2015 Heavy Element Chemistry and Separations Science Principal Investigators' Meeting

Gaithersburg, MD
April 19–22, 2015

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

2015 Heavy Element Chemistry and Separations Science Principal Investigators' Meeting

Gaithersburg Marriott
Washingtonian Center
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Office of Basic Energy Sciences
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U.S. Department of Energy

Cover photo: District of Columbia Cherry Blossom Festival (Philip Wilk, 12 April 2014).

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Foreword

This abstract booklet provides a record of the thirteenth U.S. Department of Energy contractors' meeting in separations sciences and the eighth in heavy element chemistry. This year the meeting is co-chaired by Dr. Jaqueline Kiplinger (Los Alamos National Laboratory) and Professor Thomas Albrecht-Schmitt (Florida State University). 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. Although these are distinct disciplines, they have much in common for many reasons, in particular because novel separations research is needed to produce pure heavy-element samples and because heavy element chemistry provides the basis for many separations processes. This is the seventh 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.

We appreciate the privilege of serving as the managers of our respective research programs. In carrying out these tasks, we 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. We also hope that this meeting will enhance your research efforts and will nurture future collaborations and initiatives.

We thank all of the researchers whose dedication and innovation have advanced our research and made this meeting possible and, we hope, productive. We also hope that all of you will build on your successes and that we will assemble in two years for our next joint meeting.

We thank Diane Marceau of the Chemical Sciences, Geosciences and Biosciences Division for her vital contributions to the administration of our programs.

Philip Wilk
Larry Rahn

Agenda

2015 Heavy Element Chemistry and Separations Principal Investigator's Meeting
Gaithersburg Marriott, Washingtonian Center

Sunday, April 19

7:00-7:10	Wilk greeting (welcome new PIs and introduce co-chairs)		
	Opening Remarks on the Technical Program		
7:10-7:20	Kiplinger	Jaqueline	LANL
	Albrecht-Schmitt	Thomas	FSU
	Keynote Speaker 1		
7:20-8:15	Düllmann	Christoph	Universität Mainz
8:15-9:30	**Spectroscopy/Bonding**		Session Chair: Professor Braley
	Kozimor	Stosh	Los Alamos National Laboratory
	Soderholm	Lynne	Argonne National Laboratory
	Cho	Herman	Pacific Northwest National Laboratory

Monday, April 20

7:30-8:30	**Breakfast (provided)**		
8:30-9:00	Pietraß	Tanja	CSGB Division Director, DOE BES
9:00-10:15	**Spectroscopy/Bonding (cont.)**		Session Chair: Professor Braley
	Abergel	Rebecca	Lawrence Berkeley National Laboratory
	Antonio	Mark	Argonne National Laboratory
	Minasian	Stefan	Lawrence Berkeley National Laboratory
10:15-10:30	**Break**		
10:30-11:45	**Theory/Gas Phase I**		Session Chair: Professor Bart
	Gibson	John	Lawrence Berkeley National Laboratory
	Autschbach	Jochen	University at Buffalo
	Clark	Aurora	Washington State University
	Nuclear Summer School Update		
11:45-12:10	Robertson	David	University of Missouri, Columbia
12:10-1:45	**LUNCH (provided) & Collaborate**		poster room will be open
1:45-3:45	**Poster Session #1**		
3:45-5:25	**Organometallics/Coordination Chemistry**		Session Chair: Professor Schelter
	Gaunt	Andrew	Los Alamos National Laboratory
	Sessler	Jonathan	University of Texas
	Hayton	Trevor	University of California, Santa Barabara
	Wilson	Richard	Argonne National Laboratory
	DINNER on your own and Collaborate		

Tuesday, April 21

7:30-8:30	**Breakfast (provided)**		
	Keynote Speaker 2		
8:35-9:15	Neidig	Michael	University of Rochester
9:15-9:30	**Break**		
9:30-10:45	**Separations/Soft Materials**		Session Chair: Professor Gagliardi
	Flood	Amar	Indiana University
	Bowman-James	Kristin	University of Kansas
	Bryantsev	Slava	Oak Ridge National Laboratory
10:45-11:00	**Break**		
11:00-12:15	**Separations/Soft Materials (cont.)**		Session Chair: Professor Gagliardi
	Alexandratos	Spiro	Hunter College
	Wishart	James	Brookhaven National Laboratory
	Jansone-Popova	Santa	Oak Ridge National Laboratory
12:15-1:45	**LUNCH (provided) & Collaborate**		poster room will be open
1:45-3:45	**Poster Session #2**		
3:45-5:25	**Theory/Gas Phase II**		Session Chair: Professor Robertson
	Becker	Udo	University of Michigan
	Scuseria	Gustavo	Rice University
	Gregorich	Ken	Lawrence Berkeley National Laboratory
	Heaven	Michael	Emory University
	DINNER on your own and Collaborate		

Wednesday, April 22

7:30-8:30	**Breakfast (provided)**		
8:30-10:10	**Inorganic/Materials/Interfaces**		Session Chair: Professor Dai
	Burns	Peter	University of Notre Dame
	Powell	Brian	Clemson University
	Skanthakumar	Suntharalingam	Argonne National Laboratory
	Cahill	Christopher	George Washington University
10:10-10:25	**Break**		
10:25-12:00	Summary from the co-chairs and grant tips with Philip & Larry		
12:00	**Lunch on your own / dismissal**		

Poster Session #1

Ellis	Ross	Argonne National Laboratory
Jin	Geng Bang	Argonne National Laboratory
Uysal	Amhet	Argonne National Laboratory
Wang	Lai Sheng	Brown University
Braley	Jenifer	Colorado School of Mines
Albrecht-Schmitt	Thomas	Florida State University
Arnold	John	Lawrence Berkeley National Laboratory
Shuh	David	Lawrence Berkeley National Laboratory
Batista	Enrique	Los Alamos National Laboratory
Boncella	James	Los Alamos National Laboratory
Kiplinger	Jaqueline	Los Alamos National Laboratory
LANL Pu NMR project		Los Alamos National Laboratory
Custelcean	Radu	Oak Ridge National Laboratory
Dai	Sheng	Oak Ridge National Laboratory
Moyer	Bruce	Oak Ridge National Laboratory

Poster Session #2

Bart	Suzanne	Purdue University
Dixon	David	University of Alabama
Evans	William	University of California, Irvine
He	Chuan	University of Chicago
Davis	Jeffery	University of Maryland
Gagliardi	Laura	University of Minnesota
Robertson	J. David	University of Missouri
Schelter	Eric	University of Pennsylvania
Pinkerton	Alan	University of Toledo
Armentrout	Peter	University of Utah
Dietz	Mark	University of Wisconsin, Milwaukee
Peterson	Kirk	Washington State University
Liu	Goukui	Argonne National Laboratory

Abstracts

Sensitizing the Luminescence of Trivalent Actinides through Sequential Antennae and Multi-Photon Excitation Processes

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Email: rjabergel@lbl.gov; Web: http://actinide.lbl.gov/gtsc/BioAn/

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

Overall research goals: The objective of this work is to enable the selective tuning of spectroscopic properties of specific trivalent 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 An(III) 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 2014-2015:

1. The first americium luminescence sensitization experiments were carried out using established ligands containing several hydroxypyridinonate and catecholate metal-binding isomers: complex formation between Am(III) and the octa-, hexa-, and tetradentate ligands 3,4,3-LI(1,2-HOPO), enterobactin, and 5-LIO(Me-3,2-HOPO), respectively, was probed in aqueous solution. Upon excitation of all three ligand π-π* transitions, structured emission patterns were observed and attributed to the Am(III) transition $^5D_0 \rightarrow {}^7F_1$ (with fluorescence quantum yields of the order of 0.01 %). These luminescence properties were also 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.

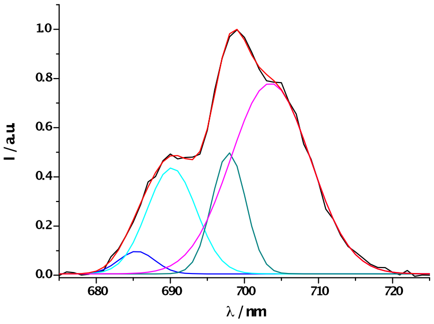

Figure 1. Deconvolution of $[Am^{III}(3,4,3\text{-}LI(1,2\text{-}HOPO))]^-$ luminescence into four Lorentzian functions, revealing the structured Am(III) emission.

2. A new experimental setup for multi-photon absorption spectroscopy with radioactive actinide complexes was implemented, using a tunable laser as an excitation source. Both hydroxypyridinonate ligands mentioned above were found to act as two-photon probes for the sensitization of several trivalent lanthanide cations and of Cm(III). This is the first example and characterization of two-photon antenna sensitization of a transuranic actinide ion in solution, which paves the way for the detailed mapping of intermediate energy levels in 5f metal complexes.

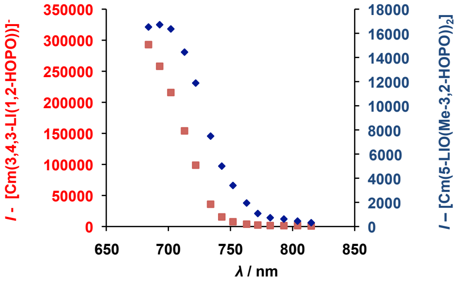

Figure 2. Luminescence intensity after two-photon excitation at various wavelengths for the Cm(III) complexes of 3,4,3-LI(1,2-HOPO) (red) and 5-LIO(Me-3,2-HOPO) (blue).

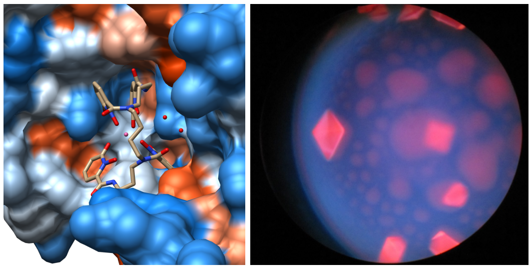

Figure 3. Crystal structure (left) and bright luminescence (right) of the Siderocalin complex of $[Cm(3,4,3\text{-}LI(1,2\text{-}HOPO))]^-$.

3. The macromolecular recognition of Ln(III) and An(III) complexes of enterobactin and 3,4,3-LI(1,2-HOPO) by the protein siderocalin was probed. Siderocalin is a mammalian protein that participates in endogenous metal homeostasis mechanisms by intercepting ferric-siderophore complexes through cation-π and Coulombic interactions. Replacing the ferric metal center by Ln and An ions affected the conformation of the resulting metal complexes and therefore their respective affinity for siderocalin. In addition, structural information on the Ln and An complexes was gained through X-ray diffraction data, with the first transuranic actinide-containing protein structures to be reported. Finally specific binding of the Eu(III) and Cm(III) complexes to the protein resulted in significant modification and enhancement of the intramolecular energy transfer luminescence processes.

Science objectives for 2015-2017:

- Use series of first identified Am(III) sensitizers to build functionalized ligand platforms with tuned actinide sensitization properties.
- Expand luminescence and thermodynamic investigations to Bk(III) and Cf(III) complexes.
- Develop further the multi-photon absorption experiments to systematically determine cross sections between different ligands and f-block metals.
- Explore the use of luminescence and thermodynamic data to build empirical trends in bonding and coordination within the 5f element series, which will in turn be correlated with theoretical predictions.
- Explore the use of macromolecular receptors to control shape and intensity in the spectroscopic signature of 5f element complexes.

Publications supported by this project 2014-2015

1. Sturzbecher-Hoehne, M.; Kullgren, B.; Jarvis, E. E.; An, D. D.; Abergel, R. J. "Highly Luminescent and Stable Hydroxypyridinonate Complexes: A Step Towards New Curium Decontamination Strategies." *Chem. Eur. J.* **2014**, *20*, 9962-9968. DOI: 10.1002/chem.201402103.
2. Sturzbecher-Hoehne, M.; Choi, T. A.; Abergel, R. J. "Hydroxypyridinonate Complex Stability of Group (IV) Metals and Tetravalent f-Elements: The Key to the Next Generation of Chelating Agents for Radiopharmaceuticals." *Inorg. Chem.* **2015**, *Accepted*.
3. 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 and Cellular Uptake of Actinides". In Preparation.
4. D'Aléo, A.; Sturzbecher-Hoehne, M.; Allred, B. E.; Abergel, R. J. "Intramolecular Sensitization of Americium(III) Luminescence in Solution: Shining Light on Short-Lived Forbidden 5f Transitions". In Preparation.

A SECOND BREAK IN THE ACTINIDE SERIES: THE TRANSITIONAL BEHAVIOR OF CALIFORNIUM

Thomas E. Albrecht-Schmitt, Principal Investigator
Samantha Cary, Teresa Eaton, Kariem Dieffenbach, Kevin Seidler, Matthew Marsh, Jared Stritzinger, T. Gannon Parker, Alexandra Arico, Shane Galley, Mark Silver *Graduate Students*
Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306
Email: albrecht-schmitt@chem.fsu.edu; Web: http://www.chem.fsu.edu/bio-t.php?userID=1230

Collaborators: David A. Dixon, Department of Chemistry, The University of Alabama, Shelby Hall, Tuscaloosa, Alabama 35487, United States; Evgeny V. Alekseev, Institute for Energy and Climate Research (IEK-6), Forschungszentrum Jülich GmbH, 52428 Jülich, Germany and Institut für Kristallographie, RWTH Aachen University, 52066 Aachen, Germany; Shelley Van Cleve, Nuclear Materials Processing Group, Oak Ridge National Laboratory, One Bethel Valley Rd, Oak Ridge, Tennessee 37830; Wulf Depmeier, Institut für Geowissenschaften, Universität Kiel, 24118 Kiel, Germany; Guokui Liu, S. Skanthakumar, Lynda Soderholm, Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439; Laura Gagliardi, Department of Chemistry, Supercomputing Institute, and Chemical Theory Center, University of Minnesota, Minneapolis, Minnesota 55455

Overall research goals:

- Understanding the origin of the change in periodicity that occurs at californium.
- Provide thorough characterization of californium compounds and complexes and compare these results with both lanthanides and lighter actinides.
- Elucidate the origin of the strong ligand-field effects in californium systems.

Significant achievements during 2013-2015: A break in periodicity occurs in the actinide series between plutonium and americium as the result of the localization of 5*f* electrons. The subsequent chemistry of later actinides is thought to closely parallel lanthanides in that bonding is expected to be ionic and complexation should not substantially alter the electronic structure of the metal ions. We have demonstrated that ligation of californium(III) by a variety of ligands results in significant deviation in the properties of the resultant complexes and compounds with respect to that predicted for the free ion. We have expanded on this by characterizing the americium and curium analogs for comparison, and have shown that these pronounced effects with californium result from a second transition in periodicity in the actinide series that occurs, in part, because of the stabilization of the divalent oxidation state. The metastability of californium(II) is responsible for many of the unusual properties of californium including the green photoluminescence.

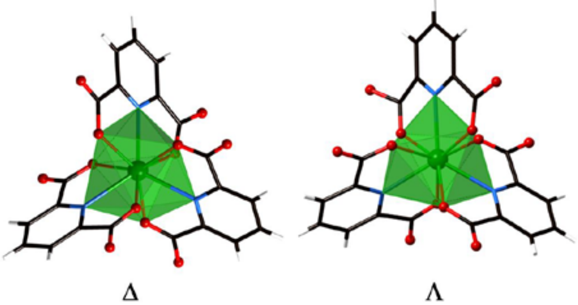

Figure 1. Views of the Δ and Λ enantiomers of $Cf(HDPA)_3$ showing the nine-coordinate, tricapped trigonal prismatic coordination environments of the Cf(III) ions created via chelation by three, monoprotonated, 2,6-dipicolinate ligands, $HDPA^{-}$.

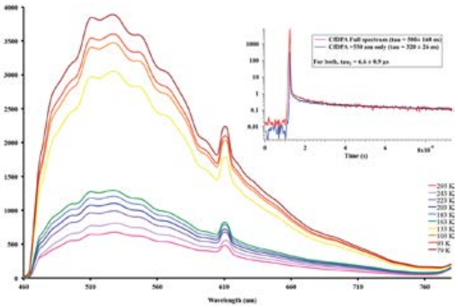

Figure 2. Photoluminescence spectra from a single crystal of $Cf(HDPA)_3{\cdot}H_2O$ upon excitation with 420 nm light as a function of temperature.

We have found that there is no basis to assign the photoluminescence to a Cf(III) 5*f*-5*f* transition. A mechanism that provides a satisfying interpretation of the spectroscopic data and is also consistent with the magnetic and thermodynamic studies is that the photoluminescence is from a ligand-to-metal charge-transfer transition that is best described as a Cf(III) to Cf(II) + h^+ (h^+ = hole in the valence band) occurring in the energy region at approximately 25,000 cm^{-1} (400 nm).

Science objectives for 2013-2016:

- Prepare isomorphous berkelium analogs and compare these compounds and complexes with californium compounds.
- Prepare Cf(III) complexes with strong π donor ligands to investigate how these perturb the electronic properties.
- Investigate the electrochemistry of Cf(III) complexes and compare these results with both lanthanides and lighter actinides. The focus will be on understand if the reduction potential to Cf(II) and be rationally tuned through ligand design.
- Interface with theoreticians to understand the quantum mechanical origins of these phenomena.

Selected Publications supported by this project 2013-2015 (out of >50)

1. 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
2. T. E. Albrecht-Schmitt, "Californium Gleaming," *Nature Chemistry*, **2014**, *6*, 840. **DOI:** 10.1038/nchem.2035.
3. M. J. Polinski, E. B. Garner III, R. Maurice, N. Planas, J. T. Stritzinger, T. G. Parker, T. D. Green, E. V. Alekseev, S. M. Van Cleve, W. Depmeier, L. Gagliardi, M. Shatruk, K. L. Knappenberger, G. Liu, S. Skanthakumar, L. Soderholm, D. A. Dixon, T. E. Albrecht-Schmitt, "Unusual Structure, Properties, and Bonding in a Californium Borate," *Nature Chemistry*, **2014**, *6*, 387-392. **DOI:** 10.1038/nchem.1896.

Polymer-supported complexants: metal ion selectivity and the variables of rational design

Spiro D. Alexandratos, Principal Investigator

Dr. Xiaoping Zhu, Post-doctoral associate

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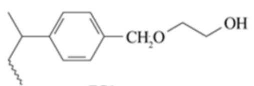
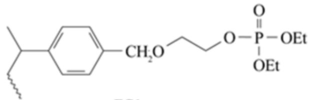
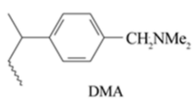
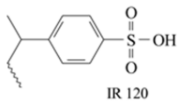
Overall Research Goals: The overall goal of this research is to understand the rational design of polymer-supported complexants wherein ionic recognition is incorporated into polymers based on the *a priori* understanding of ligand interactions; this is in contrast to the conventional empirical design wherein recognition is incorporated into polymers with ligands analogous to soluble complexants, including crown ethers, quinolines, and diphosphonic acids. This understanding of the basis for selective supported ligand – metal ion interactions is applicable to environmental remediation, the nuclear fuel cycle, sensor technology, and solid phase extraction.

Significant Achievements, 2013 – 2015: The polarizabilities of ligands immobilized onto cross-linked polymers, including those below, was successfully probed with hard (Eu(III)) and soft (Au(III)) metal ions. From a study of the affinities from solutions of varying acid strength, it was concluded that the coordinating ligands, –OH, P=O and dimethylamine can be classified as soft and the -OH in $–SO_3H$, an ion exchange ligand, can be classified as hard. The polarizability of oxygen thus depends on its microenvironment, being soft within neutral ligands and hard within ion exchange ligands. The interplay of basicity with polarizability remains to be explored given that, despite a greater basicity relative to -OH, the dimethylamine ligand is soft.


EG1


pEG1


DMA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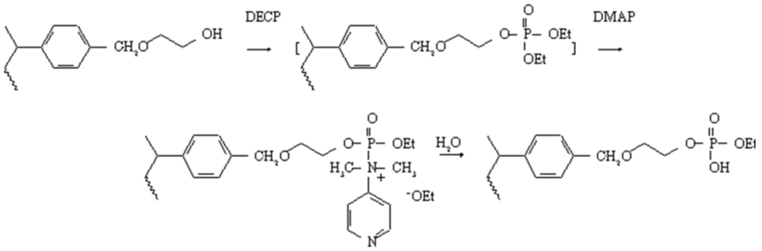
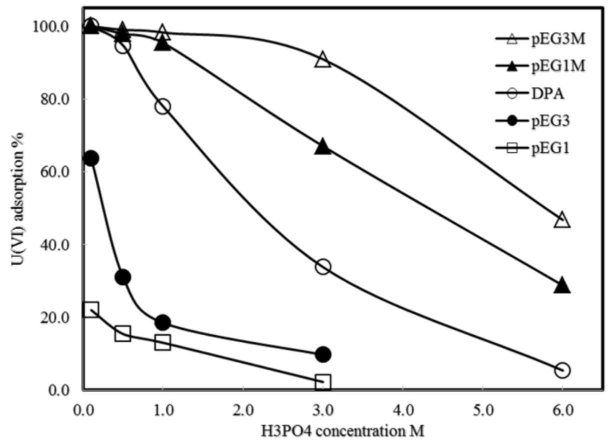
Since polarizability is a property that changes gradually rather than abruptly, it is expected that combining ion exchange and coordinating sites onto one ligand will show a mixed selectivity. A new monoprotic ligand, shown below, was thus developed. FTIR spectra show binding of Au(III) through the neutral P=O while the hard Eu(III) ion shows no change in position of the P=O but an hypsochromic shift of the P-O from 1035 to 1060 cm^{-1} due to an increased electron density from the formation of $P-O-Eu^{3+}$. Most importantly, FTIR spectra allow for the conclusion that the high metal ion affinities of the monoprotic ligand, compared to diprotic ligands, is due to decreased hydrogen bonding.



The metal ion affinity of monoprotic ligands was enhanced by the presence of auxiliary binding sites. A study of U(VI) affinities from H_3PO_4 solutions by a series of ligands on polystyrene {$–CH_2OCH_2CH_2OCH_2CH_2O-P(O)(OH)OEt$ [pEG3M], $-CH_2OCH_2CH_2O-P(O)(OH)OEt$ [pEG1M], diphosphonic acid $–CH_2P(O)(OH)_2$ [DPA], $–CH_2OCH_2CH_2OCH_2CH_2O-P(O)(OEt)_2$ [pEG3], and $-CH_2OCH_2CH_2O-P(O)(OEt)_2$ [pEG1]} gives an order of ligand strength (see figure) wherein we



conclude that aprotic ligands (pEG1, pEG3) have weak affinities; ion exchange ligands (DPA) increase binding, monoprotic ligands best balance ion exchange with a lower extent of hydrogen bonding (pEG1M), and higher affinities are evident when ion exchange is coupled to coordination by neutral donor sites (pEG3M).

Metal ion recognition can thus be optimized when substrate - ligand polarizabilities are matched and then ligands prepared capable of ion exchange, with decreased hydrogen bonding and additional coordination sites. Using these principles, a new aminophosphinate ligand was designed and found to have a high uranyl affinity from synthetic wet process phosphoric solution.

Science objectives for the next two years:

*generalize from oxygen to amine and thiol binding sites

*explore the role of basicity, superimposed on polarizability, in defining recognition.

*tune hydrogen bonding in ion exchange ligands to affect metal ion selectivities

*correlate distribution coefficients with parameters from corresponding FTIR spectra

*extend the principles from metal ion recognition to molecular and biomolecular recognition

References to publications supported by this project, 2013 – 2015:

Alexandratos, S.D.; Zhu, X. The role of polarizability in determining metal ion affinities in polymer-supported reagents: monoprotic phosphate and the effect of hydrogen bonding, New Journal of Chemistry, 2015, *in press*

Zhu, X.; Alexandratos, S.D. Development of a new ion-exchange / coordinating phosphate ligand for the sorption of U(VI) and other trivalent ions from phosphoric acid solutions, Chemical Engineering Science, 2015, 126-132. *DOI: 10.1016/j.ces.2015.01.027*

Zhu, X.; Alexandratos, S.D. The role of polarizability in determining metal ion affinities in polymer-supported reagents. I. Phosphorylated ethylene glycol, Reactive and Functional Polymers, 2014, 81, 77-81. *DOI: 10.1016/j.reactfunctpolym.2014.05.001*

Shimada, A.; Sulakova, J.; Yang, Y.; Alexandratos, S.D.; Nash, K.L. Studies on the uptake and column chromatographic separation of Eu, Th, U and Am by tetramethylmalonamide resin, Solvent Extraction and Ion Exchange, 2014, 32, 27-43. *DOI: 10.1080/07366299.2013.838492*

Alexandratos, S.D.; Zhu, X. Functionalization of polymer-supported pentaerythritol as a general synthesis for the preparation of ion-binding polymers, Journal of Applied Polymer Science, 2013, 127, 1758-1764. *DOI: 10.1002/app.37887*

Structural and Electrochemical Phenomena at Surfaces of Electrolyte Solutions in Chemical Separations

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Collaborators: Drs. M. Bera, R. Ellis, B. Qiao, L. Soderholm, A. Uysal, Chemical Sciences & Engineering Division, Argonne National Laboratory; Prof. M. Schlossman, Department of Physics, University of Illinois at Chicago, Chicago, IL 10021; Dr. W. Bu, CARS – The University of Chicago, Bldg. 434, Argonne, IL 60439

Overall research goals: The importance of liquid surface phenomena in chemical separations is significantly underestimated. Structural and electrochemical behaviors of solutes in solutions and at liquid surfaces are known to influence the kinetics and thermodynamics of solvent extraction (SX) in ways that are not well understood. Our goal is to determine the organization of solutes at liquid-vapor surfaces and at liquid-liquid interfaces, through which the transfer of selected solutes—including multivalent rare earth (*RE*) and actinide (*An*) ions—is orchestrated by neutral and acidic amphiphilic extractants. In this effort, fundamental knowledge about the influence of *RE* and *An* redox variations in organic and aqueous electrolytes alike and at interfaces between them will enable us to correlate liquid-surface structures and ion-transfer kinetics with bulk liquid-liquid extraction performance in manners not done before.

Significant achievements during 2013-2015: The electrochemistry and speciation of *An* and *RE* elements figure prominently in the practical hydrometallurgy of used nuclear fuel. Despite some six decades of use of SX for *An*-*RE*-element separation and purification, there is a dearth of fundamental insights about ion-transfer across water-organic interfaces and interfacial structures, which are otherwise primitive depictions that are based upon indirect evidence and speculation. In fact, SX is used with little understanding of interfacial speciation. Although understanding is not necessary for practical use, advances toward high performance systems by chance and random-abstract observations are doomed. To fill this void of knowledge, we have acquired initial insights about organic phases, which were formed by liquid-liquid extraction of polyoxometalate anions and erbium(III) cations from bulk aqueous media, by use of electroanalysis and X-ray scattering. As depicted in the Figure, the incorporation of heteropolyacids in organic phases with TBP leads to substantial modification of the electrochemical response compared to the aqueous phases, and the observation of an Er(III)-DHDP complex arrested at the water-oil interface confounds expectations.

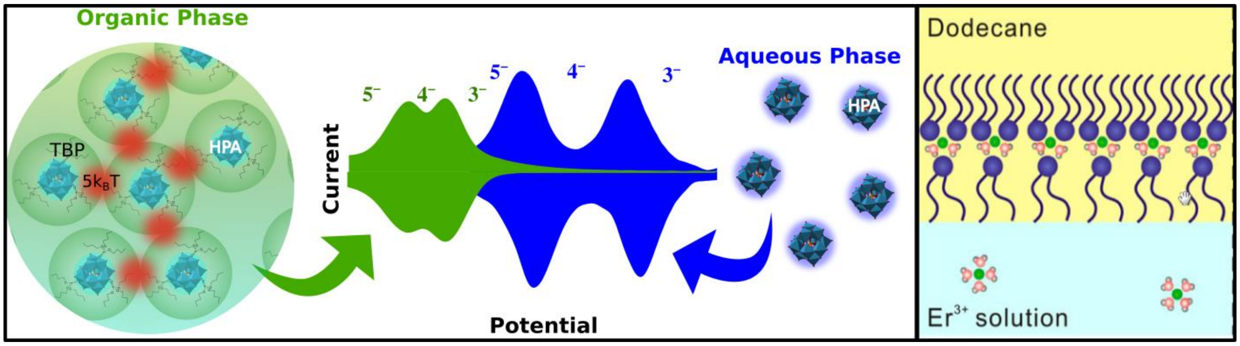

Figure. Left: Electrochemistry of dense organic "third" phases formed by solvent extraction of heteropolyacid salts, including 12-phosphotungstic acid (HPA), by using paraffinic solutions of tri-*n*-butyl phosphate (TBP) reveal redox events that are markedly shifted and less resolved than the responses in the corresponding aqueous phases due to solubilization of the charge-neutral acids.[3,6] Right: A temperature-driven adsorption transition was used to condense a two-dimensional inverted bilayer of an Er complex with di-*n*-hexadecyl phosphate (DHDP) in a paraffinic diluent at the oil–water interface, which was interrogated with synchrotron X-ray reflectivity and fluorescence measurements.[2]

Science objectives for 2015-2017: Insights into the interfacial electrochemistry and physics of liquid-liquid extraction systems are sought. Of particular interest is an understanding of ion-transfer across oil-water interfaces and structural phenomena, including the organization of extractant molecules with *An* and *RE* ions into small complexes and their aggregation into large, micellar architectures. We seek answers to a number of basic questions, including: What does the interface look like? How are solutes organized? What is the nature of metal-extractant complexes, and is it different from that in bulk aqueous and organic phases? Is cation transfer into an organic phase coupled with a concerted co-transport of anions in a single kinetic step? Or is cation transfer coupled with a concerted counter-transport of protons in two kinetic steps? As with electrochemical phenomena, where reduction is coupled with oxidation, in SX, cation transfer must be coupled with anion transfer to maintain charge neutrality. To tackle these questions, we will exploit the use of purpose-built equipment and methods, which have been developed in previous years' efforts, for surface-sensitive metrical and electrochemical measurements. For example, by use of liquid drop geometries as well as under conditions of total external reflection, we will acquire X-ray scattering and X-ray spectroscopy data in combination with electroanalytical methods. Our objectives are to obtain basic knowledge about phase-transfer behaviors and speciation of *RE*- and *An*-ions at surfaces and in-between interfaces. The results will impact our basic understanding of separation science, in general, and liquid-liquid extraction, in particular, vis-à-vis hydrometallurgical reprocessing schemes.

Publications supported by this project 2013-2015:

1. Bu, W., Mihaylov, M., Amoanu, D., Lin, B., Meron, M., Kuzmenko, I., Soderholm, L. and Schlossman, M. L., "X-ray studies of interfacial strontium-extractant complexes in a model solvent extraction system", J. Phys. Chem. B 118 (43), 12486-12500 (2014) [doi: 10.1021/jp508430e]
2. Bu, W., Yu, H., Luo, G., Bera, M. K., Hou, B., Schuman, A. W., Lin, B., Meron, M., Kuzmenko, I., Antonio, M. R., Soderholm, L. and Schlossman, M. L., "Observation of a rare earth ion-extractant complex arrested at the oil-water interface during solvent extraction", J. Phys. Chem. B 118 (36), 10662-10674 (2014) [doi: 10.1021/jp505661e]
3. Bera, M. K., Ellis, R. J., Burton-Pye, B. P. and Antonio, M. R., "Structural aspects of heteropolyacid microemulsions", Phys. Chem. Chem. Phys. 16 (41), 22566-22574 (2014) [doi: 22566-22574]
4. Ellis, R. J., Meridiano, Y., Muller, J., Berthon, L., Guilbaud, P., Zorz, N., Antonio, M. R., Demars, T. and Zemb T., "Complexation-induced supramolecular assembly drives metal-ion extraction", Chem. Eur. J. 20 (40), 12796-12807 (2014) [doi: 10.1002/chem.201403859]
5. Gorman-Lewis, D., Jensen, M. P., Harrold, Z. R. and Hertel, M. R., "Complexation of neptunium(V) with *Bacillus subtilis* endospore surfaces and their exudates", Chem. Geol. 341, 75–83 (2013) [doi: 10.1016/j.chemgeo.2013.01.004]
6. Bera, M. K., Bray, T. H., Ellis, R. J. and Antonio, M. R., "Redox chemistry of heteropolyacid microemulsions", ChemElectroChem 1 (7), 1173-1181 (2013) [doi:10.1002/celc.201402037]
7. Luo, G., Bu, W., Mihaylov, M., Kuzmenko, I., Schlossman, M. L. and Soderholm, L., "X-ray reflectivity reveals a nonmonotonic ion-density profile perpendicular to the surface of $ErCl_3$ aqueous solutions", J. Phys. Chem. C 117 (37), 19082-19090 (2013) [doi: 10.1021/jp4067247]
8. Ellis, R. J., Meridiano, Y., Chiarizia, R., Berthon, L., Muller, J., Couston, L. and Antonio, M. R., "Periodic behavior of lanthanide coordination within reverse micelles", Chem. Eur. J. 19 (8), 2663–2675 (2013) [doi: 10.1002/chem.201202880]

Activation of H_2 and CH_4 Isotopomers by Th^+ as Studied by Guided Ion Beam Mass Spectrometry and Quantum Chemistry

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Another collaborator

Overall research goals: The objective of this project is to measure accurate thermochemistry for thorium and uranium species in the gas phase and to explore their characterization using quantum chemistry.

Significant achievements during 2014-2015 (start date: 7/15/2014): Reactions of Th^+ and ThO^+ with a variety of small molecules have been explored using guided ion beam tandem mass spectrometry with these experimental results being augmented by quantum chemistry calculations. To date, two systems have been explored thoroughly and another dozen or so are approaching completion. The two systems that have progressed the most so far are:

1. The reaction of atomic thorium cations with CH_4 (CD_4) and the collision-induced dissociation (CID) of $ThCH_4^+$ with Xe are studied using guided ion beam tandem mass spectrometry. In the methane reactions, $ThCH_2^+$ ($ThCD_2^+$) is the only product at low energies (see Figure 1); however, the energy dependence of the cross section is inconsistent with a barrierless exothermic reaction as previously assumed on the basis of ion cyclotron resonance mass spectrometry results. The dominant product at higher 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 $D_0(Th^+\text{-}H) \geq 2.25 \pm 0.20$, $D_0(Th^+\text{-}CH) = 6.19 \pm 0.16$, $D_0(Th^+\text{-}CH_2) \geq 4.54 \pm 0.09$, $D_0(Th^+\text{-}CH_3) = 2.60 \pm 0.30$, 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 spin-orbit coupling are carefully considered. When spin-orbit coupling is explicitly considered, a barrier for C-H bond activation that is consistent with the threshold measured for $ThCH_2^+$ formation (0.17 ± 0.02 eV) is found at all levels of theory, whereas this barrier is only observed at BHLYP and CCSD(T) levels otherwise. 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 is thought to exist as a result of the mixed (^4F,^2D) electronic character of the Th^+ J = 3/2 ground level

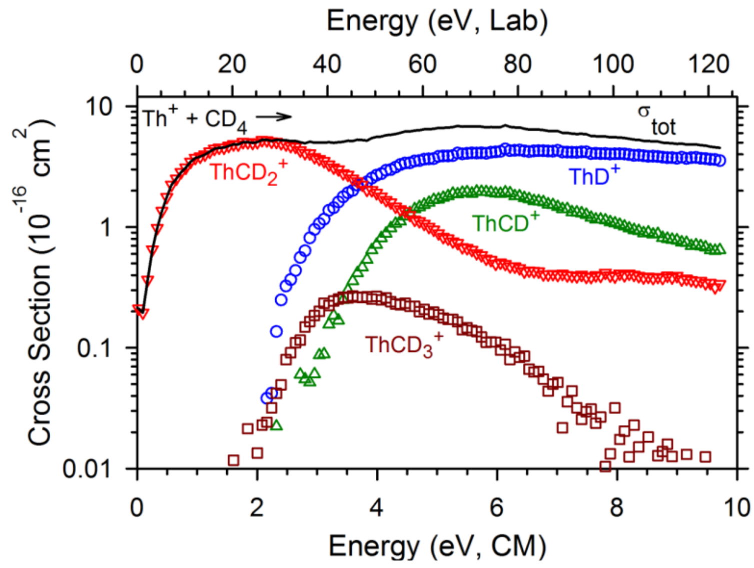

Figure 1. Cross sections for the reaction between Th^+ and CD_4 as a function of energy in the CM (lower x-axis) and Lab (upper x-axis) frames.

combined with extensive spin-orbit effects.

2. Kinetic energy dependent reactions of Th^+ with H_2, D_2, and HD were studied using a guided ion beam tandem mass spectrometer. As can be seen in Figure 2 for the D_2 system, formation of ThH^+ and ThD^+ is endothermic in all cases with similar thresholds. Branching ratio results for the reaction with HD indicate that Th^+ reacts via a statistical mechanism, similar to 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. This result is in good agreement with the result obtained in reactions of $Th^+ + CH_4$. However, $D_0(Th^+\text{-}H)$ is observed to be larger than its transition metal congeners, TiH^+, ZrH^+, and HfH^+, a result believed to be related to the $^4F - {}^2D$ mixed ground level of Th^+. These reactions were also explored using quantum chemical calculations that include a semi-empirical estimation of spin-orbit contributions. These calculations indicate that ThH^+ most likely has a $^3\Delta_1$ ground level with a $^1\Sigma^+$ low-lying excited state. Theory also provides theoretical BDEs and the reaction potential energy surfaces.

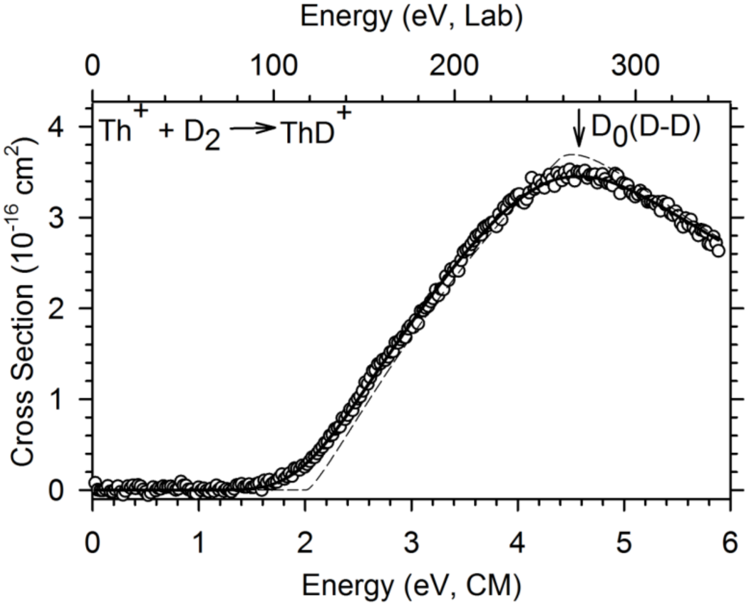

Figure 2. Cross sections for the reaction between Th^+ and D_2 as a function of energy in the CM (lower x-axis) and Lab (upper x-axis) frames. Our model of the reaction cross section is shown as a dashed line. This model convoluted over the kinetic energy and internal energy distributions of the reactants is shown as a solid line. The arrow indicates $D_0(D\text{-}D) = 4.556$ eV.

Science objectives for 2015-2017:

- Complete our experimental and computational examination of the reactions of Th^+ with O_2, CO, NO, N_2, H_2O (D_2O) and ThO^+ with O_2 and CO.
- Extend our studies to similar processes involving U^+ and UO^+.
- Begin to examine the hydration and complexation of these ions by various ligands.

Publications supported by this project 2014-2015

1. Cox, R. M.; Armentrout, P. B.; de Jong, W. A., "Activation of CH_4 by Th^+ as Studied by Guided Ion Beam Mass Spectrometry and Quantum Chemistry", *Inorg. Chem.*, submitted for publication.
2. Cox, R. M.; Armentrout, P. B., "Reactions of Th^+ + H_2, D_2, HD Studied by Guided Ion Beam Tandem Mass Spectrometry and Quantum Chemical Calculations", *J. Chem. Phys.*, in preparation.

Ligand Frameworks for the Study of Actinide Bonding to Transition Metals and Main Group Elements

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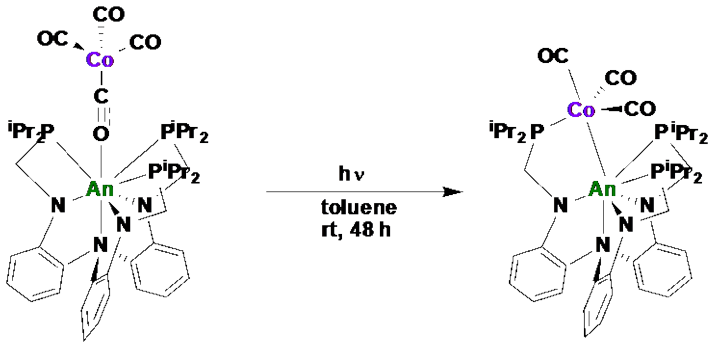
Collaborators: Dr W. Lukens, Dr S. Minasian, Dr D. Shuh, Dr N. Kaltsoyanis, Professor L. Maron

Overall research goals: The study of molecular actinide–metal bonding has been important for advancing electronic structure theory for actinide coordination compounds. Our effort focuses on new avenues to further our understanding of the fundamental bonding modes of the actinides through the preparation of new coordination compounds featuring An-E interactions (E = metal or metalloid). Following isolation, the compounds are analyzed by in-depth reactivity studies in addition to physical and theoretical characterization.

