



Program and Abstracts  
*for the*

2013 Heavy Element Chemistry  
and Separations Science  
Principal Investigators' Meeting

Gaithersburg Marriott  
Washingtonian Center  
Gaithersburg, MD  
April 21–24, 2013

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

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# Foreword

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This abstract booklet provides a record of the twelfth U.S. Department of Energy contractors' meeting in separations sciences and the seventh in heavy element chemistry. This year the meeting is co-chaired by Dr. David Shuh (Lawrence Berkeley National Laboratory) and Professor Aurora Clark (Washington 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 sixth 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, Connie Lansdon of ORISE for meeting logistics, and Dr. Dawn Adin, BES AAAS fellow, for her help in assembling this program.

Philip Wilk  
Larry Rahn

# *Agenda*

**2013 Separations and Heavy Element Chemistry Principal Investigator's Meeting**  
**Gaithersburg Marriott, Washingtonian Center**

**Sunday, April 21**

3:00 - 6:00 pm Registration and Setup

6:30 - 7:30 Reception

**Session 1**

Chair - Mark Jensen

**Materials and Separations**

7:30 - 7:45

Wilk, Rahn, A. Clark, Shuh

Welcome

7:45 - 8:10

Chuan He

Selective Recognition of Heavy Elements by Protein-Based Reagents

8:10 - 8:35

Laetitia Delmau

First Experimentally-Determined Thermodynamic Values of Francium

8:35 - 9:20

Peter Burns

EFRC Overview

**Monday, April 22**

8:10 - 8:40 am Continental Breakfast provided

8:40 - 8:55 am

John Miller

DOE Update

**Session 2**

Chair - Richard Wilson

**Spectroscopy and Coordination Chemistry**

8:55 - 9:20

Lai Sheng Wang

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

9:20 - 9:45

Corwin Booth

Investigations into 5f orbital occupancy and radiation damage in actinide intermetallics

9:45 - 10:10

James Ibers

Actinide Transition-Metal Chalcogenides and Pnictides

10:10 - 10:40

Break

**Session 3**

Chair - Udo Becker

**Synthesis and Spectroscopy**

10:40 - 11:25

Invited - Stephen Liddle

Keynote Lecture: Recent Progress in the Chemistry of Novel Uranium-Ligand Bonds

11:25 - 11:50

David Clark

Trends in Orbital Mixing for Actinide-Ligand Bonds

11:50 - 12:15

Thomas Albrecht-Schmitt

Differentiating Between Trivalent Lanthanides and Actinides

12:15 - 2:00 pm

Working lunch provided

*Session P1 – Poster Session 1*

2:00 - 4:00

P1	Amar Flood	Binding Anions Selectively with Modular Triazolophanes and Releasing them with Light
P3	Andrew Gaunt	Molecular Transuranic Discovery Science: Underpinning National Energy Security and Waste Remediation Needs – Early Career Research Program
P5	Aurora Clark	Supramolecular Organization Within Electrolyte Solutions and the Importance of Molecular Hydrophobicity to Successful Actinide Solvent Extraction
P7	David Dixon	Understanding Actinide Aggregation
P9	J. David Robertson	American Chemical Society’s Summer School in Nuclear and Radiochemistry
P11	James Wishart	An Integrated Basic Research Program for Advanced Nuclear Energy Systems based on Ionic Liquids
P13	John Arnold	Fundamental needs in actinide separation science: Developing our understanding of covalency through molecular actinide metal–metal bonds
P15	Jonathan Sessler	Ion Pair Receptors: Fundamental Studies Involving Recognition and Extraction
P19	Mark Antonio	Structured Phases and Electrochemistry at Interfaces in Separation Science
P21	Mark Dietz	An Integrated Basic Research Program for Advanced Nuclear Energy Systems based on Ionic Liquids
P23	Mark Jensen	Multi-Stage Separation of Actinides with Biomolecules
P25	Peter Burns	Topological Structural Relationships, Cation-Cation Interactions, and Properties of U(VI) and Np(V) Compounds
P27	Rene Corrales	Interfacial Transport and Liquid – Liquid Distribution of An(III) Complexes
P29	Stosh Kozimor	Evaluating Actinide-Oxygen Bonding with O K-edge XAS and TDDFT
P31	Sue Clark	Controlling Actinide Hydration in Mixed Solvent Systems: Towards Tunable Solvent Systems to Close the Nuclear Fuel Cycle
P33	Suntharalingam Skanthakumar	Electronic Structure and Magnetism in f Ion Materials
P35	Trevor Hayton	Exploring the Reactivity of the Uranyl Ion and its Chalcogen Analogues: Expanding our Understanding of Uranyl Reactivity and Behavior
P37	Wayne Lukens	Fundamental Chemistry of Technetium in Oxide Matrices Characterization of f-Orbital Bonding

<b>Session 4</b>	Chair - Trevor Hayton	<b>Actinides and Theory</b>
4:00 - 4:25	Suzanne Bart	Synthetic, Spectroscopic, and Computational Studies of Redox-Active Uranium Complexes for Fundamental Organometallic Reactions
4:25 - 4:50	Kirk Peterson	Accurate ab Initio Thermochemistry and Spectroscopy of Molecules Containing f-block Elements
4:50 - 5:15	Laura Gagliardi	Multiconfigurational Quantum Chemical Study of Actinide and Lanthanide Containing Systems
5:15 - 5:30	Break	

<b>Session 5</b>	Chair - Amar Flood	<b>Bonding and Solutions</b>
5:30 - 5:55	Lingfeng Rao	Actinide Solution Chemistry: Thermodynamics and Structure of Actinide Complexes in Solution
5:55 - 6:20	Sheng Dai	An Integrated Basic Research Program for Advanced Nuclear Energy Systems based on Ionic Liquids
6:20 - 6:45	Gengbang Jin	Actinyl Compounds with Cation-Cation Interactions (CCIs)
6:45 - 8:00	Dinner on your own	

## **Tuesday, April 23**

8:00 - 8:30 am Continental Breakfast provided

<b>Session 6</b>	Chair - Wayne Lukens	<b>Coordination Chemistry and Separations</b>
8:30 - 8:55 am	Benjamin Hay	Principles of Chemical Recognition and Transport in Extractive Separations: Molecular Modelling and Design of Ion Receptors
8:55 - 9:20	Ross Ellis	Emergent Behavior via Hierarchical Structure in Solvent Extraction Organic Phases
9:20 - 9:45	Jeffrey Davis	Self-Assembled Ionophores and Membrane Active Transporters
9:45- 10:15	Break	

<b>Session 7</b>	Chair - Andrew Gaunt	<b>Separations and Coordination Chemistry</b>
10:15 - 11:00	Invited - Ken Nash	Keynote Lecture: The TALSPEAK Process: Using Fundamental Chemistry to Unravel Complex Interactions
11:00 - 11:25	Eric Schelter	A Physicochemical Method for Separating Rare Earths: Addressing an Impending Shortfall

11:25 - 11:50	Karah Knope	Understanding Actinide Aggregation: Formation and Composition of An(IV) Clusters
11:50 - 1:30 pm	Working Lunch Provided	
<b>Session 8</b>	<b>Chair - Stosh Kozimor</b>	<b>Theory and Separations</b>
1:55 - 2:20	Enrique Batista	Theoretical Studies of Orbital Mixing in Actinide-Ligand Bonds
2:20 - 2:45	Juan Peralta	Spin-forbidden Chemical Reactions in Catalysis from First-principles
2:45 - 3:10	Robert Paine	Pre-organized and Immobilized Ligands for Metal Ion Separations

Session P2 – Poster Session 2

No Host Bar

3:10 - 5:10

P2	Wibe de Jong	Influence of Solution Phase and Interfacial Structure on the Stability of Actinide Oxidation States: A Computational Chemistry Approach
P4	Bruce Moyer	Principles of Chemical Recognition and Transport in Extractive Separations: Mechanism of Synergized Anion Exchange Using Neutral Anion Receptors
P6	Christopher Cahill	Novel uranyl bearing materials via restricted UO <sub>2</sub> <sup>n+</sup> speciation profiles and supramolecular assembly
P8	David Clark	Observation of <sup>239</sup> -Pu NMR
P10	David Shuh	Soft X-ray Synchrotron Radiation Investigations of Actinide Materials
P12	Guokui Liu	Ion-ligand Interactions in Actinyl Compounds: Analysis and Simulation of Optical Spectra
P14	Gustavo Scuseria	Accurate Theoretical Approaches for Studying Actinides and Other Heavy Elements in the Solid State
P16	Heino Nitsche	Aqueous Chemistry of Cn and Fl Homologues: Liquid-Liquid Extraction of Cd, Hg, and Pb
P18	Ilya Shkrob	Accurate ab Initio Thermochemistry and Spectroscopy of Molecules Containing f-block Elements
P20	Jochen Autschbach	Computational studies of EPR and NMR parameters for heavy-element systems
P22	John Gibson	Activation of Gas-Phase Complexes Elucidates and Expands Actinide Chemistry
P24	Lynn Francesconi	Fundamental chemistry of technetium-99 incorporated into metal oxide, phosphate and sulfide materials: towards stabilization of low valent technetium
P26	Lynda Soderholm	Understanding f-Ion Solution Speciation
P28	Michael Heaven	Spectroscopic Studies of Prototype Actinide Compounds
P30	J. Michael Simonson	Improving Chemical Separations through Understanding Weak Interactions in Condensed Phases
P32	Radu Custelcean	Ion-Pair Recognition and Separation via Self-Assembly
P34	Richard Wilson	Periodic Structural and Chemical Properties of the Early Actinide Elements
P36	Spiro Alexandratos	Polymer-Supported Complexants: Metal Ion Selectivity and the Variables of Rational Design
P38	Udo Becker	Actinide Sorption and Reduction on sulfides, oxides
5:10 - open	Dinner on your own	

## **Wednesday, April 24**

8:00 - 8:30 am Continental Breakfast provided

### ***Session 9***

Chair - Jochen Autschbach

### **Coordination Chemistry and Spectroscopy**

8:30 - 8:55 am

William Evans

Fundamental Chemistry of Actinide Complexes  
Containing An–N, An–O, and An–S Bonds

8:55 - 9:20

Paula Diaconescu

Unique Advantages of Organometallic Supporting  
Ligands for Uranium Complexes

9:20 - 9:45

Stephen Cooke

Experimentally characterizing the electronic structures  
of f-electron systems using advanced high resolution  
Fourier transform microwave spectroscopies

9:45 - 10:10

Philip Wilk

Program Business, Recommendations

10:10 - 10:40

Break

### ***Session finale***

David Shuh and Aurora Clark, Co-  
Chairs

### **Close Out Session**

10:40 - 12:00 noon

Program summaries and discussion

12:00 - open

Dismissal / Lunch on your own

Unable to attend

Abraham Clearfield

Mixed Metal Phosphonate-Phosphate Hybrid  
Exchangers for the Separation of Lanthanides from  
Actinides

# *Abstracts*

## DIFFERENTIATING BETWEEN TRIVALENT LANTHANIDES AND ACTINIDES

Thomas E. Albrecht-Schmitt, Principal Investigator

Matthew J. Polinski, Shuao Wang, Juan Diwu, Yilin Wang, Jared Stritzinger, T. Gannon Parker, Graduate Students

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306

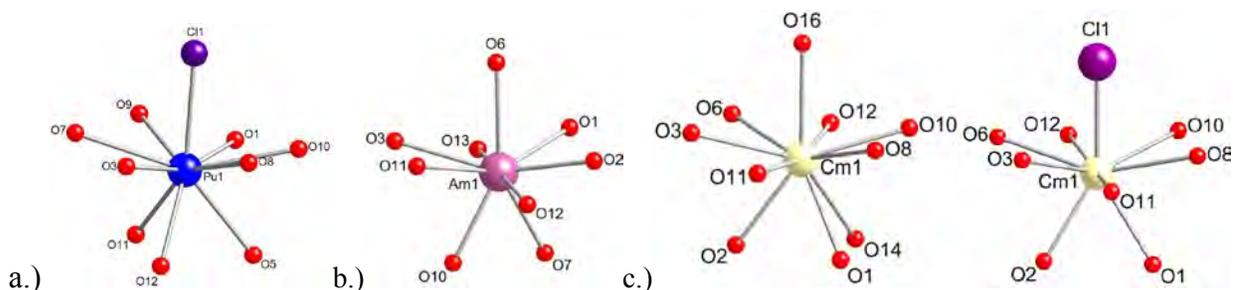
Email: [talbrechtschmitt@gmail.com](mailto:talbrechtschmitt@gmail.com); Web: <http://www.chem.fsu.edu/bio-t.php?userID=1230>

Collaborators: Laura Gagliardi, Department of Chemistry and Supercomputing Institute, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455, United States, Lynne Soderholm, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, Evgeny V. Alekseev, orschungszentrum Jülich GmbH, Institute for Energy and Climate Research (IEK-6), 52428 Jülich, Germany, Wulf Depmeier, Institut für Geowissenschaften, Universität zu Kiel 24118 Kiel, Germany

Overall research goals:

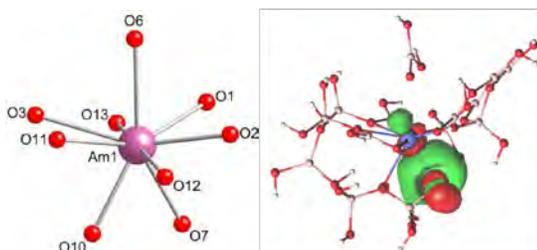
- Prepare pure samples of novel mixed-valent neptunium, plutonium, and americium borates and borophosphates
- Structurally characterize these compounds using single crystal and powder X-ray diffraction.
- Measure the magnetic susceptibility and electronic spectra of these compounds, especially on oriented single crystals.
- Develop polymeric oxoanion matrixes that are capable of bonding to both mixtures of actinides in different oxidation states, and single actinides in multiple oxidation states.
- Determine the stability of the compounds that we prepare using high-temperature calorimetry.

Significant achievements during 2010-2013: The reactions of  $\text{LnCl}_3$  with molten boric acid results in the formation of  $\text{Ln}[\text{B}_4\text{O}_6(\text{OH})_2\text{Cl}]$  ( $\text{Ln} = \text{La} - \text{Nd}$ ),  $\text{Ln}_4[\text{B}_{18}\text{O}_{25}(\text{OH})_{13}\text{Cl}_3]$  ( $\text{Ln} = \text{Sm}, \text{Eu}$ ), or  $\text{Ln}[\text{B}_6\text{O}_9(\text{OH})_3]$  ( $\text{Ln} = \text{Y}, \text{Eu} - \text{Lu}$ ). The reactions of  $\text{AnCl}_3$  ( $\text{An} = \text{Pu}, \text{Am}, \text{Cm}$ ) with molten boric acid under the same conditions yield  $\text{Pu}[\text{B}_4\text{O}_6(\text{OH})_2\text{Cl}]$  and  $\text{Pu}_2[\text{B}_{13}\text{O}_{19}(\text{OH})_5\text{Cl}_2(\text{H}_2\text{O})_3]$ ,  $\text{Am}[\text{B}_9\text{O}_{13}(\text{OH})_4] \cdot \text{H}_2\text{O}$ , or  $\text{Cm}_2[\text{B}_{14}\text{O}_{20}(\text{OH})_7(\text{H}_2\text{O})_2\text{Cl}]$ . These compounds possess three-dimensional network structures where rare earth borate layers are joined together by  $\text{BO}_3$  and/or  $\text{BO}_4$  groups. There is a shift from ten-coordinate  $\text{Ln}^{3+}$  and  $\text{An}^{3+}$  cations with capped triangular cupola geometries for the early members of both series to nine-coordinate hula-hoop geometries for the later elements.  $\text{Cm}^{3+}$  is anomalous in that it contains both nine- and ten-coordinate metal ions. Despite these materials being synthesized under identical conditions, the two series do not parallel one another.



**Figure 1.** Coordination geometries and labeled bonds in (a)  $\text{Pu}_2[\text{B}_{13}\text{O}_{19}(\text{OH})_5\text{Cl}_2(\text{H}_2\text{O})_3]$ , (b)  $\text{Am}[\text{B}_9\text{O}_{13}(\text{OH})_4] \cdot \text{H}_2\text{O}$ , and (c)  $\text{Cm}_2[\text{B}_{14}\text{O}_{20}(\text{OH})_7(\text{H}_2\text{O})_2\text{Cl}]$ . The actinide metal centers are depicted by blue (a), pink (b), or yellow (c) spheres, oxygens as red spheres, and chlorine as purple spheres.

2. Quantum chemical calculations reveal that for the Pu(III) borates a Pu  $6p$  orbital is observed with some electron density located on the O  $2p$  orbital of the basal borate ligand. For Am(III) and Cm(III) borates the equivalent An  $6p$  orbital lies much lower in energy, and an O  $2p$  orbital on the basal ligand shows delocalization to the An  $6d$  orbital. For the Ce(III) borate, the electronic structure is similar to the analogous Pu complexes where the Ce  $4f$  orbital is localized and non-interacting. However, the analogous Ce  $5p$  orbital shows no interaction with the coordinating ligands unlike the Pu  $6p$ .



**Figure 2.** Delocalization of a  $6d$  orbital with oxygen  $2p$  from borate in Americium Borate.

Science objectives for 2013-2016:

- Prepare unprecedented actinide oxoanion compounds with all available actinides from thorium to californium
- Structurally characterize these compounds using single crystal and powder X-ray diffraction.
- Measure the magnetic susceptibility and electronic spectra of these compounds, especially on oriented single crystals.
- Develop periodic trends in trivalent and tetravalent lanthanide and actinide series in order to provide evidence that  $4f$  and  $5f$  elements do not necessarily form parallel series.
- Demonstrate that some of these materials are viable advanced waste forms for storing actinides in the long-term.
- Demonstrate that the separation of americium and curium from lanthanides and from each other is possible based upon density-based flotation methods.

Selected Publications supported by this project 2010-2013 (out of >50)

1. M. J. Polinski, D. J. Grant, S. Wang, E. V. Alekseev, J. N. Cross, E. M. Villa, W. Depmeier, L. Gagliardi, T. E. Albrecht-Schmitt, "Differentiating between Trivalent Lanthanides and Actinides," *Journal of the American Chemical Society*, **2012**, *134*, 10682-10692.
2. M. J. Polinski, S. Wang, E. V. Alekseev, W. Depmeier, G. Liu, R. G. Haire, T. E. Albrecht-Schmitt, "Curium(III) Borate Reveals Coordination Environments of both Plutonium(III) and Americium(III) Borates," *Angewandte Chemie, Int. Ed.*, **2012**, *51*, 1869-1872.
3. M. J. Polinski, S. Wang, E. V. Alekseev, W. Depmeier, T. E. Albrecht-Schmitt, "Bonding Changes in Plutonium(III) and Americium(III) Borates," *Angewandte Chemie, Int. Ed.*, **2011**, *50*, 8891-8894.

## POLYMER-SUPPORTED COMPLEXANTS:

### METAL ION SELECTIVITY AND THE VARIABLES OF RATIONAL DESIGN

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Xiaoping Zhu, Post-Doctoral Researcher

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Overall research goals: The objective of this research is to probe the parameters that lead to a rational design of polymer-supported complexants. Rational design is defined as an a priori approach to preparing a complexant that has a high affinity for a targeted metal ion. It is intended as an alternative to the current method of empirical design wherein what is to be prepared is based on experimental results from what has been studied. The parameters most important to the design of polymer-supported complexants are characteristic of the ligand (polarizability and conformational rigidity), metal (polarizability, ionic radius, hydration and geometry) and polymer (conformational rigidity and polarity).

The polymer support will be poly(vinylbenzyl chloride); its rigidity will be varied by the crosslink level and the polarity will be varied with comonomers. The metal ions will be chosen based on differences in polarizability, as quantified by the Misono softness parameter for divalent ions (Pb, Cd, Cu, Ni, Zn) or the ionic potential for trivalent ions (Al, Fe, Eu, Au), and differences in ionic radius (Zn, Cd, Hg); a change in one parameter such as polarizability inevitably leads to changes in other parameters such as ionic radius and the analysis will have to account for this.

Building on research from earlier grant periods, a new set of phosphorus-based ligands will be studied as both ion-exchange and neutral coordinating sites. The new syntheses will encompass phosphates, aminoalkylphosphonates and phosphinates. The ligands will have different polarizabilities at the binding site due to the substituents on and around the phosphoryl group.

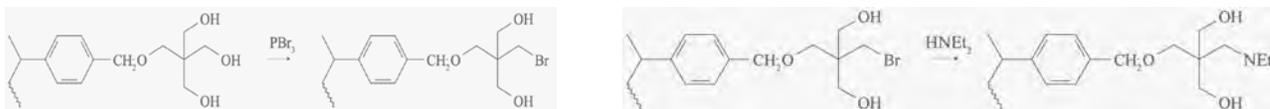
#### Significant achievements during 2011-2013:

\* Hydrogen bonding within different ligands was found to be an important variable in determining metal ion affinities. In a series of three amides / ureas, the same mechanism was found to be operative in the high affinities displayed by the polymers for lanthanide ions from acidic solutions. In the current period the urea-bound polymer had very high lanthanide affinities while operating through the same mechanism as the tetramethylmalonamide and diethylenetriamine polymers.



\* Hydrogen bonding was also critical to the high affinities displayed by a phosphorylated cyclodextrin polymer: the -OH groups of the cyclodextrin hydrogen bonded to the P=O of the phosphate and this led to a more polarizable oxygen which, in turn, had enhanced affinities for the transition metal ions studied.

\* Pentaerythritol bonded to cross-linked poly(vinylbenzyl chloride) beads (PE) provides a scaffold onto which ligands can be attached by reaction with reactive compounds such as phosphoryl halides. In order to broaden the applicability of PE for the preparation of ion-selective polymers, conditions were reported for the conversion of the hydroxyl group to the bromide, which acts as a better leaving group. The -CH<sub>2</sub>Br moiety thus provided a handle on which an array of ligands could be bound through nucleophilic substitution. Immobilization of diethylamine onto the PE and the ion-binding affinities of the resulting polymer provided a proof-of-principle.



\* A spectroscopic method was explored as a probe of metal – ligand interaction. Distribution coefficients and complementary FTIR-ATR spectra were found to be a readily accessible means of determining the mechanisms by which immobilized phosphinic acid ligands complex metal ions. The distribution coefficients were determined relative to the ligand's proton affinity from solutions of varying acidity and correlated with parameters representative of the metal ions as well as the solution pH. FTIR-ATR spectra then provided support for a molecular level interpretation of the interaction mechanism. In the initial report, the affinity of the ligand for Al(III), La(III), Lu(III), Fe(III), and In(III) was quantified from 0.01 – 6.0 M nitric acid solutions. High affinities were evident from the corresponding distribution coefficients with  $\text{In(III)} \geq \text{Fe(III)} > \text{Lu(III)} > \text{La(III)} > \text{Al(III)}$ . The affinities correlated with the softness parameter and thus the polarizability of the metal ion. The FTIR spectrum of the phosphinic acid had two incompletely separated bands at 1168 / 1126  $\text{cm}^{-1}$  associated with the P=O bond and two similar bands at 967 / 951  $\text{cm}^{-1}$  due to the P-O(H) bond. The bands at 1168 / 951 and 1126 / 967  $\text{cm}^{-1}$  were assigned to different hydrogen bonded conformers within the metal-free polymer. As metal ion binding increased, the intensity of the band at 1168  $\text{cm}^{-1}$  decreased and this was coupled to a decrease in the band at 951  $\text{cm}^{-1}$ ; the 1126 band sharpened and shifted slightly to 1133  $\text{cm}^{-1}$  while the 967 band shifted to 980  $\text{cm}^{-1}$  as a new band that depended on the metal ion formed at 1040 – 1080  $\text{cm}^{-1}$ . This new band was taken as evidence of an ion exchange interaction to give the P(O)OM moiety. Hydrogen bonding among unexchanged P(O)OH sites gave the bands at 1133 and 980  $\text{cm}^{-1}$ . FTIR-ATR spectra provided more detailed information than would be possible from the distribution coefficients and provide support for the mechanism of ion-ligand interactions.

#### Science objectives for 2013-2015:

The focus for the coming period will be on applying FTIR spectroscopy to an understanding of metal ion – immobilized ligand interactions. The ligands to be prepared are those in the overall goals summarized above.

#### Publications supported by this project 2011-2013

1. Zhu, X. and Alexandratos, S.D. "Binding of Metal Ions onto Polymers Probed by Distribution Coefficients and FTIR-ATR Spectra. I. Trivalent Ions and the Phosphinic Acid Ligand" *Inorganic Chemistry*, submitted (December 2012)
2. Alexandratos, S.D. and Zhu, X. "Functionalization of polymer-supported pentaerythritol as a general synthesis for the preparation of ion-binding polymers" *Journal of Applied Polymer Science*, 127, 1758-1764 (2013)
3. Urbano, B.; Rivas, B.L.; Martínez, F. and Alexandratos, S.D. "Novel polymer-clay nano composite ion-exchange resin based on N-methyl-D-glucamine ligand groups for arsenic removal" *Reactive & Functional Polymers*, 72, 642-649 (2012)
4. Urbano, B.; Rivas, B.L.; Martínez, F. and Alexandratos, S.D. "Equilibrium and kinetic study of arsenic sorption by water-insoluble nanocomposite resin of poly[N-(4-vinylbenzyl)-N-methyl-D-glucamine]-montmorillonite" *Chemical Engineering Journal*, 193-194, 21-30 (2012)
5. Yang, Y. and Alexandratos, S.D. "Lanthanide Complexation by Polymer-Bound Urea and the Effect of Hydrogen Bonding on Metal Ion Affinities" *Inorganica Chimica Acta*, 391, 130-134 (2012)
6. Zhu, X. and Alexandratos, S.D. "Effect of Hydrogen Bonding: Polymer-Bound Phosphorylated Cyclodextrin" *Journal of Applied Polymer Science*, 121, 1137-1142 (2011)

## Structured Phases and Electrochemistry at Interfaces in Separations Science

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Chemical Sciences & Engineering Division, Argonne National Laboratory, Argonne, IL 60439 USA

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Collaborators: Drs. M. Bera, R. Ellis, L. Soderholm, Chemical Sciences & Engineering Division, Argonne National Laboratory; Dr. W. Bu and Prof. M. Schlossman, Department of Physics, University of Illinois at Chicago, Chicago, IL 10021;

Overall research goals: The importance of liquid surface phenomena in chemical separations is significantly underestimated. Aggregation behaviors that result from the self-assembly 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 at liquid-liquid interfaces of solutes, including multivalent rare earth (RE) and actinide (An) ions as well as neutral and acidic amphiphilic extractants, and the influence of their redox speciation in organic and aqueous electrolytes. Doing so will enable a correlation of liquid surface structures and ion valences with bulk liquid-liquid extraction performance in manners not done beforehand.

Significant achievements during 2011-2013: The redox chemistry of the An and RE elements figures prominently in fundamental science and practical hydrometallurgy. Despite decades of research, controversies about high-valence Pu chemistry and ambiguous Ce valence assignments abound today. We have explored structural and electrochemical information in bulk aqueous and organic media to provide new insights into the redox speciation of these two elements. As depicted in the Figure, a direct glimpse into the tetraoxo coordination environment of Pu<sup>VII</sup>, obtained by ozonation of Pu<sup>VI</sup>, and the dioxo coordination environment of Pu<sup>VI</sup> was provided by *in situ* X-ray absorption spectroscopy.[5] It revealed 6-O coordinate molecular anions, whose interconversion is facile and reversible,  $[\text{Pu}^{\text{VII}}\text{O}_4(\text{OH})_2]^{3-} + 2\text{H}_2\text{O} + \text{e}^- \rightleftharpoons [\text{Pu}^{\text{VI}}\text{O}_2(\text{OH})_4]^{2-} + 2\text{OH}^-$ , despite the short-lived stability of Pu<sup>VII</sup>. As also depicted in the Figure, the cerium(III/IV) redox couple was shown to be a keystone that bridges the fields of separation science and electrochemistry. The first-of-kind measurements of voltammetric and spectroscopic behaviors in bulk organic phases obtained by SX affords perspectives about ion transfer across an aqueous-organic electrolyte interface and third phase redox phenomena.[8]

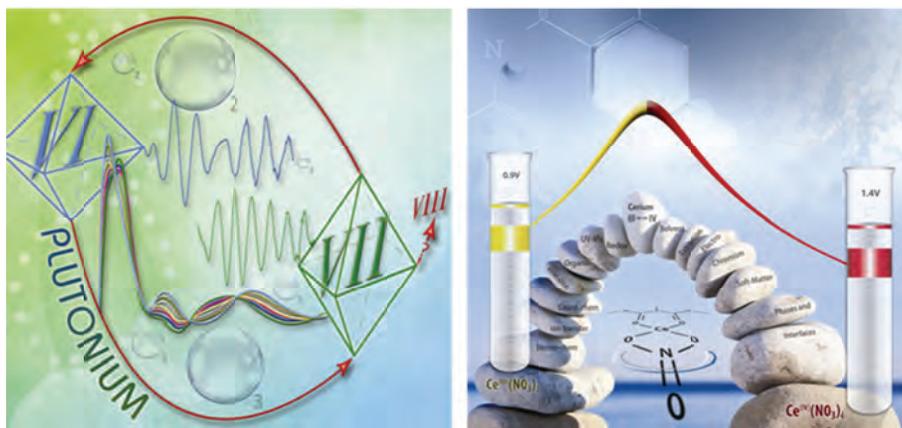


Figure. Left: A freshly prepared solution of Pu<sup>VI</sup> in 2 M NaOH was oxidized to Pu<sup>VII</sup>, via ozonolysis, while simultaneously collecting X-ray Absorption Near Edge Structure and Extended X-ray Absorption Fine Structure data.[5] Analyses revealed a dioxo coordination environment for Pu<sup>VI</sup>, PuO<sub>2</sub><sup>2+</sup>, typical for it and the hexavalent actinyl species of U and Np, and its evolution into a tetraoxo-coordination environment for Pu<sup>VII</sup>, PuO<sub>4</sub><sup>-</sup>, like that known for Np<sup>VII</sup>. Right: The electroactive nature of Ce with its renowned Ce<sup>III</sup>/Ce<sup>IV</sup> couple leads to the formation of yellow- and red-colored third phases that are correlated with Ce valence.[8] Ce<sup>III</sup> obtains in the yellow third phase and Ce<sup>IV</sup> in the red one; these are interconvertible by the polarization of an electrode at +0.9 and +1.4 V vs. Ag/AgCl, respectively.

Science objectives for 2013-2015: Strategic insights into interfacial chemistry and physics in liquid-liquid extraction systems are sought. Of particular interest is the understanding of electrochemical and molecular-scale structural phenomena, including the organization of extractant molecules and their complexes with An and RE ions, as well as supramolecular effects, including micellization and emulsification. Beginning with a simplified model, we ask the question: are redox-active metal-containing aggregates found at liquid-vapor interfaces and, if so, what is their morphology. Both of these issues, although poorly understood, are hypothesized to be critical in extraction mechanisms. The successful resolution of such issues in these activities includes, for example, the use of surface-sensitive measurements of  $AnX_4$  and  $REX_3$  electrolytes with monoanionic counter-anions, X (e.g., halides, pseudohalides, oxoanions) under conditions of total external reflection using electron-yield and fluorescence acquisition of scattering and spectroscopy data as well as electro-analytical and -chemical research. The efforts to provide basic knowledge about redox behaviors of RE- and An-ions at surfaces and interfaces are anticipated to impact research aimed at the development of high-performance SX systems. It is our objective to obtain key fundamental perspectives into the nature of metal-extractant bonding and its long-range effects on the mesoscale properties of bulk solutions and interfaces. The successful outcome of the research will have influence on our basic understanding of separation science, in general, and liquid-liquid extraction, in particular, vis-à-vis various hydrometallurgical reprocessing schemes.

Publications supported by this project 2011-2013:

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## Fundamental needs in actinide separation science: Developing our understanding of covalency through molecular actinide metal–metal bonds

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Graduate students: Ashleigh Ward, James Patton, Alison Altman, Timothy McMahon  
*Collaborators:* Dr Wayne Lukens, Dr David Shuh, Dr Stefan Minasian, Chemical Sciences Division, Lawrence Berkeley National Laboratory

*Overall research goals:* The objective of this project is to explore concepts relating to metal-metal bonding in molecular complexes of the actinide and lanthanide elements. This will address some of the crucial issues surrounding nuclear fuel reprocessing and waste remediation by developing our insight into the fundamental bonding principles for *f*-elements. We focus on the synthesis of actinide and lanthanide coordination complexes with ligands containing metal or metalloid atoms.

Our specific aims are:

- Synthesize structurally related coordination complexes of actinide and lanthanide elements containing a direct, unsupported bond to another metal or metalloid atom.
- Develop new starting materials for the exploration of actinide chemistry in various coordination geometries and oxidation states.
- Examine bonding trends as a function of the *4f* and *5f* and *6d* orbital energies, oxidation state, coordination number, and geometry of both participants in the M–M bond.

*Significant achievements during 2011-2013:*

DOE-BES funding for this program began in 2010. We have already reached several milestones, including the synthesis of a series of isostructural, isoelectronic molecules based on the (CpSiMe<sub>3</sub>)<sub>3</sub>M–ECp\* framework (M = Nd, U; E = Al, Ga; Cp\* = C<sub>5</sub>Me<sub>5</sub>). We have shown that the group 13 diyls Cp\*E are excellent An/Ln discriminators, and described a degree of covalency arising from strong Cp\*E  $\sigma$ -donation to the U *5f/6d* orbitals. Many of these molecules constitute the first example of a bond between that pair or group of elements.

In the last year, we have developed routes to actinide corroles, which represent a new class of actinide—macrocyclic ligand complex. Macrocyclic complexes of actinides, in particular of the uranyl cation, are well established in the literature with a variety of crown ethers, calixarenes, and more recently "pacman" polypyrroles. Our recent synthesis of alkali metal corroles has provided access to early transition metal and lanthanide corroles. We have employed similar methodology to prepare the first actinide corroles with both U(IV) and Th(IV) (see Figure 1) The variable temperature magnetic moment of the dimeric U corrole is in good agreement with that expected for U(IV) and a <sup>3</sup>H<sub>4</sub> ground state.

Starting materials for use in U(VI) chemistry are almost exclusively limited to uranyl systems. In order to expand this narrow range, we have been investigating the use of perfluorinated alkoxides (pfa's) as supporting ligands for high-valent uranium chemistry and have prepared several examples of tetravalent (pfa)<sub>2</sub>UX<sub>2</sub> compounds are examining their propensity to support higher valent U using electrochemical methods and chemical oxidation.

Following our work with  $N_2P_2$  and  $N_4$  donor systems, we have recently begun investigation on actinide compounds of an  $N_4P_3$  ligand. We are exploring the ability of this ligand to facilitate metal-metal bonding between an actinide coordinated to the harder N donors, and a transition metal coordinated to the softer P donor set. We have prepared Th(IV) and U(IV) starting compounds of this ligand and are investigating their reactivity toward cobalt and iron carbonylates. This has thus far resulted in both a bridging isocarbonyl cobalt complex with both U and Th, as well as a complex containing a U—Co bond.

In the last few months, we have been using X-Ray absorption spectroscopy (XAS) to probe the electronic structure of Group 13 compounds. We are in the process of preparing a well-defined series of Al (I), (II) and (III) compounds for characterization using Al K-edge XAS in order to compare differences in their electronic structures with variations in ligand donating ability, changes in aluminum oxidation state and geometry. This research will provide a baseline for comparison of complexes containing An—Al bonds and allow for better understanding of their electronic structure.

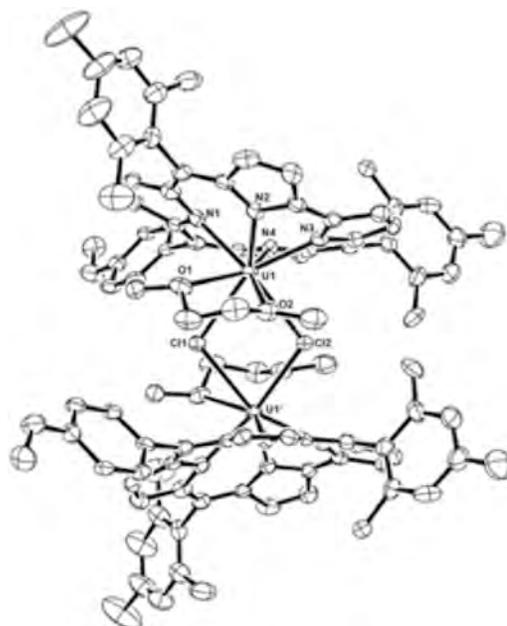


Figure 1. Molecular structure of uranium(IV) corrole

#### Science objectives for 2013-2015:

- Investigate reactions of actinide and lanthanide corrole halides with transition metal anions to prepare complexes with new M—M bonds.
- Continue studies with  $(N_4P_3)An$  species to prepare compounds with An—M bonds (M = transition metal, Ln, An).
- Probe routes to high valent, non-uranyl U complexes using oxidation-resistant supporting ligands.
- Create a series of An—M complexes with the  $N_4P_3$  donor set, and examine the nature of the M—M bonding.
- Expand the chemistry of monovalent group 13 metal complexes (with B, Al, Ga) and investigate their electronic structure using DFT and XAS.

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## Computational studies of EPR and NMR parameters for heavy-element systems

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Benjamin Pritchard & Bob Martin, Graduate Students

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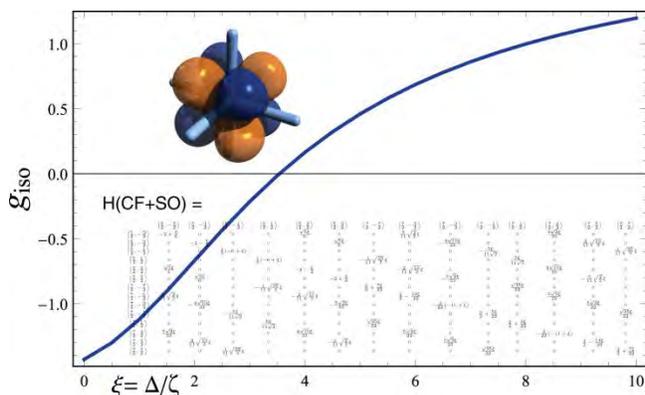
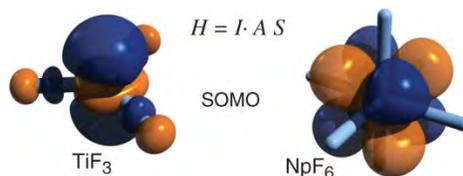
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Collaborators: N. Govind, W. de Jong, B. McNamara, PNNL. S. Patchkovskii, National Research Council, Ottawa. H. Bolvin and T. Saue, Toulouse, France. M. Reiher and D. Peng, Zurich, CH.

**Overall research goals:** The main objective of this project is to develop and understanding of the mechanisms responsible for trends in paramagnetic NMR (pNMR) and EPR spectra of f-element compounds. We apply new relativistic theoretical methods for the computation of EPR parameters and ligand pNMR chemical shifts and other NMR parameters of lanthanide and actinide complexes, and perform benchmark studies with well-characterized transition metal complexes. The project goals include developments of new relativistic methods in the open-source NWChem quantum chemistry package, the development of chemically intuitive analysis methods for the calculated molecular spectroscopic parameters, additional developments using other quantum chemistry codes, and symbolic computations.

### Significant achievements during 2011-2013:

Relativistic Density functional theory (DFT) codes were developed for calculating EPR g-factors and hyperfine coupling (hfc), using methods where spin-orbit (SO) coupling is treated either as a perturbation [5-8] or variationally [1,2]. A newly developed spin-polarized 2-component variational method in conjunction with range-separated hybrid functionals was shown to perform reasonably well for EPR parameters of  $f^1$   $AnX_6$  (X=halide) and radicals with transition metals and light elements [1,2]. Symbolic calculations



of magnetic properties for metal f-shells with a crystal-field (CF) model were set up to assist the analysis of systems that are currently being investigated (see Objectives for 2013-15). The Figure on the left shows a calculation of the g-factor of cubic  $f^1$  systems such as  $AnX_6$  depending on a CF splitting parameter  $\Delta$  and a SO coupling constant  $\zeta$  [cf. also Bolvin et al.]. Experimental data are found in the strong SO limit, with g-factors of -0.6 ( $NpF_6$ ) or below. The DFT delocalization error (DE) has a strong impact on the accuracy of the computations. We developed a fractional electron number code in

NWChem that allows to quantify the DE [1,2,6,9-11], which is of great help to understand why some functionals work better than others. Localized MO analysis tools were developed for NMR shielding, g-factors, and hfc and applied to analyse pNMR chemical shifts and EPR parameters in transition metal complexes and actinide hexahalides [4,6], to assist the data interpretation and to study the DE in detail. The NMR and EPR methods are based on the ZORA quasi-relativistic Hamiltonian. For improved accuracy of properties that depend on core orbitals, we have recently implemented DFT calculations and first-order properties such as electric-field gradients (EFGs) with an exact 2-component (X2C) Hamiltonian [3]. The picture-change effect on the  $^{235}\text{U}$  EFG in uranyl-carbonate complexes is as large as the EFG itself, rendering the 2-component transformation of property operators mandatory. X2C is expected to become the standard method for relativistic quantum chemical calculations [12], although ZORA is already quite accurate for chemical shifts [13].

## Science objectives for 2013-2015:

- Systematic studies of EPR and magnetizability data for actinyl carbonate complexes and related systems (e.g. nitrates). DFT vs. multi-reference methods. Test applicability of pNMR equation. Expt. NMR data available from PNNL, LANL. Further: what is the influence of solvent effects?
- Study magnetic properties (g-factors, hfc,  $\chi(T)$ , pNMR) for well defined 'model' systems such as LnDPA<sub>3</sub> and other Ln macrocycle complexes, Ln(C<sub>8</sub>H<sub>8</sub>)<sub>2</sub><sup>-</sup>, An(C<sub>7</sub>H<sub>7</sub>)<sub>2</sub><sup>-</sup> and related systems, using DFT and multi-reference methods.
- DFT and CC do not reproduce experimental trends for <sup>19</sup>F shifts in UF<sub>n</sub>Cl<sub>6-n</sub>, [Schreckenbach, Stanton, Saue, JA, et al., in preparation]. I.e. even in the absence of sensitive paramagnetic effects are the ligand shifts difficult to calculate. What is missing in the computational model? Can we obtain accurate density functionals for these systems? (e.g. via 'optimal tuning.' [6,9-11]).
- Further development of analysis methods, new developments of magnetic property modules

## Publications supported by this project 2011-2013

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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

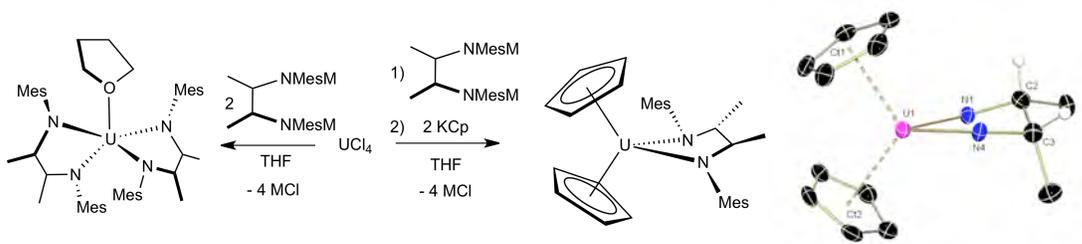
Dr. Stosh Kozimor, Los Alamos National Laboratory, Los Alamos, NM

### *i) Overall Research Goals*

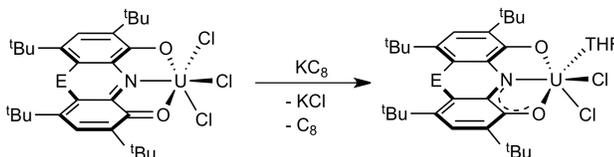
1. Determine the electronic structure of uranium species with redox-innocent butanediamine ligands. This aim will be accomplished by:
  - a. Synthesis and characterization of uranium species bearing butanediamine ligands.
  - b. Characterization by X-ray Absorption Spectroscopy, SQUID magnetometry, and computational methods
  - c. Comparison with published data describing similar studies for redox-active ligands.
2. Synthesis, characterization, and reactivity of uranium complexes bearing redox-active ONO ligands. This aim will be accomplished by:
  - a. Synthesis and characterization of redox-active uranium(III) and uranium(IV) compounds and their derivatives using  $^1\text{H}$  NMR, infrared, electronic absorption, X-ray crystallography, electrochemistry, X-ray absorption spectroscopy, SQUID magnetization, and computational methods.
  - b. Using proposed species to study fundamental organometallic reactions, including oxidative addition, reductive elimination, migratory insertion, and addition to uranium element multiple bonds.
  - c. Comparison to redox-innocent ONO uranium complexes.

### *ii) Significant Achievements during 2011-2013*

1. The project period began in July of 2012. During this time, progress has been made on all research goals. First, the use of *N,N*-bis(2,4,6-trimethylphenyl)-2,3-butanediamine ( $^{\text{Mes}}\text{BD}^{\text{Me}}\text{H}_2$ ) was explored as a redox-innocent ligand for uranium. The synthesis and characterization of  $\text{Cp}_2\text{U}(^{\text{Mes}}\text{BD}^{\text{Me}})$  and  $(^{\text{Mes}}\text{BD}^{\text{Me}})_2\text{U}(\text{THF})$  was accomplished, and the former was crystallographically characterized. This analysis provided pertinent structural parameters for comparison to the analogous species bearing the redox-active  $\alpha$ -diimine ligand framework,  $\text{Cp}_2\text{U}(^{\text{Mes}}\text{DAB}^{\text{Me}})$  and  $(^{\text{Mes}}\text{DAB}^{\text{Me}})_2\text{U}_2(\text{THF})$  ( $^{\text{Mes}}\text{DAB}^{\text{Me}} = [\text{ArN}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{NAr}]$ ; Ar = 2,4,6-trimethylphenyl (Mes)). The magnetic properties are currently being explored by our collaborator, Prof. Eric Schelter, to determine the influence, if any, that redox-active ligands have on magnetic properties by comparison to the redox-innocent ligand congeners.



2. For the second project goal, the redox-active ONO ligand,  $[\text{ONO}^{\text{cat}}]$  ( $[\text{ONO}^{\text{cat}}]\text{H}_3 = \text{N,N-bis(phenol)amine}$ ), has been explored for its ability to support uranium(IV). The ligand has been successfully synthesized and metallated, and derivatives are currently being fully characterized. Reduction and alkylation chemistry has also begun to be explored.



iii) *Science objectives for 2013-2015*

- Studies will continue with the characterization of  $\text{Cp}_2\text{U}(\text{MesBD}^{\text{Me}})$  and  $(\text{MesBD}^{\text{Me}})_2\text{U}(\text{THF})$ , including further characterization using X-ray Absorption Spectroscopy (Dr. Stosh Kozimor) and computational methods (Prof. Laura Gagliardi). These results will be compared to those for  $\text{Cp}_2\text{U}(\text{MesDAB}^{\text{Me}})$  and  $(\text{MesDAB}^{\text{Me}})_2\text{U}_2(\text{THF})$  to determine differences in the bonding character.
- Studies of  $[\text{ONO}^{\text{cat}}]\text{UCl}_3$  will continue, with exploration of reduction and alkylation chemistry. The resulting species will undergo full characterization and be tested for their ability to undergo oxidative addition, reductive elimination, and migratory insertion reactions. Use of the rigid redox-active ligand framework, 9-hydroxyphenoxazin-1-one  $[\text{ONO}^{\text{phen}}]$ , will be explored for uranium. The resulting complexes will be fully characterized.
- Uranium derivatives of both  $[\text{ONO}^{\text{cat}}]$  and  $[\text{ONO}^{\text{phen}}]$  will be explored for their ability to support uranium-element multiple bonds. The influence of the ligand reduction, if any, on the subsequent reactivity of these strong bonds will be assessed.
- Redox-innocent analogs to the ONO frameworks will be studied, and their spectroscopic properties will be compared to the redox-active compounds to determine if there are changes in the bonding character of the uranium center.

iv) *References to publications supported by this project in the last two years.*

The current work remains unpublished at this time.

## Theoretical Studies of Orbital Mixing in Actinide-Ligand Bonds

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### Overall research goals:

The goal of this project is to understand the chemical bonding between actinide species and their ligands. This understanding was sought by close coupling between experimental measurements of ligand K-edge x-ray absorption spectroscopy 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 2011-2013:

- The assignment of low-energy features in the Cl K-edge XAS of  $\text{UCl}_6^{2-}$  and  $\text{UOCl}_5^-$  to transitions into orbitals of 5f parentage provided unambiguous evidence of U(5f)-Cl(3p) covalent mixing. These conclusions add to the growing body of work indicating that covalence should be included in the description of actinide-ligand bonds. We developed a simple model based on perturbation theory of quantum mechanics to illustrate the origin of orbital mixing in actinide-ligand bonds. Two types of mixing can be deduced stemming from either orbital overlap or from favorable energy alignment of the orbital energies. Starting from the ionic limit ( $\text{M}^{4+}-\text{Cl}^-$ ) a perturbed orbital can be written as

$$\Psi = \frac{(\phi_M + \lambda\phi_L)}{\sqrt{1 + 2\lambda S_{ML} + \lambda^2}}$$

Where the overlap integral

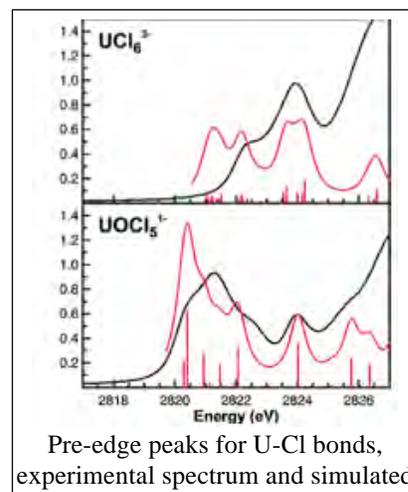
$$\lambda = \frac{H_{ML}}{E_M^0 - E_L^0}$$

Where the mixing coefficient,  $\lambda$ , is directly proportional to the coupling matrix element (overlap-driven mixing) and inversely to the energy difference (degeneracy driven mixing). The term ‘covalence’ is typically associated with buildup of charge at the midpoint of the bond due to overlapping orbital densities. However, this equation shows that this buildup will not necessarily be observed in the case of energy driven mixing. The bond energy stabilization, in a perturbation formulation, is

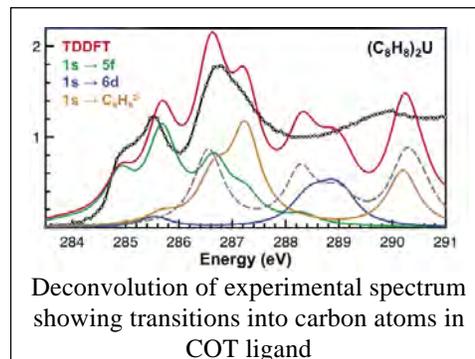
$$\Delta E = \frac{|H_{ML}|^2}{E_M^0 - E_L^0} = \lambda H_{ML}$$

Indicating that the overlap term determines the amount of stabilization and, in some sense, the strength of that bond.

