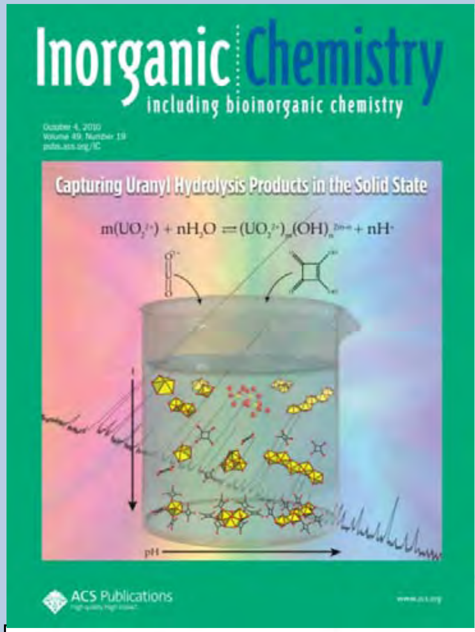
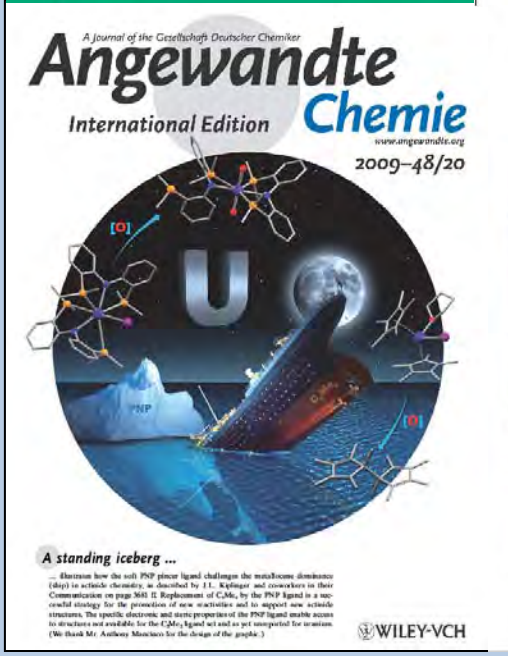
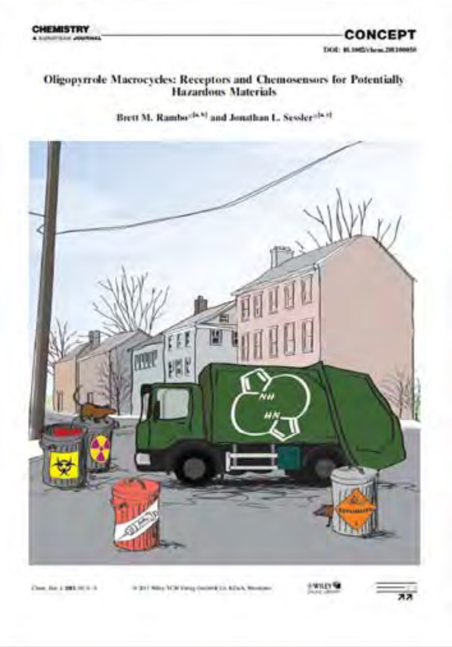
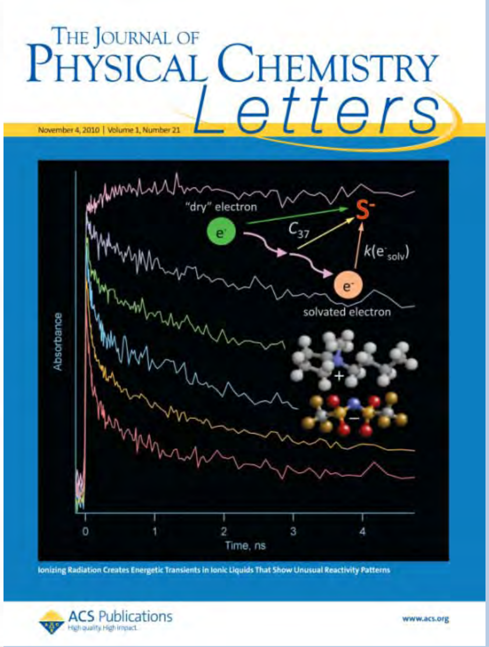
2011 Separations and Heavy Element Chemistry Research Meeting









Hyatt Regency, Baltimore, MD
April 26 - 29, 2011

U.S. DEPARTMENT OF ENERGY | Office of Science

Office of Basic Energy Sciences
Chemical Sciences, Geosciences &
Biosciences Division

Program and Abstracts
for the

2011 Separations and Heavy Element Chemistry Research Meeting

Hyatt Regency
Baltimore, MD
April 26–29, 2011

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

Cover Graphics:
The cover artwork is used by permission from the authors and journals for the associated covers. These covers are related to recently published papers by PIs speaking in this meeting's program. From left to right and top to bottom they are:

Christopher Cahill on p. 19 of this book. Also see *C. E. Rowland and C. L. Cahill (2010) "Capturing Hydrolysis Products in the Solid State: Effects of pH on Uranyl Squarates under Ambient Conditions." Inorganic Chemistry, 49(19), 8668–8673.*

Wibe A. de Jong on p. 77 of this book. Also see *V.A. Glezakou and W.A. de Jong, "Cluster-models for Uranyl(VI) adsorption on α-alumina." J. Phys. Chem. A 2011, 115, 1257 (2011).*

Jaqueline Kiplinger on p. 9 of this book. Also see *Thomson, R. K.; Graves, C. R.; Scott, B. L.; Kiplinger, J. L. "Noble Reactions for the Actinides: Safe Gold-Based Access to Organouranium and Azide Complexes," Eur. J. Inorg. Chem. 2009, 1451–1455.*

Jaqueline Kiplinger on p. 9 of this book. Also see *Cantat, T.; Graves, C. R.; Scott, B. L.; Kiplinger, J. L. "Challenging the Metallocene Dominance in Actinide Chemistry with a Soft PNP Pincer Ligand: New Uranium Structures and Reactivity Patterns," Angew. Chem., Int. Ed. 2009, 48, 3681–3684. Copyright Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.*

Jonathan Sessler on p. 17 of this book. Also see *Rambo, B. M.; Sessler, J. L. "Oligopyrrole Macrocycles: Receptors and Chemosensors for Potentially Hazardous Materials," Chem. Eur. J., in press.*

James Wishart on p. 3 of this book. Also see *Wishart, J. F., "Ionic Liquids and Ionizing Radiation: Reactivity of Highly Energetic Species," J. Phys. Chem. Lett. 2010, 1, 3225–3231. http://dx.doi.org/10.1021/jz101096b.*

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Foreword

This abstract booklet provides a record of the eleventh U.S. Department of Energy contractors' meeting in separations sciences and the sixth in heavy element chemistry. This year the meeting is co-chaired by Dr. Lynda Soderholm (Argonne National Laboratory) and Professor Sue 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 some 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. In addition, separation processes are major industrial sources of energy consumption and waste generation. This is the fifth 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, as well as invited and regular posters, organized so that papers in related disciplines are loosely clustered together. Invited presentations this year include oral and poster presentations representing an Energy Frontier Research Center and related programs in DOE Office of Nuclear Energy. 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 are pleased to collaborate with Lynda Soderholm and Sue Clark in organizing this joint meeting and appreciate their service to this community. We also 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, and Tim Ledford and Connie Lansdon of the Oak Ridge Institute for Science and Education for their important contributions to the technical and logistical features of this meeting.

Larry A. Rahn
Mark Pederson
Norman Edelstein

Agenda

2011 Separations and Heavy Element Chemistry Research Meeting
Hyatt Regency, Baltimore, MD, April 26–29, 2011

Tuesday, April 26, 2011

3:00 – 6:00	p.m.	*** Registration ***
6:00 – 7:00		*** Reception (*hors d'œuvres*) ***

Session 1 – Separations – Chuan He, Chair

7:10 – 7:20	p.m.	Welcome – John Miller, Larry Rahn, Lynda Soderholm and Sue Clark
7:20 – 8:10		**Invited speaker** – Bruce Moyer – Sigma Team for Minor Actinide Separations
8:10 – 8:35		James Wishart – An Integrated Basic Research Program for Advanced Nuclear Energy Systems based on Ionic Liquids
8:35 – 9:00		Mark Jensen – Multi-stage Separation of Actinides with Biomolecules

Wednesday, April 27

7:30 – 8:00	a.m.	*** Breakfast ***
8:10 – 8:35		Eric Rohlfing – DOE Update

Session 2 – Complexation and Coordination – William Evans, Chair

8:35 – 9:00	a.m.	Jaqueline Kiplinger – Organometallic Actinide Chemistry – Metal-Ligand Multiple Bonding and Electron Correlation
9:00 – 9:25		Wayne Lukens – Fundamental Chemistry of Technetium in Iron Oxide Matrices
9:25 – 9:50		Lynn Francesconi – Fundamental Chemistry of Technetium-99 Incorporated into Metal Oxide, Phosphate and Sulfide Materials: Towards Stabilization of Low Valent Technetium
9:50 – 10:15		Jonathan Sessler – Ion Pair Receptors: Fundamental Studies and Tests
10:15 – 10:45		*** Break ***

Session 3 – Complexation and Coordination – Thomas Albrecht-Schmitt, Chair

10:45 – 11:10	a.m.	Christopher Cahill – Control of Hydrothermal UO_2^{n+} Systems: A Solution Phase Approach to New Solid State Materials
11:10 – 11:35		Trevor Hayton – Exploring the Redox and Oxo Substitution Chemistry of the Uranyl Ion: Implications for Separations and Environmental Remediation
11:35 – 12:00		Andrew Gaunt – Molecular Transuranic Discovery Science: Underpinning National Energy Security and Waste Remediation Needs
12:00 – 1:00	p.m.	*** Working lunch ***

Session 4 – Actinides – Lynda Soderholm, Chair

1:00 – 1:50	p.m.	**Invited speaker** – Peter Burns – Energy Frontier Research Center: Materials Science of Actinides
1:50 – 2:15		Richard Wilson – Structural, and Chemical Properties of Lower Valent Actinide Complexes
2:15 – 2:40		Udo Becker – Actinide Incorporation and Radiation Effects in Layered-Structures
2:40 – 3:05		Kenneth Raymond – Actinide/Lanthanide Luminescence and Actinide Sequestration

Invited Poster Introductory Presentations

3:05 – 3:10 p.m. Tori Forbes – Synthesis and Structural Characterization of Heterometallic Actinide Nanoclusters

3:10 – 5:00 *** Interaction time and put up posters for both poster sessions ***

Session P1 – Poster Session 1

5:00 – 6:00 p.m.

P1 **Invited** – Tori Forbes – Synthesis and Structural Characterization of Heterometallic Actinide Nanoclusters

P3 Paula Diaconescu – C-H Activation Reactions by Uranium Alkyl Complexes

P5 Guokui Liu – Electronic Interactions in Actinyl Compounds: Analysis and Simulation of Optical Spectra

P7 Lætitia Delmau – Principles of Chemical Recognition and Transport in Extractive Separations, Calix[4]pyrrole Derivatives: Simple Dual Host or Ion-Pair Receptor? Thermodynamic Study of Anion Selectivity in Cesium Salt Extraction

P9 Thomas Albrecht-Schmitt – Actinide Borates

P11 Ken Czerwinski – Low Valent Technetium Acetate and Technetium Halide Metal-Metal Bonded Dimers Synthesized by Hydro-Solvothermal and Chemical Transport

P13 Chuan He – Selective Recognition of Heavy Elements by Protein-Based Reagents

P15 Robert Paine – Preorganized and Immobilized Ligands for Metal Ion Separations

P17 Heino Nitsche – Heavy Element Nuclear and Radiochemistry

P19 **Invited** – James Willit – Reproducible and Reliable Electrochemical Determination of U and TRU Concentrations

P21 S. Skanthakumar – Correlations between Structure, Magnetism, and Electronic Properties in Neptunium Compounds

P23 Sheng Dai – Tailoring Ionic Liquids for "Smart" Separation of Metal Ions

P25 Ilya Shkrob – Ionic Liquid Based Extraction Systems: From Mechanistic Aspects of Radiation Stability to Separations Chemistry

P27 Michael Morse – Spectroscopy of Organometallic Radicals

P29 **Invited** – Leigh Martin – Thermodynamics and Kinetics of Extraction Systems

P31 Richard Andersen, Corwin Booth, Wayne Lukens – Organometallic Chemistry of the f-Block Elements; Intermediate-Valence Ground States, Magnetism, and Chemistry

P33 Paul Mantica – Nuclear and Radiochemistry Summer Schools

P35 **Invited** – Ginger Sigmon – Complex Actinide Materials

P37 **Invited** – Peter Burns – Actinide Materials in Extreme Environments

6:00 – 7:00 p.m. *** Working dinner ***

Session 5 – Forensics and Characterization – Sue Clark, Chair

7:00 – 7:25 p.m. **Invited speaker** – Jon Schwantes – The Science Behind Modern Day Nuclear Forensic Analysis: Definition, Importance, and Example

7:25 – 7:50 Lester Andrews – Matrix Infrared Spectroscopic and Computational Investigations of Novel Small Uranium Containing Molecules

7:50 – 8:15 Michael Heaven – Spectroscopic Studies of Prototype Actinide Compounds

Poster Session 1 (Cont'd)

8:15 – 10:00 p.m. *** No host bar ***

Thursday, April 28

7:30 – 8:10 a.m. *** Breakfast ***

Session 6 – Electronic Structure, Characterization – Richard Martin, Chair

8:10 – 8:55 a.m. **Invited speake**r – Mark Schlossman – X-ray Studies of Liquid-Liquid Interfaces as Model Solvent Extraction Systems
9:00 – 9:25 Stosh Kozimor – Trends in Orbital Mixing for Actinide-Ligand Bonds
9:25 – 9:50 Jochen Autschbach – Computational Studies of NMR Chemical Shifts in Open-Shell Actinide and Lanthanide Systems
9:50 – 10:15 David Dixon – Understanding Actinide Aggregation

10:15 – 10:45 *** Break ***

Session 7 – Theory and Characterization – Laura Gagliardi, Chair

10:45 – 11:10 a.m. John Gibson – Actinide Coordination Chemistry: From Solution to the Gas Phase
11:10 – 11:35 Bert de Jong – Modeling the Influence of Geochemical Interfaces on the Stability of Actinide Oxidation
11:35 – 12:00 Aurora Clark – Origin of Actinide Partitioning in Biphasic Systems
12:00 – 12:25 Gustavo Scuseria – Accurate Theoretical Approaches for Studying the Chemistry of Actinides and Other Heavy Atoms

12:25 – 1:30 p.m. *** Working lunch ***

1:30 – 2:00 p.m. *** Break ***

Session P2 – Poster Session 2 *** No host bar ***

2:00 – 4:30 p.m.