Significant achievements during 2013-2015: In getting this new project off the ground with funding for a new postdoctoral felllow, we have focused on two main areas thus far:

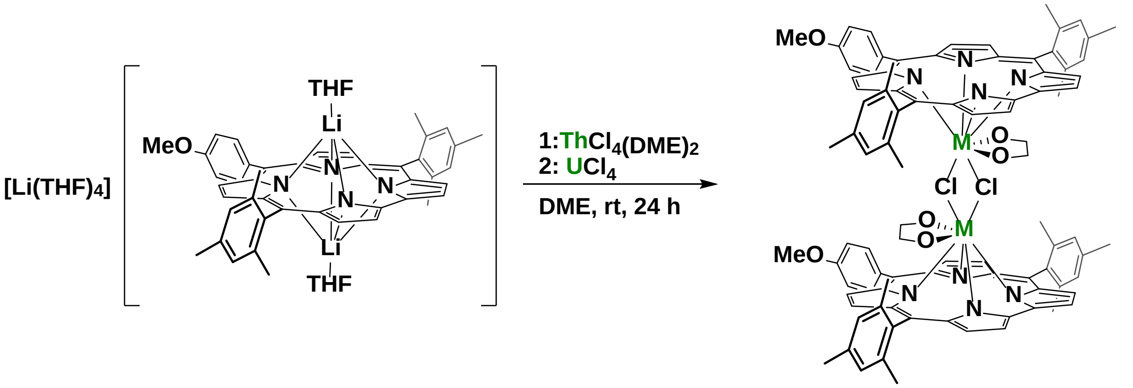
1. A series of actinide-transition metal heterobimetallics was prepared, featuring thorium, uranium and cobalt. Complexes incorporating the binucleating ligand N[*o*-(NHCH$_2$P^{i}Pr$_2$)C$_6$H$_4$]$_3$ and Th(IV) or U(IV) with a carbonyl bridged [Co(CO)$_4$]$^-$ unit were synthesized from the corresponding actinide chlorides (Th; U) and Na[Co(CO)$_4$]. Irradiation of the resulting isocarbonyls with ultraviolet light resulted in the formation of new species containing actinide-metal bonds in good yields; this photolysis method provides a new approach to a relatively unusual class of complexes. Characterization by single-crystal X-ray diffraction revealed that elimination of the bridging carbonyl and formation of the metal-metal bond is accompanied by coordination of a phosphine arm from the N$_4$P$_3$ ligand to the cobalt center. The solution state behavior of the thorium complexes was evaluated using ^{1}H, ^{1}H-^{1}H COSY, ^{31}P and variable-temperature NMR spectroscopy. IR, UV-Vis/NIR, and variable-temperature magnetic susceptibility measurements were also reported.



U: Red Blocks, 65% yield

Th: Colorless Blocks, 61% yield

2. The complexes, (Mes$_2$(*p*-OMePh)corrole)$_2$Th$_2$(μ-Cl)$_2$(DME)$_2$ and (Mes$_2$(*p*-OMePh)corrole)$_2$U$_2$(μ-Cl)$_2$(DME)$_2$, were synthesized via combination of the corresponding lithium corrole, (Mes$_2$(*p*-OMePh)corrole)Li$_3$ with ThCl$_4$(DME)$_2$ and UCl$_4$ respectively, in dimethoxyethane (DME) (Scheme 1). In the case of thorium complex, the reaction resulted in precipitation of a purple solid, while a dark red solution was observed for the uranium complex, after stirring at room temperature for 1 d.



1: M = Th; red needles, 93% yield
2: M = U; pink needles, 83% yield

Science objectives for 2013-2015:

- Pursue studies involving (N_4P_3)An species to prepare compounds with An—M bonds (An = Th, U, transuranics; M = transition metal, Ln, An) and examine the nature of the M-M bonding in series of structurally-related derivatives.
- Continue the investigation of actinide amidinate and silylamide derivatives and expand the study of their reactivity towards new substrates, with the aim of discovering new modes of reactivity and identifying new routes to An-M heterobimetallic species.
- Expand the chemistry of An-metalloids (e.g. B, Al, Ga, Si, Ge, Sn) and investigate their electronic structure using DFT and XAS.
- Develop metrics to evaluate bonding, including: thermodynamic measurement; VT magnetism and NMR; solid-state structural elucidation; electronic spectroscopies

Publications supported by this project:

1. Ward, A.L., Buckley, H.B., Lukens, W.W., Arnold, J. "Synthesis and Characterization of Thorium(IV) and Uranium(IV) Corrole Complexes" *J.Am.Chem. Soc.*, **2013**, *135*, 13965.

2. Arnold, J., Minasian, S.G., Krinsky, J.L. "Evaluating F-Element Bonding from Structure and Thermodynamics" *Chem. Eur. J.*, **2011**, *14*, 12234.

3. Ward, A.L., Lukens, W.W., Lu, C.C., Arnold, J. "Photochemical Route to Actinide-Transition Metal Bonds: Synthesis, Characterization and Reactivity of a Series of Thorium and Uranium Heterobimetallic Complexes" *J. Am. Chem. Soc.*, **2014**, *136*, 3647.

4. Kashtan, Y., Gianetti, T.L., Arnold, J. "Thorium Lends a Fiery Hand" *Nature Chem.*, **2014**, *6*, 554.

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

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Frederic Gendron, Kamal Sharkas (part time), postdoctoral researchers
Benjamin Pritchard (PhD 2014), Bob Martin (current), Graduate Students
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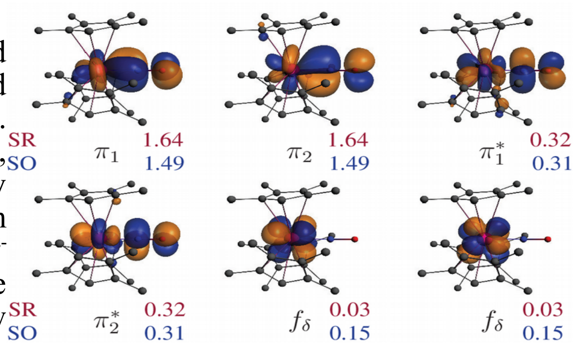
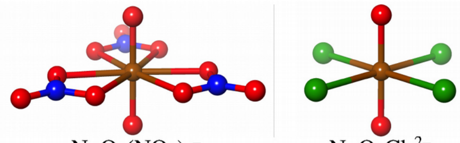
Overall research goals: We investigate magnetic properties of 4f- and 5f-element compounds (lanthanides, actinides) by using quantum chemical calculations. The main objective is to learn how observable magnetic properties are related to the geometrical structure, chemical bonding, and the nature of the 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) and magnetic susceptibilities of lanthanide and actinide complexes, and perform benchmark studies in comparison with well-characterized transition metal complexes. The project goals include developments of new relativistic quantum chemical methods in the open-source NWChem quantum chemistry package and other quantum chemistry programs.

Significant achievements during 2013-2015:



Natural orbitals and occupations of a Ar_3 U(IV)-NO complex, scalar (SR) vs. spin-orbit (SO)

Theoretical studies were carried out for selected uranium(V), uranium(IV), neptunium(VI), and plutonium(VI) compounds with unpaired electrons. Calculated EPR g-factors, magnetic susceptibilities, and the energies and compositions of low enegy electronic states were in reasonable agreement with available experimental data. For the $[NpO_2Cl_4]^{2-}$ complex ion, we demonstrated strong effects from the crystal embedding on the EPR g-factors. New theoretical methods were developed for these studies, allowing a description of chemical bonding and the distribution of the unpaired electrons and their magnetization in chemically intuitive terms, based on multi-reference (CAS-based) wavefunctions including effects from spin-orbit coupling. Further, connections of current state-of-the-art calculations with crystal field theory model were established. A new method to calculate hyperfine coupling constants for ligand atoms in f-element complexes within a CAS framework was developed and is currently being tested for various actinide complexes. Hyperfine constants probe the magnitude, shape, and spatial distribution of the magnetization from unpaired electrons in the actinide or lanthanide f-shells. Going forward, these calculations will allow us to interpret complicated nuclear magnetic resonance spectra of f-element complexes. A book chapter was written jointly with other developers of the NWChem program, highlighting its capabilities for predictive modelling of complex actinide systems. These capabilities include relativistic density functional methods for magnetic properties developed by us during previous budget periods. Results from a 2012 benchmark on paramagnetic ligand NMR shifts of 3d metallocenes were used to develop a module for our undergraduate computational chemistry laboratory. The impact of the DFT delocalization error on hyperfine coupling was investigated.



	$NpO_2(NO_3)_3^-$		$NpO_2Cl_4^{2-}$	
	$g_\parallel$	$g_\perp$	$g_\parallel$	$g_\perp$
CAS	3.55	0.24	1.76	1.51
B3LYP	3.28	0.56	1.03	1.13
expt.	3.41	0.21	1.32	1.38

EPR g-factors for neptunyl(VI)

Science objectives for 2015-2017:

- Develop relativistic quantum chemical methods for magnetic properties of open-shell f-element complexes within the density matrix renormalization group (DMRG) technique for multi-reference wavefunctions. This will allow us to treat systems with several actinide atoms such as tric-actinyl carbonate complexes, and to probe spin polarization more accurately.

- Investigate the importance of solvent effects on the magnetic properties of actinyl carbonate complexes, in particular on ligand NMR chemical shifts.

- Investigate how the surrounding of actinide complexes in crystals change their magnetic properties relative to calculations of isolated complexes

- Develop and apply quantum chemical methods suitable for studying nuclear magnetic and quadrupolar resonance of actinide nuclei.

Publications supported by this project 2013-2015:

Autschbach, J.; Govind, N.; Atta-Fynn, R.; Bylaska, E. J.; Weare, J. H.; de Jong, W. A., ‘Computational tools for predictive modeling of properties in complex actinide systems’, in Dolg, M.(editor), ‘Computational methods in lanthanide and actinide chemistry’, John Wiley & Sons, 2015. To appear.

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Gendron, F.; Le Guennic, B.; Autschbach, J., ‘Magnetic properties and electronic structures ofAr_3 U^{IV}–L complexes with Ar = $C_5(CH_3)_4H$ or C_5H_5 and L = CH_3, NO, and Cl’, Inorg. Chem. 2014, 53, 13174–13187. http://dx.doi.org/10.1021/ic502365h.

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Synthetic, Spectroscopic, and Computational Studies of Redox-Active Uranium Complexes for Fundamental Organometallic Reactions

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Prof. Laura Gagliardi, University of Minnesota, Minneapolis, MN
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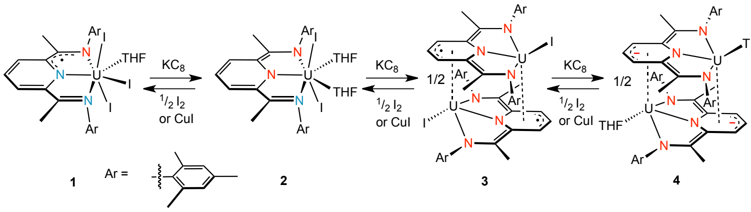
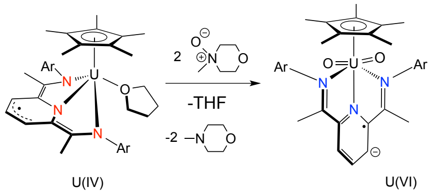
Overall Research Goals: To explore the formation of uranium complexes bearing redox-active ligands, through synthesis, characterization and reactivity studies. Analogous species bearing redox innocent ligands will be prepared for comparison to assess the role of the redox-active ligand. These species will be fully characterized using ^{1}H NMR, infrared, electronic absorption, and X-ray absorption spectroscopies (Kozimor) as well as X-ray crystallography, electrochemistry, SQUID magnetization (Schelter), and computational methods (Gagliardi).

Significant achievements during 2013-2015:



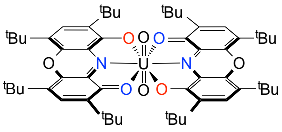
1. The electronic structures of a series of highly reduced uranium complexes bearing the redox-active pyridine(diimine) ligand, $^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$ ($^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$ = 2,6-(2,4,6-$\mathrm{Me_3}$-$\mathrm{C_6H_2}$-N=CMe)$_2$$\mathrm{C_5H_3N}$) have been investigated. The complexes, ($^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$)$\mathrm{UI_3}$(THF) (**1**), ($^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$)$\mathrm{UI_2(THF)_2}$ (**2**), [($^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$)UI]$_2$ (**3**), and [($^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$)U(THF)]$_2$ (**4**) contain uranium(IV) centers with $5f^2$ configurations and reduced ligand frameworks, specifically [$^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$]$^{\cdot/-}$, [$^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$]$^{2-}$, [$^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$]$^{3-}$ and [$^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$]$^{4-}$, respectively. The electrons stored in these ligands facilitate multi-electron reactivity, enabling the synthesis of unique uranium imido complexes, [U(NR)$_x$], including the unprecendented uranium tris(imido) family, ($^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$)U(NR)$_3$ (R = Mesityl, 2,6-diisopropylphenyl).



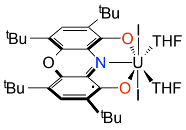
2. A series of cyclopentadienyl uranium(IV) species were generated. Cp*U($^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$)(THF), which contains a ligand trianion, generates a unique uranyl species, Cp*U($^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$)$\mathrm{O_2}$, by oxygen atom transfer from N-methylmorpholine-N-oxide. Characterization reveals this species is appropriately described as a hexavalent species with ligand radical. Cp*U($^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$)(THF) also mediates oxidative addition of dichalcogenides and dihalides, where the two electrons required are derived from the ligand, rather than the uranium, generating a family of complexes, Cp*U($^{\mathrm{Mes}}\mathrm{PDI}^{\mathrm{Me}}$)(EPh)$_2$ (E = S, Se, Te).

3. Studies were performed to generate uranium derivatives of a redox-active, dioxophenoxazine ligand. These analyses show uranium complexes bearing these tridentate ligand frameworks in

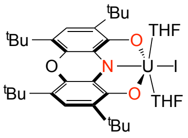
three different oxidation states: monoanionic quinone ($DOPO^{q}$), dianionic seminquinone ($DOPO^{sq}$), and trianonic catecholate ($DOPO^{cat}$).



$(DOPO^{q})_2UO_2$



$(DOPO^{sq})UI_2(THF)_2$



$(DOPO^{cat})UI(THF)_2$

Science objectives for 2015-2017:

- Expand the family of known uranium tris(imido) complexes, including variation of the substituents and oxidation states. Further probe the electronic structure and bonding of uranium tris(imido) complexes. Explore reactivity trends for uranium tris(imido) species, including generation of mixed imido species, nitrene group transfer, and redox chemistry.
- Study the reactivity of unusual ligand-radical containing uranyl species. Included will be further characterization to establish electronic structure, variation of the Cp ring, and uranyl functionalization. Influence of the ligand radical on the reactivity will also be probed.
- Further studies aimed at understanding the electronic structures of dioxophenoxazine uranium complexes. Establishing the utility of these robust ligand frameworks in mediating fundamental organometallic processes.

References to publications supported by this project 2013-2015:

1. Pattenaude, S.A.; Kuehner, C.S.; Dorfner, W.L.; Schelter, E.J.; Fanwick, P.E.; Bart, S.C.* (Spectroscopic and Structural Elucidation of Uranium Dioxophenoxazine Complexes" *Inorg. Chem.*, **2015**, *submitted.*

2. Anderson, N.H.; Kiernicki, J.J.; Fanwick, P.E.; Schelter, E.J.; Bart, S.C.* "Exploration of Uranium Tris(Imido) Complexes: Synthesis, Characterization, and Reduction Chemistry of $U(NDIPP)_3(THF)_3$" *Angew. Chem. Int. Ed.,* **2015,** *submitted.*

3. Anderson, N.H.; Odoh, S.; Williams, U.J.; Lewis, A.J.; Wagner, G.L.; Lezama Pacheco, J.; Kozimor, S.A.; Fanwick, P.E.; Gagliardi, L.; Schelter, E.J.; Bart, S.C.* "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.*, **2015**, *accepted.*

4. Anderson, N.H.; Odoh, S.; Yao, Y.; Williams, U.J.; Schaefer, B.A.; Kiernicki, J.J.; Lewis, A.J.; Goshert, M.D.; Fanwick, P.E.; Schelter, E.J.; Walensky, J.R.; Gagliardi, L.; Bart, S.C.* "Harnessing Redox-Activity for the Formation of Uranium Tris(imido) Compounds" *Nat. Chem.*, **2014**, 6(10), 919-926.

5. Kiernicki, J.J.; Fanwick, P.E.; Bart, S.C.* "Utility of a Redox-Active Pyridine(diimine) Chelate in Facilitating Two Electron Oxidative Addition Chemistry at Uranium" *Chem. Commun.* **2014**, *50(60), 8189-8192.*

6. Kiernicki, J.J.; Newell, B.S.; Matson, E.M.; Anderson, N.H.; Fanwick, P.E.; Shores, M.P.; Bart, S.C.* "Multi-electron C-O Bond Activation Mediated by A Family of Reduced Uranium Complexes" *Inorg. Chem.* **2014**, *53,* 3730-3741.

7. Matson, E.M.; Opperwall, S.R.; Fanwick, P.E.; Bart, S.C.* " 'Oxidative Addition' of Halogens to Uranium(IV) Bis(amidophenolate) Complexes" *Inorg. Chem.*, **2013**, *52*, 7295–7304.

Theoretical Studies of Orbital Mixing in Actinide-Ligand Bonds

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Stefan G. Minasian, Kevin S. Boland, Steven D. Conradson
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Overall research goals:

The ultimate 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 experimental signatures. Both hard and soft ligands, chlorine, sulfur, and carbon were studied in this cycle.

Significant achievements in 2013-2015:

- In order to obtain quantitative measurements of covalent interactions in metal-oxygen bonds, a standard of normalization had to be developed. In previous studies, those involving metal-chlorine bonds, we had used the TiCl4 reference, as this system was easily understandable and a clear mapping between experimental data and computed bonding interactions could be extracted. In order to develop a similar reference for metal-oxygen bonds we studied the family of permetalates, MO_4^{2-} (M=Cr, Mo, W) and MO_4^- (M=Mn, Tc, Re). The pre-edge features were modeled using similar techniques as the ones we used for metal-chlorine bonds. The two pre-edge features were clearly identified ad the splitting of the d manifold into e and t2 bands. These developed standards are currently being used for obtaining quantitative information about actinide-oxygen bonds which are resulting in excellent agreement with predicted values by theory and will be ready for publication shortly. (Figure 1)

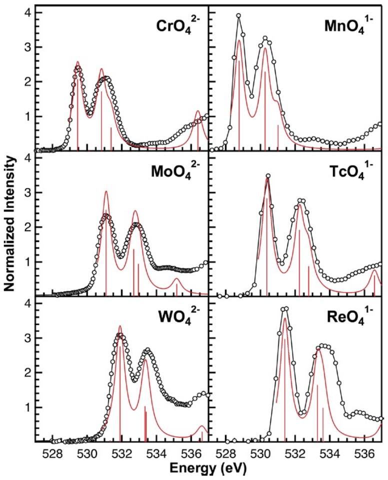

Figure 1: Pre-edge peaks for MO_4^{x-} bonds, experimental spectrum and simulated

- In the area of softer ligands, the interaction of sulphur and oxygen with metal centers (Cr, Mo, and W) were studied using k-edge spectroscopy and DFT linear response. An important development in this study consisted in the study of these systems in solution, for the measurements and for the modeling aspects. Comparison of the solid-state data with solution data allowed us to evaluate the level of error one incurs when interpreting bonding interactions in the solid-state as referents for the solution phase. The ultimate motivation for these studies is to understand the interactions of actinides with molecular extractants used in liquid-liquid separations. The interaction on functionalized thiophosphinate ligands between the phosphine and sulfur and the effect of that in the binding with actinide species was identified and tracked down to conformational effects induced by the steric nature of the ligands (Figure 2)
- We studied the coupling of uranyl with the redox active ligand, tetrathiafulvalene salphen. This is a theoretical and experimental study in collaboration with the group of Prof. Sessler, also funded by BES. Experimentally his complex was synthesized and studied via cyclic voltammetry where it was observed a reversible first reduction potential but an irreversible second wave. The DFT calculations reproduced well the reversible couple of the

ligand with minor disturbance due to the coordination of uranyl. The computational study indicated that irreversible process stemmed from a subtle rearrangement of the solvent molecules around the uranyl ion upon reduction.

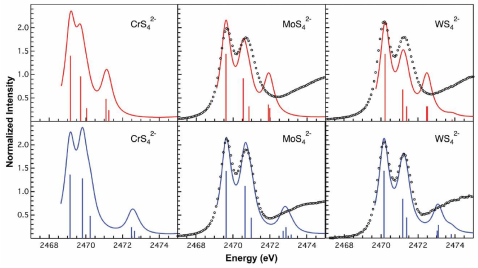

Figure 2: Comparison of gas-phase TDDFT spectra and computed spectra in solution with a CH3CN dielectric medium.

Science Objectives for 2015-2017:

In the next cycle we plan to move to the study of interactions between the metal center and delocalized/conjugated orbitals. The multi-atom type of these ligands will involve the development of a formalism that couples several spectra, one for each atom type, and convolutes them to produce the resulting molecular orbital. Besides answering basic science questions related to actinide-ligand bonds, these studies will impact questions related, for example, to separation processes where the ligands are conjugated molecules. Studies of actinide-ligand bonding in solution will also be carried out and compared with measurements from our experimental team partners.

Related publications:

- Stefan G. Minasian, Jason M. Keith, Enrique R. Batista, Kevin S. Boland, Joseph A. Bradley, Scott R. Daly, Stosh A. Kozimor, Wayne W. Lukens, Richard L. Martin, Dennis Nordlund, Gerald T. Seidler, David K. Shu, Dimosthenis Sokaras, Tolek Tyliszcxzk, Gregory L. Wagner, Tsu-Chein Weng, and Ping Yang, "Covalency in Metal-Oxygen Multiple Bonds Evaluated Using Oxygen K-edge Spectroscopy and Electronic Structure Theory," *Journal of the American Chemical Society* **2013**, *135*, 1864-1871.
- Stefan G. Minasian, Jason M. Keith, Enrique R. Batista, Kevin S. Boland, Stosh A. Kozimor, Richard L. Martin, David K. Shu, and Louis J. Vernon. "Carbon K-Edge X-ray Absorption Spectroscopy and Time-Dependent Density Functional Theory Examination of Metal-Carbon Bonding in Metallocene Dichlorides," *Journal of the American Chemical Society* **2012**, *134* 14731-14740.
- Christopher Bejger, Yong-Hui Tian, Beau J. Barker, Kevin S. boland, brian L. Scott, Enrique R. Batista, Stosh A. Kozimor, and Jonathan L. Sessler. "Synthesis and characterization of a tetrathiafulvalene-salphen actinide complex," *Dalton Transactions Communication* **2013**, *42*, 6716-6719.
- Stefan G. Minasian, Jason M. Keith, Enrique R. Batista, Kevin S. Boland, David L. Clark, Stosh A. Kozimor, Richard L. Martin, David K. Shu, Tolek Tyliszcxzk "New evidence for 5f covalency in actinocenes determined from carbon K-edge XAS and electronic structure theory" *Chemical Science* **2014**, *5*, 351-359.
- Angela C. Olson, Jason M. Keith, Enrique R. Batista, Kevin S. Boland, Scott R. Daly, Stosh A. Kozimor, Molly M. MacInnes, Richard L. Martin, and Brian L. Scott . "Using solution –a and solid-state S K-edge X-ray absorption spectroscopy with density functional theory to evaluate M-S bonding for MS$_4^{2-}$ (M=Cr, Mo, W) dianions" *Dalton Transactions* **2014**, *43*, 17283.

Actinide Sorption and Reduction on Sulfides and Oxides

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Overall research goals:

- Resolve kinetics of adsorption/reduction into sub-processes such as bulk diffusion in bulk solution, surface diffusion, stripping of hydration sphere, adsorption, overcoming activated states due to incompatible orbital symmetries or spin transitions.
- Use a combination of quantum-mechanical calculations, electrochemical powder micro-electrode measurements, batch experiments with subsequent TEM, XPS, and ICP-MS analysis, and electrochemical AFM measurements to resolve overall reaction path and mechanism and evaluate which of the sub-processes controls kinetics as function of environmental parameters (pH, pe, T, solution chemistry, and light).
- Use the information gained to help developing a strategy for optimizing reaction conditions for given applications, such as actinyl immobilization in permeable reactive barriers or geologic barriers near nuclear waste repositories, and to understand the geochemical behavior of actinyl phases in the environment.
- Move on to MOFs and actinyl nanoclusters and their redox, electronic, and catalytic properties.

Significant achievements during 2013-2015 (Renewal started in 7/12):

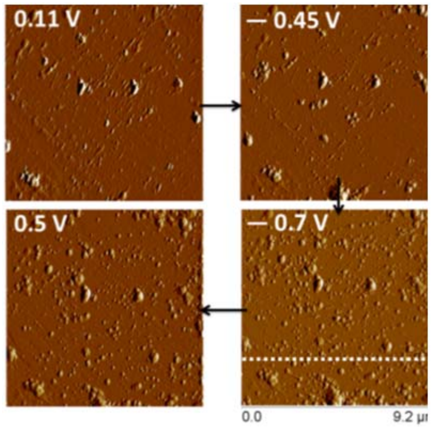

Fig. 1: Peak force error images (9.2×9.2 µm) of the magnetite electrode surfaces at electrochemical potentials of 0.11 V, -0.45 V, -0.7 V, and 0.5 V in 0.5 mM UO_2^{2+} (visible as UO_2 precipitatiesat pH = 3.4.

Method development for the characterization of actinide reduction on mineral surfaces: In five publications, the mechanism of uranium reduction on semiconducting sulfide and oxide mineral surfaces is investigated [1-5]. These studies reveal that typically, U(VI) is first reduced to U(V) before being further reduced to U(IV) or disproportionated to U(IV) and U(VI). In addition, it was found under which conditions U(V) or U(V)-containing solids form at least metastable states. In these sub-projects, significant progress has been made in method-development of the powder microelectrode, the single crystal mineral electrode, and in the use of electrochemical atomic force (EC-AFM) microscopy to study redox reaction mechanisms on mineral surfaces (Fig. 1). Electrochemical AFM allows one to observe *in situ* the growth of reduced U adsorbates on mineral surfaces as a function of solution pH, chemistry, and set electrochemical potential. In addition, samples were analyzed using EXAFS and XANES and, as a spinoff, an *in situ* electrochemical reaction cell was developed that allows for real-time structural and oxidation states changes using x-ray absorption spectroscopy [2]. Both techniques are now available for powder and single-crystal applications.

Electron transfer kinetics across actinide-mineral interfaces: In order to understand the atomistic mechanism and kinetics of actinyl redox processes, quantum-mechanical electron transfer calculations involving Marcus theory have been performed. Electron-transfer (ET) calculations on the first rate-limiting ET-step (the reduction of U(VI)aq to U(V)aq by Fe(II)aq) complement the experimental results. The homogeneous reduction of U(VI)aq to U(V)aq by Fe(II)aq is thermodynamically and kinetically favorable if an inner–sphere complex can be achieved. However, significant thermodynamic and kinetic barriers exist to proceed from an outer–sphere ET reaction to an inner–sphere ET reaction, a process that needs to overcome dehydration of the first solvation shell and hydrolysis of Fe(II)aq [1-6].

Computational and experimental determination of redox potentials of actinide-mineral interfaces: One publication from this grant reviews, evaluates, and expands the theory behind the calculation of redox potentials in solution for species such as organic compounds, inorganic complexes, actinides, battery materials, and mineral surface-bound-species [7]. Different computational approaches to predict and determine redox potentials of electron transitions are discussed along with their respective pros and cons for the prediction of redox potentials. This article reviews the importance of computational parameters, such as basis sets, density functional theory (DFT) functionals, and relativistic approaches and the role that physicochemical processes play on the shift of redox potentials, such as hydration or spin orbit coupling.

Thermodynamics, electronic, optical, and catalytic properties of actinyl metal organic frameworks: In a new line of research, we evaluate the thermodynamic, structural, electronic, optical, and catalytic properties of actinide-containing metal organic frameworks (An-MOFs) which may be used for the determination of the potential of An-MOFs for photo-enhanced catalytic processes [6, 8, 9]. Metal organic frameworks (MOFs) are a relatively new class of hybrid crystalline materials composed of metal ions or metal-clusters and organic molecules as building blocks.

Additional studies supported by this grant: Additional publications have resulted from this grant on the thermodynamics of actinyl incorporation into carbonate, sulfate, and oxide minerals[10, 11], as well as uranyl alteration phases, and the thermodynamics of the UO_2-HfO_2 solid solution to evaluate the role of burnable poisons on nuclear fuel performance [12].

Science objectives for 2015-2016:

- Activated states that control the U adsorption/reduction kinetics in photochemical processes on Mn oxides.
- Direct *photo*-electrochemically-dependent AFM observations of U adsorption/reduction, including the in-house development of a photo-sensitive electrochemical atomic force microscopy.
- Surface morphology changes of the bulk magnetite electrode in uranium solution using in-situ electrochemical AFM as a function of the potentials of the magnetite electrode.
- Continuation on MOFs and actinyl nanoclusters and their redox, electronic, and catalytic properties.

Publications supported by this project 7/2013-3/2015

1. Renock, D., et al., *The energetics and kinetics of uranyl reduction on pyrite, hematite, and magnetite surfaces: A powder microelectrode study.* Geochimica Et Cosmochimica Acta, 2013. **118**: p. 56-71.
2. Yuan, K., et al., *Electrochemical and spectroscopic evidence on the one-electron reduction of U(VI) to U(V) on magnetite.* Environmental Science & Technology, 2015. **(in revision)**.
3. Yuan, K., et al., *Uranium reduction on magnetite: Probing for pentavalent uranium using electrochemical methods.* Geochimica et Cosmochimica Acta, 2014. **(in press)**.
4. Taylor, S.D., et al., *An experimental and ab initio study on the abiotic reduction of uranyl by ferrous iron.* Geochimica et Cosmochimica Acta, 2015, in press.
5. Taylor, S.D., M.C. Marcano, and U. Becker, *Reduction of U(VI) by Fe(II) sorbed on isostructural Fe and Al (oxyhydr)oxides.* Geochimica et Cosmochimica Acta, 2015, submitted.
6. Saha, S. and U. Becker, *A first principles study of uranium-based coordination polymers for Np incorporation.* Microporous and Mesoporous Materials, 2014, submitted.
7. Arumugam, K. and U. Becker, *Computational redox potential predictions: Applications to inorganic and organic aqueous complexes, and complexes adsorbed to mineral surfaces.* Minerals, 2014. **4**(345-387).
8. Saha, S. and U. Becker *The effect of the aliphatic carboxylate linkers on the electronic structures, chemical bonding and optical properties of the uranium-based metal organic frameworks*. RSC Advances, 2015. DOI: 10.1039/C5RA01335F.
9. Saha, S. and U. Becker, *Effect of metal doping on electronic properties of different uranyl metal organic frameworks (MOFs).* 2015, in final stage of preparation.
10. Shuller-Nickles, L.C., et al., *Quantum-Mechanical Methods for Quantifying Incorporation of Contaminants in Proximal Minerals.* Minerals, 2014. **4**: p. 690-715.
11. Walker, S.M. and U. Becker, *Uranyl (VI) and neptunyl (V) incorporation in carbonate and sulfate minerals: Insight from first-principles.* Geochimica et Cosmochimica Acta, 2015. **(in press)**.
12. Yuan, K., R.C. Ewing, and U. Becker, *Thermodynamic mixing properties of the* UO_2-HfO_2 *solid solution: Density functional theory and Monte Carlo simulations.* Journal of Nuclear Materials, 2015. **(in press)**.

Organometallic Actinide Chemistry: Probing Covalency through Metal Ligand Multiple Bonding

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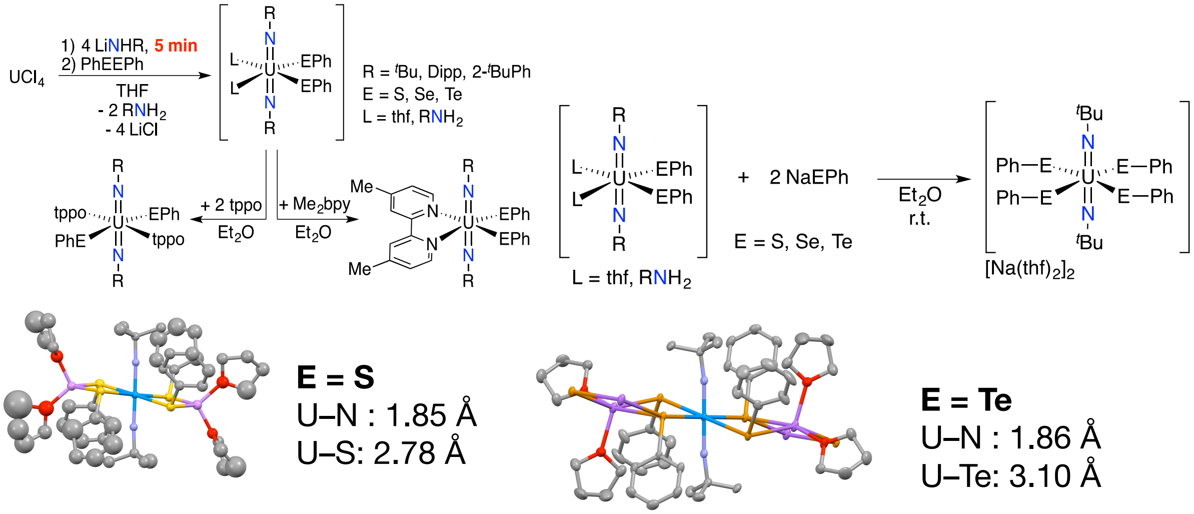
Overall research goals: The objective of this project is to synthesize novel uranium complexes with Uranium-light element multiple bonds and understand the bonding in these compounds within the context of the evolving view of actinide-ligand ligand bonding.

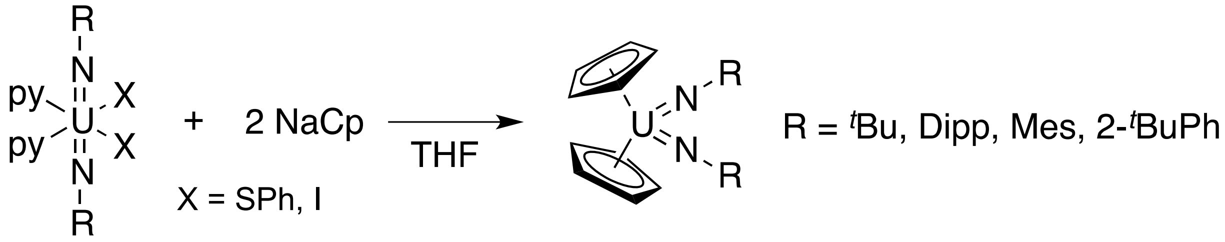
Significant achievements during 2013-2015

1. The synthesis, crystal structure and XAS characterization of uranium chalcogenolate complexes (Scheme I). Synthesis involved the generation of a putative U(IV)bis(imido) which is oxidized through reaction with PhEEPh (E = S, Se, Te). This has resulted in a general synthesis of the family of novel chalcogenolate complexes, **1- 3**, below. This family of compounds has allowed us to begin comparing the bonding in [bis(imido)U(VI)X_4]$^{2-}$ (X = halide) with the related chacogen complexes using ligand k-edge X-ray absorption spectroscopy (XAS). The synthetic procedure for these compounds is an improvement over our original synthesis of bis(imido)U(VI) complexes because the starting material is readily available UCl_4 and the isolation and purification of the resultant compounds is easier than our original procedures giving useful access to a wider range of imido groups with varying substituents.



SCHEME I

2. The synthesis of a new series of $(C_5H_5)_2U(=NR)_2$ complexes as shown in Scheme II. Access to these compounds has allowed us to investigate the origin of Temperature Independent Paramagnetism (TIP) in this class of compounds. The phenomenon of TIP in these compounds was first reported over 20 years ago with the synthesis of $(C_5Me_5)_2U(=NPh)_2$, but has not been fully investigated. With access to numerous derivatives and modern computational methods, we have been able to more fully investigate the origins of this phenomenon.



Scheme II

These studies have revealed the electronic structure of the $(C_5H_5)_2U(=NR)_2$ compounds is far more complex that we had originally thought. When R=Ph there is a low energy absorption at 920nm that is *not* due to an f-f transition, but rather an imido π to U charge transfer transition.

The results demonstrate that the ground electronic state of the $(C_5H_5)_2U(=NR)_2$ compounds is not properly described by single determinate DFT methods. They are best described using CAS-SCF calculations that show that the multi-configurational ground state is composed of 80% of one configuration plus 15 other configurations that contribute at least 0.6% to the overall electronic ground state of the molecule. This multi configurational ground state has a triplet excited state that is ~5000cm^{-1} above the ground state. Mixing of this triplet state with the ground state is responsible for the observed TIP and consequent unusual NMR chemical shifts observed in these compounds. Overall, these observations suggest that standard DFT methods may not always be the best way to understand the electronic structure of these compounds.

Science objectives for 2013-2015:

- Explore novel synthetic pathways to known and new U-E multiple bonds.
- Investigate the electronic structure of the new materials using various spectroscopic and computational techniques.

Publications supported by this project 2013-2015

1. L. P. Spencer, P. Yang, S, G. Minasian, R. E. Jilek, E. R. Batista, K. S. Boland, J. M. Boncella, S. D. Conradson, D. L. Clarke, T. W. Hayton, S. A. Kozimor, D. K. Shuh, M. P. Wilkerson *Tetrahalide Complexes of the* $[U(NR)_2]^{2+}$ *Ion: Synthesis, Theory, and Chlorine K-Edge X-ray Absorption Spectroscopy, J. Am. Chem. Soc.* **2013**, *135*, 2279 - 90.
2. R. E. Jilek, N. C. Tomson, R. L. Shook, B. L. Scott, **b** *Preparation and Reactivity of the Versatile Uranium(IV) Imido Complexes:* $U(NAr)Cl_2(R_2bpy)_2$ *(R = Me,* ^{t}*Bu) and* $U(NAr)Cl_2(tppo)_3$ *Inorg. Chem.* **2014**, *53,* 9818-26.
3. R. E. Jilek, N. C. Tomson, B. L. Scott, J. M. Boncella *[2+2] Cycloaddition Reactions a Terminal Imido Uranium(IV) Complexes to Yield Isolable Cycloadducts, Inorg. Chim. Acta.* **2014**, *422*, 78-85. (invited paper)

Targeting DOE-Relevant Ions with Supramolecular Strategies

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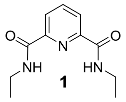
Overall research goals: The effectiveness of three popular strategies for supramolecular anion recognition is being evaluated: (1) charge and spacer complementarity, (2) ion pair hosts, and (3) molecular organic frameworks. Amide, amide/amine, urea, and urea/amine hosts have been explored targeting ions of importance to the DOE mission, with special focus on SO_4^{2-}.

Significant achievements during 2013-2015: To date we have made progress in 1) evaluating sulfate selectivity and the effectiveness of the chelate influence for amide- and urea-based hosts; 2) assessing the sensitive role of the amine functionalities and macrocyclic size on interactions with small molecules and anions; and 3) synthesizing metal-linked extended molecular host frameworks:

1) We systematically explored the influence of the sequential addition of chelating groups for two common hydrogen bonding functionalities, ureas and amides.[1] Amide-, amide/amine-, urea-, and urea/amine-based hosts (**1** – **6**) were compared with respect to (1) selectivity for SO_4^{2-} over other anions and (2) binding effectiveness in the presence of water. Not only did the urea host **6** display selectivity for SO_4^{2-} over other anions (**Figure 1**), but **6** also maintained significant binding at 25% water content ($K = 7 \times 10^3$ M^{-1}). Structure results for **5** and **6** indicate that sulfate ion is an effective template in organizing the hosts and also binds (geometry-wise) in a fashion similar to transition metal ions (**Figure 2**).



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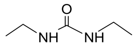

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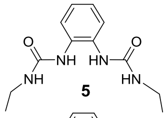

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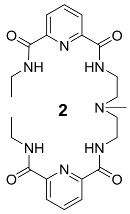

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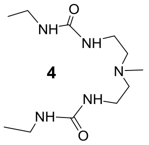

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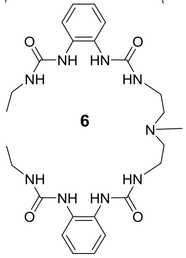

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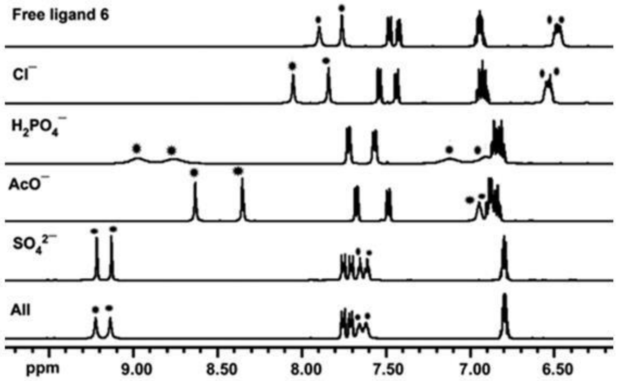

Figure 1. Partial ^1H NMR spectra in 0.05% water-mixed DMSO-d_6 of **6** in the presence of 1 equiv of selected anions and with all anions (NH signals denoted by asterisks).