- Moving towards studies of interactions of actinide species with soft-ligands we looked at sulfur compounds with the same techniques used in chlorine studies. 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



- We started studies on actinide-carbon ligand interactions. The first measurements and calculations involve actinide-metallocene complexes, which is a challenging project due to the large number of interacting orbitals. We have developed a computational approach to de-convolute these interactions as a function of the angular momentum quantum number helping the interpretation of the experimental spectra. This aspect is just starting and will continue through the next cycle.



#### Science Objectives for 2013-2015:

In the next cycle we plan to move to the study of interactions between actinide and fluorine ligands and between actinide and nitrogen ligands. The former will be studied in hexafluoride systems and metallocene difluorides, and the later ones in imido systems. Studies of actinide-ligand bonding in solution will also be carried out and compared with measurements from our experimental team partners.

#### Related publications:

- Spencer, Liam P, Ping Yang, Stefan G. Minasian, Robert E Jilek, Enrique R Batista, Kevin S Boland, James M Boncella, et al. "Tetrahalide Complexes of the  $[U(NR)_2]^{2+}$  Ion: Synthesis, Theory, and Chlorine K-Edge X-Ray Absorption Spectroscopy." *Journal of the American Chemical Society* **2013**, *135*, 2279.
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- Keith, Jason M, and Enrique R Batista. "Theoretical Examination of the Thermodynamic Factors in the Selective Extraction of Am 3+From Eu 3+by Dithiophosphinic Acids." *Inorganic Chemistry* **2012**, *51*, 13–15.
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## Actinide Sorption and Reduction on sulfides, 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, ...).
- 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.

### Significant achievements during 2012-2013 (Renewal started in 7/12):

**The energetics and kinetics of uranyl reduction on pyrite, hematite, and magnetite surfaces: a powder microelectrode study:** There are many studies describing the influence of parameters such as pH, pCO<sub>2</sub>, and complexing ligands on the sorption of the aqueous uranyl species onto mineral surfaces. However, few of these studies describe the reduction reaction mechanisms and the factors that influence the rate of reduction, despite the fact that the oxidation state of uranium is the most important factor controlling the mobility of uranium. In this study, the energetics and kinetics of the U(VI) reduction half-reaction on pyrite, hematite, and magnetite were investigated by electrochemical methods using a powder microelectrode (PME) as the working electrode. Anodic and cathodic peaks corresponding to the 1 e<sup>-</sup> redox couple, U(VI)/U(V), were identified in cyclic voltammograms of pyrite, hematite, and magnetite at pH 4.5. A second oxidation peak, corresponding to the oxidation of U(IV), was identified and provides evidence for the formation of reduced uranium phases on the mineral surfaces. In addition, uranium-containing precipitates were identified on pyrite surfaces after polarization in a PME. High Tafel slopes (> 220 mV/(log unit of current) on all minerals evaluated) suggest that uranyl reduction is mediated by insulating oxide layers that are present on the semiconducting mineral surfaces. The onset potential for uranyl reduction was determined for pyrite (>0.1 V vs. Ag/AgCl), and hematite and magnetite (between -0.02 and -0.1 V vs. Ag/AgCl). The onset potential values establish a baseline kinetic parameter that can be used to evaluate how solution conditions (*e.g.*, dissolved reductants, complexing ligands, and polarizing ions) affect the kinetics of uranyl reduction.

This is the first study that uses a PME, instead of a conventional mineral electrode, to evaluate redox processes on mineral surfaces. The results of this study demonstrate the feasibility of using PMEs to evaluate redox potentials, energetics, kinetics, and mechanisms for other environmentally-relevant mineral-analyte systems.

**Quantum mechanical calculations on U(VI) adsorption and reduction on dimer substrates:** *Ab initio* calculations using Fe- and Al-dimers are being completed to understand how electronic properties may affect the adsorption and reduction of uranyl molecules. Becker et al. (2001) have hypothesized that semiconducting minerals (such as goethite and hematite) may better facilitate electron transfer processes, thus this hypothesis is being tested through comparison of adsorption and coadsorption reactions on goethite and its insulating, isostructure diaspore. Charge-neutral Fe- and Al-dimers (X<sub>2</sub>O<sub>10</sub>H<sub>14</sub>, where X=Fe or Al), constructed from bulk goethite and diaspore minerals respectively, are being used as a simplified means to understand

whether chemical and electronic differences may affect the adsorption and reduction of uranyl via a Fe(II) reductant.

Coadsorption of  $\text{UO}_2^{2+}$  and  $\text{Fe}(\text{OH})_2$  on a goethite dimer and diaspore dimer (hematite and corundum dimers in progress) was found to be exothermic (-162.0 kJ/mol and -141.7 kJ/mol, respectively). Molecular orbital analyses are being used to qualitatively observe if orbital overlap exists within the coadsorbed complexes, potentially enabling electron transfer from one distant site to another. More orbital overlap is found in the coadsorbed complex with the goethite dimer than the diaspore dimer, supporting the idea that semiconducting minerals may better facilitate redox processes. Several charge analyses methods (Bader, Hirshfeld, and Mulliken) have also been employed to observe charge and spin redistributions throughout these reactions to quantify charge transfer. The spin redistribution shows that the uranium atom obtains a spin of  $\sim 1.0$  au (suggesting it is U(V) instead of U(VI)). All calculations are being carried out using uranyl molecules with different ligands and reductants (such as  $\text{S}^{2-}/\text{H}_2\text{S}$ ) to better understand charge and spin redistribution in these reactions. Batch adsorption experiments complementing these adsorption and reduction studies are being performed using ICP-MS in solution and XPS, Auger, and AFM on the solid to measure aqueous uranium concentrations over time to evaluate the kinetics for the adsorption and reduction of U(VI) by Fe(II) in the presence of hematite.

**Redox reactions of uranyl complexes on magnetite studied by cyclic voltammetry using the cavity microelectrode:** Magnetite can reduce  $\text{U}^{6+}$  in aqueous solution by transfer electron from the surface, probably through the ferrous iron, to uranyl species in solution. However, the kinetics of the electron transfer processes remains unclear. In this work, electrochemistry methods have been applied in order to investigate redox reactions of different aqueous uranium species on the surface of synthetic magnetite particles (200nm) using a cavity microelectrode. The redox potentials of different  $\text{U}^{6+}/\text{U}^{5+}$  complexes vary with their corresponding coordination environment. The peak separations  $\Delta E$ , of the  $\text{U}^{6+}/\text{U}^{5+}$  redox couples are greater than 56 mV for a reversible redox reaction (mass transport controlled process), indicating electron transfer-limited kinetic behavior (scan rate = 50mv/s). The first-order heterogeneous reaction rate constant,  $k^0=4.43 \times 10^{-4}$  cm/s, of  $\text{UO}_2(\text{SO}_4)_{(\text{aq})}$  was calculated from peak shift of a series of cyclic voltammograms obtained under different scan rates, which is less than the reported value measured using metallic electrodes ( $k^0=10^{-3}$  cm/s), reflecting the electron transfer may be governed by the electron density in the conduction band in addition to other kinetic barriers. The anodic peak appeared around 0.0V was assigned to the oxidation of  $\text{U}^{6+}$  to  $\text{U}^{5+}$ . The cathodic peak position was influenced by the  $\text{U}^{5+}$  disproportionation (shift to negative potential) or by absorption of  $\text{U}^{5+}$  on mineral surface (shift to positive potential).

#### Science objectives for 2013-2015:

- Activated states that control the kinetics of U adsorption/reduction
- Direct electrochemically-dependent AFM observations of U adsorption/reduction
- 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.

#### Publications supported by this project 7/2012-3/2013

Renock D.R., Mueller M., Ewing R.C., Becker U. (2013, in press) The energetics and kinetics of uranyl reduction on pyrite, hematite, and magnetite surfaces: a powder microelectrode study. *Geochimica et Cosmochimica Acta*.

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## Investigations into 5f orbital occupancy and radiation damage in actinide intermetallics

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Overall research goals: To determine the 5f orbital occupancy in actinide intermetallics and organometallics, and the magnetic, electronic, and structural ramifications of this occupancy.

Significant achievements during 2011-2013: Two significant achievements during this period were:

1. The first hard x-ray resonant x-ray emission spectroscopy (RXES) measurements of the 5f orbital occupancy were completed on elemental uranium and plutonium, as well as on several other actinide intermetallics. Together with x-ray absorption near-edge structure (XANES)  $L_3$ -edge measurements and specific heat data on an even wider range of compounds, we determined that features in the RXES data represented the occupancy of different 5f orbital configurations, demonstrating that many uranium and plutonium intermetallics have multiconfigurational character.

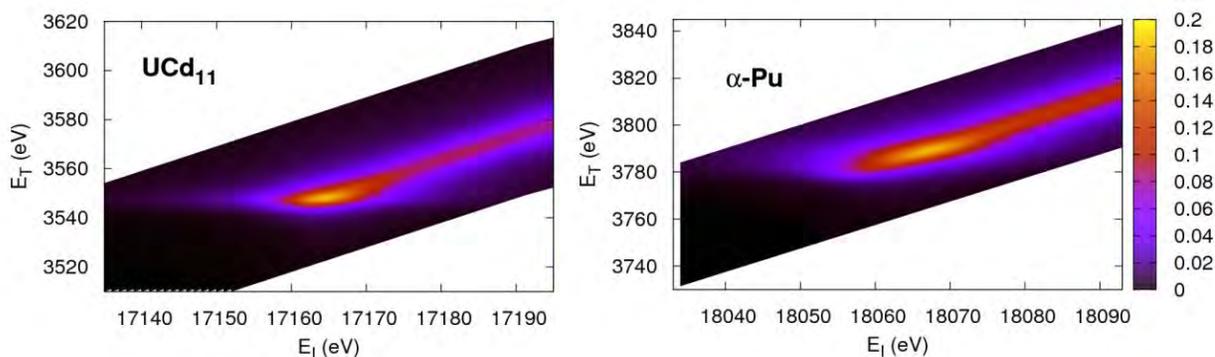


Figure 1. **Resonant x-ray emission spectra of actinide metals:** Spectra show the emitted photon intensity as a function of the incident photon beam energy,  $E_i$ , and the transfer energy,  $E_T$ . Left panel shows a sharp resonance dominated by a single uranium valence configuration. Right panel shows a broader resonance for the alpha phase of elemental plutonium that is made up of differing amounts of three resonances = three valences.

2. A complicating feature of strongly-radioactive materials with regard to understanding their electronic and magnetic properties is self-irradiation damage. We have successfully measured the radiation damage as a function of age using the local structure extended x-ray absorption fine-structure (EXAFS) technique in a variety of Pu intermetallics, and also the aging effect on  $\delta$ -Pu for a sample held below 32 K for a period of two months.

### Science objectives for 2013-2015:

- Apply RXES technique to a broader array of actinide materials to further establish the efficacy of the technique and to help settle outstanding questions in the field, such as the so-called “hidden order” state in URh<sub>2</sub>Si<sub>2</sub>.
- Remeasure  $\delta$ -Pu radiation damage properties to better determine the temperature dependence of damage annealing above 50 K.

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1. Yu Jiang, A. Huq, C. H. Booth, G. Ehlers, J. E. Greedan, J. S. Gardner, “Order and disorder in the local and long-range structure of the spin-glass pyrochlore, Tb<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>.” [J. Phys.: Condens. Matter \*\*23\*\*, 164214 \(2011\)](#). DOI: 10.1088/0953-8984/23/16/164214.
2. P. H. Tobash, Yu Jiang, F. Ronning, C. H. Booth, J. D. Thompson, B. L. Scott, and E. D. Bauer, “Synthesis, Structure, and Physical Properties of YbNi<sub>3</sub>Al<sub>9</sub>.” [J. Phys.: Condens. Matter \*\*23\*\*, 086002 \(2011\)](#). DOI: 10.1088/0953-8984/23/8/086002.
3. G. B. Jin, E. S. Choi, C. H. Booth, T. Albrecht-Schmitt, “Syntheses, Structure, Magnetism, and Optical Properties of the Ordered Interlanthanide Copper Chalcogenides Ln<sub>2</sub>YbCuQ<sub>5</sub> (Ln = La, Ce, Pr, Nd, Sm; Q = S, Se): Evidence for Unusual Magnetic Ordering in Sm<sub>2</sub>YbCuS<sub>5</sub>.” [Chemistry of Materials \*\*23\*\*, 1306 \(2011\)](#). DOI: 10.1021/cm103347u.
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6. S. A. Wang, J. Diwu, A. Simonetti, C. H. Booth, T. E. Albrecht-Schmitt, “Interstitial Incorporation of Plutonium into a Low-Dimensional Potassium Borate.” [Environ. Sci. Tech. \*\*45\*\*, 9457-9463 \(2011\)](#). DOI: 10.1021/es2028247.
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### i) Overall Research Goals

The overall goals of this research are: (1) To synthesize and determine the structures of a chemically 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 Np(V) compounds. (2) To synthesize and characterize a broad range of compounds containing highly unusual 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 properties.

### ii) Significant Achievements during 2011-2013

The Burns group and researchers at the University of Minnesota have studied cation-cation interactions in Np(V) compounds. The Burns group synthesized and characterized the structure of the novel compound  $K[(Np(V)O_2)(OH)_2] \cdot 2H_2O$ . It contains a single symmetrically unique neptunyl ion, which is coordinated by four hydroxyl ligands and one O atom belonging to a symmetrically equivalent neptunyl ion. Adjacent neptunyl pentagonal bipyramids share an equatorial edge defined by two hydroxyl groups, and these chains are linked to identical chains through cation-cation interactions, resulting in anionic sheets of polyhedra. The cation-cation configuration in  $K[(Np(V)O_2)(OH)_2] \cdot 2H_2O$  is an example of a rare side-on interaction. Each neptunyl ion both accepts and donates a cation-cation interaction. Two previously reported Np(V) structures have this type of interaction, but there are chelating ligands that bridge the neptunyl ions involved in the cation-cation interaction.

The University of Minnesota group, lead by Prof. Gagliardi, studied the electronic structure of  $K[(Np(V)O_2)(OH)_2] \cdot 2H_2O$  using a suite of quantum chemical methods ranging from density functional theory (DFT) to high level multiconfigurational methods such as the complete active space self-consistent field theory with corrections from second order perturbation theory (CASSCF/CASPT2) and the generalized active space self-consistent field (GASSCF) theory. They analyzed the topology of the electron density from DFT calculations for the high spin states of model clusters. Topological analysis of the electron density revealed two bond critical points (BCP) between the neptunium centers and the oxygen atoms. These interactions are ionic in nature since the Laplacian at the BCP is positive, but the energy density is slightly negative, which points to some dative character as well. No relevant electron density indicative of a Np-Np direct bond was found between adjacent neptunium centers.

We have report the syntheses and characterization of new compounds with U(VI) and cation-cation interactions and/or tetraoxido U(VI) $O_4$  core complexes. We synthesized a uranyl-2,2'-bipyridine coordination polymer,  $(UO_2)_2(2,2'\text{-bpy})(CH_3CO_2)(O)(OH)$ , (2,2'-bipy = 2,2'-bipyridine), hydrothermally at 165 °C. Its structural unit consists of two uranyl pentagonal bipyramids that are linked through cation-cation interactions to form chains that are truncated in the second and third dimensions by 2,2'-bipyridine. This is a rare case of cation-cation interactions through the edge-sharing polyhedra connection mode. This compound is the first U(VI) compound reported that contains CCIs in which the structural unit is one-dimensional; the others are all framework structures.

We also demonstrated that the compounds  $NH_4[(UO_6)_2(UO_2)_9(GeO_4)(GeO_3(OH))]$ ,  $K[(UO_6)_2(UO_2)_9(GeO_4)(GeO_3(OH))]$ ,  $Li_3O[(UO_6)_2(UO_2)_9(GeO_4)(GeO_3(OH))]$ , and  $Ba[(UO_6)_2(UO_2)_9(GeO_4)_2]$ , obtained in good yield via hydrothermal synthesis at 220°C, contain cation-cation interactions. There are three symmetrically independent U sites in each structure, two of which correspond to typical  $(UO_2)^{2+}$  uranyl ions and the other of which is octahedrally coordinated by six O atoms. One of the uranyl ions donates a cation-cation interaction, and accepts a different cation-cation interaction. The linkages between the U-centered polyhedra result in a relatively dense three-dimensional framework with low-valence cations contained in channels.

We have examined unusual coordination environments about U(VI) in several compounds. The compounds  $K[(UO_2)_2(UO_4)(OH)(NO_3)_2]H_2O$  and  $Ba[(UO_2)_4(UO_4)_2(OH)_2(NO_3)_4]H_2O$  contain sheets that are based on the well-known  $\beta$ - $U_3O_8$  topology but are exceptional because each contains a highly unusual  $(UO_4)^{2-}$  tetraoxido unit that is further coordinated in each case by two bidentate  $(NO_3)^-$  groups. In the case of  $(UO_2)_2[UO_4(trz)_2](OH)_2$  (trz = 1,2,4-triazole), which we prepared using a mild solvothermal reaction of uranyl acetate with 1,2,4-triazole, we demonstrated that one of the U(VI) coordination environments is intermediate between a  $(UO_4)^{2-}$  tetraoxido unit and a  $(UO_2)^{2+}$  uranyl ion. This prompted an analysis of the data in the ICSD for six-coordinated U(VI) that revealed distinct structural pathways between coordination polyhedra.

We have synthesized five novel U(VI) uranyl tungstate compounds with cation-cation interactions. As with most other structures containing such interactions, these are frameworks of uranyl (and tungstate) polyhedra. The structures contain solvent accessible voids and exchange of cations contained therein has been demonstrated.

In the course of our recent synthetic efforts designed to yield compounds with U(VI) cation-cation interactions, we documented 36 U(VI) compounds that are new to science. These compounds revealed numerous interesting features, including novel structural units, the first uranyl arsonates, new sheet and chain topologies, new framework

structures, and highly unusual mixed valence Cr uranyl compounds. In the course of our ongoing work with Th, we synthesized and characterized five phases that are new to science. We continue to construct a hierarchical arrangement of all inorganic structures that contain Th.

### iii) Science objectives for 2013-2015

The specific objectives for 2013-2015 are: (1) To continue to synthesize and determine the structures of a chemically 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 containing highly unusual U(VI) cation-cation interactions using elevated pressure hydrothermal reactions, and to delineate the conditions under which such interactions are favored. To understand the impact of U(VI) cation-cation interactions on structural 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 actinyl 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. (5) The training of 2 Ph.D. graduate students in solid-state actinide chemistry. To introduce 6 undergraduate students over three years to actinide research through providing research assistantships and supervision.

### iv) References to publications supported by this project in the last two years.

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- Ling, J., Ward, M. & Burns, P.C. (2011): Hydrothermal syntheses and structures of the uranyl tellurates  $\text{AgUO}_2(\text{HTeO}_5)$  and  $\text{Pb}_2\text{UO}_2(\text{TeO}_6)$ . *Journal of Solid State Chemistry* 184, 401-404.

Novel uranyl bearing materials via restricted  $\text{UO}_2^{n+}$  speciation profiles and supramolecular assembly

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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  $[\text{UO}_2]^{2+}$  is the norm, to lower temperature, high-anion conditions to promote restricted speciation profiles. Molecular ‘tectons’ such as the  $[\text{UO}_2\text{X}_4]^{2-}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) are assembled through supramolecular ‘synthons’ such as H-bonding and halogen-halogen interactions.

Significant achievements during 2011-2013:

1. Study of charge transfer vibronic coupling: The development of uranyl materials synthesized from high-halide media has been underway for some time; the first examples predate this award period. As such,  $(\text{C}_{10}\text{H}_{12}\text{N}_2)[\text{UO}_2\text{Cl}_4]$  and related materials have provided a family of compounds for systematic study of the electronic structure of the uranyl cation considering their isolated uranyl centers and variation of organic, second sphere cationic species. Through Absorption and emission spectra were measured at 4 K and subsequently simulated using the Huang-Rhys theory (Figure 1). These results suggest that the electronic behavior of  $[\text{UO}_2]^{2+}$  behaves more like intra 5f-configuration transitions rather than equatorial ligand-to-metal charge transfer transitions.

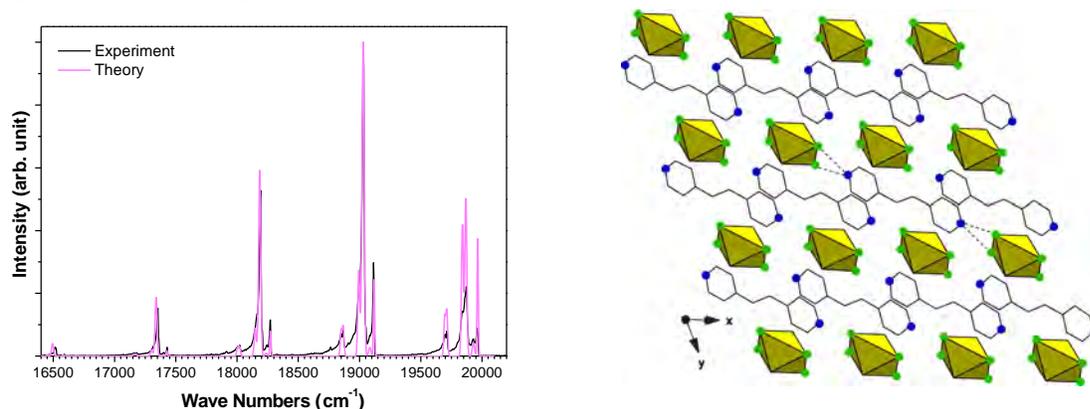


Figure 1. Left: Observed and simulated Low T emission spectra of  $(\text{C}_{12}\text{H}_{14}\text{N}_2) [\text{UO}_2\text{Cl}_4]$  (right).

2. Development of halogen-halogen interactions within  $[\text{UO}_2\text{X}_4]^{2-}$  materials: Our approach of restricted speciation and subsequent assembly of  $[\text{UO}_2\text{X}_4]^{2-}$  units is ideally suited for exploring interactions between equatorial halide groups and organic groups containing Cl, Br or I functionality. As a proof of concept, Figure 2 contains a sampling of three recently reported materials wherein either the uranyl tetrachloride or tetrabromide anion is assembled using halopyridine species. These are first of a kind materials and we are developing a ranking scheme using crystallographic parameters as indicators of interaction strength.

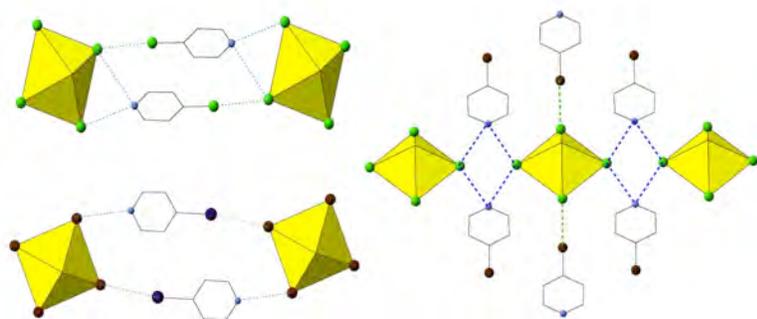


Figure 2. Top left:  $(\text{C}_5\text{H}_5\text{ClN})_2[\text{UO}_2\text{Cl}_4]$ ; Bottom left:  $(\text{C}_5\text{H}_5\text{IN})_2[\text{UO}_2\text{Br}_4]$ ; Right:  $(\text{C}_5\text{H}_5\text{BrN})_2[\text{UO}_2\text{Cl}_4]$ . H-bonding gives way to X-X interactions with increasing mass of the halogens.

### Science objectives for 2013-2015:

Objectives for the next three years include: 1) Further exploration of halogen-halogen interactions and an expansion of synthesis efforts to assess feasibility of non-traditional synthons such as X-nitrate interactions. We will continue to discern relative strengths of interactions (crystallographically) and work to develop a comprehensive ranking as relevant to crystal engineering and design. 2) Apply supramolecular concepts developed thus far for uranyl materials to Pu-Cl systems. Preliminary results in this arena suggest a fruitful endeavor wherein the chemistry does not simply mimic what is seen in uranyl systems. Anion variability to include  $[\text{PuO}_2\text{Cl}_4]^{2-}$  and  $[\text{PuCl}_6]^{2-}$  is a result of redox activity and will ultimately serve to diversify building units within these materials. 3) Ligand K-edge X-ray absorption spectroscopy of uranyl materials-collaboration with Stoh Kozimor- LANL. Preliminary Cl K-edge XAS analyses show that H-bonding between  $[\text{UO}_2\text{Cl}_4]^{2-}$  species and protonated amines (in compounds such as in Figure 1) 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 2011-2013

1. M. B. Andrews and C. L. Cahill (2013) "Uranyl bearing hybrid materials: synthesis, speciation and solid state structures." *Chemical Reviews*, In Press. DOI: 10.1021/cr300202a. *Invited*.
2. G. Liu, N. P. Deifel, C. L. Cahill, V. V. Zhurov, and A. A. Pinkerton (2012) "Charge Transfer Vibronic Transitions in Uranyl Tetrachloride Compounds." *The Journal of Physical Chemistry A*, 116(2), 855-864. DOI: 10.1021/jp210046j
3. M. B. Andrews and C. L. Cahill (2012) "Uranyl Hybrid Material Derived from In Situ Ligand Synthesis: Formation, Structure, and an Unusual Phase Transformation." *Angewandte Chemie International Edition*, 51(27), 6631-6634. DOI: 10.1002/anie.201202402
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5. N. P. Deifel and C. L. Cahill (2011) "Combining coordination and supramolecular chemistry for the formation of uranyl-organic hybrid materials." *Chemical Communications*, 47(21), 6114-6116. DOI: 10.1039/c1cc11116g.

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

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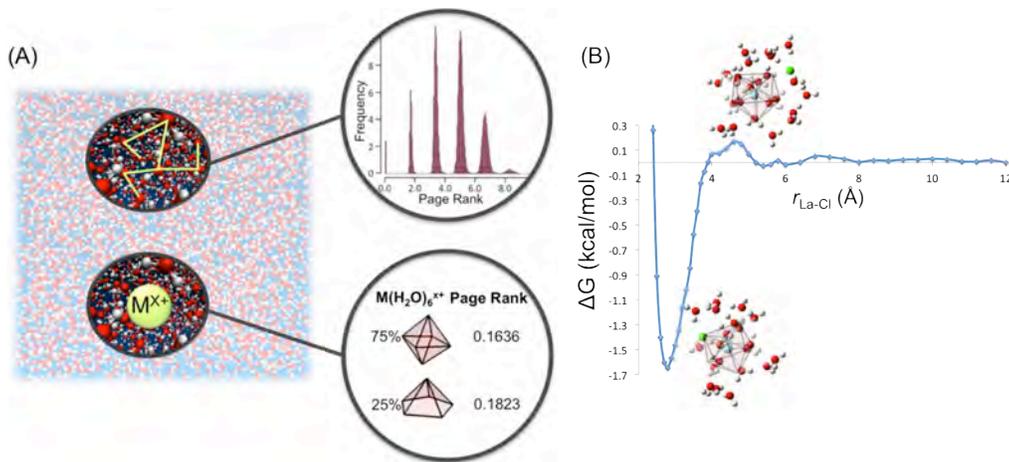
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Overall research goals: The objective of this project is to utilize DFT and MD methods to characterize solvent organization in aqueous electrolytes and to quantify molecular hydrophobicity from a dynamics and kinetics perspective. As these quantities are analyzed in the context of successful actinide extractions, new predictive chemical models can be derived to help in the rational design of novel extraction systems.

Significant achievements during 2011-2013: The most significant development has been a new graph theoretical approach for understanding solvent organization about ions, in complex solution mixtures of hydrogen bonded solvents, and of metal-ligand complexes at interfaces. This methodology has been applied to pure water, lanthanide and actinide ions in the infinite dilution limit and in lanthanide electrolyte solutions of up to 4M NaCl. Other DFT and MD studies have examined the permeability of oil:water interfaces as a function of the packing capability of the organic solvent. Significant results have emerged include:

1. The Google Page Rank algorithm can be used as a data-mining tool to determine the dynamic change in coordination environment of heavy element ions in solution and during complexation reactions.



**Figure 1.** (A) Schematic of the decomposition of molecular dynamics data into a graph based upon the hydrogen bonding network that is then Page Ranked for determination of polyhedral coordination geometries about a metal center. (B) Potential of mean force profile for chloride complexation of Ln(III) in the infinite dilution limit, illustrating how PR determines the dynamic fluctuation of the coordination environment along the reaction coordinate.

2. Network neighborhood analysis can be used to determine defects in the hydrogen bond network caused by solutes and thus a network entropy of solution can be determined from:

$$S_{\text{Defect}} = -k_B \sum_{n=1} f_n \ln(f_n) \quad (1)$$

In collaboration with Prof. Sue Clark, we are examining the correlation between the total entropy of solution phase reactions in electrolytes (based upon calorimetric experiments) with the network entropy from MD simulations.

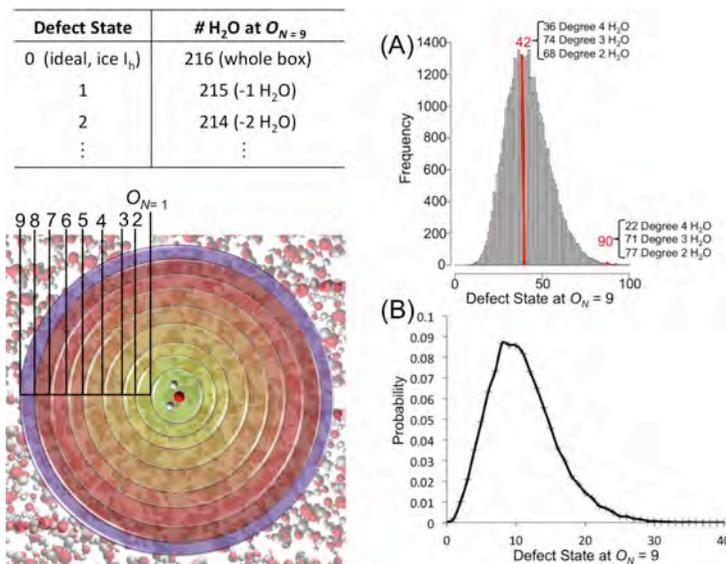


Figure 2. Network neighborhood analysis determines the total number of nearest neighbors in concentric solvation “shells” of a species, if a reference perfect network can be used, then missing species in the network define “defect” states of the system. In bulk water a Gaussian distribution of defect states is observed at 340K (panel A) which can be used to define a probability distribution at all other temperatures (panel B) and thus a network defect entropy.

#### Science objectives for 2013-2015:

- Perform MD simulations of a series of systematically more hydrophobic solutes (ML complexes) and using our graph theory methods, derive a new predictive scale of molecular hydrophobicity.
- Employ mixed QM/MM methods to determine accurate structural, dynamic, and thermodynamic information about complexation reactions in electrolyte solutions of varying concentration.
- Perform MD simulations of electrolytes and hydrophobic ML complexes at oil:water interfaces so as to understand the impact upon interfacial organization and extraction efficiency.

#### Publications supported by this project 2011-2013

1. Ozkanlar, A.; Clark, A. E. A Complete Map of the Hydrogen Bond Network of Water, *J. Phys. Chem. B*, **2013**, *submitted*.
2. Parmar, P. K.; Peterson, K. A.; Clark, A. E. Static Electric Dipole Polarizabilities of Tri- and Tetravalent U, Np, and Pu Ions, *J. Chem. Phys.*, **2013**, *submitted*.
3. Hudelson, M.; Mooney, B. L.; Clark, A. E. Determining Polyhedral Arrangements of Atoms Using PageRank, *J. Math. Chem.* **2012**, *50*, 2342.
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## Trends in Orbital Mixing for Actinide-Ligand Bonds.

**Presenting;** David L. Clark

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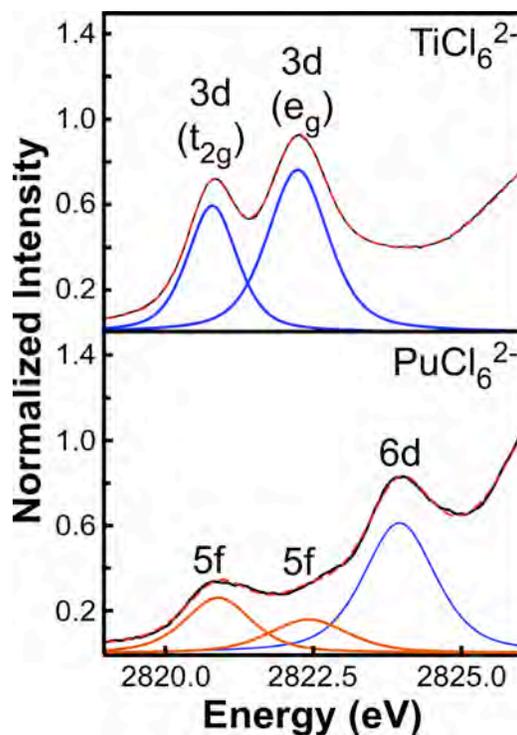
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**Objective:** The goal of this research is to advance understanding into the relative roles of the 5f vs 6d orbitals in actinide ligand bonding.

**Abstract.** Recent studies from our laboratories have focused on development of ligand K-edge X-ray Absorption Spectroscopy and electronic structure calculations for evaluating the relative roles of valence 5f and 6d orbitals in chemical bonding for actinides. Significant effort has focused on a variety of ligand types, including electronegative chloride and oxo ligands, soft sulfur-based ligands, and organometallic complexes. We find definitive spectroscopic evidence for covalent interactions using actinide 5f orbitals, and offer new views on how to think about chemical bonds that utilize 5f orbital interactions.

Chlorine K-edge X-ray absorption spectroscopy on  $MCl_6^{2-}$  ( $M = Ti, Zr, Hf$ ) compared to  $AnCl_6^{2-}$  ( $An = Th, U, Np, Pu$ ) systems indicates the presence of covalent interactions between both Cl 3p and An 5f and 6d orbitals, with the relative contributions changing across the series. Electronic structure calculations indicate the predominant covalent interactions are expected to occur through An-Cl bonding via  $t_{1u}$  and  $t_{2u}$  interactions with the An 5f orbitals, and through  $t_{2g}$  and  $e_g$  interactions with An 6d orbitals. The Cl K-edge XAS work provided a basis for study of S donor dithiophosphinic acid ( $HS_2PR_2$ ) extractants employed in minor actinide/lanthanide separation. More recently we have begun exploration of first row O and C K-edge XAS in collaboration with D. K. Shuh (LBL) to study the  $AnO_2Cl_4^{2-}$  ( $U, Np, Pu$ ), and organometallic  $An(C_8H_8)_2$  and  $(C_5R_5)_2MCl_2$  compounds.

*We gratefully acknowledge support from the*



**Fig 1.** Cl K-edge XAS spectra for  $MCl_6(PPh_4)_2$  ( $M = Ti$ , top;  $Pu$  bottom).

### **Science Objective for 2011-2013**

- (i) Synthesize a carefully selected series of compounds that contain unique bonding interactions between actinide and non-halide ligands.
- (ii) Develop the use of ligand K-edge XAS and TD-DFT calculations to evaluate actinide-ligand bonding.
- (iii) Initiate complete-active-space-self-consistent-field (CASSCF) calculations to aid in evaluating the effects of multiplet and spin-orbit coupling on the ligand K-edge spectra.

### **Publications supported by this project 2012-2013**

“Observation of  $^{239}\text{Pu}$  Nuclear Magnetic Resonance” H. Yasuoka, G. Koutroulakis, H. Chudo, S. Richmond, D. K. Veirs, A. I. Smith, E. D. Bauer, J. D. Thompson, G. D. Jarvinen, D. L. Clark, *Science*, **2012**, 901. DOI:10.1126/science.1220801

“Determining Relative f- and d-Orbital Contributions to M–Cl Covalency in  $\text{MCl}_6^{2-}$  (M = Ti, Zr, Hf, U) and  $\text{UOCl}_5^{1-}$  using Cl K-edge X-Ray Absorption Spectroscopy and Density Functional Theory” Minasian, S. G.; Keith, J. M.; Batista, E. R.; Boland, K. S.; Christensen, C. N.; Clark, D. L.; Conradson, S. D.; Kozimor, S. A.; Martin, R. L.; Schwarz, D. E.; Shuh, D. K.; Wagner, G. L.; Wilkerson, M. P.; Wolfsberg, L. E.; Yang, P. *J. Am. Chem. Soc.* **2012**, *134*, 5586-5597. DOI: 10.1021/ja2105015

“Synthesis and Structure of  $(\text{Ph}_4\text{P})_2\text{MCl}_6$  (M = Ti, Zr, Hf, Th, U, Np, Pu)” Minasian, S. G.; Boland, K. S.; Feller, R. K.; Gaunt, A. J.; Kozimor, S. A.; May, I.; Reilly, S. D.; Scott, B. L.; Shuh, D. K. *Inorg. Chem.* **2012**, *51*, 5728-5736.

“Sulfur K-edge X-ray Absorption Spectroscopy and Time-Dependent Density Functional Theory of Dithiophosphinate Extractants: Minor Actinide Selectivity and Electronic Structure Correlations.” Daly, S. D.; Keith, J. M.; Batista, E. R.; Boland, K. S.; Clark, D. L.; Kozimor, S. A.; Martin, R. L. *J. Am. Chem. Soc.* **2012**, *134*, 14408-14422. DOI: 10.1021/ja303999q

“Covalency in Metal–Oxygen Multiple Bonds Evaluated Using Oxygen K-edge Spectroscopy and Electronic Structure Theory.” Minasian, S. G.; Keith, J. M.; Batista, E. R.; Boland, K. S.; Bradley, J. A.; Daly, S. R.; Kozimor, S. A.; Lukens, W. W.; Martin, R. L.; Nordlund, D.; Seidler, G. T.; Shuh, D. K.; Sokaras, D.; Tyliszczak, T.; Wagner, G. L.; Weng, T.-S.; Yang, P. *J. Am. Chem. Soc.*, **2013**, *135*, 2279. DOI: 10.1021/ja310223b

“Tetrahalide Complexes of the  $[\text{U}(\text{NR})_2]^{2+}$  Ion: Synthesis, Theory, and Cl K-edge Absorption Spectroscopy.” Spencer, L. P.; Minasian, S. G.; Jilek, R. E.; Batista, E. R.; Boland, K. S.; Boncella, J. M.; Conradson, S. D.; Clark, D. L.; Gdula, R. L.; Hayton, T. W.; Kozimor, S. A.; Martin, R. L.; MacInnes, M. A.; Olson, A. C.; Scott, B. L.; Shuh, D. K.; Yang, P. *J. Am. Chem. Soc.* **2013**, *135*, 1864. DOI: 10.1021/ja310575j

“Covalency in f-Element Complexes,” M. L. Neidig, D. L. Clark, and R. L. Martin, *Coord. Chem. Rev.*, **2013**, *257*, 394-406.

## Controlling Actinide Hydration in Mixed Solvent Systems: Towards Tunable Solvent Systems to Close the Nuclear Fuel Cycle

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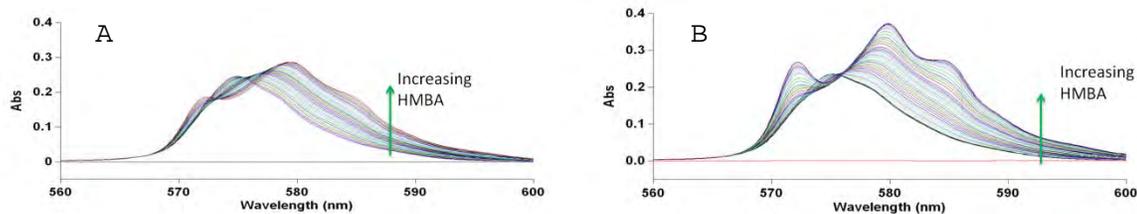
Overall research goals: The objective of this project is to develop a basis for understanding the role of hydration in the thermodynamics of f-element complexation in mixed solvent systems. Many f-element complexation reactions in aqueous systems are endothermic, but still favorable because of the entropy gain resulting from ligand displacement of hydration waters surrounding the metal center. Very limited thermodynamic data are available to describe complexation in mixed solvent systems. We are systematically investigating the role of cationic charge and solvent composition on the thermodynamics of actinide and lanthanide complexation by alpha-hydroxycarboxylic acids in methanol:water systems. We are also investigating the role of methanol in the solvation of f-elements in chromatographic, electrochemical, and mass spectrometric systems. One of the challenges in this work is to consider the role of ion pairs.

Significant achievements during 2011-2013: During this period, we installed a new micro-calorimeter that enables direct determination of the enthalpy of complexation. In addition, we continue to use other experimental tools, such as NMR, UV-VIS, fluorescence, electrochemistry, and mass spectrometry to study our systems. One team member, graduate student Luther McDonald, completed experiments using a high resolution mass spectrometry system in France via the ACTINET user facility program.

1. *Effect of solvent composition on the formation of ion pairs.* To define our thermodynamic systems accurately, we must consider the possibility of ion pair formation among all electrolytes in the system when water is replaced by methanol. This is a non-trivial challenge, and we are using conductivity and calorimetry to quantify ion pair formation as a function of solvent composition. In addition, via collaboration with A. Clark we are using computational approaches to expand our capabilities. Our experimental methodology is now fully developed.

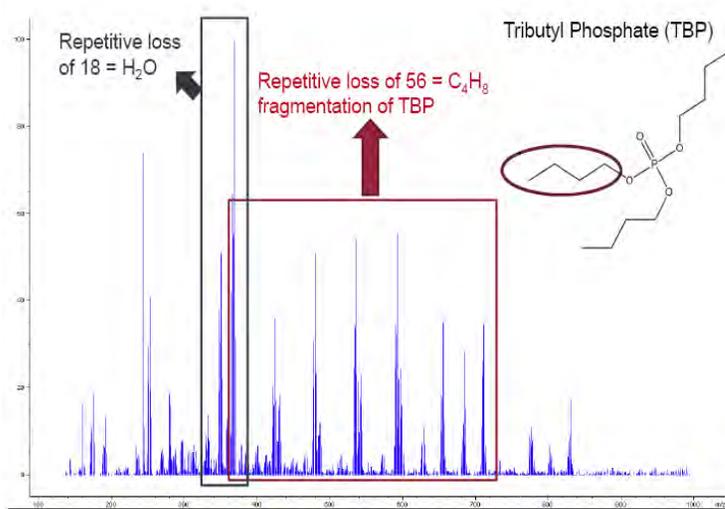
2. *Thermodynamic data in mixed solvent systems.* In these studies, we are determining stability constants, enthalpies, and entropies of complexation between f-elements and alpha-hydroxycarboxylate ligands in various compositions of methanol:water. Since complexation reactions for the f-elements are largely electrostatic, we are exploring the effect of cationic charge by comparing the tri-, tetra-, penta-, and hexavalent states. Corrections for ion pairing are made using our knowledge base developed from part (1) above. In this way, we are providing a data base that can be applied to many different complexation scenarios, rather than the typical empirical data having only limited applicability.

3. *Characterization of the f-element coordination sphere.* Various spectroscopic tools are being employed to probe changes in the coordination shell of the f-elements prior to and after complexation as a function of solvent composition. For example, UV-VIS is being employed to study the effect of the f-f hypersensitive bands of the 4f-elements (see Figure 1, next page). Similarly, we are using NMR, EXAFS, and fluorescence as additional tools, as we have done in our previous work involving aqueous systems.



**Figure 1:** Nd complexation by 2-hydroxy-2-methyl butyric acid (HMBA). 30 mM Nd(III), final ligand:metal ratio is 8:1. Ionic strength is 1.0 M (NaClO<sub>4</sub>). A. Aqueous. B. 50:50 methanol:water.

4. *Use of data in mass spectrometric applications.* The role of hydration water in the coordination shell of the f-elements plays an important role in the species observed in electrospray ionization-mass spectrometry (ESI-MS). Methanol is often used as a solvent modifier during ESI to improve the transfer of ions from the solution phase to the gas phase for detection by mass spectrometry, but the impact of the altered solvent on the observed species has not been investigated in depth.



**Figure 2:** ESI-MS of plutonium complexed with tributyl phosphate (TBP). Solvent matrix was 50:50 methanol:water. Note the fragmentation pattern for the butyl groups from TBP, and water, indicating water associated with the complex.

ESI-MS has been proposed as a possible analytical tool for materials control & accountability in reprocessing plants. The advantage offered by ESI-MS is the opportunity to observe both the accountable material (e.g. the U or Pu) along with complexants used in the separations process. However, until the impact of solvent composition on the observed species is understood, ESI-MS is simply a qualitative tool, at best. Our efforts are intended to support the development of ESI-MS as a quantitative tool for actinide speciation in mixed solvent systems.

#### Science objectives for 2013-2015:

- Implement work on ion pairs described in part (1) above to provide a basis for correction of ion pair formation in mixed solvent systems.
- Complete study of f-element complexation with HMBA in methanol:water systems.
- Use data to describe systems such as the ESI-MS data presented in Figure 2.

#### Publications supported by this project 2011-2013

1. H. Kurosaki, Daniel I. Kaplan, and S. B. Clark (accepted), "Impact of Environmental Curium on Plutonium Migration and Isotopic Signatures", Environmental Science & Technology.
2. P. D. Schumacher, J. L. Doyle, J. O. Schenk, and S. B. Clark (accepted) "Electroanalytical Chemistry of Lanthanides and Actinides", Reviews in Analytical Chemistry.
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4. C. R. Armstrong, K. L. Nash, P. R. Griffiths, S. B. Clark (2011). "Spectroscopic and thermal study of françoisite-(Nd)", American Mineralogist, 96:417-422.

# Mixed Metal Phosphonate-Phosphate Hybrid Exchangers for the Separation of Lanthanides from Actinides

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Dr. Nien-Hwa Linda Wang, Professor of Chemical Engineering, Purdue University, West Lafayette, IN

**Overall research goals:** The objective of this project is to complete separation of lanthanides from actinides and separation of actinides from each other. We intend to carry out these separations by ion exchange procedures based on materials that are highly selective for cations with plus 3 and 4 charge and non-selective for ions of lower charge. The ion exchange compounds are mixed phosphonate phosphates of  $Zr^{4+}$  and  $Sn^{4+}$ .

**Significant achievements during 2011-2013:** Project came up to speed in January 2008 with hire of Jonathon Burns and Rita Silbernagel in October 2011. To date, work has been conducted on determining the proper synthesis and uptake of the hybrids. Some highlights are as follows:

1. Synthesis and Characterization: The hybrids are prepared by hydrothermal synthesis with addition of  $ZrOCl_2 \cdot 8H_2O$  or  $SnCl_4 \cdot 5H_2O$  to 1,4-phenylene diphosphonic acid, phosphoric acid ( $H_3PO_4$ ), and heated at 120-140 °C for four days.<sup>1</sup> Partial sodium phases are obtained by substituting  $Na_3PO_4$  in place of  $H_3PO_4$ .<sup>2</sup> General compositions approximate  $M(O_3PC_6H_4PO_3)_{1-x/2}(HPO_4)_x \cdot nH_2O$ ,  $M = Zr^{4+}, Sn^{4+}$ . Using trisodium phosphate results in partial replacement of the monohydrogen phosphate protons by  $Na^+$ . We have in this way prepared four exchangers exhibiting  $K_d$  values for several cations as shown in Table 1 and shown for actinides in Table 2.<sup>1</sup>

**Table 1.**  $K_d$  values observed at pH 3 in  $HNO_3$  and reported in mL/g

Sample	$Cs^+$	$Ca^{2+}$	$Sr^{2+}$	$Nd^{3+}$	$Sm^{3+}$	
H-Zr-hybrid	32 ± 27	450 ± 30	46 ± 14	650 ± 70	29,000 ± 2,000	80,500 ± 10,000
Na-Zr-hybrid	-	3,700 ± 300	780 ± 180	≥ 5,200*	≥ 1,940,000	1,320,000 ± 380,000
H-Sn-hybrid	<1	130 ± 10	18 ± 13	140 ± 10	338,000 ± 175,000	317,000 ± 16,000
Na-Sn-hybrid	-	260 ± 60	270 ± 20	650 ± 20	480,000 ± 50,000	297,000 ± 13,000

\*The detection limit of  $Sr^{2+}$  is much lower than those of  $Ln^{3+}$

**Table 2.** The  $K_d$  values and separation factors (SF) for several actinides.  $K_d$  values are reported in (mL/g).

