. L. Scott, N. C. Tomson **,** *'A Linear Trans-bis(imido) Neptunium(V) Actinyl Analog: $Np^V(NDipp)_2(R_2bipy)_2Cl$ (Dipp = 2,6-$^iPr_2C_6H_3$, R = ^tBu)', Journal of the American Chemical Society*, **2015**, *137,* 9583-9586. **DOI: 10.1021/jacs.5b06667**.
2. J. L. Brown, A. J. Gaunt, D. M. King, S. T. Liddle, S. D. Reilly, B. L. Scott, A. J. Wooles, *'Neptunium and Plutonium Complexes with a Sterically Encumbered Triamidoamine (TREN) Scaffold'* Chemical Communications, **2016**, *52,* 5428-5431. **DOI: 10.1039/c6cc01656a.**
3. C. J. Windorff, G. P. Chen, J. N. Cross, W. J. Evans, F. Furche, A. J. Gaunt, M. T. Janicke, S. A. Kozimor, B. L. Scott, *'Identification of the Formal +2 Oxidation State of Plutonium: Synthesis and Characterization of $\{Pu^{II}[C_5H_3(SiMe_3)_2]_3\}^-$', Journal of the American Chemical Society*, **2017**, *asap article*. **DOI: 10.1021/jacs.7b00706.**

Actinide Chemistry in the Gas Phase: New Insights from Thorium through Californium

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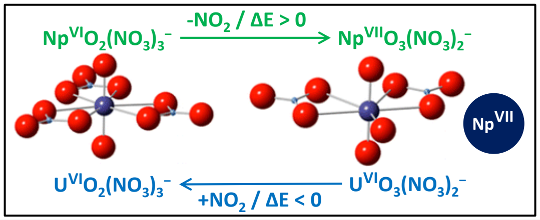
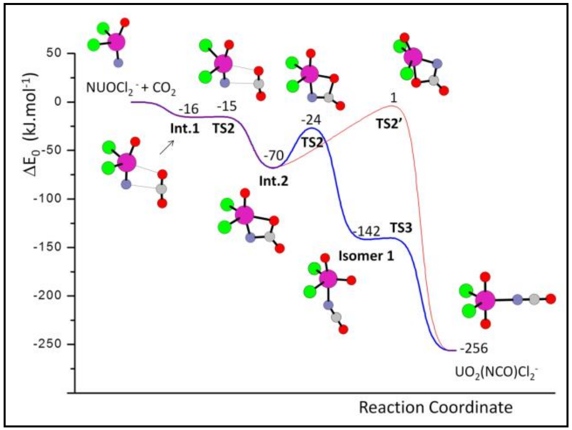
Overall research goals: Investigation of fundamental actinide chemistry in the gas phase illuminates and expands 5f element chemistry. Research on Th through Cf provides a basis to understand, control and develop condensed phase chemistry; and to interact with, evaluate and advance actinide theory.





Selected Scientific Accomplishments for 2015-2017:

- A heptavalent Np complex (**top figure**; ref. **4**)
- Oxidation of An^VO_2 (An = U, Np, Pu) by NO_2 (ref. **17**)
- A U^{6+} chelate complex: chemistry, spectroscopy, theory
- Synthesis of a Cf(II) coordination complex (ref. **5**)
- Hydrolysis of PaO_2^+ and other AnO_2^+ (refs. **13**, **19**)
- Activation of CO_2 by U≡N (**bottom figure**; ref. **9**)
- Synthesis and reactivity of Bk and Cf oxides
- An evaluation of oxo-exchange of AmO_2^+
- Comparative chemistries of Pa and U oxides (ref. **2**)
- Synthesis of a uranyl peroxide dimer (ref. **1**)

Selected Science Objectives for 2017-2019:

- Exploring new oxidation states of Cm, Bk and Cf
- Neptunyl, plutonyl and americyl peroxide dimers
- Gas-phase ion chemistry of No, Lr and transactinides
- Synthesis and characterization of hyperoxides: AnO_4^-, AnO_5^- and AnO_8^- (An = U, Np, Pu, Am)
- Chemistry/activation of neptunyl, plutonyl and americyl in multidentate coordination complexes
- IRMPD spectroscopy of uranyl complexes to elucidate bonding between U and ligands
- Effects of ligation $AnO_2(L)_n^+$ on oxo-exchange (An = U, Np, Pu): exchange enabled by electron donors
- Reactivity of actinide-halogen bonds: variations among actinides and halogens
- Synthesis and chemistry of uranyl, neptunyl and plutonyl carboxylate monomers and oligomers
- Gas-phase actinide chemistry in a low-pressure ion trap: synthesis and chemistry of reactive complexes

Publications supported by this project: April, 2015 - March, 2017

1. "A Uranyl Peroxide Dimer in the Gas Phase," P. D. Dau, P. V. Dau, L. Rao, A. Kovács, J. K. Gibson, Inorg. Chem. 56 (2017) Published online March 15, 2017 (DOI: 10.1039/c6cc07205d).

2. "Revealing Disparate Chemistries of Protactinium and Uranium. Synthesis of the Molecular Uranium Tetroxide Anion, UO_4^-," W. A. de Jong, P. D. Dau, R. E. Wilson, J. Marçalo, M. J. Van Stipdonk, T. A. Corcovilos, G. Berden, J. Martens, J. Oomens, J. K. Gibson, Inorg. Chem. 56 (2017) 3686-3694 (DOI: 10.1021/acs.inorgchem.7b00144).

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4. “Heptavalent Neptunium in a Gas-Phase Complex: $(Np^{VII}O_3^+)(NO_3^-)_2$,” P. D. Dau, R. Maurice, E. Renault, J. K. Gibson, Inorg. Chem. 55 (2016) 9830-9837 (DOI: 10.1021/acs.inorgchem.6b01617).

5. “Divalent and Trivalent Gas-Phase Coordination Complexes of Californium: Evaluating the Stability of Cf(II),” P. D. Dau, D. K. Shuh, M. Sturzbecher-Hoehne, R. J. Abergel, J. K. Gibson, Dalton Trans. 45 (2016) 12338 - 12345 (DOI: 10.1039/C6DT02414A).

6. “Hydrolysis of Thorium(IV) at Variable Temperatures,” P. L. Zanonato, P. Di Bernardo, Z. Zhang, Y. Gong, G. Tian, J. K. Gibson, L. Rao, Dalton Trans. 45 (2016) 12763-12771 (DOI: 10.1039/C6DT01868H).

7. “Thermodynamic Study of the Complexation between Nd^{3+} and Functionalized Diacetamide Ligands in Solution,” P. V. Dau, Z. Zhang, P. D. Dau, J. K. Gibson, L. Rao, Dalton Trans 45 (2016) 11968-11975 (DOI: 10/1039/c6dt01694d).

8. “Synthesis and Hydrolysis of Uranyl, Neptunyl and Plutonyl Gas-Phase Complexes Exhibiting Discrete Actinide-Carbon Bonds,” P. D. Dau, D. Rios, Y. Gong, M. C. Michelini, J. Marçalo, D. K. Shuh, M. Mogannam, M. J. Van Stipdonk, T. A. Corcovilos, J. K. Martens, J. Oomens, G. Berden, B. Redlich, J. K. Gibson, Organometallics 25 (2016) 1228-1240 (DOI: 10.1021/acs.organomet.6b00079).

9. “Gas-Phase Activation of Carbon Dioxide by a Terminal Uranium-Nitrogen Bond: A Demonstration of the Principle of Microscopic Reversibility,” P. D. Dau, P. B. Armentrout, M. C. Michelini, J. K. Gibson, Phys. Chem. Chem. Phys. 18 (2016) 7334-7340 (DOI: 10.1039/c6cp00494f).

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11. “A ‘Bare’ V^{5+} Complex Crystallized from Aqueous Solution: XRD, $^{51}V/^{17}O/^{1}H/^{13}C$ NMR; ESI-MS, and EPR Studies,” C. J. Leggett, B. F. Parker, S. J. Teat, Z. Zhang, P. D. Dau, W. W. Lukens, S. M. Peterson, A. J. P. Cardenas, M. G. Warner, J. K. Gibson, J. Arnold, L. Rao, Chemical Science 7 (2016) 2775-2786 (DOI: 10.1039/c5sc03958d).

12. “Dissociation of Gas-Phase, Doubly-Charged Uranyl-Acetone Complexes by Collisional Activation and Infrared Photodissociation,” M. J. Van Stipdonk, C. O’Malley, A. Plaviak, D. Martin, J. Pestok, P. A. Mihm, C. G. Hanley, T. A. Corcovilos, J. K. Gibson, B. J. Bythell, Int. J. Mass Spectrom. 396 (2016) 22-34 (DOI:10.1016/j.ijms.2015.12.005).

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14. “Binding of Pyrazine-Functionalized Calix[4]arene Ligands with Lanthanides in an Ionic Liquid: Thermodynamics and Coordination Modes,” S. A. Ansari, P. K. Mohapatra, W. Verboom, Z. Zhang, P. D. Dau, J. K. Gibson, L. Rao, Dalton Trans. 44 (2015) 6416-6422 (DOI: 10.1039/c5dt00049a).

15. “Electrospray Production and Collisional Dissociation of Lanthanide/Methylsulfonyl Anion Complexes: Sulfur Dioxide Anion as a Ligand,” Y. Gong, M. C. Michelini, J. K. Gibson, Int. J. Mass Spectrom. 392 (2015) 45-52 (DOI: 10.1016/j.ijms.2015.09.003).

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17. “Oxidation of Actinyl(V) Complexes by Addition of Nitrogen Dioxide is Revealed via Replacement of Acetate by NO_2,” P. D. Dau, J. Carretas, J. Marçalo, W. W. Lukens, J. K. Gibson, Inorg. Chem. 54 (2015) 8755–8760 (DOI: 10.1021/acs.inorgchem.5b01385).

18. “Solution, Solid, and Gas Phase Studies on a Nickel Dithiolene System: Spectator Metal and Reactor Ligand,” B. Mogesa, E. Perera, H. M. Rhoda, J. K. Gibson, J. Oomens, G. Berden, M. J. van Stipdonk, V. N. Nemykin, P. Basu, Inorg. Chem. 54 (2015) 7703-7716 (DOI: 10.1021/acs.inorgchem.5b00531).

19. “Elucidating Protactinium Hydrolysis: The Relative Stabilities of $PaO_2(H_2O)^+$ and $PaO(OH)_2^+$,” P. D. Dau, R. E. Wilson, J. K. Gibson, Inorg. Chem. 54 (2015) 7474-7480 (DOI: 10.1021/acs.inorgchem.5b01078).

20. “Gas Phase Uranyl Activation: Formation of a Uranium Nitrosyl Complex from Uranyl Azide,” Y. Gong, W. A. de Jong, J. K. Gibson, J. Am. Chem. Soc. 137 (2015) 5911-5915 (DOI: 10.1021/jacs.5b02420).

21. “Gas-Phase Reactions of Molecular Oxygen with Uranyl(V) Anionic Complexes. Synthesis and Characterization of New Superoxides of Uranyl(VI),” A. F. Lucena, J. M. Carretas, J. Marçalo, M. C. Michelini, Y. Gong, J. K. Gibson, J. Phys. Chem. A 119 (2015) 3628-3635 (DOI: 10.1021/acs.jpca.5b01445).

22. “Halide Abstraction from Halogenated Acetate Ligands by Actinyls: A Competition between Bond Breaking and Making,” P. D. Dau, J. K. Gibson, J. Phys. Chem. A 119 (2015) 3218-3224 (DOI: 10.1021/acs.jpca.5b00952).

Preparations for Very Heavy Element Gas-Phase Ion Chemistry

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Overall research goals: Perform gas-phase single-ion chemistry with elements from Fm(Z=100) through Sg(Z=106). Ionization potentials and bond dissociation energies will be determined.

Single ions of the heaviest elements will be produced at the LBNL 88-Inch Cyclotron in compound nucleus reactions using high-intensity beams of ^{40}Ar through ^{54}Cr with ^{208}Pb and ^{209}Bi targets, at rates ranging from a few ions/s to a few ions/h. The heavy element ions will be separated from unwanted nuclear reaction products with the Berkeley Gas-filled Separator (BGS). At the BGS focal plane, the ions will pass through a 2 μm titanium window, and stop in ultra-pure He gas inside a Radiofrequency Gas Catcher. The ions will be guided to a Radiofrequency Quadrupole Trap (RFQtrap), where they will be bunched and cooled. A small partial pressure of a reactive gas will be added to the RFQtrap, and the ions will be allowed to react for a preset reaction time interval. After the reaction time interval, both unreacted and reacted ions will be re-accelerated to 5 kV and sent through a mass separator, where they will be dispersed by their m/q ratios onto a position-sensitive detector array. The numbers of reacted and unreacted ions will be determined by monitoring their α-decay.

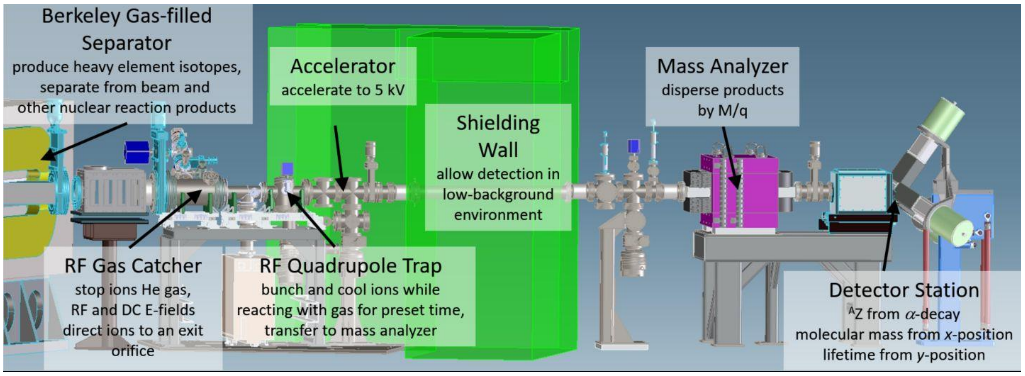

Figure 1. Layout of the Gas Catcher, RFQtrap, acceleration section, mass separator, and detector station.

By choosing various reactive gases with different ionization potentials, the ionization potentials of the heavy element ions can be determined. For example,

$$\mathrm{No}^{2+} + \mathrm{O}_2 \rightarrow \mathrm{No}^{+} + \mathrm{O}_2^{+}$$

will proceed if the electron affinity (inverse of ionization potential) of No^{2+} is sufficiently greater than the ionization potential of O_2.

By choosing various reactive gases with different bond dissociation energies, the bond dissociation energies of the heavy element ions can be determined. For example,

$$\mathrm{No}^{+} + \mathrm{O}_2 \rightarrow \mathrm{NoO}^{+} + \mathrm{O}^{\bullet}$$

will proceed only if the NoO^{+} bond strength is greater than the O_2 bond dissociation energy.

By changing the reaction time interval in the RFQtrap, the reaction rates can be determined:

$$\lambda_p = \lambda_r + \lambda_n + \lambda_c \qquad \lambda_d = \lambda_r + \lambda_m$$

$$\mathrm{nM}(t) := \frac{\mathrm{n}\cdot\mathrm{Rp}}{\lambda\mathrm{p}}\cdot\left(1 - e^{-\lambda\mathrm{p}\cdot t}\right) \qquad \mathrm{nMR}(t) := \frac{\mathrm{n}\cdot\mathrm{Rp}\cdot\lambda\mathrm{c}}{\lambda\mathrm{p}}\cdot\left(\frac{e^{-\lambda\mathrm{p}\cdot t} - e^{-\lambda\mathrm{d}\cdot t}}{\lambda\mathrm{p} - \lambda\mathrm{d}} + \frac{1 - e^{-\lambda\mathrm{d}\cdot t}}{\lambda\mathrm{d}}\right),$$

where R_p is the production rate of No^+ in the nuclear reaction, λ_p, is the total decay rate for the bare metal ion, which is composed of λ_r, the radioactive decay rate, λ_n, the neutralization rate for No^+, and λ_c, the chemical reaction rate. λ_d, is the total reaction rate of the daughter molecular ion, which is composed of λ_r and λ_m, the neutralization rate for the daughter molecular ion. The term t is the chemical reaction time interval in the RFQtrap. Simulations show that λ_c can be determined for No with one day of 88" Cyclotron beamtime.

Significant achievements during 2015-2017: The Radiofrequency Gas Catcher – RFQtrap – re-acceleration - mass separator – detector system has been constructed (with NP funding) and is presently being commissioned. We have achieved the designed mass resolution, and the overall efficiency is within a factor of two of the design goal. Equipment for controlling and measuring the reactive gas has been received.

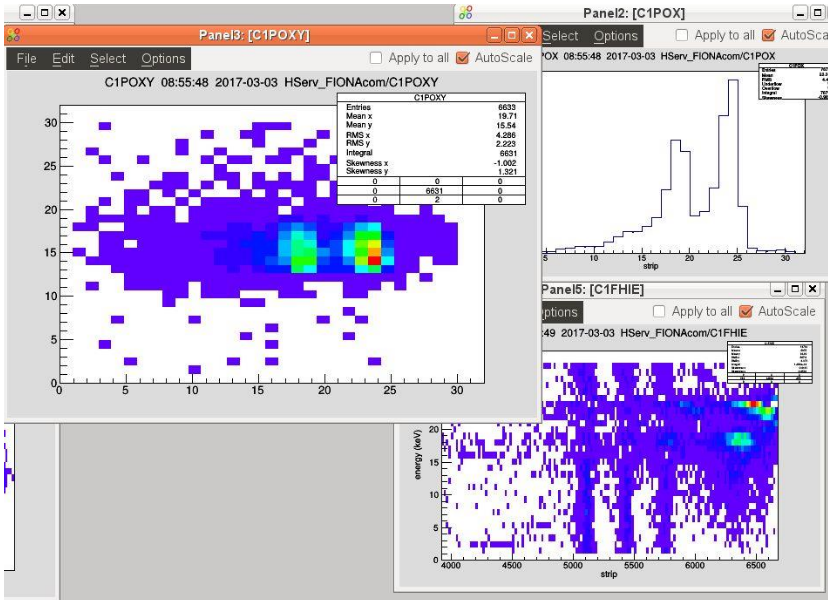

Figure 2. Screenshot from the February commissioning experiment showing separation of $^{199-201}$At produced in the ^{165}Ho(^{40}Ar,xn)$^{206-x}$At reaction.

Science objectives for 2017-2019:

- Complete commissioning of the complete system, including optimization of efficiency, mass resolution, and m/q calibration procedure
- Proof-of-principle experiment using source-generated ^{216}Po: $Po^+ + O_2 \xrightarrow{?} PoO + O^\bullet$
- Measurement of previously known reaction and rate for $Ho^+ + O_2 \rightarrow HoO^+ + O^\bullet$
- 1st heavy element gas-phase ion chem. $No^+ + O_2 \xrightarrow{?} NoO^+ + O^\bullet$, $\quad No^{2+} + O_2 \xrightarrow{?} No^+ + O_2^+$
- Additional experiments with Lr (Z=103) and Rf (Z=104)

Publications supported by this project 2015-2017

I. Usoltev, et al., Decomposition studies of group 6 hexacarbonyl complexes. Part I: Production and decomposition of $Mo(Co)_6$ and $W(Co)_6$, Radiochimica Acta **104**, 141 (2016), DOI 10.1515/ract-2015-2445.