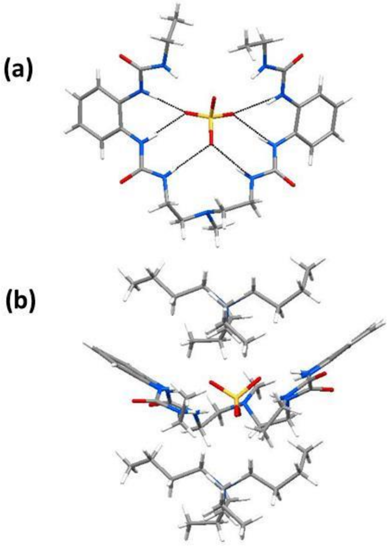

Figure 2. **(a)** Overhead view of [**6**·(SO_4^{2-})] without TBA^+ and **(b)** side view with TBA.

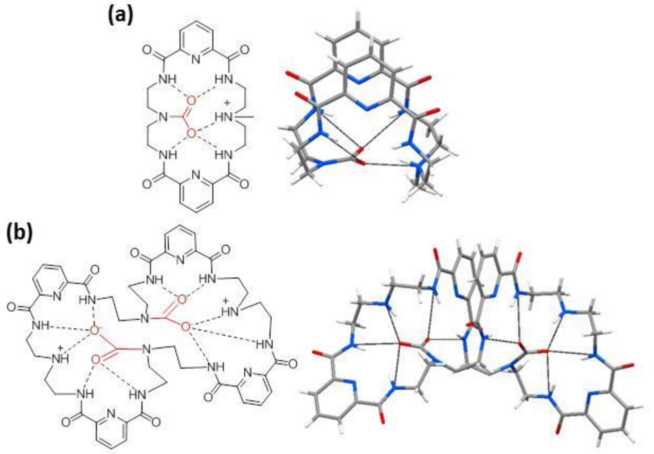

Figure 3. ChemDraw diagrams and crystallographic perspective views of the CO_2 adducts of the **(a)** 2+2 and **(b)** 4+4 macrocycles with secondary amines.

2) Our original focus for this project was on mixed amide-secondary amine macrocycles obtained by simple one-step condensation reactions between N,N-bis(2-aminoethyl)methylamine. We have now achieved a facile one-step cyclization reaction using diethylenetriamine without having to resort to N-methylation to prevent side reactions. A series of condensates, from the smaller dipincer-containing 2+2 to 3+3 and the tetrapincer-containing 4+4 macrocycle, have now been isolated in significant quantities. These macrocycles all react readily with CO_2 in the atmosphere to form a stable carbamate adduct (**Figure 3**).[2] While significant heating (100 ^{o}C) is normally required for CO_2 release,[2] we found that CO_2 is readily released in the presence of certain anions. The 4+4 macrocycle binds CO_2 in a similar, but 1:2 L:CO_2 fashion (**Figure 3(b)**).

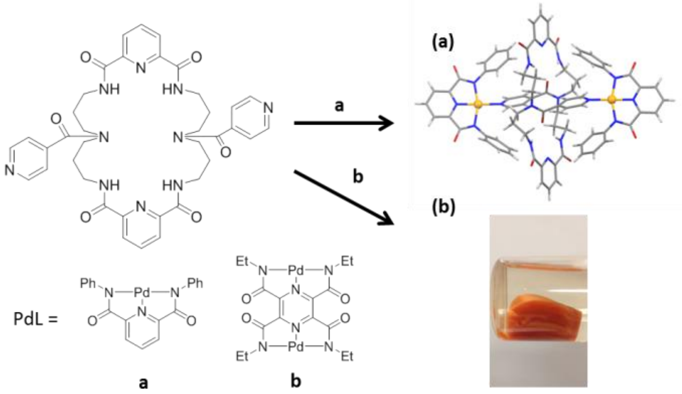

Figure 4. ChemDraw diagrams of the macrocycle and Pd(II) complexes with **a** and **b** (on the left), and **(a)** perspective view of the macrocyclic complex with **a** and **(b)** photo of the product obtained by reacting the macrocycle with **b** (on the right).

3) In exploring extended macrocyclic (MOF-like) frameworks, we synthesized several macrocycles with different pendant binding groups (pyridine and cyanobenzene) as "pre-MOFs", and explored their reactivity with metal salts. Extended $AgNO_3$-linked macrocycles were obtained, stabilized by supramolecular nitrate binding with the macrocycle. We also attached a Pd(II) pincer complex to the pendant pyridines as a prototype for extended pincer frameworks (**Figure 4(a)**), and designed a ditopic "duplex" pincer, which, when reacted with the pyridine-appended macrocycle, resulted in a porous solid (**Figure 4(b)**).

Science objectives for 2015-1016:

- Explore the supramolecular chemistry of the urea-based hosts in greater detail, including synthesis of macrocyclic and possibly bicyclic hosts.
- Explore the influence of anions on the release/activation of bound CO_2.
- Explore the synthesis and supramolecular chemistry of extended macrocyclic frameworks including duplex pincers with different metal ions.

Publications supported by this project 2013-2015:

1. Jia, C.; Wang, Q.-Q., Begum, R. A.; Day, V. W.; and Bowman-James, K. "Chelate effects in sulfate binding by amide/urea-based ligands," Submitted to *Org. & Biomolec. Chem*.
2. Wang, Q.-Q.; Day, V. W.; and Bowman-James, K. "Macrocyclic Influences in CO_2 Uptake and Stabilization," *Org. Lett.* **2014**, *16*, 3982-3985, dx.doi.org/10.1021/ol501812u.

Actinide N-Donor Thermodynamics: Expanding the f-element Covalency Dialogue

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Another collaborator

Overall research goals: The objective of this project is to assess the thermodynamic complexation data that describes actinide-aminopolycarboxylate (APC) interactions. A particular emphasis is placed on evaluating the enthalpic interaction between the nitrogen groups and the heaviest actinides to understand potentially covalent interactions in these systems.

Significant achievements during 2014-2015: Project came up to speed in the recruitment of graduate student Morgan Luckey. Morgan has been trained on stability constant determination using spectrophotometric and radioanalytical techniques using neodymium and europium-152/154, respectively. This was done in cooperation with the post-doctoral research associate, Jessica Drader. To date, submitted a review manuscript on actinide-APC interactions and are in the process of reevaluating the residual enthalpy data associated with americium APC interactions.

1. Evaluation of linear free energy relationships (LFERs) that compare trivalent actinide-lanthanide interactions with APCs. Presented inforamtion suggests that the actinide selectivity for amino-polycarboxylates decreases across the series, but data is sparse and the generated uncertainties prohibit more conclusive statements regarding the actinide-APC binding – particularly for the heaviest actinides.

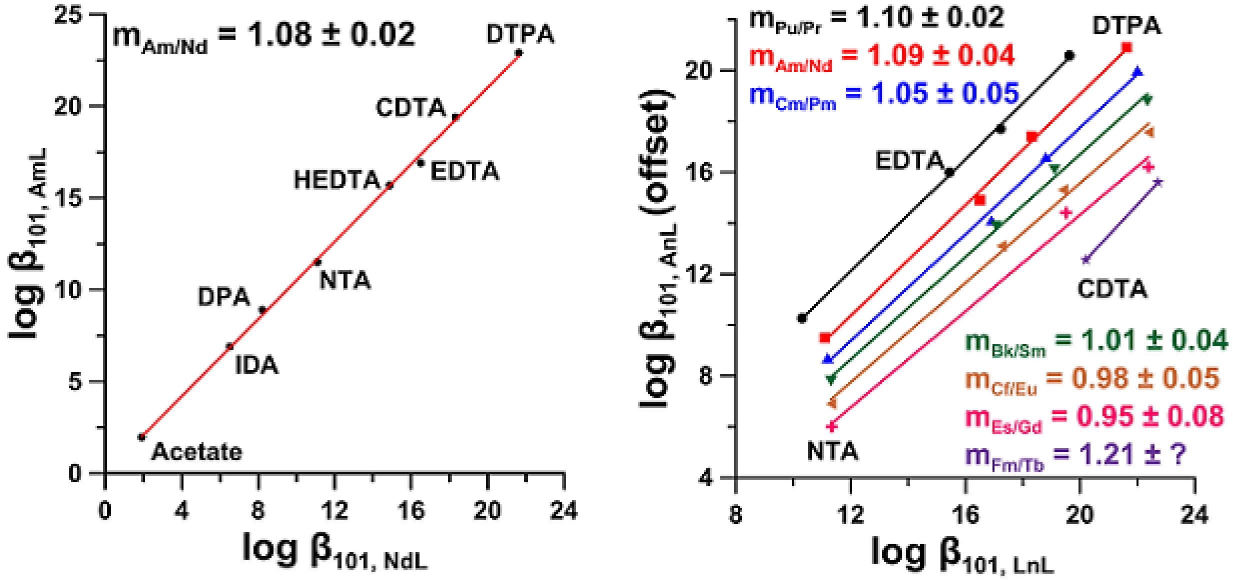
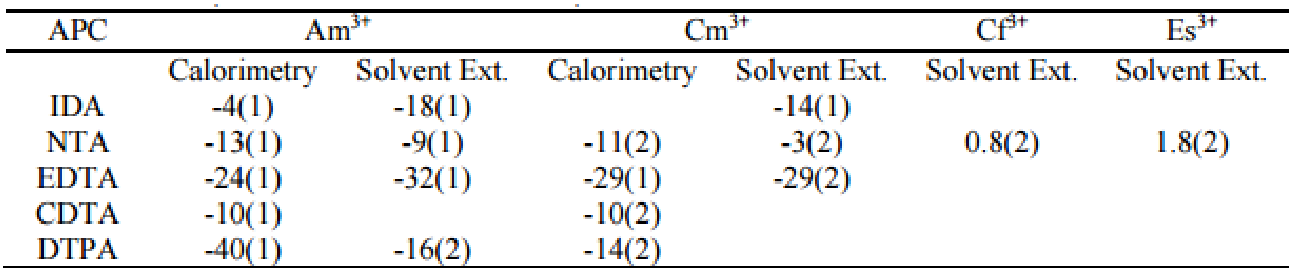


Figure 1. Left: Original LFER generated by Choppin demonstrating an approximately eigh percent increase in Am-APC interactions compared to Nd-APC interactions. Right: Expanded LFER that compares lanthanide-APC interactions with the APC interactions of the comparably sized actinide. Abbreviations of APCs are as follows: iminodiacetic acid (IDA), dipicolinic acid (DPA), nitrilotriacetic acid (NTA), N-hydroxyethyl-ethylenediamine-triacetic acid (HEDTA), ethylene-diaminetetraacetic acid (EDTA), trans-1,2-cyclohexandiamine-tetraacetic acid (CDTA), diethylenetriamine-pentaacetic acid (DTPA).

2. Assessment of currently available enthalpic data for actinide-APC interactions at comparable ionic strengths (0.5 M). Limited enthalpic data suggests a shift to more endorthermic actinide-APC interactions moving across the period.

Table 1. Enthalpic information for trivalent actinides with APC ligands at 0.5 M ionic strength and 25°C. Uncertainties are indicated in parentheses. Calorimetric and solvent extraction methods were used for enthalpic determinations. All data are presented in kJ·mol^{-1}.



APC	Am^{3+}		Cm^{3+}		Cf^{3+}	Es^{3+}
	Calorimetry	Solvent Ext.	Calorimetry	Solvent Ext.	Solvent Ext.	Solvent Ext.
IDA	-4(1)	-18(1)		-14(1)		
NTA	-13(1)	-9(1)	-11(2)	-3(2)	0.8(2)	1.8(2)
EDTA	-24(1)	-32(1)	-29(1)	-29(2)		
CDTA	-10(1)		-10(2)			
DTPA	-40(1)	-16(2)	-14(2)			

Comparisons between calorimetric and solvent extraction data demonstrate several instances where data was not reproduced and trends for a given actinide with a set of APC ligands are difficult to discern. Exceptions to this statement include the data acquired for the Cm-EDTA and Am-NTA systems. Accurate assessment of enthalpic binding components will be necessary to fully comprehend, and model, binding in heavy actinide chemistry.

Science objectives for 2015-2017:

- Evaluate stability constants and enthalpic binding information for berkelium and californium with IDA, DPA, HEDTA and CDTA.
- Complete residual enthalpy assessments for actinide-APC systems using revised acetate complexation data acquired at 0.5 M ionic strength.

  Model actinide-APC interactions with zeroth-order regular approximation of the Dirac-equation-based hybrid density functional theory (DFT) and multireference perturbation theory.

Publications supported by this project 2014 - 2015

1. Drader, J.A.; Luckey, M.; Braley, J.C., "Actinide N-Donor Solution Thermodynamics: Expanding the f-element Covalency Dialogue. Submitted Solvent Extraction & Ion Exchange

First Pseudo-Bicyclic Guanidinium-Based Receptor Favors Anion Coordination in a Symmetric Planar Orientation

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Collaborators: Dr. Radu Custelcean and Dr. Bruce A. Moyer, Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6119

Overall research goals: Our overarching research goal is to develop a rational basis for the design of fully functional receptors for binding specific oxoanions. The first step is to identify guanidinium hydrogen-bonding groups that offer increased binding affinity and rigidity upon coordination with an anion. The next step is to determine optimal linking groups that can join multiple guanidinium groups to provide a receptor with an optimal orientation and number of hydrogen bonds to a specific anion, forming a charge-neutral complex. Added lipophilicity provides the functionality to effect selective and efficient extraction.

Significant achievements during 2014–2015:

We report the first example of a planar pseudo-bicyclic guanidinium-based anion receptor rigidified by intramolecular hydrogen bonding to the bis(2-pyridyl) framework (**1**, Figure 1). Wave function and density functional theory (DFT) methods have been used to determine relative stabilities of the major conformations in a free state and when bound to the nitrate anion. Comparison with the results for the *N*,*N*'-bis(phenyl)guanidinium (**2**, Figure 1) enabled us to elucidate the role of the intramolecular hydrogen bonding on the conformation flexibility and the preferential binding motif of guanidinium ligands. We find that in contrast to **2**, the pseudo-bicyclic scaffold **1** shows a strong preference for a symmetric planar α,α-conformation when bound to an anionic species (Figure 1).

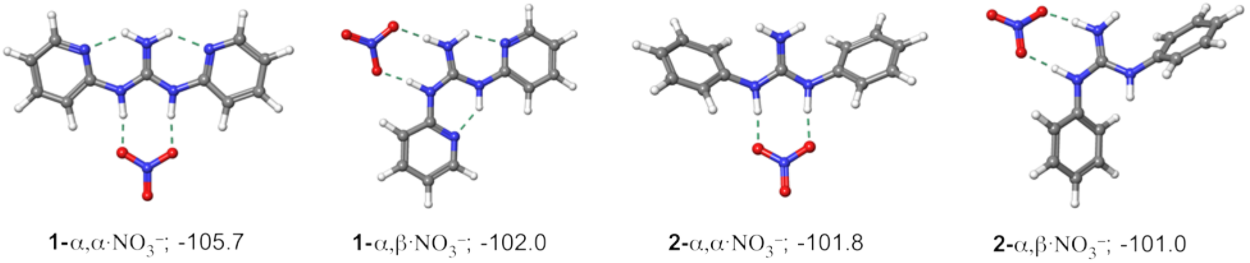
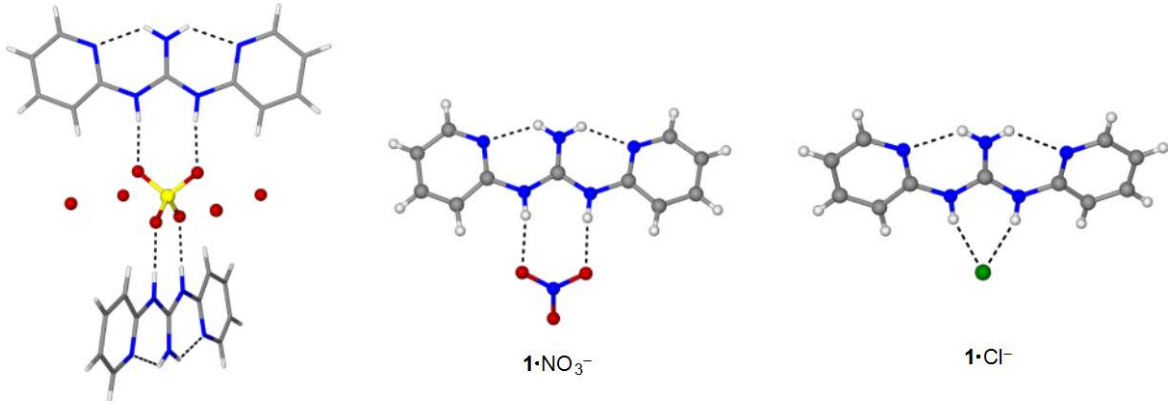

1-α,α·NO_3^-; -105.7 **1**-α,β·NO_3^-; -102.0 **2**-α,α·NO_3^-; -101.8 **2**-α,β·NO_3^-; -101.0

Figure 1. Structures and binding energies (kcal/mol) for 1:1 nitrate anion – ligand complexes in the α,α and α,β binding conformations obtained after geometry optimization at the ωB97X-D/6-311++G(3df,3pd) level of theory. Binding energies are obtained with respect to a free ligand in the most stable α,β conformation. Dashed lines indicate hydrogen bonds.

Theoretical predictions were corroborated by X-ray structural data, indicating that **1** binds to the sulfate, nitrate, and chloride anions exclusively in the α,α-orientation (Figure 2). Conversely, **2**, which does not have the intramolecular hydrogen bonds, is unable to show the same degree of structural discrimination. Furthermore, the ability of **1** to act as an effective sulfate separation agent is demonstrated by the selective crystallization of sulfate from an aqueous mixture of anions. A strong preference for one type of coordination geometry offers advantages for the design of more complex bis- and tris-guanidinum receptors with a predefined binding geometry.



1·SO_4^{2-}·$(H_2O)_4$·**1**

1·NO_3^-

1·Cl^-

Figure 2. Crystal structures of **1** bound to various anions. In all cases, **1** is planar and bound in the desired α,α conformation.

Science objectives for 2015–2017:

Develop a rational design approach for fully functional guanidinium-based receptors preorganized to bind specific oxoanions. This includes the following steps:

- Investigate various guanidinium-based scaffolds and rank them with respect to binding affinity and degree of preorganization for oxoanions.
- Develop parameters for one of the existing force-field methods to allow accurate modeling of aliphatic and aromatic guanidinium derivatives and their anion complexes. Couple this force field with the *de novo* molecule building software to generate and screen bis- and tris-guanidinium architectures for selective binding of oxoanions.
- Synthesize the target receptors and characterize their structural and thermodynamic properties in binding and extracting anions.

Publications supported by this project 2013–2015:

1. Moyer, B. A.; Custelcean, R.; Hay, B. P.; Sessler, J. H.; Bowman-James, K.; Day, V. W.; Kang, S. O. A Case for Molecular Recognition in Nuclear Separations: Sulfate Separation from Nuclear Wastes. *Inorg. Chem.* **2013**, *52*, 3473 (invited article).

2. Rajbanshi, A.; Wan, S.; Custelcean, R. Dihydrogen Phosphate Clusters: Trapping $H_2PO_4^-$ Tetramers and Hexamers in Urea-Functionalized Molecular Crystals. *Cryst. Growth Des.* **2013,** *13 (5),* 2233–2237. DOI: 10.1021/cg400336q.

3. Custelcean, R. Urea-Functionalized Crystalline Capsules for Recognition and Separation of Tetrahedral Oxo Anions. *Chem. Commun.* **2013,** *49 (22),* 2173–2182 (Invited article, featured on the front cover). DOI: 10.1039/c2cc38252k.

Hydrothermal Chemistry of UO_2^{n+} Phases: Formation and Stabilization of Pentavalent Uranium Compounds

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Ganna Senchyk, Pius Adelani, Zhehui Weng, Post-Doctoral Researchers
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Overall research goals: (1) Synthesis and characterization of a diverse suite of Np(V) compounds, to develop topological relationships within this group of structures and those of U(VI), and to study the magnetic properties of well-characterized Np(V) compounds. (2) To synthesize and characterize a broad range of compounds with U(VI) cation-cation interactions, and to delineate the conditions under which such interactions are favored. To understand the impact of U(VI) cation-cation interactions on structure stability. (3) Using the unique approach of ionothermal-based synthesis of uranyl and neptunyl compounds, probe the role of structural water in determining the connectivity of uranyl compounds. (4) Probe the mechanism of formation of dinuclear peroxide complexes in nonaqueous solution in the absence of added peroxide, and characterize the solid-state chemistry of these compounds for both uranyl and neptunyl.

Significant achievements during 2013-2015: Details of achievements are provided in published papers.[1-13]

Hybrid uranyl-vanadium oxide clusters were obtained by dissolving uranyl nitrate in the ionic liquid 3-Ethyl-1-methylimidazolium ethylsulfate that was then layered or mixed with an aqueous solution containing vanadium.[13] Where sulfate was present, wheel-shaped $\{U_{20}V_{20}\}$ crystallized and contains ten sulfate tetrahedra, and in the absence of added sulfate, $\{U_2V_{16}\}$, a derivative of $\{V_{18}\}$, was obtained. The polyhedral linkages and topology of $\{U_{20}V_{20}\}$ are intermediate between those typical of the extensive families of transition metal polyoxometalates and uranyl peroxide cage clusters (Figure 1).[13]

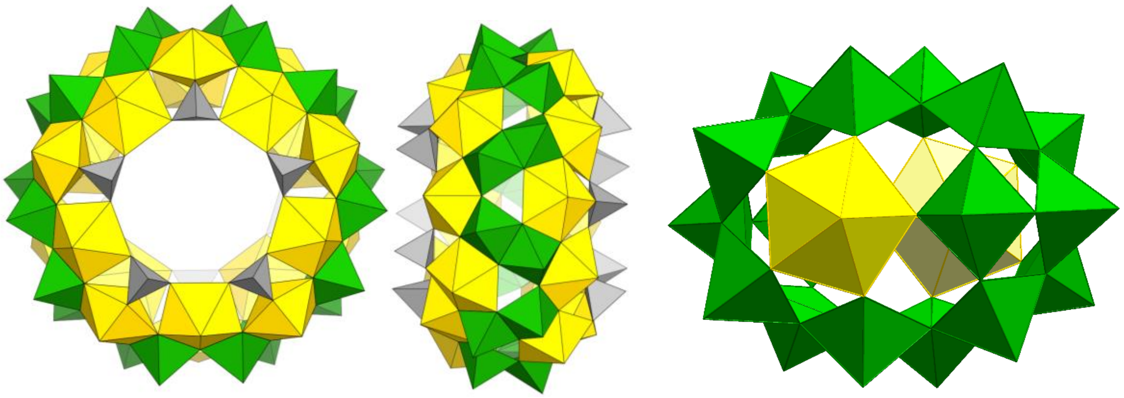

Figure 1. Hybrid uranyl-vanadium oxide clusters $\{U_{20}V_{20}\}$ (left and center) and $\{U_2V_{16}\}$ (right). Uranyl, vandyl, and sulfate polyhedra are shown in yellow, green, and gray, respectively.

We have made progress in answering longstanding questions about the origin of uranyl peroxide complexes following the sunlight photolysis of uranyl nitrate and uranyl acetate solutions in pyridine, demonstrating that they arise from photochemical oxidation of water.[7]

We developed methods for ionothermal synthesis of novel uranyl compounds, and examined relationships between their structural units and interstitial complexes.[8, 11, 12] The exclusion of water provides insights relative to typical uranyl minerals and compounds synthesized using the more common hydrothermal approach. Our efforts utilizing ionic liquids also provided a pathway to novel uranyl-vanadate clusters (see above).

Studies of cation-cation interactions in actinide solids resulted in several novel examples, including a compound with Np(V) cationic nets that was the subject of computational studies.[5, 9] We synthesized and characterized uranyl diphosphonate and arsonate compounds with new structure topologies, including nanotubular and nanocage arrangements of building units.[1-4] Studies revealed complex uranyl-based structure topologies.[6, 10]

Current work is focused on the characterization of several additional uranyl-based transition metal clusters obtained from ionic liquids, Np(V) compounds from ionic liquids, and additional examples of U(VI) compounds containing cation-cation interactions. We have also developed a new structural hierarchy of inorganic uranyl phases and intend to submit a manuscript on the topic in June.

Science objectives for 2015-2017:

- Continue development of the ionothermal synthesis approach for novel Np(V) and U(VI) compounds, and place the resulting structures within the context of our structural hierarchy.
- Completed characterization of novel uranyl-transition metal clusters.
- Conduct calorimetric measurements (using drop-solution calorimetry) for selected U(VI) compounds containing cation-cation interactions.

Publications supported by this project 2013-2015

1 P. O. Adelani, N. D. Cook, J. M. Babo and P. C. Burns, *Inorganic Chemistry*, 2014, **53**, 4169. 10.1021/ic500220d

2 P. O. Adelani, N. D. Cook and P. C. Burns, *Crystal Growth & Design*, 2014, **14**, 5692. 10.1021/cg500972w

3 P. O. Adelani, N. A. Martinez, N. D. Cook and P. C. Burns, *European Journal of Inorganic Chemistry*, 2015, 340. 10.1002/ejic.201402764

4 P. O. Adelani, G. E. Sigmon and P. C. Burns, *Inorganic Chemistry*, 2013, **52**, 6245. 10.1021/ic400827h

5 E. Balboni and P. C. Burns, *Journal of Solid State Chemistry*, 2014, **213**, 1. 10.1016/j.jssc.2014.02.001

6 S. V. Krivovichev and P. C. Burns, *Journal of Geosciences*, 2014, **59**, 135. 10.3190/jgeosci.164

7 B. T. McGrail, L. S. Pianowski and P. C. Burns, *Journal of the American Chemical Society*, 2014, **136**, 4797. 10.1021/ja502425t

8 P. A. Smith and P. C. Burns, *Crystengcomm*, 2014, **16**, 7244. 10.1039/c4ce00512k

9 B. Vlaisavljevich, P. Miro, D. X. Ma, G. E. Sigmon, P. C. Burns, C. J. Cramer and L. Gagliardi, *Chemistry-a European Journal*, 2013, **19**, 2937. 10.1002/chem.201204149

10 Z. H. Weng, Z. H. Zhang, T. Olds, M. Sterniczuk and P. C. Burns, *Inorganic Chemistry*, 2014, **53**, 7993. 10.1021/ic5007814

11 E. M. Wylie, M. K. Dustin, J. S. Smith and P. C. Burns, *Journal of Solid State Chemistry*, 2013, **197**, 266. 10.1016/j.jssc.2012.08.045

12 E. M. Wylie, P. A. Smith, K. M. Peruski, J. S. Smith, M. K. Dustin and P. C. Burns, *Crystengcomm*, 2014, **16**, 7236. 10.1039/c4ce00270a

13 G. Senchyk, E. M. Wylie, S. Prisio, J. E. S. Szymanowski, G. E. Sigmon and P. C. Burns, *Chemical Communications (submitted)*, 2015.

Novel uranyl bearing materials via restricted UO_2^{n+} speciation profiles and supramolecular assembly

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Argonne National Laboratory, Chemical Sciences &
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Overall research goals: The overall research goal of this project is to synthesize novel uranyl bearing materials using supramolecular assembly techniques. This is a transition away from hydrothermal systems wherein hydrolysis of $[UO_2]^{2+}$ is the norm, to lower temperature, high-anion conditions to promote restricted speciation profiles. Molecular 'tectons' such as the $[UO_2X_4]^{2-}$ (X = Cl, Br, NCS) are assembled through supramolecular 'synthons' such as H-bonding and halogen bonding interactions.

Significant achievements during 2013-2015:

1. Building on the success of the $[UO_2Cl_4]^{2-}$ and $[UO_2Br_4]^{2-}$ systems, we have expanded our efforts to include assembly of $[UO_2(NCS)_4H_2O]^{2-}$ bearing materials. This tecton may be formed reproducibly under high NCS^- concentration at room temperature. Assembly and precipitation with substituted pyridinium cations such as 4-XpyH (where X = CH_3, NH_2, $N(CH_3)_2$, Cl, Br, I, SCN) is a viable route to crystalline materials and large families of compounds have been produced. As such, this allows for a systematic study of synthon interactions as one may observe which manifest themselves in the solid state and (at least qualitatively) explore the strengths thereof via crystallographic metrics (e.g. bond lengths) and IR signatures. Figure 1 shows $(C_5H_5NCl)_2[UO_2(NCS)_4H_2O]$, a molecular compound exhibiting extended chains along the [010] direction containing intrachain S···H hydrogen bonds and interchain C-Cl···O and N-H···S pairings.

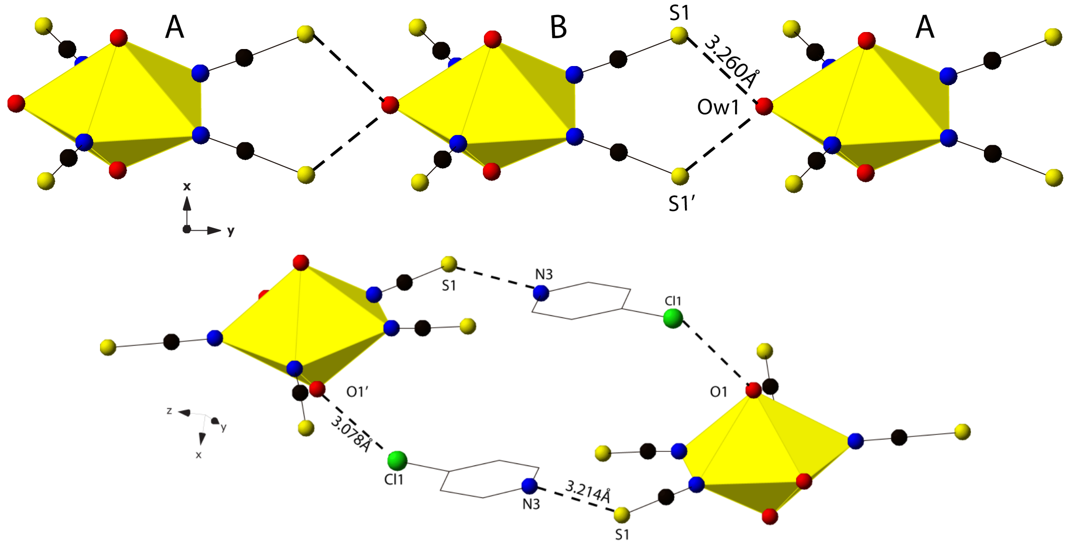

Figure 1. Top: Chain motif in $(C_5H_5NCl)_2[UO_2(NCS)_4H_2O]$ highlighting H-bonding between bound water molecules and terminal S of NCS groups. Bottom: the 4-chloropyridine H-bonds with terminal S atoms, and halogen bonds to uranyl oxygens.

2. Further reactions in high NCS$^-$ media: Pentacoordinate $[UO_2(NCS)_5]^{3-}$ tectons may be promoted in the solid state through the use of dication charge balancing species such as bipyridines. Figure 2 shows $(C_{10}H_{10}N_2)_2[UO_2(NCS)_5]\cdot SCN$ wherein tectons are linked though S···S interactions. Luminescence spectra of this family of materials contain additional peaks corresponding to uranyl coupling with the C=S stretch of isothiocyante groups. Moreover, we have begun to quantify the strengths of the supramolecular interactions involving the terminal S groups via probing the U-N and C=S stretches in the IR.

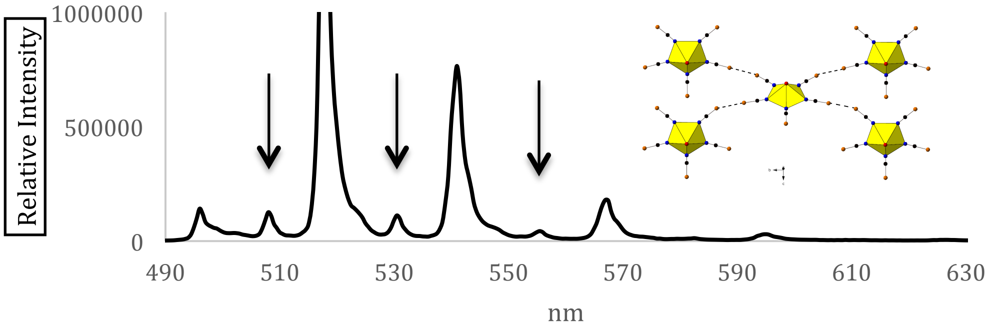

Figure 2. Emission spectrum of $(C_{10}H_{10}N_2)_2[UO_2(NCS)_5]\cdot SCN$. Arrows indicate additional bands from uranyl coupling with C=S stretches.

Science objectives for 2015-2017:

Objectives for the next three years include: 1) Further exploration of supramolecular interactions with a variety of organic cations and [UO2X4]2- (X = Cl, Br) and $[UO_2(NCS)n(H_2O)m]$ (n = 4,5; m= 0,1). After establishing families of compounds, we will continue to discern relative strengths of interactions (crystallographically and spectroscopically) and work to develop a comprehensive ranking as relevant to crystal engineering and design.

2) Ligand K-edge X-ray absorption spectroscopy of uranyl materials- continued collaboration with Stosh Kozimor- LANL. Preliminary Cl K-edge XAS analyses show that H–bonding between $[UO_2Cl_4]^{2-}$ species and protonated amines can appreciably alter U–Cl electronic structure and orbital mixing. As such, we plan a systematic study of Cl-Kedge spectra of related materials that contain both H-bonding and halogen-halogen interactions.

Selected publications supported by this project 2013-2015

1. R. E. Wilson, D. D. Schnaars, M. B. Andrews, and C. L. Cahill (2014) "Supramolecular Interactions in $[PuO_2Cl_4]^{2-}$ and $[PuCl_6]^{2-}$ Complexes with Protonated Pyridines: Synthesis, Crystal Structures, and Raman Spectroscopy.″ *Inorg. Chem.*, 53(1), 383-392. http://dx.doi.org/10.1021/ic4023294

2. R. G. Surbella III and C. L. Cahill (2014) "The exploration of supramolecular interactions stemming from the $[UO_2(NCS)_4(H_2O)]^{2-}$ tecton and substituted pyridinium cations.″ *CrystEngComm*, 16(12), 2325-2536. http://dx.doi.org/10.1039/c3ce42106f

3. M. B. Andrews and C. L. Cahill (2013) "Metal-organic hybrids involving the $[UO_2Cl_3(NO_3)]^{2-}$ tecton and the role of halogen polarizability.″ *CrystEngComm*, 15(16), 3082-3086. http://dx.doi.org/10.1039/C2CE26561C

Nuclear Magnetic Resonance Spectroscopy of Plutonium Compounds

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Overall research goals. The observation of ^{239}Pu nuclear magnetic resonance (NMR) by Yasuoka et al. has inspired interest in the potential of NMR spectroscopy for elucidating long-standing questions surrounding the electronic structure of plutonium and the remarkable ability of this element to display both covalent and atom-like behavior. Whereas the initial ^{239}Pu NMR experiments were performed at cryogenic temperatures using swept-field instruments, at PNNL we have recently initiated a study of Pu compounds with a fixed-field system with the goal of acquiring high-resolution magic-angle-spinning (MAS) spectra. This new project will evaluate magnetic resonance spectroscopy's ability, *^{239}Pu NMR in particular*, to probe the formidably complex electronic structure of Pu-containing systems.

Significant achievements during 2014-2015.

- *Development of custom instrumentation, encapsulation techniques and safety procedures for Pu experiments.* A substantial effort devoted to instrument and methods development is necessary given the challenges of experimentation with plutonium. At PNNL, we have successfully contained radioactive solid and solution samples in specially designed tubes and rotors, and more recently we have developed a custom-built sealed magic-angle-spinning probe. Our first prototype has been constructed for the 750 MHz instrument installed in the EMSL Radiological Annex. The sealed probe concept offers key improvements, including faster spinning speeds, increased filling factors, and reduced sample mass requirements.

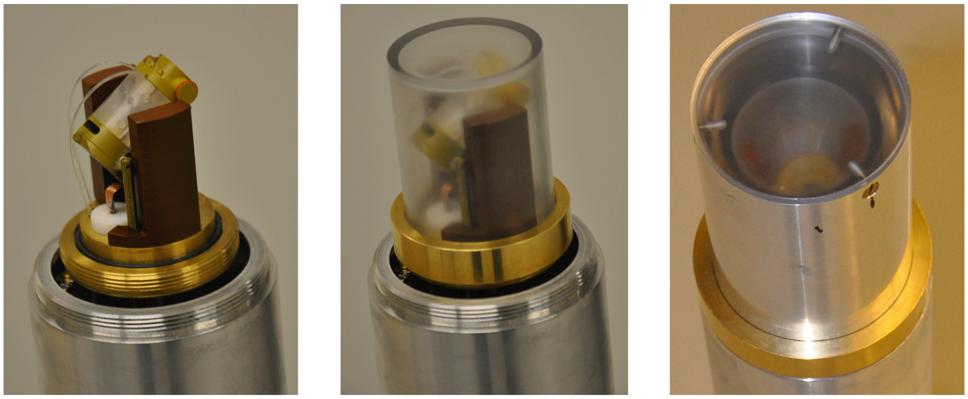

Figure 1: 750 MHz radiological magic-angle-spinning NMR probe.

- *Preparation of Pu NMR samples and preliminary measurements*. Several grams of PuO_2 have been produced using a conventional oxalate calcination method and prepared for initial NMR experiments. To enhance safety, we have developed a process for creating monolith samples from powders with the use of a mold (Fig. 2).

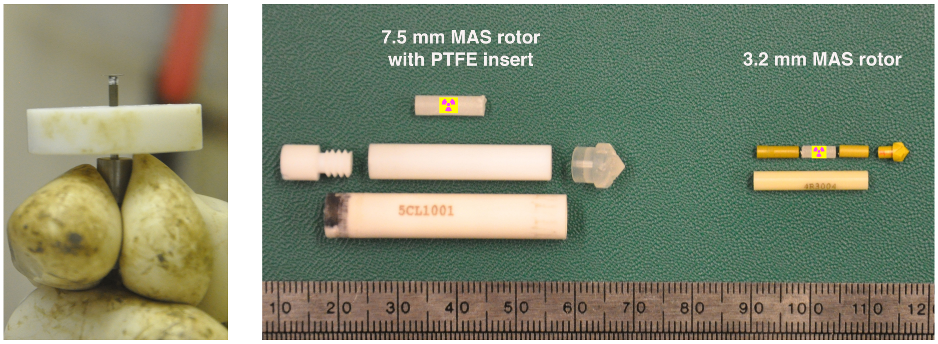

Figure 2: PuO_2 NMR pellet atop a PTFE mold (*left*) and MAS NMR rotor assemblies for pelletized radioactive sample (right).

- *Spectra of $(Me_4N)_2PuCl_6$ and PuO_2.* Low temperature experiments have been performed on $(Me_4N)_2PuCl_6$ with the swept field instrument of the LANL solid state physics group. This compound was attractive for its similarities with PuO_2: like PuO_2, $(Me_4N)_2PuCl_6$ contains a Pu(IV) center in an environment of perfect cubic symmetry. A model assuming cubic symmetry, low magnetism, and small electric field gradients has been used to analyze the data. Further work to assign spectral features is in progress.

Science objectives for 2015-2017:

- *High-resolution spectra of PuO_2.* An original goal of this project was to elucidate defect sites in PuO_2 created by oxygen atom deficiencies. This task will test the hypothesis that defects in the lattice and secondary phases will be manifested in new lines with well-defined shifts and broadening of the ^{239}Pu and ^{17}O NMR signals that may be used to infer local structure.

- *Theoretical predictions and spectral interpretation.* Electronic structure calculations are computationally demanding and at present there are many uncertainties that cloud our ability to predict and interpret NMR spectra in Pu-containing systems. Progress on fundamental theoretical issues will require close cooperation with theory colleagues.

- *Compounds beyond PuO_2, and mapping of Pu's shielding and coupling parameters.* Several Pu compounds that are *prima facie* promising for NMR study are currently available or will be synthesized at LANL. Investigation of a range of different Pu molecules will be vital for mapping the dependence of Pu chemical shifts on local environment. For a comprehensive picture of the electronic structure of the metal center, NMR spectra of covalently bonded nuclei and nearby ligands (such as ^{19}F) will also be acquired.

Publications supported by this project 2014-2015

1. "Sealed Magic Angle Spinning Nuclear Magnetic Resonance Probe and Process for Spectroscopy of Hazardous Samples," H. M. Cho, N. M. Washton, K. T. Mueller, J. A. Sears, Jr., M. R. Townsend, and R. J. Ewing, U.S. Patent Pending (Application No. 14/106,441).