P2 Abe Clearfield – Development of Pillared M(IV) Phosphonate Phosphate Materials for Lanthanide-Actinide Separations
P4 Mark Antonio – Structural Aspects of Solution Chemistry in Solvent Extraction (SX)
P6 S. Jurisson and Lynn Francesconi – Reactivity of Pertechnetate with Sulfide Containing Materials: From the Molecular Level to Solid State
P8 Corwin Booth – Local Structure and f-Orbital Localization in Fresh and Aged Uranium and Plutonium Intermetallics
P10 Lynda Soderholm – Actinide Solution Speciation: Implications for Complex Stability and Separations Chemistry
P12 William Evans – Fundamental Chemistry of Actinide Complexes Containing An-N, An-O, and An-S Bonds
P14 James Ibers – Novel Actinide Chalcogenides: $Tl_3Cu_4USe_6$ and $Tl_2Ag_2USe_6$
P16 Jeffery Davis – Self-Assembled Ionophores: New Directions
P18 Laura Gagliardi – Multiconfigurational Quantum Chemical Study of Actinide and Lanthanide Containing Systems
P20 Richard Martin – Implications of Covalency in Actinide-Ligand Bonding
P22 Ping Yang – Understanding Uranyl Adsorption at Water-Alumina Interface using First-Principles Molecular Dynamics
P24 Peter Burns – Topological Structural Relationships, Cation-Cation Interactions, and Properties of U(VI), Np(V) and Th(IV) Compounds
P26 Benjamin Hay – Principles of Chemical Recognition and Transport in Extractive Separations Molecular Modelling and Design of Ion Receptors

P28 Linfeng Rao – Actinide Solution Chemistry: Thermodynamics and Structure of Actinide Complexes in Solution
P30 Steven Conradson – Collective and Cooperative Phenomena in Actinide-Based Materials: Intrinsic Dynamical Processes in Hypervalent Urania
P32 S. Skanthakumar, L. Soderholm, M.R. Antonio, M.P. Jensen, G. Luo, R.E. Wilson – Facilitating Experiments at a Synchrotron
P34 Stephen Cooke – Experimentally Characterizing the Electronic Structures of f-Electron Systems using Advanced High Resolution Fourier Transform Microwave Spectroscopies
P36 Eric Bylaska – Parameter-Free (Approaching) Petascale Simulations for Actinide Solution Species and Geochemical Interfaces

4:30 p.m. *** Interaction time and dinner on your own ***

Friday, April 29

7:30 – 8:00 a.m. *** Breakfast ***

Session 8 – Separations – Paula Diaconescu, Chair

8:10 – 8:35 a.m. Radu Custelcean – Selectivity Principles in Anion Separation by Self-Assembled Cage Receptors
8:35 – 9:00 Amar Flood – Binding and Releasing Anions with CH Hydrogen-Bonded Receptors
9:00 – 9:25 Sue Clark – Controlling Actinide Hydration in Mixed Solvent Systems: Towards Tunable Solvent Systems to Close the Nuclear Fuel Cycle
9:25 – 9:50 Bruce Moyer – Mechanism of Synergized Anion Exchange using Neutral Anion Receptors

10:00 – 10:30 *** Break ***

Session 9 – Close Out Session – Sue Clark and Lynda Soderholm, Co-chairs

10:30 – 12:00 p.m. Program summaries and discussion
12:00 – 1:00 Working lunch – box lunch
1:00 – 3:00 Open discussion and take down posters

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Session 5 – Forensics and Characterization – Sue Clark, Chair

Session 6 – Electronic Structure, Characterization – Richard Martin, Chair

Session 7 – Theory and Characterization – Laura Gagliardi, Chair

Session P2 – Poster Session 2

Session 8 – Separations – Paula Diaconescu, Chair

Abstracts Not Presented

Session 1 – Separations

Sigma Team for Minor Actinide Separations
Directed Fundamental Research under the Office of Nuclear Energy

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Collaborators: Lætitia H. Delmau (ORNL), George S. Goff (LANL), Artem V. Guelis (ANL), Benjamin P. Hay (ORNL), David T. Hobbs (SRNL), Mark P. Jensen (ANL), Gregg J. Lumetta (PNNL), Bruce J. Mincher (INL), Kenneth L. Nash (ANL), Dean R. Peterman (INL)

Overall research goals: The Sigma Team for Minor Actinide Separation (STMAS) was formed at the beginning of FY 2009 under the overarching thesis that finding more efficient separation methods for americium and other minor actinides (MAs) can significantly improve the overall benefit of fuel recycle. Specific aims of the STMAS are essentially two-fold: to develop the scientific basis for a more robust, more efficient actinide/lanthanide (An/Ln) separation process and to develop the scientific basis for an efficient separation of americium from curium. These two aims are being pursued by integrated hypothesis-driven research mainly within the paradigm of aqueous reprocessing of used oxide nuclear fuel dissolved in nitric acid, with one exception focused on carbonate media. Questions being addressed deal with principles of selectivity through various means including aqueous-phase complexation, use of soft-donor extractants, higher oxidation states of americium, ion exchange, and crystallization/dissolution processes. Explicit attention is also paid to the question of robustness of chemical systems under conditions relevant to future technology implementation. This presentation outlines the goals of the STMAS, significance of achieving these goals, recent highlights, and future directions. There will also be a discussion of the mutual beneficial interaction between fundamental and applied research.

Significant achievements in 2009–2011:

- Proof-of-principle for the TRUSPEAK concept has been reached employing a combination of two extraction reagents to enable a one-step An(III)/Ln(III) separation in which Am(III) is selectively stripped with an aqueous chelating agent.
- Insights into the aqueous-phase complexation chemistry of the TALSPEAK process have been obtained toward a needed understanding of selectivity and pH dependence.
- A proof of principle of the thermodynamic-amplification effect was demonstrated in which two ligands just the right size to coordinate the larger Am^{3+} cation but too large to bind the smaller Cm^{3+} cation effectively select the larger cation against normal thermodynamic expectations.
- Proofs-of-principle experiments have shown that discrimination of poorly extractable Am(V) is possible vs extractable trivalent metals under TRUEX extraction

conditions. Am(V) proves to be surprisingly stable in up to 8 M nitric acid solution, though Am(VI) is reduced rapidly.

- Under the hypothesis that uranophilic ligands can preferentially stabilize Am(VI) over Cm(III) or Ln(III), one uranophile exhibited a promising complexation constant for Pu(VI) two orders of magnitude greater than that of Nd(III).
- Oxidation of Am(III) to Am(VI) as the $AmO_2(CO_3)_3^{4-}$ species, was successfully demonstrated by bubbling ozone through a solution of Am(III) in 2 M K_2CO_3, and the Am(VI) was stable for several hours. Am(III) and Nd(III) precipitate from carbonate solution with the addition of hydrogen peroxide. An Am/Nd separation factor of 1.7 was observed, a low value presumably because of co-crystallization.
- Titanate-based and hybrid zirconium phosphonate materials and conditions were identified that afforded separation of Am(III) from Ln(III) and fission products.

Questions being addressed in 2011–2013:

- Can aqueous complexation provide sufficient discrimination and operational control?
- Can the higher oxidation states of americium be stabilized and exploited?
- Are soft-donor extractants sufficiently robust and effective?
- Does ion exchange have the selectivity and robustness to operate effectively?
- Can dissolution or crystallization processes provide adequate selectivity?

Selected references of works supported by this project

1. Gelis, A. V.; Vandegrift, G. F.; Bakel, A.; Bowers, D. L.; Hebden, A. S.; Pereira, C.; Regalbuto, M. Extraction behaviour of actinides and lanthanides in TALSPEAK, TRUEX and NPEX processes of UREX+. *Radiochim. Acta* **2009**, *97*, 231–232.
2. Leggett, C. J.; Liu, G. K.; Jensen, M. P. Do Aqueous Ternary Complexes Influence the TALSPEAK Process? *Solvent Extr. Ion Exch.* **2010**, *28*, 313–334.
3. Lumetta, G. J.; Carter, J. C.; Gelis, A. V.; Vandegrift, G. F. Combining octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide and bis-(2-ethylhexyl)phosphoric acid extractants for recovering transuranic elements from irradiated nuclear fuel. In *Nuclear Energy and the Environment Symposium*; C. M. Wai and B. J. Mincher, Eds., ACS Symposium Series, Vol. 1046, Washington, DC, 2010.
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5. Martin, L. R.; Mincher, B. J.; Schmitt, N. C. Extraction of Am(VI) with a neutral organophosphorous ligand. *J. Radioanal. Nucl. Chem.* **2009**, *282*, 523–526.
6. Mincher, B. J.; Schmitt, N. C.; Case, M. E. A TRUEX-based separation of americium from the lanthanides. *Solvent Extr. Ion Exch.*, in press.
7. Runde, W. H.; Mincher, B. J. The higher oxidation states of americium: preparation, characterization and use for separations. *Chem. Rev.*, in press.

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

James F. Wishart (Lead),[a] Mark L. Dietz,[b] Sheng Dai,[c] Huimin Luo,[c] Charles L. Hussey,[d] Ilya A. Shkrob,[e] Principal Investigators
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Collaborators: T. W. Marin, S. D. Chemerisov, Argonne National Laboratory
Students: C. A. Hawkins, S. L. Garvey, A. J. Pawlak (UWM), Y. Pan (UM)

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 and electrochemical separations systems, study 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 2009-2011: Project awards were made in September 2009, and postdocs were hired in early-mid 2010.

- Previous work on the partitioning of radiostrontium between acidic aqueous phases containing NO_3^- and several imidazolium-based ILs in the presence of DCH18C6 showed a systematic shift in the predominant pathway for partitioning of Sr^{2+} from ion exchange to neutral nitrato complex extraction as the hydrophobicity of the IL cation increased. Our new results for Na^+, K^+ and Cs^+ indicate that, in contrast to Sr^{2+}, increasing IL hydrophobicity with alkyl chain length from $C_5mim^+Tf_2N^-$ to $C_{10}mim^+Tf_2N^-$ does not change the predominant ion exchange partitioning pathway; in no case is neutral complex extraction observed. The practical significance is that in the acidity range (as HNO_3) of interest in extraction processes the selectivity for Sr^{2+} considerably improves with increasing cation hydrophobicity. Work with Ca^{2+} and Ba^{2+} suggests that this enhancement of divalent *vs.* monovalent cation extraction selectivity is a general characteristic of these systems.
- Sixteen protic amide-based ionic liquids derived from dimethylformamide and other amides, with $N(SO_2CF_3)_2^-$ or $N(SO_2CF_2CF_3)_2^-$ anions, were prepared and characterized. Excellent efficiencies for separation of Sr^{2+}_{aq} and Cs^+_{aq} were found for several of these ILs using DCH18C6. Unlike in imidazolium- and ammonium-based ILs, the extraction efficiency trends in our amide-based ILs are not directly correlated with the hydrophilicity of the corresponding cations of the protic IL system. The effects on extraction efficiencies of solution acidities, anions, and alkyl chain lengths in the cations of ILs were also investigated and reported.
- A direct UV-spectroscopic method was developed to measure the ultralow vapor pressures and vaporization enthalpies of ionic liquids. This method opens up a new avenue to study the nature of ionic-liquid vapors, and by extension, the relatively low but variable solubility of ionic liquids in non-polar solvents of interest in biphasic systems.
- Literature reports about the electrodeposition of Ln metals (in this case Sm) by reducing dissolved Ln^{3+} species in neat ionic liquids were reexamined by careful experimentation using highly purified ionic liquids, which showed that this approach does not result in stable, useful

metal deposits. Therefore, we adopted an alternative strategy in which we are attempting to co-deposit metals with Sm that have been reported to form stable Sm-M alloys, e.g., M = Ag, Co, Cu, Mn, Ni, Sn, and Zn, since it has been demonstrated that these metals can be electrodeposited from ionic liquids at relatively positive potentials.

Science objectives for 2011-2013:

- Investigate the effect of IL anions on extraction of metal ions.
- Develop highly stable task-specific ILs for metal-ion extraction.
- Investigate separation mechanisms associated with rare-earth ions (fission products) in ionic liquids.
- ILs based on $N(SO_2CF_3)_2^-$ anions are inert solvents with large electrochemical windows but they are mediocre solvents for metal ions. Therefore, we began working with dicyanamide ($N(CN)_2^-$) ILs. Many metals can be electrodeposited from BuMePyr $N(CN)_2$, including Al, Cu, Mn, Ni, Sn, and Zn. We are currently using this IL for the electrodeposition of Sm-M alloys (see below) and to investigate the electrochemistry of rhenium (as a technetium surrogate).
- We will exploit the positive electrochemical potential shift that results from alloy formation to effect the electrodeposition of Sm as alloys of Ag, Co, Cu, Mn, Ni, Sn, and Zn. Some of the alloys thus formed are particularly useful as high performance magnets.
- We are using electrochemistry to determine the complex formation constants between trivalent lanthanides and *N*,*N*,*N'*,*N'*-tetra(octyl)diglycolamide (TODGA) and bis(2-ethylhexyl)phosphoric acid (DEHPA) in ionic liquids.
- Ultimately one must remove Ln^{3+} dissolved in ILs, either when solvated by the ionic liquid or complexed by TODGA. We will examine the precipitation of Ln^{3+} by electrogenerated oxide and/or oxalate ions. We are also researching methods for the electroless plating of Ln from ILs.

Publications supported by this project (separations focus) 2009-2011

1. Wang, C. M., Luo, H. M., Li, H. R. and Dai, S. "Direct UV-spectroscopic measurement of selected ionic-liquid vapors," *Phys. Chem. Chem. Phys.* **2010**, *12*, 7246-7250. http://dx.doi.org/10.1039/c001101k
2. Luo, H. M., Huang, J. F. and Dai, S. "Solvent Extraction of Sr^{2+} and Cs^+ using Protic Amide-Based Ionic Liquids," *Sep. Sci. Technol.* **2010**, *45*, 1679-1688. http://dx.doi.org/10.1080/01496395.2010.493798
3. Lee, J. S., Luo, H. M., Baker, G. A. and Dai, S. "Cation Cross-Linked Ionic Liquids as Anion-Exchange Materials," *Chem. Mater.* **2009**, *21*, 4756-4758. http://dx.doi.org/10.1021/cm902522b
4. Tsuda, T., Boyd, L. E., Kuwabata, S. and Hussey, C. L., "Electrochemistry of Copper(I) Oxide in the 66.7-33.3 mol % Urea-Choline Chloride Room-Temperature Eutectic Melt," *J. Electrochem. Soc.* **2010,** *157* (8), F96-F103. http://dx.doi.org/10.1149/1.3377117
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6. Dietz, M. L., Garvey, S. L. and Hawkins, C. A., "Mechanisms of metal ion transfer into RTILs: Implications for their use as extraction solvents", *Proceedings of the International Solvent Extraction Conference (ISEC '11)*, **2011**, in press.
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An Integrated Basic Research Program for Advanced Nuclear Energy Systems based on Ionic Liquids – Radiolytic Aspects (SISGR)

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Students: C. A. Hawkins, S. L. Garvey, A. J. Pawlak (UWM), Y. Pan (UM)

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 and electrochemical separations systems, study 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 2009-2011: Project awards were made in Sept. 2009, and a technical associate and a postdoc were hired at BNL in Sept. 2009 and April 2010 respectively.

- Magnetic resonance spectroscopy was used to study the formation of radical species in irradiated frozen glasses of many different families of ILs. We showed that radiation-induced redox reactions lead to fragmentation of the constituent ions in the ILs, however certain types of anions (derivatives of benzoate, (thio)salicylate, and certain imides) are particularly resistant to oxidative fragmentation, thus providing greater radiation stability to the solvent. Several entirely new types of organic radicals and their reactions have been discovered in these studies.
- Our studies suggest that the IL solvents frequently exhibit a radioprotective effect: the solvent diverts the radiation damage towards the constituent ions while protecting the solute from fragmentation, either in the ionized or electronically excited states (which negatively affects the performance of the extracting agents).
- We assessed the effect of radiation on the Sr^{2+} extraction performance of 1-alkyl-3-methylimidazolium bistriflimide containing crown ethers. While solvent damage was readily apparent, the extraction performance did not deteriorate but actually improved after radiolysis, resulting in steeper dependencies of the distribution coefficients on the acidity of the raffinate. We consider this behavior as an experimental confirmation of our mechanistic studies suggesting radioprotective effect of the IL solvent on the crown ether fragmentation. As a result of these studies, good understanding of the complex radiation and radical chemistry of the ionic liquids is gradually emerging and the effects of this chemistry on the extraction behavior of the IL based solvents are becoming recognized.
- Electrospray mass spectroscopic studies were conducted on gamma-irradiated imidazolium, pyridinium, and ammonium ionic liquids to identify their radiolysis products and elucidate the mechanisms of radiolytic damage to ionic liquids. Due to the slow accumulation rate of radiolysis products, the samples had to be irradiated to 2 MGy, a larger dose than expected in

practical separations use. Selective deuteration was used to identify specific sites of reactivity and fragmentation. Aerobic and anaerobic irradiations revealed previously unknown redox-sensitive mechanisms for product formation in imidazolium ILs. The identified products can now be evaluated for their impact on separations efficiency.

Science objectives for 2011-2013:

- In the next phase we will focus on chemistry of several common extracting agents for trivalent metal ions, such as the diglycolamides and bis-(2-ethylhexyl) phosphoric acid, as the IL variants of the extraction processes based on these agents being investigated by the ORNL coworkers.
- We will continue our studies of radiation effects on the extraction performance and our examination of mechanisms of radiation damage and electrochemical breakdown of ILs.
- We have already formulated several approaches for improving radiation stability of the ILs and we will investigate more of the potential classes of hydrophobic organic ions that can be used to achieve exceptional stability and superior extraction performance.
- Reaction rates of primary radiolysis products (electrons and radicals) with common extractants will be measured in several different families of ionic liquids using BNL's LEAF picosecond pulse radiolysis facility.
- We will conduct ESI-MS studies of the radiolysis products of ionic liquids containing various extractants, such as crown ethers and diglycolamides, to determine the extent of their radiolytic degradation and characterize the products obtained. The effects of water and nitric acid on radiolysis product accumulation and speciation in ILs and IL-extractant mixtures will be studied.
- 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.

Publications supported by this project (radiolysis focus) 2009-2011

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2. Wishart, J. F. and Shkrob, I. A., "The radiation chemistry of ionic liquids and its implications for their use in nuclear fuel processing," In "Ionic Liquids: From Knowledge to Application," Rogers, R. D.; Plechkova, N. V.; Seddon, K. R., Eds. Am. Chem. Soc.: Washington, **2009**; pp 119-134.
3. Wishart, J. F., "Ionic Liquids and Ionizing Radiation: Reactivity of Highly Energetic Species," *J. Phys. Chem. Lett.* **2010**, *1*, 3225–3231. http://dx.doi.org/10.1021/jz101096b
4. I. A. Shkrob, Marin, T. W., Chemerisov, S. D. and J. F. Wishart, "Radiation-induced redox reactions and fragmentation of constituent ions in ionic liquids. 1. Anions," *J. Phys. Chem. B* **2011**, *115*, in press.
5. I. A. Shkrob, Marin, T. W., Chemerisov, S. D., Hatcher, J. L. and J. F. Wishart, "Radiation-induced redox reactions and fragmentation of constituent ions in ionic liquids. 2. Imidazolium cation," *J. Phys. Chem. B* **2011**, *115*, in press.
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Multi-Stage Separation of Actinides with Biomolecules

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Professors Gayle Woloschack and Tatjana Paunesku, Northwestern University, Departments of Radiation Oncology and Radiology, Chicago, IL

Overall research goals: This program is focused on the interactions of actinides with biological or biologically inspired molecules. We are attempting to understand the structural, thermodynamic, and kinetic principles that might be used to achieve actinide separations in systems that can recognize and separate actinide-bioligand complexes. Our 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 2009-2011: We have been studying the complexes of tetravalent f-elements and their interactions with proteins in order to understand how these multi-stage systems achieve separation.