New Approaches for the Synthesis of Actinide-Ligand Multiple Bonds: Opportunities for Novel Structure, Reactivity, and Catalysis

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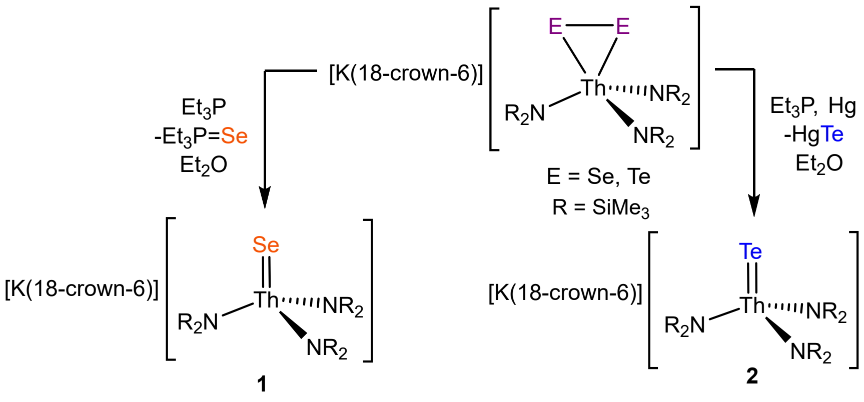
Overall research goals: Our research program has two specific aims: (*i*) develop new methods for the synthesis of actinide-ligand multiple bonds; and (*ii*) explore the reactivity and electronic structure of actinide-ligand multiple bonds, specifically to answer fundamental questions about *d* and *f* orbital participation in actinide-ligand bonding, develop actinide complexes for catalysis, and provide insight into the electronic structure of the actinyl ions.

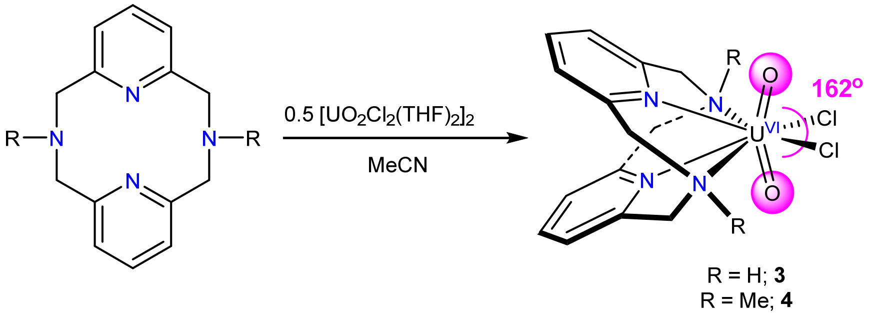
Significant achievements during 2015-2017: We recently reported the synthesis of thorium terminal chalcogenides, $[K(18\text{-crown-6})][Th(E)(NR_2)_3]$ (E = Se, **1**; E = Te, **2**) (Scheme 1). Both **1** and **2** were characterized by X-ray crystallography and were found to feature the shortest Th–Se and Th–Te bond distances yet reported. We also characterized **1** and **2** by ^{77}Se and ^{125}Te NMR spectroscopy, respectively. Interestingly, we found that the ^{77}Se and ^{125}Te NMR chemical shifts correlated with the An–E bond delocalization index, which is as a measure of the bond covalency, suggesting that NMR spectroscopy could be useful tool for understanding actinide electronic structure.

Scheme 1



We have also begun exploring the reactivity of the ubiquitous uranyl ion with macrocyclic ligands (Scheme 2). Specifically, we discovered that addition of the 12-membered macrocycles, ^{H}N4 (^{H}N4 = 2,11-diaza[3,3](2,6) pyridinophane) or ^{Me}N4 (^{Me}N4 = *N,N'*-dimethyl-2,11-diaza[3,3](2,6) pyridinophane), to $[UO_2Cl_2(THF)_2]_2$ resulted in formation of 8-

Scheme 2



coordinate uranyl complexes, (^{R}N4)UO_2Cl_2 (R = H, **3**; R = Me, **4**) These complexes exhibit some of the smallest O-U-O bond angles yet reported, which is consequence of the steric repulsion between the oxo ligands of the uranyl fragment and the macrocycle backbone.

Science objectives for 2017-2019:

- Use macrocyclic ligands to modify the *trans*-oxo stereochemistry of the uranyl ion.
- Develop new carbene transfer reagents and synthesize an actinide carbene.
- Develop ^{13}C NMR spectroscopy as a tool to evaluate covalency in actinide organometallics.

Publications supported by this project 2015-2017:

1. Smiles, D. E., Wu, G., Hayton, T.W.* Synthesis, Electrochemistry, and Reactivity of the Actinide Trisulfides, [K(18-crown-6)][An(η^3-S_3)(NR_2)$_3$] (An = U, Th; R = $SiMe_3$). *Inorg. Chem.* **2016**, *55*, 9150-9153.

2. Pedrick, E. A., Schultz, J. W., Wu, G., Mirica, L. M., Hayton, T. W.* Perturbation of the O–U–O Angle in Uranyl by Coordination to a 12-Membered Macrocycle. *Inorg. Chem.* **2016**, *55*, 5693-5701.

3. Pedrick, E. A.; Seaman, L. A.; Scott, J. C.; Griego, L.; Wu, G.; Hayton T. W.* Synthesis and Reactivity of a U(IV) Dibenzyne Complex. *Organometallics* **2016**, *35*, 494-502.

4. Smiles, D. E.; Wu, G.; Hrobárik, P.*; Hayton, T. W.* Use of ^{77}Se and ^{125}Te NMR Spectroscopy to Probe Covalency of the Actinide-Chalcogen Bonding in $[Th(E_n)\{N(SiMe_3)_2\}_3]^-$ (E = Se, Te; *n* = 1, 2) and Their Oxo-Uranium(VI) Congeners. *J. Am. Chem. Soc.* **2016**, *138*, 814-825.

5. Pedrick, E. A.; Hrobárik, P.*; Seaman, L. A.; Wu, G.; Hayton, T. W.* Synthesis, structure and bonding of hexaphenyl thorium(iv): observation of a non-octahedral structure. *Chem. Commun.* **2016**, *52*, 689-692.

6. Pedrick, E. A.; Wu, G.; Hayton, T. W.* Oxo Ligand Substitution in a Cationic Uranyl Complex: Synergistic Interaction of an Electrophile and a Reductant. *Inorg. Chem.* **2015**, *54*, 7038-7044.

7. Smiles, D. E.; Wu, G.; Hayton, T. W.* Reactivity of $[U(CH_2SiMe_2NSiMe_3)(NR_2)_2]$ (R = $SiMe_3$) with elemental chalcogens: Towards a better understanding of chalcogen atom transfer in the actinides. *New. J. Chem.* **2015**, *39*, 7563-7566.

8. Smiles, D. E.; Wu, G.; Hayton, T. W.* Thorium-ligand multiple bonds *via* reductive deprotection of a trityl group. *Chem. Sci.* **2015**, *6*, 3891-3899.

Selective Recognition of Heavy Elements by Protein-Based Reagents

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Overall research goals: Our goal is to engineer protein-based reagents that can selectively bind heavy elements in aqueous solutions. We hope to design and evolve proteins that can bind and respond to individual actinide and lanthanide ions tightly and selectively. We also hope to develop small molecules that can selectively chelate actinide ions based on principles learned from the protein work.

Significant achievements during 2015-2016: We have identified and begun to characterise proteins with nanomolar lanthanide-binding affinity from a methylotroph native to lanthanide-rich volcanic mud pots.

1. Identification and characterisation of lanthanide-binding proteins from *Methylacidiphilum fumariolicum*.

M. fumariolicum, found in an Italian volcanic mud pot, was recently revealed to possess a lanthanide-dependent methanol dehydrogenase (XOXF MDH).[a] Using competitive binding assays, we have found that XOXF MDH binds Ce^{3+} – the lanthanide that confers the greatest protein activity – with an affinity of 44 nM, and Tb^{3+} with an affinity of 1.6 nM (Figure 1a). At 67 kDa and with low recombinant expression levels, XOXF MDH is unsuited to mutation studies and engineering.

However, the existence of XOXF MDH pointed to other uncharacterized proteins in the same gene cluster likely involved in lanthanide trafficking. We have found that XOXJ and XOXGJ bind Tb^{3+} with affinities of 0.8 nM (XOXJ) and 1.5 nM (J domain of XOXGJ), despite a lack of sequence homology with the lanthanide-binding region of XOXF MDH. The J domain of XOXGJ expresses well, shares high identity with the same domain in XOXJ and is 147 amino acids in length. It is a promising candidate for the development of a highly sensitive and selective lanthanide- and actinide-binding protein. This protein has a 10-fold greater affinity for Tb^{3+} than the best lanthanide binding proteins previously identified from our computational screen, leading us to switch focus to XOXGJ.

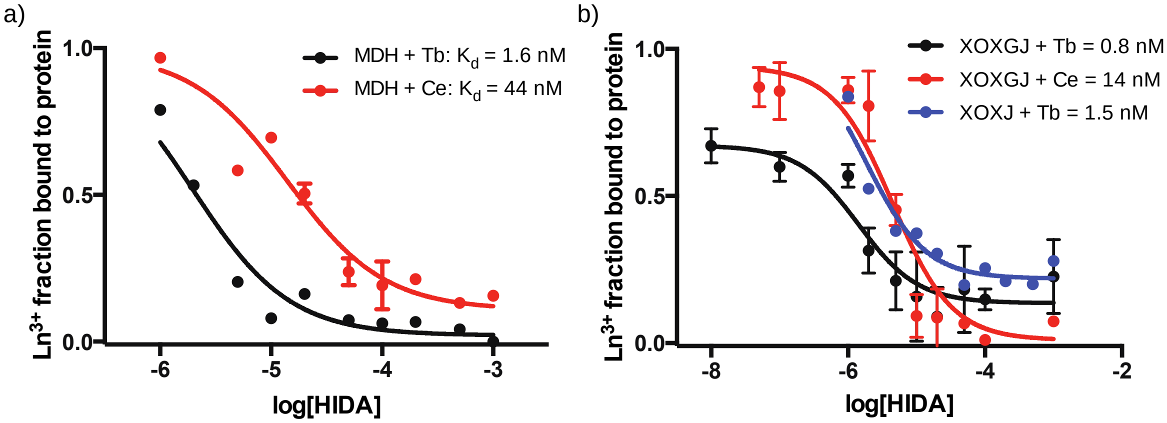

Figure 1. Competitive binding curves used to determine the lanthanide-binding affinities of (a) MDH and (b) XOXGJ and XOXJ.

Our efforts in the past year have focused on determining the crystal structure of the J domain of XOXGJ, for which there are no structural homologues in the Protein Data Bank. We have been successful in growing crystals and collecting diffraction data to a resolution of 1.3 Å. The bound lanthanides were not sufficient for the generation of an anomalous scattering signal required to solve the crystal structure. We are now working to crystallize a SeMet-substituted protein under the same conditions for multiwavelength anomalous dispersion. Crystal growth conditions have been identified for XOXJ, but studies of this protein are limited by its poor expression in recombinant systems.

Our immediate objective is to solve the crystal structure of the J domain of XOXGJ, thus revealing the lanthanide-binding site and allowing us to begin the rational mutation of amino acids around the binding site and in the second coordination sphere to improve lanthanide binding, as well as to engineer a smaller version of the protein.

[a] Pol, A.; Barends, T. R. M.; Dietl, A.; Khadem, A. F.; Eygensteyn, J.; Jetten, M. S. M.; Op den Camp, H. J. M. Rare Earth Metals Are Essential for Methanotrophic Life in Volcanic Mudpots. *Environ Microbiol* **2013**, *16*, 255–264.

2. Compiling information about the biological function of XOXJ and XOXGJ to improve our understanding of their affinity for lanthanides.

Two other methylotrophic *Verrucomicrobia* closely related to *M. fumariolicum* have been identified, both containing XOXJ and XOXGJ in the same gene cluster. All three proteins are likely perisplasmic and their homologues in Ca^{2+}-dependent MDH systems have been linked to XOXF MDH, for example as possible chaperones or electron-transfer partners. We have done BLAST searches to collect all available information about the possible biological functions of these proteins. We have also identified a small, 67 amino acid protein from one of these methylotrophs for study as a possible lanthanide-binding protein. Future work will include testing whether XOXJ and XOXGJ interact with each other and MDH and if the 67 amino acid protein is indeed a lanthanide-binding protein. We expect that in combination with the crystal structure, this information will help to guide the rational mutation of XOXGJ to improve its lanthanide-binding affinity.

Science objectives for 2017-18:

- Solve the structure of XOXGJ and use it to rationally design a smaller, more potent lanthanide- and actinide-binding protein.
- Characterise the binding of XOXGJ for different lanthanides and actinides to determine its potential for design for selective recognition.
- Gain a basic understanding of the biology of XOXJ and XOXGJ in association with MDH: do they interact? Is there a direct transfer of the lanthanide between these proteins?

Publications supported by this project 2015-2016

1. Karpus, J.; Zhang, C.; Bosscher, M.; Weekley C. M.; Luhua, L.; He, C. Development of lanthanide-binding protein through computation screening and design" submitted to *Journal of Biological Inorganic Chemistry*.
2. Karpus, J.; Bosscher, M.; Ajiboye, I.; Zhang, L.; He, C. "Chromate Binding and Removal by A Molybdate Binding Protein ModA" *ChemBioChem* on-line.

Spectroscopic Studies of Prototype Actinide Compounds

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

Significant achievements in 2015-2017: Microwave and sub-millimeter wave spectroscopy techniques can provide some of the most accurate molecular constants. However, attempts to observe direct microwave absorption spectra for actinide species other than oxides have not been successful. In collaboration with Prof. Steimle, we used a microwave-optical double resonance (MODR) technique to observe pure rotational transitions of ThS. Figure 1 shows the essential components of the MODR experiment. The molecules of interest are entrained in a molecular beam, and a CW laser is used to excite a single rotational line of an electronic transition. The laser beam is divided, so that the molecular beam can be excited at two different locations. Microwave excitation of the J-1 → J transition results in an increase of the laser induced fluorescence (LIF) signal from the second beam. By this means, we observed pure rotational transitions for ThS ranging from J=7 to J=14, with a linewidth of 25 kHz. The rotational constants $B=3275.05033\pm0.00041$ and $D=0.0006699\pm0.0000012$ MHz were derived from these data. The high sensitivity of the MODR method compensates for the low chemical yield of species such as ThS, permitting microwave studies of species that are more challenging for gas-phase production.

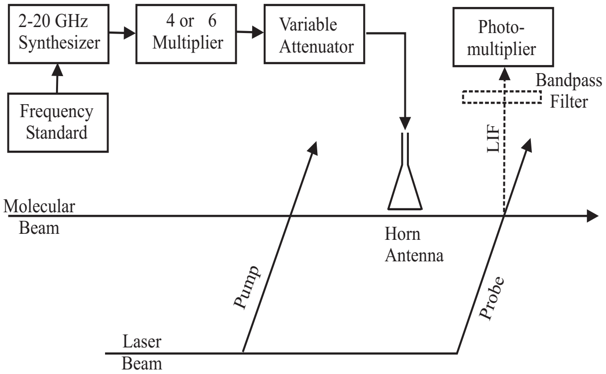

Fig 1.1 A block diagram of the MODR spectrometer used to study ThS

Spectroscopic studies of ThCl and ThCl$^+$ were carried out to test the predictions of high-level electronic structure calculations. ThCl was generated by laser ablating Th metal in the presence of a low concentration of Cl_2. LIF spectra were recorded for the ranges 18100-23600 cm^{-1} and 35000-36000 cm^{-1}. Low energy states of ThCl were observed using dispersed fluorescence measurements, as shown in Fig. 2. A striking feature of this spectrum is the long progression of the ground state vibrational levels (up to v”=10). This is consistent with initial excitation of a high vibrational level of the upper electronic state. Fitting to the band centers defined vibrational constants of ω_e=340.9(1.3) cm^{-1} and $\omega_e x_e$=0.90(14) cm^{-1}. Electronically excited states were identified at energies of 3497.7, 4075.7 and 4361.2 cm^{-1}. Pulsed field ionization – zero kinetic energy photoelectron spectroscopy established an ionization energy for ThCl of 51344(5) cm^{-1}, and the vibrational term energies of the v=1-3 levels. The zero-point level of the first electronically excited state was found at 949(2) cm^{-1}. Comparisons with high-level theoretical results indicate that the ground and excited states are Th^{2+}(7s6d)Cl$^-$ $X^3\Delta_1$ and Th^{2+}(7s^2)Cl$^-$ $^1\Sigma^+$, respectively.

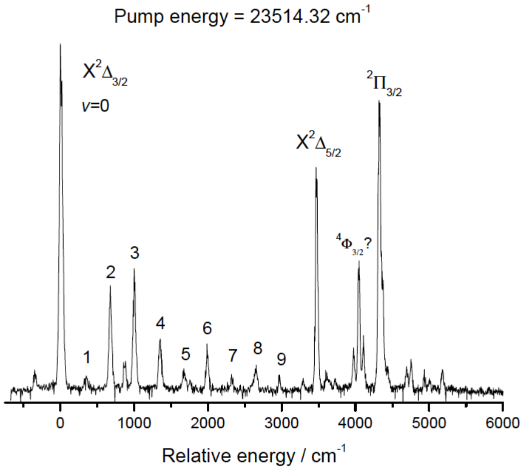

Fig. 2 Dispersed fluorescence spectrum for Th^{35}Cl

The construction and testing of a slow electron velocity map imaging (SEVI) spectrometer for actinide studies has been completed. This instrument is now being used to investigate the ground state and low-lying vibronic states of $(ThO)_m$ and $(UO)_m$ clusters.

Science objectives for 2017-2018: For the diatomic molecules we have examined, we have seen little evidence for participation of the 5f orbitals in the bonding. One question of interest is whether lowering the symmetry of the molecule will facilitate bonding contributions from the 5f orbitals? The OThF/OThF$^+$ pair will be examined as they are predicted to have bent equilibrium structures, providing an opportunity to study electronic state mixing in a low-symmetry (C_s) environment. We will further examine this question by studying organo-metallic actinide species (also of interest from the perspective of the bonding to chelating agents). The initial focus will be on the complexes of Th and U with 1,3,5,7-cyclooctatetraene (COT).

Publications supported by this project

T.C. Steimle, R. Zhang, M.C. Heaven, Chem. Phys. Lett., **639,** 304-306 (2015) http://dx.doi.org/10.1016/j.cplett.2015.09.048.
" The pure rotational spectrum of thorium monosulfide"

M. C. Heaven and K. A. Peterson in *“Experimental and Theoretical Approaches to Actinide Chemistry”* (Invited book chapter, submitted). Editors, J. K. Gibson and W. De Jong. Wiley, 2017
“*Chapter 1: Probing actinide bonds in the gas phase: theory and spectroscopy”*

R. A. VanGundy, J. H. Bartlett, M. C. Heaven, S. R. Battey and K. A. Peterson, J. Chem. Phys., 146, 054307 (2017) http://dx.doi.org/10.1063/1.4975070
“Spectroscopic and theoretical studies of ThCl and ThCl$^+$”

Remarkable Recognition of Copper Sulfate Through Self-Assembly of a Ditopic Receptor

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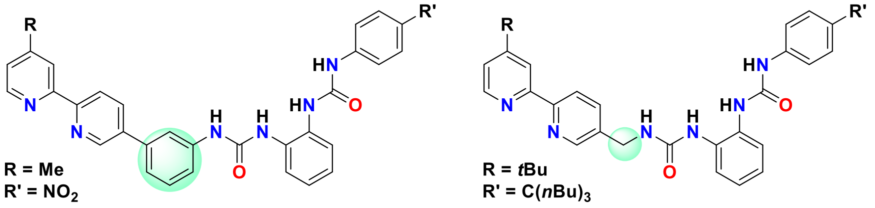
Overall research goals: This research aims to understand the self-assembly of functionalized ditopic organic ligands with metal salts to construct complex, charge-neutral architectures with predetermined structures and separation functions.