2. H. Yasuoka, et al, "NMR and Susceptibility Study of the Magnetism of $(Me_4N)_2PuCl_6$." Manuscript in preparation.

Network Analysis of Liquids and Their Phase Boundaries - Computationally Derived Process Optimization of Solvent Extraction

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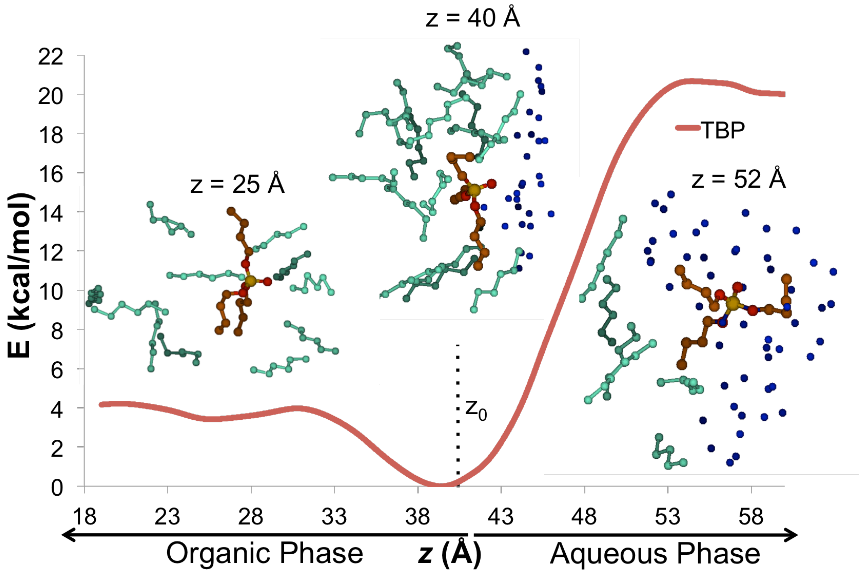
Overall Research Goals: For extraction processes to become economically feasible, to minimize waste streams, and to design new separations approaches for the next generation of nuclear reactors, it is imperative to go beyond empirical observations and understand the fundamental molecular forces and mechanisms that govern metal speciation, complexation, and transport across phase boundaries. The goal of the current work is 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. The two specific effects to be examined are ionic strength and solute hydrophobicity, both of which are experimental handles that are actively manipulated to optimize the distribution ratio of a metal-ligand complex (ML) between liquid phases, $\frac{[ML]_{org}}{[ML]_{aq}}$. A fundamental understanding of how ionic strength and hydrophobicity alter the thermodynamic and mechanistic aspects of ion extraction will enable better exploitation of experimental conditions and ligand design to achieve more efficient, predictable, and controllable separation processes. The study uses a synergistic approach composed of simultaneous density functional theory (DFT) calculations and molecular dynamics (MD) simulations that respectively provide electronic structure and ensemble correlations of molecular systems. However, novel data analysis using graph-theoretic approaches provide the key to achieving insight into the structural and dynamic effects that are imparted by high ion concentrations and the hydrophobic character of extracting ligands and of neutral metal-ligand complexes.

Significant Achievements: In prior work we have demonstrated that network analysis of graphs composed of solute-solvent interactions can be used to data-mine molecular simulation data to correlate the structural organization of a solvent to the reactivity of a simple metal ion. This has been useful for understanding the speciation of metals that include the lanthanides and actinides.[1-4] The initial approach has been expanded in the last two years to include networks that are composed of intermolecular interactions between solvent molecules in bulk liquids, with specialized analyses to understand the structure and dynamics of liquids at phase boundaries.[5-9] The current work discusses the relationships between the mesoscopic descriptors of a liquid:liquid interface (interfacial tension and width), with the fundamental dynamic process that causes interface formation and relates to interfacial permeability (microsolvation processes). Specifically, for conditions related to solvent extraction technologies – we examine how sensitive interfacial properties are to the organic solvent, aqueous electrolyte strength, and presence of ampiphilic solutes like tri-butyl phosphate and it radiolytic degradation products. The resulting data helps to decompose the dominant factors of the interface that influence the distribution coefficients of solutes relating to solvent extraction.

Figure 1. Potential of mean force profile, with inset solvation environments of TBP across the phase boundary of water and *n*-hexane. Note the change in conformation of the TBP as it enters the phase boundary and the response of *n*-hexane by adopting more perpendicular orientations to the phase boundary. This in turn has been shown to increase the microsolvation processes of *n*-hexane.



Science Objectives (next 2 years): We will continue to combine DFT and MD approaches to develop a hydrophobicity scale that is based upon our ability to now accurately calculate the solvation free energies of a variety of solutes independent of their overall charge, in combination with the response of the solvents to the solute both structurally and dynamically. Our end goal will be predict distribution coefficients apriori.

References (last 2 years):

[1]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**, *submitted.*

[2] Parmar, P., Peterson, K. A.; Clark, A. E. Static Electric Dipole Polarizabilities of $An^{5+/6+}$ and $AnO_2^{+/2+}$ (An = U, Np, and Pu) Ions *Journal of Chemical Physics*, **2014**, *141*, 234304.

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[4] Parmar, P.; Ghadar, Y.; Clark, A. E. Structural and Dynamic Dependence of Aqueous Actinides Upon Classical Force Fields, *Inorganic Chemistry*, **2015,** *In Prep.*

[5] Ozkanlar, A.; Clark, A. E. *ChemNetworks*: A Complex Network Analysis Tool for Chemical Systems, *Journal of Computational Chemistry*, **2014**, *35*, 495-505.

[6] Ghadar, Y.; Clark, A. E. Intermolecular Network Analysis of the Liquid and Vapor Interfaces of Pentane and Water: Microsolvation Does Not Trend with Interfacial Properties, *Physical Chemistry Chemical Physics*, **2014**, *16*, 12475 – 12487.

[7] Ozkanlar, A.; Zhou, T.; Clark, A. E. Towards a Unified Descriptions of Hydrogen Bond Networks of Liquid Water: A Dynamics Based Approach *Journal of Chemical Physics* **2014** *141*, 214107.

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[9] Ghadar, Y.; Christiansen, S. L.; Clark, A. E. Influence of Aqueous Ionic Strength Upon Liquid:Liquid Interfacial Structure and Dynamics, *Fluid Phase Equilibria*, **2015**, *invited article – special issue Aqueous Solutions: Bulk Fluids and Interfaces*, submitted.

Self-Assembled Architectures via Ion-Pair Coordination

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Collaborators: Peter V. Bonnesen, Santa Jansone-Popova, Benjamin P. Hay, Bruce A. Moyer, Chuandong Jia (postdoc), Oak Ridge National Laboratory

Overall research goals: We seek to understand how to effectively employ self-assembly of small organic units with selected ion pairs to construct complex molecular architectures with predetermined structures and separation functions. Our approach is to identify with the help of structure-based design multitopic ligands structurally encoded to selectively self-assemble with targeted ion pairs into high-symmetry charge-neutral ensembles (e.g., helicates, tetrahedra, cubes) that can be effectively separated by solvent extraction or crystallization.

Significant achievements during 2013-2015: In the past two years we have performed an in-depth investigation of the factors controlling the formation of triple-stranded ion-pair helicates, a new class of charge-neutral self-assembled architectures based on $NiSO_4$ or $FeSO_4$ coordination by ditopic ligands containing 2,2'-bipyridine (bpy) and o-phenylene-bis(urea) (pbu) as metal- and anion-chelators, respectively (Fig. 1). Structure-based design methods have been employed to identify geometrically complementary ditopic ligands that are structurally encoded to form ion-pair helicates with predetermined structures and stereochemistry. Single-crystal X-ray structural analysis of the prototype helicates, based on the simple methylene linker between the bpy and pbu ion-binding groups, established the homochiral (Δ,Δ or Λ,Λ) nature of this series of structures, regardless of the R group on the terminal urea. Solution NMR experiments indicated the helicate self-assembly is anion-selective, requiring the presence of tetrahedral XO_4^{2-} oxoanions such as SO_4^{2-}, SeO_4^{2-}, or $S_2O_3^{2-}$; anions of different shape or/and charge, such as Cl^-, NO_3^-, ClO_4^-, or SeO_3^{2-} formed poorly defined structures. The NMR analysis also provided insight into the mechanism of helicate formation, which appears to involve fast metal coordination, followed by the rate-limiting *mer* to *fac* isomerization of the octahedrally coordinated metal center, and finally fast anion complexation.

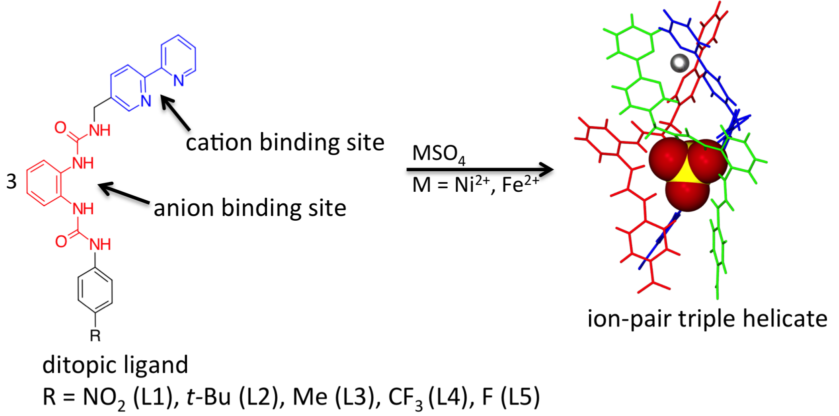

Figure 1. Self-assembly of the prototype ion-pair helicates from ditopic 2,2'-bipyridine-bis(urea) ligands and MSO_4 (M = Ni, Fe).

More recently, we began exploring the possibility of building more elaborate ion-pair architectures by self-assembly. For example, our structure-based design predicts that ligand

L6, shown in Figure 2, can self-assemble into higher-order structures such as bis-helicate, tetrahedron, or cube, all based on the ion-pair helicate as the basic structural unit. Preliminary NMR analysis showed that a high-symmetry structure does indeed form in solution when this ligand coordinates $FeSO_4$ or $ZnSO_4$. We are currently synthesizing more lipophilic analogs of L6 to allow structural analysis of the self-assembled architectures in solution by multinuclear and diffusion NMR, and small-angle X-ray/neutron scattering.

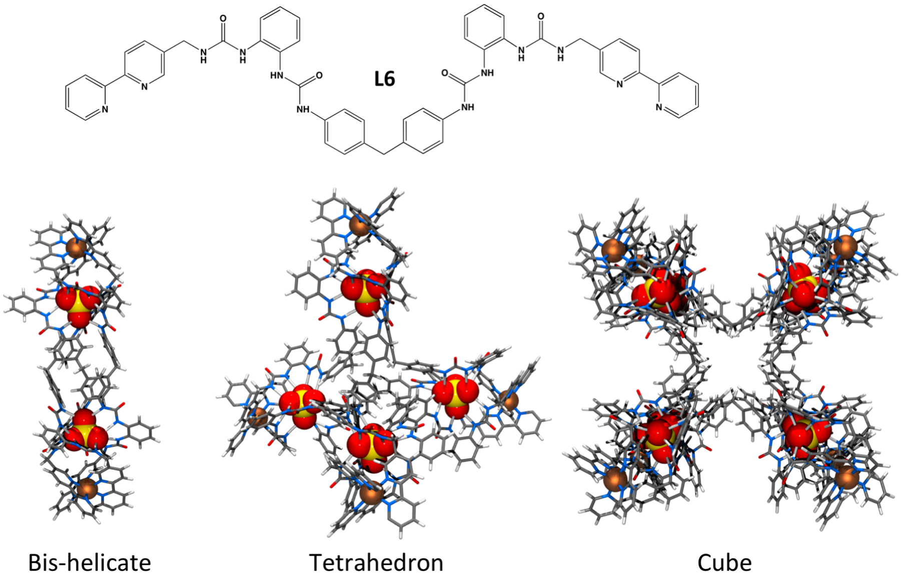

Figure 2. Higher-order structures predicted to self-assemble from L6 and MSO_4 (M = Ni, Fe).

Science objectives for 2015-2017:

- Understand the factors controlling the self-assembly of the ion-pair architectures, and gain experimental and computational insights into the roles of solvation and entropy
- Employ the self-assembled structures in selective ion-pair separation by solvent extraction

Publications supported by this project 2013-2015:

1. Custelcean, R. Urea-Functionalized Crystalline Capsules for Recognition and Separation of Tetrahedral Oxoanions. *Chem. Commun.* **2013**, *49*, 2173-2182 (invited article, highlighted on the front cover).
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Self-Assembled Ionophores: New Directions

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Prof. Srini Raghavan, University of Maryland

Overall research goals: One of our research goals is to build "self-assembled" ionophores that can selectively bind and transport ions (both cations and anions) and/or ion pairs across lipid membranes. We have used non-covalent interactions to synthesize such receptors. We have found that both lipophilic guanosine nucleosides form hydrogen bond to give G-quadruplexes that selectively bind cations. Our goals include: 1) learning how to control structure & dynamics of nucleoside self-association and ion binding; 2) design self-assembled ionophores that selectively bind various ions and 3) construct supramolecular structures that function as synthetic ion channels. More recently we have discovered how to make a remarkably stable hydrogel by adding specific salts to water solutions of guanosine. These particular hydrogels are able to bind a variety of ions and hydrophobic dyes, which make them attractive materials for separations.

Significant achievements During 2012-2015: ***Supramolecular Assemblies that Transport Small Molecules across Hydrophobic Membranes.*** We have shown that the lipophilic guanosine G **2** selectively transports cytidine (C **3**) across organic liquid membranes (Fig. 1).[1] The lipophilicity of the carrier and the and targets, and the identity of the target's sugar, are important for transport selectivity. Thus, 2′-deoxyribose nucleosides can be selectively transported and separated over ribose nucleosides. We have also modulated transport selectivity by using various additives or by forming supramolecular structures, such as a G_4-quartet or a C-G-C base-triple. Our findings suggest that supramolecular assemblies can be used to catalyse transmembrane transport of "small" biomolecules such as nucleosides, sugars and amino acids. This is an area we plan to focus on in the future.

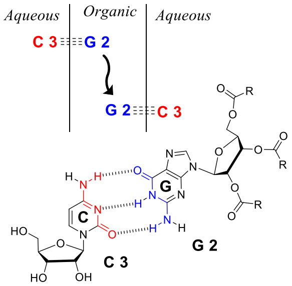


Fig. 1. Lipophilic derivative, G **2**, selectively transports C **3** across liquid membranes.

Supramolecular Hydrogels from Guanosine and Borax. We have also developed and characterized a robust hydrogel that forms with low concentrations of guanosine (G **1**) and potassium borate (Fig. 2).[2,3] The structural composition and mechanism of gelation has been extensively interrogated. We established that the hydrogel's fibrous network is the result of borate ester formation and self-assembly of borate diesters into G_4-quartets and subsequently G_4-wires. Due to the dynamic nature of the borate ester linkages and the hydrogen-bonded G_4 motif, we found that a variety of small molecules can be incorporated into the gel network, using both covalent and non-covalent bonding, suggesting the potential to use this unique hydrogel for separations and for drug delivery medium. The physical properties of these gels can be modulated by varying the cation or by addition of various cationic dyes or by adding G_4-quartet ligands.

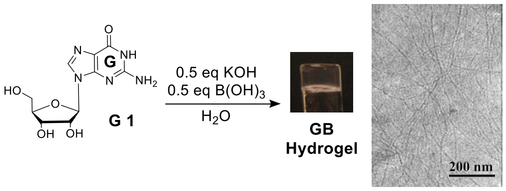
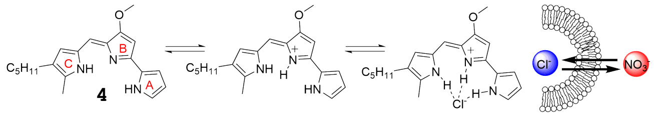


Fig. 2. A transparent hydrogel is formed from G **1** and 0.5 equiv of $KB(OH)_4$. Cryo-TEM shows the gel is composed of nanofibers.

New Synthetic Receptors That Catalyze Transmembrane Transport of Cl^- Anion. In the past grant period we have continued our research program to identify natural products and/or synthetic analogs compounds that can transport Cl^- anions across bilayer membranes.[4-5,7] In collaboration with the research group of Prof. Alison Thompson at Dalhousie University we have compared the H^+/Cl^- co-transport activity of synthetic analogs of prodigiosin **4**, a potent natural product.[4,5] These compounds' ability to transport Cl^-, to maintain a transmembrane potential, along with high activity at nM concentrations, low molecular weight and relatively straightforward and modular preparation make them all valuable leads in drug development for diseases caused by Cl^- transport malfunction. In addition to such biomedical applications these compounds also provide a framework on which to build other functional supramolecular structures that might be used for anion transport or anion separation. Moreover these studies have provided insight into the mechanism by which prodigiosin **4** and its synthetic analogs catalyzes anion exchange and transport.



__Science Objectives for 2015-2017:__ In addition to continuing our fundamental studies of self-assembled ionophores, continued emphasis in the coming years will be placed on developing self-assembled compounds that can form large pores and channels in phospholipid membranes. We also plan to use self-assembly of these lipophilic nucleosides to make other complex and functional nanostructures. We are also extremely excited about the guanosine hydrogels and their potential as functional medium for a wide variety of separations and other useful applications.

__Papers supported by this DOE Grant (May 2012-March 2015):__

1. " Controlling the Transmembrane Transport of Nucleosides." Gretchen M. Peters and Jeffery T. Davis, *Supramolecular Chemistry*, **2014**, *26*, 286-295. DOI: 10.1080/10610278.2013.872782.

2. "A $G_4 \bullet K^+$ Hydrogel Stabilized by an Anion." Gretchen M. Peters, Luke Skala, Taylor Plank, Brooke Hyman, G. N. Manjunatha Reddy, Andrew Marsh, Steven Brown, and Jeffery T. Davis, *J. Am. Chem. Soc.* **2014**, *136,* 12596-12599. DOI: dx.doi.org/10.1021/ja507506c.

3. "$G_4 \bullet M^+$ Borate Hydrogels." Gretchen M. Peters, Luke Skala, Taylor Plank, Hyuentak Oh, G. N. Manjunatha Reddy, Andrew Marsh, Steven Brown, Srini Raghavan and Jeffery T. Davis, submitted to *J. Am. Chem. Soc.* **2015**,

4. "Synthetic Prodigiosenes and the Influence of C-Ring Substitution on DNA Cleavage, Transmembrane Chloride Transport and Compound Basicity." Soumya Rastogi, Estelle Marchal, Imam Uddin, Brandon Groves, Julie Colpitts, Sherri A. McFarland, Jeffery T. Davis and Alison Thompson, *Organic & Biomolecular Chemistry*, **2013**, *11*, 3834-3845. DOI: 10.1039/C3OB40477C.

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An Integrated Basic Research Program for Advanced Nuclear Energy Systems Based on Ionic Liquids (SISGR) – Separations Aspects

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Overall research goals: We are a team of radiation and separations chemists doing fundamental studies on ionic liquid-based separations systems for the nuclear fuel cycle. We study the effects of radiation on ionic liquids (ILs) and solutes related to separations chemistry with respect to their impact on the efficiency and durability of liquid/liquid separations systems and novel IL-based separations methods, examine the principles controlling separations with ILs, and apply our findings to design new IL-based separation systems for higher efficacy, selectivity and durability.

Significant achievements during 2013-2015:

- 1-Methylimidazole (1-MIM) and 2-methylimidazole (2-MIM) are miscible in water and imidazolium based ionic liquids (ILs) and they can coordinate with soft metal ions. We have developed novel solvent extraction process for trivalent lanthanides and yttrium from aqueous solutions into ILs, which was promoted by a hydrophilic 1-MIM or 2-MIM. Slope analysis confirmed that MIM in ILs forms a 1 : 1 complex with La^{3+} and Y^{3+} and a 1 : 4 complex with Eu^{3+} and Lu^{3+}, depending on the atomic number of the metal and the metal–ligand interactions that have been characterized by FTIR spectroscopy and ESI-MS. From the temperature dependence data, the thermodynamic parameter values (ΔH, ΔS and ΔG) were calculated. The results indicated that the extraction reactions were through an endothermic process.

- Trioctylmethylammonium di(2-ethylhexyl)phosphate ([TOMA]-[DEHP]), an anion-functionalized IL extractant, was used in 1-alkyl-3-methylimidizolium bis[(trifluoromethylsulfonyl)]imide ($[C_n mim][NTf_2]$, n = 4, 6, 8, 10) and 1-alkyl-3-methylimidazolium bis(perfluoroethanesulfonyl) imide ($[C_n mim][BETI]$, n = 4, 6, 8, 10) for the separation of rare earth elements (REEs). Solvation was found to be the dominant mechanism in an ionic liquid (IL)-based extraction system for REEs. Surprisingly, very similar extraction behavior was observed even as the carbon chain length on the IL cation increased from butyl (C_4) to decyl (C_{10}). This behavior is in sharp contrast to that of conventional molecular extractants, whose extraction efficiencies are strongly dependent on the hydrophobicity of the IL cations.

- A systematic examination of the thermal properties of a series of macrocyclic polyethers of potential utility in the synthesis of new ternary ionic liquids has been undertaken. The results show that the temperature corresponding to the onset of mass loss upon heating (*i.e.*, evaporation and/or decomposition) varies with the ring size, substitution, nature of the donor atoms, and stereochemistry of the macrocycle, but is most strongly influenced by the molecular weight and aromatic content of the compound.

Science objectives for 2015-2017:

- We will continue our efforts to develop and characterize TSILs for separations, which combine the unique properties of an IL with those of an extractant. An important objective is to determine if these TSIL solvents offer significant extraction performance advantages over non-functionalized ILs. Complementary radiolytic studies will be done to determine if the attachment of functional groups affects the radiation sensitivity of the IL and the products produced. Pulse radiolysis measurements can provide kinetic data to quantify prosthetic group reactivity versus that of potential protective scavengers. EPR spectroscopy and radiolytic product analysis will identify reactive sites and suggest mitigation strategies.
- The investigation of separation mechanisms associated with fission product (*e.g.*, rare-earth ions) extraction into ionic liquids will be continued. Emphasis will be placed on controlling ion-exchange processes through use of extractants based on ionic liquids.
- Structural studies on the nanoscale using x-ray and neutron scattering will shed light on microscopic organization of ternary water-acid-IL systems in the presence of extracting agents and metal ions, pre-and post-irradiation, and the role that is played in radiation damage by system morphology. This structural work will inform pulse radiolysis studies to examine reactivity within domains and across domain boundaries. We will explore how the morphology affects the radiation susceptibility of extracting agents and how the interaction of the various components with radiation influences phase behavior.

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3. Sun, X. Q.; Luo, H. M.; Dai, S. Mechanistic investigation of solvent extraction based on anion-functionalized ionic liquids for selective separation of rare-earth ions. *Dalton Transactions* **2013**, *42*, 8270-8275.
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Understanding Actinide Aggregation

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Overall research goals: The objective of this project is to develop a fundamental understanding of actinide hydrolysis and condensation reactions, their detailed mechanisms, and the chemical, physical, and electronic properties of the resulting nanoparticles. The expected impact is a predictive insight into hydrolysis reactions in general including the role of counterions and a specific capability for chemistries related to reprocessing spent nuclear fuel and radionuclide migration in the environment.

Significant achievements during 2013-2015: The formation and evolution of polynuclear species within thorium(IV) selenate systems has been explored using complementary experimental (ANL) and computational (UA) approaches. To further understand the energetics of the formation, evolution, stability, and precipitation of polynuclear building units present within these systems, as well as to aid in the experimental data analysis, density functional theory with the COSMO self-consistent reaction field approach was used to predict the geometries, vibrational frequencies, and energetics of various model compounds based on the crystal structures. The energetics for a set of clustering reactions were predicted and these results provide further insight into the relative stabilities and energetics of mono-, di-, hexa- and octanuclear units. The energetic results for the clustering reactions highlight the important role of the anion in cluster assembly as well as the complexity of the system (Figure 1). For the monomeric complexes examined, the selenate anions are bound in a monodentate fashion whereas for the dimers, they serve to bridge Th centers and thereby bind the cluster together. The formation of the larger oligomers including the hexameric unit are entropically driven occurring with the loss of water molecules. Moreover the stabilization of the

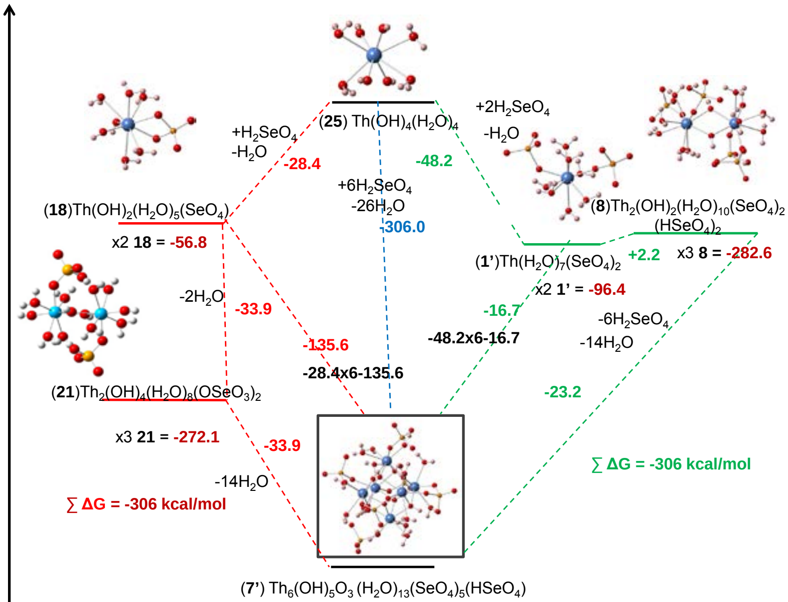

Figure 1.One clustering scheme with ΔG(aq) in kcal/mol.

anion in solution appears to be a huge driving force for the condensation of smaller oligomers. The acidity of the counterion is important and we predict that the pK_a of H_2SeO_4 at the CCSD(T)/CBS/COSMO level to be -6.9, slightly less acidic than H_2SO_4.

We are currently studying the initial steps of Pu(IV) hydrolysis with and without the presence of ‘H_2SeO_4’. The Pu structures are nearly identical to the Th structures with the same substituents. Due to the f^4 configuration on Pu, some structures found with Th were not found with Pu and are under further investigation. The exchange of H_2O by H_2SeO_4 on a monomer has a comparable energy for Th and Pu but dimerization is more favorable for Th than for Pu. The electron configuration at Pu for most of these molecules is $\sim f^4 d^1 s^{0.2}$ with no spin polarization showing that the dominant backbonding is in the d orbitals. The amount of backbonding in complexes of Pu, Am, Cm, and Cf with a variety of substituents is being studied to further benchmark the computational methods and explain experimental data.

Science objectives for 2015-2017:

- Determine if the tetravalent actinides present similar hydrolysis chemistry across the series or if the actinide contraction and subtle changes in electronic effects have a measurable influence on this chemistry. Study Pu(IV) and other actinides as appropriate.
- Determine the primary condensation reactions available to hydrolyzed actinides as they undergo initial oligomer formation. How does the $An^{n+}(H_2O)_m$ cluster shed positive charge as the condensation process occurs?
- Determine if simple chemical concepts such as electronegativity, hardness, and acidity (and their appropriate definitions) can be used as a predictive guide to aggregate speciation.
- Determine the role of anions in the hydrolysis chemistry of the actinides.

Publications supported by this project 2013-2015

1. “Thorium Fluorides ThF, ThF_2, ThF_3, ThF_4, $ThF_3(F_2)$ and ThF_5^- Characterized by Infrared Spectra in Solid Argon and Electronic Structure and Vibrational Frequency Calculations,” L. Andrews, K. S. Thanthiriwatte, X. Wang, and D. A. Dixon, *Inorg. Chem.* **2013**, *52*, 8228−8233. **DOI:** 10.1021/ic401107w
2. “Infrared Spectra of H_2ThS and H_2US in Noble Gas Matrices: Enhanced H-An-S Covalent Bonding,” X. Wang, L. Andrews, K. S. Thanthiriwatte, and D. A. Dixon, *Inorg. Chem.* **2013**, *52*, 10275–10285. **DOI**: 10.1021/ic400560k
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5. “Unusual Structure, Bonding, and Properties in a Californium Borate,” M. J. Polinski, E. B. Garner, R. Maurice, N. Planas, J. T. Stritzinger, T. G. Parker, J. N. Cross, T. D. Green, E. V. Alekseev, S. M. Van Cleve, W. Depmeier, L. Gagliardi, M. Shatruk, K. L. Knappenberger, G. Liu, S. Skanthakumar, L. Soderholm, D. A. Dixon, and Thomas E. Albrecht-Schmitt, *Nature Chem.*, **2014**, 6, 387-392. **DOI**:10.1038/nchem.1896
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Chemical Studies of the Heaviest Elements: an Overview on Recent Achievements Including the Synthesis of a First Carbonyl Complex of a Transactinide: $Sg(CO)_6$

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Overall research goals: Chemical studies of superheavy elements help shedding light on the influence of relativistic effects on chemical properties and hence benchmark the most advanced fully-relativistic quantum chemical calculations. Gas phase studies are ideally suited to study volatility and reactivity of volatile d-element complexes and volatile p-elements in their atomic state. Experiments in liquid phase are generally more time-consuming – hence limited to elements, where isotopes with sufficiently long half-lives are known – but give access to complementary observables. Generally, expanding the accessible chemical systems is of prime interest, as is the advancement of experimental techniques to give access to new observables.

Significant achievements during 2011-2013:

In my presentation, I will discuss the following examples highlighting recent progress in the field:

1. The reduction of Md^{3+} to Md^{2+}

The reduction behavior of mendelevium (Md) was studied using a flow electrolytic chromatography apparatus. By application of the appropriate potentials on the chromatography column, the more stable Md^{3+} is reduced to Md^{2+}. The reduction potential of the $Md^{3+} + e^{-} \rightarrow Md^{2+}$ couple was determined to be −0.16 ± 0.05 V versus a normal hydrogen electrode [1].

2. The first ionization potential of Lr

In heaviest elements, atomic s and $p_{1/2}$ orbitals are stabilized by relativistic effects, whereas $p_{3/2}$, d and f orbitals are destabilized, so that ground-state configurations of heavy elements may differ from those of lighter elements in the same group. The first ionization potential of Lr was experimentally obtained as 4.96 (+0.08 / -0.07) eV, measured with ^{256}Lr (half-life: 27 s) using an efficient surface ion-source and a radioisotope detection system coupled to a mass separator, cf. Figure 1. The measured value is in excellent agreement with the value of 4.963(15) eV predicted by state-of-the-art relativistic calculations. The present work [2] opens the way for similar measurements of superheavy elements (Z≥104) on an atom-at-a-time scale.

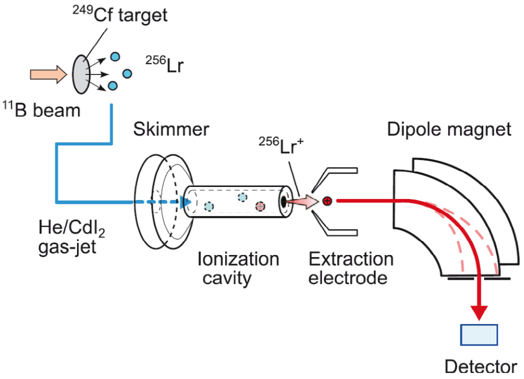

Figure 1. Experimental setup used for the measurement of the first ionization potential of Lr at JAEA Tokai, Japan.

3. Synthesis of $Sg(CO)_6$ – access to new compound classes of the transactinides

So far, in gas-phase chemical reactions, simple inorganic compounds with the transactinide in its highest oxidation state have been synthesized. Single-atom production rates, short half-lives, and harsh experimental conditions limited the number of experimentally accessible compounds. Recently, a gas-phase carbonylation technique previously tested on short-lived Mo and W isotopes allowed synthesis of a carbonyl complex of Sg, enabled by the coupling of the chemistry setup to a magnetic recoil separator to remove the intense heavy-ion beam. This successfully prevented the formation of a plasma, which would otherwise have destroyed the CO ligands and/or formed volatile complexes. The volatile Sg complex showed the same volatility and reactivity with a silicon dioxide surface as those of the hexacarbonyl complexes of the lighter homologs Mo and W. Comparison of the product's adsorption enthalpy with theoretical predictions and data for the lighter congeners supports a $Sg(CO)_6$ formulation. The work [3] opens perspectives for synthesis of carbonyl complexes also of other transition-metal transactinides, and for studying further compounds that were out of experimental reach with more conventional techniques.

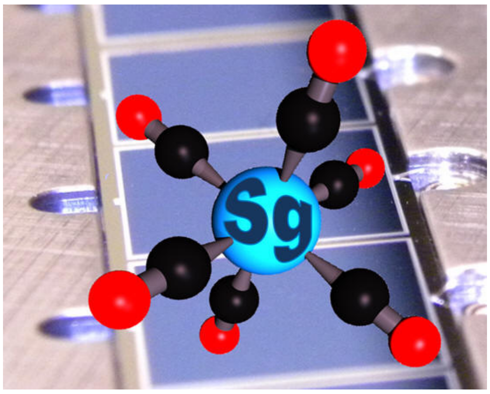

Figure 2. A $Sg(CO)_6$ molecule on silicon dioxide covered detectors.

4. Chemical properties of Fl – heaviest element whose chemical behavior has been studied to date.

The question whether Fl might behave similarly to a noble gas, owing to its quasi-closed shell electron configuration $6d^{10}7s^27p_{1/2}{}^2$ was raised in the 1970s [4]. Alternatively, trends present in group 14 suggest Fl to rather be a relatively volatile metal. First gas phase chemical results reported in 2010 favored a behavior more resembling that of an inert gas [5]. New results, obtained from an experiment where the chemistry setup was coupled to a recoil separator, similarly as in [3], but here to remove unwanted transfer products disturbing the unambiguous detection of nuclear decay chains from Fl, provide evidence for a metallic Fl [6].

5. Expansion of the periodic table: experiments on elements 115 / 117 / 119 / 120

The interesting question about the heaviest elements that can exist is still not answered, and the quest for ever heavier elements is ongoing. I will presents recent results on elements 115 [7] and 117 [8] – which are not currently recognized by the IUPAC – focusing on results obtained at GSI Darmstadt. I will also present the status of search experiments for the new elements 119 and 120.

Relevant publications

1. Toyoshima, A., Li, Z., Asai, M., *et al.*, "Measurement of the Md^{3+}/Md^{2+} reduction potential studied with flow electrolytic chromatography", Inorg. Chem. 52 (2013) 12311, doi: 10.1021/ic401571h.
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Exploring Soft Matter and Coordination Structures in Heavy Element Solvent Extraction Systems

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Overall research goals: Elucidating the structural roots of physical properties is vital in developing better materials for energy applications. In the organic phases used in solvent extraction processes for nuclear fuel separations, nanoscale structures that extend well beyond the coordination sphere of the metal ion are becoming recognized as important in driving properties that underpin the efficacy of heavy metal ion separations. However, there is currently lacking a structural paradigm that describes the solvent extraction organic phase beyond a solution of coordination complexes, due in part to a lack of appreciation for the role of both the 'soft matter' and 'coordination complex' material aspects of the fluid. Our goal is to reach a new definition of structure in the metal-loaded solvent extraction organic phase by bridging soft matter science with coordination chemistry. Such a structural model promises to generalize and rationalize the multiple equilibria that are currently used to describe processes.

Significant achievements during 2013-2015:

Over the previous 2 years, we have built an international collaborative network that collects the diverse expertise needed to cover the multidisciplinary requirements of the program, stretching from soft matter science to coordination chemistry and separations. By directly comparing simulations with experiment, we are reaching a comprehensive understanding of how solvent extraction organic phases are structured from the long range interactions between nanoscale reverse micelle aggregates down to the coordination sphere of the encapsulated metal ions, with atomistic resolution. By doing so, we begin to define the metal-loaded organic phase as a 'hybrid' (inorganic-organic) fluid, in that the structure and properties are emergent from an interplay between the aggregating (organic) 'extractant-in-oil' solvent matrix and the coordinating (inorganic) metal complexes.

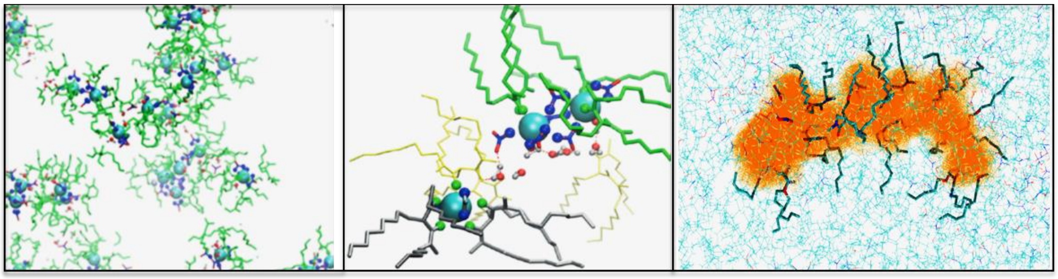

Figure. Snapshots showing structures from MD simulations of a system reflective of the DIAMEX process for lanthanide/actinide separations. The extractant DMDOHEMA is in green, nitrate in red/blue, water in red/white, and EuIII as large blue spheres (the solvent n-heptane was removed for clarity). The simulations show that the coordinating metal ion is solvated by nitrate, water and extractant that form reverse micelle-type aggregates that interact through H-bonds in the outer-sphere. The picture furthest to the right shows the time-averaged positions of the hydrophilic species as an orange cloud that reflects the morphology of nanoscale aggregates observed using experimental SAXS.

Science objectives for 2015-2017: Having built the necessary tools and expertise to explore hierarchical structure in solvent extraction organic phases of interest to heavy element separations, the next stage is to use this approach to understand the underlying energetics of extraction. Connecting structure to physical property *via* energetic language is the crux of our project aims and will draw us toward a predictive understanding of solvent extraction systems. By basing our model in material structure, we aim to build a unifying theory that generalizes and accounts for a disparate range of important system properties from mass transport and selectivity to phase stability and kinetics. This will be achieved through collaborations that center on Argonne, taking a multi-pronged approach that combines theory with experiment.

Publications supported by this project 2013-2015:

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Expanding the Fundamental Chemistry of Actinide Complexes

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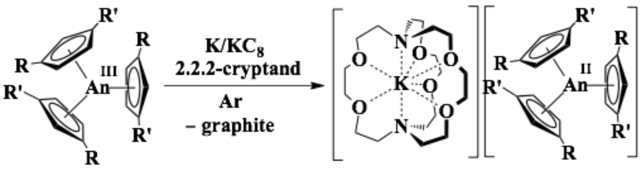
Overall Research Goals: The objective of this research is to provide new fundamental chemical information that may be useful in the development of advanced nuclear fuel cycles while training graduate students who will be the next generation of scientists skilled in the chemistry of the actinides. This project will explore the identification of new oxidation states for uranium and thorium as well as examine under-developed actinide reaction types such as those involving radicals, solid/gas reactions, and reactions between metal complexes.

Significant Achievements Since the Last PI Meeting:

Full details are presented in references 1-12. Paragraphs A-E highlight some of the results.

A. The first crystallographically characterized examples of molecular complexes containing U^{2+} (2) and Th^{2+} (11) have been prepared according to the reactions in Scheme 1. Finding new oxidation states for these heavily studied actinide elements was quite surprising particularly since the possibility of synthesizing a U^{2+} complex has been discussed in the literature since the 1980's. Now, the isolation and structural characterization of $[K(2.2.2\text{-cryptand})][(C_5H_4SiMe_3)_3U]$ provides the first example with which U^{2+} can be definitively examined. The isolation of the first molecular complex of Th^{2+}, $[K(2.2.2\text{-cryptand})]\{[C_5H_3(SiMe_3)_2]_3Th\}$, was even more unexpected since only five examples of the strongly reducing Th^{3+} are known and the Th^{3+}/Th^{2+} redox potential is estimated to be -4.9 V vs. NHE. Density functional theory indicates that the Th^{2+} complex has a $6d^2$ configuration of the type expected for Rf^{2+} or Db^{3+}.



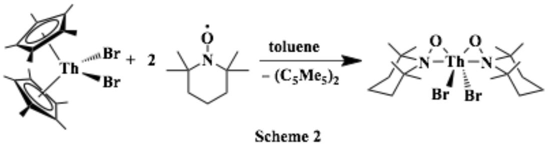
Scheme 1
(An = U, R = SiMe$_3$, R' = H; An = Th, R = R' = SiMe$_3$)

B. Magnetic susceptibility data on over 500 uranium complexes have been assembled and analyzed in the first comprehensive review. This will allow future magnetic measurements of uranium complexes to be compared with the complete set of available magnetic data rather than with selected examples as is the current practice (9).

C. ^{29}Si NMR data have been collected on paramagnetic uranium complexes and compared with data in the literature to evaluate for the first time if there are correlations of ^{29}Si NMR shifts with oxidation states, compositions, and structural classes (6).

D. Four, air-stable, volatile uranium complexes of chelating alkoxide ligands have been synthesized and evaluated as precursors for gas phase deposition of uranium oxide films (12).

E. Actinide radical chemistry was explored by examining reactions of the TEMPO radical with well-characterized thorium metallocenes. This appears to be a promising way to manipulate actinide coordination environments, e.g. Scheme 2.



Scheme 2

Science Objectives for 2015-2017: (a) We will attempt the synthesis of additional complexes of the new oxidation states, U^{2+} and Th^{2+}, to find more stable compounds to aid in the chemical and physical characterization of these new ions. (b) We will seek to find additional new actinide oxidation states on the basis of information learned in the discovery of U^{2+} and Th^{2+}. (c) We will explore the reactivity of U^{2+} and Th^{2+} for the first time. (d) We will continue to explore the reactivity of actinides with radicals. (d) We will explore thermal and gas/solid reactions of actinide complexes using data obtained by DSC and TGA measurements.

Publications supported by DE-SC0004739 from 2013-2015:

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Binding Anions Selectively with Modular Triazolophanes and Releasing them with Light

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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 2013-2015: We have been using computer-aided design of shape-persistent macrocycles to bind polyatomic anions. We have improved the binding-release differential in photofoldamers and we discovered a new mode of anion extraction inside foldamers derived from hydrophobic collapse. Two significant results have emerged:

1. Computer-aided Design of Receptors for Polyatomic Anions: Paired computation-experiment approaches are being used to deepen our understanding of anion binding in solution. Out recent computer-aided design of an anion receptor highlights that deepening understanding. Following that approach, we show how virtual experimentation can be used to rapidly screen for and tune-up the binding mode between triazolophanes (Figure 1) and bifluoride, $[FHF]^-$; a model for solvent-exposed polyatomic anion complexes.