Sample	$K_d AmO_2^+$ pH 1.99	$K_d NpO_2^+$ pH 2.11	$K_d Am^{3+}$ pH 2.00	$K_d PuO_2^{2+}$ pH 2.13	$Am^{3+}/AmO_2^+$ SF	$Am^{3+}/NpO_2^+$ SF	$Am^{3+}/PuO_2^{2+}$ SF
H-Zr-hybrid	2 ± 1	80 ± 2	4,870 ± 50	1,440 ± 50	2000 ± 1000	61 ± 2	3.4 ± 0.1
Na-Zr-hybrid	13 ± 1	3,000 ± 300	640,000 ± 30,000	240,000 ± 20,000 <sup>a</sup>	49,000 ± 4000	210 ± 20	2.7 ± 0.3
H-Sn-hybrid	14 ± 1	230 ± 5	12,000 ± 100	3,200 ± 200	860 ± 60	52 ± 1	3.8 ± 0.2
Na-Sn-hybrid	15 ± 1	480 ± 10	38,800 ± 800	6,100 ± 200	2600 ± 200	81 ± 2	6.4 ± 0.2

a:  $K_d$  obtained at pH 1.94

2. Separation of Am from Cm: Our strategy to separate Am from Cm was to oxidize Am to  $AmO_2^+$ . This was accomplished at Los Alamos Carlsbad Laboratory by using  $Na_2S_2O_8$  as the oxidizing agent in  $HNO_3$  at 80 °C.<sup>2</sup> To prevent reduction to  $Am^{3+}$  an excess of hypochlorite was added as the calcium salt. The Am(V) state persisted for five days with only a 5% reduction to  $Am^{3+}$ . The separation was carried out at the Savannah River National Lab. Only one trial with

each of the 4 hybrid exchangers was possible in the time allotted at Savannah River. The best result was obtained with the Na-Sn hybrid. In the mixed  $\text{AmO}_2^+$ - $\text{Cm}^{3+}$  solution the  $K_d$  values were 200 mL/g for  $\text{AmO}_2^+$  and 4,400 mL/g for  $\text{Cm}^{3+}$  for a separation factor of 22.<sup>3</sup> Based on the data in Table 2 we expected a much higher separation factor. This will be part of our research effort. We expect that better control of the pH of the reaction will lead to much higher separation factors. Further work will be pursued to separate lanthanides from actinides based on pH and charge in the near future.

Science objectives for 2013-2015:

- **More comprehensive determination of  $K_d$  values:** We have determined  $K_d$  values as a function of pH for only one lanthanide (Nd) and no actinides. We will continue these studies for several lanthanides and as many of the actinides as possible at Carlsbad and Savannah River National Laboratories.
- **Improvement of conditions for Cm/Am separation:** Two approaches will be tried: First, the  $K_d$  value as a function of pH will be determined for pure  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$ . We will also determine the  $K_d$  of  $\text{AmO}_2^+$ . The ideal conditions for separation based on the pH will be determined, the two actinide solutions will then be mixed,  $\text{Am}^{3+}$  oxidized, and separation executed. In the second procedure, a mixed Am-Cm solution will be prepared, the Am oxidized, pH adjusted and separation effected.
- **Separation of lanthanides from actinides:** At this stage in the fuel cycle where the solution is a mixture of lanthanides and actinides, we oxidize only Pu and Np to the oxidation states five and six (preferably five). Then pick up all the 3+ ions and return the Pu and Np left in solution to the fuel. In the recovered 3+ cation solution we now oxidize the  $\text{Am}^{3+}$  to  $\text{AmO}_2^+$  and remove all the other trivalent ions that become part of the waste. The  $\text{AmO}_2^+$  solution left behind may contain some  $\text{Cm}^{3+}$  as with the earlier raffinate. We then proceed to separate Am and Cm.
- **Ligand modification:** The actinides as a group are softer than the lanthanides because their 5f orbitals extend outside the 6d and 7s orbitals, which are close in energy. Therefore, the combination of a soft sorbent and lower pH may favor uptake of actinides over lanthanides. Another option is use of a bipyridyl pillar group. Previous work has shown that the bipyridyl pillar has performed separations and may give an added benefit with the chelate functionality of the nitrogens.<sup>4</sup>

Conclusion:

Our hybrid exchangers are unique. I know of nothing in the whole pantheon of analytical tools that can match the selectivity preferences of these materials. By use of oxidation state and pH, we have the possibility of complete separation of lanthanides from actinides and actinides from each other, including Am and Cm. By utilizing information from EXAFS, APD, and ED together with modeling and our extensive knowledge of pillared layered metal phosphonates, we may be able to unlock the reasons for their remarkable behavior and lead to further development of new materials and applications.

Publications supported by this project 2011-2013

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DOI: 10.1524/ract.2012.1929
2. J. D. Burns, M. Borkowski, A. Clearfield, D. T. Reed, *Radiochim. Acta* **2012**, *100*:12, 901-906.  
DOI: 10.1524/ract.2013.1990
3. J. D. Burns, T. C. Shehee, A. Clearfield, D. T. Hobbs, *Anal. Chem.* **2012**, *84*, 6930-6932.  
DOI: 10.1021/ac3018394
4. H. P. Perry, J. Law, J. Zon, A. Clearfield, *Micropor. Mesopour. Mater.* **2012**, *149*, 172-180.  
DOI: 10.1016/j.micromeso.2011.07.018

## **Experimentally characterizing the electronic structures of f-electron systems using advanced high resolution Fourier transform microwave spectroscopies**

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Brittany Long, Graduate Student

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### Overall research goals:

We aim to (i) provide data that directly addresses the fundamental roles of actinide valence electrons in chemical bonding, and (ii) serve to provide prototypical data for the heavy element computational chemistry community. These goals will be achieved through the first pure rotational spectroscopic measurements on prototypical systems at ultra-high resolution. These systems encompass low oxidation state uranium and thorium compounds including, but not limited to, UX and ThX, X = F, Cl, Br, I, and UY and ThY, Y = O, S, and other simple U and Th-containing compounds. Our primary experimental tools involve time-domain rotational spectroscopy achieving line widths and resolutions of a few kHz.

### Significant achievements during 2012-2013:

1. During the present funding period we have purchased two new laser ablation target rods, thorium and uranium, and made safe the locations in which the experiments are to be performed. Preliminary broadband searches were performed for several target molecules. These preliminary searches have, to date, been unsuccessful. To counter this set back we have spent several weeks working on the sensitivity of the instrumentation, and have made considerable improvements. For example, using the metal-containing spectra of tin monosulfide and lead monochloride we have improved signal to noise ratios from approximately 50 : 1, to approximately 300 : 1. Experiments suggest that this can be further improved by a factor of 2.

2. Complimentary to the broadband spectroscopy we have been working with a high resolution cavity microwave spectrometer and examining the products of the thorium plus molecular oxygen reaction. Thorium metal has been laser ablated in the presence of pure oxygen entrained in high pressure argon. The products of the ablation event have been supersonically expanded into the Fabry-Perot cavity of a time-domain microwave spectrometer. New measurements have been performed on thorium monoxide, where the  $J = 1 - 0$  transition has been recorded in the  $v = 8, 9,$  and  $10$  vibrational levels. Further to this, and most notably, a thorium-dependent spectral transition has been observed at 19251.8740(10) MHz. The carrier of this signal is to be determined, however, it requires an oxygen concentration of 0.1 % which is significantly higher than the optimal oxygen concentration required for observation of the thorium monoxide transitions. It is postulated that the presently unidentified thorium-containing compound is  $\text{ThO}_2$  which has  $C_{2v}$  symmetry. Progress on the measurement of this

spectrum, together with other thorium experiments and supporting quantum chemical calculations, will be presented at the contractors meeting.

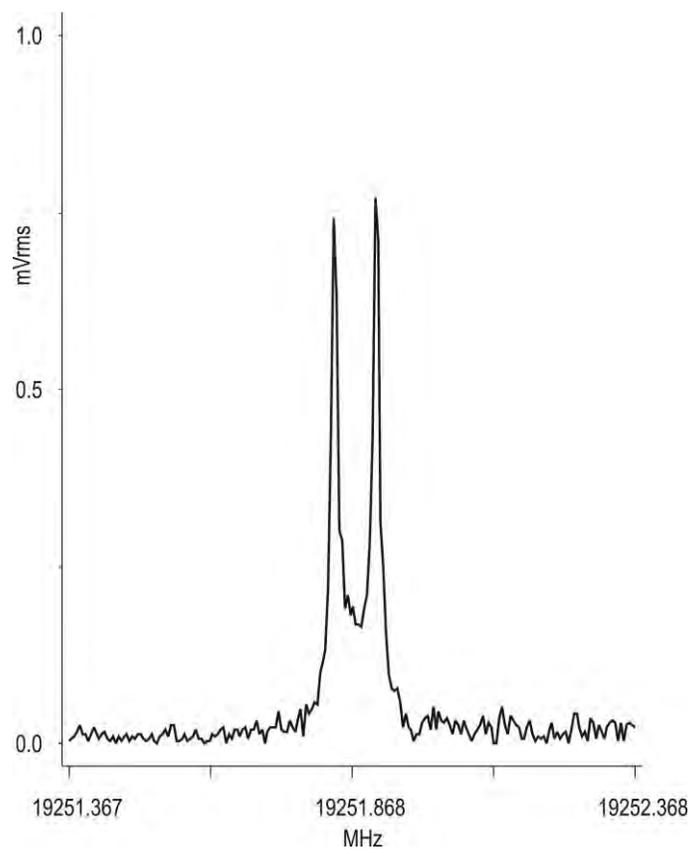


Figure 1: The postulated  $\text{ThO}_2$  transition

Publications supported by this project:

“The pure rotational spectrum of lead monochloride in the  $X^2\Pi_r$  ground state”. B. E. Long, G. S. Grubbs II, and S. A. Cooke. In preparation.

## Interfacial Transport and Liquid – Liquid Distribution of An(III) Complexes

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Overall research goals: The objective of this project is simulate An chelate complexes to characterize the role of liquid – liquid interfaces in partitioning to better understand the chelate ligand metal complex interactions with liquid – liquid interfaces of the different oxidation states of actinide ions. More generally, we are exploring the global versus local free energy changes incurred by water occupying inner and outer solvation spheres of the metal – organic ligand complexes.

Significant achievements during 2011-2013: Project was started up in September 2009 with funding provided for graduate students. To date, we have explored the use of molecular dynamics simulation methods to characterize the solvation structure and dynamics of water about ions, the interfacial structure and properties of alkane – aqueous systems, and liquid – liquid distribution properties of An(III) – ligand complexes. Significant results have emerged from analysis method development and application of developed parameters for Np(III):

1. Network graph theoretical methods have been employed to go beyond pairwise analysis of solvent shell structure and dynamics as well as to characterize surface structure and dynamics. The former has provided us with the ability to quickly evaluate ligand exchange about ions providing lifetimes of coordination structures and mechanisms of inner and outer shell exchanges. The latter provides us with a means to explore the structural response of solutes at the interface in terms of capillary wave action and surface roughness.

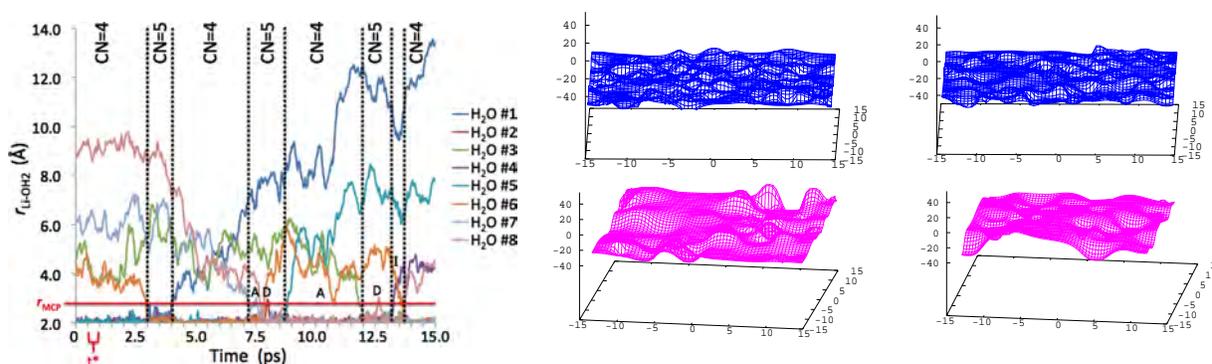
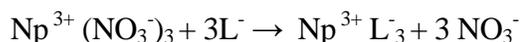


Figure 1. Left: Exchange events of water about a Na cation showing fluctuations of coordination number. Right: Surface fluctuations of liquid – vapour interface (left) and of liquid – liquid interface (right). Water (upper figures) reduces its roughness and hexane (lower) increases its roughness corresponding to a decrease and increase of surface tensions, respectively, in going from liquid – vapour to liquid – liquid interfaces.

2. The change from hydrophilic to lipophilic nature of the neptunium nitrate complex when the nitrate ligands are exchanged with typical beta-diketone ligands such as hexafluoroacetylacetonate,  $L^- = F_3CCOCHCOCF_3^-$ , :



is studied by determining the changes in their liquid – liquid distributions or their relative partition coefficients. We employ Umbrella Integration to determine the potential of mean force along a “trajectory” taking the complexes from the aqueous (raffinate) bulk phase, through a liquid – liquid interface, and into the bulk phase of the extractant hexane solution. The end points of the trajectory are identical to a thermodynamic integration determination of the free energy difference of the

complexes in each bulk phase. The advantage of the trajectory PMF is that details of the role of the interface are obtained.

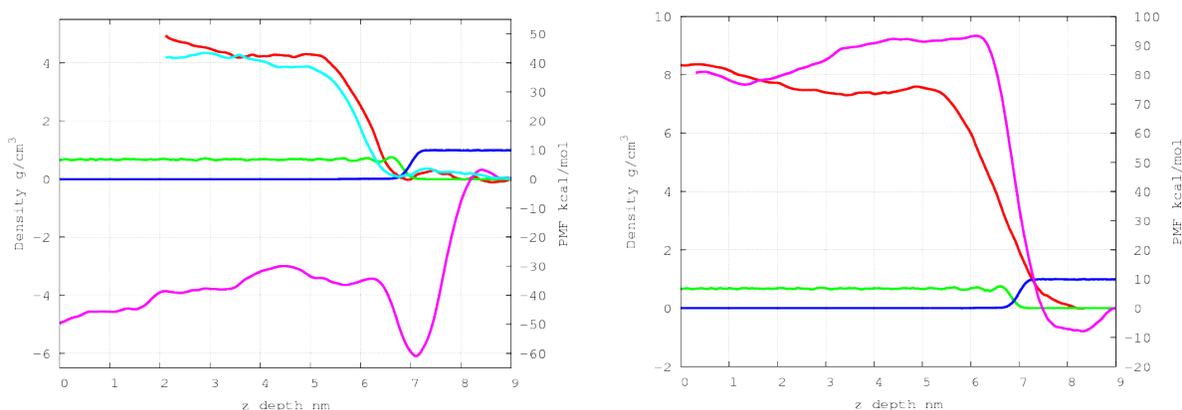


Figure 2. Left: the potential of mean force trajectories of the global minimum pathway from hexane to water at 298 K, the trajectory from water to hexane at 298 K, and from water to hexane at 328K. The global minimum path of this complex shows preferential solvation in the hexane phase and is insensitive to an increase in temperature. Right: similar forward and backward trajectories except for the nitrate complex at 298 K.

While the global minimum path has endpoints identical to those that would be determined by thermodynamic integration, the difference in forward and backward trajectories reveal that water binds to the inner solvation sphere even in the presence of the organic ligand. Thus, compromising the lipophilic nature of the organic ligand. While adding larger chain lengths to the ligands increases the lipophilic nature of the ligands, they do not necessarily reduce the number of waters entering the inner solvation sphere. Suggesting that large head groups can play an important role to enhance partitioning.

#### Science objectives for 2013-2015:

- Explore the liquid – liquid distribution behavior of An(V) and An(VI)  $\beta$ -diketonate complexes to characterize differences in solubility, coordination and water retention behavior.
- Explore different  $\beta$ -diketonate ligand systems in preference to exchange with nitrate complexes of An(III), An(V) and An(VI) at the interface.
- Expand the PMF effort to include monodentate and tridentate systems to explore crowding out water from inner solvation shell.

#### Publications supported by this project 2011-2013

1. B.L. Mooney, L.R. Corrales, A.E. Clark, 'moleculaRnetworks: an Integrated Graph Theoretic and Data Mining Tool to Explore Solvent Organization in Molecular Simulations', *J. Comp. Chem.* 2012, 33, 853. DOI: 10.1002/jcc.22917.
2. B.L. Mooney, L.R. Corrales, A.E. Clark, 'Novel Analysis of Cation Solvation Using Graph Theoretic Approaches', *J. Chem. Phys. B* 2012, 116, 3387. DOI: 10.1021/jp300193j.
3. J. Gibbs and L.R. Corrales, 'Interface Structure and Dynamics of Aqueous - Hexane Isomer Systems', to be submitted *J. Phys. Chem B*.
4. L.R. Corrales, 'Liquid – Liquid Distribution of beta-Diketone – Neptunium Complexes', to be submitted *J. Phys. Chem. B*.

## Ion-Pair Recognition and Separation via Self-Assembly

Radu Custelcean, Principal Investigator

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Collaborators: Peter V. Bonnesen, Benjamin P. Hay, Bruce A. Moyer, Oak Ridge National Laboratory

Overall research goals: This research is aimed at understanding how to employ self-assembly of small organic units with selected ion pairs to construct complex molecular architectures with predetermined structures and separation functions. The particular challenge here is to identify multitopic ligands that are 'programmed' to selectively self-assemble with targeted ion pairs into high-symmetry charge-neutral ensembles (e.g., helicates, tetrahedra, cubes, octahedra, etc.) that can be effectively separated by solvent extraction, crystallization, or other technique.

Significant achievements during 2011-2013: In our quest to achieve ion-pair recognition with self-assembled architectures, we designed and synthesized a series of  $M(L2)_3(SO_4)$  ( $M = Ni^{2+}, Fe^{2+}$ ) helicates (Fig. 1), and investigated their structures and dynamics of self-assembly by single-crystal X-ray diffraction and NMR spectroscopy. The X-ray structural analysis confirmed the formation of either helicates or mesocates, differing in the relative stereochemistry ( $\Delta\Delta$  or  $\Delta\Lambda$ ) of the metal and anion coordination centers, with both the metal cation and the sulfate anion coordinated octahedrally by six pyridyl and urea groups, respectively. The NMR analysis confirmed the persistence of the helicate structures in solution, at the same time indicating a complex dynamic behavior that requires further investigations for a detailed understanding of the self-assembly process. For instance, while monitoring the self-assembly by proton NMR, it was noted that a mixture of species of lower symmetry initially form, and that over the course of several hours the symmetrical helicate or mesocate structures grow in. Of particular interest for on-going studies are the structures and stereochemistries of the intermediate species as well as the influence of the *para*-substituent (here  $-NO_2$  or  $-tBu$ ) over the nature of the self-assembled structures (helicate vs mesocate) and their dynamics. We are also trying to understand what specific roles do the cation and anion play in the helicate self-assembly, and if there is any cooperativity between the cation and the anion binding.



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

### Science objectives for 2013-2015:

- Understand the factors governing the structures and dynamics of self-assembled ion-pair helicates.
- Investigate the self-assembly of more complex architectures based on ion-pair recognition.
- Employ these self-assembled structures for the selective separation of ion pairs by liquid-liquid extraction or/and crystallization.

### Publications supported by this project 2011-2013:

1. Borman, C. J.; Custelcean, R.; Hay, B. P.; Bill, N. L.; Sessler, J. L.; Moyer, B. A. Supramolecular Organization of Calix[4]pyrrole with a Methyl-trialkylammonium Anion Exchanger Leads to Remarkable Reversal of Selectivity for Sulfate Extraction vs Nitrate. *Chem. Commun.* **2011**, 47, 7611–7613 DOI: 10.1039/c1cc12060c.
2. Custelcean, R.; Bonnesen, P. V.; Duncan, N. C.; Zhang, X.; Watson, L. A.; Van Berkel, G.; Parson, W.; Hay, B. P. Urea-Functionalized  $M_4L_6$  Cage Receptors: Anion-Templated Self-Assembly and Selective Guest Exchange in Aqueous Solutions. *J. Am. Chem. Soc.* **2012**, 134, 8525–8534 DOI: 10.1021/ja300677w.
3. Custelcean, R.; Bonnesen, P. V.; Roach, B. D.; Duncan, N. C. Ion-Pair Triple Helicates and Mesocates Self-Assembled from Ditopic 2,2'-Bipyridine-bis(urea) Ligands and Ni(II) or Fe(II) Sulfate Salts. *Chem. Commun.* **2012**, 48, 7438–7440 (highlighted on the inside cover) DOI: 10.1039/c2cc33062h.
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## Self-Assembled Ionophores and Membrane Active Transporters

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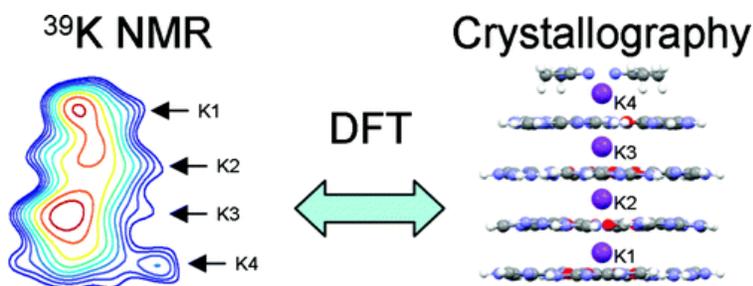
Collaborators: Prof. Philip Gale, Southampton University, UK

Prof. Alison Thompson, Dalhousie University, Canada

Prof. Gang Wu, Queen's University, Canada

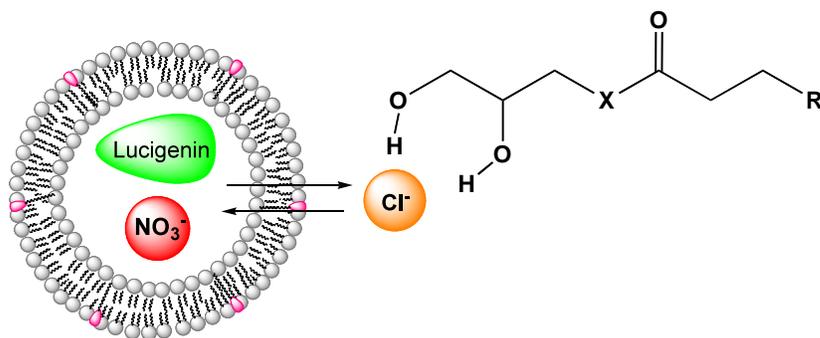
Overall research goals: Our goal is to build “self-assembled” ionophores that selectively bind and transport ions across membranes. We have used non-covalent interactions to synthesize such receptors. For example, lipophilic guanosine nucleosides hydrogen bond to give G-quadruplexes that selectively bind and transport cations. We have also developed a series of anion transporters based on molecular self-assembly strategies. Our goals include: 1) learning how to control structure & dynamics of 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.

Significant achievements during 2011-2013: **Supramolecular Assemblies that Transport Ions across Phospholipid Bilayer Membranes.** We recently prepared a novel synthetic ion channel that can move ions across phospholipid bilayer membranes. Such transporters could eventually serve as intracellular sensors or antimicrobial agents. We achieved the desired properties by attaching guanosine groups to the ends of a lithocholic acid dimer. This study is, to the best of our knowledge, the first experimental demonstration that G-quadruplexes can be used as synthetic ion channels. We are currently trying to determine the transport mechanism and develop improved analogs. Also, some of our compounds are excellent model systems for the biophysical characterization of channel like structures (see Fig. 1)



**Fig. 1.** Supramolecular G-Quadruplexes allow for Correlation of ss-NMR and X-ray data.

**New Cl<sup>-</sup> Anion Receptors/Membrane Transporters.** We extended our use of self-assembly to prepare compounds that transport Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> anions across bilayer membranes. Using liposomes we compared the H<sup>+</sup>/Cl<sup>-</sup> co-transport activity and the Cl<sup>-</sup>/HCO<sub>3</sub><sup>-</sup> anion exchange properties of a series of synthetic molecules and natural products (prodigiosins and ceramides). These compounds' ability to transport Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> at micromolar concentrations, their low molecular weight and simple preparation make them lead platforms for building new approaches toward selective ion separations.



**Fig. 2.** Ceramide Derivatives function as transmembrane anion transporters.

Science objectives for 2013-2015:

- To use self-assembled ionophores to transport nucleosides and nucleotides across membranes;
- To study new ionophores formed by covalent capture of supramolecular assemblies;
- To synthesize transmembrane anion transporters that are selective for bicarbonate anion

Publications supported by this project 2011-2013

1. "Structurally-Simple Lipid Bilayer Transport Agents for Chloride and Bicarbonate." Cally J.E. Haynes, Stephen J. Moore, Christine C. Tong, Mark E. Light, Jeffery T. Davis, William A. Harrell, Jr. and Philip A. Gale, *Chemical Science* 2011, 2, 256–260. [DOI: 10.1039/C0SC00503G](https://doi.org/10.1039/C0SC00503G)
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3. "Monoacylglycerol Analogs as Transmembrane Cl<sup>-</sup> Anion Transporters." Soheila Bahmanjah, Ning Zhang and Jeffery T. Davis, *Chemical Communications*, **2012**, 48, 4432-34. [DOI: 10.1039/C2CC18148G](https://doi.org/10.1039/C2CC18148G)
4. "Synthetic Prodigiosenes: Influence of C-Ring Substitution on Ease of Protonation, DNA Cleavage, and Transmembrane Anion Transport." Soumya Rastogi, Estelle Marchal, Imam Uddin, Brandon Groves, Julie Colpitts, Sherri A. McFarland, Jeffery T. Davis and Alison Thompson, *Organic & Biomolecular Chemistry*, **2013**, submitted.

## Influence of Solution Phase and Interfacial Structure on the Stability of Actinide Oxidation States: A Computational Chemistry Approach

Wibe A. de Jong, Principal Investigator

Samuel Odoh, Postdoctoral Fellow

Pacific Northwest National Laboratory, Richland, WA

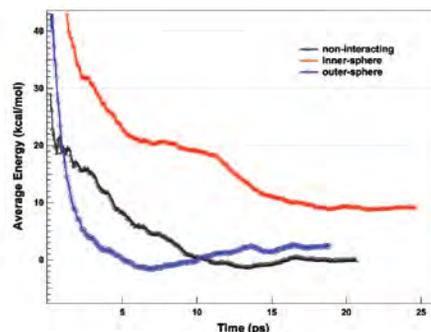
Email: [bert.dejong@pnl.gov](mailto:bert.dejong@pnl.gov)

Collaborators: - Dr. Lynne Soderholm (ANL) on EXAFS of actinides in solution  
- Dr. John Gibson (LBL), Dr. Gary Groenewold (INL), Dr. Theresa Windus (Iowa) on validating simulation methods through comparison with gas-phase experiments  
- Dr. Jochen Autschbach (SUNY) on spin-orbit NMR using our developed ZORA  
- Dr. Raymond Atta-Fynn (Univ. Texas) solvation and surface model development

Overall research goals: The goal of our program is to develop a fundamental understanding of the influence of the local molecular environment on the oxidation state of actinides, on the speciation of actinides in solution environments, and the adsorption and reduction of these actinides on mineral surfaces, to understand the effects of kinks and step edges, or accessible pores, to accurately portray actinide redox chemistry under real-world conditions using a combination of statistical and quantum mechanical methods.

Significant achievements during 2011-2013: The project has made significant progress in modeling actinides in solution and interacting with surfaces, and multiple collaborations have been developed.

1. First-principle molecular dynamics of uranyl on hydroxylated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 0001 surface demonstrate the key role of water solvation in forming surface complexes. The size of the model, especially the proper description of the water layers all the way out to 25 Å is critical to obtain correct energetics. Results from the large scale models show that when enough water layers are included direct coordination of uranyl with the surface is ~10 kcal/mol less stable compared to uranyl being further away. The uranyl does not interact with the surface, which is in contrast to the findings from simpler periodic and cluster models that only include a few water molecules.



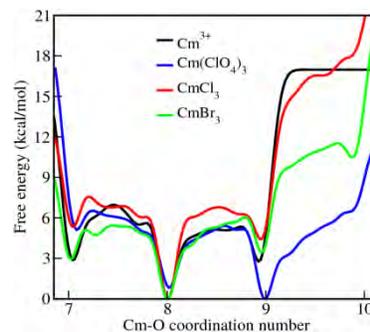
Energetics of inner simulations using large simulation cells.

2. AIMD simulations at room temperature probe the solvation structures, EXAFS, water-exchange mechanisms and the thermodynamics of hydrolysis (calculating the first acidity constant) of uranium in aqueous solution its three oxidation states IV, V, and VI. Simulated EXAFS spectra are in excellent agreement with the experimental data. The calculated acidity constants ( $pK_a$ ) of  $U^{4+}$  and  $UO_2^{2+}$  are in good agreement with available experimental values 0.93 versus 0.54 and 4.95 versus 5.24, respectively, and we predict the  $pK_a$  of  $UO^{2+}$  to be 8.5. We determined the free energy difference and activation barrier of the dissociation reaction  $[UO_2(OH_2)_5]^{2+}(aq) \rightarrow [UO_2(OH_2)_4]^{2+}(aq) + H_2O$  were 0.7 kcal and 4.7 kcal/mol respectively; the free energy difference lies with the experimental range of experimental of 0.5-2.2 kcal/mol data.

3. The role of counter ions on the complexation and hydration of aqueous Cm(III) and Th(IV) ions was studied using AIMD and metadynamics. For curium we have demonstrated that the number of water molecules coordinating with the actinides depends on the type of

counter ion ( $\text{Br}^-$ ,  $\text{Cl}^-$ , and  $\text{ClO}_4^-$ ) and concentration. For thorium the effects are more subtle, and the role of long-range dispersion is currently being investigated.

- Continued collaboration with gas-phase experiments led to insights into chemical bonding of actinide species. Multimeric species with up to 5 uranium atoms were observed by Groenewold (INL). Simulations show that the most stable structures obtained for  $[(\text{UO}_2)_2(\text{OH})_5]^-$  feature cation-cation interactions (CCI). Structures for complexes up to five uranyl hydroxyl complexes, observed in, were determined to form flat sheet structures. Experimental studies by Gibson (LBL) on uranyl-acetone complexes found 8 ligands hypercoordinating with the actinide. An integrated experimental and computational effort proved that diactone alcohol species can form species that give a perceived coordination of 8 ligands around the actinide, but that in reality the coordination number does not exceed 5, in concord with other experimental and computational findings. This work involved 2 summer students from Iowa State University and the University of Manitoba.



#### Science objectives for 2013-2015:

- Understand the role of ligands, counter-ions and oxidation state in aqueous solution on the formation, stability and charge transfer properties of multimeric U and Pu actinide species.
- Model the structure, thermodynamics, and redox (charge-transfer) chemistry of solvated U, Pu, and Np ions on reducing mineral surfaces at ambient conditions.

#### Publications supported by this project 2011-2013

- V.A. Glezakou and W.A. de Jong, "Cluster-models for Uranyl(VI) adsorption on  $\alpha$ -alumina." J. Phys. Chem. A 2011, 115, 1257 (2011), Cover
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- G.S. Groenewold, M.J. van Stipdonk, J. Oomens, W.A. de Jong, M.E. McIlwain, "The gas-phase bis-uranyl nitrate complex  $[(\text{UO}_2)_2(\text{NO}_3)_5]^-$ : infrared spectrum and structure", Int. J. Mass Spec. 308, 175 (2011)
- R. Atta-Fynn, D. Johnson, E. Bylaska, E. Ilton, G. Schenter, W.A. de Jong, "Structure and Hydrolysis of the U(IV), U(V), and U(VI) Aqua Ions from Ab Initio Molecular Simulations", Inorg. Chem. 51, 3016 (2012)
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- D.F. Johnson, E.J. Bylaska, W.A. de Jong, "Thermodynamics of Tetravalent Thorium and Uranium Complexes from First-Principles Calculations", J. Phys. Chem A, submitted (2012)

Five additional publications are in preparation, with subjects ranging from the role of counter ions on the coordination of curium and uranium, the formation of multimeric species, and *ab initio* molecular dynamics simulations of uranyl(aq) on both non-reducing and reducing surfaces.

## First Experimentally-Determined Thermodynamic Values of Francium

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Overall research goals: The objective of this project is to investigate the extraction properties of ditopic ion pair receptors. More specifically, the study involves alkali cation/halide anion extraction systems using calix[4]arene-crown combined with calixpyrroles. The entire alkali series is being considered, including francium.

Significant achievements during 2011-2013: The study involving francium was actually started in May 2012. Thermodynamic data for the solvent nitrobenzene have been determined experimentally.

The Gibbs energy of partitioning of  $\text{Fr}^+$  ion between water and nitrobenzene has been determined to be  $14.5 \pm 0.6$  kJ/mol, the first solution thermodynamic quantity for francium ever determined experimentally. This result allowed the calculation of the ionic radius and standard Gibbs energy of hydration for  $\text{Fr}^+$  to be estimated as 173 pm and  $-251$  kJ/mol, respectively. These values depart from those estimated and found in the literature. An experimental procedure was established using a cesium dicarbollide as a cation-exchanger, overcoming problems inherent to the trace-level concentrations of francium. This methodology will permit the study of the partitioning behavior of francium to other organic solvents and the determination of complexation constants for francium binding by receptor molecules.

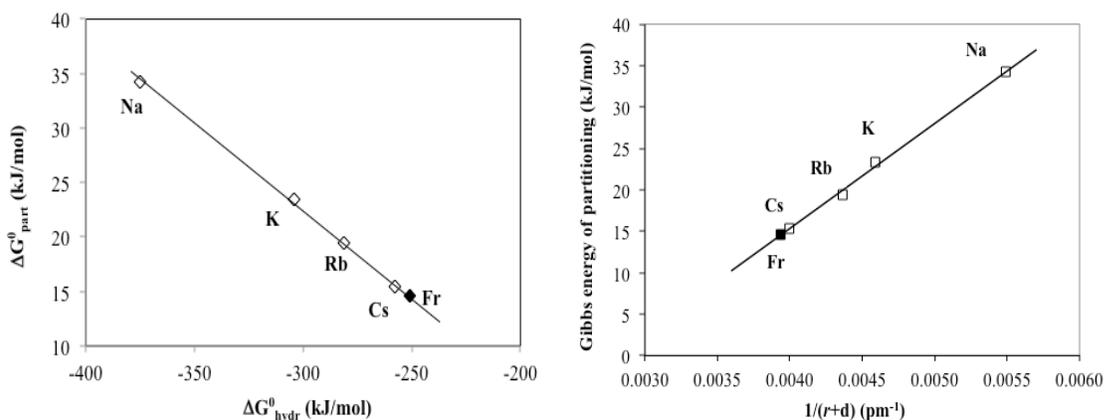


Figure 1. Left: Gibbs energy of partitioning as a function of the hydration energy for alkali cations. Right: Gibbs energy of partitioning as a function of the thermodynamic radius of alkali cations. To the radius of the different alkali cations is added the conventionally accepted 80 pm (d).

The estimates show that  $\text{Fr}^+$  ion is closer to the size and behavior of  $\text{Cs}^+$  ion than previously thought. Based on the intervals between  $\text{K}^+$  and  $\text{Rb}^+$  and  $\text{Rb}^+$  and  $\text{Cs}^+$ , the change in radius and hydration energy in the interval  $\text{Cs}^+$  to  $\text{Fr}^+$  is significantly decreased. This observation is likely to have theoretical ramifications. Having these estimates will prove useful for multiple calculations of the properties of  $\text{Fr}^+$  ion. From our own perspective, the methodology developed here will enable determination of the partitioning of  $\text{Fr}^+$  to multiple water-immiscible solvents. Determining the homogeneous binding constants for  $\text{Fr}^+$  ion will then be possible and will allow us to continue the fledgling coordination chemistry for this ion that we had previously established. Moreover, information about the thermodynamic behavior of this heavy alkali metal is critical for predicting the chemical properties of element 119, the next element to be discovered and anticipated to be placed in the alkali series under francium.

#### Science objectives for 2013-2015:

- Obtain thermodynamic data in other solvents
- From the Gibbs energy of partitioning of Fr in different solvents, determine the binding constants of various ligands for francium
- Compare the extraction behavior of francium and cesium comparison in presence of cation receptors, anion receptors, and dual host systems.

#### Publications supported by this project 2011-2013

1. Delmau, L. H.; Moine J.; Mirzadeh, S.; Moyer, B.A. First experimentally determined thermodynamic values of Francium: Hydration energy, energy of partitioning and thermodynamic radius, *submitted to J. Phys. Chem. B*

## Unique Advantages of Organometallic Supporting Ligands for Uranium Complexes

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Overall research goals: The objective of this project is to take advantage of the combination between uranium and ferrocene-based ligands in order to uncover new properties and reactivity patterns. Specifically, we are interested in understanding the electronic communication between iron and uranium in ferrocene-based complexes.

Significant achievements during 2011-2013: Uranium complexes containing ferrocene-based ligands provide an interesting platform to study the electronic interaction between iron and uranium. Two areas have emerged:

1. *Importance of f orbitals in determining interactions between iron and uranium in bis(1,1'-ferrocene diamide) complexes.* Uranium complexes containing two ferrocene-based ligands (Figure 1) allow us to study the electronic interaction between iron and uranium and how uranium mediates the electronic coupling of the two iron centers. In addition, this study offers insight into the question of the participation of f orbitals in covalent bonding, which is still a hotly debated topic. By designing a system in which uranium interacts directly with a transition metal, we have created a unique class of compounds to use as a basis to address this question.

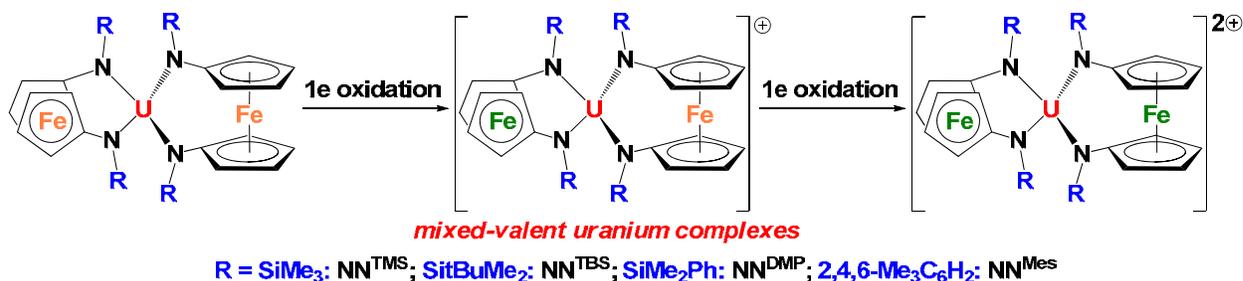


Figure 1. Bis(ferrocene diamide) complexes of uranium.

The compounds shown in Figure 1 were characterized by nuclear magnetic resonance, electrochemistry, optical and vibrational spectroscopy, as well as crystallography and magnetometry.

2. *Arene-bridged diuranium complexes* constitute a general bonding motif for low-valent organouranium compounds featuring benzene/toluene, naphthalene, biphenyl, cycloheptatrienyl, or cyclooctatetraene, as the bridging arene ligand. Our work with [(NN<sup>TBS</sup>)U]<sub>2</sub>(η<sup>6</sup>-toluene) inspired a separate project with group 3 metal complexes, namely the reduction of metal iodides, (NN<sup>TBS</sup>)MI(THF)<sub>2</sub>, with KC<sub>8</sub> in the presence of aromatic hydrocarbons. While the isolation of inverse sandwiches of naphthalene and anthracene was reminiscent of previously reported yttrium and lutetium complexes, the reduction in the presence of non-fused aromatic hydrocarbons (biphenyl, terphenyl, 1,3,5-triphenylbenzene) gave surprising results (Figure 2) and indicate an analogy with known arene-bridged uranium complexes. DFT calculations indicate that HOMO and HOMO-1 of the tetra-anionic arene group 3 metal complexes are high-lying π orbitals mixed with empty metal d or f orbitals and that a significant degree of covalency was caused by this mixing.

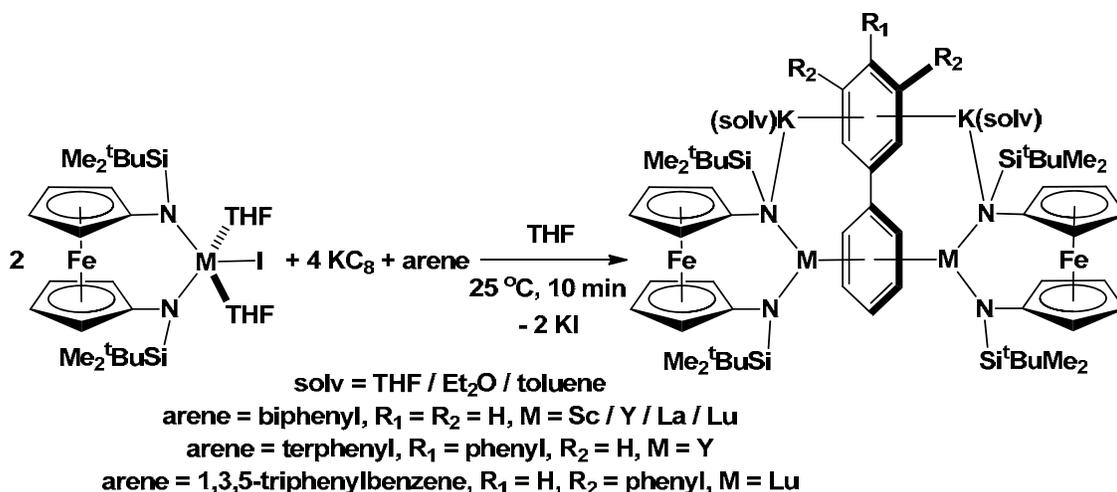


Figure 2. Synthesis of quadruply reduced biphenyl complexes of group 3 metals.

The high degree of covalency of the tetraanionic biphenyl complexes (Figure 2) together with a report that arene-bridged polyuranium clusters can exhibit single molecule magnet behaviour indicate that arene-bridged diuranium and paramagnetic dilanthanide complexes supported by 1,1'-ferrocene diamides are good candidates for single molecule magnets.

#### Science objectives for 2013-2015:

- *Importance of f orbitals in determining interactions between iron and uranium in bis(1,1'-ferrocene diamide) complexes.* We will continue to study the electronic communication between iron and uranium in ferrocene complexes in order to develop new catalytic systems and reactivity.
- *Inverse sandwiches of arene-bridged diuranium and paramagnetic lanthanides.* We propose to expand our studies on the reactivity of a diuranium toluene-bridged complex supported by a ferrocene diamide ligand reported by our group. In addition, a unique example of a quadruply reduced biphenyl-bridged group 3 dimetal complex offers new opportunities to develop single-molecule magnets based on uranium and paramagnetic lanthanides.

#### Publications supported by this project 2009-2011

1. **Redox Processes of 1,1'-Diamidoferrocene Uranium(IV) Complexes.** Duhović, Selma; Diaconescu, Paula L. **2013**, manuscript in preparation.
2. **Electronic Communication in Bis(1,1'-Diamidoferrocene) Uranium Complexes.** Duhović, Selma; Khan, Saeed I.; Diaconescu, Paula L. **2013**, manuscript in preparation.
3. **Synthesis and Characterization of Paramagnetic Lanthanide Benzyl Complexes.** Huang, Wenliang; Upton, Brianna M.; Khan, Saeed I.; Diaconescu, Paula L. *Organometallics* **2013**, DOI: 10.1021/om3010433.
4. **A six-carbon 10 $\pi$ -electron aromatic system supported by group 3 metals.** Huang, Wenliang; Dulong, Florian; Wu, Tianpin; Khan, Saeed I.; Miller, Jeffrey T.; Cantat, Thibault; Diaconescu, Paula L. *Nat. Commun.* **2013**, *4*, 1448.
5. **An Experimental and Computational Study of 1,1'-Ferrocene Diamines.** Duhović, Selma; Diaconescu, Paula L. *Polyhedron* **2013**, Werner Special Issue, DOI: 10.1016/j.poly.2012.08.063.
6. **Synthesis of symmetrically and unsymmetrically 3,5-dimethylbenzyl-substituted 1,1'-ferrocene diamines.** Lee, Jason A.; Williams, Bryan N.; Ogilby, Kevin R.; Miller, Kevin L.; Diaconescu, Paula L. *J. Organomet. Chem.* **2011**, *696* (25), 4090-4094.
7. **Molecular quadrangle formation from a diuranium  $\mu$ - $\eta^6$ ,  $\eta^6$ -toluene complex.** Monreal, Marisa J.; Khan, Saeed I.; Kiplinger, Jacqueline L.; Diaconescu, Paula L. *Chem. Commun.* **2011**, *47*, 9119-9121.

## 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 solids/nanoparticles. The expected impact is a predictive insight into hydrolysis reactions in general and a specific capability for chemistries related to reprocessing spent nuclear fuel and radionuclide migration in the environment.

Significant achievements during 2011-2013: Two discrete Th oligomeric units were isolated at ANL, a hexamer and an octamer. The highly charged hexameric unit  $[\text{Th}_6(\text{OH})_4\text{O}_4]^{12+}$ , was isolated with 12 carboxylate ligands ( $\text{RCO}_2^-$ ,  $\text{R} = \text{H}, \text{CH}_3, \text{CH}_3\text{Cl}$ ) decorating the surface. Density functional theory (DFT) calculations were used to determine the location of the four  $\mu_3$ -hydroxo and four  $\mu_3$ -oxo bridges (Figure 1). The protons are located in a tetrahedral arrangement on the faces of the cluster core, to minimize the interactions of the additional positive charges. The DFT calculations were used to assign the experimental Raman and proton NMR spectra. The average water complexation energies, the gas phase, the aqueous and DMSO acidities were predicted and the Th clusters are found to be mild to strong acids in gas phase with some acidities in the range of 250 to 270 kcal/mol yet they behave as weak acids in solution. The acidities of the model  $\text{Th}_6(\text{OH})_4\text{O}_4\text{O}_6$  complex have been calculated and these complexes are predicted to be very strong gas phase acids.

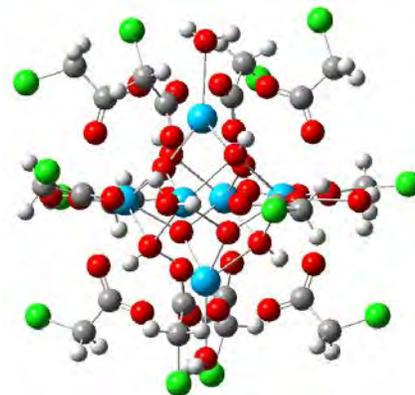


Figure 1. Optimized DFT structure of  $\text{Th}_6(\text{OH})_4\text{O}_4(\text{H}_2\text{O})_6(\text{ClCH}_2\text{COO})_{12}$

The highly charged octamers that were isolated at ANL contain an octanuclear core,  $[\text{Th}_8\text{O}_4(\text{OH})_8]^{16+}$ , built from eight Th(IV) atoms (four Th in a plane and two up and two down) linked by four “inner”  $\mu_3$ -O and eight “outer”  $\mu_2$ -OH groups. The core units are neutralized by eight ligating selenate anions, the structures differing primarily by selenate linkages and number of associated waters. DFT calculations were performed to predict the geometries, vibrational frequencies, and relative energies of different structures. Details of the calculated structures are in good agreement with experiment and the calculated frequencies were used to assign the experimental Raman spectra. Based on an analysis of the DFT results, the compound  $\text{Th}_8\text{O}_8(\text{OH})_4(\text{SeO}_4)_6$  was predicted to be a strong gas phase acid but is reduced to a weak acid in aqueous solution. Of the species studied computationally, the dication  $\text{Th}_8\text{O}_6(\text{OH})_6(\text{SeO}_4)_6^{2+}$

is predicted to be the most stable in aqueous solution at 298 K followed by the monocation  $\text{Th}_8\text{O}_7(\text{OH})_5(\text{SeO}_4)_6^+$ .

The condensation of  $\text{ThO}_2$  to form  $(\text{ThO}_2)_n$  nanoclusters for up to  $n = 6$  have been calculated as have the initial hydrolysis reactions of the clusters. The heats of formation of the clusters have been calculated based on normalized clustering energies and the experimental heat of formation of  $\text{ThO}_2$ . These are first reliable thermodynamic predictions for these species. The clustering energies converge more slowly to the bulk value than do the transition metal oxides. The average water binding energy for physisorption is  $\sim 18$  kcal/mol for thorium oxide clusters which provides the first good estimate for the physisorption energy of water onto thorium oxide surfaces. Calculations at the DFT and correlated molecular orbital theory (CCSD(T)) levels have been used to predict the structures, infrared spectra, and energetics of  $\text{Th}_x\text{O}_y$  clusters and  $\text{Th}_x\text{F}_y$  clusters, to assign the IR spectra measured in rare gas matrices. This provides a benchmark of the current methods as well as determining the structures of species with novel bonding. The potential energy surfaces for the and the reactions of  $\text{CH}_3\text{OH}$  with lanthanides and thorium have been calculated to assign the IR spectra measured in rare gas matrices and provide details on the reaction intermediates and transition states.