Significant achievements during 2015-2017: We have previously designed neutral ditopic receptors for self-assembly with metal sulfates into helical ion-pair complexes (Custelcean et al. *Inorg. Chem.*, **2014**, 3893). The poor solubility of these ligands in various organic solvents prevented their direct application in liquid-liquid extractions of metal salts. Therefore, we directed our efforts toward the synthesis of highly stable lipophilic ditopic receptors for selective ion-pair separation. Two new ditopic ligands, previously designed using HostDesigner software to be predisposed to form ion-pair helicates with $M^{II}SO_4$, were synthesized. The key structural difference between **1** and **2** is the linking group connecting *o*-phenylene-bis(urea) and bipyridine anion and cation binding sites, which is 1,3-phenylene or methylene in **1** and **2**, respectively (Figure 1).



1 **2**

Figure 1. Chemical structures of new bipyridine-bis(urea) ligands **1** and **2**.

Ligand **1** does not form triple-stranded helicates with $M^{II}SO_4$. Instead, it efficiently crystallizes with $CuBr_2$ to form a 1:1 complex in the solid state with a hydrogen bond (N–H···Br) motif (Figure 2). Ligand **2**, on the other hand, readily forms isostructural helicate complexes with several $M^{II}SO_4$ (M = Fe, Ni, Zn) salts (Figure 3, a). Observed differences in complexation ability of **2** with metal sulfates, compared to ligand **1**, can be attributed to the increased flexibility of the ligand, facilitated by the methylene linker.

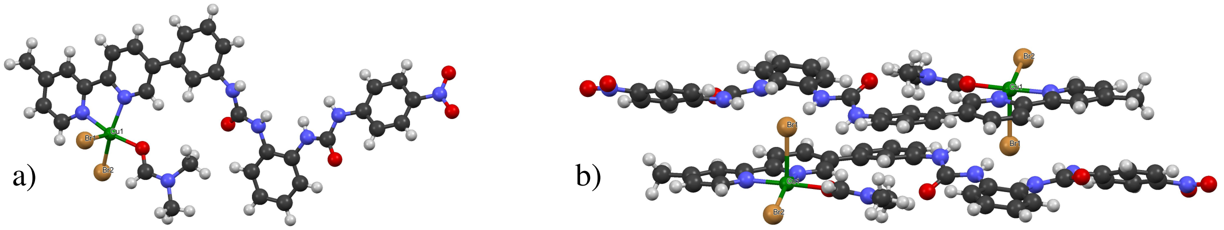


Figure 2. a) Molecular structure of the complex [(**1**)$CuBr_2$]. b) Illustration of short interactions between bromine and the four bis(urea) hydrogens.

Furthermore, ligand **2** is a very strong and selective extractant of $CuSO_4$. Within 10 minutes, majority (95%) of $CuSO_4$ is extracted by **2** in an organic diluent from an aqueous mixture containing seven different metal sulfates (Figure 3, b). Selectivity, however, changes dramatically when excess ligand is used to extract trace amounts of metal sulfate from an aqueous solution into an organic phase with a competitive and nearly complete extraction of Cu, Fe, Zn and Co sulfates taking place, while Ca, Mn and Ni sulfates remain in the aqueous phase. Based on ^{1}H NMR titration and liquid-liquid extraction studies, self-assembled species extracted in the organic phase were identified as complexes of ligand with metal sulfate with 3:1 stoichiometry. Extraction behaviour of M^{2+} by bipyridine unit in **2** does not follow the typical Irving-Williams order of stabilities, which for the 3:1 complexes increase in the order Mn<Zn<Co<Cu<Fe<Ni (Irving, H. et al. *J. Chem. Soc.*, **1962**, 5222). This suggests that the appended *o*-phenylene-bis(urea) binding site has a profound influence on the overall stability of the M^{2+} and bipyridine chelated species.

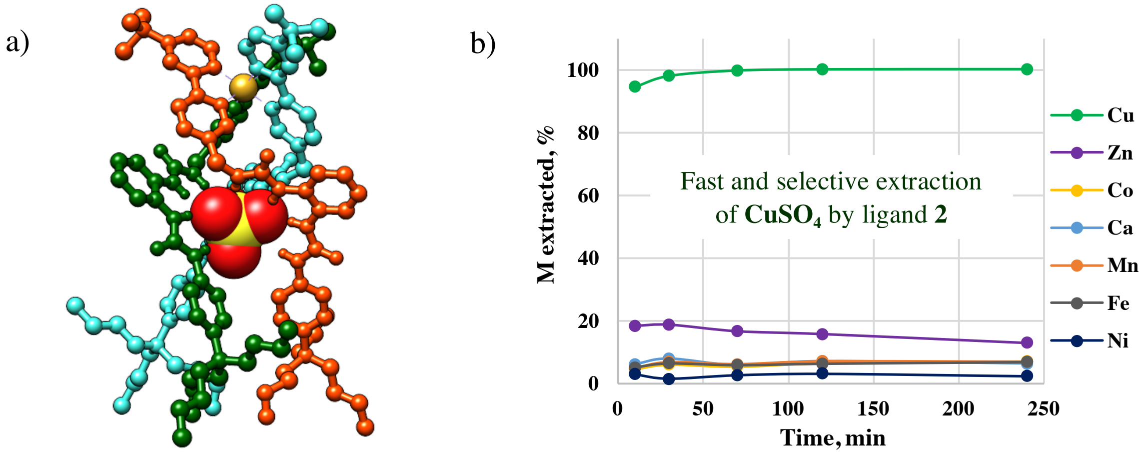


Figure 3. a) Molecular structure of the complex $[(\mathbf{2})_3NiSO_4]$. b) Metal sulfate extraction from aqueous solution ([M] = Ca, Mn, Fe, Co, Ni, Cu, Zn – 4 mM each, total $[MSO_4]$ = 28 mM) by 12 mM ligand **2** in chloroform at 25 °C as a function of time.

Science objectives for 2017-2019:

- Synthesis of new highly pre-organized ligands and their self-assembly studies with different metal salts to form complex molecular architectures (helicates, tetrahedral, cubes, etc.) with predetermined structures and separation functions will be continued.
- Design and synthesize novel functional porous materials (anion exchange polymers) decorated with cationic binding sites for selective complexation with tetrahedral oxoanions and their water clusters. This will include:
    - Identification of stable, robust framework
    - Identification and optimization of cationic binding site
    - Positioning of cationic site in the porous polymer (pre-installation or post-functionalization)
    - Testing of new materials, performance analyses.

Publications supported by this project 2015-2017:

Thevenet, A.; Custelcean, R.; Moyer, B. A., Jansone-Popova, S. “Remarkable Recognition of Copper Sulfate Through Self-Assembly of a Ditopic Receptor” In preparation for Angewandte Chemie International Edition.

Understanding the Influence of Counter Cations on the Formation of Actinide Compounds from Solution

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Overall research goals: improve our understanding of the chemistry and reactivity of the actinides in solution and ultimately advance our ability to control the formation and properties of solid actinide compounds.

Significant achievements during 2015-2017:

1. **Established a better correlation between Np(V) CCI speciation in solution and final solid products**: We conducted both in situ and ex situ experiments to monitor the crystallization of cation-cation interaction (CCI) complexes during evaporation of Np(V) solutions.[1] Our studies show that CCI entities beyond the well-known monomers and dimers are present in solution, and the assembly of these entities in solid products are extremely sensitive to evaporation conditions (Fig. 1a). Slower evaporation led to the discovery of the first example of a three-dimensional cationic network of Np(V) connected through CCIs without the support of ancillary ligands or other cations (Fig. 1b).

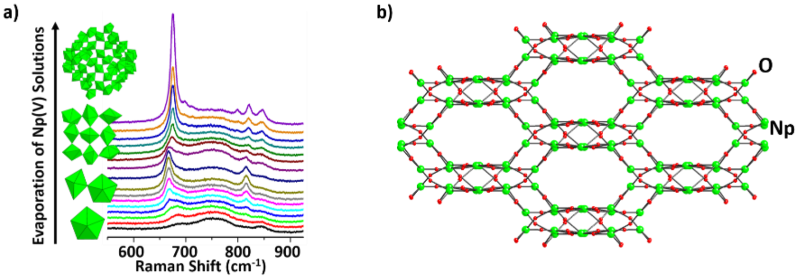

Figure 1. a). In situ Raman spectra of a slow evaporation of a Np(V) solution. b). A three-dimensional CCI network of NpO_2^+ in the structure of $NpO_2Cl(H_2O)_2$. Cl^- and H_2O are omitted for clarity.

2. **Demonstrated the substantial influence of counter cations on the formation of solid actinide compounds from evaporating solution:** Evaporation reactions of thorium nitrate solutions under acidic conditions are known to form compounds consisting of neutral $[Th(NO_3)_4(H_2O)_4]$ or $[Th(NO_3)_4(H_2O)_3]$ complexes. With addition of ANO_3 (A = monovalent counter cations) in similar evaporation reactions, we prepared a series of solid products either containing discrete monovalent $[Th(NO_3)_5(H_2O)_2]^-$ anions in the case of smaller A or discrete divalent $[Th(NO_3)_6]^{2-}$ units in the cases of larger A (Figure 2).

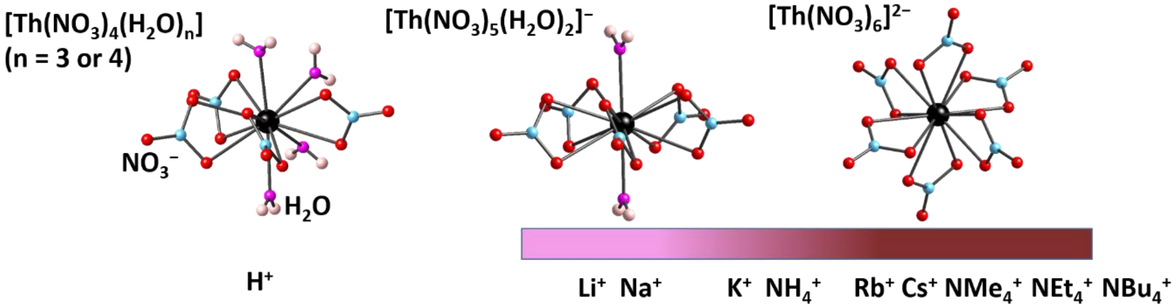

Figure 2. Formation of thorium nitrate complexes in solid as a function of A^+ in evaporation reactions of acidic solutions.

Our results suggest that large counter cations tend to stabilize higher orders of Th nitrate complexes, presumably by forming ion-pairs. These findings open a new avenue for understanding and ultimately controlling the formation mechanism of actinide complexes.

Science objectives for 2017-2019:

Understand the influence of counter cations on actinide, particularly transuranic, chemistry:

Preliminary studies on evaporation reactions of neptunyl(V) chloride solutions in the presence of large counter cations (e.g. NMe_4^+ and PPh_4^+) showed interconversion of Np(V) and Np(VI) chlorides during evaporation (Fig. 3a). Electrochemical measurements indicated substantial influence of large counter cations on the redox behavior of Np(V/VI) species in solution (Fig. 3b).

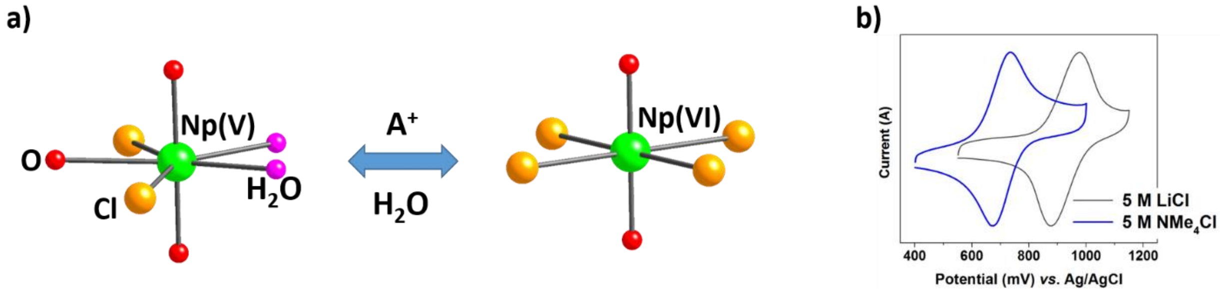

Figure 2. a). Interconversion between Np(V) and Np(VI) chloride solid compounds during the evaporation of Np(V) aqueous solution in the presence of large counter cations (A^+). b). Cyclic voltammograms of Np(V) dissolved in 5 M LiCl and 5 M NMe_4Cl.

Next Steps:

- Explore actinide speciation in solution as a function of counter cations using X-ray, UV-vis, and Vibrational spectroscopies.
- Expand electrochemical studies on the redox behavior of Np and Pu in the presence of counter cations.
- Expand in situ and ex situ studies on actinide evaporation reactions as a function of counter cations.
- Investigate the energy landscape of ion-pairs between actinide complexes and counter cations with collaborative modeling efforts.

Publications supported by this project 2015-2017

1. Jin, G. B., “A Three-Dimensional Network of Cation–Cation-Bound Neptunyl(V) Squares: Synthesis and in Situ Raman Spectroscopy Studies” Inorganic Chemistry, (**2016**), 55(5), 2612–2619. (DOI: 10.1021/acs.inorgchem.5b02955)
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4. Wilson, R. E., “Structure, Phase Transitions, and Isotope Effects in $(Me_4N)_2PuCl_6$” Inorganic Chemistry, (**2015**), 54(21), 10208–10213. (DOI: 10.1021/acs.inorgchem.5b01288) **COVER ARTICLE**
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Coordination Chemistry of +3 Actinides

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Because metal aquo ions, $M(H_2O)_x^{n+}$, are both ubiquitous and chemically important, their structures and chemical properties serve as fundamental benchmarks in exploring trends across the periodic table. Characterization of aqueous speciation provides a foundation for advances throughout chemistry and biology. For example, understanding the chemistry of metal aquo ions is essential for solving technical problems relevant to biomedical applications, metal ions in the environment, extraction, food chemistry, and so on. In this sense, metal aquo ions occupy central roles in all chemical equilibria that define complexation properties of a metal by a particular ligand in aqueous media (Eq 1).

$$M(H_2O)_x^{n+} \underset{-L}{\overset{+L}{\rightleftharpoons}} ML(H_2O)_{x-1}^{n+} \underset{-L}{\overset{+L}{\rightleftharpoons}} ML_2(H_2O)_{x-2}^{n+} \underset{-L}{\overset{+L}{\rightleftharpoons}} ML_3(H_2O)_{x-3}^{n+} \tag{1}$$

Historically, one of the first critical steps in characterizing the chemical behavior of any element involved establishing its aqueous coordination chemistry. These results provide a foundation for determining critical metrics (*i.e.* stability constants) and metal solution chemistry (*i.e.* complexation, precipitation, etc.) that enable predictive capability for metal binding affinity. These days, the aquo ion identities and reactivities for many elements are taken for granted, as they have been well established for decades.

Motivated by the recent global efforts to solve technical problems in a wide range of nuclear areas – ranging from developing advanced nuclear fuel cycles to exploiting alpha decay from actinides as promising anticancer therapeutic agent – we set out to explore actinide +3 chemical binding properties in support of chelator design. Unfortunately, an insufficient understanding for many actinides (Ac, Am, Cm etc) has considerably hindered chemical development of appropriate actinide chelators.[1] As an example, even something as fundamental as the actinium aquo ion, $Ac(H_2O)_x^{3+}$ (referred hereafter as ***Ac-aquo***), remains poorly defined. Closing this gap is one of the first steps toward establishing thermodynamic data needed for predicting actinide behavior in aqueous systems across the actinide series.

Gathering experimental information about highly radioactive actinides is difficult. As an example, consider the first actinide in the series, namely actinium. The most stable actinium isotopes – ^{225}Ac and ^{227}Ac – have very short half-lives ($t_{1/2}$) of 10.0(1) d and 21.772(3) y,[2] respectively. Additionally, only very small quantities of these isotopes are available for research. As a result, many basic properties associated with actinium have yet to be defined. Perhaps the most well defined aspect of actinium chelation chemistry is the realization that actinium's affinities for binding certain donor atoms are difficult to predict.[3] This deficiency, as well as the implications of the large actinium ionic radius on chelation, severely hampers ligand design efforts for stabilizing actinium in aqueous applications.

Herein, we overcame the sample handling and spectroscopic obstacles associated with studying the actinium(III) ($5f^0\ 6d^0$) ion in aqueous media and report the first the first actinium XAFS study reported to date. Using this method, we have characterized a series of important actinide coordination compounds in aqueous environments. This series includes, arguably, the most fundamentally important actinium coordination complex, namely the ***Ac–aquo*** ion, $Ac(H_2O)_x^{3+}$. These studies made use of X-ray absorption fine structure (XAFS) spectroscopy and molecular dynamics density functional theory (MD-DFT) calculations to evaluate actinium in comparison to other +3 actinides (Am, Cm). The results include the first actinium bond distance measurements. Overall, the results highlight the uniqueness of the Ac^{III} ion, most notably in terms of the large coordination numbers and very long $Ac–O_{H2O}$ bond distance.

Publications:

1. Justin N. Cross, Jing Su, Enrique R. Batista, William J. Evans, Stosh A. Kozimor, Brian L. Scott, Benjamin A. Stein, Cory J. Windorff, and Ping Yang, "*Covalency in Americium(III) Hexachloride*," **2017**, in preparation for JACS.
2. M.G. Ferrier, B.W. Stein, E.R. Batista, J.M. Berg, E.R. Birnbaum, J.W. Engle, K.D. John, S.A. Kozimor "*Synthesis and Characterization of the Actinium Aquo Ion*.", ACS Central Science (2017) *ASAP*
3. Cross, J. N.; Macor, J. A.; Bertke, J. A.; Ferrier, M. G.; Girolami, G. S.; Kozimor, S. A.; Maassen, J. R.; Scott, B. L.; Shuh, D. K.; Stein, B. W.; Stieber, S. C. E. "Comparisons the 2,2′–Biphenylenedithiophosphinate Binding fo Americium, with Neodymium, and Europium." *Angew. Chem. Int. Ed.* **2016**, *128*, 12947.
4. M.G. Ferrier, E.R. Batista, J.M. Berg, E.R. Birnbaum, S. Kozimor et al "*Spectroscopic and Computational Investigation of Actinium Coordination Chemistry.*" Nature Communications **7**, 12312 (2016)

References:

[1] Y. S. Kim and M. W. Brechbiel, "An overview of targeted alpha therapy," *Tumor Biol.*, vol. 33, no. 3, pp. 573–590, 2012.

[2] "National Nuclear Data Center," *Brookhave National Laboratory,*. [Online]. Available: http://www.nndc.bnl.gov/chart/.