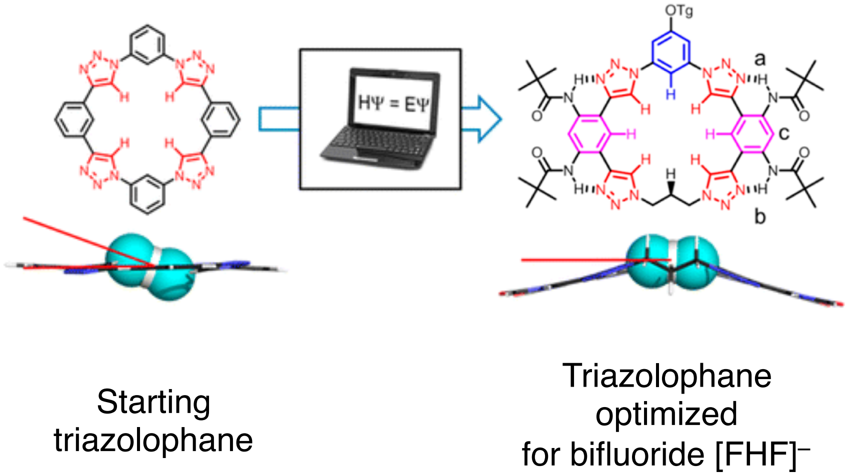


Figure 1. Computer-aided design transformed the parent triazolophane (left) into one that is complementary to bifluoride anion. In the starting structure, bifluoride binds with its two fluoride atoms (cyan) appear to be solvent accessible but in the optimized structure, the fluorides sit inside the binding sites at each end of the macrocycle.

2. Driving Anion Binding inside Foldamers by Hydrophobic Collapse: Taking inspiration from biology's halorhodopsin, a new class of light-active foldamers has been created that make use of the photoisomerizable azobenzenes (colored blue in Figure 2a). The foldamers can catch and release chloride to regulate its concentration. We then move out of organic solvents, again taking biology's lead, to tackle one of the grand challenges in host-guest chemistry: Extracting highly-hydrated ions from aqueous solutions, chloride in the present case. We were the first to discover that, when the foldamers intertwine into a duplex (Figure 2b), the hydrophobic effect provides the driving force needed to extract the hydrophilic chloride from semi-aqueous solutions. Ultimately, we found that foldamers' helical pre-organization, as controlled by their structure and solvation properties, is key to their functionality.

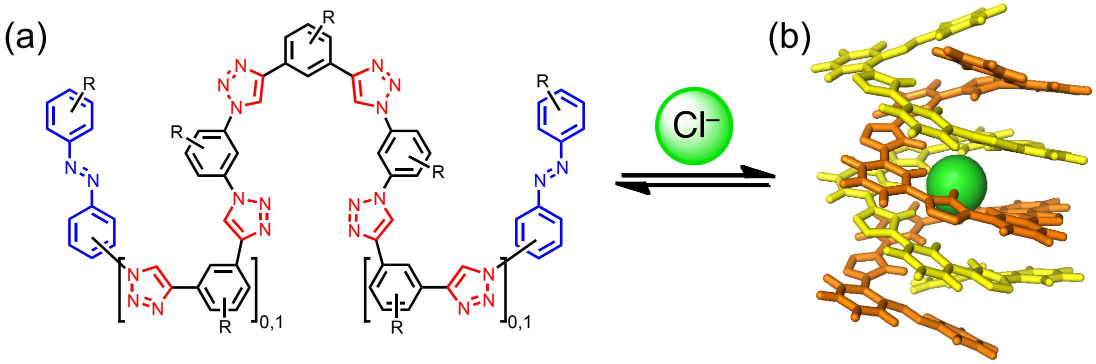
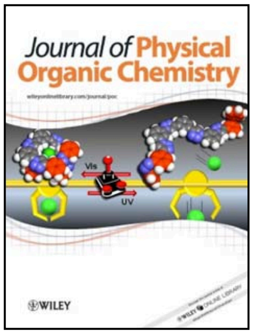


Figure 2. (a) Triazoles (colored red) are the basis for binding anions and for preparing photoactive foldamers incorporating azobenzenes (blue) that (b) can wrap up chloride ions using the hydrophobic effect.

Science objectives for 2015-2017:

- Reporting the binding of oxyanions with larger macrocycles conferring femtomolar binding
- Characterize design principles for ion-pair binding of oxyanions using Coulombic cooperativity
- Determining the impact of solvation on anion binding to shape-persistent macrocycles
- Complete fundamental studies to understand photoactivity of azobenzenes in foldamers
- Complete synthesis studies aimed improving light switching.

Publications supported by this project 2013-2015



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   http://dx.doi.org/10.1021/ja500125r

Quantum Chemical Study of Actinide and Lanthanide Containing Systems

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Overall research goals: The objective of this project is to develop and employ quantum chemical models in order to study the chemistry of systems containing actinides, lanthanides and heavy elements in the gas phase, in low temperature matrices, and in condensed phase.

Significant achievements during 2013-2015:

1) In collaboration with Paula Diaconescu we studied the electronic structure of the arene-bridged complex (μ-toluene)$U_2(N[^tBu]Ar)_4$ (Ar = 3,5-$C_6H_3Me_2$) in relation to a variety of mononuclear uranium amide complexes. The syntheses, molecular structures, and corresponding spectroscopic and magnetic properties were measured and interpreted with reference to results of density functional theory (DFT) and complete active space self-consistent field followed by second-order perturbation theory (CASSCF/CASPT2) calculations performed on model compounds.
2) In collaboration with Peter Burns we studied the electronic structure of some neptunyl complexes, in an effort to probe the nature of the side-on cation-cation interaction (CCI), and the extent to which ligand effects may alter this interaction. We employed a suite of quantum chemical methods ranging from DFT to high-level multiconfigurational methods. This analysis showed that in some of these compounds the ligand affects the CCI interaction, while in others it does not.
3) In collaboration with Al Sattleberger we studied the molecular and electronic structure, as well as the electronic absorption spectrum of $Tc_2(O_2CCH_3)_2Cl_4$ and of the trigonal-prismatic hexanuclear $[Tc_6Br_{12}]$ cluster by employing multiconfigurational quantum chemical methods. This study highlighted the nature of the Tc-Tc bonds present in these species and helped assigning the electronic transitions.
4) We characterized the electronic structure of several actinide-containing molecules recently measured by various experimental groups. In collaboration with John Gibson and Lester Andrews we investigated gas-phase molecular thorium and uranium carbide cluster cations of composition $An_mC_n^+$, with $m = 1$, $n = 2$-14, and $m = 2$, n = 3-18, as detected by Fourier transform ion-cyclotron-resonance mass spectrometry. Density functional theory computations were performed to illuminate this distinction between the thorium and uranium species. We also wrote a Chem. Rev. article together with John Gibson on Molecular Actinide Oxides.
5) In collaboration with Lester Andrews we studied the reactions of laser-ablated U atoms with N_2 molecules. In excess argon during co-deposition at 4 K it was possible to detect intense NUN and weaker UN absorptions. Annealing increased progressions of new absorptions for the $NUN(NN)_{1,2,3,4,5}$ and $NU(NN)_{1,2,3,4,5,6}$ uranium nitride complexes. Our electronic structure calculations provided support for the identification of these complexes and further characterization of the NUN and UN core molecules as terminal uranium nitrides with full triple bonds.
6) In collaboration with Susanne Bart we studied the formation of uranium tris(imido) compounds.The computational analyses of these products probed their molecular and electronic structures, which facilitated a comparison between the bonding in the tris(imido) structure and its tris(oxo) analogue.
7) In collaboration with Thomas Albrecht-Schmitt, in order to understand how the bonding changes across the actinide series, we investigated the quantum chemical properties of a Cf(III) borate.
8) In collaboration with Chuan He, we investigated the capture of uranyl, UO_2^{2+}, by a recently engineered protein by a combination of DFT, molecular dynamics, and free-energy simulations. It was found that UO_2^{2+} is coordinated to five carboxylate oxygen atoms from four amino acid residues of the super uranyl binding protein (SUP).

Science objectives for 2015-2017:

1) Develop novel force fields to study actinyl binding to different proteins 2) Explore multi-actinide single molecule magnets; study their spectroscopic and magnetic properties 3) Investigate the electronic absorption spectra of lanthanide and actinide luminescent compounds

Publications supported by this project 2013-2015

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Molecular Transuranic Discovery Science

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Overall research goals: To advance knowledge regarding transuranic coordination chemistry, bonding and electronic structure over a wide range of ligand type. Elucidating speciation, reactivity, redox trends, and covalency are all aims of the project, with information on molecules synthesized under inert atmospheric conditions in organic solvents particularly lacking. The state of the field is advanced by opening up synthetic access routes through establishing new precursors, isolating Np/Pu complexes with ligands of fuel cycle interest, comparing complexes with ligands that invoke a degree of metal-ligand orbital overlap, with trends and differences both across the 5f series and 4f series and between oxidation states of importance.

Significant achievements (2013–2015):

1. Syntheses of neutral, organic soluble, An(IV) transuranic (Np and Pu) molecular starting materials. The chemistry of tetravalent Np and Pu molecules under inert atmospheric non-aqueous conditions has been hampered by a lack of suitable precursors. Drying out a An(IV)/HCl aqueous solution with an argon gas stream, followed by dissolution of the resultant residue in a dry-box with DME (1,2-dimethoxyethane) as a coordinating solvent affords $NpCl_4(DME)_2$ and $PuCl_4(DME)_2$ (Figure 1) in synthetically useful yields to explore subsequent ligand complexation reactions. The complexes were structurally and spectroscopically characterized.

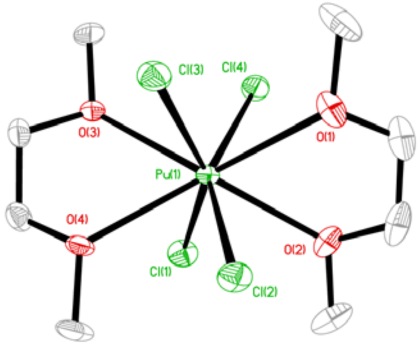

Figure 1. Solid-state structure of $PuCl_4(DME)_2$, a new organic soluble, neutral synthon. The Np(IV) analogue is isostructural.

2. Syntheses and isolation of the first non-dioxo transuranic moiety containing metal-ligand multiple bonds. The discovery of the bis-imido analog of the uranyl cation, UO_2^{2+}, by Hayton, Boncella and co-workers was one of the more surprising and impactful fundamental advances in synthetic uranium chemistry over the last decade. The characterization of the $[RN=U=NR]^{2+}$ moiety raised the possibility that the valance orbitals of transuranic metal ions may also be able to engage in similar covalent interactions. Previous attempts to synthesize such species were impeded by the difficulty in oxidizing Pu^0 to Pu(V/VI) under inert atmosphere conditions, and in the case of neptunium by the lack of access to Np^0 as a starting material. Establishment of the new $NpCl_4(DME)_2$ precursor, described above, facilitated an alternative reactivity pathway in which treatment with the parent amido, in the presence of a supporting bypyridine 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 2). Computational studies (Batista, LANL) are underway to understand electronic structure and contrast with the uranium congener.

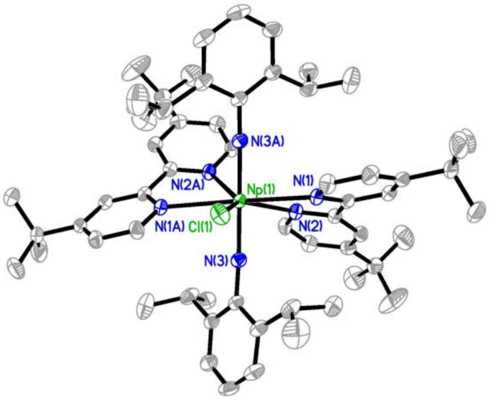

Figure 2. Solid-state structure of the Np(V) bis-imido molecule, [Np^{V}(=NDipp)$_2$(*t*Bu$_2$-bipy)$_2$Cl], the first example of a transuranic non-dioxo metal-ligand multiple bond.

3. Progress has been made on a number of other chemical systems including installation of a 'TREN' tris-amido scaffold onto Np(IV) to facilitate probing of single-site reactivity, developing precursors to terminal chalcogenide multiple bonds, new Np-dithiophosphinate structures, completion of lanthanide-amidate complexes with a tripodal ligand, publication of an invited *Chemical Reviews* article assessing the state of the field, and drafting an invited book chapter for an updated edition of the *Plutonium Handbook*, intended to be the reference text covering a wide range of research topics pertaining to element number 94.

Science objectives for 2015-2017:

- Transition Early Career project to tightly integrate into the core BES-HEC program at LANL by modifying research thrusts to both complement and collaborate with existing members.
- Explore the generality of Np-imido species and extend to Pu. Systematic k-edge XAS studies (w/Kozimor) on complexes across the 5f series to elucidate electronic structure trends.

Publications receiving support (full or partial) from this project in the period 2013-2015

1. M.B. Jones, A. J. Gaunt, J.C. Gordon, N. Kaltsoyannis, M.P. Neu, B.L. Scott, *'Uncovering f-element bonding differences and electronic structure in a series of 1:3 and 1:4 complexes with a diselenophosphinate ligand'*, *Chemical Science*, **2013**, *4*, 1189. **DOI: 10.1039/c2sc21806b.**
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Actinides in the Gas Phase: Clarifying Established Chemistry; Revealing New Chemistry

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Overall research goals: The objective is to investigate fundamental actinide chemistry in the gas phase to illuminate and expand 5f element chemistry. The studies cover the actinides from Th through Cf and provide a basis to understand, control and develop condensed phase chemistry, and to evaluate actinide theory.

Selected Scientific Accomplishments for 2013-2015:

- Activation of $[O{=}U{=}O]^{2+}$ to yield $[N{\equiv}U{=}O]^{+}$ (refs. 9,12)
- First tetrapositive metal ion complexes from solution to gas: Th^{4+}, U^{4+}, Np^{4+}, Pu^{4+} (refs. 12, 19).
- Fragmentation of actinide complexes—Th to Cm—reveals intrinsic redox chemistry (refs. 4,10).
- Structural characterization of crown ether complexes with uranyl, neptunyl and plutonyl (ref. 9).
- The effective charge of uranyl determined by fragmentation of bimetallic cluster ions (ref. 13).
- Synthesis of a complex with a $Pu^{VI}O_3^{+}$ core: a demonstration of the instability of Pu^{VII} (ref. 3).
- IR spectra of actinyl-diglycolamide complexes: an extreme red-shift in the ν_3 frequency (ref. 1).
- Hydrolysis of Ln^{IV}-O and An^{IV}-O bonds manifests intrinsic IV/III reduction potentials (ref. 2).
- Chemistry of Pa: "$PaO_2(H_2O)^{+}$" is $PaO(OH)_2^{+}$; establishing a trend across the actinide series.
- Synthesis of $[(NO)U^{VI}O]^{+}$: a side-on bonded $(NO)^{3-}$ ligand.

Science Objectives for 2015-2017:

- Fragmentation of complexes with designer ligands: formation of nitrides from azides, etc.
- Synthesis and characterization of hyperoxides: AnO_4^{-}, AnO_5^{-} and AnO_8^{-} (An = U, Np, Pu).
- IRMPD spectroscopy of uranyl complexes to elucidate covalency of bonding between U and ligands.
- Effects of ligation $AnO_2(L)_n^{+}$ oxo-exchange: can PuO_2^{+} exchange be induced by electron donation?
- Hydrolysis of Pu^{IV} from the bottom up: a comparison with hydrolysis of Th^{IV}.
- Exchange of $^{15}NH_3$ and $H_2{}^{18}O$ with $[N{\equiv}U{=}O]^{+}$: activation of U≡N versus U=O.
- Oxidation of actinyl(V) complexes by small gas-phase molecules: comparison with O_2-addition.
- Redox chemistry of Cf by fragmentation of complexes: Cf^{II} in different coordination environments.
- Stabilities of Bk^{IV} and Cf^{IV} from fragmentation and hydrolysis of nitrate complexes.
- Development and implementation of cryogenic matrix isolation synthesis/spectroscopy for transuranics.

Publications supported by this project, 2013-2015

1. "Infrared Multiphoton Dissociation Spectroscopy of a Gas-Phase Complex of Uranyl and 3-Oxa-Glutaramide: An Extreme Red-Shift of the $[O{=}U{=}O]^{2+}$ Asymmetric Stretch," J. K. Gibson, H.-S. Hu, M. J. Van Stipdonk, G. Berden, J. Oomens, J. Li, In revision for J. Phys. Chem. A.

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10. “Infrared Multiple Photon Dissociation Spectroscopy of a Gas-Phase Oxo-Molybdenum Complex with 1,2-Dithiolene Ligands,” M. J. Van Stipdonk, P. Basu, S. Dille, J. K. Gibson, G. Berden, J. Oomens, J. Phys. Chem. A 118 (2014) 5407-5418. (DOI: 10.1021/jp503222).

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16. “Synthesis and Properties of Uranium Sulfide Cations. An Evaluation of the Stability of Thio-Uranyl, $\{S=U=S\}^{2+}$,” C. C. L. Pereira, M. C. Michelini, J. Marçalo, Y. Gong, J. K. Gibson, Inorg. Chem. 52 (2013) 14162-14167. (DOI: 10.1021/ic4020493).

17. “Experimental and Theoretical Studies on the Fragmentation of Gas-Phase Uranyl-, Neptunyl- and Plutonyl-Diglycolamide Complexes,” Y. Gong, H.-S. Hu, L. Rao, J. Li, J. K. Gibson, J. Phys. Chem. A 117 (2013) 10544-10550. (DOI: 10.1021/jp4076977).

18. “Thorium and Uranium Carbide Cluster Cations in the Gas Phase: Similarities and Differences between Th and U,” C.C.L. Pereira, R. Maurice, A.F. Lucena, S. Hu, A.P. Gonçalves, J. Marçalo, J.K. Gibson, L. Andrews, L. Gagliardi. Inorg. Chem. 52 (2013) 10968-10975. (DOI: 10.1021/ic401058b).

19. “A Tetrapositive Metal Ion in the Gas Phase: Th^{4+} Coordinated by Neutral Tridentate Ligands,” Y. Gong, H.S. Hu, G. Tian, L. Rao, J. Li, J.K. Gibson, Angew. Chem. Int. Ed. 52 (2013) 6885-6888. (DOI: 10.1002/anie.201302212).

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21. “Proton Transfer in Th(IV) Hydrate Clusters: A Link to Hydrolysis of $Th(OH)_2^{2+}$ to $Th(OH)_3^+$ in Aqueous Solution,” P.X. Rutkowski, M.C. Michelini, J.K. Gibson, J. Phys. Chem A 117 (2013) 451-459. (DOI: 10.1021/jp309658x).

Heavy Element Nuclear Chemistry at Berkeley

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Overall research goals: Determining the chemical properties of the elements is the most fundamental goal in all of chemistry. Very little is known about the chemical properties of the transactinide elements ($Z > 103$). The goals of this project are to optimize production of heavy element isotopes for chemical studies, and to develop rapid single-atom chemical techniques and implement them to study the chemical properties of the elements from Rf ($Z = 104$) through Fl ($Z = 114$).

Significant achievements during 2013-2015: This project is synergistic with our study of the production, decay, and nuclear structure of the heaviest elements (performed under separate funding). Optimizing production and understanding the nuclear decay of isotopes of heavy elements are necessary for studies of their chemical properties. Similarly, chemical separation can provide the isolation-from-background necessary for studies of nuclear properties. Progress during the last few years has been focused in two areas: 1) new accelerator targets for use with the higher-intensity beams now available, and 2) microfluidic chemical separation devices that can be used with single-atoms of short-lived heavy element isotopes that are produced at rates as low as one atom per day.

1. Accelerator beams create heat as they pass through our targets. To spread out the heat and allow for cooling, large-area rotating target wheels are used. With newly–available high-intensity (10^{13} ions/sec) heavy-ion beams from the LBNL 88" Cyclotron, our targets were pushed beyond their limits. A finite-element-analysis simulation was developed to model the heating of rotating target wheels by heavy ion beams, and subsequent cooling by convection in gas and blackbody radiation. Information gained by running these simulations was employed in design of a new, larger-area target wheel (and the extensive infrastructure needed to utilize the new target wheels in the Berkeley Gas-filled Separator). A new target wheel system was fabricated and a ^{207}Bi target was run with ^{48}Ca beam intensities of 10^{13} ions/sec in the Berkeley Gas-filled Separator for over one week. The targets performed flawlwessly, resluting an a factor of 10 increase data for the decay of a high-K isomer in ^{255}Lr.

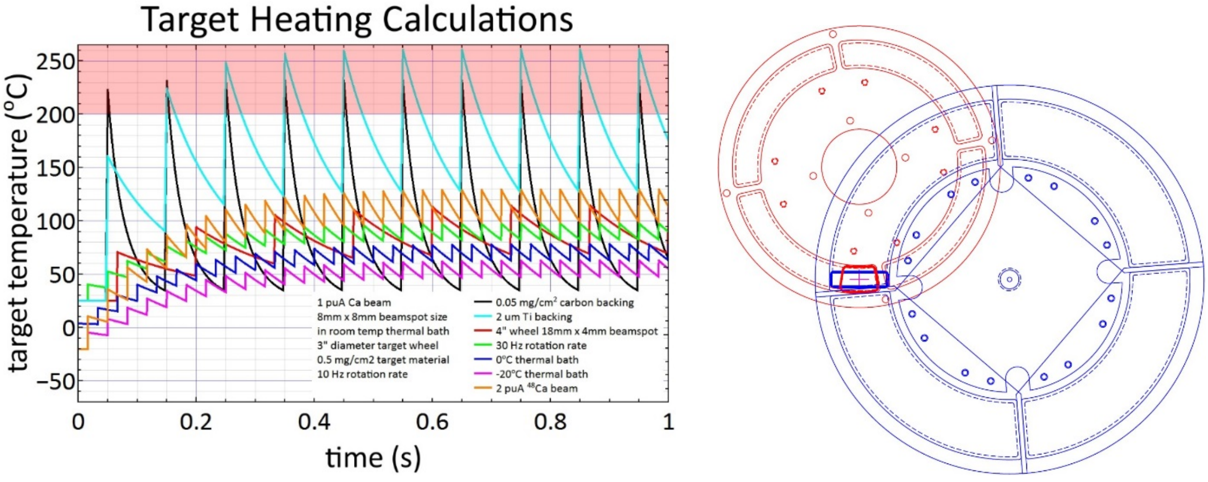

Figure 1. Left: Result of target heating simulations for old target wheel (black, cyan) and the newly designed large-area target wheel. Right: 2D CAD comparison of old (red) and new (blue) target wheels and beamspot shapes (heavy lines).

2. Atoms of the heaviest elements have half-lives of a few seconds or less, and are produced at particle accelerators with rates as low as one atom per day. To perform chemical separations with these elements, a chemical system must be fast, and run continuously for weeks at a time. We are working on a microfluidic liquid-liquid extraction system to perfrom aqueous-phase chemical separations on these short-lived single atoms. When two immiscible liquids are passed through a sub-millimeter channel, they break up into small droplets. The small droplets result in excellent phase contact, facilitating liquid-liquid extraction. Work has begun on liquid-liquid extraction and pahse separation devices. Extraction of Hg (chemical homolog of element 112) from aqueous solutions into an organic solution containing trioctylphosphine oxide has shown distribution coefficients approaching those obtained with macro-scale liquid-liquid extractions. Subsequent phase separation has been demonstrated. Devices for capture of the ions into solution, and for detection of radioactive decay by liquid scintillation after phase separation are in the conceptual phase.

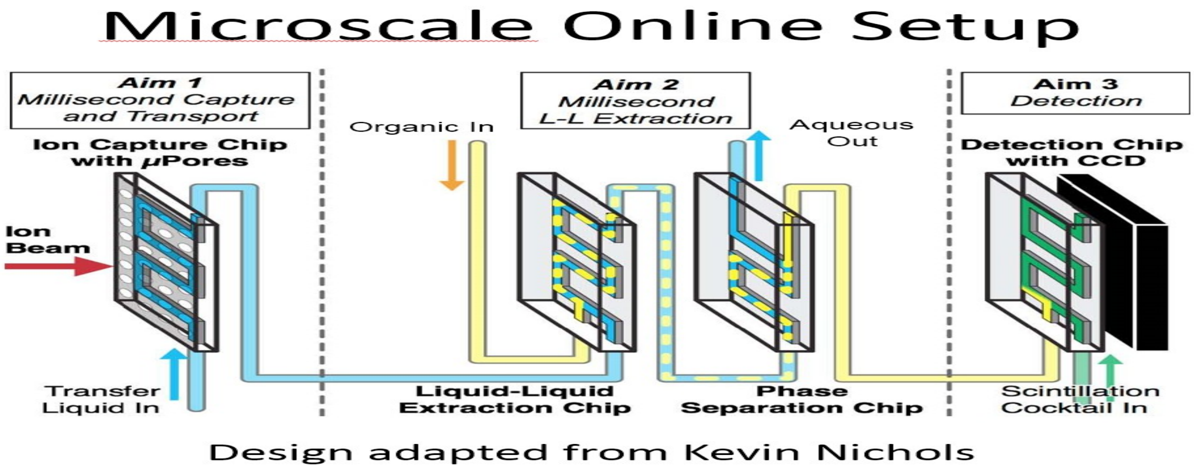

Figure 2. Schematic of microfluidic liquid-liquid extraction apparatus for chemical separations of superheavy elements.

<u>Science objectives for 2013-2015:</u>

- Extend the new target wheel capablities to actinide targets (^{243}Am, ^{248}Cm) by designing and fabricating an enlarged high-voltage electrodeposition cell.
- Continue development of the microfluidic liquid-liquid extraction devices and test them with chemical homologs of the superheavy elements.
- Find suitable liquid-liquid extraction systems for use in chemical separations of elements 104-114.

<u>Publications supported by this project 2013-2015</u>

1. Alexander Yakushev, et al., “Superheavy Element Flerovium (Element 114) Is a Volatile Metal”, Inorganic Chemistry **53**, 1624 (2014), DOI: 10.1021/ic4026766.
2. J. Runke, et al., “Preparation of actinide targets for the synthesis of the heaviest elements”, Journal of Radioanalytical and Nuclear Chemistry **299**,1081 (2014), DOI: 10.1007/s10967-013-2616-6.
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New Approaches for the Synthesis of Actinide-Ligand Multiple Bonds: Opportunities for Novel Structure, Reactivity, and Catalysis

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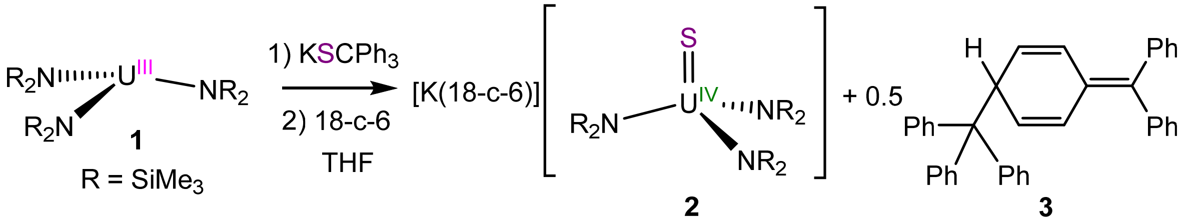
Overall research goals: Our research program has two specific aims: (*i*) develop new methods for the synthesis of actinide-ligand multiple bonds; and (*ii*) explore the reactivity and electronic structure of actinide-ligand multiple bonds, specifically to answer fundamental questions about *d* and *f*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

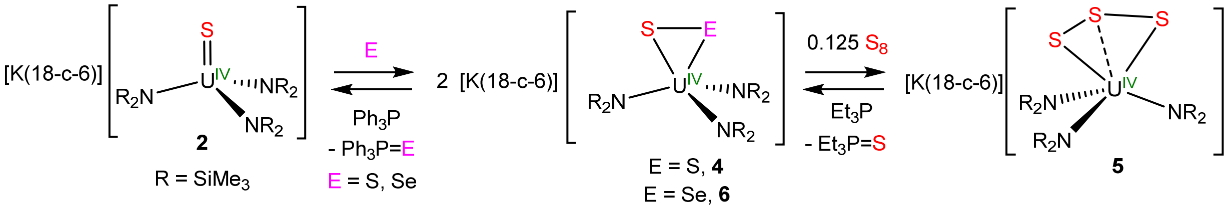
Significant achievements during 2013-2015: We recently reported the ability of $KSCPh_3$ to act as a convenient sulfur atom source. In particular, reaction of $KSCPh_3$ with **1** resulted in formation of a terminal sulfide, $[K(18\text{-crown-6})][U(S)(NR_2)_3]$ (**2**; R = $SiMe_3$), via spontaneous release of the trityl radical (**3**) (Scheme 1). Formally, $KSCPh_3$ is acting as a $1e^-$ oxidant in this transformation. No doubt, this mode of reactivity is enabled by the low C-S bond dissociation enthalpy in $[SCPh_3]^-$ coupled to the relatively high reducing power of the U(III) ion. Moving forward, we will attempt to apply the trityl 'deprotection methodology' to other chemical systems, as it should be readily transferrable to a wide variety of metals.

Scheme 1



We have also undertaken a reactivity study of the terminal sulfide complex, $[K(18\text{-crown-6})][U(S)(NR_2)_3]$ (**2**). This complex reacts with 0.125 equiv of S_8 to provide the disulfide, $[K(18\text{-crown-6})][U(\eta^2\text{-}S_2)(NR_2)_3]$ (**4**), in good yield (Scheme 2). Addition of a further 0.125 equiv of S_8 to **4** provided a novel trisulfide complex, $[K(18\text{-crown-6})][U(\eta^3\text{-}S_3)(NR_2)_3]$ (**5**), also in good yield.

Scheme 2



The scope of chalcogen atom addition to **2** is not limited to sulfur. In particular, addition of 1 equiv of Se to **2** results in formation of an exceptionally rare selenosulfide complex, $[K(18\text{-crown-}6)][U(\eta^2\text{-SSe})(NR_2)_3]$ (**6**) (Scheme 2). Interestingly, these atom transfer reactions are reversible. Thus, addition of Ph_3P or Et_3P to complexes **4**, **5**, or **6**, resulted in reformation of the terminal sulfide, $[K(18\text{-crown-}6)][U(S)(NR_2)_3]$ (**2**). This reversibility suggests that complex **2** could be developed as a catalyst for chalcogen atom transfer, and we are currently exploring this possibility.

Science objectives for 2015-2017:

- Develop terminal actinide chaclogenides into catalysts for chaclogen atom transfer.
- Use the ‘deprotection methodology’ to synthesize terminal thorium chalcogenides.
- Develop new carbene transfer reagents and synthesize an actinide carbene.

Publications supported by this project 2013-2015:

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8. Hayton, T. W. An Actinide Milestone. *Nat. Chem.* **2013**, *5*, 451. DOI: 10.1038/nchem.1643
9. Brown, J. L.; Fortier, S.; Wu, G.; Kaltsoyannis, N.; Hayton, T. W. Synthesis and Spectroscopic and Computational Characterization of the Chalcogenido-Substituted Analogues of the Uranyl Ion, $[OUE]^{2+}$ (E = S, Se). *J. Am. Chem. Soc.* **2013**, *135*, 5352-5355. DOI: 10.1021/ja402068j
10. Seaman, L. A.; Hrobárik, P.; Schettini, M. F.; Fortier, S.; Kaupp, M.; Hayton, T. W. A Rare Uranyl(VI)–Alkyl Ate Complex $[Li(DME)_{1.5}]_2[UO_2(CH_2SiMe_3)_4]$ and Its Comparison with a Homoleptic Uranium(VI)–Hexaalkyl. *Angew. Chem. Int. Ed.* **2013**, *52*, 3259-3263. DOI: 10.1002/anie.201209611
11. Hayton, T. W. Recent developments in actinide–ligand multiple bonding. *Chem. Commun.* **2013**, *49*, 2956-2973. DOI: 10.1039/C3CC39053E

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 ions tightly and selectively.

Significant achievements during 2013-2015: In the past 2 years, we have made progresses in two research areas:

1. Development of an uranyl-selective binding protein that can sequester uranyl from seawater.

Uranyl (UO_2^{2+}) is present in the ocean at a concentration of ~ 13.7 nM or 3.2 mg/ton seawater. The ocean contains 1,000 times more uranium than land, offering an enormous resource that, unlike land resources, may be tapped at minimal environmental cost. To effectively sequester uranyl from seawater requires the development of highly selective and sensitive uranyl-binding ligands. We computationally screened published protein crystal structures in the Protein Data Bank using a designed uranyl-selective binding geometry. Out of 4,000 hits we selected 10 proteins, synthesized these genes, expressed the proteins, and tested uranyl binding. Four proteins were shown to bind uranyl at nM affinities. We focused on engineering one of the uranyl-binding proteins. After several rounds of design, test, structural characterization, mutagenesis, and binding test, we obtained a robust uranyl-binding protein with a K_d of 6.1 femtomolar (fM) and > 10,000-fold selectivity over other metal ions including calcium(II).

We named this protein SUP for super uranyl-binding protein, which can repeatedly and efficiently sequester uranyl from seawater (Figure 1). The University of Chicago has patented this invention. We have also collaborated with Professor Gagliardi to computationally understand the binding of SUP to uranyl. We have set up a method to randomly mutate SUP and are in the process of using protein evolution to further improve the uranyl affinity of mutated SUP.

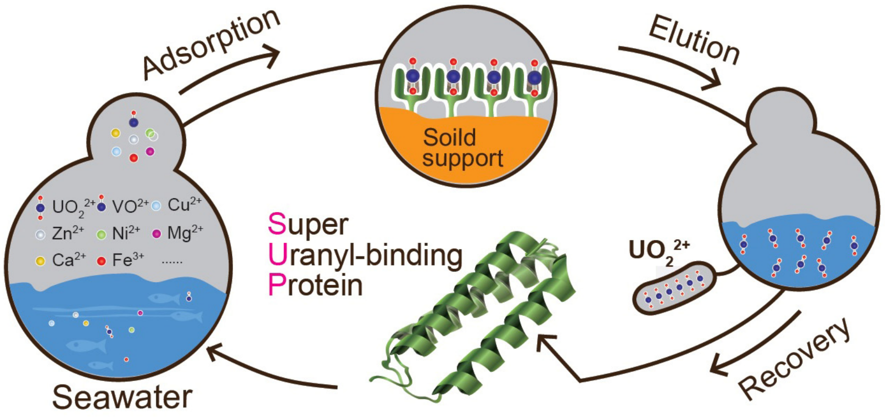

Figure 1. SUP immobilized on amylose resin can consistently remove uranyl from uranyl-contaminated water over many cycles.

2. Development and enhancement of a genetically encoded lanthanide binding protein.

After the success of SUP, we modified our initial screen to instead search the PDB for proteins containing a lanthanide-selective binding geometry. Our search revealed several hundred promising hits, and of these we selected 18 different proteins based on factors such as protein size and previously reported parameters including stability and ease of expression. These 18 genes were synthesized and the corresponding protein was expressed and tested for lanthanide binding. Four of these proteins bound terbium(III) with nM levels of affinity, and three of these four demonstrated robust expression and stability.

To further improve upon the affinity of our constructs, we are currently in the process of designing and testing a number of rational mutations. Mutations have been made to alter the binding residues, introduce intrinsic fluorescence to help with the ease of the assay, and mutate the nearby surrounding, non-binding residues. The later method proved especially effective in optimizing previously reported lanthanide-binding tags (LBTs) and will help us achieve higher levels of affinity we desire. Our current best binder binds with an affinity of 8 nM, something we seek to improve through further mutations or a possible collaboration with computational groups to help identify optimal mutation sites.

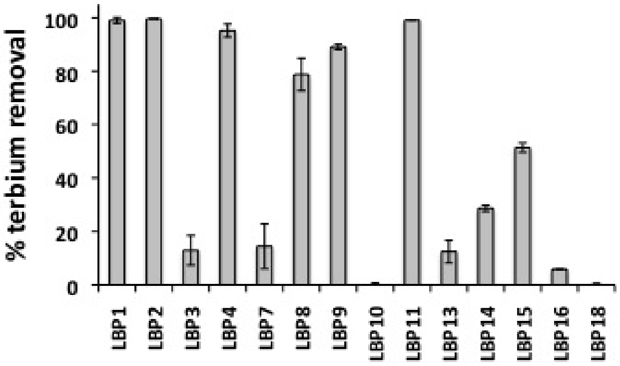

Figure 2. Ability of 10 µM of selected lanthanide binding proteins (LBPs) to bind an equimolar amount of terbium(III) in an aqueous solution.

Science objectives for 2015-2017:

- We have started protein evolution to improve the uranyl-binding affinity of SUP. We hope to achieve 100% sequestration of uranyl from seawater.
- Using the same computation-based approach we have selected potential protein scaffolds that may selectively bind lanthanide and actinide ions. We are testing these proteins.

Publications supported by this project 2013-2015

1. Zhou, L.; Bosscher, M.; Zhang, C.; Ozcubukcu, S.; Zhang, L.; Zhang, W.; Li, C. J.; Liu, J.; Jensen, M. P.; Lai, L.; He, C. “An engineered selective uranyl-binding protein with femtomolar affinity” *Nat. Chem.* **2014**, *6*, 236-241.
2. Odoh, S. O.; Bondarevsky, G. D.; Karpus, J.; Cui, Q.; He, C.; Spezia, R.; Gagliardi, L. “UO$_2^{2+}$ Uptake by Proteins: Understanding the Binding Features of the Super Uranyl Binding Protein and Design of a Protein with Higher Affinity. *J. Am. Chem. Soc.* **2014**, *136*, 17484-17494.

Spectroscopic Studies of Prototype Actinide Compounds

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Overall research goals: Spectroscopic studies of small actinide-containing molecules are the central focus of our program. The intention is to record benchmark data that can be used in the evaluation of relativistic quantum chemistry models. To obtain data that will be most suitable for comparisons with theory, experiments are conducted in the gas phase. Previously we have found that high-resolution photoionization techniques can provide complete maps of the low-lying electronic states of small actinide ions. Detailed information concerning bonding mechanisms can be deduced from the molecular constants and energy level patterns. We are now extending our experimental capabilities to permit studies of neutral molecules via photodetachment of mass-selected negative ions.

Significant achievements in 2013-2015: Experimental and theoretical studies of ThS were continued. Dispersed fluorescence spectra provided vibrational constants for the $X^1\Sigma^+$ ground state and the term energies of the $^3\Delta_1$ and $^3\Delta_2$ excited states. Multi-reference electronic structure calculations yielded results that were in good agreement with the spectroscopic data. The calculations produced a ground state wavefunction that was an admixture of the $Th^{2+}(7s^2)S^{2-}$ and $Th^+(7s^26d)S^-(3p^5)$ configurations, with a dipole moment of μ=4.2 D. To test this prediction, the dipole moment was measured by means of the Stark effect on rotational lines of the $\{18.26\}1$-$X(1)^1\Sigma^+$ transition (experiments performed at the Arizona State University). The ground state dipole was found to be 4.58(10) D, indicating a slightly larger charge separation than the theoretical calculations. Although it seems that multi-reference methods would be needed for calculations of ThS properties, we found that density functional theory (DFT) and coupled cluster methods (both single reference implementations) provided good results. This supports the use of DFT for calculations for actinide complexes that contain S-donor ligands.

The ThN/ThN$^+$ pair provides a model system for studies of actinide−nitrogen bonds. In addition, as ThN and ThO$^+$ are isoelectronic, comparisons of their low-energy states can yield further insights concerning the validity of the ligand field theory (LFT) view of actinide electronic structure. Laser induced fluorescence (LIF) and resonantly enhanced multi-photon ionization (REMPI) spectra, recorded over the 19700−21200 cm^{-1} range, exhibited a large number of optically active vibronic transitions (>20). Rotationally resolved spectra for ThN confirmed that the ground state was Th(7s)N, $X^2\Sigma^+$, as predicted by both LFT and high-level electronic structure calculations. Spectra for ThN$^+$ were taken using the pulsed field ionization- zero kinetic energy photoelectron technique. Rotationally resolved data established an ionization energy of 6.3272(4) eV and a ground state symmetry of $X^1\Sigma^+$. The $v'' = 1$ level of the ground state at 1010.0 cm^{-1} was the only excited molecular ion feature appearing within 1400 cm^{-1} of the ionization threshold.

Electronic structure calculations for ThN were carried out using both single- and multi-reference methods. Comparisons to the data for ThO^+ revealed trends that were consistent with LFT expectations. The first excited states of both molecules were derived from the Th(6d)-X configuration, but these states were at higher energies for ThN due to the greater destabilization of the 6d orbital resulting from the larger charge separation and shorter internuclear distance.

Due to the potential for using spectroscopic observations of ThF^+ as a means to determine the electron electric dipole moment (eEDM), we carried out further electronic structure calculations for the low-lying electronic states. The MRCI+Q/SO method was used to obtain term energies and electric dipole transition moments. These data are essential for the design of eEDM measurements.

The construction of a slow electron velocity map imaging (SEVI) spectrometer for actinide studies is one of the primary goals of this project. This instrument will provide extensive spectroscopic data for the lower energy states of neutral molecules. A key advantage of this technique is that the negative ions can be mass selected prior to photodetachment. This avoids some the complications encountered with laser ablation sources, where the range of species produced can be difficult to control. The spectrometer is now operating and being evaluated with simple test molecules. Fig. 1 shows an image obtained by near-threshold photodetachment of AlO^-

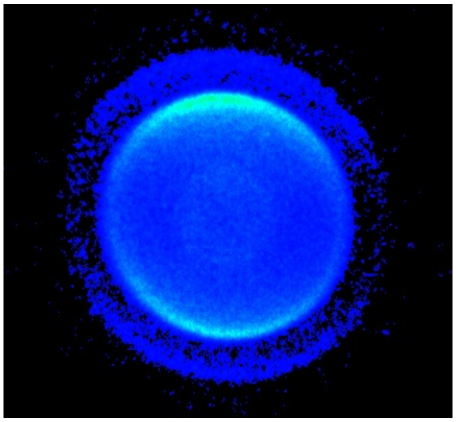

Fig. 1 Image of slow electrons from AlO- photodetachment.