#### Science objectives for 2013-2015:

- 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.
- Determine the primary condensation reactions available to hydrolyzed actinides as they undergo initial oligomer formation. How does the  $\text{An}^{n+}(\text{H}_2\text{O})_m$  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 2011-2013

1. "Reactions of Late Lanthanide Atoms and Methanol in Solid Argon: A Matrix Isolation Infrared Spectroscopic and Theoretical Study," Y. Gong, L. Andrews, M. Chen, and D. A. Dixon, *J. Phys. Chem. A*, **2011**, *115*, 14581–14592. DOI: 10.1021/jp209135a
2. "Matrix Infrared Spectra and Predicted Properties of Thorium Oxide Species:  $\text{ThO}_x$  and  $\text{Th}_2\text{O}_y$ ," L. Andrews, Y. Gong, B. Liang, V. E. Jackson, R. Flamerich, S. Li, and D. A. Dixon, *J. Phys. Chem. A*, **2011**, *115*, 14407–1441. DOI: 10.1021/jp208926m
3. "Thorium(IV) molecular clusters with a hexanuclear core," K. E. Knope, R. E. Wilson, M. Vasiliu, D. A. Dixon, and L. Soderholm, *Inorg. Chem.*, **2011**, *50*, 9696-9704. DOI: 10.1021/ic2014946
4. "Thorium(IV)-Selenate Clusters containing an Octanuclear Th(IV) Hydroxide/Oxide Core," K. E. Knope, M. Vasiliu, D. A. Dixon, and L. Soderholm, *Inorg. Chem.* **2012**, *51*, 4239-4249. DOI: 10.1021/ic202706s
5. "Spectroscopic and Energetic Properties of Thorium(IV) Molecular Clusters with a Hexanuclear Core," M. Vasiliu, K. E. Knope, L. Soderholm and D. A. Dixon, *J. Phys. Chem. A*, **2012**, *116*, 6917–6926. DOI: 10.1021/jp303493t
6. "Methane to Methanol Conversion Induced by Thorium Oxide through the  $\text{CH}_3\text{Th}(\text{O})\text{H}$  Intermediate in Solid Argon," Y. Gong, L. Andrews, V. E. Jackson, and D. A. Dixon, *Inorg. Chem.* **2012**, *51*, 11055-11060. DOI: 10.1021/ic301595h

## Emergent Behavior via Hierarchical Structure in Solvent Extraction Organic Phases

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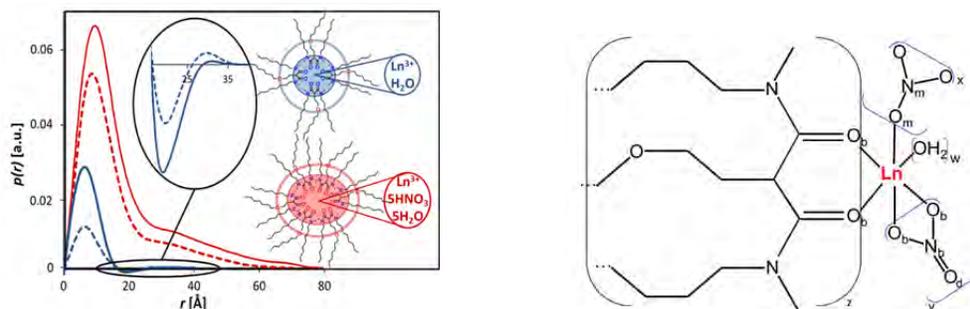
Overall research goals: Hierarchical structures, extending from molecular associations to nano-scale reverse micelles and their mesoscopic association into even larger aggregates, comprise the complex morphologies in solvent extraction organic phases. Yet, despite this rich structural landscape, research into the macroscopic behavior of solvent extraction systems is tethered largely to the structures of metal-extractant complexes, where extractant molecules are thought of as organic soluble ligands. This approach fails to explain much of the complex and dynamic properties of solvent extraction systems.

This research is not restricted to these small structural scales, but seeks to understand solvent extraction as a soft-matter ‘surfactant-in-oil’ system containing metal ions, where the structural hierarchies from the molecular through the nano- and meso-scales are interconnected and affect the key extractive and physical properties. We strive to understand how the structural architectures seen in solvent extraction organic phases link together to give emergent system behavior.

Significant achievements during 2011-2013:

- By incorporating recent techniques for small-angle X-ray scattering data interpretation (namely the Generalized Indirect Fourier Transform – GIFT – method) into the project we have further developed our understanding of the fundamental origins of ‘third phase formation’. For more than a decade, third phase formation was understood by the accepted ‘Baxter model for hard sticky spheres’, where small reverse micelle aggregates of constant size and shape interact with increasing potential until they are said to spontaneously condense into the separate third phase. Our studies have shown that the interactions produced by extraction cause the small reverse micelles of approximately globular shape to assemble into meso-scale structures of increasing curvature until third phase formation is reached. This model is more in line with current understanding of cloud-point behaviour in a variety of soft matter systems and explains the structured nature of the third phase that was unaccounted for in the previous model.
- We have studied how pH affects Ce(III) extraction and the hierarchical structure of reverse micelles in an organic phase consisting a malonamide extractant in dodecane. Acid significantly increased the water content of the organic phase, swelling the reverse micelles to produce a ‘water-in-oil microemulsion’. Metal coordination in these swollen hydrated structures is also different compared to the relatively ‘dry’ aggregates formed in the neutral system. These hydrated, swollen nano-scale environments are attributed to the increased extraction efficiency produced by the presence of acid.
- Trends in lanthanide(III) coordination were investigated within the nano-confined solvation environments offered by reverse micelles formed with malonamide amphiphiles in n-heptane. Structural aspects of the Ln(III) complex formation and the RM morphology were obtained by use of XAS (X-ray absorption spectroscopy) and SAXS (small-angle X-ray scattering) and hydration numbers for the Eu species were measured using TRLIFS (time-resolved laser-induced fluorescence spectroscopy). The picture that emerges from a system-wide perspective of the Ln-O interatomic distances and number of coordinating oxygen atoms for the extracted complexes of

Ln(III) in the first half of the series is that they are different from those in the second half of the series: the number of coordinating oxygen atoms decrease from 9O for early lanthanides to 8O for the late ones, a trend consistent with the lanthanide contraction. These findings showed that the coordination chemistry of lanthanides within nanoconfined environments is neither equivalent to the solid nor bulk solution behaviors.



Left:  $P(r)$  functions from [1]. Neutral system reverse micelles were significantly smaller (blue) than the acidic (red). Dotted lines for no metal, solid lines for organic phase containing  $Tb^{III}$ . Inset shows high- $r$  positive and negative regions in neutral system, indicative of reverse micelles with 'core-shell' character.

Right: General view of  $Ln^{III}$  coordination environment in complexes formed within the reverse micelle architecture.[1] The total O CN is given as the sum:  $w + x + 2y + 2z$ . This depended on both the nature of the reverse micelle, shown in the left-hand figure, as well as the type of lanthanide(III) ion.

#### Science objectives for 2013-2015:

Continuing on from our work in 2011-2013, we plan to reach a more comprehensive understanding of how the physical parameters in solvent extraction systems influence the hierarchical structure of organic phases, and how this in turn influences the separation properties. A major thrust toward this goal involves investigating how mixtures of different extractants change the coordination and aggregated structures in the organic phase and how this is connected to the macroscopic behavior. Particularly in this regard, we will look at the phenomena known as *synergism* and *antagonism* that describe the enhancing or diminishing effect on the extractive properties brought about by the mixtures. This concept is exploited in many modern solvent extraction systems, though the fundamental origins yet remain unclear.

#### Resulting Publications for 2011-2013:

1. Ellis, R. J.; Meridiano, Y.; Chiarizia, R.; Berthon, L.; Muller, J.; Couston, L.; Antonio, M. R. Periodic Behavior of Lanthanide Coordination within Reverse Micelles. *Chem.--Eur. J.* **2013**, *19*, 2663.
2. Ellis, R. J.; Audras, M.; Antonio, M. R. Mesoscopic Aspects of Phase Transitions in a Solvent Extraction System. *Langmuir* **2012**, *28*, 15498.
3. Ellis, R. J.; Antonio, M. R. Coordination Structures and Supramolecular Architectures in a Cerium(III)-Malonamide Solvent Extraction System. *Langmuir* **2012**, *28*, 5987.
4. Ellis, R. J.; Antonio, M. R. Redox chemistry of third phases formed in the cerium/nitric acid/malonamide-*n*-dodecane solvent extraction system. *ChemPluschem* **2012**, *77*, 41.
5. Ellis, R. J.; D'Amico, L.; Chiarizia, R.; Antonio, M. R. Solvent Extraction of Cerium(III) Using an Aliphatic Malonamide: The Role of Acid in Organic Phase Behaviors. *Sep. Sci. Technol.* **2012**, *47*, 2007.

## Fundamental Chemistry of Actinide Complexes Containing An–N, An–O, and An–S Bonds

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Postdoctoral Students: Ming Fang, Joy H. Farnaby

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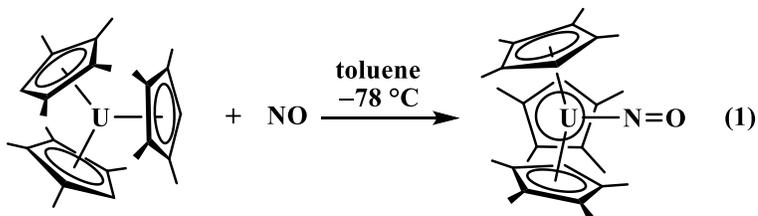
Email: [wevans@uci.edu](mailto:wevans@uci.edu); Web: <http://www.chem.uci.edu/people/faculty/wevans/>

**Overall Research Goals:** The objective of this research is to expand the knowledge of actinide chemistry to provide fundamental information on actinide metal-ligand bonding that may be useful in the development of advanced nuclear fuel cycles. In addition, this research provides training for graduate students in the chemistry of the f orbital metals, the lanthanides and actinides. Recent studies of the reaction chemistry of uranium and thorium have shown that surprising new structures and reactivity patterns can be exhibited from well-established classes of actinide complexes, some of which have been known for decades. These studies indicate that further expansion is possible so that a wider range of actinide chemistry is available to form a better basis for developing nuclear energy.

**Significant Achievements during 2011-2013:** Only two of the results [1-7] are described here.

**1. Radical Chemistry.** The radical chemistry of well-defined organoactinide complexes is being studied to obtain more information about the reactivity of actinide-element bonds with radicals. Examination of NO as a radical reagent provided the first  $(\text{NO})^{1-}$  nitrosyl complex of any f element, lanthanide or actinide, namely  $(\text{C}_5\text{Me}_4\text{H})_3\text{U}(\text{NO})$ , eq 1 [3]. Since the  $(\text{NO})^{1-}$  ligand is a pseudohalide and the f elements form many types of complexes with true halides, it was surprising that this ligand had never before been found in complexes of these metals.

$(\text{C}_5\text{Me}_4\text{H})_3\text{U}(\text{NO})$  proved to be unusual since it had a linear U–N–O linkage characteristic of  $(\text{NO})^{1+}$ , but the N–O bond length was in the range characteristic of a double bond of an  $(\text{N}=\text{O})^{1-}$  ligand which classically forms bent MNO linkages. Moreover, the U–N bond was short

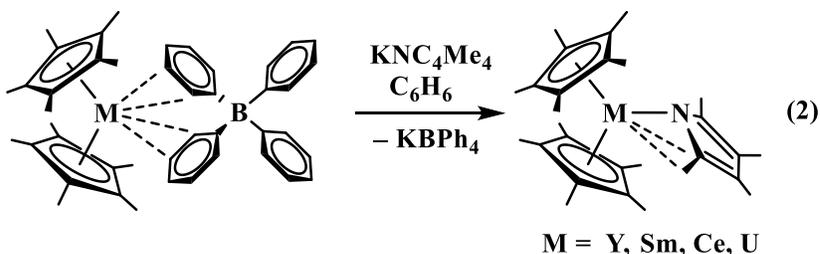


and more consistent with a U=N double bond which does not match either of the conventional models for binding NO to metals. This complex, therefore, shows a new aspect of actinide-element multiple bonding, and also expands NO chemistry in general by revealing a new type of metal–NO connection. Since reactions similar to eq 1 with  $(\text{C}_5\text{Me}_5)_3\text{U}$  and  $(\text{C}_5\text{Me}_4\text{SiMe}_3)_3\text{U}$  did not provide isolable nitrosyl complexes, this result emphasizes how subtle changes in ancillary ligands can lead to new results in uranium chemistry.

### 2. Lanthanide vs Actinide Comparisons with the Heterocyclic Nitrogen Ligand, Tetramethylpyrrolyl.

The  $(\text{NC}_4\text{Me}_4)^{1-}$  anion (TMN) forms a homologous series of organometallic complexes,  $(\text{C}_5\text{Me}_5)_2\text{M}(\text{NC}_4\text{Me}_4)$  (M = U, La, Ce, Sm, Y), that allows comparison of lanthanide versus actinide binding with a ligand that displays an unusual binding mode involving M–N bonds [7]. Although the  $(\text{C}_5\text{Me}_5)^{1-}$  ligands in these complexes display their conventional pentahapto binding, the TMN ligands coordinate asymmetrically through the nitrogen with one ring carbon and its attached methyl also oriented toward the metal, eq 2. Crystals in two different space groups were obtained for U and these had more than one crystallographically independent molecule in each unit cell. Yttrium also formed crystals in two different space groups. In one case, two crystals picked from the same mother liquor gave

significantly different metrical parameters for the TMN–metal interaction. Overall, a total of twelve crystallographically independent variants of TMN–metal structures were identified in this study. This revealed the extensive variation possible with this secondary bonding and demonstrated that there is considerable structural flexibility with both lanthanides and actinides.



#### Science Objectives for 2013-2015:

- Explore the properties and reactivity of the first crystallographically characterized molecular  $U^{2+}$  complex.
- Examine the use of solvent-free reactions of actinide complexes with gases to improve selectivity over solution-phase syntheses.
- Study thermal conversion of molecular species to solid-state materials of interest such as uranium nitride (UN).
- Explore the chemistry of actinide–element bonds with radical species in well-defined molecular environments.

#### Publications Supported by this Project in 2011-2013:

1. "Insertion, Isomerization, and Cascade Reactivity of the Tethered Silylalkyl Uranium Metallocene ( $\eta^5$ - $C_3Me_4SiMe_2CH_2$ - $\kappa C$ ) $_2U$ " Nathan A. Siladke, Joseph W. Ziller, and William J. Evans, *J. Am. Chem. Soc.* **2011**, *133*, 3507-3516. **DOI:** 10.1021/ja109491k
2. "Unprecedented Bending and Rearrangement of f-Element Sandwich Complexes Induced by Superbulky Cyclooctatetraenide Ligands" Volker Lorenz, Benjamin M. Schmiege, Cristian G. Hrib, Joseph W. Ziller, Anja Edelmann, Steffen Blaurock, William J. Evans, and Frank T. Edelmann, *J. Am. Chem. Soc.* **2011**, *133*, 1257-1259. **DOI:** 10.1021/ja109604t
3. "Synthesis, Structure, and Magnetism of an f Element Nitrosyl Complex,  $(C_5Me_4H)_3U(NO)$ " Nathan A. Siladke, Katie R. Meihaus, Joseph W. Ziller, Ming Fang, Philipp Furche, Jeffrey R. Long, and William J. Evans, *J. Am. Chem. Soc.* **2012**, *134*, 1243-1249. **DOI:** 10.1021/ja2096128
4. "Uranium and Thorium Hydride Complexes as Multielectron Reductants: A Combined Neutron Diffraction and Quantum Chemical Study" Daniel J. Grant, Timothy J. Stewart, Robert Bau, Kevin A. Miller, Sax A. Mason, Matthias Gutmann, Laura Gagliardi, and William J. Evans, *Inorg. Chem.* **2012**, *51*, 3613-3624. **DOI:** 10.1021/ic202503h
5. "Synthesis and Insertion Chemistry of Mixed Tether Uranium Metallocene Complexes" Nathan A. Siladke, Jennifer LeDuc, Joseph W. Ziller, and William J. Evans, *Chemistry, A European Journal* **2012**, *18*, 14820-14827. **DOI:** 10.1002/chem.201201908
6. "Synthesis and  $CO_2$  Insertion Reactivity of Allyl Uranium Metallocene Complexes" Christopher L. Webster, Joseph W. Ziller, and William J. Evans, *Organometallics* **2012**, *31*, 7191-7197. **DOI:** 10.1021/om3007536
7. "DFT and X-ray Analysis of the Structural Variability in  $\eta^5, \eta^5, \eta^1$ -Tris(ring) Rare Earth/Actinide Tetramethylpyrrolyl Complexes,  $(C_5Me_5)_2M(NC_4Me_4)$ " Christopher L. Webster, Jefferson E. Bates, Ming Fang, Joseph W. Ziller, Philipp Furche, and William J. Evans *Inorganic Chemistry* **2013**, *52*, published on line but waiting for completion of the Inorganic Chemistry Forum on "Aspects of Inorganic Chemistry Related to Nuclear Energy." **DOI:** 10.1021/ic300905r

## Binding Anions Selectively with Modular Triazolophanes and Releasing them with Light

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

Overall research goals: The objective of this project is to synthesize macrocycles and foldamers for binding large oxyanions and to release them using light-based stimuli.

Significant achievements during 2011-2013: Three significant results have emerged:

### 1. Conformational Space of Receptors with an Aliphatic CH Donor

The small conformational space that is associated with a pre-organized receptor is highlighted in a study where we observed entropy-enthalpy compensation. Swapping a phenylene CH donor in the original tetraphenylene triazolophane for a propylene CH donor (**Figure 1**) weakens anion binding on enthalpic grounds but the receptor's greater flexibility partially offsets this on entropic grounds. This claim would have been impossible to investigate, let alone support, without the benefit of computations. Therefore, this work serves to highlight the advantage of conformational simplicity provided by the rigid triazolophanes, and to underscore again the essential role of theory. These two features *together* distinguish our approach from the efforts of others; and we intend to continue this tradition in this proposal.



Figure 1. Left: Two types of CH donors (blue) are compared and (right) the quantitative understanding of multiple equilibria were ascertained.

### 2. Naphthalimide Building Blocks

We have employed a naphthalimide building block (blue in **Figure 2**) and imbued it with a new pattern of substitution that will enable the macrocyclization of larger receptors. Furthermore, we were the first to identify and exploit the fact that the naphthalimide offers an activated pair of CH hydrogen bond donors that we describe as isosteric to urea. The design of this receptor, **Figure 2**, also takes advantage of the pre-organization identified in prior work by using more robust amide NH groups. We found that the naphthalimide helps the receptor to bind anions because the CH H-bond donors are activated by the electron-withdrawing imide functionality. This fact, once again, was verified with the aid of computations. We will capitalize on this naphthalimide unit for selective binding to polyatomic anions in the expanded triazolophanes.

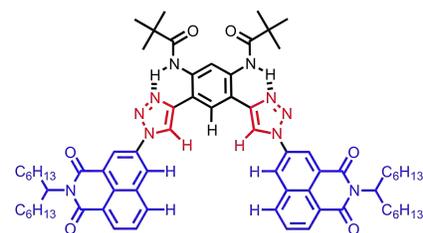


Figure 2. This receptor employs urea-like naphthalimide (blue) and amide pre-organization (black)

### 3. Polyatomic Anions – Cyanide

With the focus of this proposal on polyatomic anions, CoPI Raghavachari took the opportunity to look at the binding of the diatomic cyanide ion,  $\text{CN}^-$  to a tetraphenylene triazolophane (**Figure 3**). As a testament to the *predictive* power of theory, the strong binding affinity for cyanide with the rigid triazolophane receptor was subsequently confirmed by experiment. Theoretical calculations showed that in the gas phase cyanide has a planar minimum energy structure with a binding energy almost as strong as chloride (**Figure 3**); this prediction was shown to be true from solution phase studies where the experimentally determined binding free energies (in dichloromethane) for both ions was  $-36.8 \pm 0.5 \text{ kJ mol}^{-1}$ . This outcome is different from expectations based on chemical intuition that the more basic  $\text{CN}^-$  should have been more tightly bound than the less basic  $\text{Cl}^-$ . Second, the computational results show low-energy pathways for in-plane and out-of-plane rotations of the cyanide in the cavity, opening up the chance for fluxional behavior not previously seen in anion complexes.

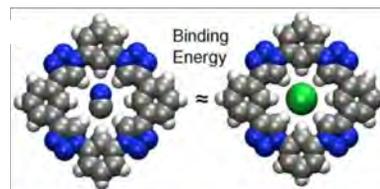


Figure 3. Cyanide binds as well as chloride

#### Science objectives for 2013-2015:

- Optimize photoactive foldamers to bind and release anions with better performance, i.e., improve upon the 9:1 change in anion binding efficiency.
- Use foldamers to bind  $\text{Cl}^-$  in aqueous solutions.
- Expand the computer aided design approach to prepare and understand receptors for the capture of larger polyatomic anions, e.g., bifluoride ( $\text{HF}_2^-$ ), azide ( $\text{N}_3^-$ ), perchlorate ( $\text{ClO}_4^-$ ) and perhennate ( $\text{ReO}_4^-$ )

#### Publications supported by this project 2011-2013

1. Hua, Y.; Ramabhadran, R. O.; Uduehi, E. O.; Karty, J. A.; Raghavachari, K.; Flood, A. H., Aromatic and aliphatic CH hydrogen bonds fight for chloride while competing alongside ion pairing within triazolophanes, *Chem. Eur. J.* **2011**, *17*, 312-321  
<http://onlinelibrary.wiley.com/doi/10.1002/chem.201002340/abstract>
2. Zahran, E. M.; Hua, Y.; Lee, S.; Flood, A. H.; Bachas, L. G., Ion-selective electrodes based on a pyridyl-containing triazolophane: Manipulating halide selectivity by mixing dipole-promoted cooperativity with hydrogen bonding, *Anal. Chem.* **2011**, *83*, 3455-3461. <http://dx.doi.org/10.1021/ac200052q>
3. Ramabhadran, R. O.; Hua, Y.; Flood, A. H.; Raghavachari, K., From Atomic to Molecular Anions: A Neutral Receptor Captures Cyanide using Strong C–H Hydrogen Bonds, *Chem. Eur. J.* **2011**, *17*, 9123-9129. <http://onlinelibrary.wiley.com/doi/10.1002/chem.201002340/pdf>
4. McDonald, K. P.; Ramabhadran, R. O.; Lee, S.; Raghavachari, K.; Flood, A. H., Polarized Naphthalimide CH Donors Enhance  $\text{Cl}^-$  Binding Within an Aryl-Triazole Receptor, *Org. Lett.* **2011**, *13*, 6260-6263. <http://pubs.acs.org/doi/abs/10.1021/ol202729z>
5. McDonald, K. P.; Hua, Y.; Lee, S.; Flood, A. H., Shape Persistence Delivers Lock-and-Key Chloride Binding in Triazolophanes, *Chem. Commun.* **2012**  
<http://pubs.rsc.org/en/Content/ArticleLanding/2012/CC/C2CC17459F>
6. Lee, S.; Flood, A. H., Photoresponsive receptors for binding and releasing anions, *J. Phys. Org. Chem.* **2013**, *26*, 79-86. **Cover Art** <http://onlinelibrary.wiley.com/doi/10.1002/poc.2973/abstract>

**SISGR: Fundamental chemistry of technetium-99 incorporated into metal oxide, phosphate and sulfide materials: towards stabilization of low valent technetium.**

Lynn C. Francesconi, Principal Investigator

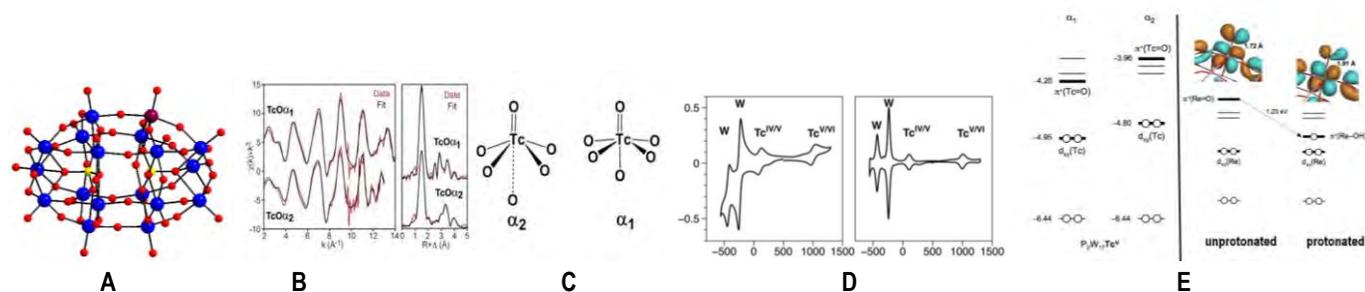
Email: [lfrances@hunter.cuny.edu](mailto:lfrances@hunter.cuny.edu)

**Overall SISGR Research Goals:**  $^{99}\text{Tc}$  ( $\beta_{\text{max}}$ : 293.7 keV, half-life:  $2.1 \times 10^5$  years) is a major product of U-235 fission in nuclear reactors and large amounts of  $^{99}\text{Tc}$ , formed during early plutonium production activities, are present in radioactive waste stored in underground tanks and in the environment. The complex redox activity of  $^{99}\text{Tc}$  poses problems for closing the fuel cycle, remediation of waste and removal from environment. The overall research goals of this SISGR is to elicit molecular level understanding of the chemical bonding, speciation, and redox stability of  $^{99}\text{Tc}$  incorporated into inorganic materials. This information should be useful in controlling the redox chemistry of  $^{99}\text{Tc}$  and in identification of separation strategies and stable waste-forms for  $^{99}\text{Tc}$  based on the fundamental chemistry of the element.

**SISGR Team:** The SISGR team is investigating  $^{99}\text{Tc}$  containing materials that range in size from molecules (nanometer-sized polyoxometalates) to sulfide, halide, phosphate, and carbonate solid-state materials. Lynn Francesconi, PI (Hunter College), Silvia Jurisson, co-PI (University of Missouri, Columbia), Ken Czerwinski, co-PI (UNLV), Wayne Lukens, collaborator (LBNL)

**Francesconi (Hunter College) Research Goals:** Polyoxometalates (POMs) are excellent models for inorganic oxides because they possess well characterized “defect” and surface binding sites. 1. Synthesis and analytical/inorganic/radiochemistry of Tc POMs where Tc is incorporated into these sites can inform Tc oxidation state stability, surface movement and coordination chemistry on the molecular level. 2. Identification of new strategies for reduction of  $\text{TcO}_4^-$ , stabilization of the low valent Tc and separation of Tc.

**Significant Achievements during 2011 – 2013:**

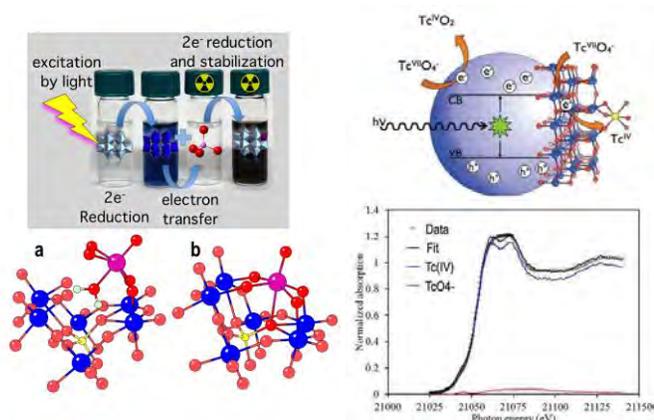


**Figure 1. Aqueous soluble  $[\text{TcVO}(\alpha_2/\alpha_1\text{-P}_2\text{W}_{17}\text{O}_{61})]^{7-}$ :** **A:**  $\text{Tc}^{\text{VO}}(\alpha_1)$ : The  $\text{Tc}^{\text{V}}$  is substituted in the “belt” region (maroon). **B:** EXAFS data for  $\text{Tc}^{\text{VO}}(\alpha_1)$  and  $\text{Tc}^{\text{VO}}(\alpha_2)$  show that the  $\text{Tc}^{\text{V}}$  in  $\text{Tc}^{\text{VO}}(\alpha_1)$  is pulled into the W framework while the  $\text{Tc}^{\text{VO}}(\alpha_2)$  shows the Tc in a coordination sphere where the Tc-phosphate “bond” is long and similar to metal ions in the lacunary framework (**C**). The coordination environment of  $\text{Tc}^{\text{VO}}(\alpha_1)$  is consistent with the ease of reduction and pH independence of the  $\text{Tc}^{\text{V}}-\text{Tc}^{\text{IV}}$  redox process. Electrochemistry data for  $\text{Tc}^{\text{VO}}(\alpha_1)$  are shown in **D**. DFT calculations are consistent with electrochemistry (**E**). The  $\text{Tc}^{\text{VO}}\text{-}\alpha_1$  is not protonated upon reduction, but the  $\text{M}^{\text{VO}}\text{-}\alpha_2$  ( $\text{M}=\text{Tc, Re}$ ) and  $\text{Re}^{\text{VO}}\text{-}\alpha_1$  must undergo protonation upon reduction. Protonation would form a Tc-O single bond that is preferred for  $\text{Tc}^{\text{IV}}$ . The  $\text{M}^{\text{IV}}$  ( $\text{M}=\text{Tc, Re}$ ) species prefer octahedral M-O single bonds that would be formed upon protonation in the case of  $\text{M}^{\text{VO}}\text{-}\alpha_2$  ( $\text{M}=\text{Tc, Re}$ ) and  $\text{Re}^{\text{VO}}\text{-}\alpha_1$ .

**1. Electrochemistry and DFT calculations work in consort to understand the redox processes of  $\text{Tc}^{\text{VO}}$  complexes of Wells-Dawson POM isomers.** Electrochemistry as a function of pH shows that  $\text{M}^{\text{III}}$ ,  $\text{M}^{\text{IV}}$ ,  $\text{M}^{\text{V}}$  and  $\text{M}^{\text{VI}}$  ( $\text{M}=\text{Tc, Re}$ ) oxidation states are accessible. Tc derivatives are always more readily reduced than their Re analogs because the electrons added always occupy lower energy orbitals. The first Tc-like orbitals are very low in energy and cannot be completely depopulated resulting in a maximum oxidation state of VI. Tc is reduced more readily in the  $\alpha_1$  site as compared to the  $\alpha_2$  site due to the orientation of the internal phosphate positioning a basic oxygen in the vacancy.

DFT calculations are consistent with the electrochemistry as a function of pH: for all species, except the  $\text{Tc}^{\text{VO}}\text{-}\alpha_1$  species,  $\text{M}^{\text{V/IV}}$  reduction process must occur with protonation of the terminal  $\text{M}=\text{O}$  to render the  $\pi^*(\text{M}=\text{O})$  orbitals the LUMOs and accessible to the addition of electrons (Figure 1, E). These data are consistent with EXAFS and XANES data that reveal that the  $\text{Tc}^{\text{V}}$  is “pulled” into the  $\alpha_1$  framework, essentially forming a dative metal-metal bond with a framework W site. The disposition of Tc in the  $\alpha_1$  framework facilitates its reduction and the stabilization of lower Tc oxidation states. This study highlights the inequivalency of the  $\alpha_1$  and  $\alpha_2$  sites, and their impact on the chemical properties of incorporated Tc.

**2. Photoactivated reduction of  $TcO_4^-$  and incorporation of reduced Tc into the defect:** POMs can be photoactivated in the presence of 2-propanol to transfer electrons to  $^{99}TcO_4^-$ , and stabilize the reduced Tc. When the  $\alpha_2$ - $[P_2W_{17}O_{61}]^{10-}$  is employed, the reduced  $^{99}Tc$  is covalently incorporated into the  $\alpha_2$ - framework to form the  $^{99}Tc^V O$  species,  $Tc^V O-\alpha_2$ . This occurs via the formation of an intermediate species. EXAFS and XANES analysis and multinuclear NMR, show that the intermediate consists of a  $^{99}Tc(IV)$   $\alpha_2$ - species where the  $^{99}Tc(IV)$  is bound



**Figure 2. Reduction of  $TcO_4^-$  by photoactivation of the  $\alpha_2$ - $[P_2W_{17}O_{61}]^{10-}$  POM.** Top left: sequence of the reaction and colors. Bottom left: a. the  $Tc^{IV}-\alpha_2$  intermediate according to EXAFS and XANES data; b. the fully condensed  $Tc^V O-\alpha_2$  product. Top right: Cartoon illustrating photoactivated reduction of  $TcO_4^-$  to  $Tc(IV)$  by  $TiO_2$ . The  $Tc(IV)$  is either adsorbed to surface  $TiO_2$  or incorporated into defects. Bottom right: XANES spectrum and fit for  $TiO_2$  solid containing adsorbed or incorporated  $Tc(IV)$ . Data are fit to 95%  $Tc(IV)$  and 5%  $TcO_4^-$  remaining on solid.

to 2 of the 4 W-O oxygen atoms in the  $\alpha_2$ - $[P_2W_{17}O_{61}]^{10-}$  defect. This intermediate oxidizes and converts to the  $Tc^V O-\alpha_2$  product. The reduction and incorporation of  $^{99}TcO_4^-$  was monitored as a function of time using multinuclear NMR ( $^{31}P$ ,  $^{99}Tc$ ) and radio TLC ( $^{99}Tc$  and  $^{188}Re$ ). The process was further probed by the “step-wise” generation of reduced  $\alpha_2$ - through bulk electrolysis followed by the addition of  $^{99}TcO_4^-$ . The reduction and incorporation of  $ReO_4^-$ , as a non-radioactive surrogate for  $^{99}Tc$ , does not proceed through the intermediate species, and possesses faster kinetics to produce the  $Re^V O-\alpha_2$  product. This may be ascribed to the potential of  $ReO_4^-$  for expansion of coordination sphere to form a  $ReO_4^-$ :  $\alpha_2$  “complex” that may facilitate electron transfer to form  $Re^V O-\alpha_2$ . This study illustrates the differences between the chemistry of technetium and rhenium.

**3. Photoactivated reduction of  $TcO_4^-$  by solid-state  $TiO_2$  and separation from aqueous solution:** Keggin ions with no defect sites and solid-state  $TiO_2$  photocatalytically reduce  $TcO_4^-$  to  $Tc(IV)$ . In the latter

case, the  $Tc(IV)$  is adsorbed onto the  $TiO_2$  and can be separated. TEM with EDX analysis showed Tc present in the  $TiO_2$  solid. XANES analysis shows 95%  $Tc(IV)$  adsorbed to the  $TiO_2$  solid and 5% as  $TcO_4^-$ . EXAFS data is required so that we can determine if the  $Tc(IV)$  is present as isolated  $Tc(IV)$  adsorbed on  $TiO_2$ , as a surface precipitate, or incorporated into the  $TiO_2$  lattice defects ( $Tc(IV)$  replacing  $Ti(IV)$ ).

**Science Objectives:** 1. Investigate Tc bound to “surface” and multiple defect sites of POMs: stability, redox properties, surface dynamics. 2. a. Examination of the photochemical mechanism for the reduction of  $^{99}TcO_4^-$  by  $TiO_2$  and identify the mode of adsorption of the reduced  $Tc(IV)$  to the  $TiO_2$  surface. b. Identify new  $TiO_2$  materials that will facilitate optimal reduction of  $TcO_4^-$  and optimize adsorption of the reduced  $Tc(IV)$  and that will enhance photoreduction by visible light. c. Identify the  $Tc(IV)$  coordination environment and phases upon sintering the  $Tc(IV)/TiO_2$  materials.

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- Poineau, F.; Weck, P.F.; Burton-Pye, B.P.; Denden, I.; Kim, E.; Kerlin, W.; Maruk, A.; Kirakosyan, G.; German, K.E.; Fattahi, M.; Francesconi, L.C.; Sattelberger, A.P.; Czerwinski, K.R. “Reactivity of Pertechnetate in Sulfuric Acid: Technetium Sulfates Complexes Revealed by X-ray Absorption Spectroscopy and First Principles Calculations”, *Dalton Trans.*, **2013**, in press. DOI: 10.1039/C3DT32951H; website: <http://pubs.rsc.org/en/Content/ArticleLanding/2013/DT/c3dt32951h>
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- Radivojevic, I.; Bazzan, G.; Burton-Pye, B.P.; Ithisuphalap, K.; Saleh, R.; Durstock, M.F.; Francesconi, L.C.; Drain, C.M. “Zirconium(IV) and Hafnium(IV) Porphyrin and Phthalocyanine complexes as new dyes for solar cell devices” *J. Phys. Chem. C.*, **2012**, 116, 15867-15877. Dx.doi.org/10.1021/jp301853d
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- Burton-Pye, B.P.; Radivojevic, I.; McGregor, D.; Mbomekalle, I.M.; Lukens, W.W., Jr.; Francesconi, L.C. “Photoreduction of  $^{99}Tc$  pertechnetate by nanometer-sized metal oxides: new strategies for formation and sequestration of low-valent technetium”. *J. Amer. Chem. Soc.*, **2011**, 133 (46) 18802-18815. DOI: 10.1021/ja2060929

**SISGR: Fundamental chemistry of technetium-99 incorporated into metal oxide, phosphate and sulfide materials: towards stabilization of low valent technetium.**

Lynn C. Francesconi, Principal Investigator

Email: [lfrances@hunter.cuny.edu](mailto:lfrances@hunter.cuny.edu)

**University of Missouri**, participants: Dr. David Rotsch (August 2011-present), Graduate student: Kim Mason Reinig, Undergraduate students: Anna Taylor, Maggie Priebe.

**Jurisson (Missouri) Research Goals:** Provide an understanding of the features of metal sulfides and mixed metal oxides/ sulfides that promote reduction of  $\text{TcO}_4^-$  and incorporation of reduced Tc. Obtain an understanding of the molecular level structure and the stability of the  $^{99}\text{Tc}$  incorporated materials.

**Significant Achievements during 2011-2013:**

1. Iron sulfide appears to be a suitable material for the immobilization of  $\text{TcO}_4^-$  in groundwater. To further understand the immobilization process, solid supports of reduced Goethite, silica, and sand have been evaluated for retaining  $\text{TcO}_4^-$  under normal and reducing conditions. Reducing conditions (pre-treatment with  $\text{Na}_2\text{S}$ ) results in immobilization of pertechnetate on the Goethite under aerobic conditions at pH 7-8.

2. Reaction of  $\text{TcO}_4^-$  with olefinic acids in the presence of sulfide result in addition of sulfide across the double bond to form the mono and dithiolate organic acid analogues and their Tc(V) complexes with mono and dimercaptosuccinic acid; authentic samples of these Tc(V) complexes were prepared for comparison. EXAFS and XANES experiments were run on these samples; we are awaiting the results of the studies (Jeff Terry, ANL and IIT).

3. The Tc and Re chemistry with the tetradentate Schiff base ligand  $\text{sal}_2\text{ibn}$  ( $\alpha,\alpha'$ -[(1,1-dimethylethylene)dinitrilo]di-*o*-cresol) result in both mononuclear and dinuclear complexes of Re in oxidation states +5, +4 and +3, and mononuclear and dinuclear complexes of Tc in oxidation states +5 and +4. The dinuclear +4 Tc/Re complexes are quite unique ( $\mu$ -oxo and with capping halides) and the +5 mononuclear complex of Re with a coordinate NCS moiety renders the complex very stable (kinetically) based on NMR studies. This manuscript is currently in its final stages of writing and will be submitted soon.

**Science Objectives for 2013-2015:**

1. Continue studies on immobilization of pertechnetate under reducing conditions using Fe containing minerals and natural soils.

2. Initiate phosphinimine chemistry containing potential fluor molecules for selectivity for pertechnetate for potential applications in separations and sensing.

3. Initiate studies on the interaction of  $^{99}\text{TcO}_4^-$  with iron sulfide nanoparticles with high surface area. The higher surface area of the nanoparticles should provide better interactions with the pertechnetate.

**Publications:** Four meeting abstracts in 2012-2013 and several publications in preparation.

**UNLV**, UNLV Research Team: Bradley Childs, Maryline Ferrier, William Kerlin, Eric Johnstone, Frederic Poineau, Paul Forster, Ken Czerwinski

**Czerwinski (UNLV) Research Goals:**

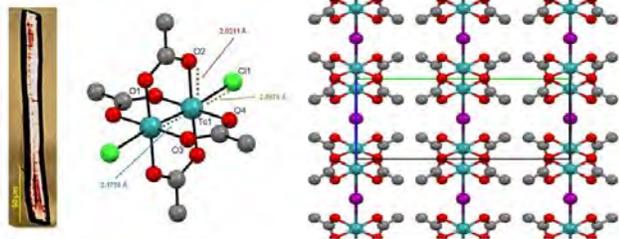
The overarching goal is to understand reaction mechanisms so synthesis conditions can be tailored for the production of specific low-valent Tc compounds. Hydrothermal synthesis focusing on halide and phosphate materials and thermal reactions for the production of low valent Tc compounds are performed. First principle modeling and simulations will be leveraged to enhance an understanding of the electronic structure and thermodynamic systematic of the solid-state prepared materials.

**Significant Achievements during 2011-2013**

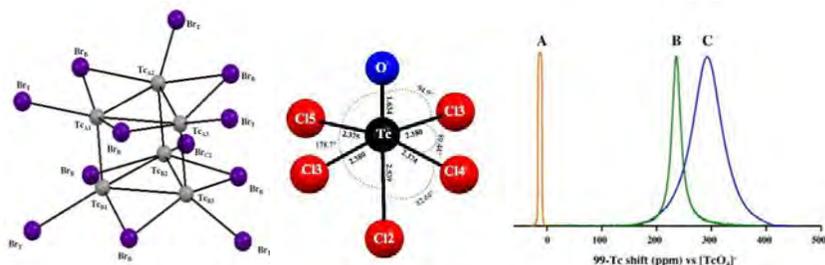
1. **Hydrothermal Synthesis:** Reactions of  $\text{TcO}_4^-$  with excess mono-carboxylic acids; glacial acetic acid, propanoic acid, benzoic acid, and halogen acids under an 30 - 70 atmosphere of hydrogen gas formed from sodium borohydride at 210 °C, 72 hrs, affords single crystals of penta(carboxylato) ditechneate(II, III) chains and tetraacetatodihalogen ditechneate(III,III) dimers with yields up to 75 %. The Tc-Tc bond distance slightly increases as the size of the carbon chain carboxylato group increases; 2.104 to 2.114 to 2.124 Å for acetato, propionate, and benzoate respectively. The difference in formation of the Tc-Tc (II, III) dimer polymer chain versus Tc-Tc (III, III) dimer molecular species is the addition of a halogen acid (HCl, HBr, and HI) at various molar ratios to  $\text{TcO}_4^-$ . All compounds synthesized under hydrothermal conditions show potential waste form application due to the insoluble nature in strong acids, water, and organic solvents.

**2. Thermal Reactions:** The compound  $\text{Na}[[\text{Tc}_6\text{Br}_{12}]_2\text{Br}]$  has been obtained from the decomposition of  $\text{TcBr}_4$

under vacuum in Pyrex ampoules at 450 °C. The stoichiometry of the compound has been confirmed by Energy Dispersive X-ray (EDX) spectroscopy and its structure determined by single crystal X-ray diffraction (SC-XRD). The compound contains a trigonal prismatic hexanuclear  $[\text{Tc}_6\text{Br}_{12}]$  cluster. The cluster is composed of two triangular  $\text{Tc}_3\text{Br}_6$  units linked by multiple Tc-Tc bonds. In the  $\text{Tc}_3\text{Br}_6$  unit, the average Tc-Tc distance (2.68 Å) is characteristic of Tc-Tc single bonds while the average Tc-Tc distance between the two triangular units (2.17 Å) is characteristic of  $\text{Tc}\equiv\text{Tc}$  triple bonds. The electronic structure of the  $[\text{Tc}_6\text{Br}_{12}]$  cluster was studied by first-principles calculations, which confirm the presence of single and triple Tc-Tc bonds in the cluster.



Crystal structure of tetraacetatodichloro ditechneum(III),  $\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$ . Left: Crystal packing of tetraacetatiodo ditechneum (II,III) polymer chains,  $\text{Tc}_2(-\text{O}_2\text{CCH}_3)_4\text{I}$ , viewed along the a-axis. Legend: Tc-turquoise, O-red, C-gray, I-purple, H removed for clarity



Left:  $\text{Tc}_6\text{Br}_{12}$  cluster: Tc: grey; Br: purple; Middle:  $\text{TcOCl}_5^-$  complex; Right:  $^{99}\text{Tc}$  NMR spectra obtained after dissolution of  $\text{NH}_4\text{TcO}_4$  in A) 15.6M  $\text{HNO}_3$ ; B) 13.87 M  $\text{HClO}_4$ ; C) 18M  $\text{H}_2\text{SO}_4$

Solvothermal and thermal reactions using red phosphorus and metal chloride species of elements that exist in both group 7 (Re, Mn) and period 5 (Mo, Ru) provide synthetic strategies that will be employed with Tc with the goal to achieve binary Tc phosphides.

Speciation of  $\text{Tc}^{\text{VII}}$  in  $\text{HClO}_4$  shows formation of pertechnetetic acid,

$\text{HTcO}_4$ , similar to the speciation in  $\text{H}_2\text{SO}_4$ . Dissolution of  $(\text{NH}_4)\text{TcO}_4$  in 12 M  $\text{HCl}$  at 0°C and careful precipitation with  $\text{KCl}$  results in crystals of  $\text{K}_2\text{TcOCl}_5$ . Crystallographic data is consistent with the DFT calculations.

### Science objectives for 2013-2015

The research will continue to examine hydrothermal and thermal reactions of technetium. It is expected efforts will focus on formation of iodide species and phosphorus reactions. The halide compounds produced will be used as starting agents in further reactions. The phosphorus reactions should produce a new range of technetium compounds, enhancing comparisons with neighboring elements.

### Publications (2011-2013) that cite this funding:

- Poineau, F.; Weck, P.F.; Burton-Pye, B.P.; Denden, I.; Kim, E.; Kerlin, W.; Maruk, A.; Kirakosyan, G.; German, K.E.; Fattahi, M.; Francesconi, L.C.; Sattelberger, A.P.; Czerwinski, K.R. "Reactivity of Pertechnetetic Acid in Sulfuric Acid: Technetium Sulfates Complexes Revealed by X-ray Absorption Spectroscopy and First Principles Calculations", *Dalton Trans.*, **2013**, in press. DOI: 10.1039/C3DT32951H; website: <http://pubs.rsc.org/en/Content/ArticleLanding/2013/DT/c3dt32951h>
- Poineau, F.; Burton-Pye, B.P.; Maruk, A.; Kirakosyan, G.; Denden, I.; Rego, D.B.; Johnstone, E.V.; Sattelberger, A.P.; Fattahi, M.; Francesconi, L.C.; German, K.E.; Czerwinski, K.R. "On the Nature of Heptavalent Technetium in Concentrated Nitric and Perchloric Acid", *Inorganica Chimica Acta*, **2013**, available on-line Dec 29, 2012; website: <http://dx.doi.org/10.1016/j.ica.2012.12.028>
- Poineau, F., Malliakas, C.D., Weck, P.F., Scott, B.L., Johnstone, E.V., Forster, P.M., Kim, E., Kanatzidis, M. G., Czerwinski, K.R., Sattelberger, A.P.: "Technetium Dichloride: A New Binary Halide Containing Metal-Metal Multiple Bonds" *Journ. Amer.Chem. Soc.* **2011** 133(23), 8814-8817.
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- Kerlin, W., Poineau, F., Czerwinski, K.R., Forster, P.M., and Sattelberger, A.P.: "Hydrothermal synthesis and solid-state structure of  $\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$ ", *Polyhedron*, **2012**, available on-line, <http://dx.doi.org/10.1016/j.poly.2012.09.064>.
- McGregor, D.; Burton-Pye, B.P.; Howell, R.C.; Mbomekalle, I.M.; Lukens, W.W., Jr.; Bian, F.; Mausolf, E.; Poineau, F.; Czerwinski, K.R.; Francesconi, L.C. "Synthesis, structure elucidation and redox properties of  $^{99}\text{Tc}$  complexes of lacunary Wells Dawson polyoxometalates: insights into molecular  $^{99}\text{Tc}$  – metal oxide interactions", *Inorg. Chem.* **2011**, 50, 1670 – 1681. DOI: 10.1021/ic102111t

## Multiconfigurational 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 and lanthanides in the gas phase, in low temperature matrices, and in condensed phase.

Significant achievements during 2011-2013: During this period we have studied actinide-and lanthanide-containing systems in the gas phase, multimetallic systems of uranium and neptunium and actinide and lanthanide systems in solution. We have collaborated closely with experimental groups that are performing state of the art experiments on actinide and lanthanide chemistry. In the following we will report some significant results obtained in selected projects.

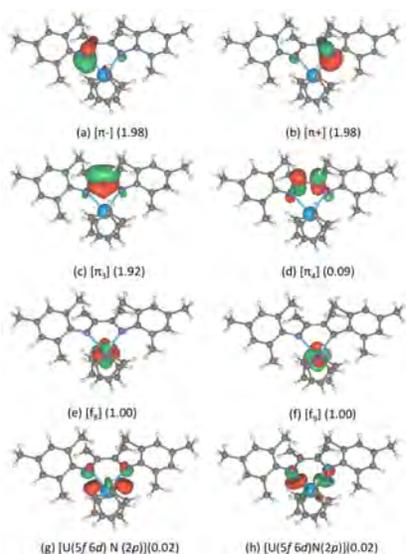


Figure 1. Active molecular orbitals for the CAS(8,8) model of **2** in its ground spin state (triplet). The occupation number for each orbital is given in parenthesis.