[3] H. W. Kirby and L. R. Morss, "Actinium," pp. 18–51, 1994.

Chemistry of Technetium, Americium, and Curium in Oxide Hosts

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Overall research goals: The objective of to Tc project is to incorporate Tc into durable metal oxides using mild aqueous conditions. The objectives of the Am/Cm project are to prepare Am^{4+} and Cm^{4+} doped CeO_2 and ThO_2 as well as AmO_2 and CmO_2 to study their electronic structures.

Significant achievements during 2015-2017:

1. Doped Tc^{4+} into Fe_3O_4 and MFe_2O_4 from HNO_3 using Fe metal and NH_4OH. Starting from TcO_4^- in 5 M HNO_3, the solution was denitrated using formic acid. $Fe(NO_3)_2$ was formed *in situ* from Fe powder. Neutralization of the solution with NH_4OH followed by heating to 95 °C for 90 minutes resulted in the removal of Tc from solution largely as Tc^{4+} replacing Fe^{3+} on octahedral sites of Fe_3O_4. Heating of the solution for 16 hr results in the formation of hematite, presumably with Tc^{4+} replacing Fe^{3+} and charge balancing by Fe^{2+} as in ilmenite ($TiFeO_3$).

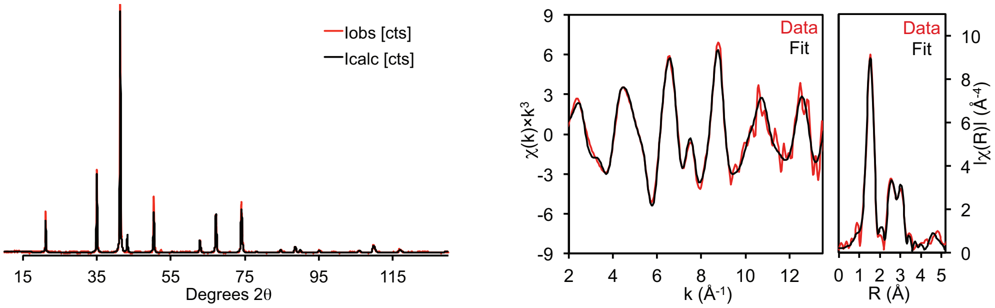

Figure 1. Diffraction pattern (left) and EXAFS spectrum (right) for Tc^{4+} doped into Fe_3O_4.

2. Doped Tc^{4+} into TiO_2 by two routes. Starting from TcO_4^- in 5 M HNO_3, the solution was denitrated using formic acid. In the first route, Ti^{3+} was formed *in situ* from Ti powder and NH_4F. In the second route TiO_2 and NH_4F were added along with hydrazine to reduce TcO_4^- to Tc^{4+}. Heating either mixture to reflux for 16 hr results in Tc doped TiO_2 with Tc^{4+} replacing Ti^{4+}.

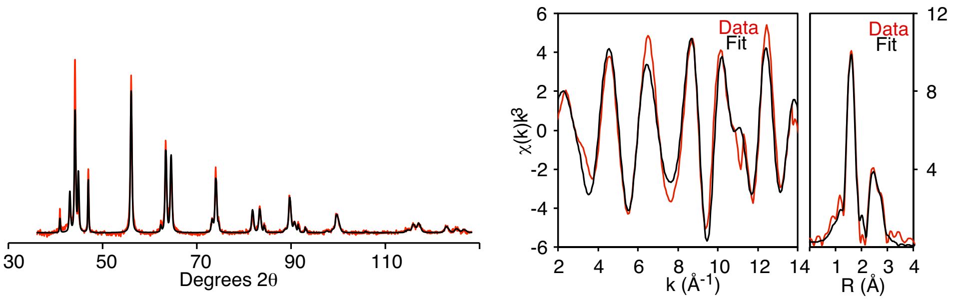

Figure 2. Diffraction pattern (left) and EXAFS spectrum (right) for Tc^{4+} doped into anatase (TiO_2).

Science objectives for 2017-2019:

- Prepare Am^{4+}/Cm^{4+} doped CeO_2 and ThO_2 as well as AmO_2 and CmO_2.
- Measure the magnetic moments and optical spectra of the Am^{4+} and Cm^{4+} in these matrices with an emphasis on the charge transfer bands.
- In collaboration with Stefan Minasian and Corwin Booth, measure the O K-edge XANES spectra of AmO_2 and CmO_2 and the L_3-edge EXAFS and RXES spectra of Am and Cm in these materials, respectively.
- Study the electronic structure using a configuration interaction model.

Selected publications supported by this project 2015-2017

1. Weaver, J.; Soderquist, C.Z.; Washton, N.M.; Lipton, A.S.; Gassman, P.L., Lukens, W.L.; Kruger, A.A.; Wall, N.A.; McCloy, J.S. “Chemical Trends in Solid Alkali Pertechnetates” Inorg. Chem. 2017, 56, 2633-2544. DOI:10.1021/acs.inorgchem.6b02694.
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3. Behrle, A.C.; Myers, A.J.; Rungthanaphatsophon, P.; Lukens, W.W.; Barnes, C.L.; Walensky, J.R. “Uranium(III) and thorium(IV) alkyl complexes as potential starting materials” Chem. Commun. 2016, 52, 14373-14375. DOI:10.1039/C6CC08105C.
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6. Lukens, W. W.; Speldrich, M.; Yang, P.; Duignan, T. J.; Autschbach, J.; Kogerler, P. “The roles of 4f- and 5f-orbitals in bonding: a magnetochemical, crystal field, density functional theory, and multi-reference wavefunction study” Dalton Trans. 2016, 45, 11508-11521. DOI:10.1039/C6DT00634E.
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10. Mason, J.A., Darago, L.E., Lukens, W.W.; Long, J.R. “Synthesis and O_2 Reactivity of a Titanium(III) Metal-Organic Framework” Inorg. Chem. 2015, 54, 10096-10104. DOI: 10.1021/acs.inorgchem.5b02046.
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A Chemist's View of Bonding in Actinide Extended Structures

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Overall research goals: Recent studies have provided a clearer picture of the role that actinide 5f orbitals have in bonding and the extent to which f electrons are localized on the metal. However, the interplay between 5f and 6d orbitals is still difficult to probe experimentally. In some cases, indirect exchange processes mediated by the 6d orbitals have been invoked to explain unusual electronic, magnetic, and structural phenomena. In this study, aluminum K-edge X-ray absorption spectroscopy and density functional theory (DFT) calculations were used to evaluate the electronic structure of the dialuminides, $LnAl_2$ and $AnAl_2$ (Ln = Ce, Sm, Eu, Yb, Lu and An = U, Pu). Because the 6d orbitals are more diffuse than the 5f orbitals, we hypothesized that enhancement in 6d orbital mixing would be closely tied to energetic stabilization due to orbital mixing.

Significant achievements during 2013 – 2015: Because of the limited historical precedent for Al K-edge studies, our work began with the measurement and interpretation of Al K-edge XAS for a series of molecular aluminum compounds with a range of oxidation states and a variety of supporting ligands and oxidation states (*J. Am. Chem. Soc.*, 2015). Al K-edge XAS measurements were conducted with the scanning transmission X-ray microscopes (STXMs) at the Advanced Light Source (11.0.2) and Canadian Light Source (10-ID1). Features in the Al K-edge spectra were fully assigned through a comprehensive polarization study and by comparison with the results of simulations using the eXcited-electron Core-Hole (XCH) approach. Results were interpreted within a molecular orbital framework, providing unique insight that could not be obtained from analysis of NMR or metrics from single-crystal X-ray diffraction. The Al K-edge XAS work also built upon results from our recent oxygen K-edge XAS studies of lanthanide sesquioxides, which showed that changes in O 2p mixing with the 5d states were directly related to established trends in the chemical behavior of the 4f electrons (*Dalton Trans.*, 2016).

Samples of the dialuminides were prepared by arc- or induction-melting of the elements. Figure 1 shows the background-subtracted and normalized Al K-edge XAS for selected dialuminides $YbAl_2$, $LuAl_2$, and $PuAl_2$. The edge onset for each alloy is 0.4 to 0.8 eV lower in energy than observed for pure Al metal and – in the case of $YbAl_2$ and $LuAl_2$ – well-resolved features are observed. XCH-DFT calculations were used to develop spectral assignments, which showed that the first low energy features near 1558.5 eV involved directional, σ-type bonding interactions between the Al 3p and Ln or An d orbitals. At higher energy, the broad features observed at 1565-1566 eV involved states derived from a σ-antibonding interaction between the Al 3p and Ln or An d orbitals.

A simple theoretical framework was developed to rationalize these results, which suggested that the increases in mixing with the high energy Al 3p orbitals were correlated with both the energy and radial extension of the 5d and 6d orbitals (Figure 1). The results showed that changes in the energy and occupancy of the f-orbitals impacted the energy of the lanthanide 5d and actinide 6d orbitals,

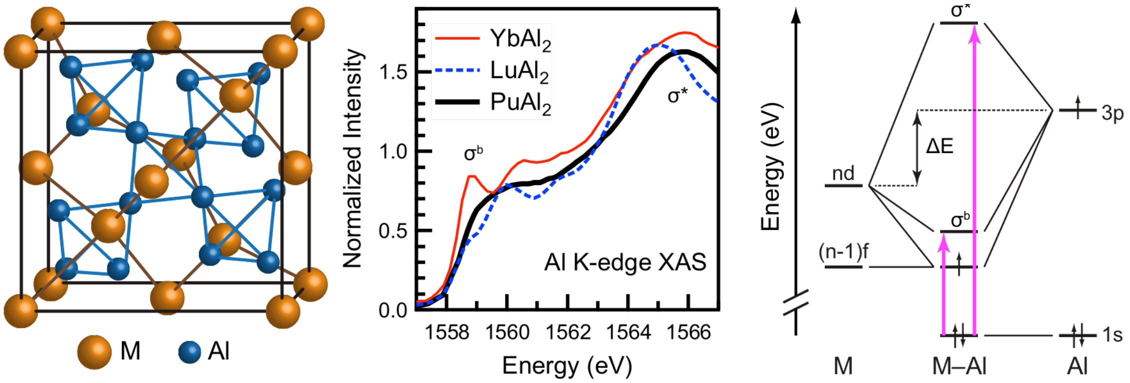

Figure 1. (Left) The cubic Cu_2Mg structure of the dialuminides, MAl_2 (M = Ce, Sm, Eu, Yb, Lu, U, Pu). (Middle) Al K-edge XAS of selected MAl_2. (Right) Proposed spectral interpretation in a simplified molecular orbital framework.

which indirectly impacted the amount of mixing with the Al 3p orbitals and the composition of the conduction band. Furthermore, trends in the amount of Al 3p and lanthanide 5d or actinide 6d mixing were influenced by changes in spatial overlap, which was strongly tied to the energetic stabilization due to orbital mixing. This intuitive model was used to explain periodic differences in electron localization and the magnetic properties of the dialuminides. In fact, over the short UAl_2, $NpAl_2$, and $PuAl_2$ portion of the series, these materials are excellent examples of the failure of the Hill criterion for describing magnetic ground states since they have similar actinide–actinide distances (3.365 Å to 3.391 Å), yet very different ground states. The findings may also have important implications for controlling bond energies, phase stabilities, and mechanical properties of actinide intermetallics by enhancing overlap with the diffuse 6d orbitals.

Science objectives for 2017 – 2019:

- Measure changes in Al 3p – An 6d orbital mixing for the dialuminides with variable temperature Al K-edge XAS using a cryogenic STXM sample stage (CLS 10-ID1).
- Use oxygen K-edge XAS to probe correlations between in 5f orbital occupancy and O 2p – An 6d orbital mixing in the transplutonium sesquioxides, An_2O_3 (An = Am, Cm, Bk, Cf) for
- Apply insights developed from the study of well-defined molecules and extended solids towards the study of complex materials with three-dimensional structure and multiple components.

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2. Altman, A. B., Pacold, J. I., Wang, J., Lukens, W. W., Minasian, S. G. "Evidence for 5d-σ and 5d-π covalency in lanthanide sesquioxides from oxygen K-edge X-ray absorption spectroscopy" *Dalton Trans.* **2016**, *45*, 9948-9961. DOI: 10.1039/C6DT00358C
3. Altman, A. B., Pemmaraju, C. D., Camp, C., Arnold, J., Minasian, S. G., Prendergast, D., Shuh, D. K., Tyliszczak, T. "Theory and X-ray absorption spectroscopy for aluminum coordination complexes – Al K-edge studies of charge and bonding in (BDI)Al, (BDI)AlR_2, and (BDI)AlX_2 complexes" *J. Am. Chem. Soc.* **2015**, *137*, 10304-10316. DOI: 10.1021/jacs.5b05854

Selective Liquid-Liquid Extraction with Novel Anion Receptors

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Overall research goals: The overarching goal of this research is to understand the principles of molecular recognition and self-assembly leading to selectivity and control in ion separations in liquid-liquid extraction. It has been of particular interest to combine charge complementarity with size and shape complementarity under the expectation of enhanced selectivity through formation of charge-neutral, coordinatively-saturated organic-phase complexes. Two types of systems are examined here: calix[4]pyrroles [C4Ps] as versatile ion-pair receptors and 2) tailored guanidiniums. A pervasive question has been how to append lipophilic substituents to achieve functional extraction systems.

Significant achievements during 2015–2017: We have shown that the versatile C4P platform in the role of ion-pair receptor can effect extractions in three different ways: 1) direct ion-pair extraction (e.g., for CsCl), 2) synergistic anion exchange (e.g., for Cl^- exchange) in combination with lipophilic cations such as quaternary ammonium ions, and 3) synergistic cation exchange (e.g., for Cs^+) in combination with lipophilic acids such as *p-tert*-butylphenol (Fig. 1). To aid in extraction studies, a lipophilic C4P isomer bearing four unidirectional *n*-hexyl alkyl chains (Hx_4C4P) was synthesized in good yield. An equilibrium model of binding and extraction in which Hx_4C4P and C4P form ion-pair complexes with tributylmethylammonium chloride was determined by $^{36}Cl^-$ tracer distribution and NMR spectroscopy, revealing a direct relationship between NMR binding constants and extraction constants. EXAFS results provided the first direct evidence of the residence of Cs^+ ion in the C4P cup in the ion-pair extraction of CsBr.

Guanidinium type anion receptors featuring dual unidirectional N–H hydrogen-bond donors (HBDs) and a built-in positive charge prove effective for oxoanion extraction. Greater understanding of how to control the guanidinium binding conformation has been achieved with remarkable selectivity. Bis(pyridyl)guanidinium gains stability by internal hydrogen bonding to form a pseudo bicyclic structure in complexing the opposite edges of sulfate (Fig. 2), and a lipophilic analog is an effective sulfate extractant in competition with chloride. Although it proved difficult to directly attach HBD groups to the guanidinium core, imine links from condensation of aldehydes or ketones with bis(amino)guanidine allowed convenient derivatization. A resulting highly lipophilic bis(imino)guanidinium (BIG) exhibits unprecedented sulfate selectivity (Fig. 3), and a bis-amido BIG derivative featuring added HBD groups has been synthesized.

Science objectives for 2017–2019:

- Elucidate the selectivity implications for C4P in the role of synergist for cation exchange.
- Expand the functionality of guanidinium type anion receptors for liquid-liquid extraction, especially to learn how to append neutral HBD groups for greater complementarity.
- Understand the extraordinary sulfate selectivity of lipophilic bis(iminoguanidinium) anion receptors and the nature of the aggregated species in the solvent phase.

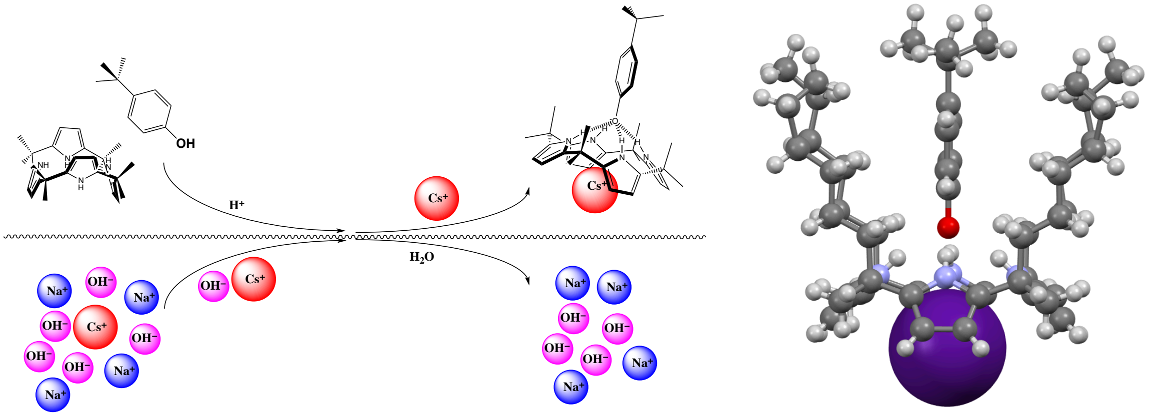

Figure 1. Left: Calix[4]pyrrole extracts Cs^+ ion by synergism of cation exchange by *p-tert-*butylphenol in which the effective receptor is the C4P-phenolate complex that binds the cation within the C4P cup. Right: Crystal structure of tetra-*n*-hexylcalix[4]pyrrole binding Cs^+ cation and *p-tert-*butylphenolate anion. This lipophilic C4P isomer is a much stronger synergist than the parent C4P.

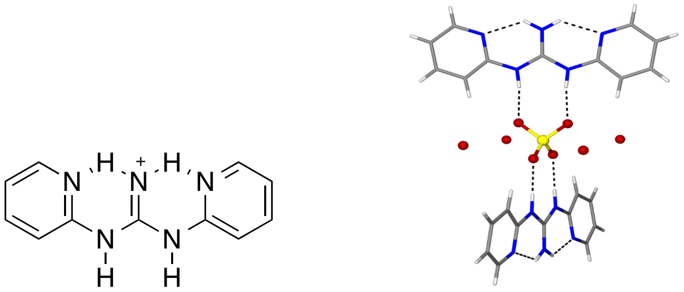

Figure 2. Left: *N,N'*-bis(2-pyridyl)guanidinium. Right: crystal structure of its 2:1 complex with sulfate (right); the O atoms of four waters are shown as red dots in the equatorial region of sulfate.

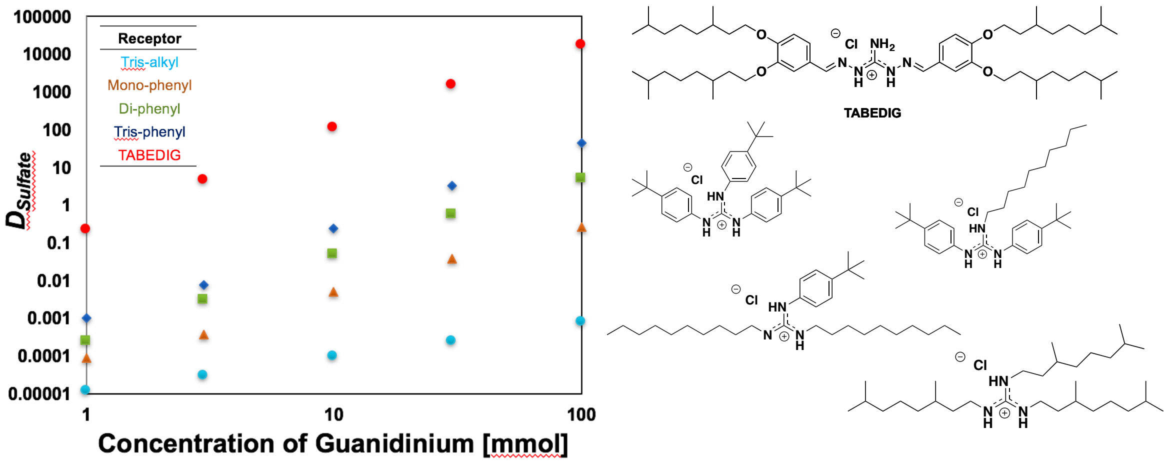

Figure 3. Tetra-alkyl-benyzlidene-diether-diiminoguanidinium (TABEDIG) exhibits unprecedented sulfate affinity and outperforms simple tri-substituted guanidiniums by more than three orders of magnitude. Aq = 10 mM NaCl, 0.1 mM Na_2SO_4. Org = 1,2-dichloroethane.