Science objectives for 2013-2015: Studies of the electronic spectra of the UCl/UCl^+ and UN/UN^+ pairs will be carried out. Extensive electronic structure calculations will be used to explore the bonding in these molecules. The SEVI instrument will be used to measure the electron affinities of Th and U, and explore the dimers Th_2 and U_2. These data are important for the understanding of actinide metal-metal bonds and evaluation of relativistic quantum chemistry models. In addition, anion photodetachment techniques will be used to study the low-lying states of organometallic complexes, starting with U-benzene and Th-benzene.

Publications supported by this project

I. O. Antonov and M. C. Heaven, J. Phys. Chem. A **117**, 9684 (2013).
"Spectroscopic and Theoretical Investigations of UF and UF^+"

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A. Le, M. C. Heaven, and T. C. Steimle, J. Chem. Phys. **140**, 024307/024301-024307/024305 (2014)
"The Permanent Electric Dipole Moment of Thorium Sulfide, ThS"

M. C. Heaven, B. J. Barker and I. O. Antonov, J. Phys. Chem. A, 118, 10867, (2014):
Invited Feature Article, Editors Choice
"Spectroscopy and Structure of the Simplest Actinide Bonds"

Self-Assembly of Ditopic Ligands with Metal Salts to Construct New Helicate and Cube Architectures

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

Significant achievements during 2014-2015: Structure-based design study by Custelcean et al. has identified ditopic ligands that specifically direct the formation of helicates or cubes upon self-assembly with metal salts. We are further exploring the ability of functionalized ligands with various linkers (methylene vs 1,3-disubstituted phenylene) between the metal and anion coordination centers (ligand **L1**, Figure 1) to self-assemble with selected metal salts into helicate structures. In order to explore the formation of more complex self-assembled charge-neutral architectures, such as cubes, we initiated our study by preparing the relatively rigid ditopic 2,2'-bipyridine-bis(urea) ligand **L2** with 1,4-disubstituted phenylene linker and investigated its self-assembly with $ZnSO_4$ by NMR spectroscopy. The NMR analysis confirms the persistence of one major complex formed in the solution where ligand **L2** to $ZnSO_4$ ratio is 3:1. Thorough characterization is underway to elucidate the precise geometry of the self-assembled framework. Moreover, both ligand **L1** and **L2** (R = CH(*n*Bu)$_2$) exhibit good solubility in organic solvents, which can be further improved (R = C(alkyl)$_3$ and R' = alkyl) so they can be used as extracting agents for selective separation of ion pairs.

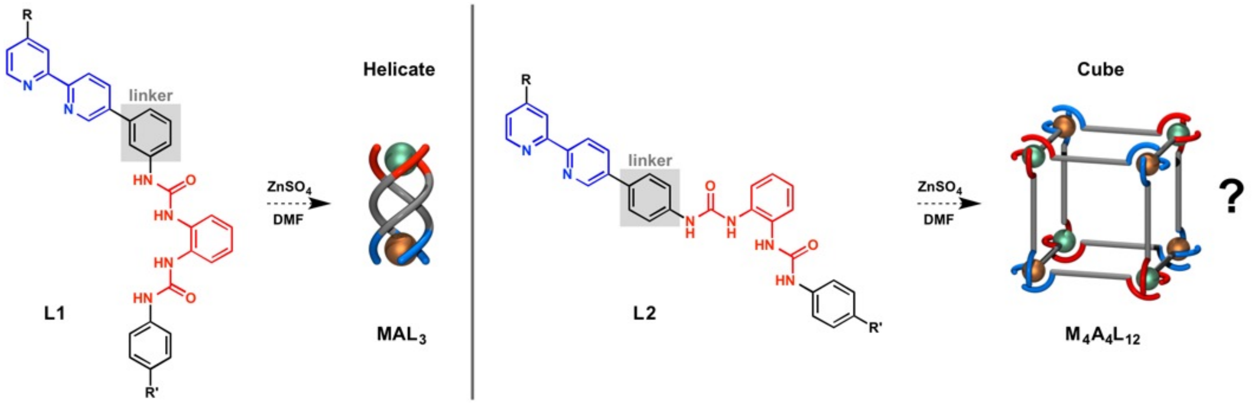

Figure 1. Self-assembly of bipyridine-bis(urea) ligands with $ZnSO_4$, leading to helicate and cube arhitectures.

Science objectives for 2015-2017:

- Understand the factors governing the geometry of the self-assembled complexes from ditopic 2,2'-bipyridine-bis(urea) ligands and metal salts.
- Improve the solubility of ligands **L1** and **L2** in organic solvents to explore their selectivity in liquid-liquid distribution systems.

- Synthesize new highly pre-organized ligands, study their self-assembly with metal salts to form complex molecular architectures (helicates, tetrahedral, cubes, etc.) with predetermined structures and separation functions.

Publications supported by this project 2013-2015:

1. Jia, C.; Hay, B. P.; Custelcean, R. De Novo Structure-Based Design of Ion-Pair Triple- Stranded Helicates. *Inorg. Chem.* **2014**, *53*, 3893.

Actinide Chalcogenides and Pnictides

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Overall research goals: The objective of this project is to understand the electronic interplay of actinides with soft-chalcogenide and -pnictide anionic environments. More specifically, we are focusing on synthesizing and characterizing valence ambiguous actinide materials, taking advantage of flexible bonding and valence behavior of actinides and anion sublattices.

Significant achievements during 2013-2015: We hypothesize that the 5f electrons of Np in chalcogenide environments sit on the border between the itinerant and localized regimes thus allowing Np^{3+}/Np^{4+} redox couples with the chalcogenide sublattice. To test this idea, we have identified some unique Np chalcogenides that may capture a 5f electronic state that is transitional between localized and delocalized. Recent extension to the actinide phosphides has been fruitful. Electronic interactions between actinide and anionic environments have been systematically studied through chemical, structural and optical- and magnetic-property characterizations. Significant results include:

1. Two binary Np selenides have been synthesized and characterized. Both compounds display clear deviations from other actinide analogues in chalcogen–chalcogen and metal–chalcogen interactions despite their similar compositions and structures. Single-crystal X-ray diffraction, X-ray spectroscopy, and magnetic susceptibility results suggest Np valence states between +3 and +4. The discrepancy between these Np compounds and other actinide analogues is primarily attributed to the different redox capabilities and ionic radii of actinides. These phases demonstrate the key role of Np in understanding the behavior of actinide chalcogenides, a result consistent with our hypotheses.

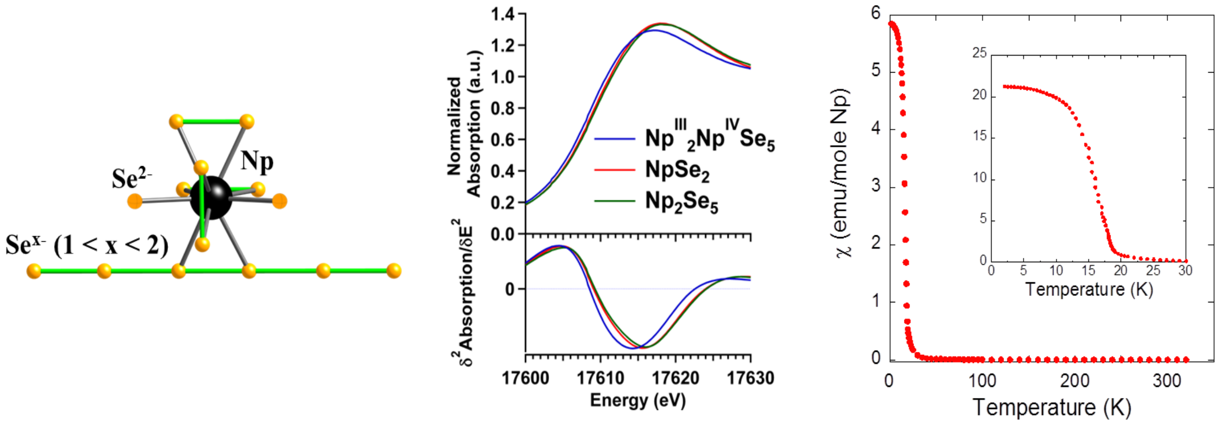

Figure 1. From left to right: local connectivities in Np_2Se_5, XANES spectra of Np selenides, magnetic susceptibility of Np_2Se_5.

2. Th^{IV} phosphides have been explored to test reaction space and serve as a tetravalent actinide benchmark for later actinide systems. Four new binary or ternary Th phosphides have been synthesized under solid-state reaction conditions using various fluxes and vapor transport agents. The discovery of these compounds demonstrates rich actinide pnictide chemistry, which has not been well studied. With even more flexible anionic sublattices than chalcogenides, these phosphides have shown a wide range of Th–P and P–P interactions. A broader range of electronic properties of actinide phosphides awaits exploration when moving to more redox active heavier actinides.

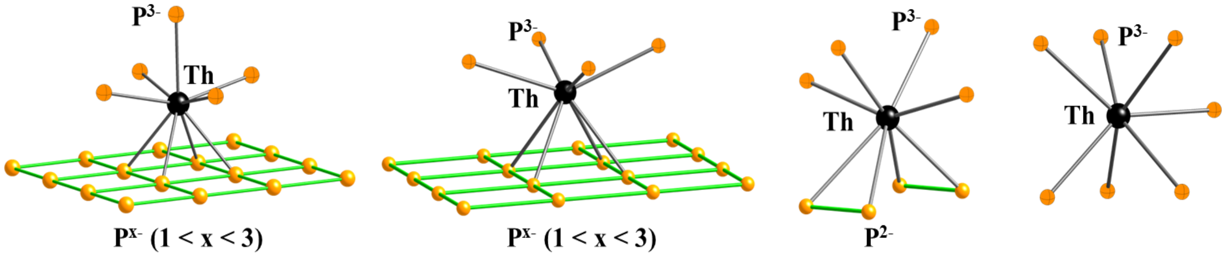

Figure 2. From left to right: local connectivities in ThP_3, $ThCu_2P_{2.5}$, $ThCuP_2$, and $ThCu_2P_2$.

Science objectives for 2015-2017:

- Expand the Np chalcogenides by introducing other metals to modify the degree of ionicity or covalency of the neptunium–chalcogen bonds using the concept of the inductive effect.
- Explore U, Np, and Pu phosphides to systematically study the interplay between the anion networks and redox active actinides.
- Expand X-ray spectroscopic studies to include both metals and anion sublattices. Also include magnetic susceptibility measurements to probe the actinide electronic states.
- Explore the electrochemical behavior of conducting, actinide-bearing crystals to obtain new insights into redox variations (of selected metals and anions). This study will provide a new approach to quantifying relationships between electronic and thermodynamic properties as well as their structures and electrochemistry.
- Conduct electrical resistivity measurements and collaborative theoretical calculations to investigate the chemical bonding, electronic structures, and potential phase transitions.

Publications supported by this project 2013-2015

1. Jin, G. B., Hu, Y-J., Bellott, B., Skanthakumar, S., Haire, R. G., Soderholm, L. and Ibers, J. A. “Reinvestigation of Np_2Se_5: A Clear Divergence from Th_2S_5 and Th_2Se_5 in Chalcogen–Chalcogen and Metal–Chalcogen Interactions” Inorganic Chemistry, (**2013**), 52(15), 9111-9118**.** [doi: 10.1021/ic401384t]
2. Jin, G. B., Christos, D. M., Skanthakumar, S., Ibers, J. A. and Soderholm, L. “Neptunium Diselenide: an Archetype Demonstrating the Key Role of Np in Understanding the Behavior of Actinide Chalcogenides” In prep for Angewandte Chemie International Edition.

Organometallic Actinide Chemistry: Probing Covalency in Metal-Ligand Multiple Bonding

Jaqueline L. Kiplinger, Principal Investigator. Co-Investigators: D. E. Morris, E. R. Batista, R. L. Martin, B. L. Scott, J. M. Boncella, M. J. Monreal, N. E. Travia, A. G. Lichtscheidl, and J. M. Dorhout. Collaborators: S. A. Kozimor and A. J. Gaunt.

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Overall Research Goals: This project explores the existence and manifestations of covalent metal-ligand bonding, including the generation and investigation of actinide-ligand multiple bonds, in complexes of uranium and other light actinides over a broad range of ligand sets and structure types through the combination of synthetic organometallic chemistry, electronic and vibrational structural characterization, and density functional theory to probe the involvement of metal 6d/5f orbitals and f-electrons in chemical bonding and to demonstrate reaction patterns unique to f-elements.

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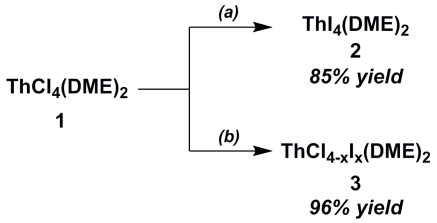
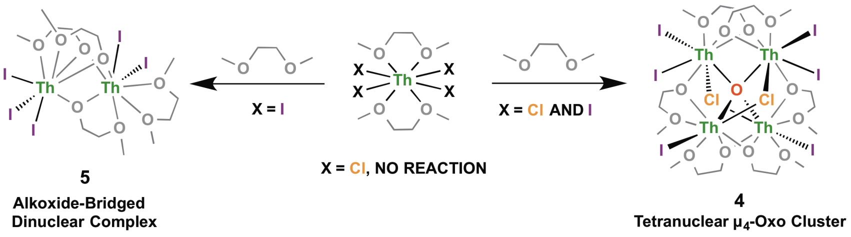
Significant Achievements in 2013-2015:

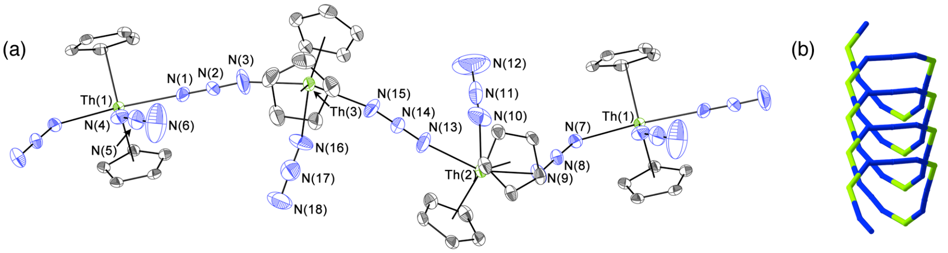
- Over the past two decades, thorium metal has become increasingly difficult to obtain. This shortage has greatly hindered the ability to perform much needed thorium research in chemistry, materials science and fuel cycle applications. Seeking a better approach, our team reacted $ThCl_4(DME)_2$ (**1**, DME = 1,2-dimethoxyethane) with excess trimethylsilylidodide (Me_3SiI) at room temperature to produce the thorium(IV) tetraiodide complex, $ThI_4(DME)_2$ (**2**) in high yield. Importantly, this route avoids the use of thorium metal as a reagent and represents a powerful new strategy for accessing thorium research. In previous work, our team reported that $ThCl_4(DME)_2$ could be easily prepared in quantitative yields from thorium nitrate, and this work was succesfully extended to transuranic actinide systems.



- Our team synthesized two rare multinuclear thorium complexes, which are formed by the unexpected carbon-oxygen bond cleavage of 1,2-dimethoxyethane (DME) by thorium iodide complexes. If the halide exchange between $ThCl_4(DME)_2$ and trimethylsilyl iodide (Me_3SiI) to prepare $ThI_4(DME)_2$ (**2**) is incomplete, the mixed-halide compound $ThCl_{4-x}I_x(DME)_2$ (**3**) is produced. Although, DME is normally a robust ligand for actinide chemistry, this mixed-halide complex (**3**) and **2** rapidly react with DME under mild conditions to form the μ_4-oxo cluster $Th_4(\mu_4\text{-}O)(\mu\text{-}Cl)_2I_6[\kappa^2(O,O')\text{-}\mu\text{-}O(CH_2)_2OCH_3]_6$ (**4**) and the dinuclear complex $Th_2I_5[\kappa^2(O,O')\text{-}\mu\text{-}O(CH_2)_2OCH_3]_3(DME)$ (**5**), respectively. These novel multimetallic complexes are formed reproducibly in good yield and result from the cleavage of multiple C-O bonds. The formation of complexes **4** and **5** highlights new reaction chemistry for the actinides and represent the first examples of actinide metal halide complexes reacting with DME to give well-defined C–O cleavage products.



- Our team has synthesized and characterized a new series of metallocene thorium diazide complexes. Their solid-state structures are governed by ancillary ligand steric effects. The two thorium diazide complexes with the least sterically bulky cyclopentadienyl ligands are coordination polymers in the solid-state. Both are 1D infinite chains; the smallest cyclopentadienyl (C_5Me_5) leads to chains of thorium centres doubly bridged by EE azides, while a slightly larger cyclopentadienyl (C_5Me_4Et) leads to thorium centres singly bridged by EE azides. Evidence from DOSY suggests that both coordination polymers break up in solution. The thorium diazide complex supported by the most sterically bulky cyclopentadienyl ligand (1,2,4-^{t}Bu$_3$-C$_5$H$_2$) is mononuclear. The formation of the extended structure of the $[(C_5Me_5)_2Th(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_3)_2]_\infty$ coordination polymer was circumvented by the addition of triphenyl phosphine oxide, allowing a mononuclear C_5Me_5 thorium diazide complex to be isolated and characterized.



<u>Science Objectives for 2015-2017</u>: We will continue our efforts to introduce new members to the family of actinide complexes containing multiply bound ligands. Further exploration into the control of organoactinide azide structure, with an eye towards the number and nature of the azide ligands, as well as the conversion of these new organometallic thorium azides into nitrides, is planned. These synthetic studies will be coupled with spectroscopy (e.g., C and N K-edge XAS, Raman) and theory. Based upon our observation that thorium can serve as a superb synthetic test bed for what will work transuranic systems, will be using this as a platform for extending our thorium studies to transuranic systems in collaboration with Dr. Andrew Gaunt.

<u>Selected publications supported by this project (2012-2015)</u>:

1. "Thorium-Mediated Ring-Opening of Tetrahydrofuran and the Development of a New Thorium Starting Material: Preparation and Chemistry of $ThI_4(DME)_2$," Travia, N. E.; Monreal, M. J.; Scott, B. L.; Kiplinger, J. L. *Dalton Transactions* **2012**, 41, 14441-14716.
2. "Thorium(IV) and Uranium(IV) Halide Complexes Supported by Bulky β-Diketiminato Ligands," Marisa J. Monreal, Robert J. Wright, Jeffrey T. Golden, Robert K. Thomson, David E. Morris, Brian L. Scott, Philip P. Power, and Jaqueline L. Kiplinger, *Organometallics* **2013**, *32*, 1423-1434.
3. "Organometallics Roundtable 2013−2014," John A. Gladysz, Robin B. Bedford, Makoto Fujita, Françǫis P. Gabbai, Karen I. Goldberg, Patrick L. Holland, Jaqueline L. Kiplinger, Michael J. Krische, Janis Louie, Connie C. Lu, Jack R. Norton, Marina A. Petrukhina, Tong Ren, Shannon S. Stahl, T. Don Tilley, Charles Edwin Webster, M. Christina White, and Gregory T. Whiteker, *Organometallics* **2014**, *33*, 1505-1527.
4. "Enhancing the Synthetic Efficacy of Thorium Tetrachloride Bis(1,2-dimethoxyethane) with Added 1,2-dimethoxyethane: Preparation of Metallocene Thorium Dichlorides," Marisa J. Monreal, Brian L. Scott, and Jaqueline L. Kiplinger, *Inorganic Chemistry Communications* **2014**, *46C*, 51-53.
5. "A Rare Tetranuclear Thorium(IV) μ^4-Oxo Cluster and Dinuclear Thorium(IV) Complex Assembled by Carbon-Oxygen Bond Activation of 1,2-Dimethoxyethane (DME)," Nicholas E. Travia, Brian L. Scott and Jaqueline L. Kiplinger, *Chemistry – A European Journal* **2014**, 20, 16846-16852.

IDENTIFYING DIFFERENCES IN ORBITAL MIXING BETWEEN 4F- AND 5F-ELEMENTS

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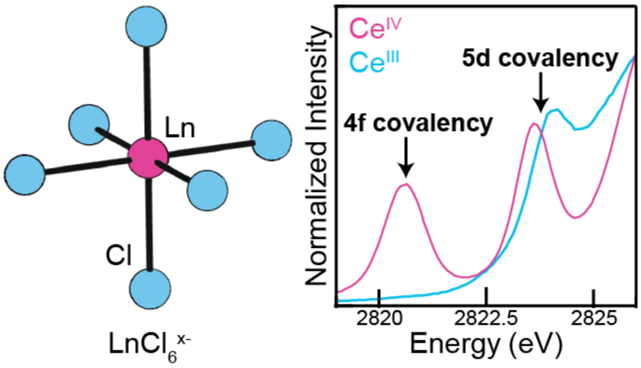
Overall Research goals: Covalency is a fundamental concept in chemistry used to describe chemical bonding in *s*-, *p*-, *d*-, and *f*-block elements. However, given the restrictions of existing experimental techniques, the degree of covalency of a given bond is difficult to measure and is often estimated or inferred. This situation was recently altered by the pioneering work of Solomon, Hedman, and Hodgson who used ligand K-edge X-ray Absorption Spectroscopy (XAS) to directly quantify covalency in bonding. Our goal is to expand this technique to complexes that contain heavy atoms in an effort to improve contemporary descriptions of covalency, electronic structure, and bonding in actinides and lanthanides. These studies are providing unique insight to evaluate the relative roles of *d*- and *f*-orbitals in bonding.

Significant achievements in 2013-2015

Despite recent advances, it remains of considerable interest to better define the roles that *f*- and *d*-orbitals play in chemical bonding in lanthanides and actinides. Advent of new theory and spectroscopic techniques have provided insight into *f*- and *d*-orbital mixing in actinide metal–ligand bonds. However, bonding for the 4*f*-lanthanide (Ln) elements is often described as primarily ionic, largely because previous calculations indicated that the 4*f*-orbitals do not extend significantly beyond the core orbitals. The viewpoint that lanthanide–ligand interactions are best described using ionic bonding models finds support in the literature from many reactivity studies and physical measurements. Most notably, optical spectroscopy suggests that the 4*f*-orbitals are core-like and only weakly influenced by ligand fields. However, a number of 4*f*-element compounds have been isolated where covalency in bonding may be important, and a growing number of studies suggested that the 5*d*-orbitals should be considered when evaluating lanthanide–ligand bonding. As the use of rare earth elements is increasing in many industrial processes – e.g. in catalysis, energy production, medicine, high-performance alloys, magnets, and areas relevant to national security – it is becoming more important to understand these anomalies and advance descriptions of lanthanide electronic structure and covalent bonding.

Covalency in Ln–Cl bonds of O_h-$LnCl_6^{x-}$ (x = 3 for Ln = Ce^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}; x = 2 for Ln = Ce^{IV}) anions has been investigated, primarily using Cl K-edge X-ray absorption spectroscopy (XAS) and time-dependent density functional theory (TDDFT); however, Ce $L_{3,2}$-edge and $M_{5,4}$-edge XAS were also used to characterize $CeCl_6^{x-}$ (x = 2, 3). The $M_{5,4}$-edge XAS spectra were modeled using configuration interaction calculations (CTM4XAS). The results have been evaluated as a function of (*1*) the lanthanide (Ln) metal identity, which was varied across the series from Ce to Gd, and (*2*) the Ln oxidation state (when practical, i.e. formally Ce^{III} and Ce^{IV}). Pronounced mixing between the Cl 3*p*- and Ln 5*d*-orbitals (t_{2g}* and e_g*) was observed. Experimental results indicated that Ln 5*d*-orbital mixing decreased when moving across the lanthanide series and when increasing the formal oxidation state of Ce from Ce^{III} to Ce^{IV}. For $LnCl_6^{3-}$ (formally Ln^{III}), the 4*f*-orbitals participated only marginally in covalent bonding, which was consistent with historical descriptions. Surprisingly, there was a marked increase in Cl 3*p*- and Ce^{IV} 4*f*-orbital mixing (t_{1u}* + t_{2u}*) in $CeCl_6^{2-}$. This unexpected 4*f*- and 5*d*-orbital participation in covalent bonding is presented in the context of recent studies on both tetravalent transition metal and actinide hexahalides, MCl_6^{2-} (M = Ti, Zr, Hf, U, Pu).



Chlorine K-edge XAS: spectra acquired from $CeCl_6^{2-}$ (pink) and $CeCl_6^{3-}$ (aqua) showing evidence for 5d- and 4f-orbital mixing with Cl 3p orbitals.

Science objectives for 2015-2017:

- We are focused on developing methods for interpreting effects from mulitiplets on the ligand K-edge XAS spectra. This is of particular importance for Pu and the other actinides.
- A significant thrust is focused on developing understanding of how covalency changes for the trans-plutonium elements.

Publications receiving support (full or partial) from this project in the period 2013-2015

"Covalency in Lanthanides. An X-ray Absorption Spectroscopy and Density Functional Theory Study of $LnCl_6^{x-}$ (x = 3, 2)" Löble, M. W.; Keith, J. M.; Altman, A. B.; S. Chantal E. Stieber, Batista, E. R.; Boland, K. S.; Conradson, S. D.; Clark, D. L.; Pacheco, J. L.; Kozimor, S. A.; Martin, R. L.; Minasian, S. G.; Olson, A. C.; Scott, B. L.; Shuh, D. K.; Tyliszczak, T.; Wilkerson, M. P.; Zehnder, R. A. *J. Am. Chem. Soc.* **2015**, *137*, 2506-2523.

"New Evidence for 5f Covalency in Actinocenes Determined from Carbon K-edge XAS and Electronic Structure Theory." Minasian, S. G.; Keith, J. M.; Batista, E. R.; Boland, K. S.; Clark, D. L.; Kozimor, S. A.; Martin, R. L.; Shuh, D. K.; Tyliszczak, T. *Chem. Sci.* **2014**, *5*, 351.

"A Carbon K-edge X-ray Absorption Spectroscopy and Time Dependent Density Functional Theory Examination of Metal–Carbon Bonding in Metallocene Dichlorides." Minasian, S. G.; Keith, J. M.; Batista, E. R.; Boland K. S.; Kozimor S. A.; Martin, R. L.; Shuh, D. K.; Tyliszczak, T.; Vernon, L. J. *J. Am. Chem. Soc.* **2013**, ***135***, 14731.

Charge Transfer in Heavy Element Complexes: All about Ion-Ligand Interactions

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Overall research goals: The objective of this project is to conduct experimental and theoretical studies of electronic properties and ion-ligand interactions aimed at achieving a fundamental and predictive understanding of heavy-elements complexation and separation.

Significant achievements during 2013-2015: By measuring the energies (reduction potentials) and dynamics of charge-transfer (CT) transitions of ions in complexes and compounds, fundamental understanding has been achieved on various consequences of ion-ligand interactions, including the stabilities of f-element ions in reduced oxidation states.

1. Ligand-to-metal CT in Cf(III) compounds for creation of a metastable divalent Cf(II) has provided new insides into actinide electronic properties. We have identified a CT transition band in the absorption spectra and analyzed photoluminescence from the CT state in crystals of Cf[HDPA]$_3$.H$_2$O and Cf[B$_6$O$_8$(OH)$_5$]. As shown in Fig.1, such a CT luminescence broadened by strong vibronic coupling has not been reported previously in any trivalent actinide compounds. Our work confirms a transition of the periodicity in the actinide series that occurs at Cf(III). In combination with the increased ion-ligand interaction measured by significantly strong ligand-field strength, this transition is given arising from stabilization of the divalent oxidation state Cf(II)5f^{10}.

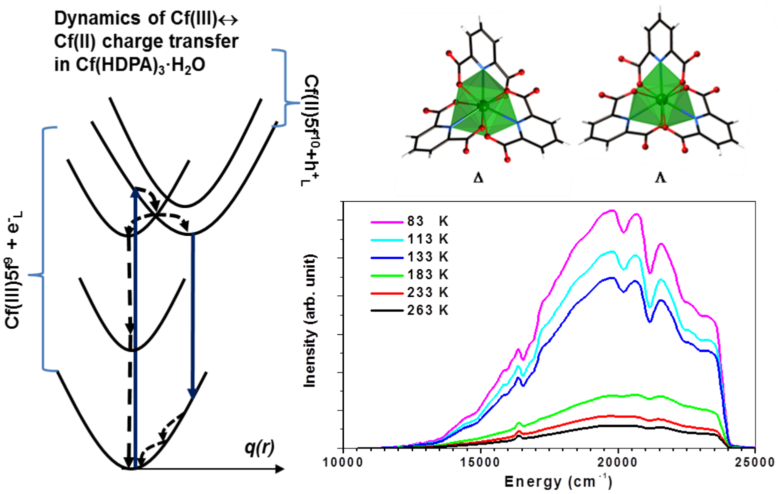

Figure 1. Temperature dependence of Cf(III)-Cf(II) CT luminescence from Cf[HDPA]$_3$·H$_2$O is interpreted with the potential and configuration coordinate in the left. There are both photon emission (solid arrow) and non-radiative relaxation (dashed arrows) from the metastable state Cf(II)5f^{10}.

2.Theoretical analysis of the CT spectra of actinyl complexes achieved quantification of complexation. Absorption spectra of uranyl ions in various tridentate ligands exhibited the characteristics of CT vibronic transitions and were utilized for characterization of complexation. Developed a new analytical method with which electronic energy levels, vibrational frequencies and vibronic coupling strength were extracted from fitting of the spectra to a semi-imperial model. It enabled us to quantitatively determine the complexation as a function of ligands and ligand charges.

3. Hybridization of Ce^{3+} 5d with ligand state 2p leads to substantial changes in bonding and spectroscopic properties. As shown in Fig. 2, an anomalous thermal quenching of the photoluminescence of Ce^{3+} at the 6H

site in $Ca_2Gd_8(SiO_4)_6O$ is attributed to Ce-O covalence. Electronic transitions between the 4f and 5d2p states were studied in characterization of Ce^{3+}-lattice interactions. Theoretical calculations suggest a weak Ce-O covalence bond formed between Ce^{3+} and the free-oxygen at the 6H site. In combination of experimental and theoretical studies, this work provides a comprehensive understanding of ionic and covalent interactions of lanthanide ions in dielectric crystals.

Science objectives for 2016-2018:

- Investigate the systematic trend of the reduction potentials of An(III)-An(II) couples [An=Pu, Am, Cm, Bk, and Cf] in various compounds. To determine the variations in the reduction potential as a function of ion-ligand interactions.
- Investigate CT luminescence of Cf(III) in various compounds to determine the correlation between Cf(II) stability and ligand environments.
- Experimental and theoretical studies of CT transitions and 5f-5f transitions in actinyl compounds. Comparing ion-ligand interaction of actinyl ions in 5f states and charge transfer states σf .

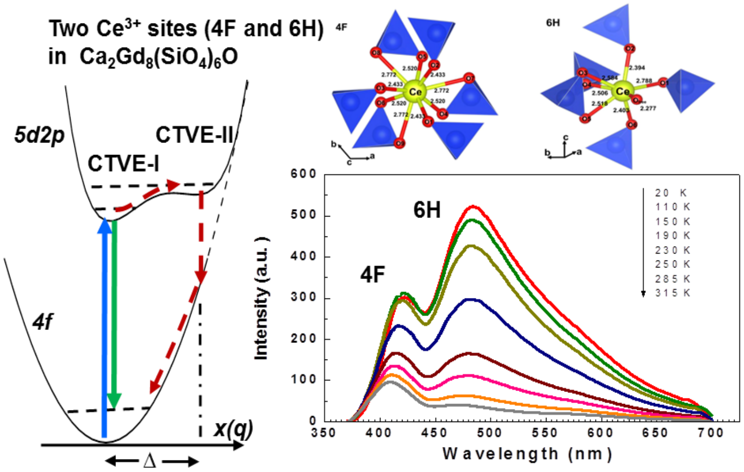

Figure 2. Temperature dependence of Ce^{3+} luminescence from $Ca_2Gd_8(SiO_4)_6O$ which has two Gd (Ce) sites 4F and 6H. At 6H a free-oxygen forms covalent bond with Ce^{3+} 5d in the excited state. Charge transfer vibronic excitation (CTVE) leads to a modification of the excited state potential as shown in the left. As a result, non-radiative relaxation (dashed arrows) quenches the Ce^{3+} photoluminescence at the 6H site.

Publications supported by this project 2013-2015

1. Guokui Liu, “Advances in the Theoretical Understanding of Photon Upconversion in Rare–Earth Activated Nanophopshors”, Chem. Soc. Review, 2015, 44 (6), 1635 – 1652[DOI: 10.1039/c4cs00187g].
2. Yanqiu Yang, Zhicheng Zhang, Guokui Liu, Shunzhong Lua, Linfeng Rao, “Effect of temperature on the complexation of NpO^{2+} with benzoic acid: pectrophotometric and calorimetric studies”, J. Chem. Thermodynamics 80 (2015) 73–78[dx.doi.org/10.1016/j.jct.2014.08.022].
3. Matthew J. Polinsk, Edward B. Garner, Re´mi Maurice, Nora Planas, Jared T. Stritzinger,T. Gannon Parker, Justin N. Cross, Thomas D. Green, Evgeny V. Alekseev, Shelley M. Van Cleve,Wulf Depmeier, Laura Gagliardi, Michael Shatruk, Kenneth L. Knappenberger, Guokui Liu, S. Skanthakumar, Lynda Soderholm, David A. Dixon and Thomas E. Albrecht-Schmitt, “Unusual structure, bonding and properties in a californium borate”, Nature Chemistry, 6, 387-392 (2014)[DOI: 10.1038/NCHEM.1896]
4. Dengyun Zhai, Lixin Ning, Yucheng Huang, and Guokui Liu, “Ce−O Covalence in Silicate Oxyapatites and Its Influence on Luminescence Dynamics” J. Phys. Chem. C 118, 16051−16059 (2014) [dx.doi.org/10.1021/jp5049293].
5. Guokui Liu, “A Degenerate Model of Vibronic Transitions for Analysing 4f–5d Spectra”, J. Luminescence, 152, 7-10(2014)[dx.doi.org/10.1016/j.jlumin.2013.12.010].
6. Guokui Liu, Guoxin Tian, Linfeng Rao, “Theoretical analysis and quantification of the absorption spectra of uranyl complexes with structurally-related tridentate ligands” , Phys. Chem. Chem. Phys. 15, 17487-17495(2013)[DOI: 10.1039/c3cp52900b]
7. Chao Xu, Guoxin Tian, Simon J. Teat, Guokui Liu, and Linfeng Rao, “Thermodynamic and structural trends in hexavalent actinyl cations: complexation of dipicolinic acid with NpO_2^{2+} and PuO_2^{2+} in comparison with UO_2^{2+}”, Chemistry, Euo. J. 19, 16690 – 16698(2013)[DOI: 10.1002/chem.201302119].

Metal–Oxygen Orbital Mixing in Actinide Molecules and Solid-State Materials

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Overall research goals: The research objectives are to synthesize high quality analytical samples of coordination compounds and solid-state materials with An–O multiple bonds (An = Th to Cm) for characterization using oxygen K-edge and hard X-ray absorption and emission spectroscopies (XAS and XES). Together with a comprehensive theoretical study, the work aims to show how changes in An–O orbital mixing are influenced by differences in 5f occupation and 5f/6d energies, and how An–O bonding impacts stability/reactivity, redox potentials, and magnetic properties.

Significant achievements during 2013 – 2015: Crystalline samples of the actinyl tetrachlorides, $AnO_2Cl_4^{2-}$ (An = U, Np, Pu), were synthesized with non-coordinating tetramethylammonium, Me_4N^{1+}, countercations and characterized using O K-edge XAS. To ensure that accurate pre-edge peak intensities were obtained, spectra were measured in transmission using the scanning transmission X-ray microscope (STXM) of Advanced Light Source (ALS) beamline 11.0.2. Imaging studies revealed a number of thin crystallites, which provided both short pathlengths for X-ray radiation and the ability to average over a large sample area. Spectra obtained at the actinide $M_{5,4}$-edge provided branching ratios that increase with the anticipated increase in 5f-orbital occupation from $5f^0$ (U) to $5f^1$ (Np) to $5f^2$ (Pu), and provide confidence that radiation damage was minimized during scans (Figure 1). Peak intensities were compared with those of the formally tetravalent lanthanide dioxides, LnO_2 (Ln = Ce, Pr, Tb), which serve as O K-edge orbital-mixing benchmarks based on complementary lanthanide L_3-edge measurements.

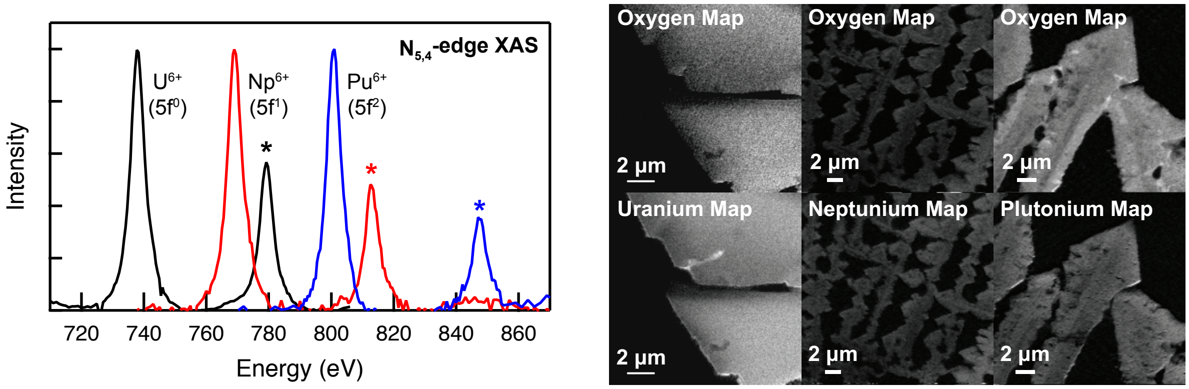

Figure 1. Actinide $N_{5,4}$-edge XAS (left) and elemental maps (right) obtained using STXM for crystalline particles of $(Me_4N)_2AnO_2Cl_4$ (An = U, Np, Pu). The measurements show that photon damage from the X-ray beam was minimized.

In the first phase, O K-edge XAS and DFT results of $UO_2Cl_4^{2-}$ were compared with measurements on the monooxo pentachloride complex, $UOCl_5^{1-}$. A marked increase in the amount of σ-type 5f and O 2p-orbital mixing as a possible consequence of the inverse *trans* influence (ITI). The ITI is a unique phenomenon for 5f-elements that has been in a variety of theoretical studies, but difficult to observe directly by experiment.

Moving across the actinide series, both the experimental O K-edge XAS and TDDFT (Figure 2) show that transitions associated with 5f-orbitals decrease in energy and become broader from $UO_2Cl_4^{2-}$ ($5f^0$) to $NpO_2Cl_4^{2-}$ ($5f^1$) to $PuO_2Cl_4^{2-}$ ($5f^2$). The experimental transition intensities, TDDFT calculated oscillator strengths, and Mulliken population analysis all suggest that 5f and O 2p orbital mixing is greatest for $NpO_2Cl_4^{2-}$ relative to either $UO_2Cl_4^{2-}$ or $PuO_2Cl_4^{2-}$. These results are surprising given that other physical observables for the actinyl ions such as An–O bond length, stretching frequency ν_1, and gas-phase basicity exhibit monotonic trends as the actinide series is traversed.

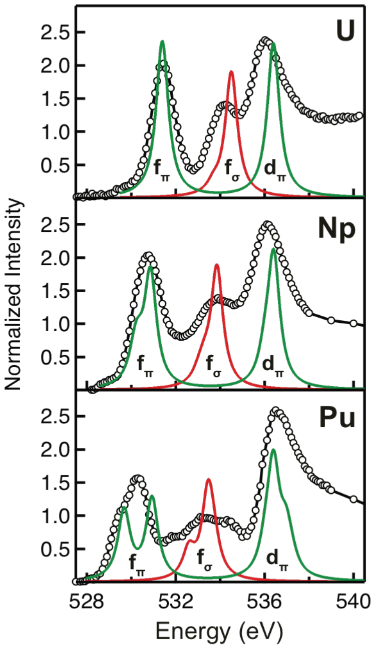

Figure 2. Oxygen K-edge XAS (black circles) of $(Me_4N)_2AnO_2Cl_4$ (An = U, Np, Pu). Time-dependent density functional theory simulated spectra (green and red) are separated into two components that are associated with final state orbitals that have σ- or π-symmetry with respect to the An–O bonds.

Science objectives for 2015 – 2017:

- Synthesize and measure O K-edge XAS for the pentavalent actinyl tetrachlorides $NpO_2Cl_4^{1-}$ and $PuO_2Cl_4^{1-}$ to evaluate how keeping Z_{eff} constant while changing 5f-orbital occupancy effects electronic structure and – in particular – the inverse *trans* influence.
- Compare changes in An–O orbital mixing for the tranuranium and transplutonium oxides as a result of the steady stabilization of the 5f-orbitals.
- Implement new methodology and instrumentation for liquid-phase measurements in order to determine reaction mechanisms and characterize intermediates during chemical transformations.