1. Computational Insights into Uranium Complexes Supported by Redox-Active  $\alpha$ -Diimine Ligands. This project has been performed in collaboration with the group of Professor Susan Bart, Purdue. The electronic structures of two uranium compounds supported by redox-active  $\alpha$ -diimine ligands,  $(^{\text{Mes}}\text{DAB}^{\text{Me}})_2\text{U}(\text{THF})$  (**1**) and  $\text{Cp}_2\text{U}(^{\text{Mes}}\text{DAB}^{\text{Me}})$  (**2**) ( $^{\text{Mes}}\text{DAB}^{\text{Me}} = [\text{ArN}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{NAr}]$ ; Ar = 2,4,6-trimethylphenyl (Mes)), have been investigated using both density functional theory and multiconfigurational self-consistent field methods. Results from these studies have established that both uranium centers are tetravalent, that the ligands are reduced by two electrons, and that the ground states of these molecules are triplets. Energetically low-lying singlet states are accessible, and some transitions to these states are visible in the electronic absorption spectrum.

2. Synthesis and Characterization of the First 2D Neptunyl Structure Stabilized by Side-on Cation-Cation Interactions. The group of Professor Peter Burns, Notre Dame, has synthesized a novel sheet structure,  $\text{K}[(\text{Np}^{\text{V}}\text{O}_2)(\text{OH})_2] \cdot 2\text{H}_2\text{O}$  (**1**), which provides a rare example of side-on Cation-Cation

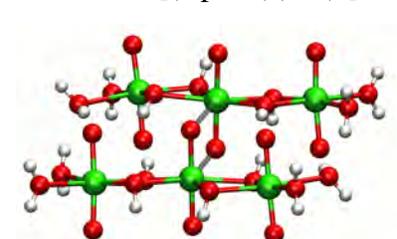


Figure 2.  $[(\text{Np}^{\text{V}}\text{O}_2)_6(\text{OH})_8(\text{H}_2\text{O})_8]^{2-}$  (**1**).

Interactions, CCIs. We have characterized it with electronic structure calculations, together with other existing CCI structures and some model compounds. Our study showed that, in contrast with side-on CCIs previously reported, the Np-Np interaction in **1** is not induced/stabilized by ligands (i.e., through chelation). Analysis of the electronic structure of **1** shows no direct Np-Np bond. Bonding in the CCI is instead localized between the neptunium and oxo centers of adjacent neptunyl moieties.

### Science objectives for 2013-2015:

- Determine accurate structures and energetics of actinide cations in the gas phase
- Explore multi-uranium single molecule magnets; study their spectroscopic and magnetic properties
- Investigate the electronic absorption spectra of lanthanide and actinide luminescent compounds

### Publications supported by this project 2011-2013

1. Wang, X. F.; Andrews, L.; Vlaisavljevich, B.; Gagliardi, L., "Combined Triple and Double Bonds to Uranium: The N U=N-H Uranimine Nitride Molecule Prepared in Solid Argon." *Inorg. Chem.* 2011, 50 (8), 3826-3831. DOI: 10.1021/ic2003244
2. Wang, X. F.; Andrews, L.; Ma, D. X.; Gagliardi, L.; Goncalves, A. P.; Pereira, C. C. L.; Marcalo, J.; Godart, C.; Villeroy, B., "Infrared spectra and quantum chemical calculations of the uranium-carbon molecules UC, CUC, UCH, and U(CC)(2)." *J. Chem. Phys.* 2011, 134 (24), 11. DOI: 10.1063/1.3602325
3. Ricks, A. M.; Gagliardi, L.; Duncan, M. A., "Uranium Oxo and Superoxo Cations Revealed Using Infrared Spectroscopy in the Gas Phase." *J. Phys. Chem. Lett.* 2011, 2 (14), 1662-1666. DOI: 10.1021/jz2006868
4. Vlaisavljevich, B.; Miro, P.; Cramer, C. J.; Gagliardi, L.; Infante, I.; Liddle, S. T., "On the Nature of Actinide- and Lanthanide-Metal Bonds in Heterobimetallic Compounds." *Chem. Eur. J.* 2011, 17 (30), 8424-8433. DOI: 10.1002/chem.201100774
5. Li Manni, G.; Dzubak, A. L.; Mulla, A.; Brogden, D. W.; Berry, J. F.; Gagliardi, L., "Assessing Metal-Metal Multiple Bonds in CrCr, MoMo, and WW Compounds and a Hypothetical UU Compound: A Quantum Chemical Study Comparing DFT and Multireference Methods." *Chemistry A European Journal* 2012, 18 (6), 1737-1749.
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7. Gagliardi, L., "The Study of Actinide Chemistry with Multiconfigurational Quantum Chemical Methods." *Int. J. Quantum Chem.* 2011, 111 (13), 3302-3306. DOI: 10.1002/qua.22992
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9. D. J. Grant, T. J. Stewart, R. Bau, K. A. Miller, S. A. Mason, M. Gutmann, G. J. McIntyred, L. Gagliardi, and W. J. Evans "Uranium and Thorium Hydride Complexes as Multielectron Reductants: A Combined Neutron Diffraction and Quantum Chemical Study." *Inorganic Chemistry*, 51 (6) 2012, pp 3613-3624 DOI: 10.1021/ic202503h
10. R. Spezia, C. Beuchat, R. Vuilleumier, P. D'Angelo, L. Gagliardi "Unravelling the Hydration Structure of ThX<sub>4</sub> (X=Br, Cl) Water Solutions by Molecular Dynamics Simulations and X-Ray Absorption Spectroscopy" *Journal of Physical Chemistry B*, 116(22) 2012, pp 6465-6475 DOI: 10.1021/jp210350b
11. B. Vlaisavljevich, P. Miro', D. Koballa, T. K. Todorova, S. R. Daly, G. S. Girolami, C. J. Cramer, and L. Gagliardi "Volatilities of Actinide and Lanthanide N,N-Dimethylaminodiboranate Chemical Vapor Deposition Precursors: A DFT Study." *The Journal of Physical Chemistry C*, 116 2012, pp 23194-23200 DOI: 10.1021/jp305691y
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13. B. Vlaisavljevich, P. Miro', D. Ma, G. E. Sigmon, P. C. Burns, C. J. Cramer, L. Gagliardi "Synthesis and Characterization of the First 2D Neptunyl Structure Stabilized by Side-on Cation-Cation Interactions." *Chemistry A European Journal*, 19 2013, pp 2937-2941 DOI: 10.1002/chem.201204149
14. A. Quemet, P. Vitorge, A. Cimas, S. Liu, J.-Y. Salpin, C. Marsden, J. Tortajada, L. Gagliardi R. Spezia, M.-P. Gaigeot, R. Brennetot "Reactivity of lanthanoid mono-cations with ammonia: A combined inductively coupled plasma mass spectrometry and computational investigation." *International Journal of Mass Spectrometry*, 334 2013, pp 27-37 DOI: 10.10216/j.ijms.2012.10.005

## Molecular Transuranic Discovery Science: Underpinning National Energy Security and Waste Remediation Needs – Early Career Research Program

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Overall research goals: To develop transformative knowledge regarding transuranic coordination chemistry with a focus upon elucidating bonding properties with both hard and soft donor ligands. The aim is to help rationalize and facilitate development of novel actinide separations.

Significant achievements (2011–2013): Efforts have focused on syntheses, characterization, and publication of transuranic synthetic precursors, coordination chemistry of hard oxygen donor extraction agents, and 4f versus 5f bonding comparisons with soft donor ligands.

1. Syntheses of  $[\text{NBu}_4]_2[\text{Pu}(\text{NO}_3)_6]$  and  $[\text{NBu}_4]_2[\text{PuCl}_6]$ . These molecules are ideal starting materials for Pu(IV) non-aqueous chemistry (under both air-stable and air-sensitive regimes).

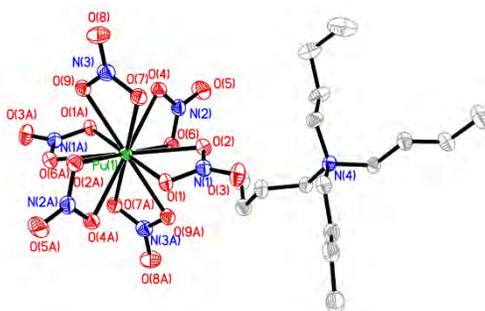


Figure 1. Solid-state structure of  $[\text{NBu}_4]_2[\text{Pu}(\text{NO}_3)_6]$ , a new starting material.

2. Bonding comparisons with soft donor ligands. Diselenophosphinates can be considered as ‘softer’ analogs of known S donors that display An(III) selectivity over Ln(III) ions. Characterization of a series of 1:3 and 1:4 trivalent complexes (Figure 2) revealed differences that were consistent a modest enhancement of metal-ligand orbital overlap in An-Se vs. Ln-Se bonding, while in 1:4 U(IV) and Np(IV) complexes the bonding differences were satisfactorily accounted for by ionic bonding models.

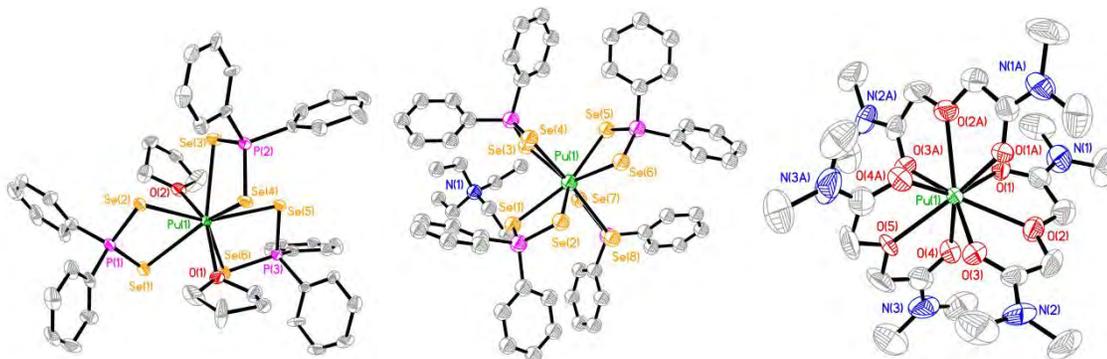


Figure 2.  $\text{Pu}^{\text{III}}(\text{Se}_2\text{PPh}_2)_3(\text{THF})_2$  (left),  $[\text{Pu}^{\text{III}}(\text{Se}_2\text{PPh}_2)_4]^-$  (middle), and  $[\text{Pu}^{\text{IV}}(\text{TMDGA})_3]^{4+}$  (right).

The chemistry of neutral soft nitrogen donor extractants has also been studied, with initial results indicating reduction of Pu(IV) to Pu(III) in organic solvent.

3. Pu(IV) chemistry with diglycolamides. We studied the speciation of Pu(IV) ions towards shorter chain TODGA-extractant derivatives, such as TMDGA (tetramethyl diglycolamide), which allowed complexes to be crystallized and structurally elucidated (Figure 2). Optical spectroscopy showed excellent correlation in the electronic transition profiles between the Pu(IV)-TMDGA speciation and the Pu(IV)-TODGA speciation, meaning that structural insights obtained for TMDGA is of relevance to the separation chemistry/actinide speciation of the TODGA extractant, which itself is not likely to form complexes that can be crystallized due to the oily nature of the octyl groups.

#### Science objectives for 2013-2015:

- Expand studies to ‘very-soft’ donor ligands, explore competition reactions, hydration effects, and utilize organometallic frameworks to aid isolation of lower group 15 neutral donor complexes.
- Reinforce collaborative efforts to extend bonding probes to synchrotron XAS techniques and electronic structure calculations (interfacing with core LANL program and external links).

#### Publications receiving support (full or partial) from this project in the period 2011-2013

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](https://doi.org/10.1039/c2sc21806b).
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3. S.D. Reilly, A. J. Gaunt, B.L. Scott, G. Modolo, M. Iqbal, W. Verboom, M.J. Sarsfield, ‘*Plutonium(IV) complexation by diglycolamide ligands-coordination chemistry insight into TODGA-based actinide separations*’, *Chemical Communications*, **2012**, 48, 9732. DOI: [10.1039/c2cc34967a](https://doi.org/10.1039/c2cc34967a).
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6. D.D. Schnaars, A. J. Gaunt, T.W. Hayton, M.B. Jones, N. Kaltsoyannis, I. May, S.D. Reilly, B.L. Scott, G. Wu, ‘*Bonding Trends Traversing the Tetravalent Actinide Series: Synthesis, Structural, and Computational Analysis of An<sup>IV</sup>(<sup>Ar</sup>acnac)<sub>4</sub> Complexes (An = Th, U, Np, Pu)*’, *Inorganic Chemistry*, **2012**, 51, 8557. DOI: [10.1021/ic301109f](https://doi.org/10.1021/ic301109f).
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8. D.D. Schnaars, E.R. Batista, A.J. Gaunt, T.W. Hayton, I. May, S.D. Reilly, B. L. Scott, and G. Wu, ‘*Uranium(IV) and plutonium(IV) complexes with a β-ketoiminato N,O donor ligand: an experimental and theoretical bonding comparison*’ *Chemical Communications*, **2011**, 47, 7647. DOI: [10.1039/c1cc12409a](https://doi.org/10.1039/c1cc12409a).
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## Activation of Gas-Phase Complexes Elucidates and Expands Actinide Chemistry

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Overall research goals: The broad objective is to investigate fundamental aspects of actinide chemistry in the simplified environment of the gas phase. The results provide a basis to understand, control, and expand condensed phase actinide chemistry, and to evaluate and refine theoretical methodologies for actinides.

Significant achievements during 2011-2013 [see publications]:

- New type of complex  $\text{UO}_2(\text{CH}_3\text{SO}_2)(\text{SO}_2)^-$  exhibits bidentate O,O coordination of  $\text{SO}_2$  to U [1]
- Proton transfer in small thorium hydrate clusters elucidates Th(IV) hydrolysis in solution [2]
- Synthesis and properties of novel heavy transition metal oxide dicationic molecular ions [3,8]
- Characteristics of acetone and diacetone alcohol in actinyl coordination complexes [4,13]
- Fundamental aspects of actinyl oxo-exchange confirms and illuminates enigmas in solution behavior [6]
- Hydration and oxidation of  $\text{UO}_2^+$ ,  $\text{NpO}_2^+$  and  $\text{PuO}_2^+$  reveals variations across the actinyl(V) series [7]
- A new type of gas-phase activation: addition of inert spectator ligands to coordination complexes [9]
- Abundances of lanthanide halide clusters correlate with structural variations across the series [10]
- Disparate behaviors of actinyl complexes upon fragmentation show trends from  $\text{UO}_2^{2+}$  to  $\text{PuO}_2^{2+}$  [11]
- Actinyl ( $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^{2+}$ ,  $\text{PuO}_2^{2+}$ ) coordination complexes by electrospray: solution versus gas [12,16]
- Reactions of  $\text{An}^+$  and  $\text{An}^{2+}$  ions ( $\text{An} = \text{Th} - \text{Cm}$ ) with hydrocarbons: role of electronic structure [14,18]
- Thermodynamics of  $\text{AnS}$  molecules: extension beyond and comparison with  $\text{AnO}$  ( $\text{An} = \text{Th} - \text{Cm}$ ) [15]

Science objectives for 2013-2015:

- Fragmentation of actinide complexes produced by ESI to produce new types of actinide-ligand bonds
- Transfer of intact actinide species from solution to gas by ESI, with a focus on multiply-charged cations
- Actinyl oxo-exchange with various O-atom donors to reveal variations in actinyl bonding from U to Pu
- Determine “effective size” of  $\text{Ln}^{3+}$  and  $\text{An}^{3+}$  ions in gas-phase complexes; contrast with condensed radii
- Explore lanthanide and actinide redox properties by gas-phase chemistry; elucidate condensed behavior
- Interactions of actinide ions with model molecules to elucidate and model key actinide-bio interactions
- Activation of  $\text{An}=\text{O}$  bonds by fragmentation of actinyl complexes; provide guidance for syntheses
- Elucidate hydrolysis and other solution phenomena through chemistry of gas-phase complexes
- Fundamentals of actinide-ligand binding explored by gas-phase ligand-exchange reactions
- Develop new approaches to explore and illuminate gas-phase actinide chemistry
- Establish relationships between gas and condensed phases; understand and control condensed chemistry

Journal articles supported by this project published during 2011-2013

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*Additional manuscripts submitted and in preparation.*

## Principles of Chemical Recognition and Transport in Extractive Separations *Molecular Modelling and Design of Ion Receptors*

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Overall research goals: The overarching goal of this project is to provide new understanding of the theoretical, structural, and thermodynamic principles of molecular recognition leading to unprecedented selectivity and control of ion separations. A major objective is to develop and apply computational techniques to design molecules with desired functionality. Efforts are focused on understanding the guiding principles for the computer-aided design of components that self-assemble with ions to yield charge-neutral ensembles, ditopic receptors for binding ion pairs, and charge-complementary receptors for single ions. The theoretical effort is closely integrated with experimental efforts in which subsequent synthesis and testing of designed molecules validates the efficacy of the computational approach.

Significant achievements in 2011-2013: Following the development of computer-aided molecular design software, we have deployed *de novo* structure-based design and high-throughput screening methods to guide the discovery of a variety of ion receptors including sulfate receptors from bis-urea tweezers and self-assembled  $M_4L_6$  cages.<sup>1</sup> Further attention has focused on the question of how to design molecular shapes encoded to form high-symmetry coordination assemblies. Crystal structure evidence reveals that prior design criteria, based on the concept of complementary bonding vector angles, fail to predict the majority of known cases. After understanding the reasons for this failure, we have shown that *de novo* structure-based design methods provide an alternative approach that successfully identifies component shapes in observed assemblies.<sup>2</sup>

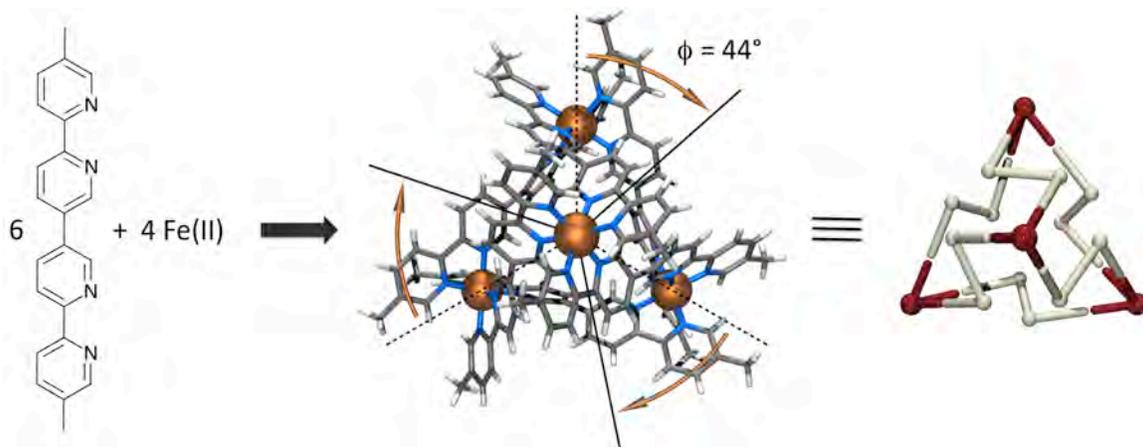


Figure 1. The most common reason why prior vector-based design rules fail is concerted vertex rotation.<sup>2</sup> In the example shown above, a rotationally distorted,  $T$  symmetric  $M_4L_6$  assembly, the degree of vertex rotation,  $\phi$ , is defined as the angle between a vertex bonding vector (solid black line) and the plane containing the  $C_2$  axis of the edge (dotted line). Previously published design rules apply only when  $\phi = 0$  or  $180^\circ$ .

Design of ion-selective hosts entails an understanding of the structural and energetic aspects of host-guest binding interactions and the ability to model them correctly. A series of computational chemistry studies have contributed to this understanding, providing a basis for future design efforts. These include theoretical investigation of: self-assembled  $M_4L_6$  anion receptors;<sup>3</sup> the structure and stability of four possible ion pair binding motifs exhibited by calix[4]arene-strapped calix[4]pyrrole ditopic receptors;<sup>4-6</sup> anion selectivity exhibited by tripodal pyrrole receptors;<sup>7</sup> how the shape of tetraalkylammonium cations influences binding with the bowl-shaped cavity formed in calix[4]pyrrole anion complexes;<sup>8</sup> why formally tridentate ligands bind trivalent metal cations in a bidentate fashion;<sup>9</sup> metal ion selectivity of oxoacid extractants, such as carboxylic acids,  $\beta$ -diketonates, and alkylphosphoric acids.<sup>10</sup>

#### Science objectives for 2013-2015:

- Elucidate the geometric and energetic aspects governing host-guest interactions via electronic structure calculations and evaluation of the Cambridge Structural Database.
- Computer-aided design of ditopic receptors for ion pairs and charge-complementary receptors for single ions.
- Computer-aided design of molecules that direct the self-assembly with ions to yield charge-neutral polygons, polyhedra, and frameworks.

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## Exploring the Reactivity of the Uranyl Ion and its Chalcogen Analogues: Expanding our Understanding of Uranyl Reactivity and Behavior

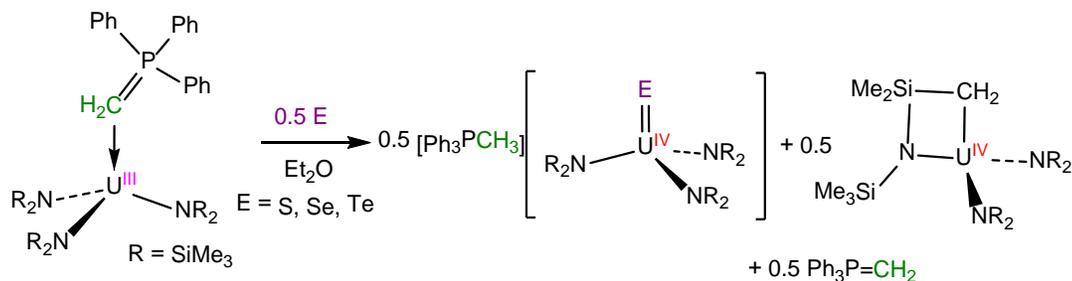
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Overall research goals: Our research program has two specific aims: (i) Explore the redox chemistry of uranyl and discover new transformations for oxo ligand functionalization and substitution; and (ii) improve the understanding of the uranyl ion by synthesizing and studying new uranyl analogues, specifically the chalcogen analogues of uranyl,  $[E=U=E]^{2+}$  (E = S, Se, Te).

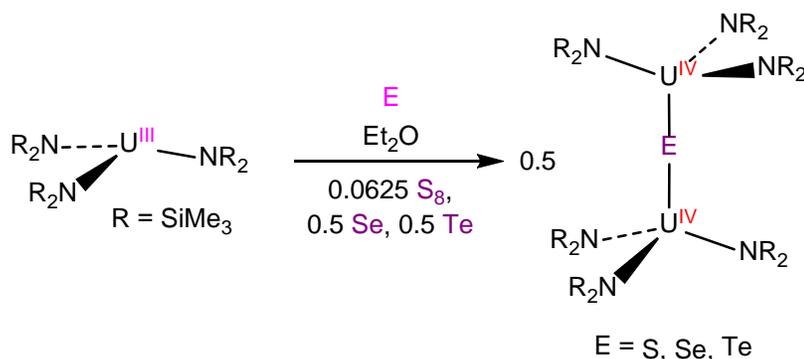
Significant achievements during 2011-2013: We recently reported the synthesis of the first complete family of terminal uranium chalcogenides, namely,  $[Ph_3PCH_3][U(E)(N(SiMe_3)_2)_3]$ , formed by reaction of  $U(NR_2)_3(CH_2=PPh_3)$  with elemental chalcogens (E = S, Se, Te) (Scheme 1). Most notably, the selenium and tellurium derivatives represent the first terminal selenide and telluride complexes of the actinides. Their isolation is also notable because most attempts to generate terminal chalcogenides produce complexes containing bridging chalcogenide ligands. To account for the formation of  $[Ph_3PCH_3][U(E)(NR_2)_3]$ , we argued that the ylide ligand in the starting material plays an important trapping role, by deprotonating a transient U(IV) hydrochalcogenide complex,  $U(EH)(NR_2)_3$ . We plan to use this mechanistic insight to promote the formation of uranium-ligand multiple bonds in other systems.

### Scheme 1



We also reported the synthesis of the bridging chalcogenide complexes,  $[(R_2N)_3U]_2(\mu-E)$  (E = S, Se, Te; R = SiMe<sub>3</sub>), by oxidation of  $U(NR_2)_3$  with the elemental chalcogens (Scheme 2). These complexes are isolable in 40-60% yields by crystallization from non-polar solvents. All three complexes were characterized by X-ray crystallography. Interestingly, crude samples of  $[H_3CPPh_3][U(S)(NR_2)_3]$  (see Scheme 1) also contain small amounts of  $[(R_2N)_3U]_2(\mu-S)$ , suggesting that multiple S-atom transfer pathways are operative upon reaction of chalcogens with  $U(H_2C=PPh_3)(NR_2)_3$ .

## Scheme 2



On several occasions, the reaction of  $\text{U}(\text{NR}_2)_3$  with elemental sulfur also resulted in the formation of a second product, namely, the bridging disulfide complex  $[(\text{R}_2\text{N})_3\text{U}]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-S}_2)$ , which is a very rare example of an actinide complex featuring an  $\text{S}_2^{2-}$  ligand. The factors that result in the production of this complex are still unknown, and we are currently investigating its mechanism of formation.

### Science objectives for 2013-2015:

- Discover new electrophiles capable of activating the U=O bonds of the uranyl ion.
- Develop new methods and reagents for chalcogen atom transfer.
- Synthesize the chalcogen analogues of the uranyl ion,  $[\text{E}=\text{U}=\text{E}]^{2+}$  (E = S, Se, Te).

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## Selective Recognition of Heavy Elements by Protein-Based Reagents

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Overall research goals: The objective of this project is to engineer protein-based reagents that can selectively bind heavy elements in aqueous solutions. Our long-term goal is to design and evolve proteins that can bind and respond to individual actinide ions tightly and selectively.

Significant achievements during 2011-2013: In the past 2 years, we have made significant progresses in two research areas:

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

The concentration of uranyl in seawater is surprisingly high at 3.2 mg/ton of seawater (13 nM). 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 uranyl-binding ligands with femtomolar or higher affinity to uranyl and > 1 million-fold selectivity over calcium(II) and other abundant metal ions present in ocean. *No existing small molecule or protein-based ligands can achieve this daunting task.*

We computationally screened all published protein crystal structures in the Protein Data Bank for uranyl-selective binding sites. 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 performed further rational protein engineering on 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. We showed that when immobilized on a polymer support or displayed on a cell surface, SUP can repeatedly and efficiently sequester uranyl from seawater. Up to 60% of uranyl in synthetic seawater can be effectively sequestered (Figure 1). The University of Chicago has patented this invention.

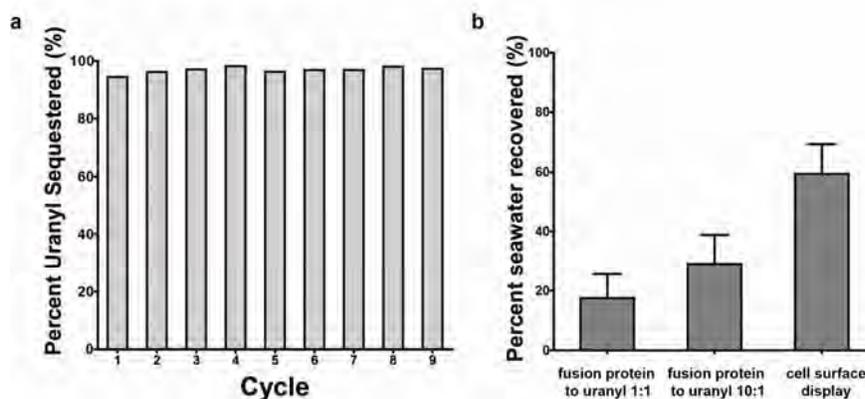


Figure 1. **a**, SUP immobilized on amylose resin can consistently remove uranyl from uranyl-contaminated water over many cycles. **b**, Both protein display by fusion with maltose-binding protein and immobilization on amylose resin by fusion with OmpA and display on live *E. coli* cells allow for effective recovery of uranyl in synthetic seawater.

## 2. Lanthanide-sensing bacteria.

The survival and growth of *E. coli* and *Salmonella* species require iron as one of the essential nutrients. They have evolved a PmrA/PmrB two-component system to sense the presence of iron(III) in the environment and to regulate the response of the bacteria. We have replaced the iron(III)-sensing motif in PmrB with a lanthanide/actinide-binding tag. The newly engineered bacterium can sense presence of 1  $\mu\text{M}$  lanthanide and respond with fluorescence or motility.

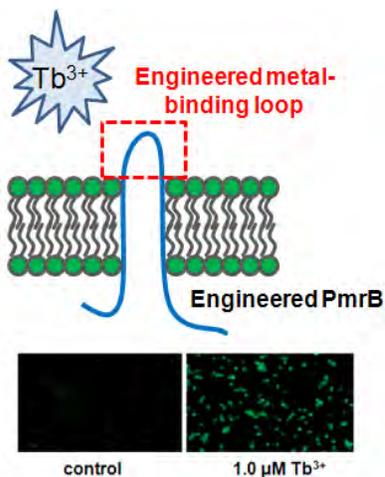


Figure 2. The *Salmonella* PmrA/PmrB two-component system that senses ferric level can be engineered to selectively respond to lanthanide ions in living bacteria (*J. Am. Chem. Soc.* **2013**, *135*, 2037).

### Science objectives for 2013-2015:

- Improve uranyl-binding affinity of SUP and other candidate proteins. We hope to achieve 100% sequestration of uranyl from seawater.
- Develop actinide-sensing bacteria. We plan to develop an uranyl-sensing bacteria. We also hope to evolve/improve the current lanthanide-binding bacteria. In collaboration with Dr. Mark Jensen we hope to construct actinide-sensing bacteria.

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## Spectroscopic Studies of Prototype Actinide Compounds

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Collaborators: Timothy C. Steimle (Arizona State University), Kirk A. Peterson (Washington State University), Vladimir E. Bondybey (University of Munich)

Overall research goals: Understanding the influence of electrons in partially filled *f*- and *d*- orbitals on bonding and reactivity is a key issue for actinide chemistry. This subtle question can be investigated using a combination of well-defined experimental measurements and state-of-the-art theoretical calculations. Gas phase spectroscopic data are particularly valuable for the evaluation of theoretical models. The primary objectives of this research program are to obtain gas phase spectra for small actinide and lanthanide compounds. Development of the tools for recording such spectra is also a component of this endeavor. To complement the experimental effort we are investigating the potential for using relativistic *ab initio* calculations and semi-empirical models to predict and interpret the electronic energy level patterns for *f*-element compounds.

Significant achievements in 2011-2013: In addition to being interesting model species for understanding the bonding in metal fluorides, the ions  $\text{HfF}^+$  and  $\text{ThF}^+$  are thought to be excellent candidates for studies of the electron electric dipole moment (eEDM). During the past two years we have completed our experimental and theoretical studies of  $\text{HfF}^+$ . On paper,  $\text{ThF}^+$  is an even better candidate for eEDM studies as it is capable of generating a higher internal electric field and has only one isotope with significant natural abundance. However, prior to the work reported here there were no spectroscopic data for  $\text{ThF}$  or  $\text{ThF}^+$ . We characterized several electronic transitions of the neutral molecule using laser induced fluorescence (LIF) and multi-photon ionization techniques. It was confirmed that the ground state was  $X^2\Delta_{3/2}$ , as expected from ligand field theory. The low-lying states of  $\text{ThF}^+$  were characterized using pulsed field ionization - zero electron kinetic energy spectroscopy (PFI-ZEKE). Rotationally resolved spectra were recorded for 14 vibronic states. LIF was used to probe a small number of higher energy electronic states. It was demonstrated that the state of interest for eEDM measurements ( $^3\Delta_1$ ) is either the ground state, or a state that lies just  $315\text{ cm}^{-1}$  above the ground state.

$\text{UF}$  and  $\text{UF}^+$  are valuable species for studies of the actinide - fluorine bond.  $\text{UF}$  has been the subject of several previous theoretical investigation. The electronic structure of  $\text{UF}^+$  is of additional interest as it is isoelectronic with  $\text{UO}$ , for which there is a significant body of spectroscopic data. LIF and multiphoton ionization spectra were recorded for  $\text{UF}$  in the  $18000\text{-}20000\text{ cm}^{-1}$  range. Rotationally resolved data were obtained, and the analysis of a band at  $18624\text{ cm}^{-1}$  yielded a ground state rotational constant of  $0.2348\text{ cm}^{-1}$ . The electronic ground state was clearly identified as  $|\Omega|=4.5$ , confirming the theoretically predicted  $\text{U}^+(5f^37s^2)\text{F}^-$  configuration. Dispersed fluorescence spectra revealed low-lying electronic states that were assigned as  $|\Omega|=3.5$  ( $435\text{ cm}^{-1}$ ) and

2.5 (650 cm<sup>-1</sup>). The ground state and fifteen electronically excited states of UF<sup>+</sup> were characterized using PFI-ZEKE spectroscopy. The ground state was found to be | $\Omega$ |=4, as it is for the isoelectronic molecule UO, and with vibrational constants of  $\omega_e$ =649.92 and  $\omega_e x_e$ =1.83 cm<sup>-1</sup>. Excited states of UF<sup>+</sup> with | $\Omega$ | spanning all values in the range 0-6 were observed. Relativistic ab initio calculations (CASSCF/CASPT2 with spin-orbit coupling) yielded predictions that were in good agreement with the ground and low-lying states of both UF and UF<sup>+</sup>.

Ionization of ThO, HfO and HfS reduces the bond energies. Paradoxically, the vibrational frequencies increase and the bond lengths shorten. We have further explored this trend by applying fluorescence and PFI-ZEKE spectroscopy to characterize ThS/ThS<sup>+</sup>. To date, we have observed the  $v=0-7$  levels of the ThS<sup>+</sup> ground state, and the 0-3 levels of the first electronically excited state (with  $T_0=2934$  cm<sup>-1</sup>). Harmonic vibrational constants of 512.6 and 495.2 cm<sup>-1</sup> were determined. By analogy with ThO<sup>+</sup>, it was expected that the first two states would be Th<sup>3+</sup>(7s)S<sup>2-</sup> X<sup>2</sup> $\Sigma^+$  and Th<sup>3+</sup>(6d)S<sup>2-</sup> <sup>2</sup> $\Delta_{3/2}$ . The observation of a smaller vibrational constant for the excited state is consistent with this ordering. These assignments were also supported by our CASSCF/MRCI/spin-orbit calculations, which predicted low-lying states at  $T_e=2136$  (<sup>2</sup> $\Delta_{3/2}$ ) and 4424 cm<sup>-1</sup> (<sup>2</sup> $\Delta_{5/2}$ ). The ground state vibrational constant from the DFT/B3LYP calculations for ThS<sup>+</sup> ( $\omega_e=514$  cm<sup>-1</sup>) was also close to the measured value.

Science objectives for 2011-2013: Ongoing studies of ThS/ThS<sup>+</sup> and ThN/ThN<sup>+</sup> will be completed. Over the next two years we will measure the electron affinities of Th and U, and explore the dimers Th<sub>2</sub> and U<sub>2</sub> using anion photodetachment spectroscopy. These data are important for the understanding of actinide metal-metal bonds and evaluation of relativistic quantum chemistry models. In addition, anion detachment techniques will be used to study the low-lying states of UO, UO<sub>2</sub>, and CUO.

#### Publications supported by this project

F. Wang, A. Le, T. C. Steimle, and M. C. Heaven, J. Chem. Phys. **134**, 031102/1 (2011)

*"The permanent electric dipole moment of Thorium monoxide, ThO"*

B. Barker, I. O. Antonov, V. E. Bondybey and M. C. Heaven, J. Chem. Phys.

**134**, 201102/1-201102/4 (2011)

*"Spectroscopic measurements for HfF<sup>+</sup> of relevance to the investigation of fundamental constants"*

B. J. Barker, I. O. Antonov, and M. C. Heaven, J. Mol. Spectrosc. **275**, 35-40 (2012)

*"Low-lying states of HfS<sup>+</sup> and the ionization energy of HfS"*

B. J. Barker, I. O. Antonov, M. C. Heaven and K. A. Peterson, J. Chem. Phys. **136**, 104305 (2012)

*"Spectroscopic investigations of ThF and ThF<sup>+</sup>"*

I. O. Antonov and M. C. Heaven, J. Phys. Chem. A. Publication Date (Web): January 29, (2013) DOI: 10.1021/jp312362e

*"Spectroscopic and theoretical investigations of UF and UF<sup>+</sup>"*

## Actinide Transition-Metal Chalcogenides and Pnictides

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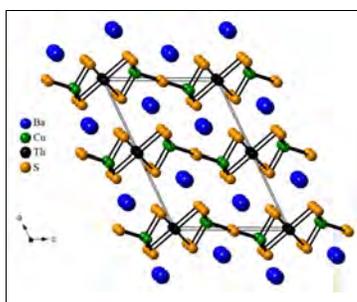
**Collaborator: Dr. Lynda Soderholm**

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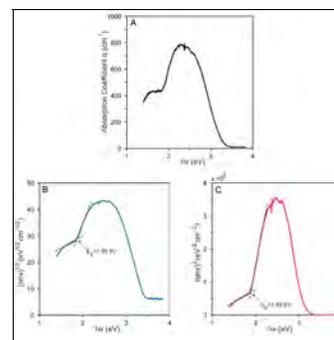
**Overall research goal:** The overall objective is to increase our knowledge and understanding of Th, U, and Np solid-state chemistry.

**Significant achievements during 2011-2013:** Most of these achievements are embodied in the publications listed below. Here we discuss some unpublished results.

The compound  $\text{Ba}_2\text{Cu}_2\text{ThS}_5$ <sup>a</sup> has been synthesized by the reaction of BaS, S, Cu, and Th at 1173 K. It crystallizes in the  $\text{Ba}_2\text{Cu}_2\text{US}_5$  structure type in the monoclinic space group  $C_{2h}^3 - C2/m$ . The structure (Fig. 1) comprises  $\text{Ba}^{2+}$  cations and  $[\text{Cu}_2\text{ThS}_5]^{4-}$  layers. The two dimensional layers are formed by the connection of  $\text{ThS}_6$  octahedra and  $\text{CuS}_4$  tetrahedra along [001] with a sequence ... *oct tet tet oct tet tet*....

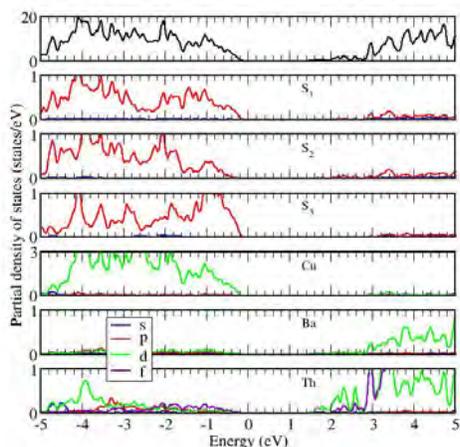


View of the structure of  $\text{Ba}_2\text{Cu}_2\text{ThS}_5$  along [010]

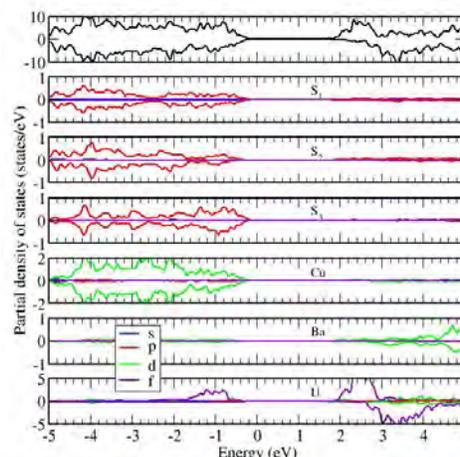


Upper, experimental; bottom left, indirect; bottom right, direct

Optical measurements (Fig. 2) performed on  $\text{Ba}_2\text{Cu}_2\text{ThS}_5$  indicate an indirect band gap of 1.86 eV. DFT calculations performed with the HSE06 functional yield band gaps of 1.7 eV for  $\text{Ba}_2\text{Cu}_2\text{ThS}_5$  and 1.5 eV for  $\text{Ba}_2\text{Cu}_2\text{US}_5$  (Fig. 3). The fact that the DFT calculation of the band gap for  $\text{Ba}_2\text{Cu}_2\text{ThS}_5$  is in excellent with experiment indicates that the HSE06 functional is a suitable tool to study the electronic structures of materials containing actinides.



Top: DOS Th



Top: DOS U

Science objectives for 2013-2014: We will continue our syntheses of new Np-containing chalcogenides and pnictides and compare their structures and properties to those of related U and Th. compounds. We will complete and submit for publication all remaining results.

Selected publications supported by this project 2012-2013

1. Bugaris, D.E.; Choi, E.S.; Copping, R.; Glans, P.-A. Minasian, S.G.; Tyliczszak, T.; Kozimor, S.A.; Shuh, D. K.; Ibers, J. A. *Inorg. Chem.* **2011**, *50*, 6656-6666.  
Pentavalent and Tetravalent Uranium Selenides,  $Tl_3Cu_4USe_6$  and  $Tl_2Ag_2USe_4$ : Syntheses, Characterization, and Structural Comparison to Other Layered Actinide Chalcogenide Compounds.
2. Jin, G. B.; Skanthakumar, S.; Haire, R.G.; Soderholm, L.; Ibers, J. A. *Inorg. Chem.* **2011**, *50*, 9688-9695.  
Neptunium Thiophosphate Chemistry: Intermediate Behavior between Uranium and Plutonium.
3. Andrews, L.; Wang, X.; Liang, B.; Ruipérez, F.; Infante, I.; Raw, A.D.; Ibers, J.A. *Eur. J. Inorg. Chem.* **2011**, 4457-4463.  
Matrix Infrared Spectroscopy and a Theoretical Investigation of SUO and  $US_2$ .
4. Oh, G. N.; Ringe, E.; Van Duyne, R. P.; Ibers, J. A. *J. Solid State Chem.* **2012**, *185*, 124-129.  
Synthesis, structure, and optical properties of  $CsU_2(PO_4)_3$ .
5. Bugaris, D. E.; Ibers, J. A. *Inorg. Chem.* **2012**, *51*, 661-666.  
 $Ba_8Hg_3U_3S_{18}$ : A Complex Uranium(4+)/Uranium(5+) Sulfide.
6. Raw, A. D.; Ibers, J. A. *J. Solid State Chem.* **2012**, *186*, 177-181.  
Syntheses and crystal structures of the quaternary uranium lanthanide oxyselenides  $UYb_2O_2Se_3$  and  $U_2Ln_2O_4Se_3$  ( $Ln = Pr, Sm, Gd$ ).
7. Raw, A. D.; Ibers, J. A. *J. Solid State Chem.* **2012**, *187*, 282-285.  
Synthesis and structural characterization of the new compound  $UEr_2O_2S_3$  and the evidence for the old compound  $U_2ErO_2S_3$ .
8. Raw, A. D.; Ibers, J. A.; Poeppelmeier, K. R. *J. Solid State Chem.* **2012**, *192*, 34-37.  
Syntheses and structure of hydrothermally prepared  $CsNiX_3$  ( $X=Cl, Br, I$ ).
9. Oh, G. N.; Ibers, J. A. *J. Solid State Chem.* **2012**, *192*, 81-86.  
Synthesis, structure, and electrical resistivity of  $Cs_3U_{18}Se_{38}$ .
10. Oh, G. N.; Choi, E. S.; Ibers, J. A. *Inorg. Chem.* **2012**, *51*, 4224-4230.  
Syntheses and Characterization of Nine Quaternary Uranium Chalcogenides Among the Compounds  $A_2M_3UQ_6$  ( $A = K, Rb, Cs; M = Pd, Pt; Q = S, Se$ ).
11. Malliakas, C. D.; Yao, J.; Wells, D. M.; Jin, G. B.; Skanthakumar, S.; Choi, E. S.; Balasubramanian, M.; Soderholm, L.; Ellis, D. E.; Kanatzidis, M. G.; Ibers, J. A. *Inorg. Chem.* **2012**, *51*, 6153-6163.  
Oxidation State of Uranium in  $A_6Cu_{12}U_2S_{15}$  ( $A = K, Rb, Cs$ ) Compounds.
12. Koscielski, L. A.; Ringe, E.; Van Duyne, R. P.; Ellis, D. E.; Ibers, J. A. *Inorg. Chem.* **2012**, *51*, 8112-8118.  
Single-Crystal Structures, Optical Absorptions, and Electronic Distributions of Thorium Oxychalcogenides  $ThOQ$  ( $Q = S, Se, Te$ ).
13. Oh, G. N.; Choi, E. S.; Lu, J.; Koscielski, L. A.; Ward, M. D.; Ellis, D. E.; Ibers, J. A. *Inorg. Chem.* **2012**, *51*, 8873-8881.  
Syntheses and Characterization of Six Quaternary Uranium Chalcogenides  $A_2M_4U_6Q_{17}$  ( $A = Rb$  or  $Cs; M = Pd$  or  $Pt; Q = S$  or  $Se$ ).
14. Bellott, B. J.; Haire, R. G.; Ibers, J. A. *Z. Anorg. Allg. Chem.* **2012**, *638*, 1777-1779.  
The Synthesis and Crystal Structure of  $NpSe_3$ .
15. Koscielski, L. A.; Ibers, J.A. *Z. Anorg. Allg. Chem.* **2012**, *638*, 2585-2593.  
The Structural Chemistry of Quaternary Chalcogenides of the Type  $AMM'Q_3$ .
16. Bellott, B.J.; Ibers, J.A. *Z. Anorg. Allg. Chem.* **2012**, *638*, 2473-2476.  
Synthesis and Structure of the Rubidium Uranium Selenophosphate  $Rb_4U_2P_5Se_{17}$ .
17. Mesbah, A.; Ringe, E.; Lebègue, S.; Van Duyne, R.P.; Ibers, J.A. *Inorg. Chem.* **2012**, *51*, 13390-13395.  
 $Ba_2An(S_2)_2S_2$  ( $An = U, Th$ ): Syntheses, Structures, Optical and Electronic Properties.
18. Bellott, B.J.; Malliakas, C.D.; Koscielski, L.A.; Kanatzidis, M.G.; Ibers, J.A. *Inorg. Chem.* **2013**, *52*, 944-949.  
Synthesis, Properties, and Complex Crystal Structure of  $Th_2Se_5$ .
19. Mesbah, A.; Ibers, J.A. *J. Solid State Chem.* **2013**, *199*, 253-257.  
Syntheses and crystal structures of three barium uranium sulfides.

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<sup>a</sup>Mesbah, Lebègue, Klingsporn, Stojko, Van Duyne, & Ibers, JSSC, accepted (2013)

## Multi-Stage Separation of Actinides with Biomolecules

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Overall research goals: This program is focused on understanding the structural, thermodynamic, and kinetic principles that could be used to separate actinide-ligand complexes in multi-stage systems patterned after biological metal-ion separations. These separation systems use multiple interactions, such as protein-protein complexes for recognition and separation. The goal is to lay a foundation for highly selective systems that move beyond the intrinsic strength of metal-ligand bonds as the principal means for separating actinide ions.

Significant achievements during 2011-2013: We have been studying the complexes of tetravalent f-elements and their interactions with proteins or biological small-molecules in order to understand how multi-stage systems can achieve actinide separation.

1. Conformationally-driven Separations. Separations based on the transferrin-transferrin receptor system behave differently than common actinide separations. The separation is driven by the conformation of the actinide-transferrin complex, not the intrinsic strength of the metal-ligand bonds in the complex. We have found that the metal-binding site, in the part of the protein that shows the conformational difference for the actinides, contains two co-ligands instead of the normally encountered single co-ligand motif. One of the two co-ligands is readily exchangeable, opening the possibility to study the influence of the number and nature of the co-ligand on the conformation of actinide-protein complexes.

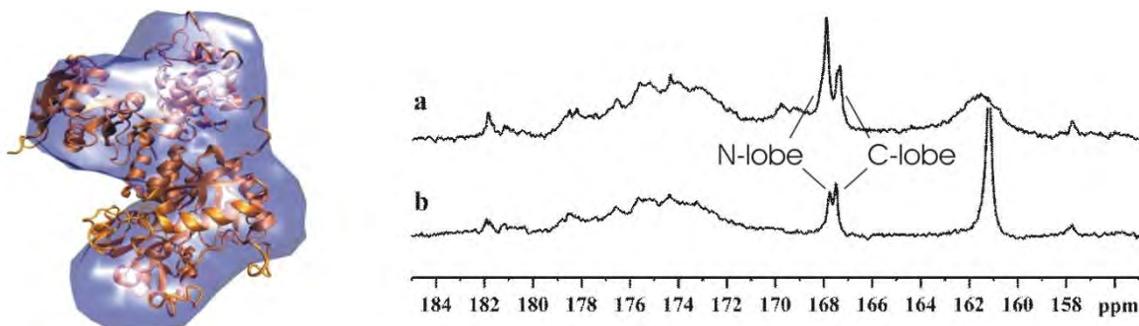


Figure 1. Left: Low resolution solution structure of a plutonium-containing transferrin (blue) docked to a crystal structure of transferrin with an open N-lobe at the top of the structure (orange, ref. 3QYT). Right,  $^{13}\text{C}$  NMR of dicerium(IV)-transferrin shows 2 equivalents of  $^{13}\text{CO}_3^{2-}$  bind in the open N-lobe (a) and that this excess carbonate can be replaced by other co-ligands (b) while the N-lobe is in the open configuration.