Structure, Bonding and Mechanism in f-Element Chemistry

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

Significant achievements during 2016-2017: The project was initiated in July 2016 focusing on *C*-tern MCD spectroscopy with Valerie Fleischauer (PhD student) and Dr. Yonaton Heit (post-doctoral scholar since September 2017, joint with Buffalo) with two new first year graduate students also joining the project in January 2017 for studies of transient species. To date, we have worked on the development of *C*-term MCD spectroscopy of f-element systems, including collaborative studies with Prof. Jochen Autschbach to develop theoretical tools for the simulation of *C*-term MCD spectra of f-element complexes. More recently, we have also initiated synthetic studies of thermally unstable uranium complexes as precursors for the study of their transient reaction chemistry in order to broaden our understanding of fundamental f-element chemistry to transient species. Two significant results have emerged:

1. The *C*-term MCD spectra of $(PPh_4)UCl_6$ in the charge-transfer region has been utilized as the initial test case for the application of *C*-term MCD spectroscopy to obtain electronic structure insight. In a collaboration with Prof. Jochen Autschbach, a theoretical framework for the interpretation of these spectra has been developed and a manuscript on this work is currently in the final stages of preparation.[1]

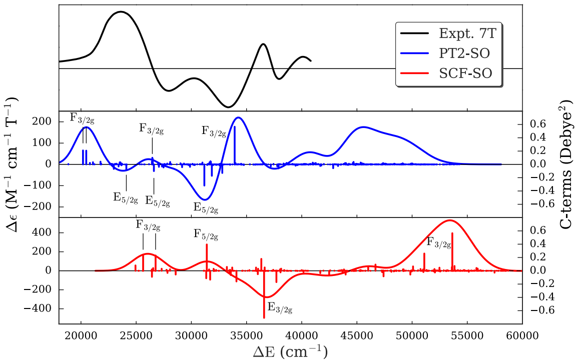

Figure 1. MCD spectrum of $(PPh_4)UCl_6$. Calculations at the SCF-CO and PT2-SO levels. The experimental spectrum (arbitrary units) was collected at 5 K.

These studies are currently being extended to One area of particular interest are low valent lanthanide complexes of the type [K(2.2.2-cryptand)][$(C_5H_4SiMe_3)_3Ln$] in collaboration with Prof. Bill Evans (UC-Irvine).

2. Our laboratory has developed novel methods for the preparation and, more importantly, handling of highly thermally unstable complexes for detailed characterization including X-ray analysis and reaction studies. We have utilized these capabilities to initiate studies on the isolation of transient and unstable uranium complexes in order to broaden our understanding of the types of complexes accessible at low temperature and their transformations. Initial studies have focused on homoleptic alkyl and aryl complexes that can subsequently serve as precursors to detailed studies of reduction pathways. Several complexes have been synthesized and structurally characterized, including UPh_6^{2-} formed from the reaction of UCl_4 and PhLi at -80 °C.[2] Initial studies have demonstrated that multiple new types of unstable uranium complexes are accessible with these capabilities which should continue to provide access to novel, transient uranium complexes.

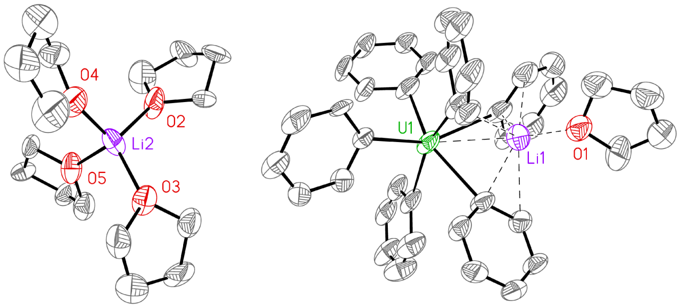

Figure 2. X-ray crystal structure of $[Li(THF)_4][(THF)LiUPh_6]$

Science objectives for 2017-2019:

- Expand C-term MCD spectroscopy development (and theoretical simulations) to lower symmetry uranium complexes (ex. D_{4h}), as well as f^2 and f^3 systems.
- Continued exploration of homoleptic alkyl and aryl uranium complexes that form from reactions of simple uranium salts and nucleophiles, focusing on the reduced uranium species formed along the subsequent reaction pathways to uranium metal.
- Expand studies of transient uranium complexes to intermediates in chemical transformations, including reduced species formed in-situ with KC_8 for subsequent reactivity.

Publications supported by this project 2016-2017

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

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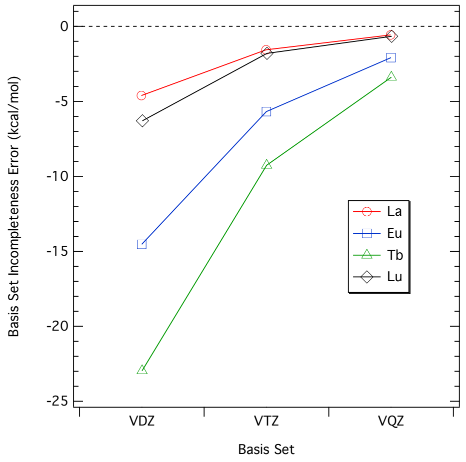
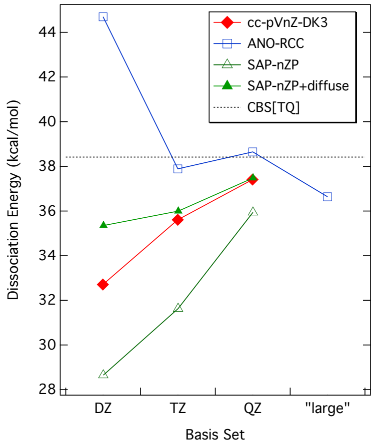
Overall research goals: Develop and apply a systematic quantum chemistry methodology that will be capable of providing chemically accurate thermochemistry (within 1 kcal/mol) and accurate spectroscopic properties (bond lengths to a few mÅ and vibrational frequencies better than 10 cm^{-1}) for molecules involving *f*-block elements, i.e., the lanthanides and actinides.

Significant achievements during 2015-2017:

1. Provided accurate theoretical predictions to assist in the observation and assignment of UFO/UFO$^-$, ThO$^+$ and ThC$^+$, and ThCl/ThCl$^+$ in collaboration with experiment (Wang, Armentrout, and Heaven, respectively).
2. Completed new correlation consistent relativistic (all-electron DK3 and X2C) basis sets for the lanthanide elements La – Lu and successfully applied the FPD composite approach to Ln ionization potentials and the thermochemistry of small Gd molecules.



Basis set convergence relative to the estimated CBS limits for the frozen-core CCSD(T) correlation energy

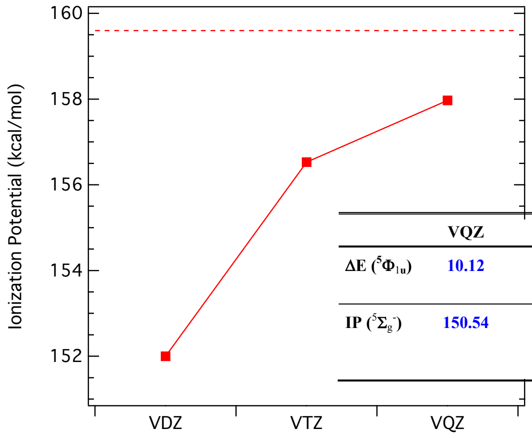


Comparison of the DK3-CCSD(T) basis set convergence of the dissociation energy of Gd_2

contributions for the 3rd ionization potentials of La, Eu, Tb, and Lu (in kcal/mol).

(kcal/mol). The rightmost basis set, "large", corresponds to the ANO-RCC-Large set.

3. Completed new correlation consistent relativistic (all-electron DK3 and X2C) basis sets for Ac and the transuranium elements (Np – Lr). The utility of these new sets was demonstrated by FPD composite calculations on the first three ionization potentials of the actinide atoms as well as the ionization potential and heat of formation of PuO_2.



Ionization potential and first excitation energy for PuO_2 (kcal/mol)

	VQZ	ΔCBS	ΔCV	ΔSO	ΔQED	ΔPW91	ΔZPE	Total
ΔE ($^5\Phi_{1u}$)	10.12	+0.77	–0.26	+4.02	+0.74	–1.40	+0.55	14.5
IP ($^5\Sigma_g^-$)	150.54	+0.83	+0.36	+6.91	+0.18	–0.80	+0.78	158.8 (162±3) (152)

4. Completed a suite of all-electron X2C relativistic basis sets for the transactinide Og atom.

5. Initiated a new thermochemical network for uranium oxides within the Active Thermochemical Tables (ATcT, see http://atct.anl.gov).

Science objectives for 2017-2019:

- Finish coupled cluster FPD study of actinyl cation-cation interactions, ranging from UO_2^+ to AmO_2^+, as well as investigate metal-metal bonding systems, particularly 5d transition metal-actinide molecules.
- Extend the study of the potential energy surfaces of $H_2O + AnO_2^+$ to transuranium elements.
- Populate thermochemical networks for Th through Pu by combining existing experimental data with new ab initio results (using the FPD composite method) on primarily their halides and oxides.
- Accurately determine the first 6-7 ionization potentials of the transuranium elements using the FPD approach with accurate multireference configuration interaction methods.
- Develop explicitly correlated F12 basis sets for the actinide elements and conventional X2C relativistic basis sets for the transactinide elements (already completed for Og).
- Continue to provide theoretical support for the experimental groups of Heaven and Armentrout.

Experimental Electron Density Distribution in Actinide Compounds – an Experimental Atoms in Molecules (AIM) Approach

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Overall research goals: The overall goal of this project is to characterize the bonding, particularly the covalent interactions, in compounds of thorium and uranium in various oxidation states, and to compare with bonding to cerium (III) and (IV). The metrics to be used are the experimentally determined electron density distribution and the properties derived from an analysis of its topology.

Methodology: Extremely accurate single crystal X-ray diffraction data is collected at very low temperature (< 20 K) to very high resolution ($\sin\theta/\lambda_{max} > 1.3$ Å^{-1}). The structural model is then refined against the observed data. Simple structural analysis refines positions of spherical atoms undergoing thermal motion. We are able to also refine the non-spherical electron density distribution for each atom using an atom based multipole expansion of the electron density, where the pole populations are refineable parameters, but radial functions are available from theory.

$$\rho_{atomic}(\mathbf{r}) = \rho_{core}(r) + P_v \kappa'^3 \rho_{valence}(\kappa' r) + \sum_{l=0}^{l_{max}} \kappa''^3 R_l(\kappa'' r) \sum_{m=-l}^{l} P_{lm} y_{lm}(\mathbf{r}/r)$$

For light atoms an averaged radial function is used, but for heavy atoms, several radial functions are required. We have used a superposition of up to five valence expansions to construct a satisfactory model for uranium. Topological analysis of the total electron density derived from the multipole expansion allows characterization of bond critical points, assignment of atomic charges, etc.

Significant achievements during 2015-2017: Significant improvements to our data integration and scaling programs have been introduced, including consideration of $\lambda/2$ contamination and its dependence on absorption and anomalous scattering. We have been collaborating with Dr. Christian Jelsch at the Université de Lorraine in France to develop and test a new version of his program MoPro to include terms up to $l = 6$, essential for the proper treatment of f electrons. In addition, the application of selective restraints into the refinements has proven useful. The following figure shows the deformation density (the total electron density minus the contribution from spherical atoms) and the residual density for the $[UF_6]^-$ ion.

Science objectives for 2017-2019:

- Crystallize and collect high resolution X-ray data on additional simple thorium and uranium compounds, such as UCl_4, simple salts of the MX_6^{n-} anions, as well as the cerium (III) and (IV) analogs, and refine appropriate multipole models for their electron density distribution.
- Evaluate the use of standard AIM descriptors for these heavy atom systems.

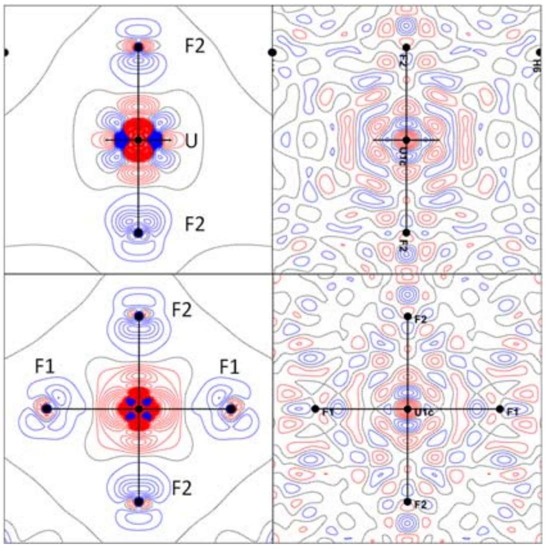

Figure 1. $[UF_6]^-$. Deformation density (left) and residual density plots (right) for the plane containing the U-F2 line and bisecting the F1-U-F1 angle (top) and for the F1-U-F2 plane (bottom). Contours are at +/-0.1 e^-A^{-3}. Blue contours denote positive charge density and red contours denote charge depletion.

Bond	ρ_b, $e^-Å^{-3}$	$\nabla^2\rho_b$, $e^-Å^{-5}$	*g, au*	*v, au*	*h, au*	$\|v\|/g$	h/ρ_b
U^V-F1 expt	0.93	7.68	0.1586	-0.2375	-0.0789	1.5	-0.57
U^V-F1theory	0.83	11.88	0.1703	-0.2173	-0.0470	1.28	-0.38
U^V-F2 expt	0.90	6.30	0.1439	-0.2224	-0.0785	1.55	-0.59
U^V-F2 theory	0.81	11.58	0.1642	-0.2083	-0.0441	1.27	-0.37
U^V-Cl1 expt	0.61	4.77	0.0850	-0.1205	-0.0356	1.42	-0.39
U^V-Cl1theory	0.57	3.72	0.0720	-0.1054	-0.0334	1.46	-0.40
U^V-Cl2 expt	0.57	5.11	0.0823	-0.1117	-0.0293	1.36	-0.35
U^V-Cl2 theory	0.58	3.77	0.0739	-0.1087	-0.0348	1.47	-0.41
U^V-Cl3 expt	0.62	4.82	0.0865	-0.1230	-0.0365	1.42	-0.40
U^V-Cl3 theory	0.57	3.72	0.0720	-0.1054	-0.0334	1.46	-0.40
U^{VI}-Cl expt	0.49	3.28	0.0585	-0.0829	-0.0245	1.42	-0.34
U^{VI}-O expt	1.70	15.77	0.3962	-0.6288	-0.2326	1.59	-0.93

Table 1. Bond critical point properties for U-X bonds.

Publications supported by this project 2015-2017

1. Gianopoulos, C.G.; Zhurov, V.V.; Minasian, S.G.; Batista, E.R.; Jelsch, C.; and Pinkerton, A.A., "Bonding in Uranium(V) Hexafluoride Based on the Experimental Electron Density Distribution Measured at 20 K," *Inorg. Chem.*, **2017**, 56, 1775−1778, DOI: 10.1021/acs.inorgchem.6b02971.

2. Gianopoulos, C.G.; Chua, Z.; Zhurov, V.V.; and Pinkerton, A.A., "λ/2 Contamination in X-ray diffraction data – the impact of heavy atoms," *J. Appl. Cryst.*, in press, https://doi.org/10.1107/S160057671700317X.

Examination of actinide chemistry at solid-water interfaces to support advanced actinide separations

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	Prof. Apparao Rao, Physics and Astronomy, Clemson University
	Prof. Ramakrishna Podila, Physics and Astronomy, Clemson University
	Dr. Daniel Olive, University of California – Berkeley

Overall research goals: The overarching objectives of this work are to provide a mechanistic conceptual model and a quantitative sorption model describing actinide behavior at solid-water interfaces based on a molecular level understanding of the chemical processes involved. Particular attention is focused on understanding underlying mechanisms of actinide sorption to differing solid phases including frequent observations of hysteretic or irreversible sorption and quantifying surface mediated redox reactions.

Significant achievements during 2015-2017: We have continued to work with various model solid phases to probe changes in actinide speciation at solid:water interfaces. Work over the past few years has focused on graphene oxide, titanomagnetite, and rutile.

Actinide interactions with graphene oxide

We have published one paper and will have three more submitted by May 2017 analyzing actinide sorption to graphene oxide. Using batch sorption work, we have developed a quantitative, surface complexation model of actinide binding to carboxyl and sulfone functional groups on the graphene oxide surface. These data show that graphene oxide has a remarkable capacity for binding actinides. A strongly correlated linear free energy relationship (LFER) was developed to relate actinide complexation with carbonate in aqueous systems with actinide binding with carboxyl functional groups. The model for Eu(III) and U(VI) binding to graphene oxide was published in 2016 (Xie et al., ES&T, 2016). The manuscript for the Np(V) and Th(IV) system showing the LFER will be submitted by April 2017.

In an attempt to understand the energetic driving forces behind strong actinide partitioning to graphene oxide and other solid phases, we have performed isothermal titration microcalorimetry experiments to measure the enthalpy of actinide binding to graphene oxide. Analysis of the calorimetry data using the surface complexation model described above, we have determined the enthalpy of Eu(III) and U(VI) sorption to graphene oxide as 13 kJ/mol and 17.5 kJ/mol, respectively.

Our work with plutonium has shown reduction of Pu(V) to Pu(IV) on a wide range of mineral surfaces (Powell, 2016). We have also demonstrated that Pu(V) will reduce to Pu(IV) on graphene oxide surfaces in the absence of an obvious electron donor (Wylie and Powell, 2017). Therefore, we have an interest in demonstrating that the reduction potential of a sorbed species is indeed different than that of the aqueous ions. Cyclic voltammetry studies using graphene oxide electrodes has shown the U(VI)/U(V) reduction potential to be approximately 0.3V higher than the aqueous reaction (Bliznyuk et al., 2017). We will continue this work with Pu on metal oxide electrodes to gain a deeper understanding of the autoreduction of Pu(V) observed on many surfaces.

Actinide interactions with rutile

Solid-water interface reactions were carried out using actinides in multiple oxidation states (Am(III), Pu(IV), Np(V), and U(VI)) in dependence of pH, temperature, and ionic strengths. This work has utilized batch sorption experiments, ATR-FTIR spectroscopy, and isothermal titration microcalorimetry. The results show that actinide sorption increases with increasing temperature and verified that sorption is an endothermic process. Thus, frequently observed strong sorption of the actinides appears to be an entropically driven process that we propose is due to the dehydration of the actinide ion and mineral surface upon sorption. An example of the calorimetry data is shown in Figure 1 where the sorption of U(VI) to rutile was monitored at 25 °C.