Publications supported by this project 2013 – 2015:

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5. Meihaus, K. R., Minasian, S. G., Lukens, W. W., Kozimor, S. A., Shuh, D. K., Tyliszczak, T., Long, J. R., "Influence of Pyrazolate vs *N*-Heterocyclic Carbene Ligands on the Slow Magnetic Relaxation of Homoleptic Trischelate Lanthanide(III) and Uranium(III) Complexes," *J. Am. Chem. Soc.*, **2014**, 136, 6056. DOI: 10.1021/ja501569t.
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Diversifying the Supply of Critical Materials, An Application of Separation Science and Technology

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Critical Materials Institute (CMI) Leadership Team: Alex King (Director, Ames Lab), Rod Eggert (Deputy Director, Colorado School of Mines), Karl Gschneidner (Chief Scientist, Ames Lab), Bruce Moyer, Tom Lograsso (Developing Substitutes Focus Area Lead, Ames Lab), Eric Peterson (Improving Reuse and Recycle Focus Area Lead, Idaho National Laboratory), Eric Schwegler (Crosscutting Research Focus Area Lead, Lawrence Livermore National Laboratory)

Overall research goals: The mission of CMI is to assure the supply chains of materials critical to clean energy technologies—enabling innovation in U.S. manufacturing and enhancing U.S. energy security. Critical materials provide essential and specialized properties to advanced engineered products or systems, have no easy substitutes, and are vulnerable to supply risk. The USDOE has evaluated the criticality of materials according to these criteria for clean energy, namely for wind energy, solar energy, energy efficient lighting, and electric vehicles. Within its five-year life, the CMI aims to develop technologies that will be adopted by industry in three areas: diversification of supply, development of substitutes, and reducing waste. Materials specifically under investigation by CMI include the five rare earths (RE) Nd and Dy for magnets and Eu, Tb, and Y for phosphors together with the light element Li for batteries. To diversify the supply of these metals and to recycle them will require the development of new separation technologies, and thus a significant investment of research effort in the CMI focuses on separation science and technology related to particular gaps in the supply chain (Figure 1). Science needs being addressed involve aspects of interfacial properties, coordination chemistry, transport, molecular recognition, structure, thermodynamics, and computational modeling all aimed at developing new beneficiation techniques to concentrate RE from ores and lean wastes and tailings, selectively separating RE from the concentrates, separating RE from one another to high purity, and conversion to oxides and metals and alloys.

Significant achievements during 2013–2015: Accomplishments in the area of separations for Diversifying Supply in the two-year operation of CMI include:

- Design of new separation agents for RE. The interfacial structure for two RE minerals bastnaesite and xenotime have been determined, enabling design of new flotation agents; computational methods for ligand design have been accelerated and expanded; and the first prototype RE extractants have been designed.
- Increased separation factors for adjacent lanthanides, a CMI grand challenge. Selectivity for Pr/Nd extraction has been tripled vs industry practice; a selective dissolution method has produced a useful light-heavy RE split; extraction of RE by an ionic-liquid system has achieved a La/Ce separation factor exceeding 300.
- Progress in froth flotation. Mineralogical characterization of four RE ore types has been completed, and an ancylite-strontianite separation has been obtained.
- Extraction of RE from phosphate. New solvent extraction chemistry for RE extraction from wet process phosphoric acid has been developed along with methods for leaching RE from process solids such as phosphogypsum.
- Lithium separation technology. New sorbents and membranes for recovery of lithium as a by-product from geothermal energy production have been developed.
- Improved RE separation processing. Acid-base consumption, a major contributor to the cost of RE separation, has been reduced using new commercial reagents.

Figure 1. Supply chain for rare earths leading to clean energy.

Science objectives for separations of critical materials 2015–2017:

- New science and developed technology for concentrating critical materials from raw materials, separating critical materials from concentrates, purifying critical materials, and converting the purified forms to oxides and metals.
- Selective, high-yield froth-flotation techniques for RE ores, improved recovery of RE from phosphate rock processing, and better sorbents and membranes for Li recovery.
- Transformational processing technology for adjacent lanthanide separation, RE separation using ionic liquids, fast ligand design, and conversion of RE to metal.

Publications related to separations 2013–2015:

1. Izatt, R. M.; Isatt, S. R.; Bruening, R. L.; Izatt, N. E.; Moyer, B. A. Challenges to achievement of metal sustainability in our high-tech society. *Chem. Soc. Rev.* **2014,** *43 (8),* 2451–2475. DOI: 10.1039/C3CS60440C.
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Spectroscopic Elucidation of Electronic Structure, Bonding and Mechanism: From Transition Metals to f-Element Chemistry

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Overall research goals: The objective of our research program is to develop insight into structure, bonding and mechanism in transition metal and f-element chemistry. These studies include projects on iron-catalyzed cross-coupling, iron- and cobalt-catalyzed direct C-H functionalization and iron- and cobalt-pincers. Recently, we have begun to expand our studies to f-element electronic structure, bonding and reaction chemistry, including the development of novel approaches for the characterization of transient species.

Significant achievements during 2013-2015:

1. Base Metal Electronic Structure, Bonding and Mechanism

We have pioneered the application of a novel experimental approach combining inorganic spectroscopic methods (e.g. magnetic circular dichroism, electron paramagnetic resonance, Mossbauer, resonance Raman, stopped-flow absorption/RFQ) combinined with density functional theory studies, organometallic synthesis and reaction studies for iron-based catalysis in organic transformation. This experimental methodology has permitted the first direct determination of an active iron species in iron-bisphosphine cross-coupling, the identification of $[FeMe_4]^-$ in iron salt catalysis with catalytically relevant Grignard and solvent and insight into fundamental bonding and electronic structure in iron(II)-NHCs. These physical inorganic methods have also been applied to fundamental electronic structure and bonding in iron(II)-pincer complexes with both potentially redox innocent and non-innocent ligands.

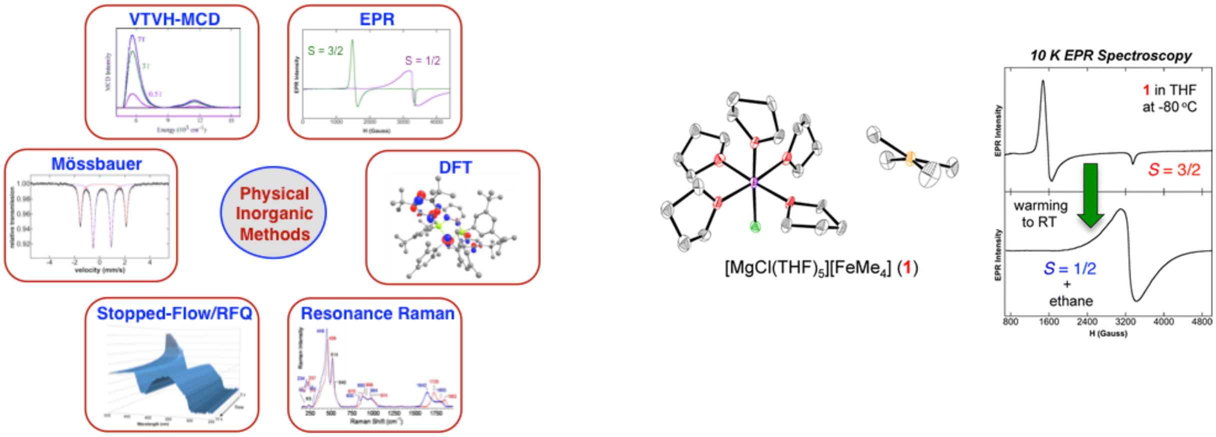

Figure 1. Left: Physical-inorganic methods for the elucidation of electronic structure and bonding in metal complexes. Right: Application of this methodology to the isolation, characterization and reactivity of $[MgCl(THF)_5][FeMe_4]$.

2. Spectroscopic Investigations of Bulk and Molecular Uranium Species

Analogous application of these inorganic spectroscopic methods to f-element systems offers the possibility for unprecedented insight into electronic structure, bonding and, when combined with freeze-trap methods, the nature of transient and high reactive species in f-element chemistry. Initial studies have focused on the determination of the spectroscopic properties of high symmetry Ucl$_6^-$ and Ucl$_6^{2-}$ using magnetic circular dichroism to define the spectroscopic features obtainable using this method. Additional studies have focused on the use of electron paramagnetic resonance for studies of electronic structure in UO$_{2+X}$ species.

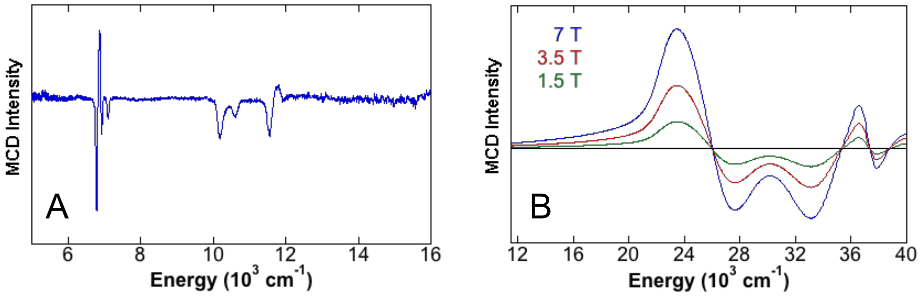

Figure 2. (A) 2.1 K, 7T NIR MCD spectrum and (B) magnetic field dependent UV-Vis MCD spectra of UCl$_6^-$.

Science objectives in f-element chemistry for 2015-2017:

- Further explore the use of MCD for the characterization of high-symmetry uranium complexes; extensions include the determination of the polarizations of transitions in randomly oriented samples, the detailed investigation of higher energy transitions (d-f and CT) and the definition of the spectroscopic features in MCD as a function of oxidation state, geometry and coordination number to serve as a foundation for in-situ studies.
- Establish new collaborations to extend our spectroscopic studies to low symmetry uranium complexes in order to develop a broad methodology across uranium coordination chemistry
- Initiate studies of transient species in uranium chemistry through the use of freeze-trap methods combined with spectroscopic and theoretical studies
- Identify synergistic opportunities to support the characterization of well-defined f-element complexes originating from the synthetic f-element community

Additional areas of interest

- Extend our studies to Np chemistry; we have an interest in the development of Np Mössbauer capabilities as well which are not currently available in the US
- Ligand hyperfine EPR spectroscopy for the evaluation of covalency in f-element complexes

Selected Publications

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

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Prof. Dr. Michael Dolg, Institut für Theoretische Chemie, Universität Köln, D-50939 Köln, Germany

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 2013-2015: The first two years of this project focused on the development of new systematically convergent correlation consistent basis sets for the f-block elements, modifying the FPD approach for heavy elements, as well as investigating different methods for the accurate calculation of spin-orbit coupling.

1. New correlation consistent basis sets based on both PP and all-electron DKH Hamiltonians were developed from double- to quadruple-zeta quality for the actinide atoms thorium and uranium (Ac and Pa in progress). Since the analogous MCDHF-adjusted PPs used for Ac-U are not currently available for the transuranic elements or the lanthanides, DKH3-based basis sets are being developed for these latter elements (valence and core-valence sets).

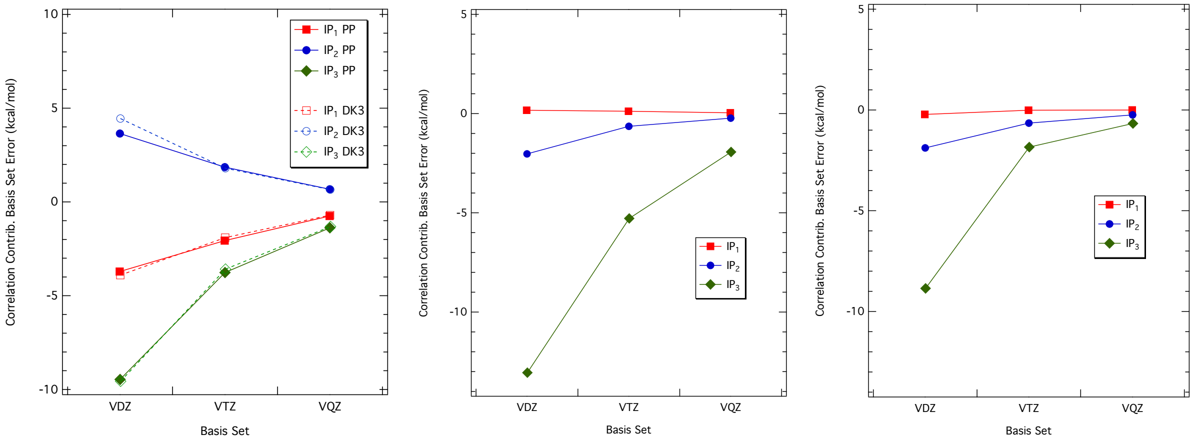

Figure 1. Frozen-core MRCI+Q correlation contributions of the 1st 3 ionization potentials (IPs) of U, Sm, and Pu relative to their estimated CBS limits. Only DK3 results are shown for the latter two species.

2. The accurate coupled-cluster-based FPD composite methodology was adapted for use on molecules containing f-block elements using new PP and all-electron DK3 correlation consistent basis sets. The scheme employed complete basis set (CBS) extrapolations, outer-core correlation, spin-orbit coupling, and quantum electrodynamics (Lamb shift). The DK3-based results for Th- and U-containing species were within the experimental uncertainties in all cases (almost all for PP-based calculations). The errors due to using a PP were found to strongly increase with increasing change in the oxidation state of the actinide.

Table I. Composite thermochemistry calculations of bond dissoc. and atomization energies (kcal/mol).

	ΔOx	PP	DK3	Expt.
$UF_6 \rightarrow UF_5 + F$	-1	72.1	73.9	71(3)/75(4)
$UF_5 \rightarrow UF_4 + F$	-1	94.4	95.7	98(4)/93(5)
$ThF_4 \rightarrow ThF_3 + F$	-1	162.7	161.7	159 ± 3
$ThF_3 \rightarrow ThF_2 + F$	-1	157.2	156.1	156 ± 3
$ThF_2 \rightarrow Th + 2F$	-2	325.3	321.5	325 ± 4
$ThF_3 \rightarrow Th + 3F$	-3	482.5	477.6	481 ± 5
$ThF_4 \rightarrow Th + 4F$	-4	647.2	641.3	639 ± 2
$ThO_2 \rightarrow Th + 2O$	-4	373.4	368.7	368 ± 3

Science objectives for 2015-2017:

- Develop PP-based basis sets for lanthanides and actinides using the older Stuttgart PPs for use in geometry optimizations and frequency calculations. These will also form the foundation for new explicitly correlated F12 basis sets which will also be initiated. These will be particularly useful for outer-core correlation calculations and larger molecules.

- Use our new basis sets and FPD extensions to investigate the thermochemical properties of actinide halides, oxyhalides, and carbonyls. Compare and contrast these results to analogous lanthanide-containing species.

- Carry out CASPT2 and MRCI studies of the low-lying electronic states of fundamental actinide species, such as UF/UF^+, UCl/UCl^+, UN/UN^+, $FUO/FUO^+/FUO^-$, $O_2F/O_2F^+/O_2F^-$, that are of interest to the Heaven and Wang experimental programs.

Publications supported by this project 2013-2015

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4. T. Mikulas, M. Chen, D.A. Dixon, K.A. Peterson, Y. Gong, and L. Andrews, "Reactions of lanthanide atoms with oxygen difluoride and the role of the Ln oxidation state", Inorg. Chem. **53**, 446 (2014). http://dx.doi.org/10.1021/ic402422h
5. P. Parmar, K.A. Peterson, and A.E. Clark, "Static electric dipole polarizabilities of $An^{5+/6+}$ and $AnO_2^{+/2+}$ (An=U, Np and Pu) Ions", J. Chem. Phys. **141**, 234304 (2014). http://dx.doi.org/10.1063/1.4903792
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7. K.A Peterson and K.G. Dyall, "Gaussian basis sets for lanthanide and actinide elements: Strategies for their development and use", in Computational Methods in Lanthanide and Actinide Chemistry, ed. by M. Dolg (Wiley and Sons, Chichester, 2015).
8. K.A. Peterson, "Correlation consistent basis sets for actinides. I. The thorium and uranium atoms", J. Chem. Phys. **142**, 074105 (2015). http://dx.doi.org/10.1063/1.4907596
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Experimental Electron Density Distribution in Actinide Compounds – an Experimental Atoms in Molecules (AIM) Approach

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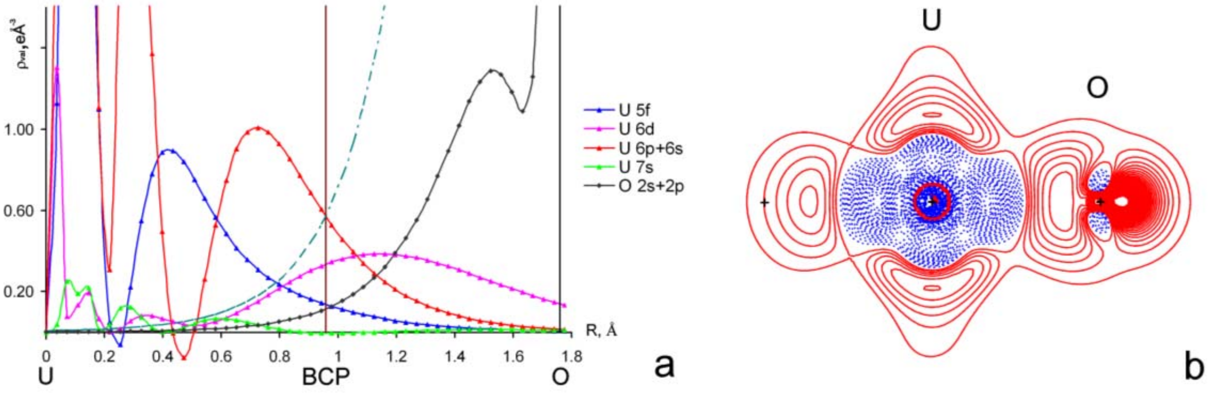
Overall research goals: The overall goal of this project is to characterize the bonding, particularly the covalent interactions, in compounds of thorium and uranium. The metrics to be used are the experimentally determined electron density distribution and the properties derived from an analysis of its 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. Whereas simple structural analysis refines positions of spherical atoms undergoing harmonic thermal motion, we are able to additionally refine the non-spherical electron density distribution for each atom. This methodology uses an atom based multipole expansion of the electron density where the pole populations are refineable parameters, but radial functions are available from theory.

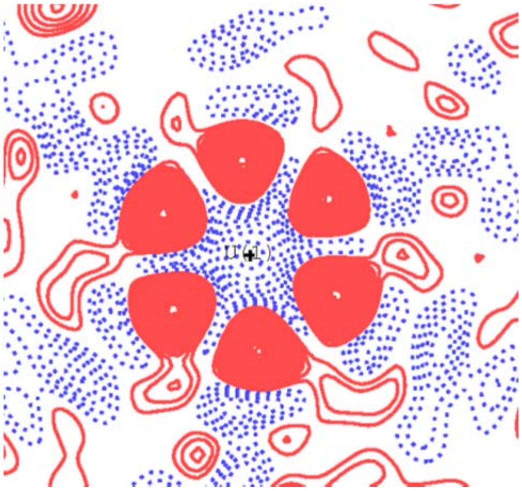
$$\rho_{atomic}(\mathbf{r}) = \rho_{core}(r) + P_v \kappa'^3 \rho_{valence}(\kappa' r) + \sum_{l=0}^{l_{max}} \kappa''^3 R_l(\kappa'' r) \sum_{m=-l}^{l} P_{lm} y_{lm}(\mathbf{r}/r)$$

For light atoms a single average radial function is sufficient, but for heavy atoms, several radial functions are required. Topological analysis of the total electron density requires the first and second derivatives of the density. This information allows characterization of bond critical points, space partitioning to assign atomic charges, etc. Preliminary results for $Cs_2UO_2Cl_4$ follow.



In a) the radial distribution of the valence density for separate U and O terms along the U-O line is shown. R is the distance from the uranium atom. The vertical line corresponds to the bond critical point position. In b) the deformation density map (the difference between the total electron density and that derived from neutral spherical atoms) calculated from the uranium and only one oxygen atom is shown to emphasize the extension of the uranium density into the oxygen atom, the U≡O triple bond, and the single lone-pair associated with oxygen. Positive contours are red, negative are blue. Contour interval is 0.05 eÅ^{-3}.

Significant achievements during 2014-2015: The project came up to speed in December 2015 with hire of Dr. Christopher Gianopoulos. To date, we have grown crystals and collected an extensive data set for sodium uranyl acetate. Data analysis is ongoing, but the residual density (shown below perpendicular to the UO_2 axis) after a spherical atom refinement looks promising.



We are currently revisiting the $Cs_2UO_2Cl_4$ experiment described above. At the time of that experiment, the highest multipole available in our software was 4th order. This is inadequate to rigorously treat *f*-type density functions. We now have a beta-test version of a new refinement program that will allow refinement up to 6th order, which we anticipate will provide significant improvement in the refinement model.

Science objectives for 2015-2017:

- Establish the viability of the use of higher poles to model the electron density associated with *f*-electron systems.
- Crystallize and collect high resolution X-ray data on a series of thorium and uranium compounds, starting with simple salts of the MCl_6^{2-} anions, and refine appropriate multipole models for their electron density distribution.
- Evaluate the use of standard AIM descriptors for these heavy atom systems.

Publications supported by this project 2014-2015:

none

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

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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 2013-2015:
For our first year, this project has been focused on actinide interactions with graphene oxide and titanomagnetite nanoparticles. Using these two disparate solid phases, provide a range of interfacial environments for comparison of quantitative speciation models of the sorbed complex.

Actinide interactions with graphene oxide

Graphene oxide (GO) made by Hummer's method has been characterized using FTIR, XRD, SEM, BET surface area analysis, elemental analysis, and potentiometric titration. Batch experiments examining Eu(III), Th(IV), Np(V), and U(VI) sorption onto graphene oxide as a function of pH (1-8) and actinide concentrations (10^{-9} to 10^{-7} M) were performed and sorption of Eu(III) and U(VI) was quantified using a thermochemically based, double layer surface complexation model (DLM). Sorption affinity increased as Th(IV) > U(VI) > Eu(III) > Np(V) which follows the trend of decreasing effective charge of the free ion. The variable concentration sorption isotherm experiments indicated remarkably high maximum U(VI) and Eu(III) concentrations of 286 mg_U/g_{GO} and 74 mg_{Eu}/g_{GO}, respectively.

The reactive surface species on GO have been identified as both carboxylic [$=CO_2H$] and sulfonic [$=SO_3H$] functional groups using the DLM. These models capture the range of the chemical environments the functional groups occupy using protonation/deprotonation constants. The site density (mol_{site}/g_{GO}) and protonation/deprotonation constants have been determined from least squares fitting of potentiometric titrations using the DLM. Based on the model fitting, sorption of the actinides (and Eu) is dominated by complexation with sulfonic groups at low pH and carboxylate groups at high pH. Previous studies which have not used this modeling approach to describe the data have not identified the importance of this sulfonic acid functional group. This work has shown that GO is a robust sorbent for actinides and sorption can be accurately quantified using a DLM. The DLM sorption constants are linearly related to 1:1 actinide:carbonate stability constants (Figure 1) likely due to the similarity between carbonate and carboxylate functional groups.

Attempts to examine Tc(VII) sorption to this graphene oxide indicated little interaction in 0.01 to 5 M HCl. However, relatively strong sorption of Tc(VII) was observed on epoxide functionalized graphene sheets and sorption increased with increasing HCl concentration from 0.01 M to 5 M. The exact mechanism of sorption is not understood but is believed to be associated with degradation of the epoxide functional group in the strong acid. This is currently under examination.

Actinide interactions with titanomagnetite

Titanium-doped magnetite nanoparticles were synthesized to examine the effects of systematically increasing the Fe(II)/Fe(III) ratio and Ti content in magnetite on the adsorption of light actinides and Eu with a range of oxidation states. Preliminary results indicate that increased Ti concentration (and the resulting increase in Fe(II)) results in increased absorption of actinides in the pentavalent and hexavalent oxidation states at low pH (~3, Figure 2). These results demonstrate that 'tunable' solid phases provide control over actinide partitioning in complex aqueous solutions and may be useful in understanding environmental distribution and in the development of actinide separation processes. Acid extraction followed by LaF_3 coprecipitation indicated that, under anaerobic conditions, U and Np were sorbed as tetravalent species on the titanomagnetite surface. TEM and XAS experiments are underway to determine the Np coordination environment and examine the potential for NpO_2 surface precipitates. These data will compliment previously published uranium-titanomagnetite XANES/XAFS data. Additionally, a release of radionuclides from the nanoparticles was observed when the suspensions were subjected to an oxidizing environment. A systematic study has been initiated that examines this re-oxidation step and the effects of 'aging' on the process.

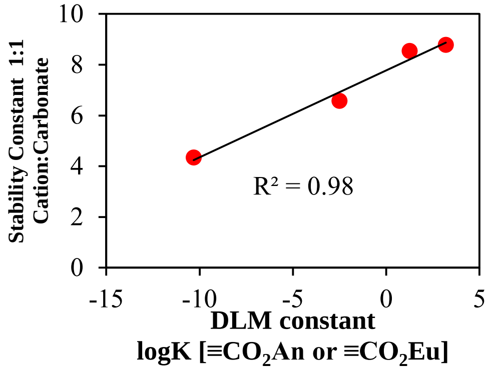

Figure 1. Linear relationship between aqueous carbonate complexation stability constants and DLM constants describing actinide sorption to carboxylate surface sites on GO.

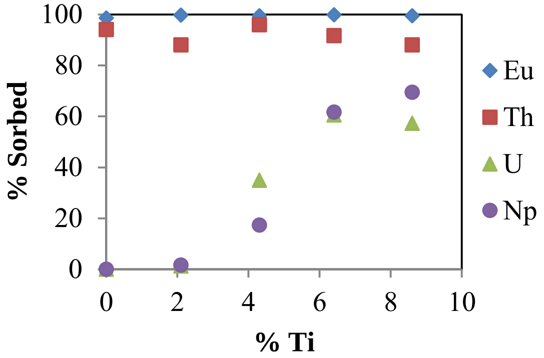

Figure 2: Sorption of Eu(III), Th(IV), Np(V), and U(VI) as a function of Ti(IV) content in titanomagnetite at pH 3. LaF_3 coprecipitation and XANES analysis indicate reduction of U(VI) and Np(V) to tetravalent species.

Science objectives for 2015-2017:

- Examine the enthalpy of actinide sorption to titanomagnetite and graphene oxide using isothermal titration calorimetery
- Characterize actinide speciation on graphene oxide and titanomagentite surfaces using x-ray photoelectron spectroscopy and x-ray absorption 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
- Determine stability constants for U(VI) and Np(V) aqueous amino acid complexes to facilitate studies of ternary solid-ligand-actinide surface complex formation

Publications supported by this project 2015-present

1. Xie, Y., Helvenston, E., Shuller-Nickles, L., Powell, B. A., "Surface complexaton and quantum mechanical modeling of Eu(III) and U(VI) sorption to graphene oxide" In preparation for Langmuir
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3. Wylie, M., Olive, D., Powell, B. A., "Neptunium(V) sorption and reduction on titanomagnetite nanoparticles" In preparation for Environmental Science and Technology

Radionuclide Waste Disposal: Development of Multi-scale Experimental and Modeling Capabilities

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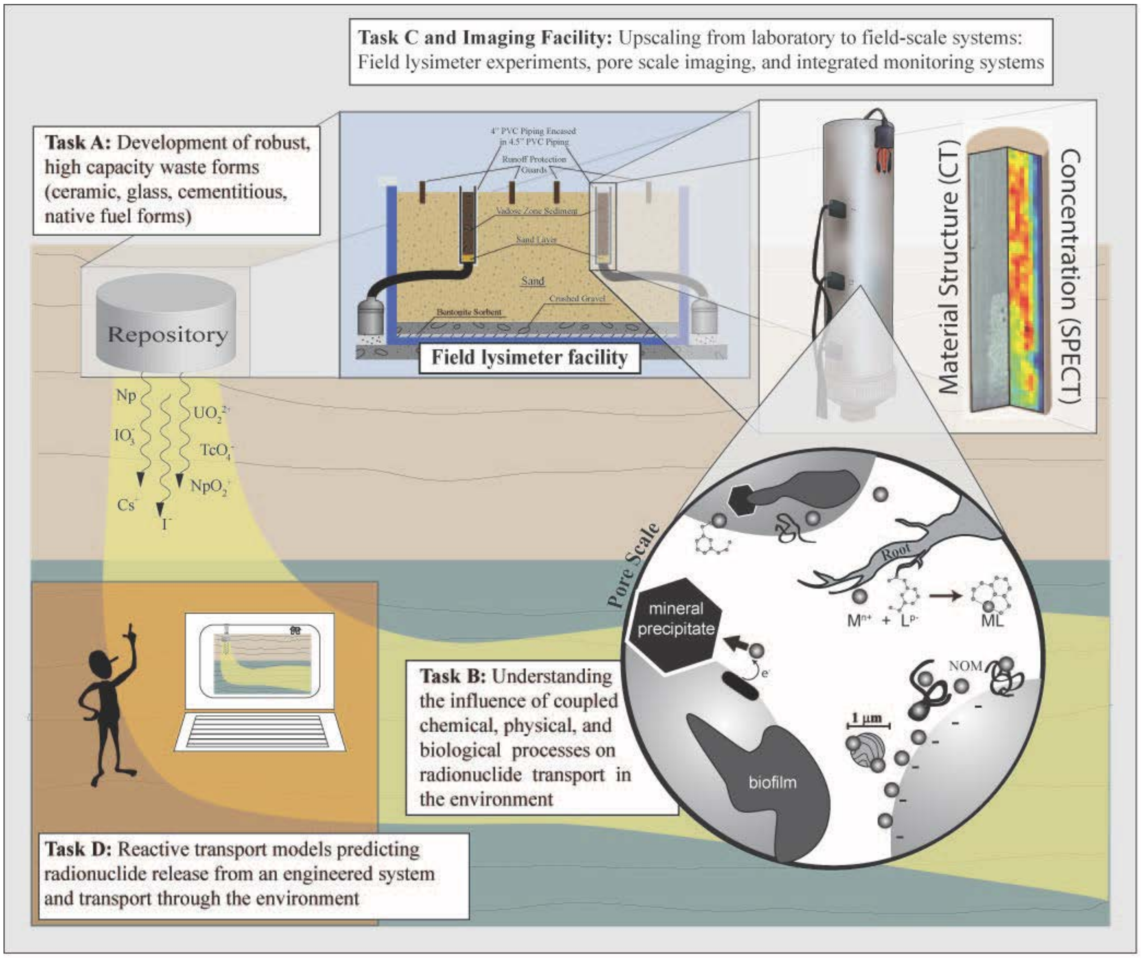
Overall research goals: This project is a Department of Energy, Experimental Program to Stimulate Competitive Research (EPSCoR) Implementation Grant started in September 2015 with supporting funding coming from the BES Heavy Element Chemistry program and the BER Subsurface Biogeochemical Research Program. The experimental and modeling efforts of this project are guided by the overarching scientific question:

> *What are the major molecular level chemical, biological, and microbial interactions that control the mobility of radionuclides in natural and engineered systems and how can these molecular and pore scale processes be properly defined and quantified for incorporation into larger scale, coupled experimental systems and reactive transport modeling efforts?*

The key issues to be addressed include identifying source terms for contaminants in geologic disposal scenarios, determining the reactivity and chemical speciation of risk-driving radionuclides (*e.g.*, Np, Tc, Cs, U, I) within engineered waste forms and natural subsurface environments, and delineating how coupled chemical, physical, and biological processes influence radionuclide mobility. The project is undertaken by an interdisciplinary team from three South Carolina universities. The project is divided into four major tasks as well as the development of a new imaging facility capable of monitoring the 2D and 3D transport of radionuclides through engineered waste forms and natural soils (shown in the conceptual figure below). The experimental plan will focus on multi-scale experimental and modeling techniques ranging from molecular to intermediate field scales. Radionuclide chemical/physical speciation within engineered waste forms will be linked to release rates and subsequent transport through subsurface environments. A variety of batch, microfluidics, column and field lysimeter experiments will be used to characterize the biogeochemical reactions controlling the mobility of the radionuclides in subsurface environments.

Major accomplishments of the project to date include:

- Testing of Single Photon Emission Computed Tomography (SPECT) imaging systems using a column with an idealized soil structure.
- Design and groundbreaking on a field lysimeter facility used to monitor transport of U, Tc, Np, I, and Cs under natural conditions.
- Experimental and quantum-mechanical modeling studies of hollandite compositions of the form $Ba_xCs_{2.32-2x}Ga_{2.32}Ti_{5.68}O_{16}$ are underway with varying A site (Ba/Cs) composition.
- Characterization of Tc behavior in reducing grout/cementitious waste forms under controlled laboratory and field conditions have examined the rate of Tc(IV) oxidation to Tc_2S_7 and TcO_4^-. Complimentary studies are underway to examine the use of graphitic nanoreinforcements to alter strength and porosity of the waste form.
- A kinetic model describing competitive ion sorption processes has been developed which can account for competition between weakly and strongly sorbing ions across a wide range of concentrations.



Task C and Imaging Facility: Upscaling from laboratory to field-scale systems: Field lysimeter experiments, pore scale imaging, and integrated monitoring systems

Task A: Development of robust, high capacity waste forms (ceramic, glass, cementitious, native fuel forms)

Task B: Understanding the influence of coupled chemical, physical, and biological processes on radionuclide transport in the environment

Task D: Reactive transport models predicting radionuclide release from an engineered system and transport through the environment

<u>Science objectives for 2015-2017:</u>

- Utilize computational and experimental techniques to examine radionuclide (Cs, Np, U, Tc) behavior within ceramic and cementitious waste forms
- Develop imaging techniques such as Single Photon Emission Computed Tomography (SPECT) techniques to examine 3D radionuclide distribution during disposition in cementitious waste forms and transport through unsaturated soil systems.
- Examine the kinetics of UO_2(s), TcO_2(s), and NpO_2(s) formation and dissolution during reductive precipitation and oxidative dissolution, respectively, within microfluidic cells with various geometries.
- Develop thermodynamic sorption models describing the influence of microbial and plant exudates on U, Np, Tc, and Cs sorption to sandy loam soil from the DOE Savannah River Site.
- Characterize water flow and transport of radionuclides within 2D tanks containing sandy loam soils. Experiments will also examine the influence of plant roots on radionuclide mobility and development of preferential flow pathways.
- Design and build a unique field lysimeter facility for monitoring transport of U, Np, Tc, I, and Cs in unsaturated sandy loam soil under natural conditions.
- Utilize quantum mechanical, pore network, pore continuum, and multi-scale hybrid modeling approaches to describe the behavior of U, Np, Tc, and Cs in waste form and soil transport research efforts described above

American Chemical Society's Summer Schools in Nuclear and Radiochemistry

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Collaborators: Dr. Louis Pena, Brookhaven National Laboratory, Biological, Environmental & Climate Sciences, Upton, NY 11973-5000.
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Overall goals: Since the 1940s our nation recognized the strategic need for research and training in nuclear science, nuclear chemistry and radiochemistry. These disciplines are essential to the foundation of many 21st century technologies including energy production in the context of carbon dioxide abatement, the development of nuclear medicine and radiopharmaceuticals, technologies that probe the structure and properties of materials, and national security. Although the subjects of nuclear chemistry and radiochemistry were once prominent in the undergraduate curricula of most US colleges and universities, these courses have slowly disappeared at many academic institutions due to faculty retirements and reductions in research funding in these areas. The manpower shortages that resulted have been a concern for many years.

NUCLEAR
CHEMISTRY
SUMMER
SCHOOL

In response to the decline in educational opportunities in the field of nuclear and radiochemistry and concomitant lack of student exposure to the field, the American Chemical Society's Nuclear and Radiochemistry Summer Schools were initiated to help address the need for an undergraduate pipeline into the field. The objective of the Summer Schools in Nuclear and Radiochemistry is to increase the number of outstanding physical science and engineering undergraduate students introduced to the fields of nuclear chemistry and radiochemistry. The goals of the Summer School are to:

1. Provide fundamental training in nuclear and radiochemistry principles, particularly to physical science and engineering students from institutions that do not have such programs.
2. Stimulate interest in physical science and engineering undergraduates in graduate studies in fields founded in nuclear and radiochemistry.
3. Generate awareness and acceptance of nuclear technologies and application in society.

Significant achievements during 2012-2014:

- 50% of the recent U.S. Ph.D.'s in nuclear and radiochemistry were initially trained at one of the Nuclear and Radiochemistry Summer Schools
- Three recent nuclear and radiochemistry faculty were participants in the Nuclear and Radiochemistry Summer Schools
    - Jennifer Braley, Assistant Professor of Chemistry, Colorado School of Mines, recipient of DOE Early Career Award
    - Amy Hixon, Assistant Professor Civial & Environmental Engineering, University of Notre Dame
    - Zachary Kohley, Assistant Professor of Chemistry, Michigan State University
- Fourteen of the 24 participants (58%) of the 2012 Summer School class are pursuing graduate degrees in the nuclear sciences.

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

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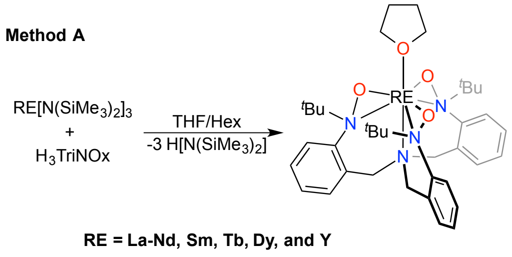
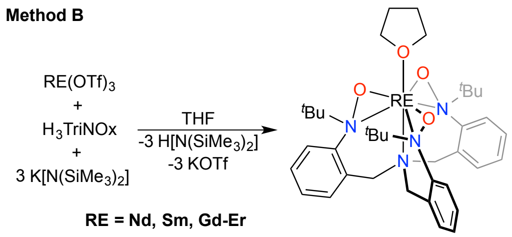
Overall research goals: The overall goal of this project is to develop a new methods for the solution separation of rare earth metals. We have been developing new redox active nitroxide compounds as ligands for lanthanide ions. Our hypothesis for the project is that electron-hole coupling in complexes of certain lanthanide metals with redox active ligands can be used to manifest chemical distinctiveness and affect separations. We are currently targeting the separations of Nd and Dy to incentivize the recycling of end-of-life magnetic materials.

Significant Achievements during 2013–2015: Initial attempts to improve upon rare earth separations prior to 2013 involved the use of pyridyl nitroxide ligands, which were expected to bind preferentially to Ce, Pr, Nd and Tb through oxidative intermediate valence effects. We successfully showed that the tetrakis pyridyl nitroxide framework significantly stabilized the tetravalent oxidation state of Ce. However, extension of this chemistry to Pr and Tb failed as a result of facile ligand dissociation pathways for the neutral radical form of the ligand. To overcome the shortfalls of the pyridyl nitroxide system, we developed a tripodal nitroxide ligand, tris(2-*tert*-butylhydroxylaminato)benzylamine, $((2\text{-}^t\text{BuNOH})\text{C}_6\text{H}_4\text{CH}_2)_3\text{N}$ (H_3TriNOx). The development of this ligand lead to three significant results:

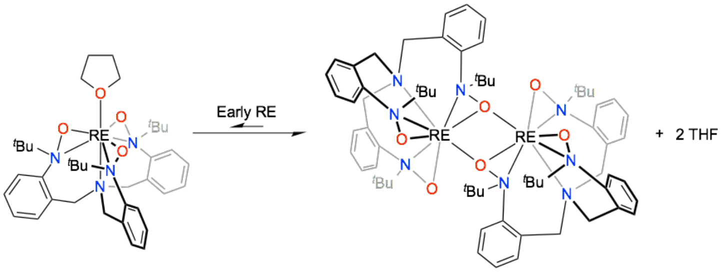
1. A series of RE(TriNOX)THF, RE = La–Er, complexes were successfully synthesized through two alternate routes:



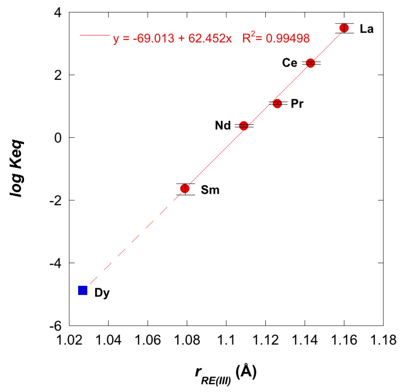


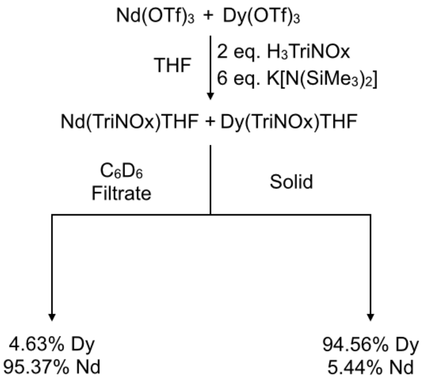
These complexes were characterized using X-ray crystallography, NMR spectroscopy, elemental analysis, and solution electrochemistry experiments.

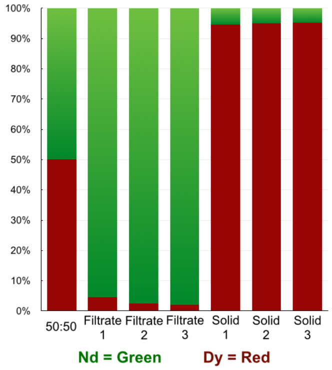
2. A self-association equilibrium was observed comprising RE(TriNOx)THF (monomer) and $[\text{RE(TriNOx)}]_2$ (dimer) species, RE = La – Sm, based on rare earth metal cationic radius and solvent polarity. Through the use of ^{1}H-NMR spectroscopic titration experiments the value of the equilibrium constants for these dimerization equilibria in benzene were determined and correlated to RE metal cationic radius.