The protein transferrin and the resulting multi-protein complexes that form through its interactions with a second protein, the transferrin receptor, are capable of separating tetravalent actinide species such as Pu from other metals. In this work, we have identified several critical features that distinguish the recognition and separations of tetravalent actinides in this system. Separations based on the transferrin-transferrin receptor system behave differently than common actinide separations. The separation is not driven by the stoichiometry or composition of the metal-transferrin complexes, the identity of the metal-binding groups, or the intrinsic strength of the metal-ligand

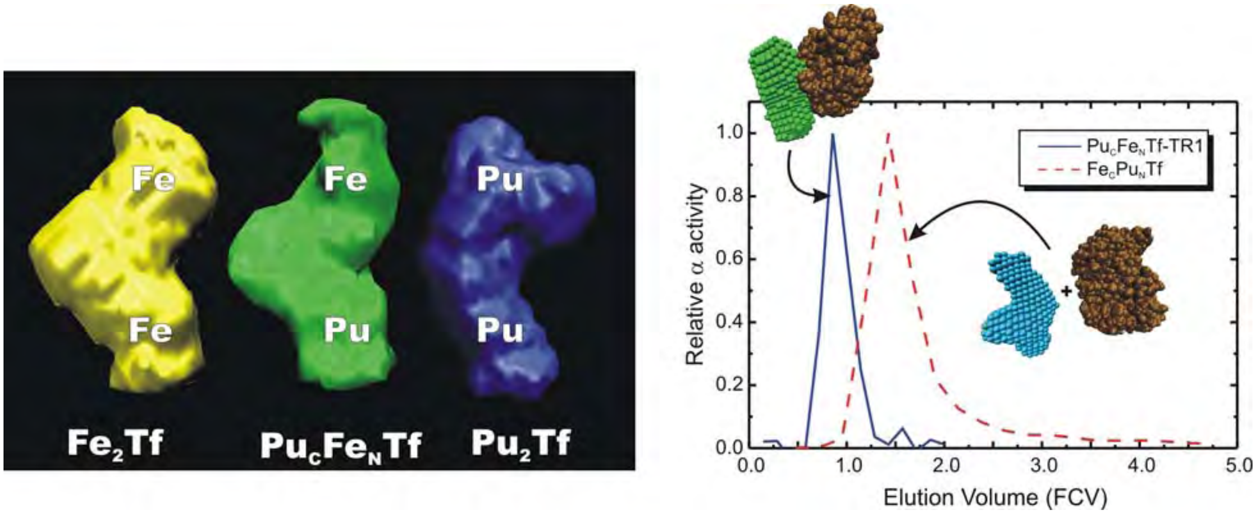

Figure 1. Left: Low resolution solution structures of transferrins containing iron or plutonium reconstructed from small-angle X-ray scattering show that binding Pu in one of the two metal binding sites of transferrin produces a different conformation in the metal-protein complex. Right: The interactions of actinide-transferrins with the transferrin receptor protein are governed by the protein conformation and can be used for separations.

bonds in the transferrin complex. In short, the thermodynamics of the metal-ligand bonds formed in these complexes do not drive this separation. Instead, the recognition and separation is based on the influence of the metal ions on the conformation of the transferrin and the subsequent interaction between the metal-transferrin complexes and the transferrin receptor protein. These interactions take place on length scales that are much longer than the actinide-ligand bonds in these complexes.

We have also been investigating how to subvert bio-based small molecules intended for transport and acquisition of transition metals, which is a natural form of separation. Substituting tetravalent actinides for the target transition metals produces complexes that remain well recognized by naturally-occurring binding proteins. This occurs despite the differences in the size and charge of the normal transition metal target ions and the tetravalent actinides. This opens the possibility of using such systems in multi-stage recognition of the actinide complexes.

Science objectives for 2011-2013:

- Elucidate specific chemical features that drive or inhibit the multi-stage interactions between the initial actinide-complexes and the secondary binding proteins.
- Investigate possible mechanisms for exercising greater control over actinide chemistry by using actinide-biomolecule complexes to stabilize actinides such as Am in difficult to access oxidation states.
- Explore the influence of actinide substitution on the kinetics of multi-stage recognition and separation.

Publications supported by this project 2009-2011

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Session 2 – Complexation and Coordination

Organometallic Actinide Chemistry – Metal-Ligand Multiple Bonding and Electron Correlation

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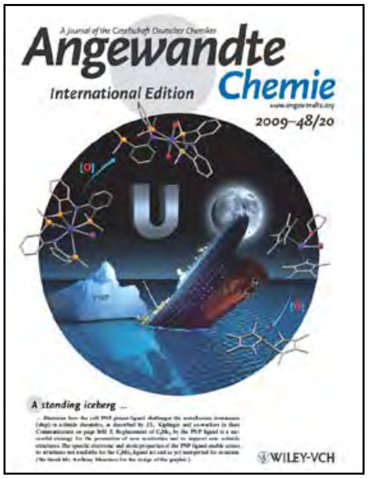
Overall Research Goals: This project explores the existence and manifestations of covalent metal-ligand bonding, including the generation and investigation of actinide-ligand multiple bonds, in complexes of uranium and other light actinides over a broad range of ligand sets and structure types through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

Significant Achievements in 2008-2011:

Synthesis and Reactivity of a Terminal Uranium Nitride Complex. Nuclear power is a key element of our global energy mix and uranium nitride $[U{\equiv}N]_x$ is a promising alternate nuclear fuel that has great potential for the expanding future of nuclear power; however, very little is known about the $U{\equiv}N$ functionality. Since the physicochemical properties of extended ceramic materials such as $[U{\equiv}N]_x$ are challenging to study, well-defined uranium nitride compounds are ideal for the controlled study of this bond fragment. Nitrides remain a rare functional group for uranium and to date there have been no examples of a discrete molecular terminal uranium nitride for scientists to study. This has changed with our recent report in which we made a uranium azide that interacts with light to lose nitrogen and produce a uranium nitride. This is the first uranium nitride to be accessed through photolysis; it is reactive and cleaves a strong carbon-hydrogen bond to form new nitrogen-hydrogen and nitrogen-carbon bonds. This important discovery demonstrates that the $U{\equiv}N$ fragment is not inert and can undergo reactions with strong bonds. Interestingly, DFT analysis shows that the observed carbon-hydrogen bond activation is strikingly similar to the oxidation of alkanes to alcohols by the enzyme cytochrome P450, which is required to oxidize organic substances in nearly all living organisms. These first reactivity studies are anticipated to improve our understanding of the chemistry of uranium nitride with small molecules and cladding materials as well as its behavior in nuclear waste and in the environment resulting in breakthroughs in materials compatibility issues, waste processing and environmental remediation. This work was selected by the Editor to be featured on the cover of *Nature Chemistry*.

Challenging the Metallocene Dominance in Actinide Chemistry with a Soft PNP Pincer Ligand. Actinide chemistry is largely founded on carbon-based metallocene complexes such as "$(C_5Me_5)_2U$" (Me = CH_3) but many of these compounds are unstable because the cyclopentadienyl ligands fall off the metal and form $(C_5Me_5)_2$ dimer during oxidation reactions. This year we circumvented



this problem by using a ligand combining 'soft' and 'hard' coordination environments. Compared to the C_5Me_5 ligand, which only displays η^5-coordination to uranium, this PNP pincer ligand is able to adopt a variety of coordination modes ranging from κ^2-(*P*,*N*) to κ^3-(*P*,*N*,*P'*) and provides more steric crowding and greater electronic density at the metal center. By replacing the conventional bis(C_5Me_5) framework of a classic uranium metallocene with a set of two phosphorus-nitrogen-phosphorus pincer, or PNP, ligands, the we obtained a uranium complex, which acts as a new synthetic equivalent for uranium(II) when in the presence of graphite intercalation compound KC_8. This "$(PNP)_2U$" uranium(II) synthon shows different reactivity patterns than the classic "(C_5Me_5)U" synthon, resulting in the first hydrazonido complex of an actinide. This features a C=N-N group where one nitrogen forms a double bond and the other a dative bond with the uranium center. The uranium(II) synthon "$(PNP)_2U$" also reacted with strong oxidant pyridine N-oxide leading to uranyl(VI) complex that cannot be obtained with metallocenes because the cyclopentadienyl ligands are released as $(C_5Me_5)_2$ dimer under the same conditions. This work was selected by the Editor to be featured on the cover of *Angewandte Chemie*.

Specific objectives for 2011-2013:

We will continue our efforts to introduce new members to the family of actinide complexes containing multiply bound ligands (e.g. alkylidenes, alkylidynes, carbides, nitrides), either by redox reactions, photochemistry, insertion chemistry, or by ligand transfer methods. Our synthetic studies will be coupled with spectroscopy and theory.

Selected references of work (out of 25 total) that was supported by this project (2008-2011)

1. Thomson, R. K.; Graves, C. R.; Scott, B. L.; Kiplinger, J. L. "Noble Reactions for the Actinides: Safe Gold-Based Access to Organouranium and Azide Complexes," *Eur. J. Inorg. Chem.* **2009,** 1451-1455. **Featured on the cover of *European Journal of Inorganic Chemistry*.**
2. Cantat, T.; Graves, C. R.; Scott, B. L.; Kiplinger, J. L. "Challenging the Metallocene Dominance in Actinide Chemistry with a Soft PNP Pincer Ligand: New Uranium Structures and Reactivity Patterns," *Angew. Chem., Int. Ed.* **2009**, *48*, 3681-3684. **Featured on the cover of *Angewandte Chemie International Edition.***
3. Graves, C. R.; Kiplinger, J. L. "Pentavalent Uranium Chemistry – Synthetic Pursuit of a Rare Oxidation State," Invited Feature Article, *Chem. Commun.* **2009**, 3813-3968. **Featured on the cover of *Chemical Communications***
4. Cantat, T.; Scott, B. L.; Kiplinger, B. L. "Convenient Access to the Anhydrous Thorium Tetrachloride Complexes $ThCl_4(DME)_2$, $ThCl_4(dioxane)_4$ and $ThCl_4(THF)_{3.5}$ using Commercially Available and Inexpensive Starting Materials," *Chem. Commun.* **2010**, *46*, 919-921. **Designated as a *Chemical Communications* HOT ARTICLE by Editor. Featured in *C&EN News.***
5. Thomson, R. K.; Cantat, T.; Scott, B. L.; Morris, D. E.; Batista, E. R.; Kiplinger, J. L. "Uranium Azide Photolysis Results in C-H Bond Activation and Provides Evidence for a Terminal Uranium Nitride," *Nature Chemistry* **2010**, 2, 723-729. **Featured on the cover of *Nature Chemistry*. Featured in *Chemistry World*. Featured in *C&EN News*. Featured in *New Scientist*.**

Fundamental Chemistry of Technetium in Iron Oxide Matrices

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Dr. Ken Czerwinski, Department of Chemistry, University of Nevada, Las Vegas, NV.
Dr. Frederic Poineau, Department of Chemistry, University of Nevada, Las Vegas, NV.
Dr. David Shuh, Chemical Sciences Division, Lawrence Berkeley National Laboratory.
Dr. Tolek Tyliszczak, Advanced Light Source, Lawrence Berkeley National Laboratory.
Dr. Wooyong Um, Geosciences Group, Pacific Northwest National Laboratory, Richland, WA.

Overall research goals: The objective of this project is to understand the factors that control the chemistry of technetium during the formation and corrosion of iron oxides especially spinel ferrites such as magnetite.

Significant achievements during 2009-2011: Project began in 2009. The initial goal 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. A series of samples with the target composition $M_xTc_{0.1}Fe_{3-x-0.1}O_4$, where M =Mg, Mn, Fe, Co, and Ni and x= 0.2 or 1.1 have been prepared by two routes, oxidation of Fe(II) and coprecipitation. The materials have been characterized by X-ray diffraction (XRD) to determine the crystalline phases present, Tc K-edge X-ray absorption fine structure (XAFS) spectroscopy to determine the speciation and local structure of Tc, and chemical analysis to determine the Fe(II)/Fe(III) ratio. The following are the main results.

1. Materials with the composition $M_{1.1}Tc_{0.1}Fe_{1.8}O_4$ are difficult to make cleanly by either synthetic route, but materials with the composition $M_{0.2}Tc_{0.1}Fe_{2.7}O_4$ can be prepared cleanly by the oxidation route. As shown in Figure 1, attempted preparation of $Ni_{1.1}Tc_{0.1}Fe_{1.2}O_4$ by the oxidation route results in the formation of nickel hydroxide in addition to the desired spinel ferrite while attempted preparation of $Ni_{0.2}Ti_{0.1}Fe_{2.7}O_4$ results in the formation of the desired spinel structure (goethite impurity is due to aerobic oxidation of ferrous hydroxide).

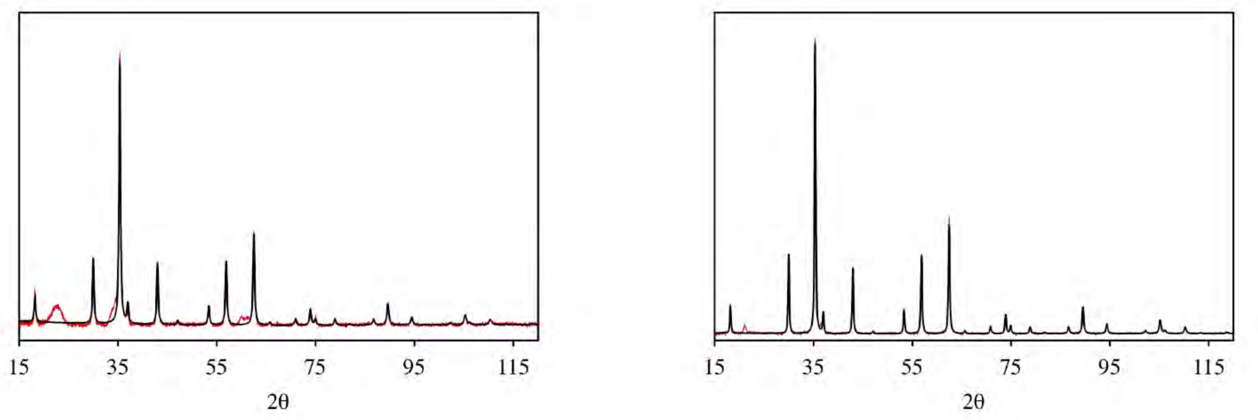
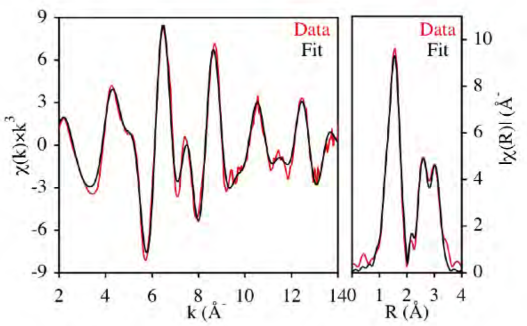


Figure 1. Red line is data. Black line is fit using the spinel structure. Left: Product of attempted synthesis of $Ni_{1.1}Tc_{0.1}Fe_{1.8}O_4$; additional peaks are due to nickel hydroxide hydrate. Right: product of attempted synthesis of $Ni_{0.2}Tc_{0.1}Fe_{2.7}O_4$; small peak at 2θ = 18° is goethite due to aerobic oxidation of ferrous hydroxide.

2. In all cases, the local structure of Tc(IV) is consistent with incorporation of Tc into the spinel lattice through replacement of Fe(III) in the octahedral site by Tc(IV). When other phases are present, Tc is still found in the spinel phase. Figure 2 shows the extended X-ray absorption fine structure (EXAFS) spectrum of Tc in magnetite and compares the local structure of Tc to the structure of the octahedral site in magnetite.



EXAFS fit parameters

Atom	#	Distance	Fe_3O_4 (O_h site)
O	5.8(1)	2.03 Å	2.06 Å
Fe	3.0(6)	3.08 Å	2.97 Å
Tc	1.1(4)	3.08 Å	2.97 Å
Fe	3.0(6)	3.50 Å	3.48 Å
O	5.8(1)	3.58 Å	3.57 Å

Figure 2. Local structure of Tc in $Tc_{0.1}Fe_{2.9}O_4$. Left: EXAFS spectrum and its Fourier Transform. Right: Fit parameters for the EXAFS spectrum

- EXAFS studies on Tc in polyoxometallates in collaboration with Lynn Francesconi reveal that the coordination environment of Tc(V) in the “cap” of the Wells-Dawson (WD) ion is significantly different from that of Tc(V) in the “belt” of the WD ion. The different environments are consistent with differences observed in the NMR spectra and redox potentials of the two complexes.

- EXAFS studies of Tc in goethite in collaboration with Wooyong Um of Pacific Northwest National Laboratory are consistent with Tc(IV) replacing Fe(III) in the goethite lattice.

<u>Science objectives for 2011-2013:</u>

- Test the hypothesis that corrosion/alteration of technetium-bearing, lower-valent iron waste forms, especially magnetite, will result in the incorporation of Tc(IV) into the lattice of the ferric corrosion products (goethite, lepidocrocite, hematite, maghemite, etc).

- 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.

- Continue to determine the local structure of Tc in polyoxometallates in collaboration with Lynn Francesconi.

- Study chemical denitration of 10 M nitric acid containing TcO_4^- to determine the speciation of technetium.