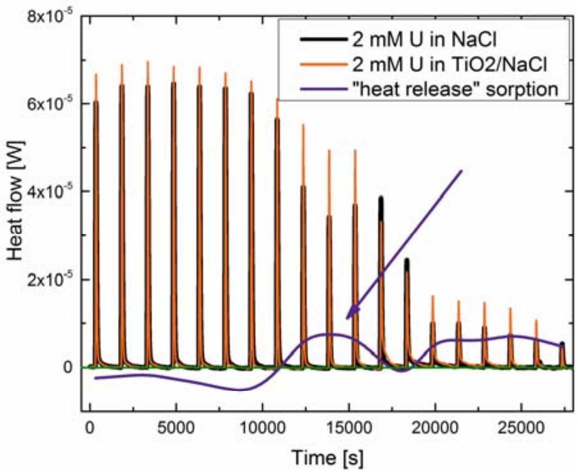

Figure 2: ITC acid-base titrations of U(VI) [2 mM] in NaCl (10 mM; black) and with TiO_2 (5 g/L) in NaCl (10 mM; orange) were performed. Net heat release of the U(VI) sorption process is shown (purple) (right).

Science objectives for 2015-2017:

- Examine the enthalpy of Np(V), U(VI), Th(IV), and Pu(IV) sorption to rutile and graphene oxide using isothermal titration calorimetery
- Characterize actinide speciation on graphene oxide and rutile surfaces using ATR-FTIR, XANES, and EXAFS spectroscopy
- Continue development of quantitative models describing actinide sorption to these phases. The models will include incorporation of an "aging" factor to describe the hysteretic or irreversible sorption

Publications supported by this project 2015-2017

Xie, Y, Helvenston, E., Shuller-Nickles, L., Powell, B. A., "Surface Complexation Modeling and Quantum-mechanical Calculations of Eu(III) and U(VI) Interactions with Graphene Oxide" Environmental Science and Technology, 2016, 50(4), 1921-1827.

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Bliznyuk, V.N., Conroy, N., Xie, Y., Rodila, R., Rao, A., Powell, B. A. "Modification of redox reactions of uranyl due to its interaction with graphene oxide surfaces: physical versus chemical factors, Submitted, Applied Materials and Interfaces, 2017

Wylie, E. M., Powell, B. A., "Pu(V) adsorption and reduction on graphene oxide" Submitted, Environmental Science and Technology, 2017

Actinide Solution Chemistry:
Thermodynamics and Structure of Actinide Complexes in Solution

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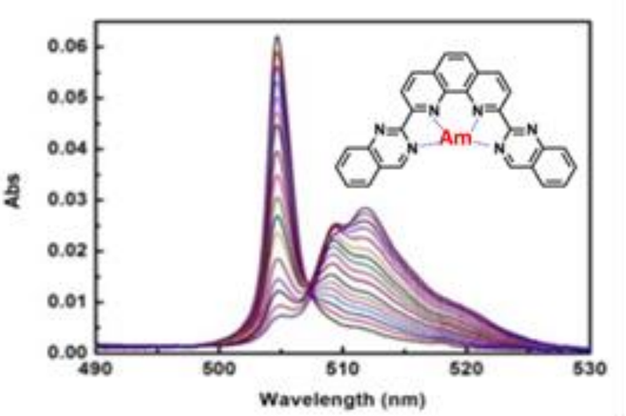
Overall research goals: (1) To improve the fundamental understanding of thermodynamic principles governing the chemical behavior of actinides in solution. (2) To reveal the structures of actinide complexes in solution in comparison with those in solids, and help to understand the thermodynamic trends as well as the nature of f-orbital bonding in actinide complexes.

Significant achievements during 2014-2016:

1. Thermodynamics of the complexation of trivalent actinides (Am(III), Cm(III)) and lanthanides (Nd(III), Eu(III)) with "softer" donor ligands that have potential use in actinide/lanthanide separations was studied under identical experimental conditions to compare the Gibbs free energy and enthalpy of complexation between the actinides and lanthanides. Results have clearly demonstrated that An(III) forms stronger complexes with N- and S- donor ligands than Ln(III), resulting from more exothermic enthalpy of complexation for An(III) than Ln(III) due to higher co-valence in the An(III) complexes.



2. In conjunction with DOE NE project of the recovery of uranium from seawater, research efforts under the BES program helped to synthesize a rare non-oxido vanadium(V) complex with glutaroimide-dioxime, $Na[V(L)_2]$, that formed in and crystalized from aqueous solutions, and unprecedentedly demonstrated the reaction mechanism by multiple techniques including $^{1}H/^{13}C/^{51}V$ NMR, EPR, and ESI/MS. The data helped to interpret the extremely strong competition of vanadium with uranium for sorption that was difficult to understand before these discoveries.

Science objectives for 2017-2018:

- To develop calorimetric methodology to directly measure the enthalpy data for actinide interactions in two-phase systems, including liquid-liquid solvent extraction, solid-liquid dissolution, and solid-liquid sorption. The unique precision solution calorimeter at LBNL provides the possibility of conducting such experiments in a temperature range from 25 to 80°C. Fundamental thermodynamic data including enthalpy and heat capacity of actinide species will provide insight into the strength and nature of actinide complexation, as well as help interpret and predict the chemical behavior of actinides in separations and environmental transport.
- To explore new and unusual actinide complexes forming in and crystalized out from aqueous solutions. Built on our recent results on a rare non-oxido vanadium(V) complex that formed in and crystalized out from aqueous solution, efforts have been made to synthesize non-oxido neptunium(V) complex in aqueous solutions but were unsuccessful. Such efforts will be continued by tuning the experimental conditions (L/M ratio, acidity, redox control, kinetics, etc.).

Publications supported by this project in 2015-2016 :

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The f Elements in Bondage: From Basics to Business

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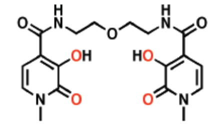
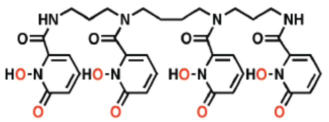
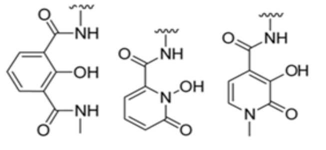

5-LIO(Me-3,2-HOPO)

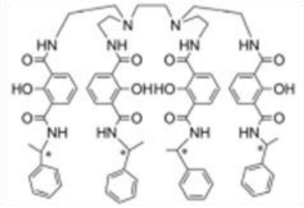

3,4,3-LI(1,2-HOPO)

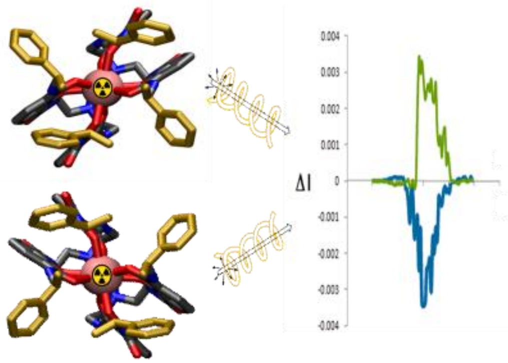

IAM 1,2-HOPO 3,2-HOPO

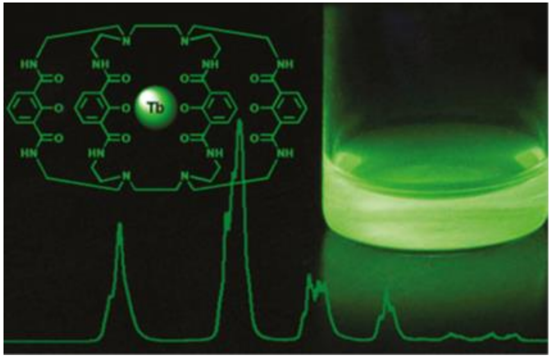
Selective complexation of metal ions is a matter of fundamental science and of practical application. Nature provides many examples of selectivity in metal complexation and transport that can be used to design selective chelators. However, the lanthanides and actinides, because of their variable coordination number, highly ionic nature and lability, provide a particular challenge to the chemist. The lanthanides and actinides are oxophiles and so selective and strong chelators for them should contain oxygen donors.

In a 30 year program at LBNL, highly selective actinide sequestering agents were developed using the siderophore hypothesis, [1] based on the fact that the toxicity of Pu(IV) is due to its biochemical similarity to Fe(III). Modeled after the siderophore enterobactin, actinide sequestering agents are composed of catecholate and HOPO chelating subunits attached to various molecular backbones via amide linkages. Some of these compounds, such as those shown (with the coordinating atoms in red), are being developed for clinical use in the case of human contamination by the actinides. [2,3]

A large family of multidentate sequestering agents based on three types of ligand groups has been developed. These groups are shown above right. In each case the wavy line denotes a point of attachment to a skeletal group of a larger molecule. Remarkably, these groups are often very effective antenna ligands for photoexcitation of the f element center. This was first found for the IAM complexes of Tb(III) (discussed later). Chiral derivatives of the IAM family of ligands are able to generate circularly polarized luminescence from their metal complexes. Using several different chiral chelating ligands, the world’s first actinide Circularly Polarized Luminescence (CPL) spectra with curium (III) complexes were reported.[4]

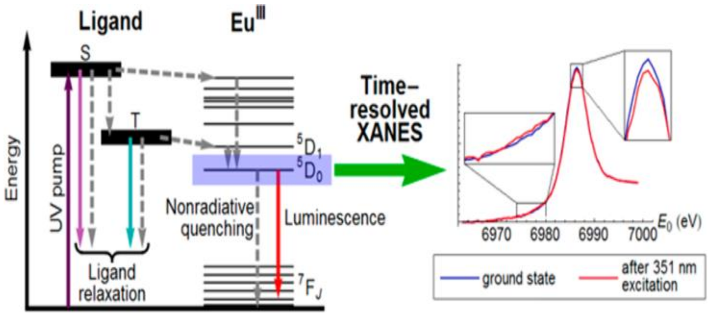


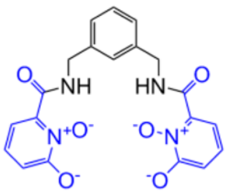




The actinide luminescent studies were preceded by those for lanthanides. Highly luminescent Ln(III) complexes (with Ln = Tb, Eu) for applications in biotechnology have been developed. The 2-hydroxyisophthalamide (IAM) chelate for Tb(III) exhibits highly efficient emission ($\Phi_{total} > 50\%$), large extinction coefficients ($\varepsilon_{max} > 20{,}000\ M^{-1}\ cm^{-1}$), and long luminescence lifetimes (τ_{H2O} > 2.45 ms) at dilute concentrations in standard biological buffers. Tri-macrocyclic Tb(III) complexes in this class (figure) display long-term stability, with little if any change in their spectral properties (including lifetime, quantum yield, and emission spectrum) over time or in different chemical environments. Functionalized derivatives with terminal amine, carboxylate, and N-hydroxysuccinimide groups suitable for derivatization and protein bioconjugation have also been developed and are in use commercially for human, veterinary and forensic diagnostic assays as well as new drug development.[7]

However, the remarkable properties of these compounds begs the question of why they are so efficient. That is the subject of the current project, which is based on the Berkley campus but continues collaboration with Dr. David Shuh and coworkers at LBNL. We have begun with a series of europium complexes that show a high variability of quantum yield in their $Eu(L)_2$ complexes. The preliminary experiments show the feasibility of this approach. [8] Now we propose to experimentally identify the dominant energy transfer process that enables ligand-to-metal energy transfer in a set of high-quantum-yield lanthanide complexes. Second, we propose studies of the effects of bonding and coordination on the efficiency of the energy transfer. The physical properties of the Ln 4f shell pose unique experimental challenges that are being addressed with a combination of UV/visible and X-ray spectroscopy, including time-resolved measurements with resolution ranging from femtoseconds to microseconds. We have an ideal, modular, ligand library, and we have access to the spectroscopic probes needed to address the important energy transfer mechanisms in these materials. The long excited state lifetimes of the lanthanides make them ideal candidates for time-resolved X-ray spectroscopy that can examine the electronic structure of the excited state.





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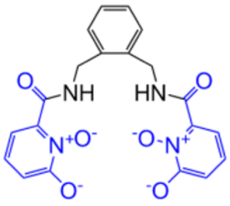

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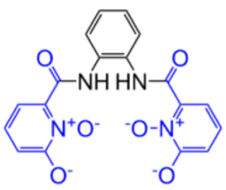

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Possible mechanisms for the sensitizer to lanthanide energy transfer include resonant Coulomb interactions, including Förster dipole−dipole transfer, or charge exchange (Dexter transfer), which involves wave function overlap. We speculate that the high quantum yields in these systems are due to Dexter transfer, which is in turn due to ligand field effects caused by increased 5d character in the 4f excited state.

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A Physicochemical Method for Separating Rare Earths: Addressing an Impending Shortfall

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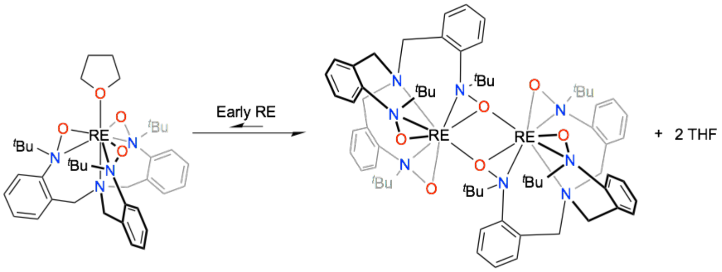
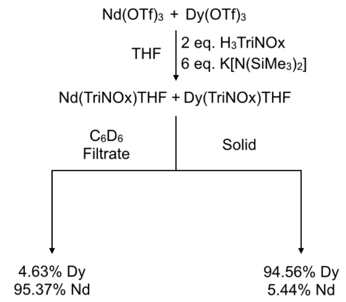
Overall research goals: The overall goal of this project is to is to develop targeted separations chemistry for 4f-elements based on molecular design principles and/or redox chemistry.

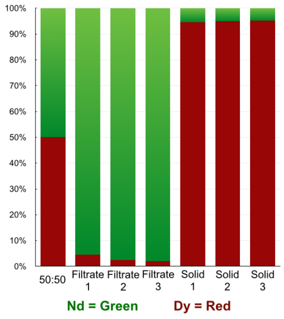
Significant achievements during 2015-2017: This Early Career Project ended in 2016 and a new project will start in 2017. The end period of the project resulted in 19 publications (*vide infra*), with 32 total for the project. The most significant results on rare earth separations are summarized below.

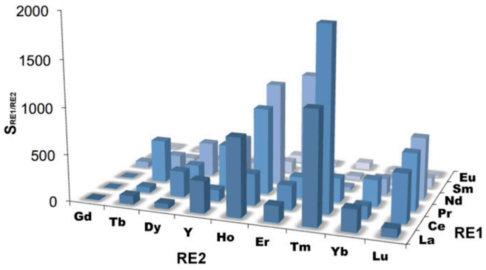
A self-association equilibrium was discovered comprising RE(TriNOx)THF (monomer) and $[RE(TriNOx)]_2$ (dimer) species, RE = La–Sm, which derived from rare earth metal cationic radius and solvent polarity. Through the use of ^1H-NMR spectroscopic titration experiments the values of the equilibrium constants for these dimerization equilibria in benzene were determined and correlated to RE metal cationic radius.



Solubility between the RE(TriNOx)THF and $[RE(TriNOx)]_2$ species were exploited to achieve separations of 54 pairwise combinations of early/late lanthanide binary mixtures, with the largest separations factor $S_{M1/M2}$ approaching 2000. For the technologically critical Nd/Dy mixtures S = 359 was obtained starting from mixtures of Nd and $Dy(OTf)_3$ salts. Stripping of the $TriNOx^{3-}$ ligand with oxalic acid enabled a ligand recycling process and allowed for the isolation of pure $RE_2(C_2O_4)_3$ salts and the recovery of $H_3TriNOx$, which could be used in subsequent chemistry.







Science objectives for 2017-2019:

- Develop separations chemistry based on redox and photoredox processes.
- Explore electronic structure of lanthanide complexes of redox active ligands.
- Design and explore ligands that produce oligomerization equilibria connected to solubility that can be leveraged for separations.

Publications supported by this project 2015-2017

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Novel Wavefunction Approaches for Studying Actinides and Other Heavy Elements

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Dr. Matthew R. Hermes, Postdoctoral Researcher (partial support)
Dr. Ireneusz W. Bulik, Graduate Student (PhD June 2015)
Dr. Alejandro J. Garza, Graduate Student (PhD July 2016)
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Overall research goals:

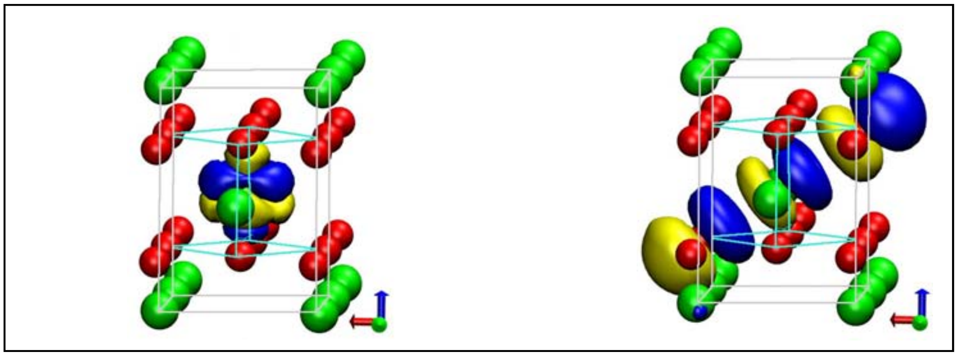
The methodological development and computational implementation of quantum chemistry methods for the accurate calculation of electronic structure and properties of molecules, solids, and surfaces containing actinides and other heavy elements.

Significant achievements during 2016-Present:

We implemented a combination of singlet-paired coupled cluster theory (CCD0) for dealing with static correlation with density functionals for dynamic correlation and applied it to actinide molecules [1]. CCD0 is a simplification of coupled cluster doubles that relinquishes a fraction of dynamic correlation in order to be able to describe static correlation. Combinations of CCD0 with density functionals that recover specifically the dynamic correlation missing in the former were developed recently. In this work, we assessed the accuracy of CCD0 and CCD0+DFT as compared to well-established quantum chemical methods for describing ground-state properties of singlet actinide molecules. The f^0 actinyl series (UO_2^{2+}, NpO_2^{3+}, PuO_2^{4+}), the isoelectronic NUN, and thorium (ThO, ThO^{2+}) and nobelium (NoO, NoO_2) oxides were studied. In general, restricted single-reference coupled cluster theory truncated to single and double excitations accurately describes weakly correlated systems, but often breaks down in the presence of static or strong correlation. Good quality coupled cluster energies in the presence of degeneracies can be obtained by using a symmetry-broken reference, such as unrestricted Hartree-Fock, but at the cost of good quantum numbers. A large body of work has shown that modifying the coupled cluster ansatz allows for the treatment of strong correlation within a single-reference symmetry-adapted framework. Our CCD0 method is one such model, which recovers correct behaviour for strong correlation without requiring symmetry breaking in the reference. In work supported by this grant [2], we extended CCD0 for application to open shell molecules via restricted open-shell singlet-paired coupled cluster singles and doubles (ROCCSD0). The ROCCSD0 approach retains the benefits of standard coupled cluster theory and recovers correct behaviour for strongly correlated, open-shell molecules using a spin-preserving ROHF reference. In singlet-paired coupled cluster, eliminating the triplet-pairing channel recovers reasonable qualitative behaviour for strong correlation at the cost of a decreased description of dynamical correlation in weakly correlated situations. This behaviour seems to hold for both closed- and open-shell systems. In other work supported by this grant [3], we explored the coupling of the singlet- and triplet-pairing channels of the doubles amplitudes and attempted to recouple them in order to recover dynamical correlation without reintroducing catastrophic failure due to strong correlation. In the weakly correlated regime, these pairing channels are only weakly coupled, and a simple recoupling scheme gives good results. However, as strong correlation dominates, the coupling strength between the singlet- and triplet-pairing channels increases, making it difficult to perturbatively recouple them in this regime.