3. Differences in solubility between the RE(TriNOx)THF and $[\text{RE(TriNOx)}]_2$ species were exploited to achieve improved separations of Nd and Dy starting from mixtures of Nd and Dy(OTf)_3 salts. Stripping of the TriNOx^{3-} ligand with oxalic acid completed the recycling process and allowed for the isolation of pure $\text{RE}_2(\text{C}_2\text{O}_4)_3$ salts and the recovery of H_3TriNOx, which could be used in subsequent recycling processes.







Science objectives for 2015–2017:

- Obtain separations factors, $S_{RE1/RE2}$, for the complete series of rare earth metal combinations.
- Replace the *tert*-butyl groups of H_3TriNOx with R groups of varying sterics in order to study the sensitivity of the self-association equilibrium constants to small changes in steric environment around the metal center.
- Extend the coordination chemistry of the rare earth metals in tripodal nitroxide ligand frameworks to the bench-top.

Publications supported by this project 2013–2015:

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Accurate Theoretical Approaches for Studying Actinides and Other Heavy Elements in Solid State

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Dr. Carlos A. Jimenez-Hoyos, Post-Doctoral Researcher (partial support)
Dr. Thomas M. Henderson, Post-Doctoral Researcher (partial support)
Mr. Alexander Rusakov, Graduate Student (PhD October 2013)
Mr. Irek W. Bulik, Graduate Student (partial support)
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Collaborators: Dr. Richard L. Martin, Los Alamos National Laboratory; Dr. Xiao-Dong Wen, Los Alamos National Laboratory.

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.

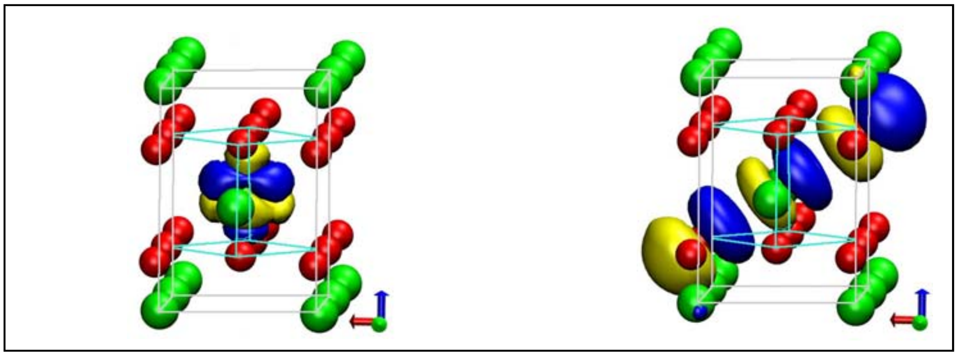
Significant achievements during 2013-Present:

Applications to actinide systems using density functional methods were carried out in collaboration with Xia-Dong Wen and Richard L. Martin from LANL (Papers 1, 2, 4, 5, 6). Applications to solid state actinide systems using the HSE functional developed in the PI's group are part of a long standing collaboration with the theory LANL group. On the other hand, methodological developments were done exclusively at Rice and involved multiple topics:

- A novel noncollinear density functional theory approach that is particularly important for heavy elements (Paper 3).
- The implementation of full space symmetry group in our periodic boundary conditions code that will allow for much faster computations of crystalline solids (Paper 7).
- The treatment of residual correlations not included by symmetry breaking and restoration (SB&R) techniques using a linearized Jastrow-type approach (Paper 8).
- Development of a quantum embedding theory that will allow for accurate wavefunction calculations using Wannier functions on solids containing actinides (Paper 9).
- Utilizing our SB&R wavefunction nodal surfaces in constrained-path quantum Monte Carlo calculations (Paper 10) and partially supported by a DOE CMCSN award.
- A thorough study of the sign problem in FCI-QMC (Paper 11)
- Application of a novel coupled cluster method to the Uranium dimer (Paper 12, in preparation).

Science objectives for 2015-2016:

Overall, progress has been substantial on multiple fronts and we are very happy with our recent achievements. We expect in 2015-2016 to continue progressing toward the objectives outlined in our proposal. The short term focus will be on ***accurate wavefunction*** calculations on small actinide molecules. For this purpose, we are finalizing a code that will allow us to efficiently compute dimers and trimers of actinide molecules, their carbides, nitrides, and other interesting cases for which some experimental data is available. These systems are currently approachable via (approximate) DFT methods but they are outside the realm of accurate techniques like CAS (exact diagonalization). We plan to fill this void using our recently developed coupled cluster wavefunctions. For solid state, our quantum embedding DMET/DET method (Paper 10) in conjunction with Wannier functions (unpublished, see Figure below) looks extremely promising for accurate calculations of solids using wavefunction methods as impurity solvers.



Wannier Functions depicting U 5*f* and O 2*p* bands near the Fermi energy. These localized orbitals will be used as a basis for first-principles computations of accurate wavefunctions in solid UO_2 using the quantum embedding method described in Paper 9, symmetry breaking and restoration techniques of Paper 8, and novel coupled cluster methods appropriate for multireference systems, as impurity solvers.

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Functional Ion Pair Receptors Targeting Cesium, Lithium, Sulfate, and Uranyl

(DE-FG02-01ER15186)

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MS J514, Los Alamos National Laboratory, Los Alamos, NM 87544

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 CsCl and LiCl, 2) chromophore-modulated calixpyrroles as sensors for CsCl, and 3) new sulfate anion extractants and redox active receptors for the uranyl cation.

Significant achievements during 2013-2015: This project has been focused on addressing two of the above objectives, namely the development of controlled ion pair receptor systems that allow very specific recognition of a particular cation anion pair. Extraction and transport are used as read-out functions. Controlled release through competitive cation complexation is a recurring theme.

1. Several new ion pair receptors based on the use of a pseudo dimeric calixpyrrole-calixarene motif were prepared. On the basis of numerous studies, the determinants that regulate cation co-complexation in these and related ion pair receptors were worked out (Fig. 1). Building on these findings, we were able to achieve controlled release of specific cations, extraction of targeted ion pairs, and produce systems where recognition was used to control the calixarene conformation.

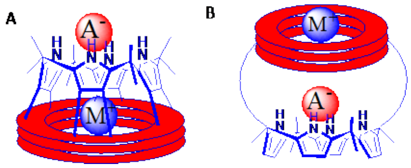

Fig. 1. In-cup (A) vs. subunit-based (B) cation recognition in calixpyrrole ion pair complexes.

2. Efforts to extend the calixpyrrole ion pair receptor design concept to recognize salts of lithium and, separately, sulfate were made. This work has advanced to the point where basic, X-ray diffraction-based structural studies have been completed. Some progress in sulfate, but not yet lithium salt, extraction has been made.

3. A new expanded porphyrin uranyl complex that switches from non-aromatic to aromatic on metal coordination was prepared and characterized in solution and in the solid state.

4. The ability of one particular set of pyridine strapped calixpyrrole receptors to function as a NaCl co-transporter was explored in a biological context. For the first time with a fully synthetic system, a causal relationship between the into-cell transport of the chloride anion and the induction of apoptosis was established. Separate, more health-related funding for this project, which involves a collaboration with the groups of Prof. Injae Shin (cell biologist; Yonsei University) and Prof. Philip A. Gale (model transport studies; Southamption University), is now being sought.

Science objectives for 2015-2017:

- Modulate various calixpyrrole-calixarene hybrid systems to create Cs^+ sensors.
- Synthesize new receptors for the sulfate anion, including ones that function in real-life milieus.
- Develop addition ion pair receptors for lithium salts. Demonstrate their utility in extraction
- Continue efforts to create new, redox active receptors for the uranyl cation.

- Push forward with an incipient collaboration with Dr. Kevin John of Los Alamos looking at water soluble texaphyrins as cancer-localizing carriers for radioactive Bi, Pb, and Ac isotopes.

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Soft X-ray Synchrotron Radiation Investigations 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/intermediate energy X-ray synchrotron radiation techniques for actinide investigations.

Significant achievements in 2013-2015: 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/computations to obtain electronic structure information from range of actinide materials with light atom constituents in collaboration with Kozimor et al. of LANL.[1-3] An outstanding highlight of the collaborative soft X-ray studies has been a detailed understanding of bonding in the metallocene dichlorides, thorocene, and uranocene from C K-edge XAS measurements and time-dependent density functional theory (TDDFT). These investigations yielded information on the electronic structures and orbital mixing plus direct experimental evidence for ϕ-bonding in the latter.[1,2] Figure 1 shows the C K-edge spectra obtained from thorocene and uranocene as well as the bonding *f*–orbital (e_{3u}) from thorocene. Soft XAS was also used to complement hard XAS studies of the actinide hexacyanoferrates with a more in-depth investigations of the soft X-ray edges (C K-edge, N K-edge, Fe $L_{3,2}$-edges) underway.[4] Spectromicroscopy was used to bracket the oxidation states in minute amounts of novel MU_8Q_{17} materials with Ibers et al.[5] Resonant inelastic X-ray spectroscopy (RIXS) was employed to determine the oxidation state of U and Np on Fe coupons following exposure to the respective actinyl solutions.[6]

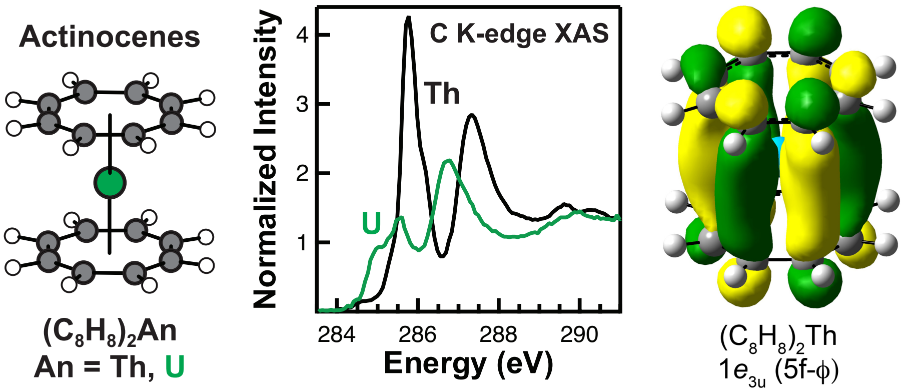

Figure 1. Left: Actinocenes; Center: Carbon K-edge spectra from thorocene (black) and uranocene (green) collected with the STXM at ALS Beamline 11.0.2; and the bonding *f*–orbital (e_{3u}) for $(C_8H_8)_2Th$.[2]

Science objectives for 2015-2017:

- Actinide STXM investigations will continue to be performed on transuranic materials, reference materials, and complexes to quantitatively determine electronic structure complemented by theoretical calculations. As materials preparation capabilities mature, more transuranic materials produced from LBNL will be examined and a near-term focus will be transuranic oxides. New emphasis will be on nitrogen K-edge spectroscopy of nitrides and separations complexes.
- The X-ray emission spectroscopy (XES) and RIXS investigations, components of this project for many years, will be re-started to examine actinide reference materials, oxides, and complexes with an emphasis on transuranics for electronic structure determination purposes.
- LBNL laboratory efforts will focus on the implementation of new growth systems, glove boxes, and infrastructure for synthesis of purpose specific materials and for the spectroscopic projects.

Publications supported by this project 2013-2015:

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Quantifying Actinide Speciation in Solution

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Overall research goals: Our objective for this research program is an understanding of a dissolved-ion's energy partitioning in solution and to do so with the accuracy necessary to inform ongoing efforts by theorists to develop predictive modeling relevant to chemical separations. Theoretical predictions of a metal-ion's solution behavior rely on a detailed representation of its coordination environment, a requirement currently hampered by a lack of metrical information about competing ligation and complex formation. Most of the available structural information is limited to first-coordination-sphere ligation, which are generally too limited for theory to adequately represent the very small energy differences that drive many systems of interest. Extending our efforts to use high-energy X-ray scattering (HEXS) to probe a targeted ion's coordination environment and provide thermodynamic free energies tied directly to structural moieties, we will begin to explore the more subtle impact of solution effects and how they can be modeled.

Significant achievements during 2013-2015:

To fill this knowledge gap, we are using HEXS as a direct structural probe of solution speciation. By studying dissolved ions as a function of varying solute concentration, we are able to obtain stability constants for the equilibrium of interest. Although these experiments are done with solutions far from ideal, we have demonstrated our ability to directly correlate the energetics determined via bulk-scale thermodynamic experiments with atomic-level structure. We are using this approach to provide metrical details about the metal ion speciation, including bond distances and ligation numbers. Of particular focus have been comparisons between coordination environments of trivalent Ln – An halides and pseudohalides. We are currently working with theorists interested in further developing force fields for use in molecular dynamics simulations of systems relevant to chemical separations.

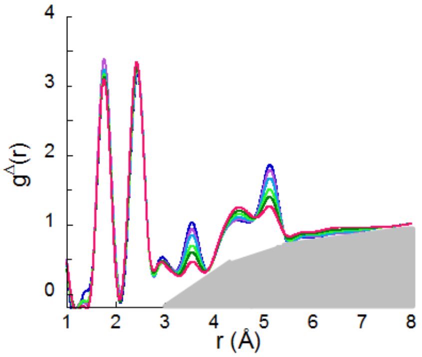

Figure 1. HEXS generated dPDFs generated from a series of uranyl thiocyanate solutions. The coordination of –NCS is unusually well defined, providing the opportunity to probe approaches for assigning coordination numbers to the second coordination sphere. The gray area represents the contribution of solution disorder within our current modeling scheme.

Science objectives for 2015-2017: We have two specific areas on which we wish to focus moving forward. The first of these involves extending our differential pair-distribution function (dPDF) methodology to provide metrical information regarding second-coordination sphere ligation. For most of the examples we have studied, in which the solute is a monomeric-metal ion, the dPDF show clear evidence for the onset of solvent disorder at the second coordination sphere. To date, we have been treating this scattering component with a simple modified error function (m-erf), an approach that works well when

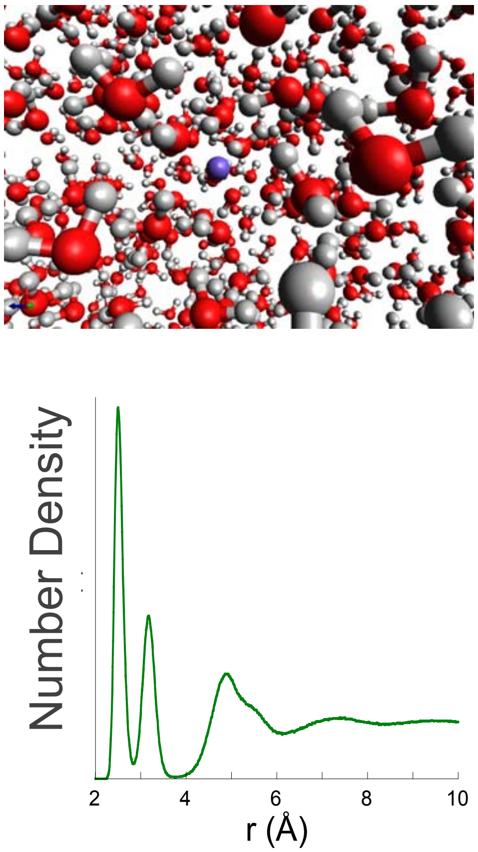

Figure 2. By performing molecular dynamics simulations (top) and determining the number of correlating ions as a function of distance (bottom) it is possible to generate a distribution function for comparison with experiments. This approach will allow us to realize a more quantitative approach to analysing the HEXS results

examining changing ligation over a controlled series of samples but provides little insight into the chemistry and dynamics occurring in this distance region. Our next step is to move toward a more quantitative and metrical approach to understanding how a metal ion organizes the solvent in which it is dissolved. Our first and simplest approach will be to extend our current modeling to a series of thiocyanate solutions, which have a dPDF profile that significantly restricts the parameter space within an m-erf fitting scheme. In conjunction with this approach we are using Argonne's large computing facilities (Blues) to investigate how to analyze results from molecular dynamics (MD) simulations within the context of the energetics associated with inner/outer sphere ligation.

Our second focus area centers on interrogating our HEXS data for information about higher coordination spheres. Selected data show evidence of solution correlations that extend beyond the second coordination sphere, information that is not otherwise experimentally available. Using this unique information as a guide we want to begin to understand the underlying forces governing these correlations. We will build on our efforts within our separations-centric program (see abstract of ANL PI Ross Ellis) to understand soft-matter interactions using a MD approach. A additional objective of this work is to compare the longer range correlations observed experimentally with those calculated using MD to test and inform theorists about their choice of force-fields at these longer distance.

Publications supported by this project 2013-2015:

1. L. Soderholm, R.E. Wilson, R. Chiarizia, S. Skanthakumar; *Solvent extraction system for plutonium colloids and other oxide nano-particles*. PATENT: U.S. (2014), US 8741237 B1 20140603.
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Actinide Compounds and Complexes

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Overall research goals: The actinide elements demonstrate a fascinating chemical diversity that remains largely unexplored. With properties that range from transition-metal, *d*-like electronic behavior to strongly localized characteristics consistent with the lanthanide, 4f-block, the actinides provide us with a flexible and tunable series with which to explore a wide variety of chemical and physical properties. By studying a variety of compounds that form, and the underlying factors that influence their structures, this research seeks insights into a unified understanding of metal-ion chemistry across the periodic table.

Significant achievements during 2013-2015: The hydrolysis and condensation of tetravalent metal ions have been studied in an effort to provide a predictive understanding of how to control this chemistry. Building on our earlier studies with Th^{IV}, we showed that the anion present in solution during hydrolysis can play a critical role in condensation. This was done by electrolytically increasing the pH of a Th solution and studying the solution speciation using high-energy X-ray scattering (HEXS). We demonstrated that hydroxo bridged dimers were formed and remained stable in solution over weeks, however immediately upon the addition of glycine hexameric units were seen to assemble from the dimers. The hexameric cationic unit $[Th_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]^{12+}$ with glycinate as the counterion was isolated and its crystal structure determined. Other work included systematic investigations of actinyl, U(VI), Np(VI) and Pu(VI) halide complexes, their structures and spectroscopic properties. These studies highlighted the sensitivity of the actinyl vibrational frequencies to both inner-coordination sphere and outer-sphere ligands.

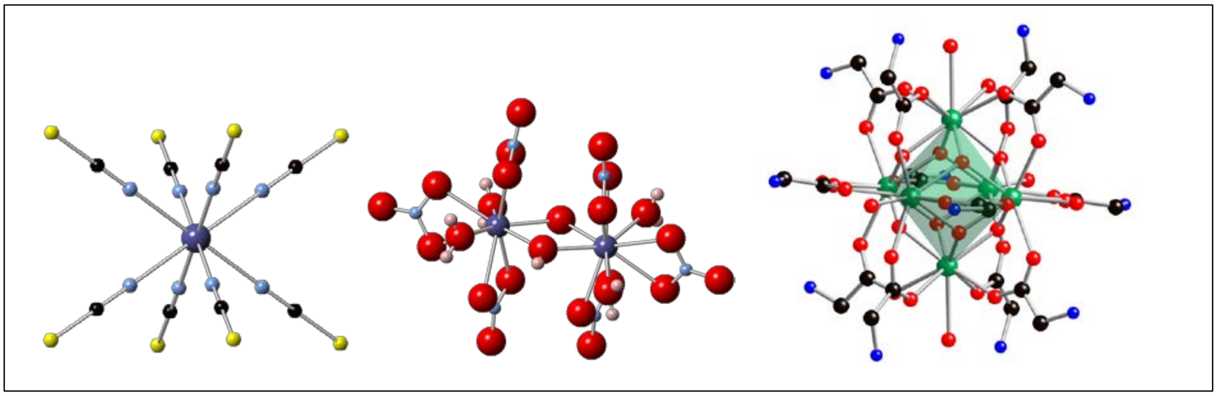

Figure 1. The molecular coordination of three Pu^{IV} compounds, a monomeric isothiocyanate (left), a hydroxo-bridged nitrate (center) and a oxo-hydroxo bridge hexameric cluster (right). The hexameric Pu moiety, decorated with glycinate, is isostructural with the previously isolated Th analog.

Science objectives for 2015-2017:

The scientific focus going forward will center on furthering the understanding of actinide structural chemistry through the synthesis of structurally-related series of compounds, achieved by varying the actinide ion. Of continuing interest will be the exploration of An^{IV} hydrolysis chemistry. Directed by our hypothesis that both ion hardness and changing *f/d* character combine to create different behaviors for Zr^{IV} and Hf^{IV} than is seen for the series Th^{IV} - Pu^{IV}. The actinide series is ideal for probing the extent to which the underlying metal-ion electronic structure influences the compounds that form. In a related project we will synthesize and characterize actinide-ion series of halides and pseudohalides, looking for electonically-driven structural changes. This work will be coupled with theoretical studies that seek to provide insights into the competing role of mixing *f-d* orbital character in actinide compounds and their exhibited physical properties.

Publications supported by this project 2013-2015:

1. L. Soderholm, R.E. Wilson, R. Chiarizia, S. Skanthakumar; *Solvent extraction system for plutonium colloids and other oxide nano-particles*. PATENT: U.S. (2014), US 8741237 B1 20140603.
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Molecular Scale Understanding of Interfaces Related to Heavy Element Separations

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Overall research goals: One of the most challenging tasks in nuclear-waste processing is the separation of trivalent actinides from lanthanides through solvent extraction. Utilization of extractant molecules, especially those with nitrogen and sulfur rich moieties, in order to exploit the subtle differences between 4f and 5f orbitals, is a promising way to approach this challenge. Although extractant molecules are thought to play a key role in effecting a separation by bridging the aqueous/solvent interface, our molecular-level understanding of this process is very limited. Our goal is to develop an integrated, experimental-models strategy in close connection with conventional separations experiments and computational simulations to address this challenge. Through this strategy we will investigate the structural aspects of the extractant interactions with targeted heavy-element ions in the interfacial region. Our overall goal is to create an experimentally-validated, molecular-level picture of the solvent-extraction processes.

Significant achievements during 2013-2015:

This is a new project, starting in 2015.

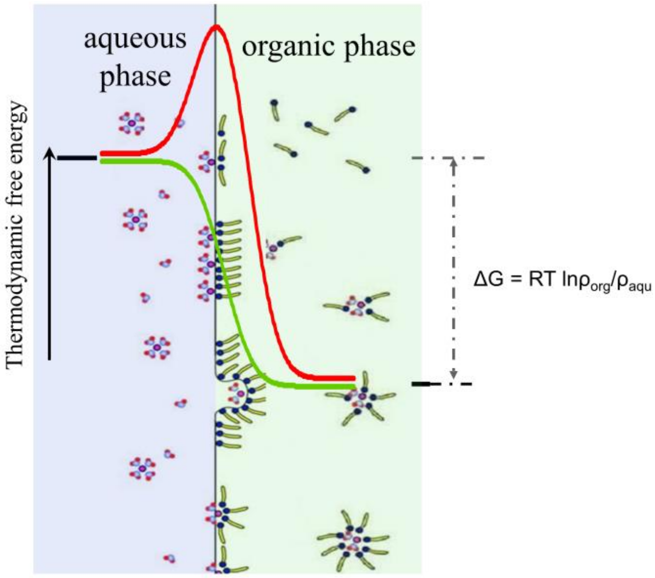

Figure 1. A schematic describing the transfer of metal ions from aqueous phase to organic phase.

Science objectives for 2015-2017: Efficient transfer of metal ions from the aqueous phase to the organic phase in a solvent extraction process relies on multiple factors. In the simplest terms, metal ions interact with extractant molecules at the interface to partially lose their hydration shell and form a soluble complex in the organic phase (Figure-1). Although we know that the initial and the final structures in this picture have very similar free energies ($\Delta G \sim k_BT$), where and how atomic correlations form and complexes assemble is unknown. From a kinetics perspective, the underlying structural factors influencing the size and nature of any energy barrier (if it exists) is also unknown. Our current goal is to initiate an integrated experimental-models strategy to understand the fundamentals of the metal-ligand complexation at the interface. The strategy involves designing model systems at three different interfaces: liquid/solid, liquid/air, and liquid/liquid (Figure-2). Through these models we aim to monitor the interactions of metal ions with extractant molecules in a well-controlled flat interface and significantly limit the effecting factors and the possible outcomes. The simple models, such as the ones at the solid/liquid interface, are advantageous because they allow comparison to computer models and simulations. Significantly more challenging are experimental studies involving the liquid/liquid interface, which provide a direct comparison to real solvent extraction systems. Finally, the liquid/air interface experiments are expected connect the two experimental models we described. Comparisons between all the levels of this hierarchy are expected to provide different perspectives on this complex problem and Figure 2 is only a first approximation to our integrated experimental models strategy. Our goal in this two-year process is to create a framework of models that can be used to inform interfacial processes in solvent extraction through the combination of new experimental tools and computational insights at the molecular scale.

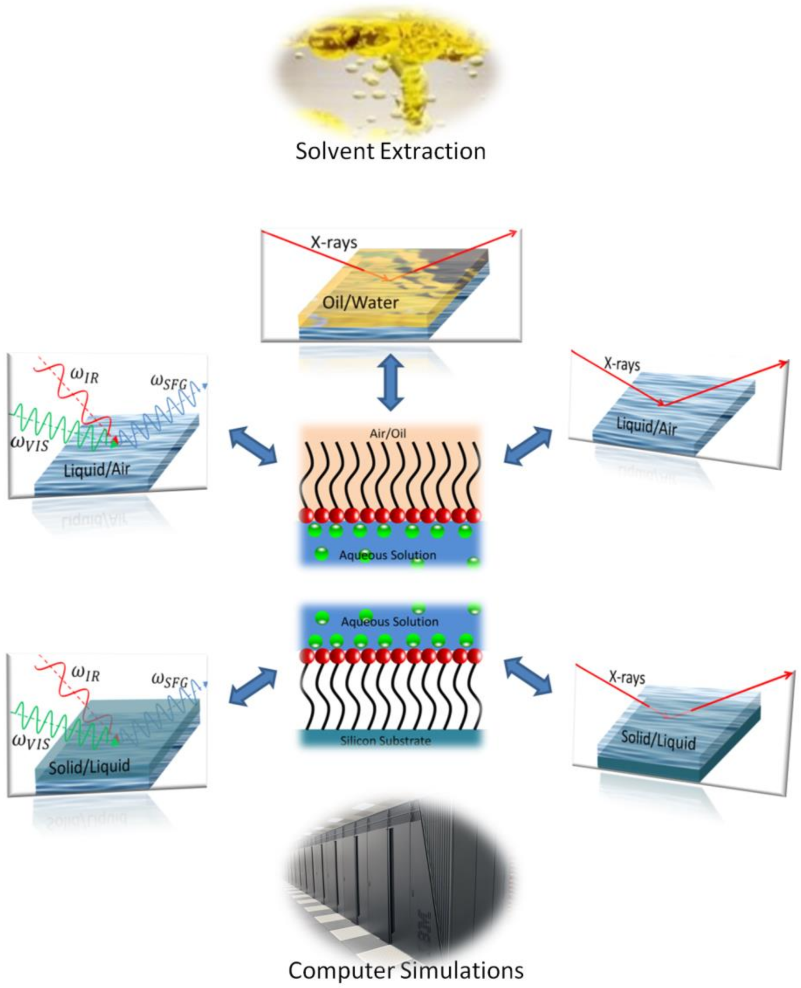

Figure 2: A schematic of Integrated Experimental Models strategy that aims to provide an experimentally validated molecular level understanding of interfacial processes relevant to solvent extraction of heavy elements.

Probing the Actinide-Ligand Binding and the Electronic Structure of Gaseous Actinide Molecules and Clusters Using Anion Photoelectron Spectroscopy

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Overall research goals: The objective of this project is to probe the electronic structure of gaseous actinide molecules and clusters using photodetachment photoelectron spectroscopy and to provide accurate spectroscopic data for the validation of new theoretical methods aimed at actinide chemistry.

Significant achievements during 2013-2015: In this period, we have focused on the investigations of various mono-uranium halides (UF_x^- and UCl_x^-) and oxide species UO_x^- (x = 1−5). Experimental electronic structures information has been obtained for the first time for several of the low oxidation states halide and oxide species. Quantum calculations were carried out in a number of cases to help interpret the experimental data and to obtain structural and chemical bonding information. High-resolution photoelectron imaging has been applied to UO^- and UO_2^-, resulting in highly accurate electron affinities for UO and UO_2 and vibrational information for several low-lying electronic states of the tow simple oxide species.

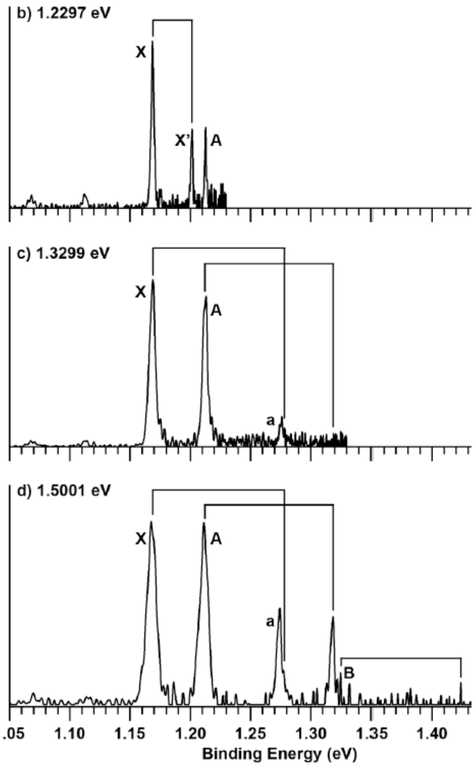

Fig. 1. High-resolution photoelectron spectra of UO_2^- at three photon energies.

1. High-Resolution Photoelectron Imaging of UO_2^- and the Low-Lying Electronic States and Vibrational Frequencies of UO_2

We have studied UO_2^- using both our magnetic-bottle photoelectron spectroscopy apparatus and our new high-resolution photoelectron imaging apparatus. The magnetic-bottle data at high photon energies reveal extensive multi-electron detachment transitions, suggesting strong electron correlation effect in UO_2^-. The spectra for UO_2^- obtained from the high-resolution imaging apparatus (Fig. 1) are consistent with, but much better resolved than data obtained from the magnetic-bottle apparatus. High-resolution data are also obtained for UO^-. The electron affinity (EA) of UO is measured for the first time as 1.1407(7) eV, whereas a much more accurate EA is obtained for UO_2 as 1.1688(6) eV. The symmetric stretching modes for the neutral and anionic ground states, and two neutral excited states for UO_2 are observed, as well as the bending mode for the neutral ground state. The stretching vibrational modes for the ground state and one excited state are observed for UO. The results for UO and UO_2 are compared with previous theoretical calculations including relativistic effects and spin-orbit coupling. The accurate experimental data provide more stringent tests for future theoretical methods for actinide-containing species.

2. Observation of Gaseous UCl_6^- and UCl_6^{2-} Anions: The Electronic Structures and Chemical Bonding of Uranium Hexachlorides

We have produced two gaseous uranium chloride anions, UCl_6^- and UCl_6^{2-} and studied their electronic structure and chemical bonding using photoelectron spectroscopy and theoretical calculations. The EA of UCl_6 is measured for the first time as 5.3 eV and its second EA is measured to be 0.60 eV. We find that the one-electron molecular orbital picture and Koopmans' theorem break down for the strongly correlated U-5f^2 valence shell of the tetravalent UCl_6^{2-}. Insight into the trend of the chemical bonding from $U(VI)Cl_6 \rightarrow U(V)Cl_6^- \rightarrow U(IV)Cl_6^{2-}$ is obtained.

Science objectives for 2015-2017:

- Investigation of the electronic structures of UFO^- and $UF_xO_y^-$ mixed uranium oxide ad fluoride molecules.
- Investigations of the U−U bonding $U_2O_x^-$ type oxide clusters.
- Production of $U_2F_x^-$ clusters using laser vaporization and systematic investigations of the U−F and U−U bonding in different U oxidation states.
- Production of low-oxidation uranyl complexes using electrospray and investigations of their electronic structure.

Publications supported by this project 2013-2015

1. "Probing the Electronic Structure and Chemical Bonding in Tricoordinate Uranyl Complexes $UO_2X_3^-$ (X = F, Cl, Br, I): Competition between Coulomb Repulsion and U–X Bonding" (J. Su, P. D. Dau, Y. H. Qiu, H. T. Liu, C. F. Xu, D. L. Huang, L. S. Wang, and J. Li), *Inorg. Chem.* **52**, 6617-6626 (2013). DOI: 10.1021/ic4006482
2. "A Joint Photoelectron Spectroscopy and Theoretical Study on the Electronic Structure of UCl_5^- and UCl_5" (J. Su, P. D. Dau, C. F. Xu, D. L. Huang, H. T. Liu, F. Wei, L. S. Wang, and J. Li), *Chem. Asian J.* **8**, 2489-2496 (2013). DOI: 10.1002/asia.201300627
3. "Probing the Electronic Structures of Low Oxidation-State Uranium Fluoride Molecules UF_x^- (x = 2−4)" (W. L. Li, H. S. Hu, T. Jian, G. V. Lopez, J. Su, J. Li, and L. S. Wang), *J. Chem. Phys.* **139**, 244303 (8 pages) (2013). DOI: 10.1063/1.4851475
4. "Strong Electron Correlation in UO_2^-: A Photoelectron Spectroscopy and Relativistic Quantum Chemistry Study" (W. L. Li, J. Su, T. Jian, G. V. Lopez, H. S. Hu, G. J. Cao, J. Li, and L. S. Wang), *J. Chem. Phys.* **140**, 084306 (9 pages) (2014). DOI: 10.1063/1.4867278
5. "High Resolution Photoelectron Imaging of UO^- and UO_2^- and the Low-Lying Electronic States and Vibrational Frequencies of UO and UO_2" (J. Czekner, G. V. Lopez, and L. S. Wang), *J. Chem. Phys.* **141**, 244302 (8 pages) (2014). DOI: 10.1063/1.4904269
6. "Photoelectron Spectroscopy and Theoretical Studies of Gaseous Uranium Hexachlorides in Different Oxidation States: UCl_6^{q-} (q = 0−2)" (Jing Su, P. D. Dau, H. T. Liu, D. L. Huang, Fan Wei, W. H. E. Schwarz, J. Li, and L. S. Wang), *J. Chem. Phys.*, In press (2015).

Early Career: Periodicity and the role of the 5f electrons at protactinium

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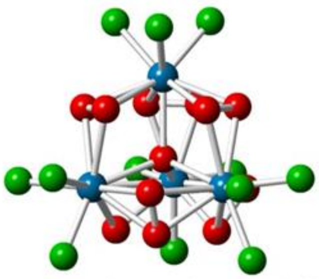
Overall research goals: This research program is focused on the chemistry of protactinium (Z=91). Protactinium is the first actinide element to possess a 5f electron, and is situated at a position where the 5f actinide orbitals and 6d transition metal orbitals cross in energy and may be nearly degenerate. Because protactinium sits at this periodic intersection of actinide f- and transition metal d- chemistries we are studying the chemistry of this unique element with the goal of understanding the relative roles of both the 5f and 6d orbitals in directing the geometry, structure and reactivity of protactinium compounds relative to its actinide and transition metal homologues.

Significant achievements during 2013-2015: Experimental efforts into the chemistry of protactinium have focused on systems for which there are clear descriptive differences between the chemistry of the actinide elements and the chemistry of the transition metals. Two ligand classes that have been identified as demonstrating well defined f- and d- element chemistries are fluoride, and peroxide. Our experimental efforts couple chemical synthesis with physical characterization methods including solid-state and solution structures, along with complementing spectroscopic probes. Collaborative efforts in experimental gas phase chemistry, as well as quantum chemical calculations are providing significant insight into the chemistry and electronic properties of Pa.

We have investigated the solid-state and solution structural chemistry of protactinium(V) in both fluoride and peroxide media. Single crystal X-ray diffraction studies have demonstrated a variety of fluoride coordination numbers and geometries, from mononuclear Pa(V) fluoro complexes to multinuclear homoleptic Pa(V) fluoro complexes. Complementary studies using both Raman spectroscopy and synchrotron based X-ray absorption spectroscopy at the Advanced Photon Source have allowed us to develop and identify quantitative differences between the chemistry of Pa(V) and its transition metal homologues Nb(V) and Ta(V) within both the fluoride and peroxide systems. Chief among these observations is the distinct absence of the previously observed protactinium mono-oxo bond under the conditions of our experiments, while such a species is readily observed for Nb and Ta. Significantly, quantum chemical calculations demonstrate that these differences in the observed chemistry can be traced to the changing electronic properties and the participation of both d- and f- states in the chemistry of Pa(V).



$Cs_2PaF_7 + H_2O_2 \rightarrow Cs_6Pa_4O(O_2)_6F_{12}$

Exploiting the simple fluoride salts of Pa(V) as starting materials, we are able to synthesize a series of unique tetranuclear Pa(V) clusters.

Science objectives for 2015-2017:

- Identify crystalline complexes containing the mono-oxo Pa(V) bond in order to investigate its reactivity, structure, and spectroscopic properties.
- Synthesize and study the chemistry of Pa(IV) complexes in both the solution and the solid-state in order to more fully understand and quantify the effects of the 5f electrons on the chemistry of protactinium.
- Continue studies into the gas phase chemistry and reactivity of Pa targeting molecular complexes of Pa with a variety simple ligand systems, O_2^{2-}, S_2^{2-}, Cl^- in order to more fully understand the periodic chemical properties of protactinium.
- Coupling the experimental efforts and computational collaborators, quantitatively describe the differences between protactinium, its actinide and transition metal homologues.

Publications supported by this project 2013-2015

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2. R. E. Wilson**.** *Retrieval and Purification of an Aged ^{231}Pa Source from its Decay Daughters*. *Radiochimica Acta.* 2014. [DOI: 10.1515/ract-2013-2169].

3. S. M. DeSio**,** R. E. Wilson *Structural and Spectroscopic Studies of Fluoroprotactinates. Inorganic Chemistry*. 53 1750-1755 2014. [DOI: 10.1021/ic402877a]

An Integrated Basic Research Program for Advanced Nuclear Energy Systems based on Ionic Liquids (SISGR) – Radiolysis Aspects

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Overall research goals: We are a team of radiation and separations chemists doing fundamental studies on ionic liquid-based separations systems for the nuclear fuel cycle. We study the effects of radiation on ionic liquids (ILs) and solutes related to separations chemistry with respect to their impact on the efficiency and durability of liquid/liquid separations systems and novel IL-based separations methods, examine the principles controlling separations with ILs, and apply our findings to design new IL-based separation systems for higher efficacy, selectivity and durability.

Significant achievements in during 2013-2015:

Radiolysis: Cation stability for five different classes of ILs has been studied and several extremely stable cations have been identified. The significant findings include the discovery of pi-stack pairing in the radical cations and trications of 6-atom heterocycle cations (such as 1-benzylpyridinium) that significantly increases the cation stability. We have also systematically studied variation of the radiolytic stability for 5-atom heterocycles, invented "antioxidant" cations for ILs (that can be used in the EUV photolithography), and discovered the unexpected stability of guandinium cations that are particularly useful as a versatile platform to tune solvent properties (as demonstrated by our collaborators at ORNL).

We complemented our study of the radiation chemistry of bisoxalatoborate anion with other such derivatives and conducted an in-depth study of another IL-forming inorganic anion, bis(fluorosulfonyl) imide (that gives one of the most fluid ILs) and of the largest family of ILs that are based on the halide anions. For the latter, we found that the radiolytically-oxidized anions readily form halide atom-heteroatom complexes that subsequently yield dihalide radical anions. In addition to the separations sciences, these studies have great significance for energy storage research, as the ILs and salts of these anions are presently used to develop new types of lithium batteries, where redox reactions identical to the radiolytic ones occur near the electrodes. We have demonstrated and explored such connections that enrich both of the fields.

We studied the radiation chemistry of choline and betainium task-specific ILs (TSILs) that are used in pioneering TALSPEAK-inspired separations (described below) and found them to be adequate for the job. This may not seem remarkable but the crystalline halide salts of those cations are the most radiolytically "hypersensitive" compounds known. The source of the hypersensitivity was poorly understood until we established the mechanism and demonstrated that it is possible only in certain crystals due to a unique confluence of factors.

Separations: In most separations studies, ILs replace the *organic* phase. We broke the paradigm by using ILs to replace water. Using TSILs such as choline NTf_2 and betainium NTf_2, we "reinvented" the TALSPEAK process for lanthanide/minor actinide separations while avoiding its notorious pH sensitivity. The ligand is an IL-soluble functionalized aminocarboxylic acid formed by direct reaction with the IL, and via the formation of a 1:2 complex with six soft nitrogen donors, a considerably higher Eu/Am selectivity than aqueous TALSPEAK was observed. We demonstrated Ln/MA group separation and tested a process based on our TSIL scheme.

Science objectives for 2015-2017:

- Looking ahead, our focus will shift from ILs as passive diluents to functionalized, task-specific, and switchable ILs that we believe have great potential to be targeted for specific separations. Though highly valuable, functionalities and switchability result in new potential pathways for radiolytic interference, which we will quantify as we continue to develop better ILs for separations.

- One large and versatile class of IL anions that we have yet to investigate is aromatic heterocycle anions (AHAs) and their carboxylated forms. The importance of these systems is that they are the simplest switchable ILs. Usually, carboxylated anions cannot be used in high radiation fields due to oxidative decarboxylation, but in these ILs the loss is reversible by CO_2 expansion of the solvent.

- Informed by structural work on the microscopic organization of multiphase systems (see Separations abstract), we will examine radiolytically-induced reactivity within domains and across domain boundaries, explore how system phase morphology affects the radiolysis of extracting agents, solutes and diluents, and how cumulative radiolysis changes phase behavior.

Publications supported by this project 2013-2015

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