<u>Publications supported by this project 2009-2011</u>

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2. McGregor, D.; Burton-Pye, B.; Howell, R.; Mbomekalle, I.; Lukens, W.; Bian, F.; Mausolf, E.; Poineau, F.; Czerwinski, K; and Francesconi, L. “Synthesis, structure elucidation, and redox properties of ^{99}Tc complexes of lacunary Wells−Dawson polyoxometalates: insights into molecular ^{99}Tc−metal oxide interactions,” Inorg. Chem., 2011, ASAP.
3. Um, W.; Chang, H.; Icenhower, J.; Serne, R.; Qafoku, N.; Westsik, J.; Buck, E.; Kukkadapu, R.; Smith, S.; and Lukens, W.. “Immobilization and limited reoxidation of technetium-99 by Fe(II)-goethite,” Environ. Sci. Technol. Submitted.

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

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Overall SISGR Research Goals:

The isotope ^{99}Tc (β_{max}: 293.7 keV, half-life: 2.1 x 10^5 years) is of interest and concern for two reasons: 1) ^{99}Tc is a major product of U-235 fission in nuclear reactors and 2) large amounts of ^{99}Tc, formed during early plutonium production activities, are present in the radioactive waste stored in underground tanks at Hanford and Savannah River. The physical properties of ^{99}Tc and its complex redox activity pose a problem for both closing the nuclear fuel cycle and remediation of waste tanks.

The *overall research goals* of this SISGR is to elicit molecular level understanding of the chemical bonding, speciation, and redox stability of ^{99}Tc incorporated into inorganic materials. This information should be useful towards controlling the extensive redox chemistry of ^{99}Tc and towards identifying appropriately stable waste-forms for ^{99}Tc based on the fundamental chemistry of the element.

SISGR Team: The SISGR team is investigating ^{99}Tc containing materials that range in size from molecules (nanometer-sized polyoxometalates and phosphates) to sulfide, phosphate, 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 Research Goals: are to provide molecular level understanding of chemical bonding, speciation and redox stability of ^{99}Tc incorporated within the bonds of polyoxometalates (POMs) and phosphate materials. 1: to identify features of POM and polyphosphate binding sites that enhance stability of low valent ^{99}Tc; 2: To identify new strategies for reduction of TcO_4^- and stabilization of the low valent Tc.

Significant Achievements during 2009 – 2011:

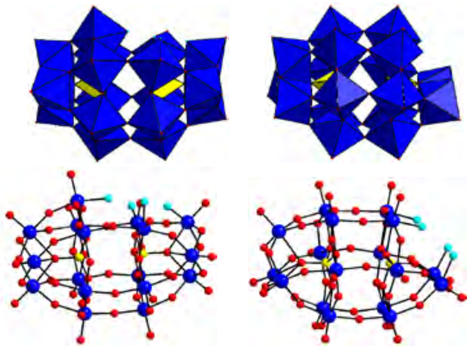
$[\alpha_1\text{-}P_2W_{17}P_{61}]^{10-}$ $[\alpha_2\text{-}P_2W_{17}P_{61}]^{10-}$

Figure 1. Polyoxometalates (POMs): ideal models for metal oxides to extract molecular level understanding of ^{99}Tc interactions with metal oxides. Top: polyhedral representation; Bottom: ball and stick representation. The well defined defect structures (shown in cyan) possess distinct and different electronic and steric features that impact chemical and redox speciation of ^{99}Tc .

1. The $(\alpha_2\text{-}P_2W_{17}O_{61})^{10-}$ (α_2) and $(\alpha_1\text{-}P_2W_{17}O_{61})^{10-}$ (α_1) isomers (Figure 1) model metal oxide solid-state materials. The "defect sites" in these isomers possess different steric and electronic environments that impact the binding strength to ^{99}Tc and the redox properties of the bound ^{99}Tc. ^{99}Tc complexes of the α_2 and α_1 isomers were prepared; the formation of $TcO_2•xH_2O$ was suppressed by employing ethylene glycol as a "transfer ligand". The solution structures, formulations, and purity of $Tc^VO\text{-}\alpha_1/\alpha_2$ were determined by multinuclear NMR and X-ray Absorption Spectroscopy. The α_1- defect is unique in that a basic oxygen atom is positioned toward the α_1- site and the Tc^VO center appears to form a dative metal-metal bond with a framework W site. These attributes may lead to the assistance of protonation events that facilitate reduction. Dr. Wayne Lukens and Professor Ken Czerwinski and UNLV contributed to this work.

2. A detailed electrochemistry study of ^{99}Tc and Re-α_1/α_2 as a function of pH determined that, at all pH values, the $Tc^V\text{-}\alpha_1$-species is easily reduced to the Tc(IV) analog compared to the $Tc^V\text{-}\alpha_2$ analog. This suggests that electrons are more easily introduced into the more basic α_1 defect site. The Tc POMs are more easily reduced compared to the Re analogs; Re analogs tend to remain oxidized (Figure 2). The HOMO and LUMO profiles for the protonated and unprotonated $^{99}Tc^VO\text{-}\alpha_1/\alpha_2$ and $Re^VO\text{-}\alpha_1/\alpha_2$ species, obtained from the cyclic voltammograms, quantitate these trends and are consistent with recent theoretical treatments by J. M. Poblet and X. Lopez. The pK_a values for the $Re^VO\text{-}\alpha_1/\alpha_2$ and $^{99}Tc^VO\text{-}\alpha_1/\alpha_2$ materials, determined from electrochemistry as a function of pH, show distinct differences. The Re^V - α_1/α_2 species are more acidic than the $^{99}Tc^V\text{-}\alpha_1/\alpha_2$ analogs. This study and the following study (3, below) demonstrates differences between ^{99}Tc and Re, often considered as a non-radioactive surrogate for ^{99}Tc.

3. A new strategy for the reduction of $^{99}TcO_4^-$, pertechnetate and complexation of the low valent ^{99}Tc has been identified (Figure 3). Irradiation of $(\alpha_2\text{-}P_2W_{17}O_{61})^{10-}$ with UV or white light produces the reduced $(\alpha_2\text{-}P_2W_{17}O_{61})^{12-}$ ("heteropolyblue") that can in turn reduce $Tc^{VII}O_4^-$ to a Tc^V "intermediate" species. Over time the Tc^V intermediate incorporates into the α_2-defect to form the $Tc^VO(\alpha_2\text{-}P_2W_{17}O_{61})^{7-}$. There are salient differences between Re and ^{99}Tc: reduction of $Re^{VII}O_4^-$ results in Re^V immediately incorporated into the POM defect. The "intermediate" species is not observed for Re.

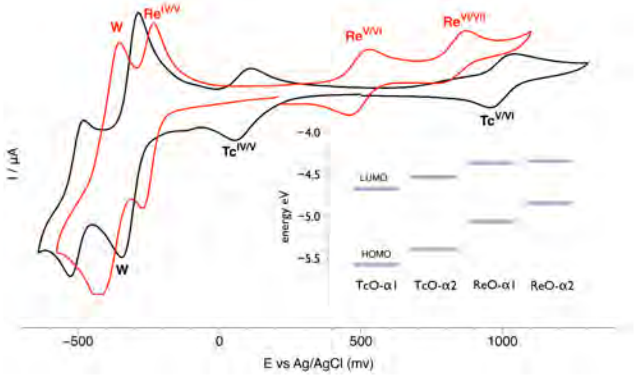

Figure 2. Cyclic voltammograms of $^{99}Tc^VO(\alpha_1\text{-}P_2W_{17}O_{61})^{7-}$ (black) and $Re^VO(\alpha_1\text{-}P_2W_{17}O_{61})^{7-}$ (red) in water, pH 1, shows facile reduction for the Tc analog compared to the Re analog. Re $^{IV, V, VI, VII}$ oxidation states can be accessed while Tc^{VII} is not accessible under these conditions. The HOMO LUMO gaps, determined from the $E_{1/2}$ values of the $M^{IV/V}$ and $M^{V/VI}$ waves, agree with theoretical calculations performed by Poblet and Lopez.

Science objectives for 2011 – 2013:

1. Investigate the use of "plenary" Keggin $(XW_{12}O_{40}^{n-})$ ions for the reduction of $Tc^{VII}O_4^-$. The reduction potentials can be tuned by altering the heteroatom (X). Speciation and product characterization will be accomplished by EXAFS, XANES, multinuclear NMR as well as techniques to assess colloidal or nanoparticle formation. Dr. Wayne Lukens, Dr. Eric Weis and Professor Silvia Jurisson are contributors to this work.

2. Investigate the ^{99}Tc chemistry of cyclic polyphosphates that support high valent and low valent metal ions.

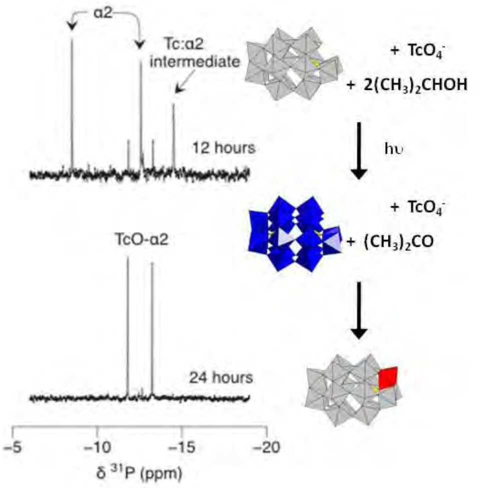

Figure 3. Strategy for reduction of $^{99}TcO_4^-$ and incorporation of low valent Tc into a metal oxide material. $(\alpha_2\text{-}P_2W_{17}O_{61})^{10-}$ is reduced by irradiation in the presence of IPA. Reduced $(\alpha_2\text{-}P_2W_{17}O_{61})^{12-}$ (blue color) reduces $^{99}TcO_4^-$. The reduced ^{99}Tc binds into the vacancy to form the $^{99}Tc^VO\text{-}\alpha_2$. This process is monitored by ^{31}P NMR and radio-TLC (^{99}Tc).

3. Investigate the synthesis, characterization and stabilities of ^{99}Tc POMs that model two scenarios: low valent ^{99}Tc, such as $^{99}Tc^I(CO)_3^+$, bound to surfaces and multiple ^{99}Tc cores (such as $^{99}Tc^V{=}O$) complexed within the metal-oxide bonds.

Publications supported by this grant (Sept 15, 2009 – February, 2011):

1. 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}Tc complexes of lacunary Wells Dawson polyoxometalates: insights into molecular ^{99}Tc – metal oxide interactions", *Inorg. Chem*. **2011**, ASAP article.

2. Burton-Pye, B.P.; Francesconi, L. C. "Speciation of organic-soluble Europium (III) α1-Wells-Dawson complexes", *Dalton Trans*., **2011**, DOI: 10.1039/c0dt01309a, in press.

3. Antonio, M.R.; Jing, J.; Burton-Pye, B.P.; Francesconi, L.C. "Series Behavior of lanthanoid(III) complexes with the α-1-Wells-Dawson heteropolyanion in acetonitrile: electrochemistry and Ln coordination", *Dalton Trans*., **2010**, 39, 7980 – 7992.

Manuscripts to be submitted in March, 2011:

4. Burton-Pye, B.P.; Radivojevic, I.; McGregor, D.; Mbomekalle, I.-M.; Francesconi, L.C. "Photoreduction of ^{99}Tc pertechnetate by nanometer-sized metal oxides: new strategies for formation and sequestration of low valent technetium", to be submitted to Inorganic Chemistry, March 2011.

5. Burton-Pye, B.P.; McGregor, D.; Lopez, X.; Mbomekalle, I.-M.; Poblet, J.M.; Francesconi, L.C., "Redox Properties of Tc and Re derivatives of Dawson Heteropolyanions: Part I. pH dependence of the redox processes and α_1/α_2 Relative Stability", to be submitted to Inorganic Chemistry, March 2011.

6. Romo, S.; Lopez, X.; Mbomekalle, I.-M.; Burton-Pye, B.P.; McGregor, D.; Francesconi, L.C.; Poblet, J.M., "Redox Properties of Tc and Re derivatives of Dawson Heteropolyanions: Part II. Theoretical calculations and molecular orbital comparison", to be submitted to Inorganic Chemistry, March 2011.

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

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Jurisson Research Goals: Provide an understanding of the features of metal sulfides and mixed metal oxides/ sulfides that promote reduction of TcO_4^- and incorporation of reduced Tc.

Previous studies indicated that TcO_4^- was reduced to TcO_2 and incorporated into the FeS matrix. Preliminary stability studies suggested good long-term stability under both anaerobic and aerobic environments. Additional studies are designed to obtain an understanding of the molecular level structure and the stability of the ^{99}Tc incorporated materials.

Significant Achievements during 2009-2011 include (1) the identification of a model compound to study the sulfide-technetium interaction, and (2) progress toward understanding how certain components of humic substances may interfere with Tc_2S_7 formation.

1. There is some evidence that iron sulfide may be a suitable material for the immobilization of pertechnetate in groundwater. Studies to date have been performed on amorphous or bulk iron sulfide, making the characterization of the molecular-scale interactions between the Tc and the S difficult. A model system has been identified for probing these interactions in the class of polyoxometalates containing transition metals sulfides., We have synthesized the necessary precursor materials, K_8 γ-$SiW_{10}O_{36}$, Mo_2S_{12}, and $W_2O_2S_{10}$. Dr. Eric Weis spent a month in Lynn Francesconi's laboratories learning polyoxometallate chemistry and had brought this chemistry to Missouri.

2. There is some evidence that olefinic acids will interfere with the formation of Tc_2S_7, and olefins make up a small part of the humic substances in contaminated ground. We have identified mercaptans from reactions of $^{99}TcO_4^-$ with low-molecular weight olefinic acids and sulfide. The low-molecular weight olefinic acids include acrylic acid, crotonic acid, citraconic acid and maleic acid; all contain unsaturation in their structure. These four acids were reacted with $^{99}TcO_4^-$ in the presence of sulfide and yielded soluble products. In the absence of the sulfide, no reaction occurred. Additionally, mercaptosuccinic acid and its methyl ester were directly reacted with $^{99}TcO_4^-$ (no sulfide added) and soluble products formed. Characterization of these complexes is ongoing.

Science Objectives for 2011-2013 include continuation of the above two projects and investigating the interactions of pertechnetate with iron sulfide nanoparticles.

1. The 3 precursors (K_8-γ-$SiW_{10}O_{36}$, Mo_2S_{12}, and $W_2O_2S_{10}$) will be reacted to generate the sulfur-containing POM model compound. This species will then be reacted with $^{99}TcO_4^-$ as a function of pH, in the presence of potential interfering species, in the presence/absence of oxygen, etc. Characterization will include NMR studies, liquid scintillation counting to monitor the reaction, EXAFS/XANES, chromatography, etc. as appropriate. The stability of these species will be assessed.

2. The Tc-99 containing species formed on reaction with the olefinic acids in the presence of sulfide will be characterized by NMR, IR, chromatography, X-ray crystallography, EXAFS/XANES, etc. This will yield information on potential interferences in the environment to immobilization of Tc-99.

3. Initiate studies on the interaction of $^{99}TcO_4^-$ with iron sulfide nanoparticles with high surface area. The higher surface area of the nanoparticles should provide better interactions with the pertechnetate.

Personnel and publications: Dr. Eric Weis will be leaving in May 2011 to begin a position at Los Alamos National Laboratory. Graduate student Kim Mason has begun working on this project and will take over from Eric Weis. Another postdoctoral fellow will be brought onto the project but will need to be identified.

We anticipate at least 2 manuscripts from Eric Weis' work. No manuscripts have been submitted or published since he began working on this project in January 2010.

Czerwinski Research Goals: Hydrothermal techniques will be employed to synthesize low valent Tc compounds, focusing on carbonate and phosphate materials and Tc-Tc dimers. Concurrently, thermal reactions for the production of low valent Tc halide compounds and Tc-Tc dimers will also be performed.

UNLV: W. Kerlin, E. Johnstone, D. Rego, F. Poineau, P. Weck, P. Forster, A. Sattelberger, K.Czerwinski

Significant Achievements during 2009-2011

1. Hydrothermal studies: Reaction of K $Tc^{VII}O_4^-$ or NH_4 $Tc^{VII}O_4^-$ with a 2:1 ratio acetic acid to HCl in an atmosphere of H_2 gas yields red hexagonal crystals of $Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$ (Figure 1). The oxidation state of each Tc in the Tc-Tc dimer is +3. Another Tc dimer, $Tc_2(\mu\text{-}O_2CCH_3)_3Cl_2(H_2O)_2{\cdot}H_2O$, was isolated from the same reaction (Figure 2). This complex possesses an average oxidation state of Tc +2.5, and may be an intermediate in the reaction for the formation of $Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$. The complexes were analyzed by single crystal XRD.

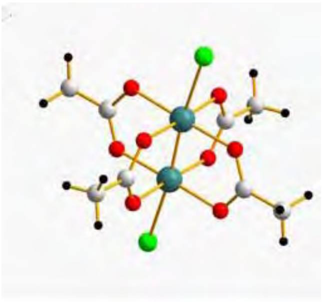
Figure 1

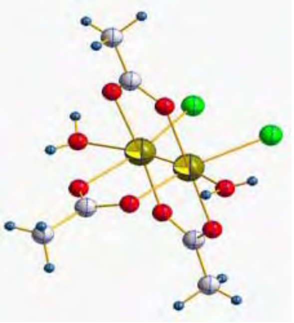
Figure 2

2. Thermal Reactions: The discovery of two new Tc binary halides $TcCl_2$ and $TcCl_3$ prompted further studies on their synthetic mechanisms and characteristics. The structure of Tc_3Cl_9 is isomorphous with Re_3Cl_9. DFT calculations showed that the conformation, presented in Figure 3, was the most stable. A number of Tc-Tc dimer compounds with halides were prepared and characterized through spectroscopic and computational methods.