Other multi-stage systems with less conformational flexibility are proving to have interesting properties for intra-actinide separations. Equilibrium thermodynamics show proteins that bind normally iron(III)-small molecule complexes show some Fe(III)/Pu(IV) selectivity (Separation Factor  $\sim 10$ ), but they show a significant Pu(IV)/Th(IV) selectivity (S.F.  $\geq 100$ ) even though the small molecule ligands studied are not themselves discriminate between Th(IV) and Pu(IV). While these small-molecule ligands display much less conformational flexibility than a protein like

transferrin, the multi-stage interactions between the actinide-small molecule complexes and the receptor protein distinguish between Th(IV) and Pu(IV).

2. New Multi-stage Systems Capable of Actinide Separation. The biological systems we have been studying for multi-stage actinide separations thus far have been based on molecules that normally bind Fe(III) in nature. Few other actinide binding sites have been identified in biological systems. Are those Fe(III) binding motifs the only way to achieve actinide separations? Could other proteins be avid actinide-binders with distinctive multi-stage binding motifs? Using proteomics techniques, we isolated more than 20 potential Pu(IV)-binding proteins, identifying 7 of them. None of the identified proteins had previously been suspected as binding Pu, and none are known to bind Fe(III) *in vivo*. Instead, most of these proteins bind divalent metals, such as Mg, Ca, Cu, Zn, or Pb, and one of the proteins, galectin-1, has never been reported to bind any metal ion. Further investigation of galectin-1 revealed that it is not a Pu-binding protein, rather it binds to a second protein, which in turn binds plutonium in a multi-stage interaction.

#### Science objectives for 2013-2015:

- Investigate the role of co-ligands in driving the inter-lobe conformational differences in transferrins essential to multi-stage receptor or anti-body based actinide separations.
- Explore structural and thermochemistry of the size-based recognition of actinide-small molecule complexes by receptor proteins.
- Develop proteomic discoveries by examining multi-stage actinide separations using newly identified biomolecules outside the iron(III)-binding paradigm.

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1. Liang, H.; Deng, X.; Bosscher, M.; Ji, Q.; Jensen, M. P.; He, C. "Engineering Bacterial Two-Component System PmrA/PmrB to Sense Lanthanide Ions." *J. Am. Chem. Soc.* **2013**, *135*, 2037-2039. DOI: 10.1021/ja312032c
2. Jensen, M. P.; Aryal, B. P.; Gorman-Lewis, D.; Paunesku, T.; Lai, B.; Vogt, S.; Woloschak, G. E. "Submicron Hard X-ray Fluorescence Imaging of Synthetic Elements." *Anal. Chim. Acta* **2012**, *722*, 21-28. DOI: 10.1016/j.aca.2012.01.064
3. Aryal, B. P.; Paunesku, T.; Woloschak, G. E.; He, C.; Jensen, M. P. "A proteomic approach to identification of plutonium-binding proteins in mammalian cells." *J. Proteomics* **2012**, *75*, 1505-1514. DOI: 10.1016/j.jprot.2011.11.023
4. Özçubukçu, S.; Mandal, K.; Wegner, S.; Jensen, M. P.; He, C. "Selective Recognition of Americium by Peptide-Based Reagents." *Inorg. Chem.* **2011**, *50*, 7937-7939. DOI: 10.1021/ic201094e
5. Jensen, M. P.; Gorman-Lewis, D.; Aryal, B.; Paunesku, T.; Vogt, S.; Rickert, P. G.; Seifert, S.; Lai, B.; Woloschak, G. E.; Soderholm, L. An Iron-dependent and Transferrin-mediated Cellular Uptake Pathway for Plutonium. *Nature Chem. Biol.* **2011**, *7*, 560-565. DOI: 10.1038/nchembio.594
6. Gorman-Lewis, D.; Aryal, B. P.; Paunesku, T.; Vogt, S.; Lai, B.; Woloschak, G. E.; Jensen, M. P. Direct Determination of the Intracellular Oxidation State of Plutonium. *Inorg. Chem.* **2011**, *50*, 7591-7597. DOI: 10.1021/ic200588p

## Actinyl Compounds with Cation-Cation Interactions (CCIs)

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Overall research goals: The objective of this project is to explore the origins of the unusual bonding motif known as a CCI interaction and their impact on physical properties. CCI interactions involve the bonding of the oxo moiety on one actinyl center as an equatorial ligand on a neighboring ion. These bonding motifs result in structural connectivities that can be thought of in terms of fractal lattice dimensionalities, consequently CCI materials provide an ideal venue to study the effects of bonding on the interplay between single-ion and collective properties.

Significant achievements during 2011-2013: We hypothesize that CCIs are invoked to fulfill the bonding requirements of actinyl oxygen atoms, completing the actinyl cation's coordination requirements. To test this idea, we have synthesized a series of neptunyl(V) sulfates, selenates, and selenites with different CCI connectivities and dimensionalities by introducing varying amounts of  $\text{Na}^+$  cations and ligating anions into the systems. Complementing and informing our understanding of the structures, we have used Raman spectra and magnetic susceptibilities of these compounds to study structure-property relationships. Examples of significant progress include:

1. As the molar ratios of  $\text{Na}^+$  ions and ligands to the  $\text{NpO}_2^+$  cations increase, the resultant CCI networks in solid products change from 3-D frameworks to 2-D sheets and ribbons, 1-D chains to no CCIs. This phenomenon is well exemplified in the selenate systems, as shown in Figure 1. The presence of other cations that can bind to actinyl oxygen, or ligands that coordinate to the metal center, play an important role in the formation of CCIs, consistent with the aforementioned hypothesis.

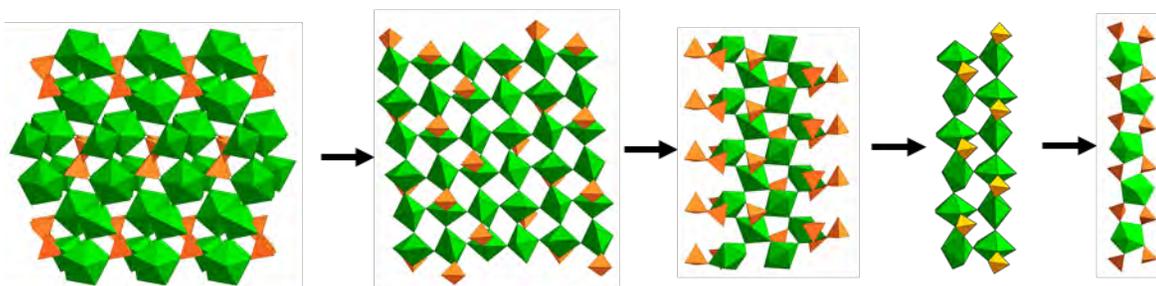


Figure 1. From left to right: neptunyl(V) sublattice of  $(\text{NpO}_2)_2(\text{SeO}_4)(\text{H}_2\text{O})$ ,  $(\text{NpO}_2)_2(\text{SeO}_4)(\text{H}_2\text{O})_4$ ,  $\text{Na}(\text{NpO}_2)(\text{SeO}_4)(\text{H}_2\text{O})$ ,  $(\text{NpO}_2)_2(\text{SeO}_4)(\text{H}_2\text{O})_6$ , and  $\text{Na}_3(\text{NpO}_2)(\text{SeO}_4)(\text{H}_2\text{O})$ .

2. One of the selenites contains the first example of one  $\text{NpO}_2^+$  cation joining five CC bonds with other neptunyl(V) units. This suggests more new connectivities involving CCIs await discovery that will further enrich the structural chemistry of neptunyl(V) compounds.

3. Magnetic measurements for samples containing 2-D sheets or ribbons of “cationic squares” indicated ferromagnetic ordering of Np moments less than 10 K, as shown in Figure 2. The magnetic results of these phases fit well into the class of magnetic behavior reported for other neptunyl(V) compounds with a similar square organization of  $\text{NpO}_2^+$  cations. This CCI square arrangement of  $\text{NpO}_2^+$  units appears to promote ferromagnetic interactions between Np(V) centers for reasons not yet fully understood.

4. By selectively measuring the Raman spectra from several neptunyl(V) selenates and sulfates with related structural features, most of vibrational bands attributed to the neptunyl moiety and ligands

can be unambiguously separated. Significant shifts of  $\nu_1$  bands of  $\text{NpO}_2^+$  to a much lower frequency are observed as the CCIs weaken the neptunyl bonds, while the Raman forbidden  $\nu_3$  bands of the  $\text{NpO}_2^+$  units are observed in Raman spectra as CCIs lower the site symmetry of the units (Figure 3). These results are consistent with the interatomic distances and coordination environments for the neptunyl cations obtained from the structural studies.

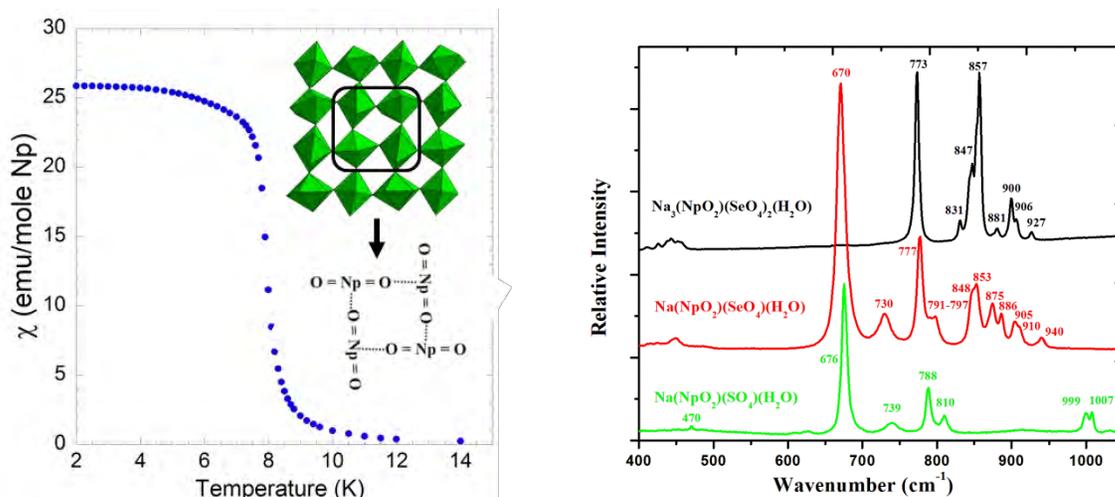


Figure 2 (left). The magnetic behaviour of  $(\text{NpO}_2)_2(\text{SeO}_4)(\text{H}_2\text{O})_4$  at low temperatures with 2-D sheets of ‘‘cationic squares’’.

Figure 3 (right). Raman spectra of  $\text{Na}_3(\text{NpO}_2)(\text{SeO}_4)(\text{H}_2\text{O})$  without CCIs and isostructural  $\text{Na}(\text{NpO}_2)(\text{TO}_4)(\text{H}_2\text{O})$  ( $T = \text{S}, \text{Se}$ ) with CCIs.

#### Science objectives for 2013-2015:

- Further investigate the roles of other ions in the formation of actinyl CCIs by using various cations (eg. alkali earth metal and transition metal cations) and ligands (eg. halides and hydroxide) with different complexing abilities and binding modes.
- Expand magnetic studies to other actinyl compounds with different CCI linkages and dimensionalities to illustrate the correlations between magnetic behaviors and CCI connectivities and the overall neptunyl lattice dimensionalities.
- Systematically investigate the Raman and IR spectra of neptunyl(V) compounds with CCIs using structural studies of solids for guidance.

#### Publications supported by this project 2011-2013

1. Jin, G. B., Skanthakumar, S. and Soderholm, L., ‘‘Cation–Cation Interactions: Crystal Structures of Neptunyl(V) Selenate Hydrates,  $(\text{NpO}_2)_2(\text{SeO}_4)(\text{H}_2\text{O})_n$  ( $n = 1, 2,$  and  $4$ )’’ *Inorganic Chemistry*, (2011), 50(11), 5203-5214. [doi: 10.1021/ic200479m]
2. Jin, G. B., Skanthakumar, S. and Soderholm, L., ‘‘Two New Neptunyl(V) Selenites: a Novel Cation-Cation Interaction Framework in  $(\text{NpO}_2)_3(\text{OH})(\text{SeO}_3)(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$  and a Uranophane-type Sheet in  $\text{Na}(\text{NpO}_2)(\text{SeO}_3)(\text{H}_2\text{O})$ ’’ *Inorganic Chemistry*, (2011), 50(13), 6297-6303. [doi: 10.1021/ic200696g]
3. Jin, G. B., Skanthakumar, S. and Soderholm, L., ‘‘Three New Sodium Neptunyl(V) Selenate Hydrates: Structures, Raman Spectroscopy, and Magnetism’’ *Inorganic Chemistry*, (2012), 51(5), 3220–3230. [doi: 10.1021/ic202703j]
4. Jin, G. B., Skanthakumar, S. and Soderholm, L., ‘‘Raman Spectroscopic Study of Cation-Cation Interactions between Neptunyl(V) Ions’’ In prep for *Inorganic Chemistry*.

## Understanding Actinide Aggregation: Formation and Composition of An(IV) Clusters

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Professor David A Dixon and Dr. Monica Vasiliu, The University of Alabama, Department of Chemistry, Tuscaloosa, AL 99352.

Overall research goals: The objective of this project is to understand the effects that the actinide contraction (as it relates to metal ion hardness and acidity), anion complexation, and solution conditions have on the formation, composition, structures, and stabilities of dissolved metal ions and their condensation products. Towards this end, we are interested in synthesizing and characterizing tetravalent actinide clusters that form through hydrolysis and condensation reactions that occur in aqueous solution.

Significant achievements during 2011-2013: We have used a number of organic and inorganic complexing ligands to isolate well defined An(IV) clusters. Two examples are highlighted below.

1. The synthesis and characterization of carboxylate decorated hexameric  $[\text{Th}_6(\text{OH})_4\text{O}_4]^{12+}$  cluster cores. The cationic, hexameric  $[\text{Th}_6(\text{OH})_4\text{O}_4]^{12+}$  unit was crystallized from aqueous solution using a series of three carboxylate functionalized ligands (Figure 1) that decorate the surface of the cluster and serve as charge-balancing counter-ions. The presence of the cluster cores in solution was confirmed by high energy X-ray scattering. Moreover, electronic calculations done at the DFT level compare well with experiment and were used to guide the experimental peak assignment of Raman and proton NMR spectra.

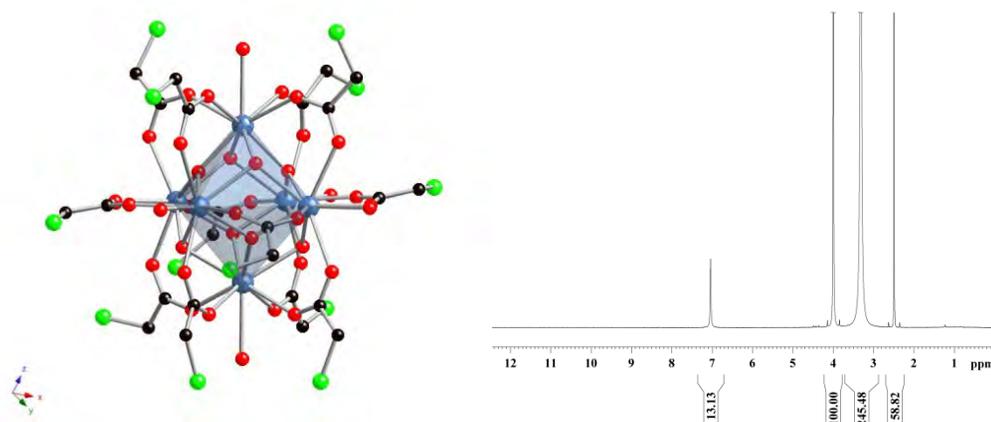


Figure 1. Right: The chloroacetate decorated hexameric  $[\text{Th}_6(\text{OH})_4\text{O}_4(\text{H}_2\text{O})_6]^{12+}$  core wherein each of the  $\text{Th}^{4+}$  ions (blue) are linked to four additional Th via a combination of four  $\mu_3$ -hydroxo and four  $\mu_3$ -oxo bridges (red). Left:  $^1\text{H}$ -NMR spectrum of the chloroacetate complexed cluster. Electronic calculations aided in the assignment of the peak at  $\sim 7\text{ppm}$  which is attributed to the protons of the  $\mu_3$ -OH group.

2. The synthesis and characterization of four Th(IV) hydroxide/oxide octanuclear clusters from aqueous solution (Figure 2). Four compounds each consisting of an octanuclear core,  $[\text{Th}_8\text{O}_4(\text{OH})_8]^{16+}$ , that is built from eight Th(IV) atoms linked by four “inner”  $\mu_3$ -O and eight “outer”  $\mu_2$ -OH groups were isolated. In each of the structures, the core units are stabilized by eight complexing selenate anions with the structures differing primarily by selenate linkages and number of associated waters. Density functional theory calculations were performed to predict the geometries, vibrational frequencies, and relative energies of

different structures. Details of the calculated structures are in good agreement with experiment and the calculated frequencies were used to assign the experimental Raman spectra.

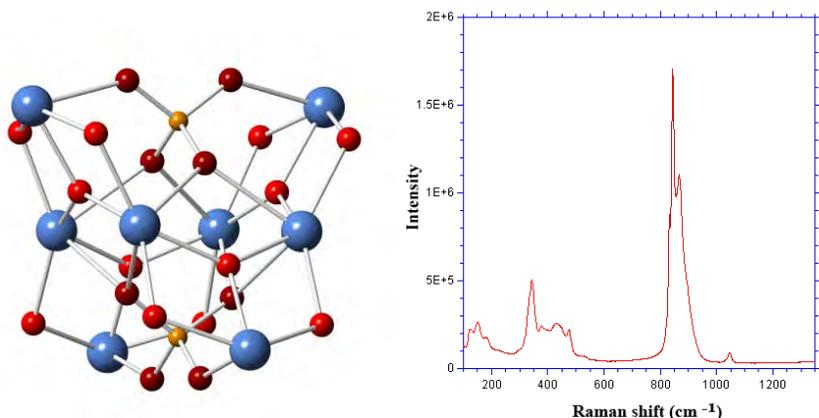


Figure 2. Left: The octameric  $[\text{Th}_8\text{O}_4(\text{OH})_8]^{16+}$  unit demonstrating the different packing of the Th(IV) ions as compared to the hexanuclear unit as well as the incorporation of the selenate anion into the core structure. Right: Raman spectrum of the Th-hydr(oxo)-selenate compound.

Both the hexanuclear and octanuclear clusters include combinations of  $\mu_3$ -hydroxo and  $\mu_3$ -oxo bridges, suggesting that they form from a combination of olation and oxolation reactions. This is in contrast to Pu(IV), the other end member of the tetravalent metal ion series, which is found to form exclusively oxo bridged oligomers. Differences in the composition of Th(IV)- as compared to Pu(IV) oligomers may be attributed to the mechanism of condensation which is related to the size, charge, electronegativity, and acidity of the metal ion.

#### Science objectives for 2013-2015:

- Study the mechanism of Th(IV) cluster formation via solution scattering techniques and NMR and Raman spectroscopic studies aimed at a more detailed knowledge of the underlying factors that play a role in metal ion condensation and cluster assembly.
- Investigate how solution conditions affect the condensation behavior of actinide ions, Th-Pu. Complementary solution and solid state characterization techniques will be used to map the compositional space defined by such variables.
- Probe the surface reactivity and stability of An(IV) clusters.
- Examine the magnetic and electronic properties of clusters of various sizes. Of interest are how, for example, the magnetic behavior changes as a function of cluster nuclearity, and how the behavior relates to the parent oxide.

#### Publications supported by this project 2011-2013

1. Knope, K. E., Soderholm, L. (2013). "Solution and Solid-State Structural Chemistry of Actinide Hydrates and Their Hydrolysis and Condensation Products." *Chemical Reviews* **113**(2): 944-994. DOI 10.1021/cr300212f.
2. Knope, K.E., Vasiliu, M., Dixon, D.A., Soderholm, L., (2012). "Thorium(IV) Selenate Clusters Containing an Octanuclear Th(IV) Hydroxide/Oxide Core." *Inorganic Chemistry* **51**(7): 4239-4249. DOI 10.1021/ic202706s.
3. Vasiliu, M., Knope, K.E., Soderholm, L., Dixon, D.A., (2012). "Spectroscopic and Energetic Properties of Thorium(IV) Molecular Clusters with a Hexanuclear Core." *The Journal of Physical Chemistry A* **116** (25): 6917-6926. DOI 10.1021/jp303493t.
4. Knope, K. E., Wilson, R.E., Vasiliu, M., Dixon, D.A., Soderholm, L., (2011). "Thorium(IV) Molecular Clusters with a Hexanuclear Th Core." *Inorganic Chemistry* **50**(19): 9696-9704. DOI 10.1021/ic2014946.

## Evaluating Actinide-Oxygen Bonding with O K-edge XAS and TDDFT

**Presenting;** Stosh A. Kozimor

**Principal Investigator;** David L. Clark;

**Co-authors;** Stefan G. Minasian,<sup>1,2</sup> Jason M. Keith,<sup>1</sup> Enrique R. Batista,<sup>1</sup> Kevin S. Boland,<sup>1</sup> Joseph A. Bradley,<sup>3</sup> Scott R. Daly,<sup>1</sup> Stosh A. Kozimor,<sup>1</sup> Matthias W. Löble,<sup>1</sup> Wayne W. Lukens,<sup>2</sup> Richard L. Martin,<sup>1</sup> Dennis Nordlund,<sup>4</sup> Angela C. Olson,<sup>1</sup> Gerald T. Seidler,<sup>5</sup> David K. Shuh,<sup>2</sup> Dimosthenis Sokaras,<sup>4</sup> Tolek Tyliczszak,<sup>2</sup> Gregory L. Wagner,<sup>1</sup> Tsu-Chien Weng,<sup>4</sup> and Ping Yang<sup>6</sup>

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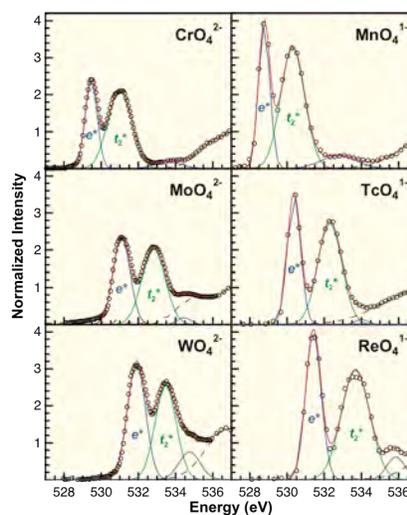
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**Overall Research Goals.** The goal of this research is to advance understanding of electronic structure and covalent actinide ligand bonding.

**Abstract:** Whether the 5f and 6d-electrons in actinide molecules, compounds, metals and some alloys are involved in bonding has been a central and integrating focus for the fields of actinide chemistry and physics. Many studies have focused on investigating actinide bonding, and despite key experimental breakthroughs and significant advances in theory, it remains experimentally and computationally difficult to assess 5f- vs. 6d-orbital participation in bonding. Of the experimental methods for measuring orbital mixing, Cl and S K-edge XAS have emerged as powerful technique for evaluating orbital mixing in metal – ligand bonding for inorganic and bioinorganic systems. In light of such successes, it seems that developing the use of synchrotron-generated radiation to quantify covalency for ligands other than Cl and S would have wide impact. This is especially true for light atoms (i.e. C, N, O, F), because they form the basis of many common ligands and have a propensity to form multiple bonds with unusual reactivity that are largely attributed to covalent metal-ligand bonding. Although the same principles that direct Cl and S ligand K-edge XAS can be used for low Z experiments, a number of experimental challenges face the development of this new area of study. For example, light-atom K-edge XAS probes  $1s \rightarrow 2p$  transitions (180 to 800 eV) that are significantly lower in energy than the  $1s \rightarrow 3p$  transitions (2200 to 2800 eV) associated with Cl and S K-edge XAS. Hence, light atom measurements are extremely sensitive to surface contamination, self-absorption, and saturation effects, any of which yield uncontrolled errors in quantifying orbital mixing. These issues are magnified when radioactive non-conducting molecular systems are analyzed since surface contamination cannot be removed by standard techniques, e.g. cleaving crystals under vacuum or cleaning surfaces using laser ablation.

To demonstrate that relative changes in orbital mixing can be quantitatively evaluated using light atom K-edge XAS we recently published results from a collaborative effort that combined expertise in materials science, chemistry, and physics from three national laboratories, the University of Washington, and three DOE-user synchrotron facilities. The research focused on addressing one of the most basic questions in chemistry, “How do  $\sigma$ - and  $\pi$ - orbital mixing change as the periodic table is



**Fig 1.** The O K-edge STXM transmission data (○), the curve-fit (red trace), and the functions used to fit the pre-edge regions (blue, green, and purple traces).

traversed left-to-right or down a given Group triad?” This research effort exploited recent upgrades in non-resonant inelastic X-ray scattering (NIXS), scanning transmission X-ray microscopy (STXM), and ultra-high vacuum XAS techniques to analyze a coherent sequence of metal-oxo compounds ( $\text{MO}_4^{x-}$ ; M = Cr, Mo, W, Mn, Tc, Re), **Fig 1**. These analytes were chosen because they have been central in developing modern theories of bonding. The study ran the gamut from synthesis, spectroscopy, group theory analysis, and “state-of-the-art” hybrid DFT. Strikingly consistent results were obtained from the experimental and theoretical techniques.

The O K-edge XAS measurements on  $\text{MO}_4^{x-}$  discussed above provides confidence and credibility that quantitative analysis of An–O orbital mixing is also possible. Recently, we leveraged this insight to conduct O K-edge STXM measurements in collaboration with David Shuh (beam line 11-0-2; ALS) on  $\text{UO}_2\text{Cl}_4^{2-}$ ,  $\text{NpO}_2\text{Cl}_4^{2-}$ , and  $\text{PuO}_2\text{Cl}_4^{2-}$ , **Fig 2**. During this experiment, we used horizontally, vertically, and elliptically polarized light to selectively “turn-on” (or “turn-off”) transitions involving  $\pi$  or  $\sigma$  An–O bonds. Although making use of polarization effects is useful for interpreting the spectra, it precludes qualitative analysis for orbital mixing. This is related to the  $\text{O}\equiv\text{An}\equiv\text{O}^{2+}$  units being uniformly arranged in the  $\text{Cs}_2\text{AnO}_2\text{Cl}_4$  crystal, whose orientation in the polarized beam cannot be controlled with the current instrumentation. This poster-presentation will describe the implication of the above-mentioned results on our efforts to advance understanding of actinide electronic structure, and present the data in the context of our recent efforts to quantitatively assess 5f vs 6d orbital mixing in actinide-ligand bonding.

*We gratefully acknowledge support from the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, US Department of Energy.*

### Science Objectives for 2013-2015

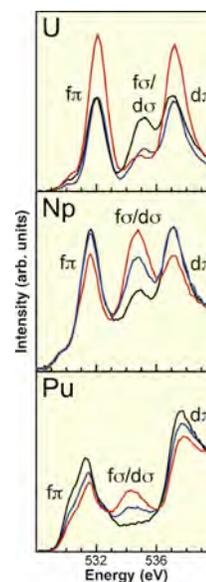
- (i) Develop the use of ligand K-edge XAS and TD-DFT calculations to evaluate actinide-ligand bonding.
- (ii) Initiate complete-active-space-self-consistent-field (CASSCF) calculations to aid in evaluating the effects of multiplet and spin-orbit coupling on the ligand K-edge spectra.

### Publications supported by this project 2012-2013

“Determining Relative f- and d-Orbital Contributions to M–Cl Covalency in  $\text{MCl}_6^{2-}$  (M = Ti, Zr, Hf, U) and  $\text{UOCl}_5^{1-}$  using Cl K-edge X-Ray Absorption Spectroscopy and Density Functional Theory” Minasian, S. G.; Keith, J. M.; Batista, E. R.; Boland, K. S.; Christensen, C. N.; Clark, D. L.; Conradson, S. D.; Kozimor, S. A.; Martin, R. L.; Schwarz, D. E.; Shuh, D. K.; Wagner, G. L.; Wilkerson, M. P.; Wolfsberg, L. E.; Yang, P. *J. Am. Chem. Soc.* **2012**, *134*, 5586-5597. DOI: 10.1021/ja2105015

“Covalency in Metal–Oxygen Multiple Bonds Evaluated Using Oxygen K-edge Spectroscopy and Electronic Structure Theory.” Minasian, S. G.; Keith, J. M.; Batista, E. R.; Boland, K. S.; Bradley, J. A.; Daly, S. R.; Kozimor, S. A.; Lukens, W. W.; Martin, R. L.; Nordlund, D.; Seidler, G. T.; Shuh, D. K.; Sokaras, D.; Tyliszczak, T.; Wagner, G. L.; Weng, T.-C.; Yang, P. *J. Am. Chem. Soc.* **2013**, *135*, 2279. DOI: 10.1021/ja310223b

“Tetrahalide Complexes of the  $[\text{U}(\text{NR})_2]^{2+}$  Ion: Synthesis, Theory, and Cl K-edge Absorption Spectroscopy.” Spencer, L. P.; Minasian, S. G.; Jilek, R. E.; Batista, E. R.; Boland, K. S.; Boncella, J. M.; Conradson, S. D.; Clark, D. L.; Gdula, R. L.; Hayton, T. W.; Kozimor, S. A.; Martin, R. L.; MacInnes, M. A.; Olson, A. C.; Scott, B. L.; Shuh, D. K.; Yang, P. *J. Am. Chem. Soc.* **2013**, *135*, 1864. DOI: 10.1021/ja310575j



**Fig 2.** O K-edge XAS obtained using STXM for  $\text{AnO}_2\text{Cl}_4^{2-}$  (An = U, Np, Pu) with horizontally (black), vertically (red), or circularly (blue) polarized light.

## Recent Progress in the Chemistry of Novel Uranium-Ligand Bonds

Stephen T. Liddle, Keynote Lecture

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**Overall research goals:** The objectives of our research are to study the structure, bonding, reactivity, magnetism, and spectroscopy of non-aqueous depleted uranium compounds by probing carbene, nitride, oxo, and arene derivatives.

**Significant achievements to date:**

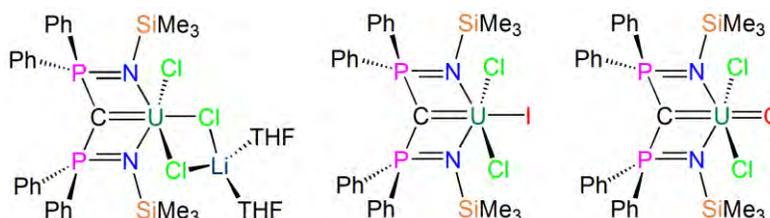


Figure 1. Examples of uranium-carbenes with uranium oxidation states IV, V, and VI.

1. We have prepared a range of uranium-carbenes with oxidation states IV, V, and VI for uranium. This has enabled us to probe the variance of the composition (5f vs 6d) of the U=C bond as a function of the oxidation state of uranium. The evidence to date is that these react with carbonyl compounds to furnish alkenes. This is comparable to transition metal alkylidene reactivity towards ketones and aldehydes but different to analogous lanthanide carbenes which instead activate C-H bonds.

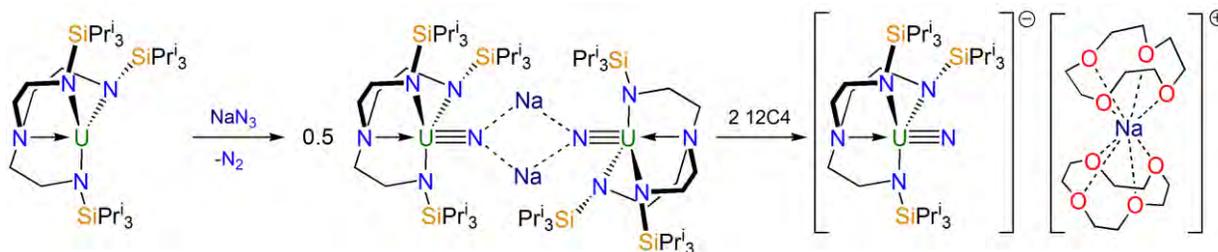


Figure 2. Synthesis of a terminal uranium(V)-nitride triple bond.

2. We have prepared the first molecular uranium-nitride triple bonds under ambient conditions. This has been achieved through the use of a very bulky triamidoamine ligand via mild oxidation of a uranium(III) complex with sodium azide followed by removal of the stabilizing sodium ion using 12-crown-4 ether. This terminal nitride is proving to be a versatile platform for exploitation in this new area of uranium chemistry.

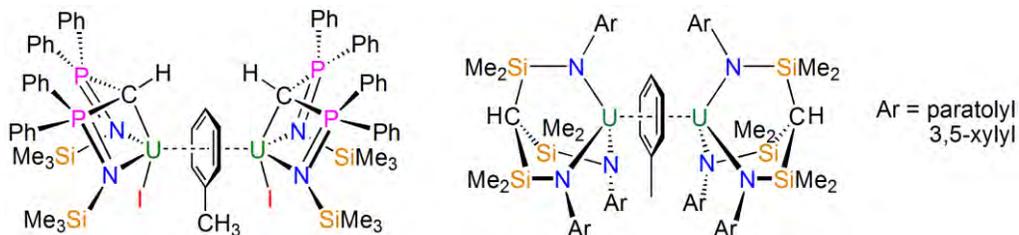


Figure 2. Left: a uranium(III) arene single molecule magnet. Right: high valent uranium(V) toluene tetraanion complexes.

3. We have prepared inverted sandwich uranium arene complexes with unusual properties. One, best formulated as containing uranium(III) and a toluene dianion, is a single molecule magnet. Two others are best formulated as containing uranium(V) and  $10\pi$ -toluene tetraanions. The latter are proving to be capable of supporting novel multi-electron redox chemistry.

#### Selected publications supported by this project

1. Uranium-Carbon Multiple Bonding: Facile Access to the Pentavalent Uranium Carbene  $[U\{C(PPh_2NSiMe_3)_2\}(Cl)_2(I)]$  and Comparison of  $U^V=C$  and  $U^{IV}=C$  Double Bonds  
O. J. Cooper, D. P. Mills, J. McMaster, F. Moro, E. S. Davies, W. Lewis, A. J. Blake, and S. T. Liddle, *Angew. Chem. Int. Ed.* **2011**, *50*, 2383-2386.
2. A delocalised arene-bridged diuranium single molecule magnet  
D. P. Mills, F. Moro, J. McMaster, J. van Slageren, W. Lewis, A. J. Blake, and S. T. Liddle, *Nature Chem.* **2011**, *3*, 454-460.
3. A Formal High Oxidation State Inverse-Sandwich Diuranium Complex: A New Route to f-Block-Metal Bonds  
D. Patel, F. Moro, J. McMaster, W. Lewis, A. J. Blake, and S. T. Liddle, *Angew. Chem. Int. Ed.* **2011**, *50*, 10388-10392.
4. Homologation and Functionalization of Carbon Monoxide by a Recyclable Uranium Complex  
B. M. Gardner, J. C. Stewart, A. L. Davis, J. McMaster, W. Lewis, A. J. Blake, and S. T. Liddle, *Proc. Nat. Acad. Sci. USA* **2012**, *109*, 9265-9270.
5. Synthesis of a Uranium(VI)-Carbene: Reductive Formation of Uranyl(V)-Methanides, Oxidative Preparation of a  $[R_2C=U=O]^{2+}$  Analogue of the  $[O=U=O]^{2+}$  Uranyl Ion (R =  $Ph_2PNSiMe_3$ ), and Comparison of the Nature of  $U^{IV}=C$ ,  $U^V=C$  and  $U^{VI}=C$  Double Bonds  
D. P. Mills, O. J. Cooper, F. Tuna, E. J. L. McInnes, E. S. Davies, J. McMaster, F. Moro, W. Lewis, A. J. Blake, and S. T. Liddle, *J. Am. Chem. Soc.* **2012**, *134*, 10047-10054.
6. Synthesis and Structure of a Terminal Uranium Nitride Complex  
D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, and S. T. Liddle, *Science* **2012**, *337*, 717-720.

## Ion-ligand Interactions in Actinyl Compounds: Analysis and Simulation of Optical Spectra

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Overall research goals: We seek a fundamental understanding of electronic properties of actinides in complexes and compounds. The consequences of ion-ligand electronic and vibronic interactions are revealed from spectroscopic experiments and theoretical analyses.

Significant achievements during 2011-2013: Ion-ligand interactions of uranyl and neptunyl in complexes and compounds have been investigated in spectroscopic experiments and theoretical calculations. Luminescence and absorption spectra have been theoretically analyzed and simulated to assign the electronic states of different configurations and to characterize the electronic and vibronic transitions of different origins commonly known as ligand-to-metal charge transfer and f-f transitions. Both types of electronic transitions involve states of mixed orbitals, and provide information on ionic and covalent behavior of actinyl ions in complexes. Our calculations of electronic energy levels and simulations of vibronic transitions, as shown in Fig. 1 for  $\text{Cs}_2\text{Np}(\text{U})\text{O}_2\text{Cl}_4$ ,

have provided a quantitative understanding of actinyl electronic interactions in terms of electron exchange interaction, spin-orbit coupling, crystal-field interaction, and ion-ligand vibronic coupling. The method we developed for empirical simulations of optical spectra has been used for evaluating the stability of the  $\text{An}=\text{O}$  bond in various ligand environments. Using a phenomenological model of electrostatic and vibrational potential, we have derived a theoretical relationship between the ligand charge and the

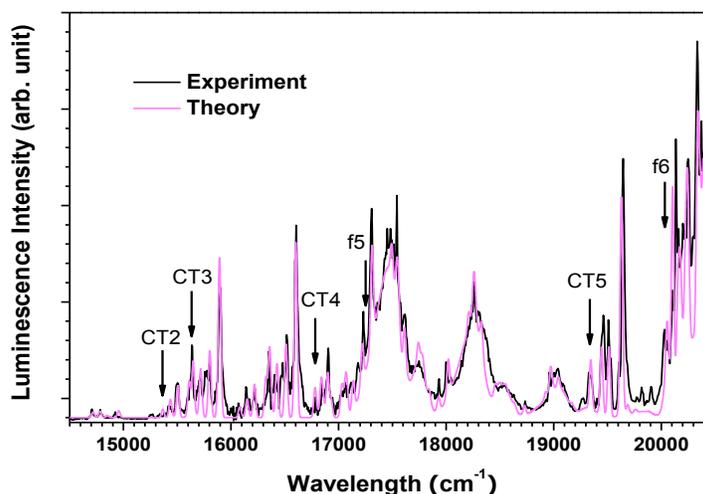
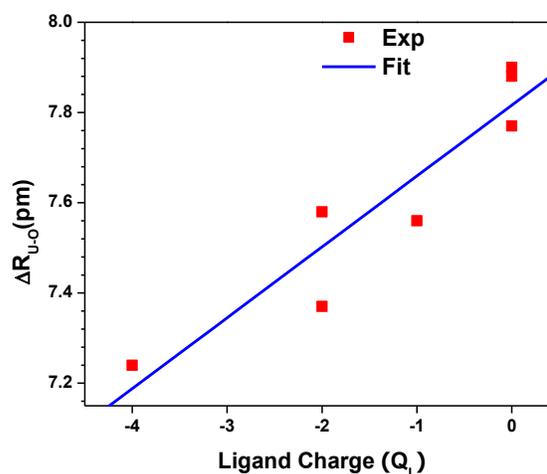


Fig. 1 Experimental and simulated excitation spectra of  $\text{Cs}_2\text{Np}(\text{U})\text{O}_2\text{Cl}_4$  at 75 K. The zero-phonon lines of CT and f-f transitions are marked by the arrows.

stability of uranyl bond (change in U-O bond length):  $\Delta R(Q_L) = A + BQ_L$ , with  $A=7.8$  pm and  $B=0.157$  pm/e for the uranyl complexes of  $\text{UO}_2\text{-L}_{0,1,2}$  ( $L=\text{ODA}$ ,  $\text{DMOGA}$ ,  $\text{TMOGA}$ ) as shown in Fig. 2. The systematic trend revealed in our spectroscopic studies is consistent with that demonstrated in thermodynamics.

Fig. 2. Dependence of O=U=O bond expansion ( $\Delta R_{\text{U-O}}$ ), after excitation into the low-lying excited states of uranyl, on the charge ( $Q_L$ ) carried by the ligand species in the uranyl complexes of  $\text{UO}_2\text{-L}_{0,1,2}$  ( $L=\text{ODA}$ ,  $\text{DMOGA}$ ,  $\text{TMOGA}$ ).



Science objectives for 2011-2013: Experimental and theoretical studies will be conducted systematically on the actinyl series, including  $\text{AnO}_2^{2+}$  ( $\text{An}=\text{U}$ ,  $\text{Np}$ ,  $\text{Pu}$ ) and  $\text{PaO}_x^{n+}$  species in various ligand environments of different coordination geometries and electrostatics. Information on ion-ligand covalence and bonding properties will be obtained through a combination of spectroscopic experiments, to monitor the ligand-to-metal charge transfer transitions, 5f-5f (6d) transitions and Raman shifts, and XRD structural characterization, to link the observed electronic behavior to physical structure. Analyses and calculations will be performed to interpret the bonding and coordinate behaviors of the actinyl systems in terms of electronic interactions.

#### Publications supported by this project 2011-2013

1. ANALYSIS OF ELECTRONIC STATES AND ENERGY LEVEL STRUCTURE OF URANYL IN COMPOUNDS  
G. K. Liu  
*J. Chem. Phys. A* 2011, 115, 12419- [dx.doi.org/10.1021/jp208012q]; 2012, 116, 7443-7443[DOI: 10.1021/jp3043472].
2. CHARGE TRANSFER VIBRONIC TRANSITIONS IN URANYL TETRACHLORIDE COMPOUNDS  
Guokui Liu, Nicholas P. Deifel, Christopher L. Cahill, Vladimir V. Zhurov and A. Alan Pinkerton  
*J. Phys. Chem. A* 2012, 116, 855-864[dx.doi.org/10.1021/jp210046j].
3. ELECTRONIC TRANSITIONS AND VIBRONIC COUPLING IN NEPTUNYL COMPOUNDS  
Guokui Liu, Shuao Wang, Thomas E. Albrecht-Schmitt, and Marianne P. Wilkerson  
*J. Phys. Chem. A* 2012, 116, 8297-8302[dx.doi.org/10.1021/jp302679q].

## Fundamental Chemistry of Technetium in Oxide Matrices Characterization of f-Orbital Bonding

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Dr. John McCloy, Radiological Materials & Technology Development, Pacific Northwest National Laboratory.

Dr. Trevor Hayton, Department of Chemistry and Biochemistry, University of California, Santa Barbara.

Dr. Norman Edelstein, Chemical Sciences Division, Lawrence Berkeley National Laboratory.

Dr. Corwin Booth, Chemical Sciences Division, Lawrence Berkeley National Laboratory.

Dr. Richard Andersen, Department of Chemistry, University of California, Berkeley.

Overall research goals: The objective of the technetium project is to understand the factors that control the chemistry of technetium during incorporation into oxide matrices including nuclear waste forms, waste form surrogates, and model systems. The objective of the f-orbital bonding project is modeling and quantifying f-orbital contributions to bonding using electronic spectroscopy (UV-Vis-near IR, EPR, XANES) and other physical measurements.

Significant achievements during 2011-2013:

1. The initial goal of the Tc project was to test the hypothesis that conditions under which magnetite is formed in solution will result in the incorporation of tetravalent technetium ions into the magnetite lattice, which has been completed. Subsequently, the focus has been on understanding the behavior of Tc as these materials corrode and exploring the chemistry of  $\text{TcO}_4^-$  in nitric acid during denitration. In the latter case, the goal has been to directly incorporate Tc(IV) into either iron or titanium oxide during denitration, which has been largely unsuccessful with the exception of incorporating Tc into magnetite in analogy with previous work. The focus will shift to understanding the chemistry of Tc during denitration to understand why attempts to incorporate Tc into oxides during denitration have been unsuccessful. In addition, work with collaborators has investigated the behavior of Tc and Re (the usual nonradioactive surrogate for Tc) in nuclear waste forms related to closure of the Hanford Site as well as work with Lynn Francesconi on the behavior of Tc in polyoxometallate complexes.

2. The goal of the f-orbital bonding project is to characterize and quantify the participation of the f-orbitals in bonding using experimental approach (especially EPR, UV-Vis-nearIR, and magnetic susceptibility) coupled with simple models. In collaboration with Trevor Hayton, the f-orbital contribution to bonding in octahedral  $f^1$ -complexes has been quantified in the complexes recently reported by the Hayton group. The bonding in these complexes has been compared to those of the well-known  $f^1$  actinide hexahalide complexes ( $\text{PaX}_6^{2-}$ ,  $\text{Ux}_6^-$ ,  $\text{NpF}_6$ ). In analyzing the data, the role of covalency in reducing spin-orbit coupling itself (in addition to reducing orbital angular momentum) was found to be important. The strength and covalency of  $\pi$ - and  $\sigma$ -bonds in these systems has been quantified using the revised model and data from near IR and EPR spectroscopy.

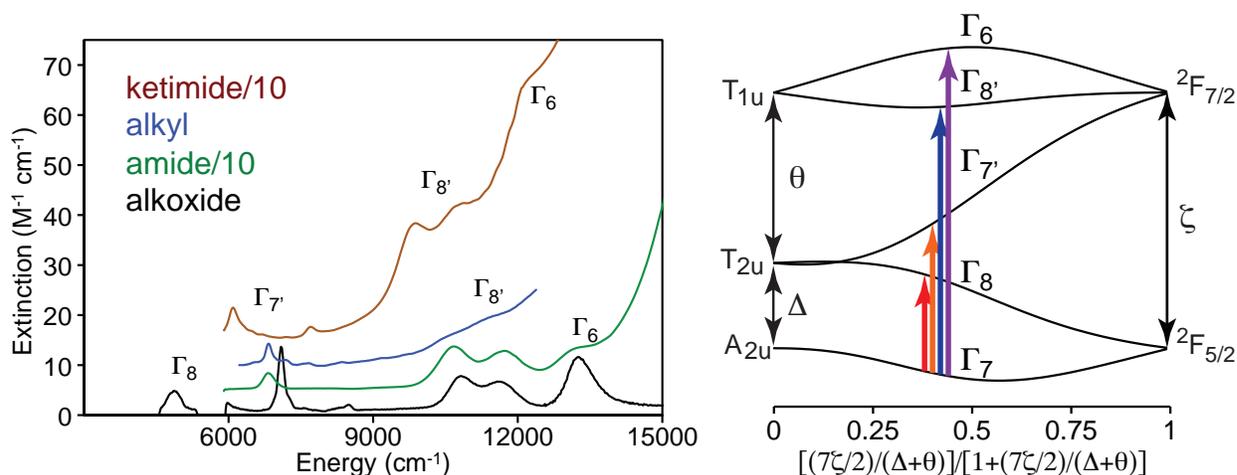


Figure 1. Left: near IR spectra of the octahedral,  $f^1$   $UX_6^-$  complexes prepared by Trevor Hayton's group; from top to bottom, X is ketimide ( $-\text{N}=\text{C}^t\text{BuPh}$ ), alkyl ( $-\text{CH}_2\text{SiMe}_3$ ), amide ( $-\text{NC}_5\text{H}_{10}$ )b and alkoxide ( $-\text{O}^t\text{Bu}$ ). The peaks are labeled with the final state of the transition (the initial state is  $\Gamma_7$  in all cases). Right: The low-lying states of f-parentage in  $O_h$  symmetry; on the left side, spin orbit coupling is zero and on the right side, the crystal field splitting is zero.

#### Science objectives for 2011-2013:

- Study chemical denitration of 5 M nitric acid containing  $\text{TcO}_4^-$  to determine the speciation of technetium as a function of denitration agent (formic acid, sugar, hydroxylamine, hydrazine)
- Test the hypothesis that iron oxides, especially a mixture of magnetite and maghemite/hematite, can buffer the oxygen fugacity at high temperature and stabilize Tc(IV) in the matrix.
- Determine the chemical speciation of Tc in model complexes (polyoxometallates).
- Extend study of bonding in  $f^1$  complexes to other species.