Science objectives for 2017-2018:

Overall, progress has been substantial and we are very happy with our recent achievements. We expect in 2017-2018 to continue progressing toward the objectives outlined in our proposal. One major focus will be on applying accurate ***wavefunction*** methods to solid state actinides using the quantum embedding techniques (DMET/DET) previously developed in our group with HEC funding. The first major obstacle for *ab initio* modelling of realistic materials using these ideas is reliable code for obtaining Wannier functions needed in the Hamiltonian projection of fragment and bath. We have achieved significant progress on this front (unpublished, see Figure below). The second obstacle is a reliable impurity solver for dealing with large number of electrons and orbitals (e.g., solid UO_2). Here our CCD0+DFT theory looks very promising. But alternative solvers based on the combination of coupled cluster theory with symmetry breaking and restoration techniques are becoming available in our group and will be employed for the solid state modelling pertinent to this proposal and alluded above.



Wannier Functions depicting U 5*f* and O 2*p* bands near the Fermi energy. These localized orbitals are needed in first-principles calculations of solid UO_2 using quantum embedding and novel coupled cluster methods appropriate for multireference systems as impurity solver.

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Functional Ion Pair Receptors Targeting Cesium, Lithium, Sulfate and Uranyl
(DE-FG02-01ER15186)

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Overall research goals: Synthesis and study so-called ion pair receptors, systems that bind concurrently both anions and cations within a single molecular framework. Within this broad paradigm, particular emphasis will be placed on 1) new strapped calixpyrroles for the recognition and extraction of lithium salts, 2) chromophore-modulated calixpyrroles as sensors for CsCl, 3) new sulfate anion extractants, and 4) expanded porphyrin-based receptors for the uranyl cation.

Significant achievements during 2015-2017: Good progress towards all four sub-goals was made during the time since the last Contractors Meeting in the spring of 2015. Particular progress was made in the further development of modified calixpyrroles as extractants for targeted ions and a new set of expanded porphyrins has been prepared that shows promise for uranyl and possibly related actinide cation recognition was made. A new type of lanthanide MOF was prepared that acts as a "ship in a breakable bottle" was also constructed. Control of function, including both binding and release, through competitive modulation of the external environment remains a recurring theme.

1. Several new calixpyrrole ion pair receptors based on the use of specific capping elements were generated. Using these, it proved possible to prepare the first-ever (to our knowledge) working extractant for the lithium cation (as its nitrite salt). This chemistry is shown in Figure 1. Gratifyingly, this work was the initial trigger that led to a C&E News article highlighting the importance of extraction and which called attention to the work of several other BES-supported programs: "Extracting inorganic ions organically," Jyllian Kemsley, C & E News, **2016**, *94(24)*, 18-19.

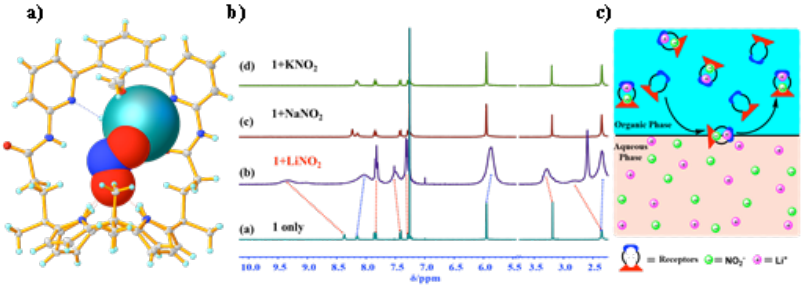

Fig. 1 a) Single crystal structure of the complex **1**•LiNO$_2$, b) ^{1}H NMR spectral changes associated with the liquid-liquid extraction of LiNO$_2$ from D$_2$O into a CDCl$_3$ phase by receptor **1**, and c) cartoon representation of the liquid-liquid aqueous-organic extraction of LiNO$_2$ by the hemispherand calix[4]pyrrole **1**.

2. A first generation chromophore-appended calixpyrrole ion pair receptor capable of acting as a sensor for cesium salts was prepared. It allowed for the concurrent extraction and color-based sensing of the cesium cation under both liquid-liquid and liquid-solid extraction conditions.

3. A new expanded porphyrin that contains pyridines as well as pyrroles was prepared and, in as-yet-unpublished work, shown to form very selectively (relative to transition metal and lanthanide cation salts) a stable uranyl complex. Work with collaborators is ongoing to extend this effort past the uranyl cation to include neptunyl cation precursors.

4. The ability of one particular functionalized calixpyrrole to serve as a backbone for MOF preparation was explored in the context of lanthanide-based frameworks (Fig. 2). Control over structure could be achieved by using fluoride anion to release the lanthnide (as a salt), without destroying the calixpyrrole. Extensions to other cations are underway.

Science objectives for 2017-2019:

- Continue to develop calixpyrrole-based cation sensors, including those that can work in more competitive environments.
- Create receptors that can target more than one ion pair concurrently. Focus particular attention on sulfate anion salts
- Develop additional ion pair receptors for lithium salts. Demonstrate their utility in the extraction of LiCl under competitive, real world conditions.

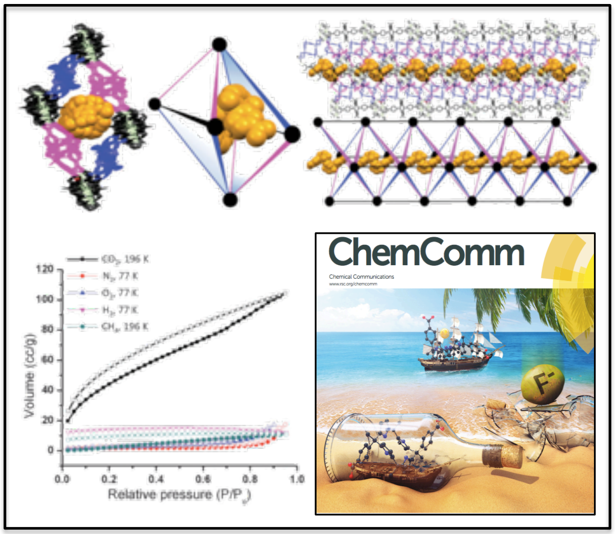

Fig. 2. Representations of the non-complexed calix[4]pyrrole within the cage-like pore (upper left). Side view of the 1-dimensional mesoporous channels containing free ligand (upper right). Gas sorption behavior for test gases (lower left) and cover image of *ChemComm* (lower right).

- Pursue the idea of decreasing the pH of aqueous solutions via the extractive removal of NaOH.
- Explore the use of less conventional molecular forms, including sol-gel transitions, to achieve sensing and extraction.
- Continue efforts to create new, redox active receptors for the uranyl cation. Extend the efforts to the transuranics.

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Soft X-ray Synchrotron Radiation Spectroscopy of Actinide Materials

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Overall research goals: The research objectives are to elucidate and understand the roles of the 5f electrons in the chemical bonding of the actinides; characterization of the electronic structures of actinide materials to understand reactivity; and the development of soft/tender energy X-ray synchrotron radiation techniques for actinide investigations.

Significant achievements in 2015-2017: Several investigations focused on soft X-ray absorption spectroscopy (XAS) measurements at the Molecular Environmental Science (MES) Beamline of the Advanced Light Source (ALS) with the scanning transmission x-ray microscope (STXM) and were coupled to theory/computation to obtain electronic structure information from a diverse range of radioactive materials with light atom constituents. These studies have included carbon and nitrogen ligand K-edge spectroscopy studies of the f-element ferrocyanides, as well as a novel study of porous aromatic frameworks that exhibited promise as separations materials for f-elements.[3,5,9] The complementary use of soft XAS and X-ray emission spectroscopy (XES) at the oxygen K-edge were utilized for studies on actinide dioxides (UO_2, NpO_2, PuO_2) and coupled to theory/computation to determine the level of electron correlation in these materials.[2] Soft XAS studies were also conducted at the actinide $N_{6,7}$-edges (4f → 6d transitions) of the actinide oxides that included the first data obtained from NpO_2, PuO_2, and UO_3.[4] The resulting spectra were evaluated within the same theory/computation framework used for the actinide dioxides in Ref. 2. Figure 1 shows and compares spectra obtained from the actinide $N_{6,7}$-edges from the actinide dioxides.

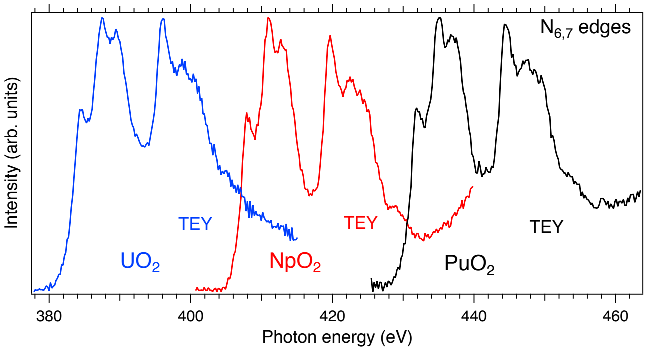

Figure 1. X-ray absorption spectra at $N_{6,7}$ (4f-to-5g, 6d transitions) edges of UO_2, NpO_2, and PuO_2, measured in the total electron yield (TEY) mode.[4]

Science objectives for 2015-2017:

- STXM investigations will be performed on transuranic materials and complexes to determine electronic structure complemented by theoretical calculations. As materials preparation capabilities mature, more transuranic materials produced from LBNL will be examined. New studies will be on light atom K-edge spectroscopy of actinide nitrides, borides, carbides, specific fluorides, separations complexes, mixed light element compounds, and heavy actinide oxides.
- XES will be re-kindled at the ALS as capabilities return to examine actinide materials and complexes with light atom constituents for complementary electronic structure determinations. The development of unique ALS spatially-resolved capabilities for tender and structural X-ray actinide studies will continue.
- Lab efforts will develop of new growth systems and infrastructure for spectroscopic projects. New preparation methods such as focused ion beam (FIB) will be implemented.

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Determining metal coordination and energetics in solution

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Overall research goals: Critical to modelling the behavior of dissolved ions in solution is a fundamental understanding of the competing equilibria that influence the complexes that form, particularly their relative energetics. Among the factors to be considered when describing the complex chemistries involved are the ion-ion correlations that develop. For actinide ions, the correlations include predominantly metal-ligand, metal-solvent, and solvent-ligand. We previously developed a novel approach to analysing X-ray scattering data to produce metal-centric, difference-pair-distribution functions (dPDF). Attempts by theorists to reproduce experimental results from even the simplest of these systems, Th^{IV} in acidic aqueous Br^- solutions, have largely been unsuccessful, suggesting the need to specifically include the anion in the calculations. In order to do this, anion-solvent interactions must be understood and quantified. Our specific objective is to extend our dPDF approach to X-ray scattering data analysis to include anion-solvent interactions and also metal speciation in non-aqueous solvents.

Significant achievements during 2015-2017:

Speciation of anion in aqueous solution. In general there is much less known about anion coordination environments and their concentration dependence than for their cationic counterparts, thus providing little guidance for the theorist wishing to include all solution components in their solution calculations. To address this issue we have performed high-energy X-ray scattering (HEXS) experiments on a series of aqueous HBr solutions, spanning a wide concentration range, and developed a methodology for quantitatively determining the central anion (Br) coordination environment. The results of our efforts are presented in Figure 1. Using this approach we were able to determine the number of coordinating waters, the Br-O correlation distances, and some information about Br-H interactions. Our results show that the coordination environment of Br is relatively invariant to solution conditions, in contrast to our general findings for cation behaviors in solution.

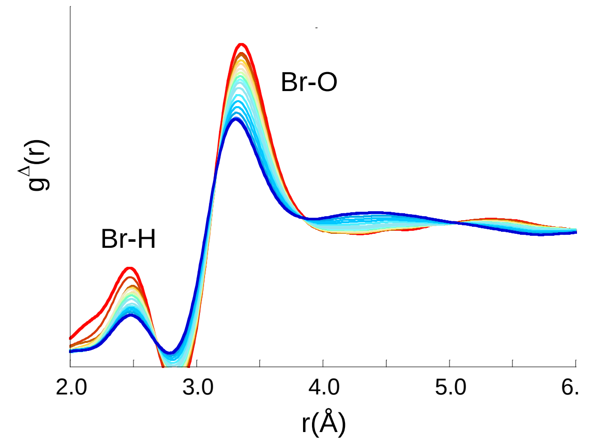

Figure 1. dPDF data obtained from a series of aqueous HBr solutions with Br concentrations ranging from 0.5 to 9 molal.

Science objectives for 2017-2019:

- Use the metrical information obtained about the anion coordination environment to optimize force-fields and then calculate the full coordination environment of Th^{IV} in aqueous solution, explicitly including anions in appropriate concentrations.

- Extend this new approach used to model $\mathrm{Th^{IV}}$ data in $\mathrm{Pu^{IV}}$ bromide solutions to determine the underlying structure(s) of Pu-Br complexes for comparison with thermodynamic stability constants and free energies. The results from the two systems will be compared with respect to details of the competition between $\mathrm{Br^-}$ and solvent waters for metal ligation. Later aspects of this approach will include performing similar measurements on $\mathrm{Cl^-}$ systems to assure a robust interpretation of the relative forces impacting $\mathrm{An^{IV}}$ ligation.

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Impact of Actinide Solution Speciation Solid Precipitates

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Valérie Vallet and Florent Réal, CNRS, University of Lille, France.

Overall research goals: The HESS group's efforts are largely focused on quantifying a metal ion's speciation in solution and to put it in the context of competing equilibria and their associated free energies. A component of this effort naturally extends to the role played by preformed solution correlations and complexes on the formulation and structure of resulting solid precipitates. Taking advantage of our development of high-energy X-ray scattering (HEXS) as a tool for quantitatively identifying polyatomic solution correlations, and coupling it with available X-ray single-crystal and surface reflectivity studies, we are striving to understand how a metal ion's solution speciation correlates with the structure of the solids that precipitate. Of particular recent focus has been the role of redox chemistry on surface-mediated actinide precipitation.

Significant achievements during 2015-2017:

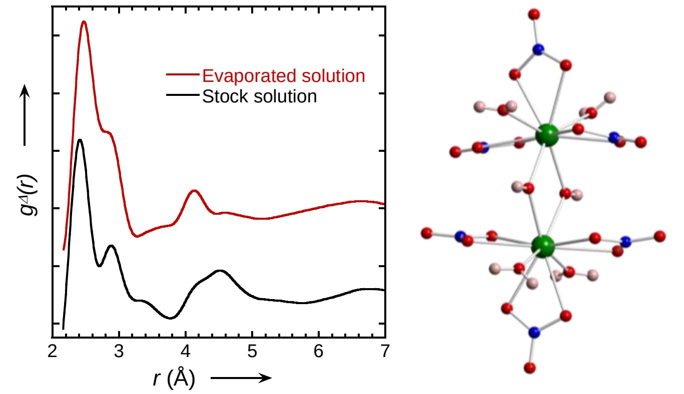

Figure 1. (Left) Metal-centric dPDF patterns, obtained from HEXS data, depicting changes in correlations during evaporation of an acidic Pu nitrate solution. The peaks in the pattern represent Pu-nitrate, Pu-Pu, or Pu-solvent correlations. Their assignments are guided by single-crystal structural refinements of the Pu molecular dimers (Right) that precipitate from solution.

Changing plutonium nitrate speciation in solution. The slow evaporation of acidic Pu nitrate solutions results in the precipitation of crystals built from discrete $Pu_2(OH)_2(NO_3)_6(H_2O)_4$ di-hydroxo bridged dimers. Each Pu is capped with three bidentate-bound nitrates, which limit further polymerization. High-energy X-ray scattering (HEXS) data, obtained from mother liquors at various stages during evaporation, were analysed to produce the metal-centric, difference pair-distribution functions (dPDF) shown in Figure 1. By comparing the correlations obtained from a single-crystal structure solution of the dimer, it is possible to assign the species present and to quantify changing speciation as the solution evaporates. We learn that nitrate exhibits only bidentate coordination to the Pu and that Pu dimers are present only a very low concentration, even after Pu reaches a concentration of 405 mM.

Comparing the roles of reduction and polymerization of Pu^{VI} and U^{VI} on the formation of surface adsorbates. In contact with a non redox-active phyllosilicate surface, aqueous solutions containing either PuO_2^{2+} or UO_2^{2+} formed very different adsorbate complexes. In neither case was the -yl(VI) species identified on the surface. For the case of Pu, results from X-ray surface-scattering studies were consistent with the formation of an adsorbed, concentration-enhanced layer of reduced Pu^{IV}. Together with its distribution profile perpendicular to the planar surface, the result is similar to those obtained from our previous studies for the same surface in contact with a solution containing either Pu^{III} or PuO_2-like nanoparticles. In contrast, U showed no evidence of surface adsorption. The significant difference in surface coverage between the two actinyl(VI) solution ions is consistent with both the more facile standard reduction potential for the plutonyl(VI) to Pu^{IV} reaction and the subsequent hydrolysis and condensation to PuO_2-related nanoparticles. A similar reaction scheme does not occur for U under our solution conditions in the presence of a redox-inactive surface. Assuming the major difference in the two systems can be attributed to differences in their formal reduction potentials, as opposed to the sorption potentials of the hexavalent cations, it can be concluded by comparison that the approximately 1 V increased relative potential required for the UO_2^{2+} (aq) to UO_2(c) half-cell reaction over that for the plutonyl reduction is outside of the range provided by the phyllosilicate surface. This information provides important insights into the relative role of differing redox behavior on the synthesis of U versus Pu compounds.

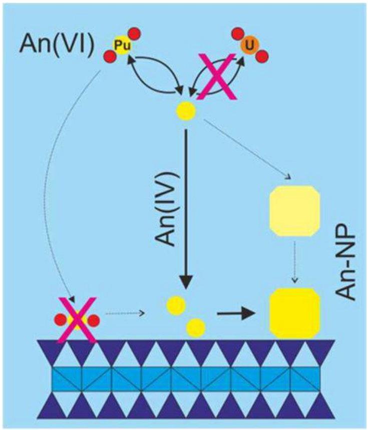

Figure 2. Although similar reaction schemes can be envisioned for UO_2^{2+} and PuO_2^{2+}, our results indicate that surface complexation behaviors of the two actinyl (VI) solution species are very different.