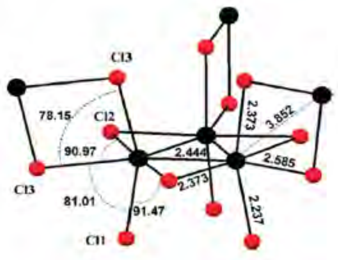

Figure 3. Ball and stick representation of Tc_3Cl_9 cluster in $TcCl_3$

Science objectives for 2011-2013: 1. Hydrothermal reactions: The use of *in situ* H_2 generationand alternative reducing agents will be explored. The exploitation of a recently developed pressure vessel array will be pursued to provide a rapid evaluation of reaction conditions for understanding mechanisms and optimizing specific product synthesis. 2. High temperature reaction efforts will continue to explore reaction mechanism of the Tc binary halides and Tc-Tc dimers.

Publications supported by this project in the last two years

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2. Briggs, B.N., McMillin, D.R., Todorova, T.K., Gagliardi, L., Poineau, F., Czerwinski, K.R., and Sattelberger, A.P.: First Emission Studies of $Tc_2X_8^{2-}$ Systems (X = Cl, Br). Dalton Trans., **39(47)**, 11322-11324 (2010).

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4. Weck, P.F.; Kim, E.; Czerwinski, K.R. First-principles study of the hexahalogenotechnetate(IV) ions TcX_6^{2-} [X = Cl, Br]. Chemical Physics Letters, **487(4-6)**, 190-193 (2010).

5. Poineau, F., Weck, P.F., Forster, P.M., Sattelberger, A.P. and Czerwinski, K.R.: Synthesis, structure, and first-principles calculations of $[TcBr_2(PMe_3)_4]$ and$[Tc_2Br_4(PMe_3)_4]$ complexes. Dalton Trans., 10338-10342 (2009).

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7. Weck, P.F.; Kim, E.; Poineau, F.; Rodriguez, E.E.; Sattelberger, A.P.; Czerwinski, K.R.: Technetium(IV) Halides Predicted from First-Principles. Inorg. Chem. **48(14)**, 6555-6558 (2009).

8. Poineau, F., Rodriguez, E.E., Forster, P.M. Sattelberger, A.P., Cheetham, A.K., Czerwinski, K.R.: Preparation of the Binary Technetium Bromides: $TcBr_3$ and $TcBr_4$. J. Amer. Chem. Soc., **131(3)**, 910-911 (2009).

Ion Pair Receptors: Fundamental Studies and Tests Involving Sulfate Anion and Thorium Cation Extraction

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Overall research goals: Synthesis and study of so-called ion pair receptors, systems that bind concurrently both anions and cations within a single molecular framework. Within this broad paradigm, particular emphasis will be placed on 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 indicators and extractants for the thorium(IV) cation.

Significant achievements during 2009-20011: This project has been focused on addressing two of the above objectives, namely the development of controlled ion pair receptor systems and the preparation of colorimetric receptors and extractants for Th(IV). Progress was made on both fronts.

1. Several new ion pair receptors based on the use of a pseudo dimeric calixpyrrole-calixarene motif were prepared. One system, bearing propoxy substituents, was studied in detail. It revealed multiple binding modes for the bound ion pair, allowing three limiting scenarios to be defined as illustrated in Fig. 1. One of the many crystal structures of bound ion pairs is also shown in this figure.

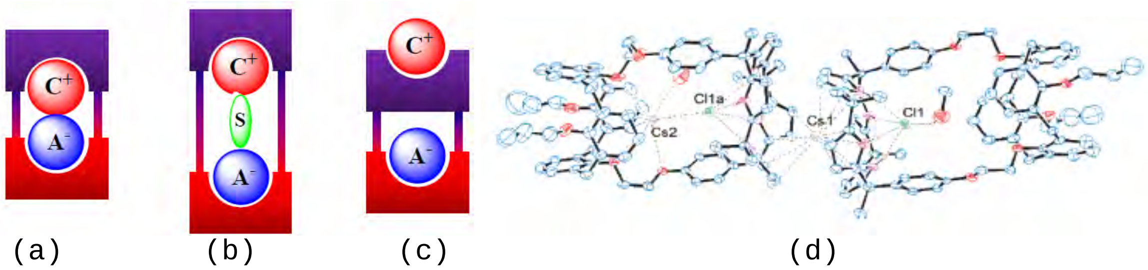
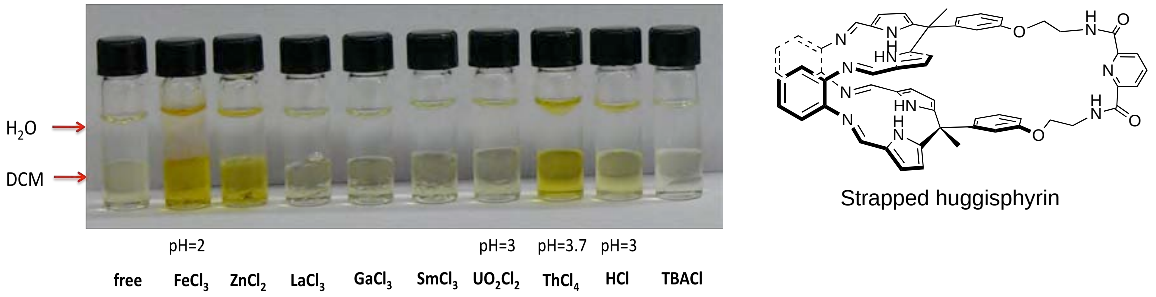


Figure 1: Schematic representation of the limiting ion-pair interactions relevant to receptor-mediated ion-pair recognition: (a) Contact, (b) solvent-bridged, and (c) host-separated. In this schematic, the anion is shown as “A^-”, the cation as “C^+”, and the solvent if present as “S”. Also shown is the CsCl complex (d) obtained from a propoxy functionalized calix[4]arene calix[4]pyrrole hybrid receptor. Note: the presence of both contact- and receptor-separated binding modes within this one receptor-ion pair complex.

2. The second major point of emphasis involved the preparation of derivatives of the so-called huggisphyrins (also known as pacman ligands) that were expected to allow for an improved colorimetric response when used as extractants for the Th(IV) cation. One such system is the strapped huggisphyrin shown in Figure 2. It undergoes a color change in the presence of Fe(III) and Th(IV), and to a lesser extent Zn(II) under mixed organic-aqueous conditions. Related systems based on TTF subunits and even simpler pyrrolic systems, including modified acetylacetone derivatives, were also tested, with the underlying studies still ongoing.



Strapped huggisphyrin

Figure 2: Left: Color changes seen when the strapped huggisphyrin (structure shown at right) in dichloromethane is exposed to aqueous solutions of various metal salts. The pH is not buffered and is approximately 3.7 in the case of the Th(IV) salt.

Finally, efforts were devoted to the preparation of new hydrogen sulfate anion receptors based on tripod arrangements, as were ones associated with the preparation of polymeric materials containing calixarene motifs capable of recognizing and extracting the cesium cation.

Science objectives for 2011-2013:

- Analyze various extant and to-be-prepared calixpyrrole-calixarene hybrid systems as receptors for MX salts. Correlate changes in receptor structure to key binding-related parameters, such as affinity, specificity, and overall complex geometry. Codify the nature of the ion pair interactions (if seen) in terms of contact, solvent separated, and receptor bridged, as appropriate.
- Synthesize new receptors for the sulfate anion, including ones based on triazole subunits. Modify these systems so as to incorporate cation binding sites. Study the resulting systems as ion pair receptors and, in conjunction with the ORNL group, as sulfate extractants.
- Study further our new strapped huggisphyrin as a Th(IV) chemosensor and extractant. Elucidate the nature of the underlying complex and the determinants of the colorimetric change.

Publications supported by this project 2009-2011

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Session 3 – Complexation and Coordination

Control of hydrothermal UO_2^{n+} systems: A solution phase approach to new solid state materials

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Overall research goals: As outlined in our proposal, we have three main focus areas: 1. High Energy X-ray Scattering of aqueous uranyl-organic solutions; 2. In situ ligand synthesis: mechanism elucidation and new reactions; and 3. Targeting materials for elucidation of charge transfer vibronic coupling mechanisms. Significant progress in area #2 has been made and we therefore emphasize these results.

Significant achievements during 2009-20011:

We have made considerable progress in the area of disulfide bond formation as a route to novel topologies in uranyl bearing materials. Figure 1 highlights a significant result that has been published in Crystal Growth and Design (Publication #2, below). In this study, we compared the influence of beginning with 3-mercaptobenzoic acid vs. 3,3'-dithiobenzoic acid as ligands for $[UO_2]^{2+}$. In the publication, we describe how different topologies (framework vs. chain) are obtained whether one uses an in situ formation route or if one utilizes a preformed ligand.

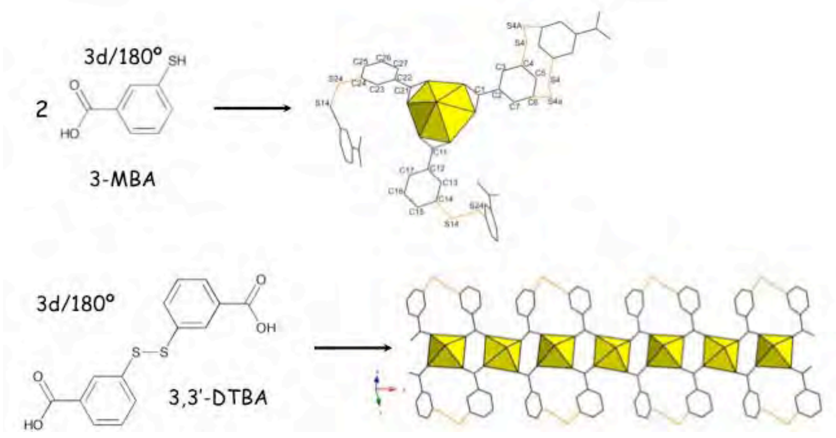

Figure 1. Top: $UO_2(C_7H_4O_2S)_3•H_2O$ as formed from the in situ oxidation of two equivalents of 3-MBA.
Bottom: The crystal structure of $UO_2(C_7H_4O_2S)_3$ as prepared from the pre-formed disulfide containing ligand.

Science objectives for 20011-2013:

We will continue to explore hydrothermal in situ ligand synthesis reactions as routes to new materials. We have recently revisited a commonly reported reaction- namely, oxalate formation from conjugated N-containing precursors. Specifically, we are looking at both oxidation and hydrolysis of 2-pyrimidinecarbonitrile (2-pymcn; Figure 2) to form carboxylate groups and, under certain conditions, oxalate anions. As shown in the figure, reaction with the uranyl cation gives rise to a novel U-pyrimidinecarboxylate, whereas reaction with harder Ln(III) ions results in oxalate formation. We are thus exploring the role of the metal with respect to facilitating oxalate formation.

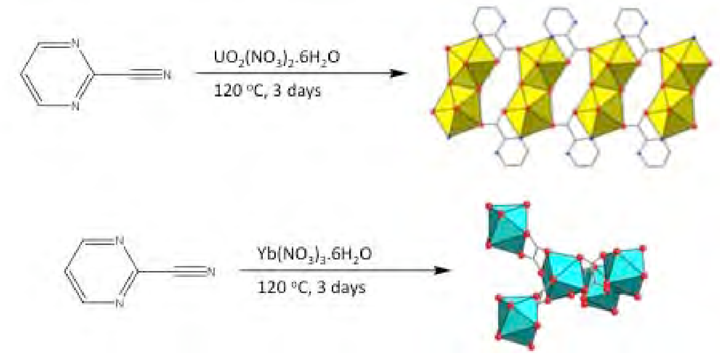

Figure 2. Top: $[UO_2(C_5H_3N_2O_2)(OH)]$ as formed by the oxidation of the nitrile group on 2-pymcn.

Bottom: X[Yb(C2O2)2] formed from the complete hydrolysis of 2-pymcn. ($X=NH_4^+$ or H_3O^+)

Publications supported by this project 2009-2011

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8. P. M. Cantos, M. Frisch, and C. L. Cahill (2010) "Synthesis, structure and fluorescence properties of a uranyl-2,5-pyridinedicarboxylic acid coordination polymer: The missing member of the UO22+-2,n-pyridinedicarboxylic series." Inorganic Chemistry Communications, 13(9), 1036-1039.
9. N. P. Deifel and C. L. Cahill (2009) "The uranyl tetrachloride anion as a tecton in the assembly of U(VI) hybrid materials.″ *CrystEngComm*, 11(12), 2739-2744.

Exploring the Redox and Oxo Substitution Chemistry of the Uranyl Ion: Implications for Separations and Environmental Remediation

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David D. Schnaars, Graduate Student
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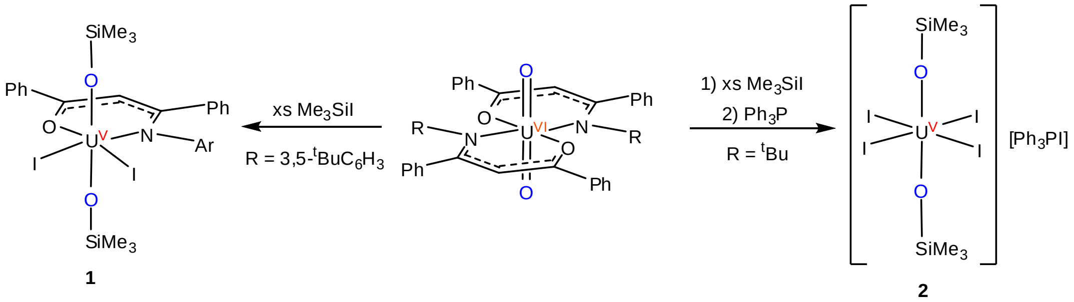
Overall research goals: Our proposed research program has two specific aims: (*i*) Understand the fundamental coordination chemistry of UO_2^+ ions; and (*ii*) Explore the redox conversion of uranyl and discover new transformations for oxo ligand functionalization and substitution.

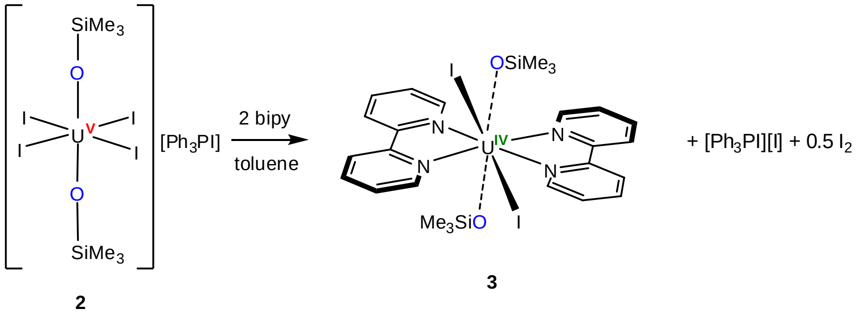
Significant achievements during 2010-2011: We are currently exploring the ability of the β-ketoiminate ligand platform (^{R}acnac = R*N*C(Ph)CHC(Ph)*O*) to both stabilize the reduced UO_2^+ ion and promote oxo functionalization in the parent uranyl ion, UO_2^{2+}. Gratifyingly, we have found that these strongly donating ligand platforms, in combination with electrophilic substrates, can promote a number of oxo functionalization reactions. For instance, reaction of $UO_2(^{Ar}acnac)_2$ (Ar = 3,5-$^tBu_2C_6H_3$) with Me_3SiI generates $(^{Ar}acnac)U(OSiMe_3)_2I_2$ (**1**) a pentavalent uranium silyloxide complex (Scheme 1). Ligand design likely plays a critical role in favoring this reactivity, as we believe the very strongly electron-donating β-ketoiminate ligands serve to weaken the U=O bond. We have also explored the reactivity of $UO_2(^{tBu}acnac)_2$ (^{tBu}acnac = ^{t}Bu*N*C(Ph)CHC(Ph)*O*) with Me_3SiI, in the presence of Ph_3P. This results in abstraction of both ^{tBu}acnac ligands and formation of $[Ph_3PI][U(OSiMe_3)_2I_4]$ (**2**). The different reaction outcome in this example is due to the bulky *tert*-butyl substituent on the ^{tBu}acnac ligand, which promotes the ligand abstraction step.

Scheme 1.



Interestingly, the reaction of **2** with various Lewis bases, such as 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen), results in *reduction* of uranium center and isolation of the U(IV) complexes $U(OSiMe_3)_2I_2(bipy)_2$ (**3**) and $U(OSiMe_3)_2I_2(phen)_2$ (**4**), respectively (Scheme 2).

Scheme 2.



Normally the uranyl ion is challenging to reduce to U(V) or U(IV); however, our results reveals that a rich redox chemistry can be accessed by silylation of the uranyl moiety. The observed redox chemistry appears to be "turned-on" by the oxo functionalization step, an observation which may have implications for the bio-remediation of uranyl in the environment and the remediation of uranyl in spent nuclear waste.