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1. Wenshan Ren, Wayne W. Lukens, Guofu Zi, Laurent Maron, and Marc D. Walter "Is the bipyridyl thorium metallocene a low-valent thorium complex? A combined experimental and computational study" *Chem. Sci.*, 2013, 4, 1168-1174. DOI:10.1039/C2SC22013J
2. 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. Shuh, Dimosthenis Sokaras, Tolek Tyliczszak, Gregory L. Wagner, Tsu-Chain Weng, Ping Yang "Covalency in Metal-Oxygen Multiple Bonds Evaluated Using Oxygen K-edge Spectroscopy and Electronic Structure Theory" *J. Am. Chem. Soc.*, 2013, 135, 1864–1871. DOI: 10.1021/ja310223b
3. John S. McCloy, Brian J. Riley, Ashutosh Goel, Martin Liezers, Michael J. Schweiger, Carmen P. Rodriguez, Pavel Hrma, Dong-Sang Kim, Wayne W. Lukens, Albert A. Kruger, "Rhenium Solubility in Borosilicate Nuclear Waste Glass: Implications for the Processing and Immobilization of Technetium-99" *Environ. Sci. Technol.*, 2012, 46, 12616–12622. DOI: 10.1021/es302734y
4. Wooyong Um, Hyunshik Chang, Jonathan P. Icenhower, Wayne W. Lukens, R. Jeffrey Serne, Nik Qafoku, Ravi K. Kukkadapu, Joseph H. Westsik Jr., "Iron oxide waste form for stabilizing  $^{99}\text{Tc}$ " *J. Nucl. Mat.* 2012, 429, 201-209. DOI: 10.1016/j.jnucmat.2012.06.004
5. Lani Seaman, Guang Wu, Norman Edelstein, Wayne Lukens, Nicola Magnani, and Trevor Hayton, "Probing the 5f Orbital Contribution to the Bonding in a U(V) Ketimide Complex" *J. Am. Chem. Soc.* 2012, 134, 4931-4940. DOI: 10.1021/ja211875s
6. Benjamin P. Burton-Pye, Ivana Radivojevic, Donna McGregor, Israel M. Mbomekalle, Wayne W. Lukens, Jr., and Lynn C. Francesconi "Photoreduction of  $^{99}\text{Tc}$  Pertechnetate by Nanometer-Sized Metal Oxides: New Strategies for Formation and Sequestration of Low-Valent Technetium" *J. Am. Chem. Soc.*, 2011, 133, 18802-18815. DOI: 10.1021/ja2060929

## Principles of Chemical Recognition and Transport in Extractive Separations: Mechanism of Synergized Anion Exchange Using Neutral Anion Receptors

Bruce A. Moyer, Principal Investigator

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Collaborators: Peter V. Bonnesen, Radu Custelcean, Lætitia H. Delmau, and Benjamin P. Hay, Oak Ridge National Laboratory; Prof. Kristin Bowman-James, University of Kansas; Prof. Emmanuel Makrlík, Czech Academy of Sciences; and Prof. Jonathan L. Sessler, University of Texas, Austin

Overall research goals: The overarching goal of our research program is to understand the factors underlying selectivity in the separation of ions by novel receptors and to learn how such factors can be manipulated by design to yield predictable behavior. The specific aim motivating the studies described herein entails understanding the role of coulombic interactions in determining the selectivity and behavior of anion receptors and how these effects can be harnessed in cooperation with other donor interactions. We have been exploring this question in the context of synergistic anion exchange (SAE), an approach to enhanced liquid-liquid extraction of anions in which a neutral lipophilic anion receptor is mixed with an anion-exchange vehicle such as a lipophilic quaternary ammonium salt. While the anion-exchanger has a selectivity of its own favoring charge-diffuse anions determined largely by ion pairing and solvation, the addition of an anion receptor to the organic phase potentially introduces new selectivity via structured hydrogen-bond donor (HBD) interactions. Does the anion receptor do this independently of the anion-exchange vehicle, or are there cooperative effects that can be identified and exploited to enhance selectivity?

Significant achievements during 2011–2013: Efforts to understand SAE were brought to a fruitful conclusion. Confirming hypothesis, neutral anion receptors can indeed perturb the selectivity of a lipophilic quaternary ammonium salt ( $Q^+X^-$ ) such as methyltri- $C_{8,10}$ -ammonium chloride (Aliquat 336 or A336). However, the effect is most striking when R

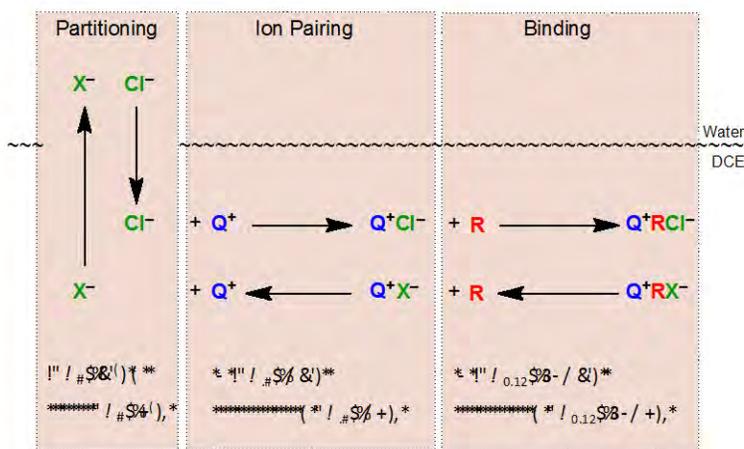


Figure 1. Thermochemical model for synergized anion exchange for univalent anions  $Cl^-$  (reference anion) and  $X^-$ , univalent lipophilic cation  $Q^+$ , and anion receptor R, in 1,2-dichloromethane (DCE).

and  $Q^+$  behave cooperatively. A thermochemical model was developed and validated for univalent anion exchange for 10 anions using A336 mixed with *meso*-octamethylcalix[4]pyrrole (C4P) in 1,2-dichloroethane. As shown in Figure 1 for  $Cl^-$  exchange with a competing anion  $X^-$ , the affinity of R for ion pair  $Q^+Cl^-$  vs  $Q^+X^-$  determines

the exchange selectivity. Although C4P exhibits a known high affinity for chloride ion, it has little effect on the selectivity of anion exchange when the lipophilic cation is tetraheptylammonium. When the lipophilic cation is A336, however, the synergistic effect is strong enough to overcome the normal strong exchange selectivity for nitrate. This remarkable effect of the cation structure is interpreted in terms of insertion of the methyl group of the A336 cation into the cup formed by C4P in its cone conformation, as supported by X-ray crystallography. Overall, we learned that a coulombic penalty weakens SAE generally but can be overcome if there is supramolecular *cooperativity* between the lipophilic cation and the anion receptor, such as that observed for C4P and A336. We accordingly hypothesize that an even greater enhancement of anion-exchange selectivity may be obtained with more fully functional receptors that incorporate the positive charge within their molecular frameworks.

#### Science objectives for 2013–2015:

- Synthesize and structurally characterize a series of guanidinium anion extractants, in which the HBD groups bear a positive charge. Combine the guanidinium groups with urea groups to obtain charge and shape complementarity for target anions such as sulfate.
- Examine the selectivity of the new guanidinium-urea extractants by liquid-liquid extraction toward understanding charge complementarity as a selectivity criterion.
- Investigate more complex architectures toward recognition of ion multiples.

#### Publications supported by this project 2011–2013:

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**, (invited forum review) DOI: 10.1021/ic3016832.
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5. Makrlík, E.; Toman, P.; Vaňura, P.; Moyer, B. A. Interaction of the Cesium Cation with Calix[4]arene-bis(*t*-octylbenzo-18-crown-6): Extraction and DFT Study. *J. Mol. Struct.* **2012**, *1033*, 14–18.
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7. Moyer, B. A. Milestones and Future Directions in the Solvent Extraction of Caesium. In *Proc. International Solvent Extraction Conference ISEC 2011*, Santiago, Chile, Oct. 3–7, 2011; Valenzuela F., Moyer, B. A., Eds.; Gecamin: Santiago, 2011; (Plenary lecture).

## **The TALSPEAK Process:**

### ***Using Fundamental Chemistry to Unravel Complex Interactions***

Ken Nash, Keynote Lecture

Department of Chemistry, Washington State University, Pullman, WA 99164

There are two principal modes of operation for U-Pu nuclear fuel cycles, the open (once through) and closed (incorporating recycle) options. The open cycle offers the apparent economic advantage of limited treatment of used fuel, but the long term challenge of proving that it is possible to isolate these materials from human intrusion for hundreds of millennia. The fully-closed cycle demands increased up front expenses for separations and actinide-burner reactors/transmutation systems, but a drastically shortened time line (several hundred years) for isolation and increased proliferation resistance through continuous recycle and transmutation of heavy actinides. Presently the U.S. operates its nuclear power system as an open cycle, utilizing something less than 1% of the total power potential of the fuel as it is extracted from the earth.

At present the most mature option for closing the fuel cycle relies on aqueous processing, based principally on liquid-liquid extraction. Solvent extraction uniquely offers the option of continuous operation, a very attractive feature considering the 72,000 tons of fuel from power reactors needing disposal. In this context, the primary unresolved challenge is separating transplutonium actinides from lanthanide fission products. At present, the best candidate for accomplishing this separation in the current framework is some variation on the TALSPEAK process. This Ln/An separation system, developed in the 1960s at ORNL, matches a cation exchanging solvent extraction reagent against a water-soluble, actinide-selective complexant, typically an aminopolycarboxylic acid. Though process development engineers have demonstrated at some level that TALSPEAK could be operated at the plant scale, it is projected as a difficult process to control and so to operate efficiently. A more robust option would be welcome.

As process development work commenced on TALSPEAK (in the context of advanced treatment options and the UREX process) several years ago, it became apparent to us that there were some significant gaps in knowledge of the molecular scale interactions that allowed the process to operate. We seized this opportunity and began an examination of the basic chemistry of the process. The first unusual feature of TALSPEAK chemistry (relative to the usual practice of solution chemistry or even of solvent extraction) was the need for a very high concentration (> 1.0 M) of a carboxylic acid buffer to control pH. Previous reports established that a 1 M lactate buffer controlled reasonably well the preferred pH of 3.0-3.5, offered protection against the effects of radiolysis, and most importantly to improve lanthanide phase transfer kinetics. But process performance was unpredictable and sometimes inconsistent.

Our investigation of the fundamental chemistry of TALSPEAK began with thermodynamic modeling, which established a “disconnect” between thermodynamic predictions and operational characteristics of the process. Thermodynamic data from the literature predicted a flat to rising pH dependence in conventional TALSPEAK, while the observed acid dependence was exactly the opposite (Figure 1). Similar observations in the prior literature were variously explained as arising from changing stoichiometry of the extraction reaction, to mixed ligand complexes, to lack of attainment of thermodynamic equilibrium, to inaccurate/inappropriate thermodynamic data and several others. These explanations suffered one notable limitation: they were based more on rationalization and indirect characterization of the possible interactions than on direct examination of the molecular scale interactions between solute molecules, metal ions, and solvent. We determined that there was considerable insight to be gained from a detailed, molecular scale examination of the fundamental chemistry of this complex, far-from-ideal system.

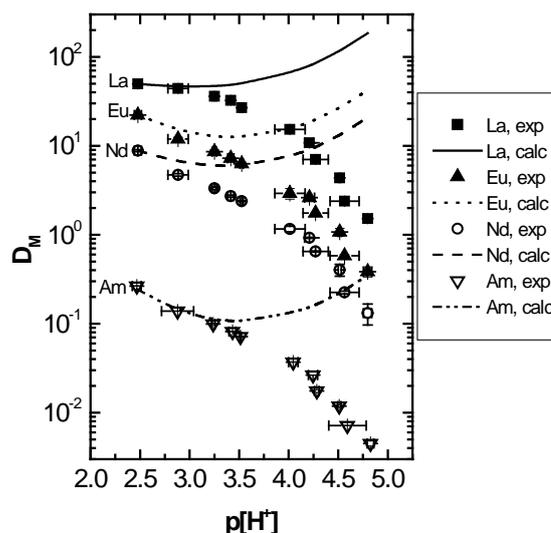


Figure 1. Distribution ratios of americium, lanthanum, neodymium and europium as a function of  $p[H^+]$ . Experimental conditions were for the aqueous phase: 1M  $Na^+$ , 1 M lactic acid, 0.05 M DTPA, 1 mM (total) Ln + Y. For the organic phase: 0.5 M HDEHP in 1,4-DIPB, extraction carried out in room temperature.

Our subsequent investigations involved the efforts of numerous graduate students and postdoctoral associates who applied a variety of different complementary analytical methods to deconstruct the fundamental chemistry of the TALSPEAK process. In sum, the investigation established that both  $Na^+$  and lactic acid partition into the organic phase and compete with lanthanides for the extractant (HDEHP), that lanthanide ligand exchange kinetics in the aqueous phase (stopped flow spectrophotometry), the organic phase ( $^{31}P$  NMR spectroscopy), and in the biphasic system were considerably impacted by the concentration of lactate ion. Redetermination of thermodynamic data established the essential validity of the thermodynamic modeling predictions, but also indicated some anomalies. Electrospray Ionization Mass Spectrometry (ESI-MS), Small Angle Neutron Scattering (SANS) and Fluorescence measurements indicated that, at high concentrations of extracted lanthanide ions and in the presence of lactate, complex supramolecular organization of solutes and solvent in the extractant phase was important. These insights have pointed the way towards an improved Advanced TALSPEAK process based on variations in each category of reagent (extractant, complexant and buffer) promising significantly simplified approaches to lanthanide-actinide separations. These results will be summarized in this presentation.

Work supported by the Department of Energy, Office of Nuclear Energy, Nuclear Energy Research Initiative, Nuclear Energy University Program, and Fuel Cycle R&D Program, Sigma Team for Minor Actinide Separations and in part by subcontracts with the Idaho National Laboratory.

## Aqueous Chemistry of Cn and Fl Homologues: Liquid-Liquid Extraction of Cd, Hg, and Pb.

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Ken Gregorich, Co-PI, Senior Staff Scientist<sup>i</sup>

Philip Mudder, Graduate Student Researcher<sup>ii</sup>

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Overall research goals: The objective of this new project is to explore the aqueous chemistry of the superheavy elements copernicium (<sup>112</sup>Cn) and flerovium (<sup>114</sup>Fl). To begin with, we are exploring aqueous separation schemes using the homologues mercury (Hg) and cadmium (Cd), and lead (Pb) to evaluate the periodic behavior of Cn and Fl, respectively.

Significant achievements during 2012-2013: Work began in May 2012 with the production of radionuclide tracers for homologue separations. This has led to separations of Hg and Cd from various organic extractants and solvents. The main result from these separations is shown below in Figure 1 with the selective extraction of Hg in weakly acidic solutions with Cyanex 923 ligand.

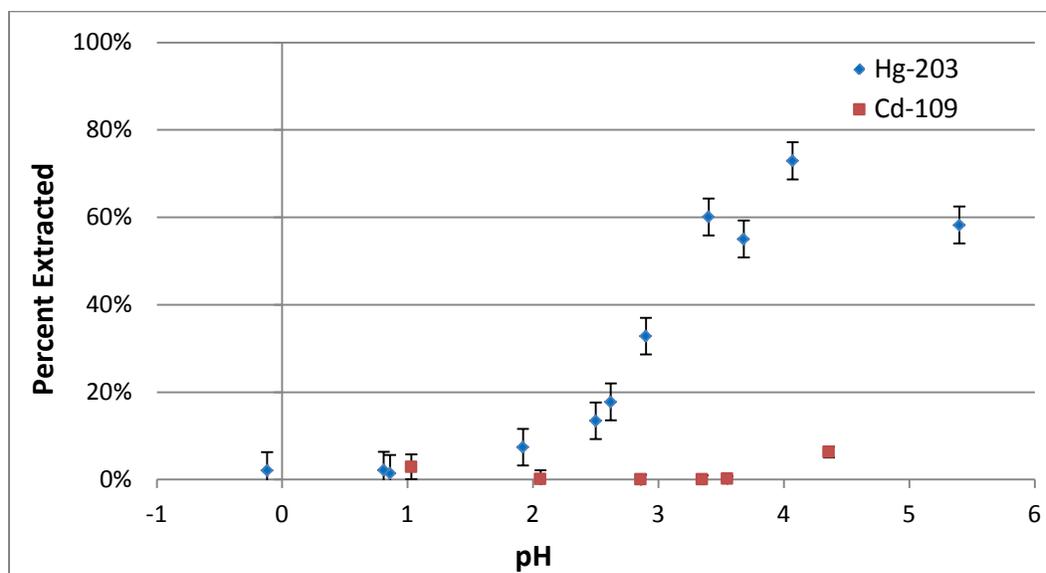


Figure 1. Extraction of <sup>109</sup>Cd and <sup>203</sup>Hg with 0.1M Cyanex 923 in toluene (pH adjusted with H<sub>2</sub>SO<sub>4</sub>)

### Science objectives for 2013-2016:

- Complete homologue extractions to determine the optimum procedures to use in atom-at-a-time studies at the BGS.
- Produce a microfluidic device capable of performing a liquid-liquid extraction and detection of accelerator produced ions under 100 ms.
- Test the microfluidic device off-line with homologue extraction systems.
- Test the microfluidic device with homologue extraction systems coupled to the RFQ trap/gas catcher/BGS at the 88" cyclotron.
- Perform microfluidic liquid-liquid extractions of copernicium and flerovium.

Publications supported by this project: None at this time

The goal of this new project is to conduct experiments exploring the aqueous nature of the superheavy elements copernicium ( $^{112}\text{Cn}$ ) and flerovium ( $^{114}\text{Fl}$ ). Relativistic effects dominate the chemistry of superheavy elements, which may lead to deviations from periodic trends in the electron orbitals. The short half-lives of Cn and Fl have thus far prevented effective studies on their aqueous chemistry. We are developing a microfluidic separation device to decrease the separation time into the millisecond range. To begin with, we are exploring aqueous separation schemes using the homologues mercury (Hg) and cadmium (Cd), and lead (Pb) to evaluate the periodic behavior of Cn and Fl, respectively. The Cn homologues are being extracted with Cyanex 923 in toluene with Hg extracting in weakly acidic solutions and Cd not showing any significant extraction at any pH. The liquid-liquid extractions are performed using radioactive tracers of these homologues as an offline separation. The extraction properties will then be tested by one-atom-at-a-time chemistry at the Berkeley Gas-filled Separator. This requires the development of a microfluidic extraction device for online separation. Ultimately, this microfluidic device will be used to test the aqueous nature of these superheavy elements in comparison to their homologues.

## Pre-organized and Immobilized Ligands for Metal Ion Separations

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(University of Nevada-Reno), Andrew J. Gaunt (Los Alamos National Laboratory)

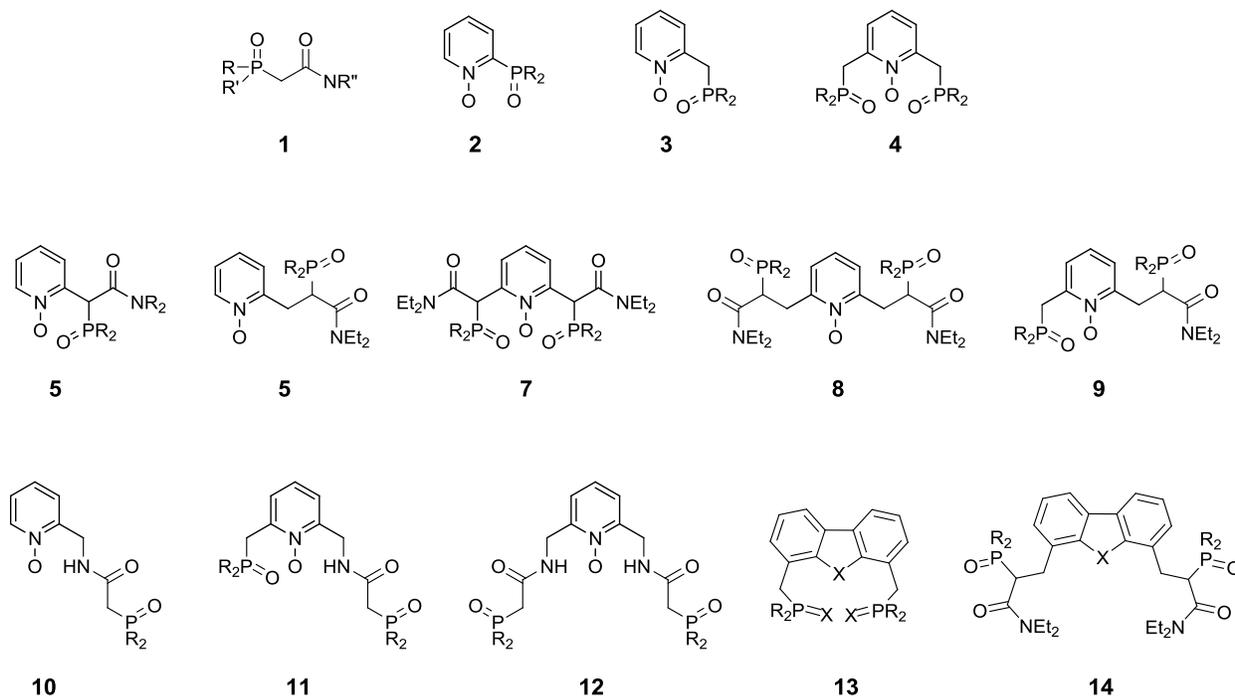
Overall Research Goals: Computational molecular modeling, organic synthesis, lanthanide coordination chemistry, spectroscopy and X-ray crystal structural analyses are used to construct and optimize new ligand environments for f-element ions. These studies reveal the fundamental and complex interplay between electronic, steric and architectural organization features that influence selective recognition of these unique ions by receptor molecules in solution. In turn, the basic science approach sheds light on molecular features that impact practical solution-based separation problems that exist in the DoE complex. The university studies of lanthanide ions as actinide surrogates is complimented by collaborative actinide chemistry at National Laboratory sites that includes quantitative solvent extraction analyses and actinide ion coordination chemistry.

### Significant Achievements during 2011-2013:

*Ligand design/synthesis/Ln coordination chemistry activities:* Hybrid multifunctional P=O, C=O and N-O donor decorated ligand architectures of the types illustrated by **1-4** have previously been shown to provide unique coordination environments for f-element cations. Furthermore, examples of **1** are well known to act as selective extractants for f-element cations, and they are the key component in TRUEX and related processes used to partition f-element cations from highly acidic aqueous nuclear materials solutions. During the last two years we have continued our efforts to expand on the knowledge core regarding the structure-function characteristics of these ligands and to develop additional architectures that lead to enhanced ligand binding, selectivity and improved separation performance. In particular, we have devoted attention to new architectures that marry the CMPO-type fragment, (**1**) to pyridine, pyridine N-oxide, dibenzofuran and dibenzothiophene platforms. These efforts have resulted in new multidentate structure types depicted by **5-14**. Efficient synthetic pathways have been devised, lanthanide coordination chemistry explored, structural characterization of coordination environments completed and selected extraction analyses performed.

Science objectives for 2013-2014: The program for robust, all O-atom donor ligand design and synthesis, lanthanide coordination chemistry and extraction analyses will be continued with primary attention

given to evolution of new examples of platforms **5-14**. In addition, efforts to prepare and study the actinide ion coordination chemistry of donor “softened” examples of **7**, **9**, **11** and **13** will be continued.



Publications supported by this project 2011-2013:

1. J.M. Camus, S. Pailloux, C.E. Shirima and R.T. Paine “Synthesis of 2,5-bis(phosphinoylmethyl)- and 2,5-bis(thiophosphinoylmethyl)-thiophenes” *Main Group Chem.*, **2011**, *10*, 25-36. DOI: **10.3233/MGC-2010-0022**
2. S. Pailloux, C.E. Shirima, E.N. Duesler, K.A. Smith and R.T. Paine “Synthesis and lanthanide coordination chemistry of 2[(phosphinoyl)methyl]-4,5-dihydrooxazole and 2-[(phosphinoyl)methyl]benzoxazole ligands” *Polyhedron*, **2011**, *30*, 2746-2757. DOI: **10.1016/j.poly.2011.08.012**
3. M. Chakravarty, S. Pailloux, E.N. Duesler, K.A. Smith, R.T. Paine, N.J. Williams and R.D. Hancock “Synthesis and metal coordination chemistry of (phenyl)(pyridine-2-ylmethyl)phosphinodithioic acid, [2-C<sub>5</sub>H<sub>4</sub>N]CH<sub>2</sub>P(S)(SH)(Ph)” *Polyhedron*, **2012**, *33*, 327-335. DOI: **10.1016/j.poly.2011.11.041**
4. J. Sulakova, R.T. Paine, M. Chakravarty and K.L. Nash “Extraction of Lanthanide and Actinide Nitrate and Thiocyanate Salts by 2,6-Bis[(bis 2-n-octyl)phosphino)methyl]pyridine N,P,P’-trioxide in Toluene” *Sep. Sci. Tech.*, **2012**, *47*, 2015-2023. DOI: **10.1080/01496395.2012.697323**
5. D. Rosario-Amorin, E.N. Duesler, R.T. Paine, B.P. Hay, S. Reilley, B.L. Scott and A. J. Gaunt “Synthesis and Coordination Chemistry of Phosphino Oxide Decorated Dibenzofuran Platforms” *Inorg. Chem.*, **2012**, *51*, 6667-6681. DOI: **10.1021/ic.300301d**
6. D. Rosario-Amorin, S. Ouizem, D.A. Dickie, Y. Wen, R.T. Paine, J. Gao, J. K. Grey, A. de Bettencourt-Dias, B.P. Hay and L.H. Delmau “Synthesis, Coordination Chemistry and Liquid-Liquid Extraction Performance of CMPO-decorated Pyridine and Pyridine N-oxide Platforms” *Inorg. Chem.* accepted

## Spin-forbidden Chemical Reactions in Catalysis from First-principles

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Overall research goals: The purpose of this project is to develop computational tools for the first-principles modeling of reactions that involve intercrossing of spin-states, with particular emphasis on catalytic reactions with transition metals and heavy elements.

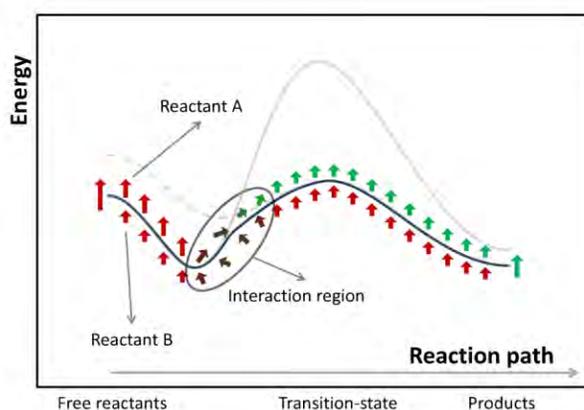


Figure 1: Schematic representation of a spin-forbidden chemical reaction.

### Significant achievements during 2011-2013:

- The student working on the project was hired in 2011. During this period we have developed a search algorithm to find the minimum energy crossing point (MECP) between two (spin adiabatic) energy surfaces of different spin-multiplicity (Table 1). Using this we analyzed the performance of different density functional methods to characterize the geometric parameters and energetics of the MECP in a set of small molecules where comparison with accurate wave-function methods is feasible.

Table 1: Mean absolute error (in kcal mol<sup>-1</sup>) for the minimum energy crossing point (MECP) and energy gap between different-spin structures ( $\Delta E$ ) for a set of 8 small molecules. CCSD(T) values are used as reference.

	MECP	$\Delta E$
LSDA	11.7	12.5
PBE	8.0	8.6
PBEh	6.8	6.8
MP2	9.0	7.6
MP4	6.3	4.4

- We have finalized the methodology to calculate spin-torques between different pairs of magnetic centers. Although this is in connection to the evaluation of magnetic

exchange coupling constants and related to another project, it is the starting point for the third science objective below.

Science objectives for 2013-2015:

- Improve the MECP search code and implement an approximate Hessian update to make it more efficient.
- Implement the evaluation of the spin-orbit operator matrix elements between both adiabatic spin-states and the evaluation of the transition probability using the Landau-Zerner approximation.
- Develop an algorithm to find the (spin diabatic) MECP that is compatible with the use of noncollinear spin density functional theory.

Publications supported by this project 2011-2013:

- A comparison of minimum energy crossing point structures and energies with different density functional approximations, B. Abate and J. E. Peralta (in preparation for Chem. Phys. Lett.).
- Site-specific polarizabilities from linear-response perturbation theory, J. E. Peralta and K. A. Jackson (in preparation for J. Phys. Chem. C)

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

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**Overall research goals:** Develop a 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<sup>-1</sup>) for molecules involving *f*-block elements, i.e., the lanthanides and actinides

**Significant achievements during 2011-2013:** Since this project was initially funded in August of 2012, some important initial work has already been completed.

- 1) New correlation consistent basis sets, cc-p(C)*VnZ*-PP, ranging from double- to quadruple-zeta quality have been developed for the uranium atom based on the accurate MCDHF relativistic pseudopotential of Dolg and Cao. In addition to valence sets designed for correlation down to the 6s electrons, core-valence sets designed for 5d correlation have been developed. These basis sets are being used in 1- and 2-component benchmark calculations of the structural and thermodynamic properties of uranium species such as UF<sub>6</sub>, UF<sub>5</sub>, UO<sub>3</sub>, UO<sub>2</sub>(OH)<sub>2</sub>, and UO<sub>2</sub>F<sub>2</sub>, using a composite ab initio scheme based on the Feller-Peterson-Dixon CCSD(T) approach. In one such project, preliminary calculations have predicted the enthalpy of formation of UO<sub>3</sub> using two reaction schemes, one based on W and another on S, together with the accurately known heat of formation of UF<sub>6</sub>. The two resulting values agree to within 3 kcal/mol, and both fall within the ±3.6 kcal/mol experimental uncertainty. The accuracy of these results hinged on the ability to reliably extrapolate the new basis sets to the complete basis set limit, as well as to accurately account for correlation effects involving the outer core electrons, e.g., 5d for U, which were found to only slowly converge with increases in the basis set.

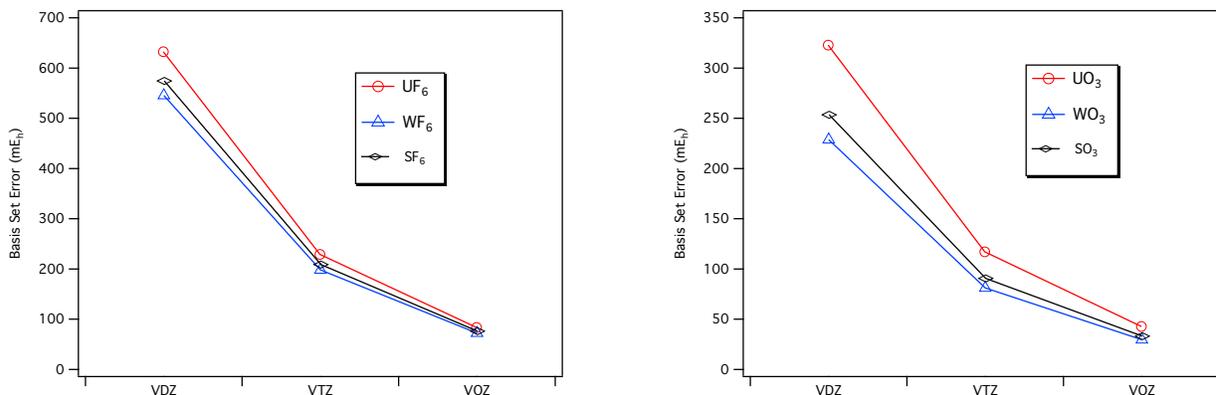


Figure 1. Comparison of the basis set convergence of the CCSD(T) correlation energies of (a) XF<sub>6</sub> (X=S, W, U) and (b) XO<sub>3</sub> (X=S, W, U) using newly developed basis sets for U with cc-p*VnZ*-PP for W, cc-p*V(n+d)Z* for S, and aug-cc-p*VnZ* for O and F. Values are given relative to their separate extrapolated CBS limits.

- 2) The importance of second-order spin-orbit coupling effects are being evaluated in both 4- and 2-component calculations for the molecules noted above, as well as for the spectroscopic properties (ground state ro-vibrational) of the closed-shell, linear MCN molecules (M=Cu, Ag, Au) and the ionization potentials of 4*p*-block atoms. In the reaction schemes alluded to above for determining the heat of formation of UO<sub>3</sub> (UF<sub>6</sub> + XO<sub>3</sub> → XF<sub>6</sub> + UO<sub>3</sub>, with X=S or W) all molecules are formally closed-shell species. The spin-orbit coupling effects on the reaction enthalpies, however, were non-negligible: -1.7 kcal/mol for the S-based reaction and -0.5 kcal/mol for the W-based reaction. Hence even in a reaction scheme approach with closed-shell molecules, one can not completely rely on spin-orbit effects cancelling.

#### Science objectives for 2013-2015:

- Continue to investigate the development and use of reaction schemes within composite ab initio methodologies to obtain accurate thermodynamic properties for molecules containing actinide elements. Particular attention will be given to approaches for accurately recovering spin-orbit coupling contributions.
- Utilize 1- and 2-component methods (MRCI, KRCI, CCSD(T)) to predict spectroscopic properties for both ground and excited electronic states of small neutral uranium molecules and their cations for comparison and interpretation of ongoing high resolution spectroscopic experiments (Heaven group). Initial studies currently involve UF/UF<sup>+</sup> and UCl/UCI<sup>+</sup>.
- Develop correlation consistent basis sets for Th, Pa, Np, and Pu and test their efficacy in molecular calculations.
- Investigate the use of new explicitly correlated methods for the actinides, particularly with the aim of efficiently recovering the important effects of outer core correlation with only modest sized basis sets.

#### Publications supported by this project 2011-2013

1. J.G. Hill, A.O. Mitrushchenkov, K.A. Peterson, "Ab initio ro-vibrational spectroscopy of the group 11 cyanides: CuCN, AgCN, and AuCN", *J. Chem. Phys.*, submitted.
2. N.J. DeYonker and K.A. Peterson, "Is near-"spectroscopic accuracy" possible for heavy atoms and coupled cluster theory? An investigation of the first ionization potentials of the atoms Ga – Kr", *J. Chem. Phys.*, submitted.
3. P.K. Parmar, K.A. Peterson, and A.E. Clark, "Static electric dipole polarizabilities of tri- and tetravalent U, Np and Pu ions", *J. Phys. Chem. A*, submitted.
4. K.A. Peterson, "Correlation consistent basis sets for actinides. Double- through quadruple-zeta basis sets for uranium". In prep for *The Journal of Chemical Physics*.

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

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

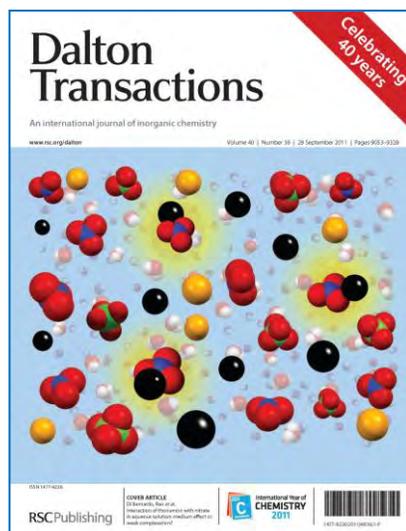
Significant achievements during 2011-2013:

1. Advanced microcalorimetry has unequivocally demonstrated the formation of weak inner-sphere  $\text{Th}(\text{NO}_3)^{3+}$  complex in aqueous solutions, and helped to answer a fundamental question regarding the medium effect and weak complexation in aqueous solutions (Dalton Transactions cover article, Publication #5).

2. Effect of temperature on the cation-cation interactions of Np(V)-U(VI) was studied. The cation-cation complex between  $\text{NpO}_2^+$  and  $\text{UO}_2^{2+}$  was weak and became stronger as the temperature was increased from 283.15 K to 358.15 K. The molar enthalpy of complexation was directly determined for the first time by microcalorimetry to be  $(4.2 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}$  at 298.15K. The small and positive enthalpy and entropy of complexation support the argument that the cation-cation complex between  $\text{NpO}_2^+$  and  $\text{UO}_2^{2+}$  is of inner-sphere type. Implications of cation-cation interactions in the distribution of Np(V) in spent nuclear fuel reprocessing were discussed (Publication #3).

3. Experimental and computational methods were jointly used to illustrate the energetics and structure of uranium(VI) – acetate complexes in dimethyl sulfoxide (Publication # 2).

4. The studies on the hydrolysis of Pu(VI) at elevated temperatures were completed and published. Three hydrolysis reactions involving  $\text{PuO}_2(\text{OH})^+$ ,  $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ , and  $(\text{PuO}_2)_3(\text{OH})_5^+$  were identified in slightly acidic solutions of Pu(VI) ( $\text{pC}_\text{H} < 5.5$ ) in the temperature range from 283 K to 343 K. All three hydrolysis reactions are significantly enhanced by the increase in temperature,



which could have a great impact on the migration behavior of plutonium in the geological environment. (Publication #8).

Science objectives for 2013-2015:

- Continue the studies on actinide complexation with ligands of importance in advanced actinide separations. The studies have been broadened to include ligands with N and S donors. On the basis of the thermodynamic and structural information on the complexation of actinides in aqueous solutions, the interactions of actinides with the ligands of importance in separations will be studied in more complex systems such as the two-phase conventional solvent extraction.
- Continue the studies on the complexation of U(VI), Np(VI) and Pu(VI) with a series of structurally related ligands. The focus is on the development of structure-property relationship.
- Investigate the effect of solvation on the complexation of actinides and lanthanides in media with drastically different solvating strength, including mixtures of alcohol/water and ionic liquids.

Publications supported by this project in the last two years:

1. C. Xu, G. Tian, S. J. Teat, L. Rao, Complexation of U(VI) with Dipicolinic Acid: Thermodynamics and Coordination Modes, *Inorg. Chem.*, DOI: 10.1021/ic4000389, Article ASAP.
2. P. Di Bernardo, P. Zanonato, F. Benetollo, A. Melchior, M. Tolazzi, L. Rao, Energetics and Structure of Uranium(VI)-Acetate Complexes in Dimethyl Sulfoxide, *Inorg. Chem.* 2012, 51 (16), 9045-9055.
3. L. Xian, G. Tian, W. Zheng, L. Rao, Cation-Cation Interactions between  $\text{NpO}_2^+$  and  $\text{UO}_2^{2+}$  at Different Temperatures and Ionic Strengths, *Dalton Trans.*, 2012, 41 (28), 8532 - 8538.
4. G. Tian, L. Rao, Complexation of Np(V) with Oxalate at 283 – 343 K: Spectroscopic and Microcalorimetric Studies, *Dalton Trans.*, 2012, 41, 448-452.
5. P. Di Bernardo, P. Zanonato, L. Rao, A. Bismondo, F. Endrizzi, Interaction of Thorium(IV) with Nitrate in Aqueous Solution: Medium Effect or Weak Complexation? *Dalton Trans.* 2011, 40, 9101-9105.
6. L. Rao, Application of Thermodynamic and Spectroscopic Techniques to the Studies of Actinide Complexation in Solution, *Progress in Chemistry*, 2011, 23 (7), 1295-1307.
7. W. A. Reed, A. G. Oliver, L. Rao, Tetra(tetramethylammonium) uranyltricarboxylate octahydrate, *Acta Cryst.* 2011, C67, m301-m303.
8. L. Rao, G. Tian, P. Di Bernardo, P. Zanonato, Hydrolysis of plutonium(VI) at variable temperatures (283 – 343 K). *Chem. Eur. J.* 2011, 17, 10985-10993.
9. G. Tian, L. R. Martin, Z. Zhang, L. Rao, Thermodynamic, Spectroscopic and Computational Studies of Lanthanide Complexation with Diethylenetriaminepentaacetic acid: Temperature Effect and Coordination Modes, *Inorg. Chem.*, 2011, 50 (7), 3087-3096.
10. G. Tian, N. M. Edelstein, L. Rao, Spectroscopic Properties and Hydration of the Cm(III) Aqua Ion from 10 to 85°C, *J. Phys. Chem. A*, 2011, 115 (10), 1933-1938.

## American Chemical Society's Summer School in Nuclear and Radiochemistry

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Dr. Herbert Silber, San Jose State University, Department of Chemistry, San Jose, CA 95192.

Overall research goals: Numerous reports over the last decade have raised concerns regarding the number of well-trained nuclear scientists available to address critical national needs in defense, energy, medical sciences, and fundamental research. The Nuclear and Radiochemistry Summer Schools were initiated to help address the need for an undergraduate pipeline in response to the decline in educational opportunities in the field and concomitant lack of student exposure to 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 nuclear chemistry and radiochemistry.

The Summer Schools are intensive, six-week courses in fundamental principles of nuclear and radiochemistry, held at San Jose State University (SJSU) and at Brookhaven National Laboratory (BNL). Each site serves 12 students annually. Participating students are introduced to course materials and activities that they would not be exposed to at their home institutions, broadening their perspective on this vital field of chemistry. As a result of their participation, approximately 20% of the 577 graduates of past summer schools chose to pursue advanced degrees in nuclear science disciplines and have subsequently found career positions in research or applied nuclear science fields, including positions with the US Department of Energy National Laboratories.

Significant achievements during 2011-2013: The 2012 Summer Schools received 110 applications. The 24 participants (14 male/10 female) came from small colleges (14) and research universities (10) and had an average GPA of 3.8. Lecture topics included natural radioactivity, modes of decay, decay rates, interactions of radiation with matter, nuclear reactions, nuclear structure, fission and fusion, accelerators and reactors, nuclear power, actinide chemistry, nuclear waste management, environmental radiochemistry, and fundamentals of nuclear medicine. The laboratory exercises covered a sequence of experiments that illustrate fundamentals of radiation detectors and data acquisition systems, nuclear-based methods of chemical quantitative analysis, and preparation and purification of a radiopharmaceutical compound. At BNL, students toured the Relativistic Heavy Ion Collider, the Brookhaven LINAC Isotope Producer, the National Synchrotron Light Source, and the Indian Point Nuclear Power Plant. At SJSU, students visited the National Ignition Facility, the Seaborg Institute, the Center for Accelerator Mass Spectrometry and the Synchrotron Light Source and Linear Accelerator Center at Stanford University.

One "Outstanding Student" from each site was selected based on their performance during the six-week program. In both locations, the competition was stiff for this honor. John Gray of Georgia Institute of Technology was named the 2012 Outstanding Student at SJSU. Justin Vadas of Earlham College was the 2012 Outstanding Student at BNL. Both students have been invited to attend the 245<sup>th</sup> National Meeting of the American Chemical Society in New Orleans, April 7-11, 2013, as guests of the ACS Division of Nuclear Chemistry and Technology and this program.

Specific Aims for 2013: The near term tasks and objectives are:

- Advertise the 2013 Summer Schools programs (October 2012)
- Select the 2013 participants (February 2013)
- Hold the 2013 Summer Schools (June 17 – July 26, 2013)

Presentations supported by this project 2011-2013

1. Invited presentation on the Nuclear Chemistry Summer Schools at the National Academy of Science symposium for the release of “Assuring a Future U.S.-Based Nuclear and Radiochemistry Expertise (2012)”, May 18, Washington, D.C.

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

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Justin A. Bogart, Graduate Student Researcher, Walter Dorfner, Graduate Student Researcher, Andrew J. Lewis, Graduate Student Researcher  
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104

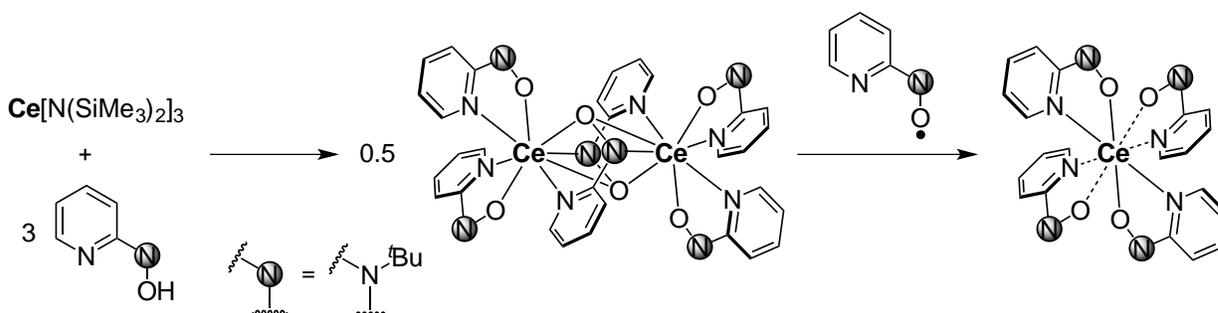
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Collaborator: Dr. Corwin H. Booth, Chemical Sciences Division, Lawrence Berkeley National Laboratory, MS 70A-1150, 1 Cyclotron Rd., Berkeley, CA 94720-8175

Overall research goals: The overall goal of this project is to develop new chemical methods for the simple separation of rare earth ions. We have been developing the chemistry of lanthanide ions, especially cerium, with redox active nitroxide ligands to observe electronic/magnetic coupling and redox chemistry between metal 4f electrons and ligand electron holes.

Significant achievements during 2011-2013: Building on discoveries from the first year of the project, the use of pyridyl appended nitroxide ligands has been expanded to encompass a total of six congeners with varying electron donation/with drawing abilities.

1. The synthesis, and characterization of six pyridyl-nitroxide Ce<sup>III</sup> complexes and six Ce<sup>IV</sup> complexes has been achieved:



Scheme 1. General synthesis of cerium(III) and cerium(IV) pyridyl appended hydroxylamine complexes.

It is now possible to predict properties of 4:1 hydroxylamine cerium complexes using Hammett parameters. This data is also useful to baseline the physical properties of the compounds.

2. Characterization of the full series of complexes has been made using solution electrochemistry experiments,  $L_{III}$  edge X-ray absorption spectroscopy, and density functional theory. In particular, electron donating groups appended to the pyridyl groups have been found to shift the Ce(III/IV) redox wave to more than  $-2.0$  V versus ferrocene.

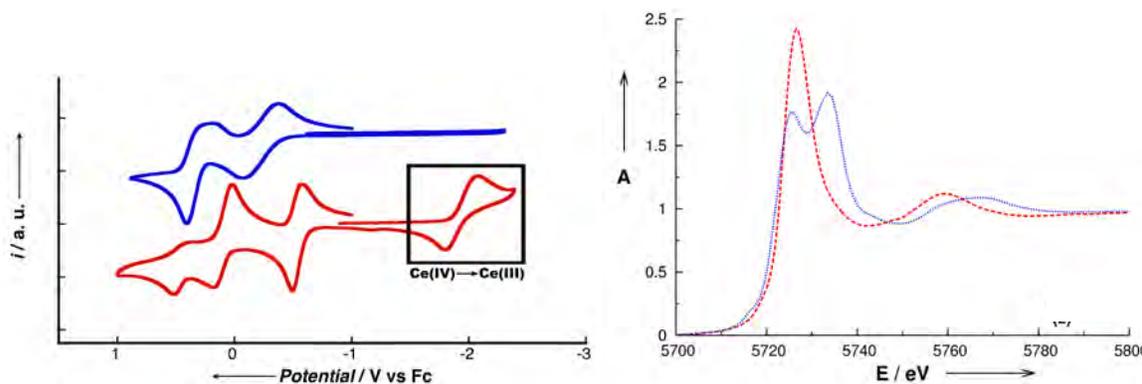


Figure 1. Left: solution electrochemistry of the parent pyridyl appended hydroxylamine ligand (blue trace) and Ce(IV) complex recorded in CH<sub>2</sub>Cl<sub>2</sub>. Right: cerium *L*<sub>III</sub> edge X-ray absorption spectra for the parent cerium(III) and cerium(IV) pyridyl-appended hydroxylamine complexes.

Furthermore, the XAS data confirm the compounds are bona fide Ce<sup>IV</sup> complexes. The physicochemical data suggest they are the most strongly thermodynamically stabilized Ce<sup>IV</sup> compounds that have been reported. In order to understand the origin of this unprecedented stabilization, DFT calculations were performed on the compounds.

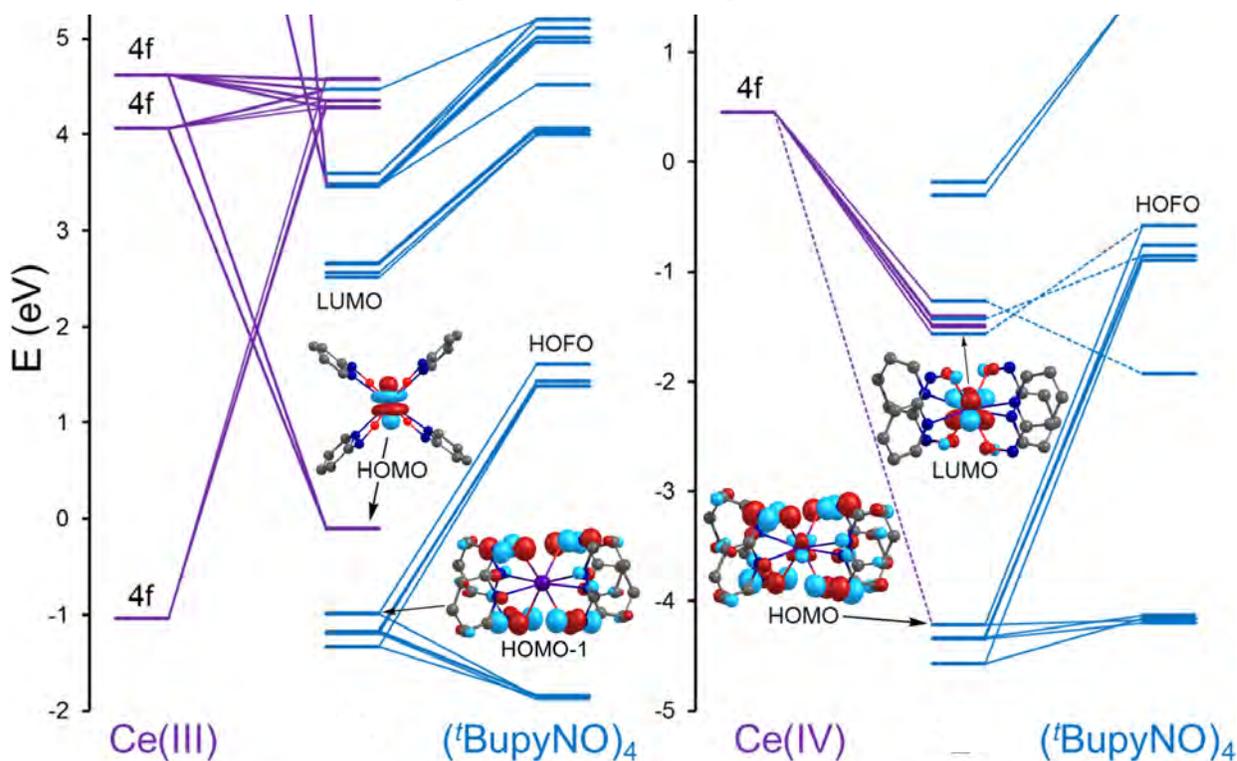


Figure 2. Fragment molecular orbital correlation diagrams for Ce[2-(<sup>t</sup>BuNO)py]<sub>4</sub> (right) and its anion (left). A small but important covalent 4f orbital contribution to bonding is found in Ce[2-(<sup>t</sup>BuNO)py]<sub>4</sub> but not in its anion.