Science objectives for 2017-2019:

- Compare the impact of the nitrate ion on the solution speciation of tetravalent Ce, Th, Np, and Pu and the crystalline compounds that form. Very few studies report structures of simple binary actinide nitrates, despite their obvious relevance to both fundamental structure/bonding relationships and the solvent-extraction chemistry used in *f*-ion purification and reprocessing.
- Complete surface-complexation studies by examining the role of the counterion and its concentration on surface-complexation chemistry, with a focus on the nitrate anion.

Publications supported by this project 2015-2017

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(5) Hellebrandt, S.; Schmidt, M.; Knope, K. E.; Lee, S. S.; Lussier, A. J.; Stubbs, J. E.; Eng, P. J.; Soderholm, L.; Fenter, P. *Redox dependent interfacial reactivity of hexavalent radionuclides*; 2191-8708; Argonne National Laboratory: 2016; p 27.
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Competitive Ion Adsorption at Interfaces in Highly Concentrated Solutions

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Overall research goals: Transfer of a target ion from an aqueous phase into an organic phase in solvent extraction (SX) includes a few-nanometer-long but important journey through the interface. The molecular scale details of the processes at this interface are not well-understood, although they are expected to have significant impact on transfer kinetics and phase stability. Our goal is to determine the fundamental physical and chemical processes at aqueous interfaces related to heavy element separations.

Significant achievements during 2015-2017:

The combination of interfacial X-ray scattering and spectroscopy techniques with surface specific vibrational sum frequency generation (VSFG) spectroscopy provided a unique opportunity in our interfacial investigations. An example of the success of this approach was the elucidation of important aspects of competitive adsorption of chlorometallate anionic complexes at air/solid and air/water interfaces. These model systems allow well-controlled, systematic studies of ion distribution and ion-extractant interactions at the interface. It has long been known that the hydration shell of the ions and the interfacial hydrogen bonded water networks have significant effects on ions at the interface, but very few studies actually studied these effects for heavy elements.

We have discovered a two-step adsorption process for chlorometallates, such as $PtCl_6^{2-}$, in highly concentrated solutions similar to the real SX systems. The two-step process was firstly discovered at solid/liquid interface in an indirect way. Later, we expanded studies to the air/water interface and investigated the water structures with VSFG spectroscopy and the ion distribution with x-ray scattering and spectroscopy (Figure, left and right respectively). The combination of these techniques, integrated with atomistic molecular dynamics (MD) simulations, suggest that the chlorometallate complexes adsorbed in the Stern layer lead to a unique, weakly-bonded interfacial water structure that has not been observed before with lighter anions or anionic complexes, such as halides or sulfate. The emergence of this new interfacial water structure can nicely be linked to the two-step adsorption of chlorometallates.

Science objectives for 2017-2019: There are several factors that need to be considered during the transfer of a metallate ion from aqueous phase into the organic phase. Especially the role of the interfacial water, the solvation shell of the metals, and the formation of ionic species specific to the interface are not well-understood. Our research program will continue to investigate these effects with an integrated experimental and computational approach. Specifically, we will expand our research program into two major directions based on the experimental and conceptual tools we have developed in the first two years. The first direction will be a systematic investigation of lanthanides and the interfacial solute structures related to them. It is well-known that the kinetics of some conventional extraction processes for trivalent ions strongly depend on the conditions in the aqueous phase, such as temperature and pH. The interfacial studies are going to shed light on the molecular scale origins of these effects. The second direction will be the integration of the interfacial studies with the conventional SX experiments and with the bulk studies on either sides of the interface. Although, this has already been the fundamental approach of our group in general; with the proven capabilities of the interfacial techniques, we will be able to design more advanced experiments that will address the challenges in Lanthanide-Actinide separations.

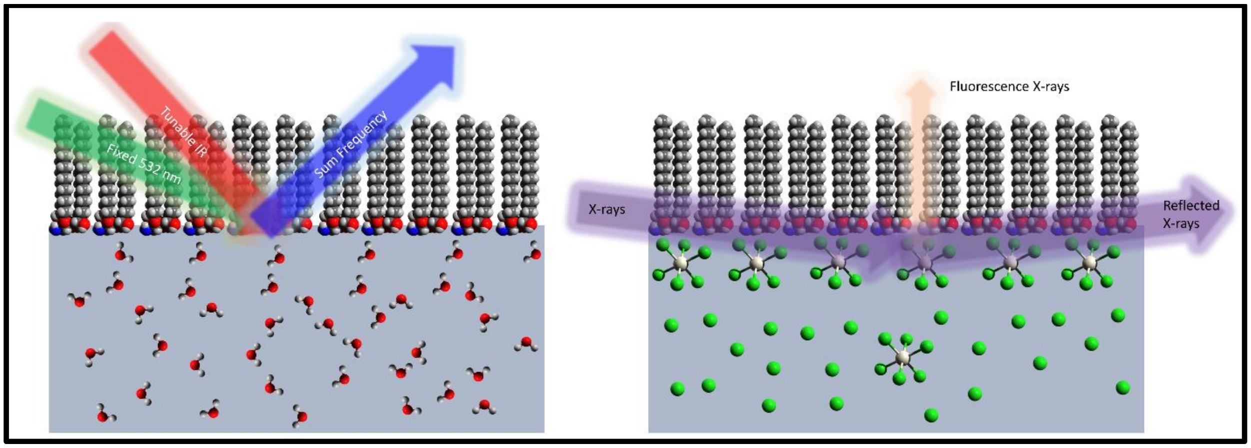

Figure: Studies of model extractants at the aqueous chlorometallate/air interface with vibrational sum frequency generation (VSFG) spectroscopy (left) and x-ray scattering and spectroscopy (right). While VSFG spectroscopy is sensitive to interfacial water structures, x-rays provide information about metallate ion distribution. Integration of these techniques provide a complete picture of the interfacial structures forming in these model extraction systems.

<u>Publications supported by this project 2015-2017:</u>

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2. Hellebrandt, S., Lee, S. S., Knope, K. E., Lussier, A. J., Stubbs, J. E., Eng, P. J., Soderholm, L., Fenter, P., & Schmidt, M. "A Comparison of Adsorption, Reduction, and Polymerization of the Plutonyl (VI) and Uranyl (VI) Ions from Solution onto the Muscovite Basal Plane" Langmuir, <u>32</u> (41), 10473-10482 (2016)
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5. Antonio, M. R., McAlister, D. R., & Horwitz, E. P. "An europium (III) diglycolamide complex: insights into the coordination chemistry of lanthanides in solvent extraction" Dalton Transactions, 44(2), 515-521 (2015)
6. Schmidt, M., Hellebrandt, S., Knope, K. E., Lee, S. S., Stubbs, J. E., Eng, P. J., Soderholm, L., & Fenter, P. "Effects of the background electrolyte on Th (IV) sorption to muscovite mica" Geochimica et Cosmochimica Acta, <u>165</u>, 280-293 (2015)

Organothorium Chemistry with Phosphorus and Arsenic

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Overall research goals: The objective of this project is to investigate the fundamental chemistry of actinides, hard Lewis acids, with phosphorus and arsenic, soft Lewis bases.

Significant achievements during 2015-2017: The chemistry of the actinides with phosphorus and arsenic has been virtually ignored and we have developed rare thorium complexes with these elements including the isolation of a bridging phosphinidene species. Some of the first reactivity studies of these complexes have been explored.

1. The synthesis, crystal structure and reaction pathway was determined for the first thorium bridging phosphinidene complex from the reaction of two equivalents of $(C_5Me_5)_2Th(CH_3)_2$ with $H_2P(2,6\text{-}^iPr_2C_6H_3)$.

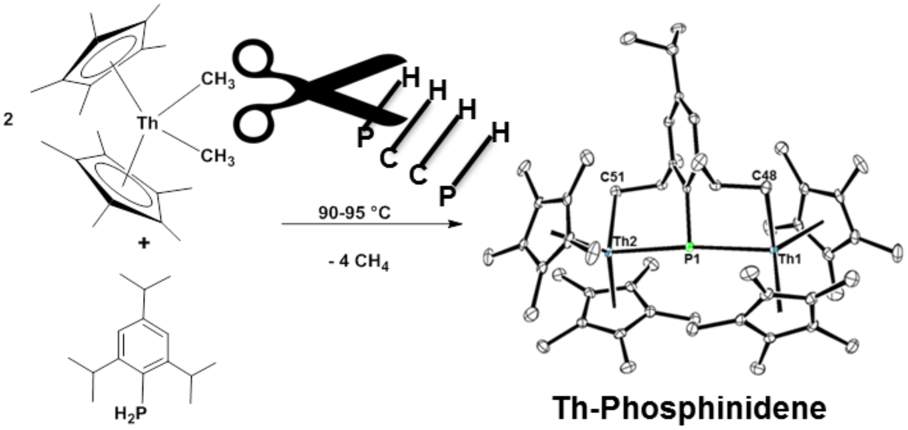

Figure 1. Synthesis and crystal structure of the bridging thorium phosphinidene complex.

2. The reactivity of $(C_5Me_5)_2Th[EH(2,6\text{-}^iPr_2C_6H_3)]_2$ with ^tBuNC to form the first phosphaazaallene and arsaazaallene complexes of the actinides.

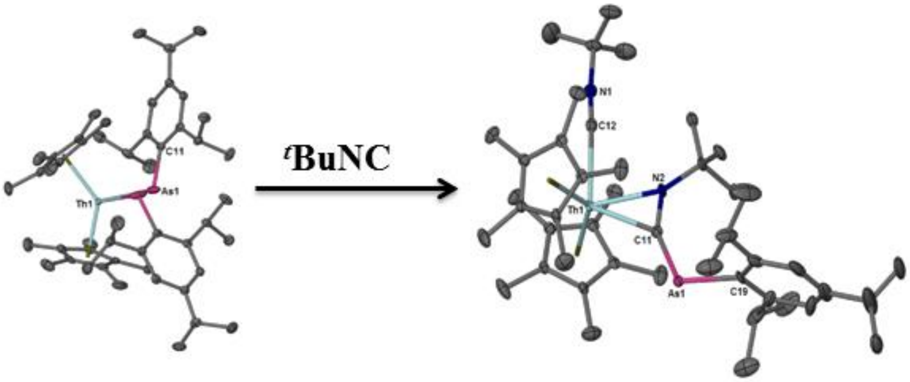

Figure 2. Formation of the arsaazaallene moiety.

3. The synthesis of new U(III) and Th(IV) alkyl complexes has been achieved using the dimethylbenzylamide ligand.

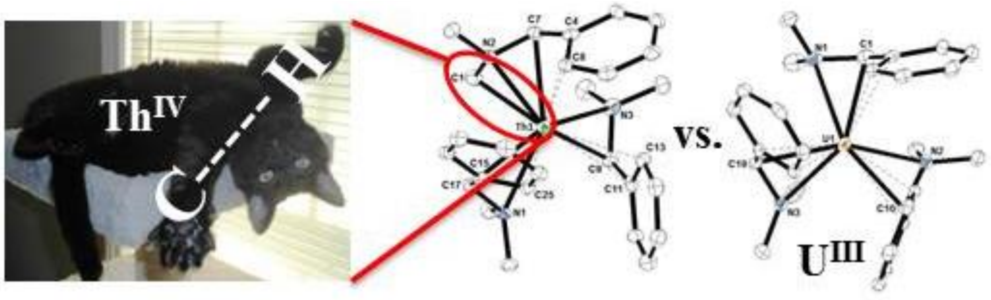

Figure 3. Synthesis of new Th(IV) and U(III) alkyl species. Only three dimethylbenzylamide ligands can coordinate so a C-H bond activation occurs with Th(IV). Attempts with Np(IV) are currently underway.

Science objectives for 2017-2020:

- Explore the chemistry of sulfur- and selenium- complexes previously done with thorium and uranium with neptunium, including the synthesis of new organometallic neptunium(IV) and neptunium(III) complexes. Examine differences in covalency between thorium, uranium, and neptunium.
- Forge into actinide-ligand multiple bonding with phosphorus and arsenic ligands and look for differences in covalent character.
- Synthesis of heterobimetallic phosphinidene and arsinidene complexes to provide insight into push-pull covalent bonding between transition metals and actinides.

Publications supported by this project 2015-2017

1. Behrle, A. C.; Castro, L.; Maron, L.; Walensky, J. R. Formation of a Bridging Thorium Phosphinidene Complex, *J. Am. Chem. Soc.* **2015**, *137*, 14846.
2. Behrle, A. C., Walensky, J. R. Insertion of ^{t}BuNC into Thorium-Phosphorus and Thorium-Arsenic Bonds: Phosphaazaallene and Arsaazaallene Moieties in *f* Element Chemistry, *Dalton Trans.* **2016**, *45*, 10042 (Invited for special issue on New Talent: Americas).
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Chemical Periodicity in the Early Actinide Elements: The Interplay of the 5f and 6d electrons

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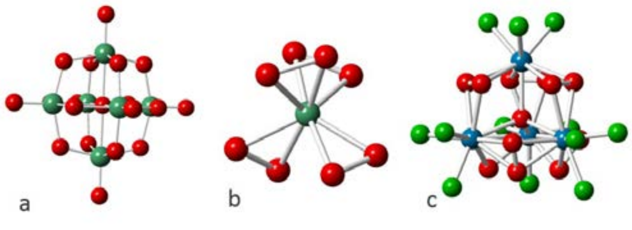
Overall research goals: This research program was formerly focused exclusively on the chemistry of protactinium (Z=91). Protactinium is the first actinide element to possess a 5f electron, and is situated at a position where the 5f actinide orbitals and 6d transition metal orbitals cross in energy. Though at this nexus of f- and d- chemistries, protactinium is only one member of the cis-curium elements, where the combination of relativistic effects and spin-orbit coupling along with the filling of the 5f shell give rise to a rich chemistry in both reactivity and structure. The overall goal of this research program is to develop a comprehensive understanding of the changing roles of the 5f and 6d electrons in the early actinide elements, Th to Cm, combining both molecular synthesis of model complexes and their study by spectroscopic, structural, and computational methods.

Significant achievements during 2015-2017: Our efforts have focused on understanding the relationship between protactinium, its transition metal homologues and the remainder of the early actinide series. These have been accomplished by combining synthesis, structural and spectroscopic characterization with computational studies and gas phase reactivity studies supported by collaborations within and external to the Heavy Elements program. Our own studies focused on the comparison of the fluoride complexes of the Group V transition metal elements, Nb and Ta, with those of Pa revealing significant differences in the chemistry of these closed shell pentavalent ions. It was demonstrated that the major differences in the observed chemistries between Nb, Ta, and Pa arose because of the influence of relativistic effects on the chemistry of these elements.



Structures investigated for studying the comparative chemistries of the actinide and transition metal complexes, a. $M_6O_{19}^{8-}$ polyoxometalates, b. $M(O_2)_4^{3-}$ molecular peroxides, and c. $M_4O(O_2)_6F_{12}^{6-}$ tetranuclear clusters.

Inspired by these results and our synthesis of a tetranuclear protactinium complex, we investigated the alkaline chemistry of Pa to investigate whether or not we would be able to form a protactinate anion or a polyoxometalate, much like those of the form $Nb_6O_{19}^{8-}$. Despite considerable experimental efforts we were unable to synthesize an alkaline soluble polyprotactinate ion. However, computational work directed at the comparison of the stability and electronic properties of transition metal and actinide polyoxometalates, synthesized *in-silico* demonstrated an important periodic relationship between the changing roles of the 5f and 6d electrons between Pa and U. An increase in the participation of the 5f orbitals for the uranium versus the protactinium bearing polyoxometalate was observed resulting in the distortion of the structure arising from the formation of asymmetric uranyl like bonding motifs in the clusters. This work reinforces the periodic trends highlighted in the gas phase reactivity studies conducted on the actinyl ions of the early actinide ions and the complementing theoretical work that highlighted the increasing participation of the 5f electrons in the chemistry of the early actinide elements.

Science objectives for 2017-2019:

- Expand the synthetic work beyond Pa to include the early actinides inclusive to Cm in order to fully develop the changing participation of the 5f electrons and the effect it has on the structural properties and reactivities of the early actinide elements.
- Explore the effects of chemical periodicity in the higher oxidation states of the actinide elements including the penta-, hexa-, and heptavalent states with a particular focus on the structure and bonding properties of these unique ions.
- Continue collaborations into the gas phase chemistry and reactivity of the early actinide elements inclusive of protactinium targeting simple ligand systems that include O_2^{2-}, S_2^{2-}, and halogen species for comparison with reactivity studies with the transition metals and actinides.
- Explore the chemistry of tetravalent protactinium the first $5f^1$ chemical system.

Publications supported by this project 2015-2017

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4. R. E. Wilson, *Structure, Phase Transitions, and Isotope Effects in $(Me_4N)_2PuCl_6$. Inorganic Chemistry* 2015.. **COVER ARTICLE** dx.doi.org/10.1021/acs.inorgchem.5b01288

5. P. Dau, R. E. Wilson, J. K. Gibson. *Elucidating Protactinium Hydrolysis: The Relative Stabilities of $PaO_2(H_2O)^+$ and $PaO(OH)_2^+$. Inorganic Chemistry*. 2015. DOI: 10.1021/acs.inorgchem.5b01078

Theoretical Studies of Actinide-ligand Bonding Interactions and Spectroscopic Properties

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Overall research goals: The goal of the program is the study of the nature of chemical bonds between actinide elements and their ligands in a variety of coordination environments. The studies are carried out with a close cooperation between experimental probes of the electronic structure of the synthesized compounds, in the form of a variety of spectroscopic techniques and computational studies to unravel the nature of the chemical signatures.

Significant achievements during 2015-2017: Several advances on actinide-ligand bonding interactions have been made using a combination of theoretical and spectroscopic techniques during this period. Herein we highlight the work on understanding the origin of covalency across the actinide series and more information could be founded in the publications section.

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

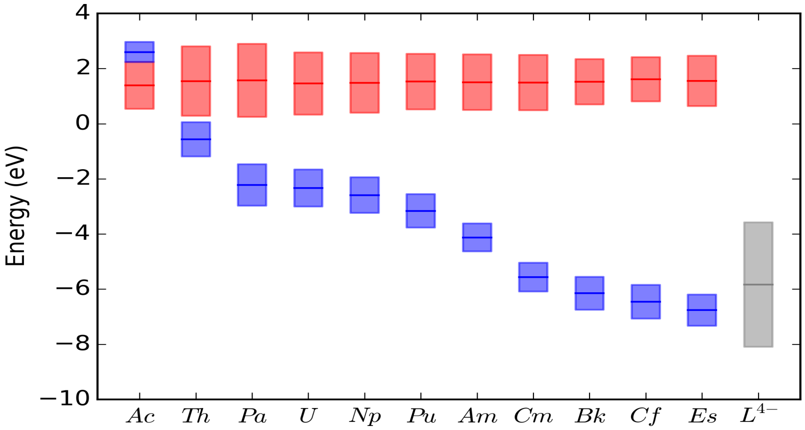

Figure. Energy levels of 5f (blue), 6d (red) and ligand (grey) orbitals in the An^{III}(HOPO)$^-$ complexes.

Science objectives for 2017-2019:

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

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2. Kelley, M.P.; Su, J.; Urban, M.; Luckey, M.; Batista, E. R.; Yang, P.; Braley, J. C. " On the oringin of covalent bonding in heavy actinides", **2017**, Submitted.
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10. Batista, E. R.; Martin, R. L.; Yang, P. "Computational Studies of Bonding and Reactivity in Actinide Molecular Complexes", **2015**, *Book Chapter 14 in 'Computational methods in Lanthanide and Actinide Chemistry".*