Science objectives for 2011-2013:

- Discover new electrophiles capable of activating the U=O bonds of the uranyl ion.
- Explore the ability of new multidentate ligands in stabilizing UO_2^+ and/or promoting oxo ligand reactivity.
- Develop ambiphilic ligands capable of simultaneously coordinating to the uranyl equatorial and the uranyl oxo ligands.

Publications supported by this project 2009-2011

1. Schnaars, D. D.; Wu, G.; Hayton, T. W. Borane-Mediated Reductive Silylation of the Uranyl Ion. Submitted to *JACS.*
2. Seaman, L. A.; Fortier, S.; Wu, G.; Hayton, T. W. Comparison of the Redox Chemistry of Primary and Secondary Amides of U(IV): Isolation of a U(VI) Bis(imido) Complex or a Homoleptic U(VI) Amido Complex. *Inorg. Chem.*, **2011**, *50*, 636–646.
3. Brown, J. L.; Wu, G.; Hayton, T. W. Oxo Ligand Silylation in a Uranyl beta-Ketoiminate Complex. *J. Am. Chem. Soc.* **2010**, *132*, 7248-7249.
4. Seaman, L. A.; Schnaars, D. D.; Wu, G.; Hayton, T. W. Isolation of a uranyl amide by "ate" complex formation. *Dalton Trans.* **2010**, *39*, 6635 - 6637.

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

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Current Collaborators: T. W. Hayton group (UCSB), E. R. Batista, S. A. Kozimor, I. May (LANL), R. T. Paine (UNM), F. Lewis (Reading, U.K.), N. Kaltsoyannis (UCL, U.K.), D. Shuh (LBNL).

Overall research goals: To develop transformative knowledge regarding transuranic coordination chemistry with a focus upon elucidating the extent to which covalent interactions are important with soft donor atom ligands, a property that has potential to be exploited in actinide separation technology for advanced nuclear fuel cycle and waste remediation strategies.

Significant achievements during project year one (April 2010 – April 2011): Efforts in year one have focused on synthetic pursuit and characterization of starting materials and molecules with a range of ligands to serve as a basis for more in-depth bonding analyses as the project progresses.

1. The synthesis, crystal structure and characterization of $Pu^{IV}I_2(^{Ar}acnac)_2$ (Figure 1), containing a β-ketoiminate mixed 'hard-soft' N, O donor ligand, afforded a rare opportunity to directly compare U(IV) to Pu(IV) bonding in a discrete molecular system (with Hayton, UCSB). Structural data revealed interesting discrepancies between the U(IV) and Pu(IV) bonding that are not adequately explained by ionic bonding and the actinide contraction alone. Initial DFT calculations (Batista, LANL) point towards metal-ligand orbital overlap differences between U(IV) and Pu(IV).

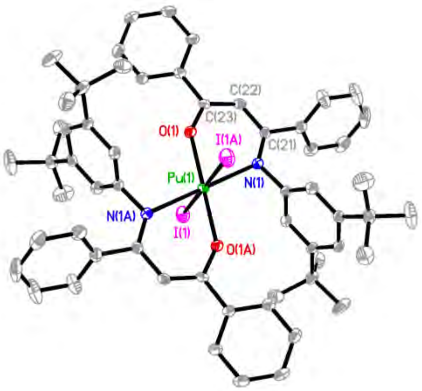

Figure 1. Thermal ellipsoid plot of the crystal structure of the $Pu^{IV}I_2(^{Ar}acnac)_2$ complex.

2. Synthetic routes have been developed to prepare Pu complexes with phosphine oxide/sulfide ligands (with Paine, UNM) and neutral polydentate nitrogen donor ligands (with Lewis ,Reading, UK) (Figure 2). Characterization of these extractant related complexes is underway.

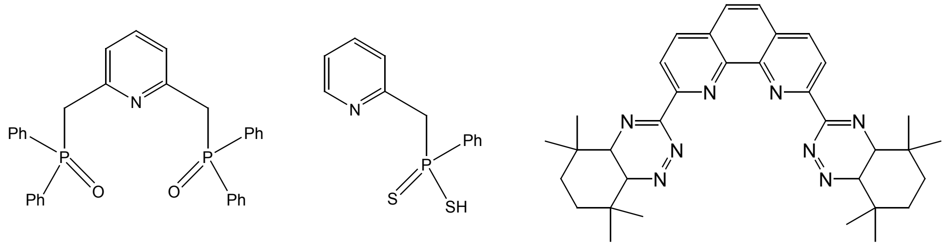

Figure 2. Ligands with O, N, and S donor atoms for transuranic coordination chemistry studies.

3. Understanding of plutonium speciation in nitric acid solutions is relevant to nuclear fuel cycles and also supports our efforts to develop new synthetic precursors from available stock solutions. We have utilized the crystal structure of the plutonyl(VI) dinitrate complex, along with solid state and solution spectroscopic data (vis-nIR and Raman) (Figure 3), to demonstrate that the dinitrate complex is not appreciably present in nitric acid, in contrast to what some have postulated. The $[PuO_2(NO_3)_2(H_2O)_2]\cdot H_2O$ solid itself may serve as a useful precursor for ligand reactivity studies.

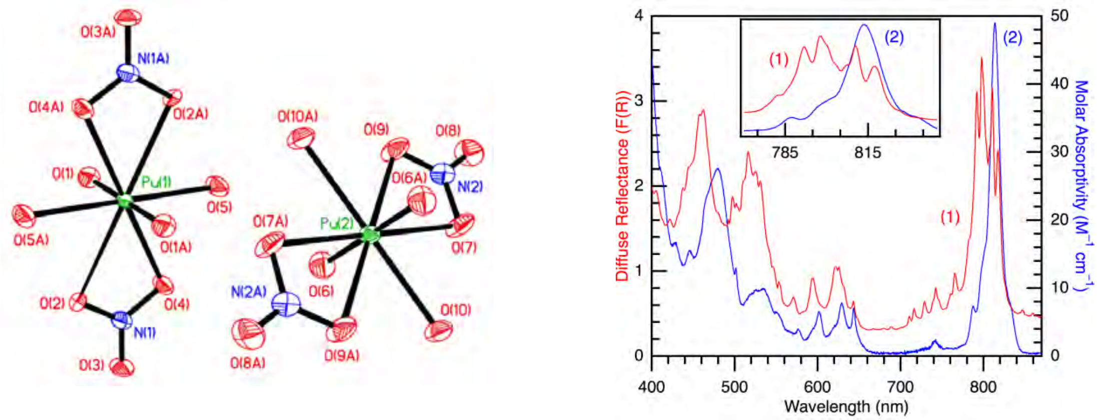

Figure 3. Crystal structure of $[PuO_2(NO_3)_2(H_2O)_2]\cdot H_2O$ (left); comparison of solid state vis-NIR of the dinitrate complex (red(1)) to Pu(VI) in 15.2 M HNO_3 (blue(2)) (both right).

Science objectives for 2011-2013:

- Complete isolation and characterization of transuranic complexes with phosphine oxides, sulfides, and polydentate N donor extractants to develop bonding trends across the An series.
- Begin to synthesize and characterize a suite of chalcogen S, Se, Te donor complexes with Np and Pu, and compare bonding to U and Ln complexes to elucidate bonding differences.
- Prepare samples for ligand K-edge X-ray absorption spectroscopic measurements at synchrotron facilities and acquire data through collaborations with Kozimor (LANL) and Shuh (LBL).
- Collaborate with theoretical colleagues, Batista (LANL) and Kaltsoyannis (UCL, UK), to model the electronic structure and bonding of the structurally characterized molecules.

Publications receiving any support from this project in year one (April 2010 – April 2011)

1. 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-ketoiminate N,O donor ligand: an experimental and theoretical bonding comparison'* manuscript in preparation to be submitted to *Chemical Communications* in early **2011**.

2. A.J. Gaunt, I. May, M.P. Neu, S.D. Reilly B.L. Scott, *'Structural and Spectroscopic Characterization of Plutonyl Nitrate Under Acidic Conditions'* manuscript to be submitted to *Inorganic Chemistry* in early **2011**.

3. A.J. Gaunt, M.P. Neu, *Recent developments in nonaqueous plutonium coordination chemistry'*, *Comptes Rendus Chemie*, **2010**, *13*, 821-831 (invited contribution to a special f-element themed issue).

Session 4 – Actinides

Energy Frontier Research Center: Materials Science of Actinides

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The mission of the Materials Science of Actinides EFRC is to create the the foundation of knowledge in actinide materials needed for an advanced nuclear energy system. This EFRC brings experimentalists, computationalists, and theorists to bear on three major research themes (Figure 1):

(1) Complex actinide materials. This theme focuses on chemical and structural complexity in a broad range of actinide materials that include potential nuclear fuels and waste forms.
(2) Nanoscale control of actinides. The focus of this theme is creation of nano-scale actinide materials with well-defined structures and potential applications.
(3) Actinide materials in extreme environments. The behaviro of materials such as those under study in themes (1) and (2) under extremes in temperature, pressure, and radiation field, as well as coupled effects.

Themes (1) and (3) will be highlighted in posters. I will discuss progress in theme (2) in this presentation.

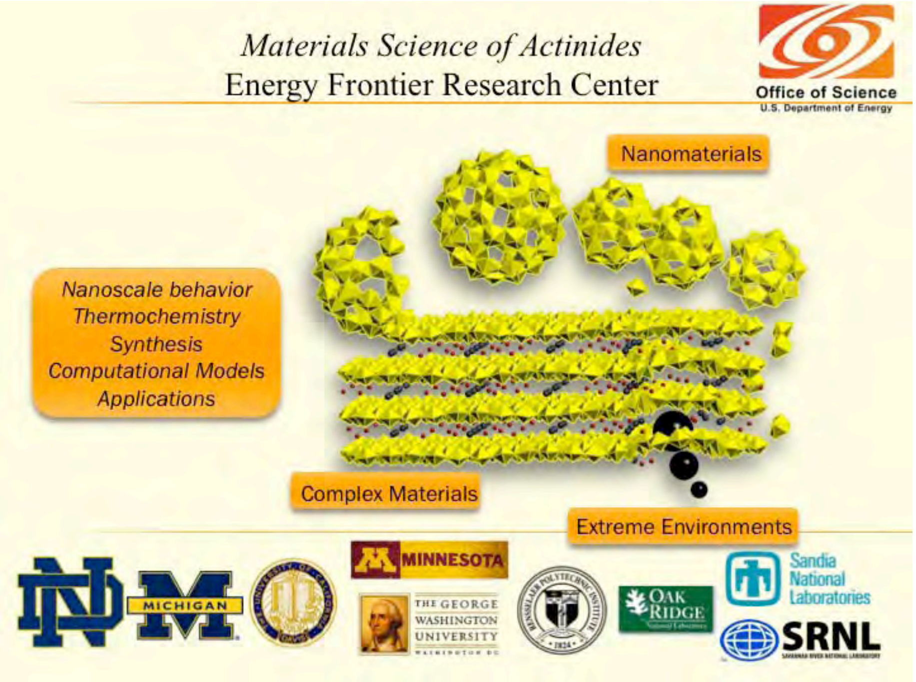

Figure 1. An overview of the EFRC Materials Science of Actinides, including theme areas and participating institutions.

Taking advantage of curvature created in structures by the uranyl-peroxide-uranyl bridge, more than 50 nano-scale clusters built from uranyl polyhedra have been synthesized and structurally characterized. These clusters self-assemble in aqueous solution under ambient conditions. Under alkaline conditions, clusters that form consist only of uranyl polyhedra with bridges corresponding to peroxide groups or polyhedral edges defined by two hydroxyl groups. Replacing hydroxyl bridges with pyrophosphate or oxalate bridges facilitates formation of complex clusters under acidic conditions as well.

Ongoing studies of clusters of uranyl polyhedra in aqueous solution using small-angle X-ray scattering (SAXS) and electrospray ionization mass spectroscopy (ESI-MS) are providing insights into the behavior of these clusters over time. Under relatively dilute conditions, clusters of U_{60} and U_{24} remain intact for at least 70 days after dissolution in ultrapure water. However, studies of mother solutions indicate polydispersity in most cases, and that growing crystals are highly selective in which clusters are incorporated.

Given the persistance of clusters built from uranyl polyhedra in solution, the relative ease of their formation, and their high masses, applications of such clusters in the separation of uranium from complex solutions is an attractive possibility that is under active examination.

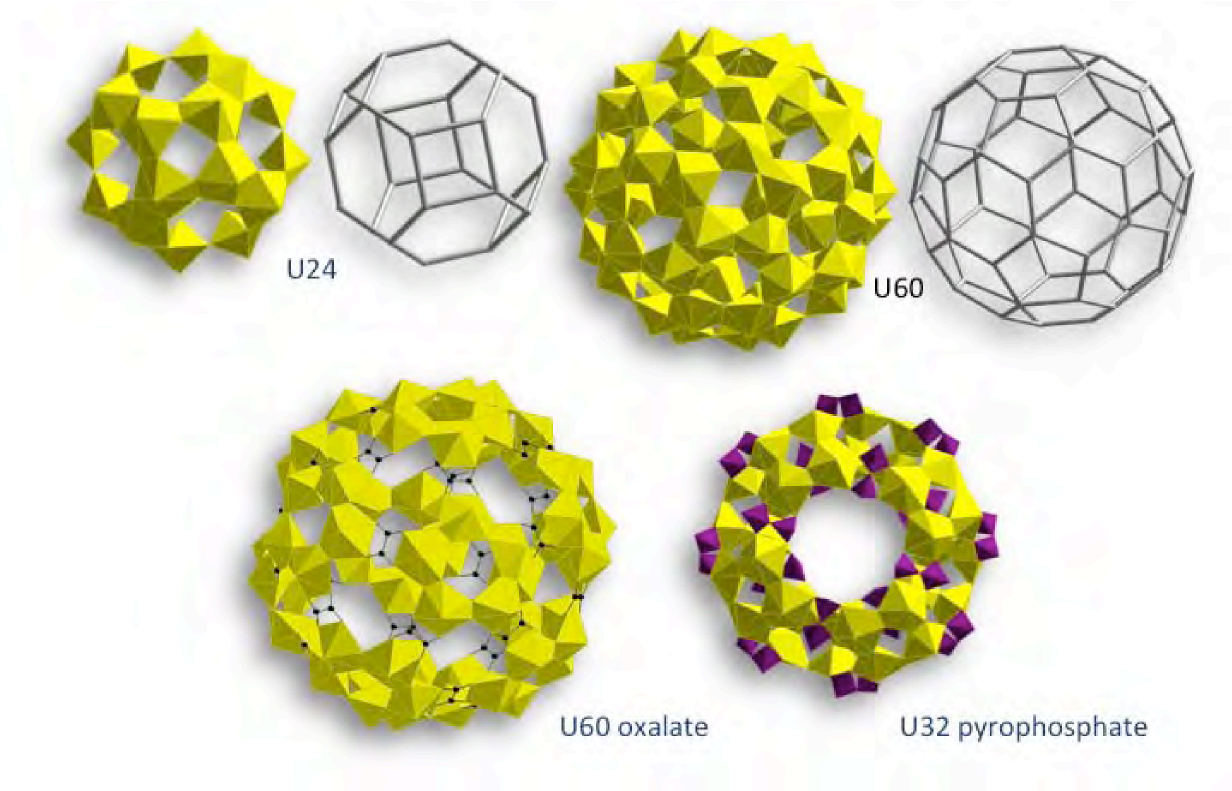

Figure 2. Examples of clusters containing uranyl polyhedra (yellow), oxalate groups (black balls and sticks), and pyrophosphate groups (purple).

Structural, and Chemical Properties of Lower Valent Actinide Complexes

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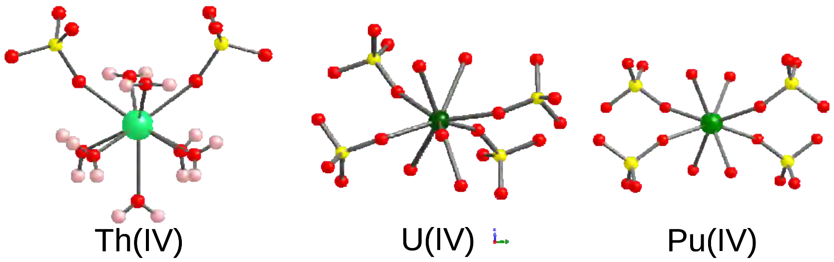
C. L. Cahill, The George Washington University, Department of Chemistry.

Overall research goals: The goal of this research is to understand the role that the periodicity imposed by the actinide contraction and the periodic effects within ligand systems has on the resulting chemical and structural properties of the actinide elements and their compounds. Our research focuses on the structural chemistry of lower-valent actinide ions in the solid state. Building on a periodic approach, a hierarchy of these complexes is sought that extends through the aqua complexes of the ions to coordination complexes with inorganic ligands.

Significant achievements during 2009-2011: Synthetic efforts in the study of actinide ions, Th to Pu, have provided significant new insight into the chemical properties of actinide inorganic complexes, their relationship across the actinide series and within the Periodic Table.

Specifically, complexes of the lower valent actinides with oxo-acid ligands and the halides have been and are currently being explored. Significant structural variety within these complexes both across the actinide series and within the Periodic Table has been noted. Across the actinide series an isostructural trend was expected within these ligand systems as observed for the binary oxides and other simple ligand systems. This was not observed to be the case. Instead significant structural variety has been observed including variations in coordination geometry, stoichiometry, and hydration state.