The DFT results revealed a critical, partial covalent contribution from the nitroxide ligand field to the Ce<sup>IV</sup> cation that serves to strongly stabilize the high oxidation state metal cation.

#### Science objectives for 2013-2015:

- Prepare second-generation nitroxide ligands including bidentate and tetradentate frameworks to increase the stability of the resulting complexes upon oxidation.
- Isolate stable Tb and Pr complexes with strongly-coupled metal-ligand electron holes
- Develop functionalized hydroxamic acid and phosphine oxide/nitroxide rare earth extractants

#### Publications supported by this project 2011-2013

1. "Synthesis, Electrochemistry and Reactivity of Cerium(III/IV) Methylene-Bis-Phenolate Complexes," Mahoney, B. D.; Piro, N. A.; Carroll, P. J.; Schelter, E. J. *Inorg. Chem.* **2013**, in revision.
2. "Homoleptic Ce(III) and Ce(IV) Nitroxide Complexes: Extreme Stabilization of the 4+ Oxidation State," Bogart, J. A.; Lewis, A. J.; Medling, S. A.; Carroll, P. J.; Booth, C. H.; Schelter, E. J. *submitted*.
3. "Electrochemical and Computational Studies of Substituted 2-Pyridyl Hydroxylamines," Bogart, J. A.; Lee, H. B.; Boreen, M. A.; Jun, M.; Schelter, E. J. *in preparation*.

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

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Collaborator (Theory): Dr. Richard L. Martin, LANL

**Overall research goals:** The methodological development and computational implementation of novel electronic structure methods for the accurate theoretical description of properties of molecules, solids, and surfaces containing actinides and other heavy elements. Applications to actinide systems.

### Significant achievements during 2011-2013

1. A paper in *Chemical Reviews* describing our efforts at modelling actinide oxides in solid state for the last 12 years, using the screened hybrid HSE functional conceived and developed in the PI's research group. See paper #10 in the list below.

2. The implementation of a solution to an important problem in density functional theory: how to extend existing exchange-correlation functionals (that go beyond the local-density approximation) to the realm of noncollinear spins having proper invariance and local torque properties. See paper #9 and FIG. 1.

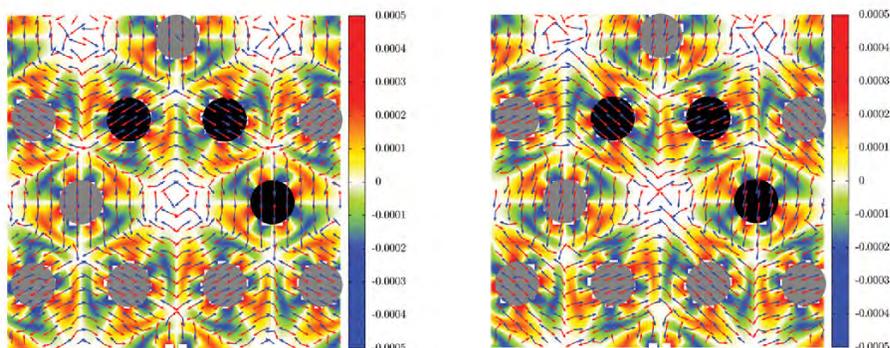


FIG. 1. The directions of the magnetization (red arrows) and the exchange-correlation magnetic field (blue arrows) obtained with the PBE functional for the Kagome lattice of (left) positive and (right) negative chirality. The color map depicts the magnitude (in atomic units) of  $\mathbf{m} \times \mathbf{B}_{xc}$  in the direction perpendicular to the Cr surface. The black points indicate the actual magnetic unit cell used in the calculations. Details on paper #9.

3. The implementation and benchmarking of Quantum Monte Carlo methods with many thousands of determinants as reference for providing an accurate fermionic nodal structure. See papers #3 and #4.

4. Several application papers to actinides in solid state in collaboration with LANL partners (papers #5, #6, #7, #8).

### Science objectives for 2013-2015

1. We shall continue our efforts on using the nodal structure of our symmetry broken and restored multi-reference projected Hartree-Fock wavefunctions for constrained-path (auxiliary field) QMC. I will present some very encouraging preliminary results in my poster.

2. Time reversal symmetry breaking and restoration may be key to understand and model “hastatic” order in the heavy-fermion compound URu<sub>2</sub>Si<sub>2</sub> [Nature **493**, 621 (2013)]. We plan on testing our proposed methodology in lattice model Hamiltonians initially.

3. We have studied UO<sub>2</sub> in solid state for many years. We are finally in a position to model its noncollinearity with the novel tools described in paper #9.

4. We will study small actinide molecules like U<sub>2</sub> and UO<sub>2</sub> with our newly developed multi-reference projected Hartree-Fock method.

### **Publications supported by this project 2011-2013**

1. Accurate treatment of solids with the HSE screened hybrid, T. M. Henderson, J. Paier, and G. E. Scuseria, *Phys. Status Solidi B* **248**, 767 (2011). [Partial support.] DOI: [10.1002/pssb.201046303](https://doi.org/10.1002/pssb.201046303)

2. Accurate prediction of the electronic properties of low-dimensional graphene derivatives using a screened hybrid density functional, V. Barone, O. Hod, J. E. Peralta, and G. E. Scuseria, *Acc. Chem. Res.* **44**, 269 (2011). [Partial support.] DOI: [10.1021/ar100137c](https://doi.org/10.1021/ar100137c)

3. Computing the energy of a water molecule using multideterminants: A simple, efficient algorithm, B. K. Clark, M. A. Morales, J. McMinis, J. Kim, and G. E. Scuseria, *J. Chem. Phys.* **135**, 244105 (2011). DOI: [10.1063/1.3665391](https://doi.org/10.1063/1.3665391)

4. Multideterminant wave functions in quantum Monte Carlo, M. A. Morales, J. McMinis, B. K. Clark, J. Kim, and G. E. Scuseria, *J. Chem. Theory Comput.* **8**, 2181 (2012). DOI: [10.1021/ct3003404](https://doi.org/10.1021/ct3003404)

5. Effect of spin-orbit coupling on the actinide dioxides AnO<sub>2</sub> (An = Th, Pa, U, Np, Pu, and Am): A screened hybrid density functional study, X.-D. Wen, R. L. Martin, L. E. Roy, G. E. Scuseria, S. P. Rudin, E. R. Batista, T. M. McCleskey, B. L. Scott, E. Bauer, J. J. Joyce, and T. Durakiewicz, *J. Chem. Phys.* **137**, 154707 (2012). DOI: [10.1063/1.4757615](https://doi.org/10.1063/1.4757615)

6. Rotational rehybridization and the high temperature phase of UC<sub>2</sub>, X.-D. Wen, S. P. Rudin, E. R. Batista, D. L. Clark, G. E. Scuseria, and R. L. Martin, *Inorg. Chem.* **51**, 12650 (2012). DOI: [10.1021/ic301133m](https://doi.org/10.1021/ic301133m)

7. Screened hybrid and DFT plus U studies of the structural, electronic, and optical properties of U<sub>3</sub>O<sub>8</sub>, X.-D. Wen, R. L. Martin, G. E. Scuseria, S. P. Rudin, E. R. Batista, and A. K. Burrell, *J. Phys. Cond. Matt.* **25**, 025501 (2013). DOI: [10.1088/0953-8984/25/2/025501](https://doi.org/10.1088/0953-8984/25/2/025501)

8. Optical band gap of NpO<sub>2</sub> and PuO<sub>2</sub> from optical absorbance of epitaxial films, T. M. McCleskey, E. Bauer, Q. X. Jia, A. K. Burrell, B. L. Scott, S. D. Conradson, A. Mueller, L. Roy, X. D. Wen, G. E. Scuseria, and R. L. Martin, *J. Appl. Phys.* **113**, 013515 (2013). DOI: [10.1063/1.4772595](https://doi.org/10.1063/1.4772595)

9. Noncollinear density functional theory having proper invariance and local torque properties, I. W. Bulik, G. Scalmani, M. J. Frisch, and G. E. Scuseria, *Phys. Rev. B* **87**, 035117 (2013). DOI: [10.1103/PhysRevB.87.035117](https://doi.org/10.1103/PhysRevB.87.035117)

10. Density functional theory studies of the electronic structure of solid state actinide oxides, X.-D. Wen, R. L. Martin, T. M. Henderson, and G. E. Scuseria, *Chem. Rev.* **113**, 1063 (2013). DOI: [10.1021/cr300374y](https://doi.org/10.1021/cr300374y)

## Ion Pair Receptors: Fundamental Studies Involving Recognition and Extraction

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Collaborators: Drs. Bruce Moyer and Ben Hay, Oak Ridge National Lab  
Dr. Stosh A. Kozimor, Los Alamos National Laboratory

**Overall research goals:** This project is concerned with the synthesis and study of so-called ion pair receptors. Ion pair receptors are systems that bind concurrently both anions and cations within a single molecular framework. Within this broad paradigm, particular emphasis will be placed on neutral systems that 1) bind alkali halide salts (MX) with high specificity, 2) permit the liquid-liquid extraction-based removal of sulfate from nitrate-rich mixtures, and 3) act as receptors and ultimately indicators and extractants for various early actinide cations.

**Significant achievements during 2011-2013:** Because it is most fundamental to understanding the difference between an ion pair receptor and a so-called dual host strategy, wherein a mixture of individual cation and anion receptors is employed for recognition and extraction, most of the emphasis over the last year was placed on exploring in detail how changes in structure modulate the recognition of alkali halide salts (Objective 1 above). Here, particular focus was devoted to ion pair receptors that allow for the binding and release of the cesium cation since this is a species of particular current interest in light of the Fukushima disaster.

To be viable an ion-pair receptor system not only has to bind the target cation (cesium for radioactive sea water) and, presumably, the dominant anion (chloride), but also release it after performing the desired function (e.g., separation via liquid-liquid extraction).

We have been collaborating with Dr. Moyer and his group at the Oak Ridge National Laboratory (ORNL) to achieve this goal. These efforts recently culminated in the creation of a crown-5 strapped calixarene-calixpyrrole hybrid.<sup>1</sup> The crown-5 calixarene subunit is selective for the potassium cation over the cesium cation. However, the chloride anion salt, Cs<sup>+</sup> is also bound by the receptor (via the calixpyrrole). After extraction into an organic solvent, exposure to the K<sup>+</sup> cation induces ion metathesis and releases the Cs<sup>+</sup> cation. Quite recently, we have prepared a related system that

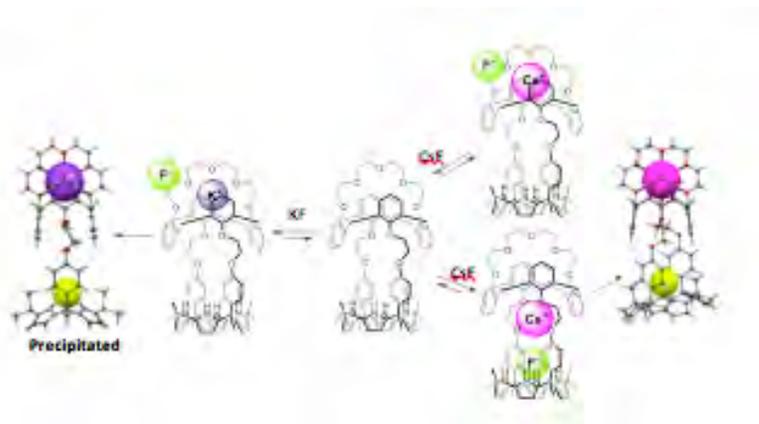


Figure 1. Schematic representation of a rationally designed ion-pair recognition system that allows capture of Cs<sup>+</sup> and its K<sup>+</sup>-induced release.

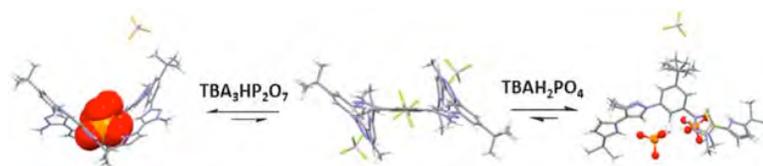


Figure 2. New Triazolium receptor and its recognition behavior

binds potassium and releases it upon exposure to cesium.<sup>2</sup>

As part of our efforts to develop receptors for the sulfate anion, we have targeted the recognition of tetrahedral anions in general. As part of this effort, we have recently prepared a new triazolium system that permits the selective recognition of pyrophosphate in polar media (Figure 2).<sup>3</sup>

Finally, in newer work carried out in conjunction with Stosh A. Kozimor, we have created a new class of tetrathiafulvalene (TTF) appended salen-type receptors. To date, we have demonstrated recognition of the uranyl cation. Plans are in place to extend this theme (Figure 3).<sup>4</sup>

#### Science objectives for 2013-2015:

- Develop ion-pair receptors for more complex analytes
- Expand the TTF-based ligand work to other actinide cations

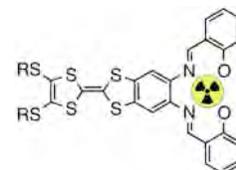


Figure 3. View of a TTF-based ligand.

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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; surface chemistry of actinide materials; and the development of soft X-ray SR techniques for actinide investigations.

Significant achievements in 2011-2013: Soft X-ray investigations focused on near-edge X-ray absorption fine structure (NEXAFS) measurements with the Molecular Environmental Science (MES) Beamline at the Advanced Light Source (ALS) scanning transmission x-ray microscope (STXM) to obtain electronic structure information from actinide materials. NEXAFS spectra were used to understand the bonding in the novel materials  $Tl_3Cu_4USe_6$  with Ibers et al.[3], a range of actinide molecules with Kozimor et al.[6,7], a diniobium sandwich complex with Arnold et al. [11], and in a series of transition-metal oxides with Kozimor et al.[9]. Figure 1 shows the U and Se NEXAFS spectra from a small particle of  $Tl_3Cu_4USe_6$  that were used to help establish the oxidation state of the compound. An outstanding highlight of the soft x-ray studies has been furthering the detailed understanding of oxygen bonding in metal oxide materials from direct O K-edge NEXAFS studies that set the stage for the direct quantification of actinide-oxygen bonding in the near future[9]. Unique studies at the MES STXM extended earlier work to the speciation of radionuclides in cement and clays, including the study of cesium in representative clay materials. Laboratory-based activities concentrated on the first studies of transuranic species in the LBNL actinide electrospray mass spectrometer[4], continued synthesis and characterization of actinide complexes with designer ligands[2], and discovering the first circularly polarized luminescence from an actinide species[8].

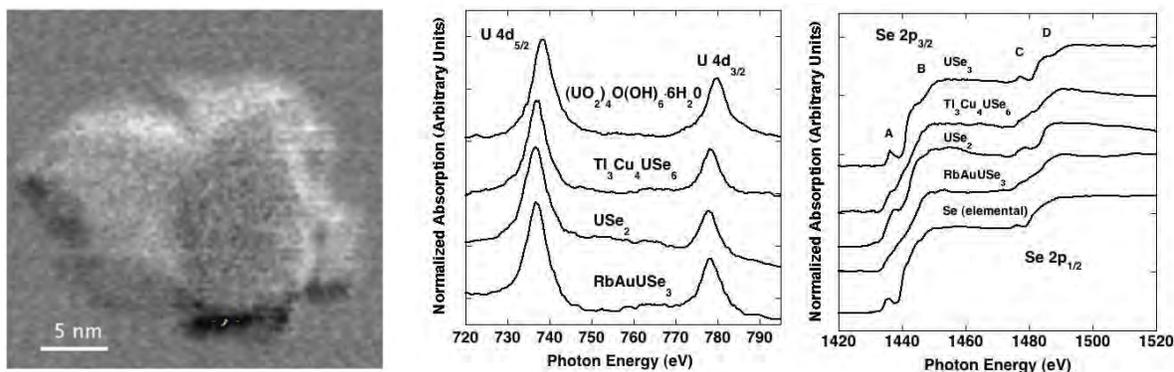


Figure 1. Left: Normal x-ray contrast image from a  $Tl_3Cu_4USe_6$ ; Center: Uranium 4d<sub>5/2,3/2</sub> x-ray absorption spectra collected from  $Tl_3Cu_4USe_6$  compared to uranium materials; and Right: selenium 2p<sub>3/2,1/2</sub> x-ray absorption spectra from  $Tl_3Cu_4USe_6$  compared to selenium materials.[3]

### Science objectives for 2013-2015:

- 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.
- The x-ray emission spectroscopy (XES) and resonant inelastic x-ray scattering (RIXS), staples of this project for many years, will be re-started to examine actinide reference materials, oxides, and complexes 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.

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## Improving Chemical Separations through Understanding Weak Interactions in Condensed Phases

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Overall research goals: The goal of this research is to achieve an improved understanding of the molecular-level interactions in solution that drive the affinity and selectivity between target ions and receptors in chemical separations. The primary approach is to combine neutron-diffraction experiments with atomistically-detailed molecular dynamics simulations to determine the local solvation structure near target ions in solution.

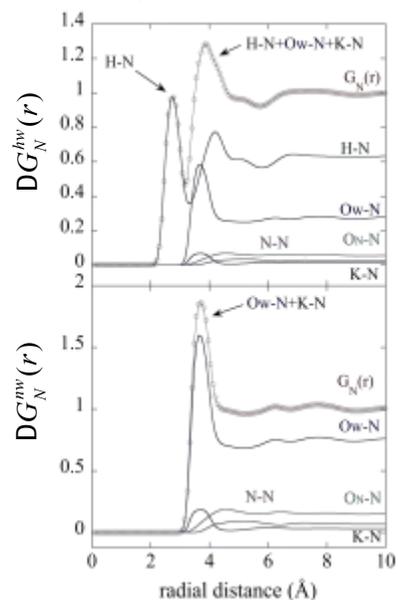
Significant achievements during 2011-2013:

The experimental approach to the project goal of understanding entropy/enthalpy contributions to ion solvation relies primarily on neutron diffraction with isotopic substitution (NDIS). For the oxyanions of interest in this project (e.g.,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) this technique depends on the scattering length differences in the core nuclei (e.g.,  $^{14}\text{N}/^{15}\text{N}$ ,  $^{32}\text{S}/^{33}\text{S}$ ). It was discovered<sup>1,3</sup> that there is a small but usable difference in the scattering length of oxygen isotopes ( $^{16}\text{O}/^{18}\text{O}$ ) that can be used to give more direct information on local solvation structure near the oxygen atoms (outer shell) of oxyanions in aqueous solution. We are using both approaches to isotopic substitution to extract new details of local solvation structure near  $\text{O}^{2-}$  in solution.

In 2012 the first measurements ever attempted for solvation using oxygen-isotope substitution were made in solutions of potassium nitrate in  $\text{D}_2\text{O}$  using a neutron diffractometer at the Spallation Neutron Source. Measurements made with nitrogen-labeled nitrate were consistent with the oxygen-substitution results, providing additional verification for the oxygen-substitution results. The results are in pre-publication, including detailed molecular dynamics simulation of solution structure as an independent verification and an aid to deconvoluting the pairwise structure factors to the measured total structure.

Similar measurements on sulfate anion with oxygen isotope substitution were scheduled late in 2012 but had to be delayed due to neutron availability issues. These experiments are scheduled to be run in spring 2013.

Results of molecular-dynamics simulations such as those



**Figure 1:** “First-order difference” of neutron-weighted distribution functions in deuterated (hw) and null (nw) aqueous solutions according to our molecular dynamics simulations (work in progress)

shown in Figure 1 above generally indicate the expectation of finding cation-anion near-neighbor interactions at relatively high salt concentrations in aqueous solution. Such charge-neutralizing interactions are expected to be important in extraction processes, and need to be understood in order to model the overall species distribution in extractive separations. Experiments on NOMAD in both this project and in collaboration with geosciences research (Stack et al.) have not shown definitively that the predicted ion pair populations are reflected in the measured distribution functions. In addition to expanding this research to include additional anions of fundamental and practical importance (e.g., phosphate, perchlorate) we will extend experimental studies to include oxyanion solvation in “null water,” where the H/D ratio is adjusted to effectively cancel the oxygen-hydrogen (or deuterium) contributions to the structure factor and correspondingly highlight oxyanion-cation interactions.

#### Science objectives for 2013-2015:

- Complete solvation experiments and modeling for solvation of nitrate and sulfate to fully demonstrate the capabilities of oxygen-isotope substitution for understanding solvation structure and entropy/enthalpy contributions near oxyanions in solution.
- Use null-water experiments to define the extent or lack of charge-neutralization ion-pair formation in solution, leading to the speciation information needed to assess separations performance.
- Use new experimental results to refine models and approaches used in molecular-dynamics simulations to improve predictive capabilities for solvation and speciation in oxyanion solutions.

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## Electronic Structure and Magnetism in f Ion Materials

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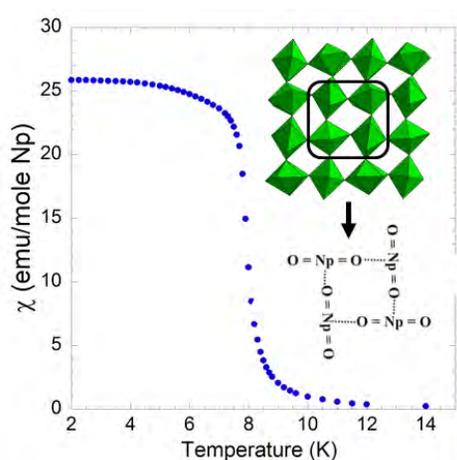
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Overall research goals: Actinide ions provide a unique opportunity to unite our understanding of electronic properties across the periodic table. Spanned by behaviors seen for the d-electrons, where electrostatic effects dominate spin-orbit coupling, and the 4f electrons, where the reverse is true, the intermediate coupling seen for the 5f series provides an opportunity we exploit in this research. Sensitive to changes in ligand-orbital radial extensions and symmetries, the low-lying electronic states are influenced by both their electrostatic charges and their abilities for metal-ligand overlap, an effect that plays a central role in bonding. We are looking at trends in a variety of systems to try to understand the subtleties of these competing effects.

Significant achievements during 2011-2013: Materials exhibiting cation-cation interactions (CCIs)



represent a class of compounds that provide an unusual opportunity to study magnetic effects. The neptunyl(V) ion has strongly axial symmetry, providing a similar electronic contribution to many of the oxidic compounds that form. In contrast, the unusual bonding patterns involved in CCIs provide a wide assortment of lattice dimensionalities, from 1D chains through ribbons and 2D planar linkages, to 3D lattices. Whereas the Np magnetic moments in these materials are similar their ordering temperatures are not, showing significant correlations with the lattice dimensionality. By synthesizing several new compounds we have been able to develop a hypothesis for the relationship between synthetic conditions and crystalline structures. We continue probing these materials seeking a predictive understanding of their cooperative magnetic

behavior and a correlation with any observable bonding effects.

Science objectives for 2013-2015: Continuing studies on cooperative magnetic effects in CCI compounds will focus on further examples of unusual structural connectivities and any resulting influence on cooperative moment ordering. Recent results provide insights into our previously determined correlation between neptunyl connectivity in the solid, the type of magnetic ordering, and the ordering temperature. Currently, for reasons not yet clear, all observed ferromagnets order at less than about 10 K whereas all antiferromagnets exhibit ordering at about 20 K or higher. By subtly tuning lattice dimensionality we hope to distinguish between several potentially competing influences on magnetic ordering behavior. Data from Raman spectroscopy, which provides a quantitative measure of bond strength, will be compared with bond distances obtained from single-crystal structural studies. To complement these studies we are also seeking structurally simple examples (one crystallographically unique Np per asymmetric unit) to probe the electronic properties in more detail. Results from these studies will be coupled with detailed magnetic measurements. Ultimately our goal is to identify electronic signatures for bonding and couple them with observed correlations in magnetic ordering.

In addition to our work on Np(V) CCIs, our interests in bonding will focus on another series of compounds, the f-ion isothiocyanates. Because of their ability to differentiate trivalent lanthanides from trivalent actinides in separations scenarios, we are interested in looking in detail at their



electronic structures. We seek slight differences in symmetry and evidence of bonding. As part of a larger program aimed at studying their coordination environments under solution conditions relevant to solvent extraction, we are characterizing solid-state behaviors in a lanthanide isothiocyanate series. Large single crystals have been synthesized and their crystal structures determined. As expected, they reveal molecularly isolated lanthanide isothiocyanate complexes, which are expected to exhibit primarily single-ion electronic properties. By studying these properties in detail, including the symmetries of their ground states, we will look for differences in their single-ion magnetic

properties, predicted from their ground-state wavefunctions, with observed magnetic responses as a function of temperature. Detailed solid-state and solution Raman studies, in addition to high-energy X-ray scattering from solutions, will provide a link between the electronic properties characterized solid-state and the complexes seen in solution.

#### Publications supported by this project 2011-2013

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## Understanding f-Ion Solution Speciation

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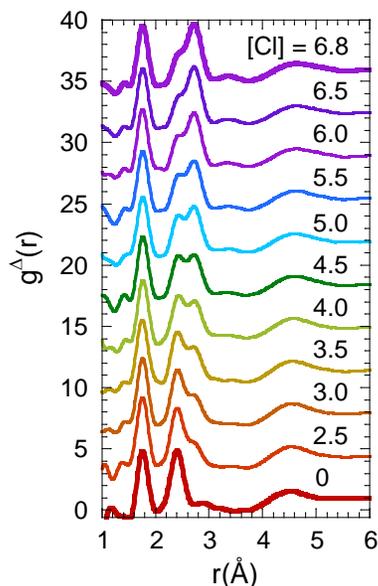
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Overall research goals: A predictive understanding of an f-ion's solution behavior awaits theoretical models that quantitatively capture the underlying interactions influencing the relative energetics of competing species. By comparing experiments designed to probe local and mid-range correlations in solution using classical molecular dynamics simulations with appropriate force fields, a more detailed understanding is sought of metal-ion coordination environments and their dynamics.

### Significant achievements during 2011-2013:

We continue to build upon recently developed methodologies for quantifying metal-ion speciation in solution using high-energy x-ray scattering (HEXS). Exemplifying our experimental program are studies to correlate published thermodynamic stability constants, for metal-ion solution complexes,



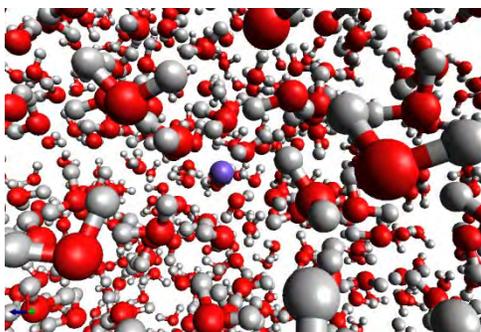
with their structures. By studying a series of solutions with varying ligand concentration, at constant ionic-strength, using HEXS, it is possible to quantitatively assess the changing coordination environment of a dissolved metal ion as a function of dissolved-ligand concentration. Pair-distribution functions derived from the data, shown in the figure to the right for a series of uranyl chloride solutions, is used to extract bond distances and coordination numbers, the latter of which are of sufficient precision to provide average numbers of ligands coordinating to the metal as a function of ligand concentration. This information is precisely that required to determine stability constants for the reaction under study. In addition, the determination of inner- vs. outer-sphere coordination, together with associated stability constants provides the metrical data that can be used to quantitatively compare details provided by theoretical calculations as well as the development of new force fields. This opportunity is particularly important when modeling complex speciation, as exemplified by  $\text{Er}^{3+}$  in acidic aqueous chloride solution, wherein both inner- and outer-sphere Er-Cl interactions

are seen to form. Applicable in the broader context, theoretical studies need to be able to reproduce changing coordination to reach an accurate, predictive, understanding of the stability and reactivity of solute ions in complex solutions.

### Science objectives for 2013-2015:

Our experimental work on metal-ion speciation will focus on extending studies of dissolved-ion speciation to specifically probe the coordination numbers and dynamics of second- and more-distant coordination-sphere interactions. Our current method of accounting for the onset of disorder in aqueous solutions, as probed by HEXS, is to include a modified error function (m-erf) in the fits,

which serves simply to parameterize the disorder. Although the m-erf parameters are seen to vary between solution series, they are subject to large uncertainties and provide little insight into molecular-level details, including dynamics, underlying the observed changes. Understanding the competing solution interactions that ultimately result in structural disorder and their distance dependence is a critical next step in characterizing and modeling solute energetics. With this in mind, we have initiated a program to couple molecular dynamics simulations with experimental x-ray scattering data. Measured solute-solute and solute-solvent correlations are compared with those generated from analyzing thousands of MD trajectories. Simulated data matching well to experiment are analysed to provide statistical insights into outer-sphere correlations. Because this methodology involves a single-ion basis to its spectral development similar to the experiment being modelled, the correlations imbedded in the trajectories provide detailed spatial and temporal information that, if analysed appropriately, should point to a new way of addressing metal ion energetics in solution.



Due to computer limitations, current MD modelling of metal-ion solution speciation relies on classical force-fields to account for ion-ion interactions. These force fields are often developed from, and tested with, other theoretical approaches. HEXS experiments, which probe ion correlations in solutions out to distances of 8 Å or longer, provide a new opportunity to further test the calculated force fields, particularly for second- or higher-order coordination spheres, where there has been a paucity of experimental data. As part of our efforts to model intermediate-range solute correlations in solution,

we will develop direct comparisons of measured and calculated interactions that can be used to further optimize and understand the force-fields themselves. In this way the results from this program are expected to clarify contributions made by both experiments and theory to the understanding of the role of structure in solution chemistry.

Publications supported by this project 2011-2013:

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5. R.E. Wilson, S. Skanthakumar, C. Cahill, L. Soderholm; "Structural studies coupling x-ray diffraction and high-energy x-ray scattering in  $UO_2^{2+} HBr_{aq}$  system", *Inorg. Chem.* **50** (2011) 10748-10754 [DOI:10.1021/ic201265s]
6. K.E. Knope, R.E. Wilson, S. Skanthakumar, L. Soderholm; "Synthesis and characterization of thorium(IV) sulfates", *Inorg. Chem.* **50** (2011) 8621-8629 [DOI:10.1021/ic201175u]
7. L. Soderholm, S. Skanthakumar, R.E. Wilson; "Structural correspondence between uranyl chloride complexes in solution and their stability constants", *J. Phys. Chem. A* **115** (2011) 4959-4967 [DOI:10.1021/jp111551t]

## 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 broad scope of this program is to better understand actinide chemistry using new spectroscopic techniques and to provide accurate spectroscopic data for the validation of new theoretical methods aimed at actinide chemistry. More specifically, we investigate ligand-uranyl ( $\text{UO}_2^{2+}$ ) interactions in gaseous anionic complexes in the form of  $[\text{UO}_2\text{L}_x]^{n-}$  produced by electrospray ionization and uranium-containing oxide ( $\text{U}_x\text{O}_y^-$ ) and fluoride clusters ( $\text{U}_x\text{F}_y^-$ ) using photoelectron spectroscopy and photoelectron imaging.

**Significant achievements during 2011-2013:** This program commenced in August 2011. To date, we have focused on the uranyl-halide complexes. We have studied  $[\text{UO}_2\text{F}_4]^{2-}$  and its  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{CN}$  solvated species,  $[\text{UO}_2\text{Cl}_4]^{2-}$ ,  $\text{UF}_5^-$  and  $\text{UF}_6^-$  complexes, as well as,  $[\text{UO}_2\text{X}_3]^-$  ( $\text{X} = \text{F-I}$ ).

1. Observation and investigation of the uranyl tetrahalide dianion ( $[\text{UO}_2\text{X}_4]^{2-}$ ,  $\text{X} = \text{F}$  and  $\text{Cl}$ ) and the solvation complexes with water and acetonitrile of  $[\text{UO}_2\text{F}_4]^{2-}$ . Bare uranyl tetrafluoride ( $\text{UO}_2\text{F}_4^{2-}$ ) and its solvation complexes by one and two water or acetonitrile molecules have been observed in the gas phase (Fig. 1) using electrospray ionization and investigated by photoelectron spectroscopy and *ab initio* calculations. The tetrachloride complex was also observed and the stability and electronic structures of the two gaseous tetrahalides are investigated and compared. Significant differences are found between the two complexes as a result of the different U-F and U-Cl interactions.

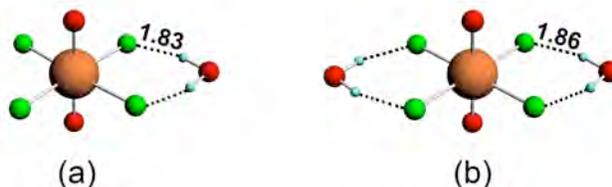


Fig. 1. Optimized structures of (a)  $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})]^{2-}$  ( $\text{C}_{2v}$ ) and (b)  $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})_2]^{2-}$  ( $\text{D}_{2d}$ ) using density functional theory. The H-bond lengths are in Å.

2. Photoelectron spectroscopy and theoretical studies of  $\text{UF}_5^-$  and  $\text{UF}_6^-$ . The  $\text{UF}_5^-$  and  $\text{UF}_6^-$  anions are produced using electrospray ionization (Fig. 2) and investigated by photoelectron spectroscopy and relativistic quantum chemistry. An extensive vibrational progression is observed in the spectra of  $\text{UF}_5^-$ , indicating significant geometry changes between the anion and the neutral ground states. Photoelectron spectra for cold  $\text{UF}_5^-$  yields an accurate electron affinity of  $3.885 \pm 0.015$  eV for  $\text{UF}_5$ , which is an important thermodynamic value, but was not accurately known before. Relativistic

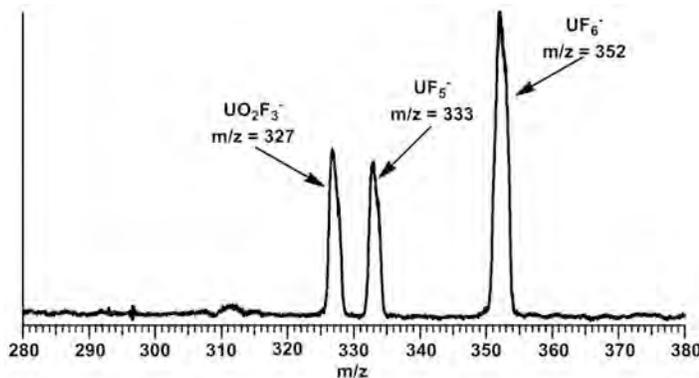


Fig. 2. Electrospray mass spectrum of  $\text{UO}_2\text{F}_3^-$ ,  $\text{UF}_5^-$ , and  $\text{UF}_6^-$ .

quantum calculations using density functional and *ab initio* theories are performed on  $\text{UF}_5^-$  and  $\text{UF}_6^-$  and their neutrals. Surprisingly, despite the strong mass signal of  $\text{UF}_6^-$  from our electrospray source, no photoelectron spectrum could be observed for  $\text{UF}_6^-$  due to the extremely low detachment cross section from the  $5f_{xyz}$ -based HOMO of  $\text{UF}_6^-$ .

3. Probing the electronic structure and chemical bonding in tricoordinate uranyl complexes  $\text{UO}_2\text{X}_3^-$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ): Competition between Coulomb repulsion and U–X bonding. The uranyl halide complexes  $[\text{UO}_2(\text{halogen})_n]^{2-n}$  ( $n = 1, 2, 4$ ) are ubiquitous, while the tricoordinate species have relatively unknown until very recently. We have used photoelectron spectroscopy and relativistic quantum chemistry to investigate the bonding and stability of the gaseous tricoordinate uranyl complexes,  $\text{UO}_2\text{X}_3^-$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ). The isolated  $\text{UO}_2\text{X}_3^-$  ions are produced by electrospray ionization and observed to be highly stable with very large adiabatic electron detachment energies. Theoretical calculations reveal that the frontier molecular orbitals are mainly of uranyl U–O bonding characters in  $\text{UO}_2\text{F}_3^-$ , but they are from the ligand valence  $np$  lone pairs in the heavier halogen complexes. Extensive bonding analyses are carried out for  $\text{UO}_2\text{X}_3^-$ , as well as for the doubly-charged tetracoordinate complexes ( $\text{UO}_2\text{X}_4^{2-}$ ), showing that the U–X bonds are dominated by ionic interactions with weak covalency. The U–X bond strength decreases down the periodic table from F to I. The Coulomb barriers and dissociation energies of  $\text{UO}_2\text{X}_4^{2-} \rightarrow \text{UO}_2\text{X}_3^- + \text{X}^-$  are calculated, revealing that all the gaseous dianions are in fact metastable. The dielectric constant of the environment is shown to be the key in controlling the thermodynamic and kinetic stabilities of the tetracoordinate uranyl complexes via modulation of the ligand-ligand Coulomb repulsions.

#### Science objectives for 2013-2015:

- Investigation of the electronic structures of  $\text{UCl}_5^-$  and  $\text{UCl}_6^-$  and comparisons with the fluoride counterparts.
- Investigations of  $\text{UO}_x^-$  ( $x = 1-4$ ) and  $\text{U}_2\text{O}_x^-$  ( $x = 1-6$ ) clusters and the U-U bonding.
- Production of  $\text{UF}_x^-$  ( $x = 1-6$ ) and  $\text{U}_2\text{F}_x^-$  ( $x = 1-8$ ) clusters using laser vaporization and systematic investigations of the U-F and U-U bonding in different U oxidation states.

#### Publications supported by this project 2011-2013

1. "Observation and Investigation of the Uranyl Tetrafluoride Dianion ( $\text{UO}_2\text{F}_4^{2-}$ ) and Its Solvation Complexes with Water and Acetonitrile" (P. D. Dau, J. Su, H. T. Liu, J. B. Liu, D. L. Huang, J. Li, and L. S. Wang), *Chem. Sci.* **3**, 1137-1146 (2012). (DOI: 10.1039/c2sc01052f)
2. "Photoelectron Spectroscopy and Theoretical Studies of  $\text{UF}_5^-$  and  $\text{UF}_6^-$ " (P. D. Dau, J. Su, H. T. Liu, D. L. Huang, F. Wei, J. Li, and L. S. Wang), *J. Chem. Phys.* **136**, 194304 (2012). (DOI: 10.1063/1.4716182)
3. "Photoelectron Spectroscopy and the Electronic Structure of the Uranyl Tetrachloride Dianion:  $\text{UO}_2\text{Cl}_4^{2-}$ " (P. D. Dau, J. Su, H. T. Liu, D. L. Huang, J. Li, and L. S. Wang), *J. Chem. Phys.*, **137**, 064315 (2012). (DOI: 10.1063/1.4742062)
4. "Photoelectron Spectroscopy of Cold  $\text{UF}_5^-$ " (P. D. Dau, H. T. Liu, D. L. Huang, and L. S. Wang) *J. Chem. Phys.* **137**, 116101 (2012). (DOI: 10.1063/1.4753421)
5. "Probing the Electronic Structure and Chemical Bonding in Tricoordinate Uranyl Complexes  $\text{UO}_2\text{X}_3^-$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ): 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), submitted for publication.

## Periodic Structural and Chemical Properties of the Early Actinide Elements

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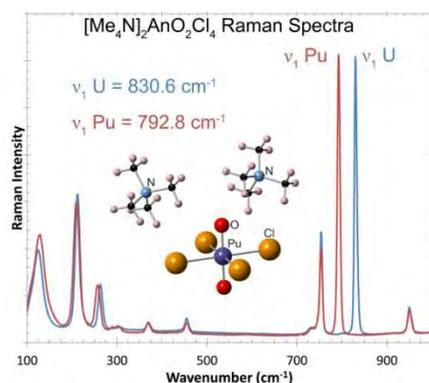
Collaborators: Drs. L. Soderholm, S. Skanthakumar, Stephanie DeSio, David Schnaars, Guokui Liu, Argonne National Laboratory.

Prof. C. L. Cahill, The George Washington University, Department of Chemistry

Overall research goals: The goal of this research is to understand the changes in both the structural and chemical properties of the actinide elements arising because of the imposition of chemical periodicity across the actinide series, the actinide contraction. Our research focuses on the synthesis of inorganic actinide complexes and their structural and spectroscopic study, both in the solid state and in aqueous solution. Using well-known trends in chemical periodicity as our guide, a hierarchy of actinide-ligand complexes is sought that extends across the early actinides, as influenced by their multiple valence states and across a series of periodic ligand systems.

Significant Achievements during 2011-2013: Synthetic, structural and spectroscopic studies of the actinide ions, Th to Pu, have provided significant new insight into the manifestation of the periodicity imposed by the actinide contraction in the chemistry of these ions.

Specifically, we have explored the sulfate coordination of Th, U(IV), and Pu(IV) monomeric species, coupling both structural studies in the solid and solution states (EXAFS and HEXS) with spectroscopic measurements of their vibrational and Raman spectra. Significant structural variety was observed in the solid state among these complexes vitiating our attempts to identify clear trends across the series. However, solution structural and thermochemical data have identified a clear chemical trend within these complexes with respect to the ligand coordination mode across this series of tetravalent actinides which we have ascribed to the increasing Lewis acidity of these ions from Th to Pu.



More recently the focus of this study has moved to the actinyl ions of U(VI), Np(VI), and Pu(VI). Unlike our earlier studies with the tetravalent ions, these ions provide us the opportunity to study a series of isostructural complexes that can be directly compared. Utilizing these complexes we are studying their vibrational spectra and their solid-state structures with the goal of building a quantitative understanding of the relationship between the vibrational frequency of the actinyl bond, its relative strength, and with more advanced spectroscopic probes, its electronic structure.

### Science Objectives for 2013-2015:

- Develop a quantitative model for the vibrational spectra of U(VI), Np(VI), and Pu(VI) incorporating data from X-ray crystallographic studies, Raman studies of oriented single crystals, and optical luminescence data.

- Interrogate ligand systems of significant promise to lanthanide-actinide separations such as thiocyanate with the trivalent actinides, Pu, Am, and Cm and the lanthanides. Using our structural and spectroscopic approach and with collaborations from theory, develop a predictive and quantitative understanding of the chemistry in these systems.
- Study the chemistry of protactinium(V) and protactinium(IV) in the solid-state and in aqueous solution with the goal of understanding the interplay and roles of the nearly degenerate 5f and 6d electronic levels in its chemistry.

Publications supported by this project 2011-2013

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6. L. Soderholm, S. Skanthakumar, R. E. Wilson. *Structural correspondence between uranyl chloride complexes in solution and their stability constants*. *Journal of Physical Chemistry A*. 115, 4959-4967, 2011.
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## An Integrated Basic Research Program for Advanced Nuclear Energy Systems based on Ionic Liquids (SISGR)

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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 extractions using ILs, and apply our findings to design new IL-based separation systems for higher efficacy, selectivity and durability.

### Significant achievements during 2011-2013:

- We have previously shown that IL cation hydrophobicity is an important factor in determining the balance between ion exchange and neutral complex (ion pair) mechanisms in Sr<sup>2+</sup> extraction from HNO<sub>3(aq)</sub> into ILs with DCH18C6. Our new results using a wider range of extraction conditions show that the charge density of the extracted metal ion, the hydration energy of the aqueous phase anion, and the hydrophilicity of the ionic liquid anion, are equally important. *These principles apply broadly for all metal ion extractions into ILs and have wide applications.*
- A series of hydroxyalkyl-substituted imidazolium-based task-specific ILs (TSILs) have been prepared and characterized as part of an effort to determine the influence of various substituents on the physicochemical properties and extraction performance of imidazolium-based ILs.
- Studies of Sr<sup>2+</sup> extraction by DCH18C6 into these new ILs have shown that over a specific range of conditions, i.e., those leading to neutral complex extraction as the predominant partitioning mode, a direct correlation exists between the Sr<sup>2+</sup> extraction efficiency and the water content of the IL phase. This mimics the behavior of several families of molecular solvents, including aliphatic alcohols, ketones and carboxylic acids, and provides the possibility of tunable control via modification of IL composition to control water solubility in the IL by design.
- The extraction of actinide ions into hydrophobic ILs was investigated using TODGA or HDEHP as extractants. Four IL compositions were used as diluents for the separation of <sup>227</sup>Th and <sup>225</sup>Ac. TODGA offered higher extraction efficiency for both Th(IV) and Ac(III) ions in C<sub>4</sub>mim NTf<sub>2</sub> and 1-butyl-2,3-trimethylimidazolium NTf<sub>2</sub>. By adjusting the aqueous phase acidity, HDEHP proved to be an excellent extractant for separation of <sup>227</sup>Th from <sup>225</sup>Ac in all four ILs.
- We have synthesized DEHP-based ammonium and phosphonium TSILs (N<sub>4444</sub>, N<sub>1888</sub>, and P<sub>666,14</sub> di(2-ethylhexyl)phosphates) and investigated them for Ln<sup>3+</sup> separation in C<sub>6</sub>mim NTf<sub>2</sub>. In contrast to most TSILs whose *cations* contain functional groups, the functionality here is incorporated into the constituent *anion*. The complexes formed by Ln<sup>3+</sup> ions and ionic

extractants have better solubilities and stabilities in the TSILs than in diisopropylbenzene, the solvent typically used for HDEHP extractions. The DEHP-based ionic extractants demonstrate better selectivities for  $\text{Ln}^{3+}$  than HDEHP because of the larger steric hindrance in the cations.

- Many classes of ILs are damaged in radiation fields due to fragmentation caused by oxidation or electronic excitation of the constituent anions. Anion fragments often attach to IL cations, modifying their properties. However, we discovered two exceptional classes of "radiation-hard" anions: aromatic imides (such as phthalimide, saccharinate, and 1,2-benzenedisulfonimide) and polycyano anions (such as 1,1,2,3,3-pentacyanopropenide and pentacyanocyclopentadienide) that do not fragment in their oxidized, reduced, and electronically excited states. In both cases, delocalization of excess charges and excited states improves radiation stability. We are assessing the separations performance of ILs based on these exceptional anions. Our early results show that the excellent  $\text{Sr}^{2+}$  neutral complex extraction behavior of  $\text{P}_{666,14}$  saccharinate IL was almost unchanged after a dose of 2 MGy.
- Extending our interest in delocalization, we systematically investigated ILs with aromatic (imidazolium, pyridinium, 1,2,4-triazolium, thiazolium) and other (guanidinium, arylsulfonium) cations. Radiolytically-generated species were detected using EPR and pulse radiolysis, while radiolysis products were identified using (LC/GC)-MS, NMR and isotopic substitution. Modification pathways for IL cations were established. In 5-atom ring aromatic cations, substituent arm elimination from the cation's reduced state correlates with the trigonality of the spin-bearing carbon and the stability of the eliminated fragment radical/carbocation. For imidazolium, reactivity at the trigonal, spin-bearing C(2) carbon causes dimerization. In the presence of water this leads to hydrophilic and potentially metal-coordinating derivatization. Having a substituent at C(2) blocks this pathway. In contrast, the analogous 6-atom ring cations are stable to fragmentation due to the formation of sandwich  $\pi$ -stack dimers observed by EPR and pulse radiolysis. Presently we are formulating principles for choosing IL constituents to minimize or mitigate radiolytic damage.
- An IL can have a radioprotective effect on extractant solutes by diverting damage towards itself. Several classes of extractants and solvent modifiers used in nuclear separations were examined. We found that aromatic ILs efficiently protect extracting agents that fragment through reductive chemistry (including the di- and tri- phosphates) but offer less protection to solutes that mainly fragment in their oxidized or excited states (including crown ethers and (di)amides).
- Since contact with nitrate may occur in some IL-based separations, we studied its effect on IL radiolysis. The reductive channel is altered because  $\text{NO}_3^-$  scavenges electrons. This helps protect solutes that decompose through the reductive channel; for example it virtually eliminated damage to di- and tri-alkyl phosphates. (There is little effect on the oxidative damage channel.) This finding begs the question of why nitrate effectively protects alkylphosphates in ILs but not in the hydrocarbon phase of the PUREX system. The difference is that nitrate is dispersed in the IL such that it can be an efficient scavenger and protectant, whereas in the molecular diluent it is confined to reverse micelles where it cannot protect extractants in the hydrocarbon phase from reductive decomposition. This distinction underscores the meso- and nanoscale structural differences between ILs and other solvents in the extraction context, which can have practical advantages in standard extraction technologies and open the door to new methods exploiting the unique combinations of properties possessed by ILs.

#### Science objectives for 2013-2015:

- 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. One objective is to determine if these TSIL solvents offer significant extraction performance advantages over non-functionalized ILs. Complementary radiolytic studies need to be done to determine if attachment of functional

groups affects the radiation sensitivity of the IL and what products are 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 rare-earth ions (fission products) in ionic liquids will be continued. Emphasis will be placed on controlling ion-exchange processes through use of extractants based on ionic liquids.
- Transfer of IL ions and water between phases has a strong influence on extraction mechanisms. We will investigate the relationship between the octanol-water partition coefficients for ILs and their performance as extraction solvents. We will also develop improved analytical (HPLC and IC) methodology for the characterization of IL-based extraction systems and radiolysis products.
- We will expand our survey of radiation damage in ILs aiming to discover more classes of radiation resistant ions through further synthetic efforts. Pulse radiolysis studies of damage transfer reactions will quantify the protective effects of radiation-resistant ions in IL mixtures. EPR and MS studies, and the new mid-IR radiolysis capabilities at BNL's LEAF, will help reveal damage mechanisms. These studies will be complemented by trials of separations performance in irradiated vs. non-irradiated IL solvents. We are the point when it becomes possible to guide synthesis of new ILs to specifically address the radiation stability requirements of particular separations processes, which vary widely in severity.
- 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. Informed by the structural work, pulse radiolysis studies will examine reactivity within domains and transfer of reactive species across domain boundaries. We will explore how the morphology affects the radiation susceptibility of certain extracting agents and how the interaction of the various components with radiation influences phase behavior.
- The effects of heavy ion radiolysis on ionic liquids (as a surrogate for alpha radiolysis during processing) will be examined using time-resolved kinetics and bulk radiolysis product studies in collaboration with the French CEA.

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