In addition to the studies on the solid-state complexes, investigations into the solution structural and chemical properties in these systems have been undertaken exploiting high-energy X-ray scattering and classical electrochemical methods. The goal of these experiments is to correlate the solution chemical behavior and structure to that observed in the solid-state, and at Pu, where an accessible III-IV redox couple exists, relative energy differences between these complexes have been measured.

Science objectives for 2011-2013:

- Extend our studies of lower-valent actinide inorganic complexes from Th to Am through the pnictide and chalcogenide oxo-acid systems and the halides.
- Attempt to develop an isomorphous series of actinide complexes within a ligand system for spectroscopic and electrochemical studies to probe the effects of chemical periodicity in the early 5f elements.

Publications supported by this project 2009-2011

1. R. E. Wilson. *Plutonium(IV) Sulfates*. *Inorganic Chemistry*. article. submitted. 2011.

2. R. E. Wilson, S. Skanthakumar, C. L. Cahill, and L. Soderholm. *Structural studies coupling X-ray diffraction and high-energy X-ray scattering in the* UO_2^{2+}- HBr_{aq} *system.* *Inorganic Chemistry*. article submitted, 2011.

3. K. E. Knope, R. E. Wilson, S. Skanthakumar, L. Soderholm. *Synthesis and Characterization of Th(IV) Sulfate..* *Inorganic Chemistry*. submitted 2011.

4. Soderholm, L.; Skanthakumar, S.; Wilson, R.E.; *Structural correspondence between uranyl chloride complexes in solution and their stability constants, J. Phys. Chem. A.* (in the press).

5. L. Soderholm, S. Skanthakumar, R. E. Wilson. *Structures and Energetics of Erbium Chloride Complexes in Aqueous Solution*. *Journal of Physical Chemistry, A.* 113(22), 6391-6397, (2009).

Actinide Incorporation and Radiation Effects in Layered-Structures

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OVERALL RESEARCH GOALS

1. ***Develop a fundamental understanding of the interactions between actinides and layered-structures, mainly uranyl phases and sheet silicates.***
2. ***Evaluate the energetics of the incorporation of actinides into layered-structures.***
3. ***Evaluate the role of different surfaces on the energetics of sorption of actinides onto layered-structures.***
4. ***Determine the structural and composition controls of layered-structures on the effects radiation damage and annealing that result from ionizing radiation.***

RESEARCH STRATEGY

This research program on actinide incorporation and sorption into layered-structures is based on four different strategies: *i.*) experimental studies in which synthetic compounds are doped with a variety of actinides; *ii.*) computational studies of the incorporation and sorption mechanisms of actinides; *iii.*) studies of naturally occurring actinide phases to understand incorporation and sorption mechanisms in complex geochemical environments; *iv.*) studies of radiation effects due to alpha-decay of actinides, utilizing electron and ion beam irradiations of synthetic and natural materials.

Np-incorporation into uranyl phases

Radionuclide incorporation into the alteration products of corroded UO_2 in spent nuclear fuel may control the release and mobility of radionuclides. Studtite, $[UO_2(O_2)(H_2O)_2](H_2O)_2$, is expected to form in the presence of peroxide produced by α-radiolysis of water in contact with the spent fuel. Experiments have indicated that the studtite structure can incorporate Np; however, due to the low concentrations in the solid (6500 ppm), the incorporation mechanism could not be determined. In this study, density functional theory is used to calculate an optimized structure, determine the electronic density of states, and calculate the energetics of the incorporation of Np^{6+} *vs*. $Np^{5+} + H^+$ into the studtite structure. The definition of the source and the final incorporation phase for the cations involved in the incorporation process greatly affects the final incorporation energy. Using hexafluorine reference phases (NpF_6/UF_6) results in negative incorporation energies (-1.42 eV and -1.36 eV for Np^{6+} and Np^{5+} incorporation, respectively), while using binary oxide reference phases (Np_2O_5/UO_3) results in positive incorporation energies (0.96 eV and 1.02 eV for Np^{6+} and Np^{5+} incorporation, respectively). In addition, Np^{6+} incorporation into studtite is energetically more favorable than Np^{5+}-incorporation as assessed from the lower incorporation energy. Estimates of the solid-solution behavior from a combination of quantum-mechanical calculations and Monte-Carlo simulation indicate that the Np^{6+}- and U^{6+}-studtite solid solution is completely miscible at room temperature provided that there is an Np^{6+}-studtite structure. Knowledge of the electronic structure provides insight into Np-bonding in the studtite structure. The fact that Np 5f orbitals are within the bandgap of studtite results in the narrow band gap of Np-incorporated studtite (1.09 eV) as compared with the band gap of studtite alone (2.29 eV).

Heterogeneous electron transfer of U(IV)-U(VI) on sorbed surfaces: Energetics and kinetics

Reduction of aqueous U(VI) species results in the precipitation of insoluble uranium phases which reduces its mobility in natural waters. In most cases, U(VI) reduction is kinetically inhibited unless a mineral surface or bacteria is present to catalyze the reaction. The role of mineral surface in catalyzing this reaction is poorly understood. There are a number of reasons for this: 1) these processes almost always involve a complex series of elementary reactions, each involving the transfer of one electron at a time, 2) it can be unwieldy to resolve the influence of individual environmental parameters in rate experiments (e.g., pH, pe, pO_2, concentration of other oxidants and reductants, other ions in solution, temperature, etc.), 3) it is challenging to differentiate rate constants for heterogeneous (surface) processes and homogeneous (solution) processes in order to assess the catalytic effects of the surface itself, and 4) rate-limiting processes such as electron spin transitions have been widely ignored thus far. Our mineral surface group has developed an innovative electrochemical-based approach to address these challenges.

An electrochemical testing station has been constructed to evaluate U(VI) reduction (energetic and kinetics) on environmentally-important semiconducting minerals. Cyclic voltammetry using a powder microelectrode (PME) has been developed specifically to evaluate U(VI) reduction rates on pyrite (FeS_2), hematite (Fe_2O_3) and galena (PbS) under controlled conditions. PME enables rapid evaluation of redox kinetics and eliminates much of the variability inherent in electrochemical experiments using conventional electrodes fabricated from minerals. It should be noted that PME has not traditionally been applied to study environmental reactions, and demonstration of its advantages (e.g., electrochemical stability and rapid evaluation) in this study will provide the community with a new technique for evaluating other actinide-mineral reactions.

The voltammetric redox peaks of pyrite and hematite have been characterized by PME at pH 4 and pH 8 and the results are in agreement with redox peaks obtained using conventional electrodes. Pyrite lacks redox peaks between -0.6 and +0.5 V (vs Ag/AgCl). The initial results of our study show a voltammetric peak associated with the reduction/oxidation of U(VI) ↔U(V) on pyrite at ~-0.22 V (vs Ag/AgCl). This peak clearly falls within the flat electrochemical window for pyrite and is dependent on the concentration of U(VI) in solution. This is the first time that the peak for U(VI) reduction on pyrite has been shown. Scan rate profiles for the U(VI) /U(V) redox couple have been obtained that will be used to determine kinetic parameters for reduction. Hematite shows a flat voltammetric profile that extends to ~-0.75 V (vs Ag/AgCl) before reduction of Fe(III) on the surface. Hematite voltammetry shows no peak that could be attributed to the U(VI) /U(V) redox couple. However, after a conditioning step (i.e. the hematite electrode is held at sufficiently cathodic potentials to initiate the reduction of Fe(III) on the surface), a small U(VI) reduction peak appears at approximately the same potential as on pyrite. This result suggests that Fe(II) on the surface may be responsible for reduction of U(VI).

Future Research Directions

Once the electrochemical properties of the mineral powders exposed to U(VI) have been characterized by PME, the next step will be to visualize redox processes as they occur on primary cleavage or growth surfaces of sheet-structures. These processes will be directly imaged in electrolyte *(in situ)* using electrochemical scanning atomic force microscopy (AFM). X-ray photoelectron spectroscopy (XPS) will be employed evaluate the chemistry and oxidation state of redox product phases formed on the mineral surface.

During this next fiscal year we will continue with a combination of experimental and computational studies. However, we have initiated some new and innovative electrochemical studies as described in the previous section. Future calculations will focus on actinide sorption onto Fe-oxide surfaces.

Recent Publications

Ewing, R.C., Runde, W., Albrecht-Schmitt, T.E. (2010) Environmental impact of the nuclear fuel cycle: Fate of actinides. *MRS Bulletin*, 35, 859-866.

Shuller, L.C., Ewing, R.C., Becker, U (2010) Quantum-mechanical evaluation of Np-incorporation into studitite. *American Mineralogist*, 95, 1151-1160.

Shuller, L.C., Ewing, R.C. Becker, U (in revision) A quantum-mechanical approach for the evaluation of Np-incorporation into uranyl phases. *Journal of Nuclear Materials*.

Actinide/Lanthanide Luminescence and Actinide Sequestration

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Christopher M. Andolina and Chengbao Ni, Postdoctoral Fellows
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Collaborators: Gilles Muller (San Jose State University)

Overall Research Goals: To explore 4f and 5f electronic structure through sensitized actinide and lanthanide luminescence. In addition, we will continue development of ligands for sequestration of actinides and assess the structure and stability of these complexes.

Significant achievements during 2009-2011

- Preliminary data has shown that several 1-hydroxypyridin-2-one (1,2-HOPO) and 2-hydroxyisophthalamide (IAM)-based ligands can sensitize Cm(III). Preliminary quantum yields range from 20% (IAM) up to 65% (1,2-HOPO).
- A chiral IAM-based ligand has been used to sensitize circularly polarized luminescence from Cm(III), representing the first actinide CPL measurement ($g_{lum} = +0.048$ at 611 nm).
- The DOE funded dye laser has been successfully installed and has enabled measurements of luminescent lifetimes of near-IR emitters.
- We have developed a series of tetradentate mixed ligands incorporating both TAM and HOPO binding units for dioxo-U(VI) sequestration. Similar CAMC (CAM-carboxylate)-HOPO mixed ligands, and pentadentate bis-HOPO ligands with IAM linkers have also been synthesized. The ligands were complexed with uranyl, and many were characterized by X-ray diffraction.
- Series of novel linear, tetradentate bis-TAM ligands were synthesized and complexed with uranyl, and the complex with 5LIO-MeTAM was characterized by X-ray diffraction. Analogous aromatic bis-TAM ligands were complexed with Ce(IV), and the structural characterization provided insight in to the relationship between backbone structure coordination geometry.
- Macrocyclic, octadentate, TREN-based ligands with four TAM binding moieties were synthesized for the sequestration of the Th(IV). A Th(IV) complex was structurally characterized, and the kinetics of association of these ligands with Th(IV) in aqueous solution was studied by UV-Vis spectroscopy.
- X-ray crystal structures of the first Ce(IV) complex with an octadentate ligand (H(2,2)-1,2-HOPO) and of Ce(IV), Th(IV), and U(IV) with the tetradentate 5LIO-MeTAM were obtained, and were useful models in studying the coordination chemistry of Pu(IV).
- New ligands incorporating IAM and HOPO units linked by backbones similar to those in the aforementioned ligands were synthesized and led to Ln(III) coordination complexes. These complexes are useful models for the structural characteristics of An(III) complexes, and their luminescent properties were investigated.

Science objectives for 2011-2013

- Linear and non-linear multidentate ligands based on the hydroxypyridinonate (HOPO) and terephthalamide (TAM) binding moieties will be targeted for the complexation of Ce(IV), Th(IV), dioxo-U(IV), U(VI), U(VI), Pu(IV) and other actinide ions.
- The coordination behavior of these complexes will be studied by spectroscopy and structural characterization in the solid state (X-ray diffraction). They will also be studied in the solution state (spectrophotometric/potentionmetric titrations) to evaluate the binding affinities of the ligands. The electrochemistry of U(IV) and Pu(IV) with these ligand systems will be explored.
- The synthesis and structural characterization of uranyl complexes will be pursued with novel and existing tetra-, penta-, hexa-, and octadentate ligands. Their solution behavior will be studied.

- Macrocyclic, octadentate, water-soluble ligands will be developed for Th(IV) complexation, and the solution thermodynamics and sequestering affinities of these ligands will be studied.
- Actinide complexes prepared with existing ligands, as well as existing complexes, will be similarly investigated. As well as luminescence studies on existing and novel Ln(III) complexes with analogous HOPO and hydroxyisophthalamide (IAM) ligands will be extended.
- Additional octadentate ligands with chiral backbones will be synthesized to achieve stronger CPL signals for Cm(III) and Am(III), in order to develop this technique further for the actinides.
- Ligands that are known to crystallize well with Ln(III)s will be used to grow X-ray quality crystals with Am(III) and Cm(III) and will be solved using the Advanced Light Source at LBNL.

Publications supported by this project 2009-2011

1.) Abergel, R., Durbin, P. W., Kullgren, B. R., Ebbe, S., Xu, J., Chang, P., Bunin, D. I., Blakely, E. A., Bjornstad, K. A., Rosen, C. J., Shuh, D. K., Raymond, K. N. “Biomimetic Actinide Chelators: An Update on the Preclinical Development of the Orally Active Hydroxypyridonate Decorporation Agents 3,4,3-LI(1,2-HOPO) and 5-LIO(Me-3,2-HOPO),” *Health Physics* **2010**, *99*, 401-407.

2.) Szigethy, G., and Raymond, K. N., “Influence of Linker Geometry on Uranyl Complexation by Rigidly Linked Bis(3-hydroxy-N-methyl-pyridin-2-one),” *Inorg. Chem.* **2010**, *49*, 6755–6765.

3.) Szigethy, G. and Raymond, K. N., “The Influence of the Linker Geometry in Bis(3-hydroxy-N-methyl-pyridin-2-one) Ligands on Solution-Phase Uranyl Affinity,” *Chem. Eur. J.* **2010**, online.

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7.) Moore, E. G., Xu, J., Jocher, C. J., Corneillie, T. M., and Raymond, K. N., “Eu(III) Complexes of Functionalized Octadentate 1-Hydroxypyridin-2-ones: Stability, Bioconjugation, and Luminescence Resonance Energy Transfer Studies,” *Inorg. Chem.* **2010,** *49*, 9928–9939.

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9.) Samuel, A. P. S., Xu, J., Raymond, K. N., “Predicting Efficient Antenna Ligands for Tb(III) Emission,” *Inorg. Chem.* **2009**, *48*, 687-698.

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13.) D'Aléo, A., Moore, E. G., Szigethy, G., Xu, J., Raymond, K. N., “Aryl Bridged 1-Hydroxypyridin-2-one: Effect of the Bridge on the Eu(III) Sensitization Process,” *Inorg. Chem.* **2009**, *48*, 9316-9324.

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Session P1 – Poster Session 1

Synthesis and Structural Characterization of Heterometallic Actinide Nanoclusters

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Overall research goals: The major goal of the Forbes research group is to determine the structures, stabilities, and fates of heterometallic actinide nanoclusters present in aqueous systems. Applications include: 1) development of clusters as geochemical model compounds for colloidal-assisted transport of actinides in natural aqueous systems and 2) novel pre-concentration methodology for separations and environmental remediation.

Science objectives for 2011-2013:

- Synthesis and structural characterization of (Th, U)/Fe and (Th, U)/Al oxyhydroxide nanoclusters.
- High-energy X-ray scattering studies of actinide-bearing aqueous solutions and amorphous/poorly crystalline solids
- Adsorption and aggregation experiments of soluble heterometallic actinide nanoclusters.

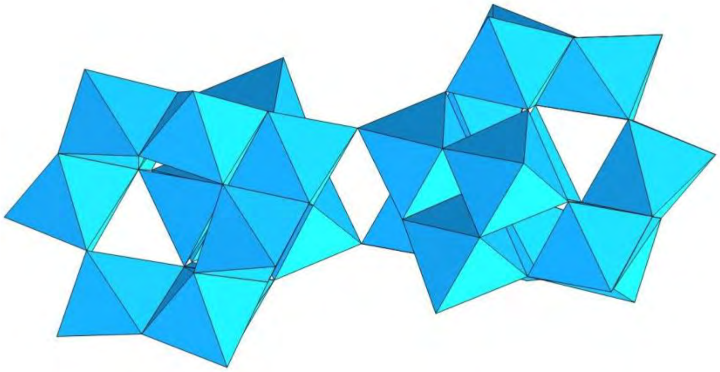

Figure 1.A new aluminum hydroxide Keggin-type nanocluster $[(AlO_4)Al_{12}(\mu\text{-}OH)_{25}(H_2O)_{10})]_2^{12+}$ was recently synthesized in the Forbes research group and will serve as a starting point for future heterometallic actinide clusters.

Recent Publications

1. Forbes, T.Z., D. McInnis, P. Horan, T. Devine, and P.C. Burns. "Alteration of secondary uranyl mineral analogues in the presence of hydrogen peroxide." (2011) *American Mineralogist* 96(1) 202-206
2. Forbes, T.Z., M. Nyman, M.A. Rodriguiz, and A. Navrotsky. "Energetics of Lanthanum Tantalate Materials." (2010) *Journal of Solid State Chemistry* 183(11) 2516-2521.
3. Radha, A. V., T.Z. Forbes, C. Killian, P.U.P.A. Gilbert, and A. Navrotsky. "Crystallization Enthalpies of Synthetic and Biogenic Amorphous Calcium Carbonate." *Proceedings of the National Academy of Sciences* (2010) 107(38) 16438-16443.
4. Forbes, T.Z., and S.C. Sevov. "Metal-Organic Frameworks with Direct Transition Metal-Sulfonate Interactions and Charge-Assisted Hydrogen Bonds." *Inorganic Chemistry (*2009*)* 48(14) 6873-6878.
5. Forbes, T.Z. and P.C. Burns "Synthesis, structure, and spectroscopy of $(NpO_2)_2(SO_4)(H_2O)_4$: prevalence of cation-cation interactions and cationic nets in neptunyl sulfate compounds." *Journal of Solid State Chemistry* (2009) 182(1) 43-48.

C-H Activation Reactions by Uranium Alkyl Complexes

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Overall research goals: The objective of this project is to study C-H activation reactions specific to uranium alkyl complexes supported by ferrocene diamide ligands. Specifically, the reactivity of these uranium complexes with aromatic heterocycles is investigated.

Significant achievements during 2009-2011: To date, we have explored the reactions of aromatic N-heterocycles with $(NN^{fc})U(CH_2Ph)_2$ (NN^{fc} = 1,1'- $fc(NSi^tBuMe_2)_2$). Two significant results have emerged:

1. The C−C coupling event between the two imidazole rings in a previously isolated uranium benzimidazole complex, $\mathbf{3^{mbi}}$, was found to be reversible (Figure 1). This finding was supported by single-crystal and powder X-ray diffraction, ^{1}H and ^{2}H variable-temperature NMR spectroscopy, and DFT calculations. Reversible bond formation has been invoked as the basis for developing switchable molecular systems, and C−C bonds of heterocycles have been recently identified as a fruitful area for exploration. In general, such systems switch between two states in response to an external stimulus. The two states coexist in solution for $\mathbf{3^{mbi}}$. The uranium system is a rare example of reversible bond formation that involves organometallic complexes and that work was highlighted by being chosen as the cover for the June 9, 2010 issue of the *Journal of American Chemical Society* (see figure to the right).

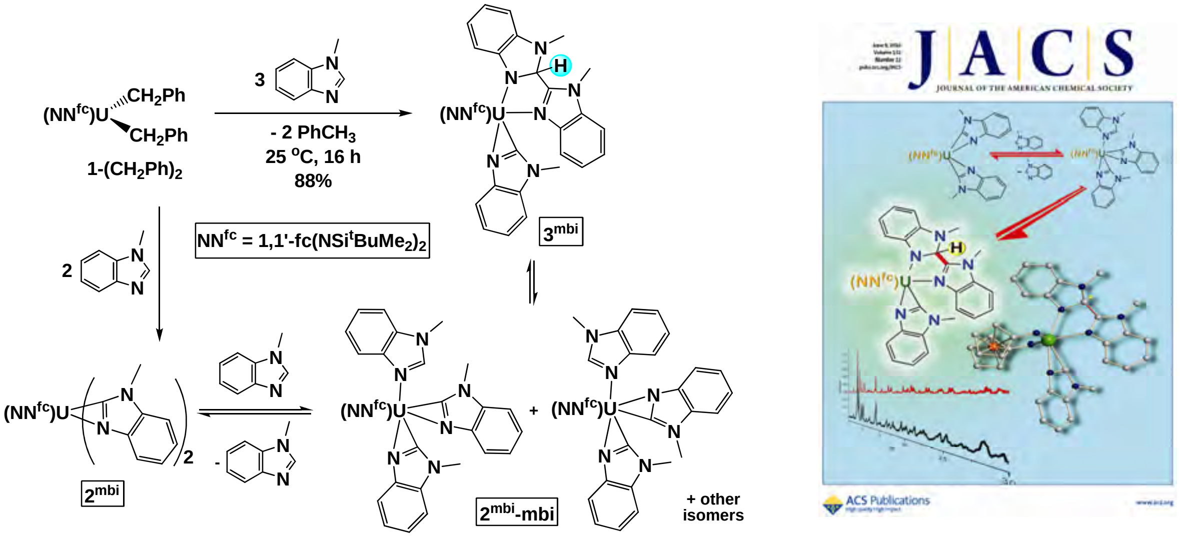

Figure 1. Proposed solution equilibria for $\mathbf{3^{mbi}}$ (left) and (cover for the June 9, 2010 issue of the *Journal of American Chemical Society*).

We have been investigating uranium complexes supported by 1,1'-ferrocene diamide ligands as an alternative to the widely studied metallocene complexes. The change to diamide ligands allows the stabilization of more electrophilic metal centers than those in metallocenes. This characteristic becomes important in the reactions with aromatic N-heterocycles, which tend to be strong Lewis bases and shut down further reactivity at the metal center.

2. A toluene-bridged diuranium complex reduced quinoxaline and formed a molecular quadrangle with uranium(IV) vertices and reduced quinoxaline as edges.

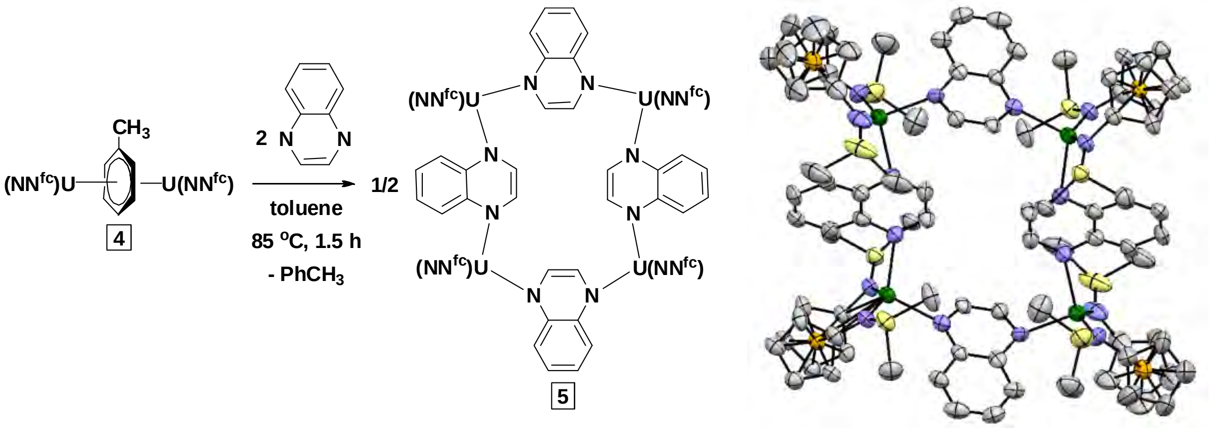

Figure 2. Molecular quadrangle formation from a diuranium μ-η^6,η^6-toluene complex.

Treatment of a ferrocene diamide uranium(IV) diiodide complex with excess potassium graphite led to the formation of a μ-η^6,η^6-toluene complex. This complex provided a convenient synthetic entry point into uranium multinuclear macrocyclic chemistry: when treated with an aromatic N-heterocycle, it lost the bridging toluene, reduced the substrate, and formed a rare uranium(IV) molecular quadrangle. The reduced nature of the bridging ligand in conjunction with the multiple uranium and iron components of this compound make it an interesting prospect for electronic and magnetic studies.

Science objectives for 2011-2013:

- Understand the electronic communication between iron and uranium in ferrocene complexes in order to develop new catalytic systems and reactivity.
- Prepare macrocycles with different linking molecules and determine the level of electronic and magnetic communication in the new family of self-assembled compounds.

Publications supported by this project 2009-2011

1. **d^0f^n-Metal Complexes Supported by Ferrocene-Based Chelating Ligands.** Diaconescu, Paula L. *Comments Inorg. Chem.* **2010**, *31*(5-6), 196 – 241.
2. **Ring Opening of Aromatic Heterocycles with Uranium Alkyl Complexes.** Duhović, Selma; Monreal, Marisa J.; Diaconescu, Paula L. *J. Organomet. Chem.* **2010**, *695*(25), 2822-2826.
3. **Reactions of Aromatic N-Heterocycles with d^0f^n-Metal Alkyl Complexes Supported by Chelating-Diamide Ligands**. Diaconescu, Paula L. *Acc. Chem. Res.* **2010**, *43*(10), 1352-1363.
4. **Reactions of Aromatic Heterocycles with Uranium Alkyl Complexes**. Duhović, Selma; Monreal, Marisa J.; Diaconescu, Paula L. *Inorg. Chem.* **2010**, *49*(15), 7165–7169.
5. **Inter- and Intramolecular Hydroamination with a Uranium Dialkyl Precursor**. Broderick, Erin M.; Gutzwiller, Nathaniel P.; Diaconescu, Paula L. *Organometallics* **2010**, *29*(15), 3242–3251.
6. **In situ Generation of Uranium Alkyl Complexes**. Duhović, Selma; Khan, Saeed; Diaconescu, Paula L. *Chem. Commun.* **2010**, *46*(19), 3390-3392.
7. **Reversible C−C Coupling in a Uranium Biheterocyclic Complex**. Monreal, Marisa J.; Diaconescu, Paula L. *J. Am. Chem. Soc.* **2010**, *132*(22), 7676-7683.
8. **Beyond C−H Activation with Uranium: Imidazole Ring-Opening Mediated by a Uranium Dialkyl Complex**. Monreal, Marisa J.; Khan, S.; Diaconescu, Paula L. *Angew. Chem. Int. Ed.* **2009**, *48*(44), 8352-8355.

Electronic Interactions in Actinyl Compounds: Analysis and Simulation of Optical Spectra

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Overall research goals: We seek a fundamental understanding of electronic interactions of actinides in complexes and compounds. Spectroscopic experiments and theoretical analysis and modeling are conducted for achieving a quantitative correlation between electronic interactions and chemical properties.

Significant achievements during 2009-2011: We have developed a framework to calculate the absorption and luminescence spectra of uranyl- and neptunyl-compounds, thus, are able to explain the intricate actinyl electronic and vibronic interactions in detail. Information such as metal-ligand bond length for different states and in different coordination geometries is obtained along with the energy levels of electronic state and vibration modes. First, electronic energy levels for uranyl in several tetrachloride compounds were calculated using a model Hamiltonian established in combination of molecular orbital theory with crystal filed theory:

$$\mathscr{H} = \mathscr{H}\left(\text{Axial field}\right) + \mathscr{H}\left(\text{Coulomb \& Exchange}\right) + \mathscr{H}\left(\text{Spin-Orbit}\right) + \mathscr{H}\left(\text{Crystal Field}\right)$$

The calculated energy levels agree generally with recent *ab initio* calculations in ordering but are much closer to those observed in experiments. Based on the electronic energy levels, transition intensities and vibronic coupling to various vibration modes were further calculated

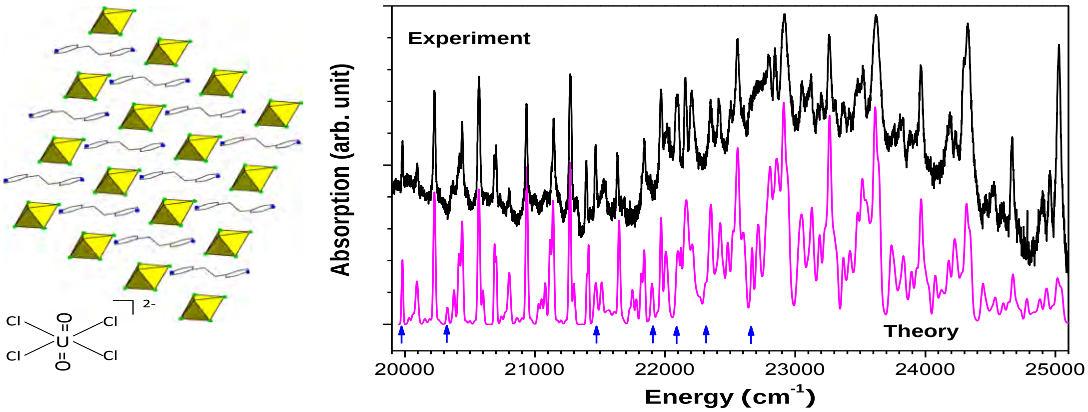

Fig.1 Comparison between theoretically calculated and experimental absorption spectrum of $[UO_2Cl_4](C_{12}H_{12}N_2)$ at 4 K. Multiple vibronic lines progress in the frequency of O-U-O symmetric stretching mode. Electronic energy levels (zero-phonon lines) are marked by the vertical arrows.

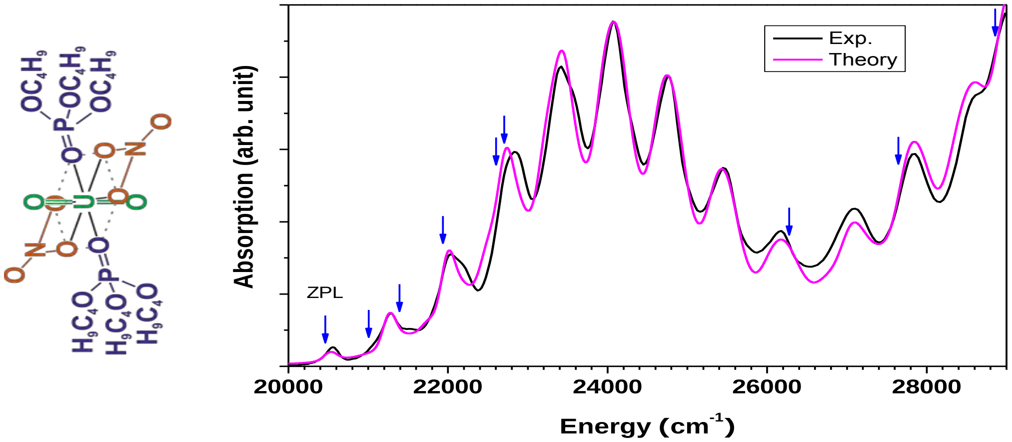

Fig.2 Theoretical simulation of the absorption spectrum of $UO_2(NO_3)_2(TBP)_2$ in solution at room temperature. Multiple vibronic lines progress in the energy of O-U-O symmetric stretching mode. Electronic energy levels (zero-phonon lines) are marked by the vertical arrows.

by using a modified Huang-Rhys theory for vibronic interactions. This theory was used previously for elucidating the progression of uranyl luminescence. Our work was, for the first time, to simulate absorption spectra of uranyl in compound and solution to extract more information. Fig. 1 and Fig. 2 compare between the calculated and experimental spectra for a crystalline compound of $[UO_2Cl_4](C_{12}H_{12}N_2)$ and for $UO_2(NO_3)_2(TBP)_2$ in solution.

Science objectives for 2011-2013

Experimental investigation and theoretical modeling will be extended to neptunium compounds in which the behavior of neptunyl is much less understood. In comparison with UO_2^{2+}, NpO_2^{2+} and NpO_2^{1+} have more complicated electronic structures. We have to deal with charge transfer transitions coupled to 5f-5f transitions. Moreover, as previously observed, cation-cation interaction (CCI) arising from two coupled neptunyl centers significantly affects coordination geometry and magnetic properties. We plan to tackle CCI in neptunyl compounds with our approach from modeling optical spectra. Our hypothesis is that, through modeling of optical spectra of systems with and without CCI, the mechanisms of CCI would be revealed, and the information resulted from the modeling will be useful for interpreting various effects, including the dynamics of magnetic ordering induced by CCI in neptunyl compounds.

Publications supported by this project 2009-2011

1. W. Wang, G. K. Liu, M. G. Brik, L. Seijo, and D. Shi, “5f-6d orbital hybridization of trivalent uranium in crystals of hexagonal symmetry: effects on electronic energy levels and transition intensities”, Phys. Rev. B 80, 155120-12(2009).
2. Y. X. Pan, W. Wang, G. K. Liu, S. Skanthakumar, “Correlation between structure variation and luminescence red shift in YAG:Ce”, J. Alloy Comp. J. Alloys and Comp. 488, 638–642(2009).
3. G. K. Liu, and M. P. Jensen, “Theoretical analysis of optical spectra of uranyl in complexes”, Chem. Phys. Letts. 499, 178–181(2010).
4. Guokui Liu, Nicholas P. Deifel, and Christopher L. Cahill, “Analysis and simulation of charge transfer vibronic transitions in tetrachloride uranyl compounds”, in preparation for JACS.

Principles of Chemical Recognition and Transport in Extractive Separations

Calix[4]pyrrole derivatives: Simple dual host or ion-pair receptor? Thermodynamic study of anion selectivity in cesium salt extraction

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Overall research goals: The objective of this project 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 focus of this research is to determine the contribution of the coulombic or ion-pairing interactions to the selectivity of anion receptors, and to determine how can these effects be harnessed in corporation with the other donor interactions.

Significant achievements during 2009-2011:
Questions about selectivity, nature of extraction mechanism, and binding strength of a receptor for both the cation and the anion of interest are being investigated using an extraction system that involves a dual host molecule, which can be compared to the combination of a cation receptor and an anion receptor. Figure 1 below summarizes the comparison between the different cesium-anion extraction systems: despite the strong polarity of nitrobenzene, it was determined that the calix[4]pyrrole anion receptor C4P could be the host of cesium halide ion pairs (demonstrated with chloride and bromide). This ion pair is dissociated when a stronger cation receptor is used (bisoctylbenzo calix[4]arene-crown-6, BOB).

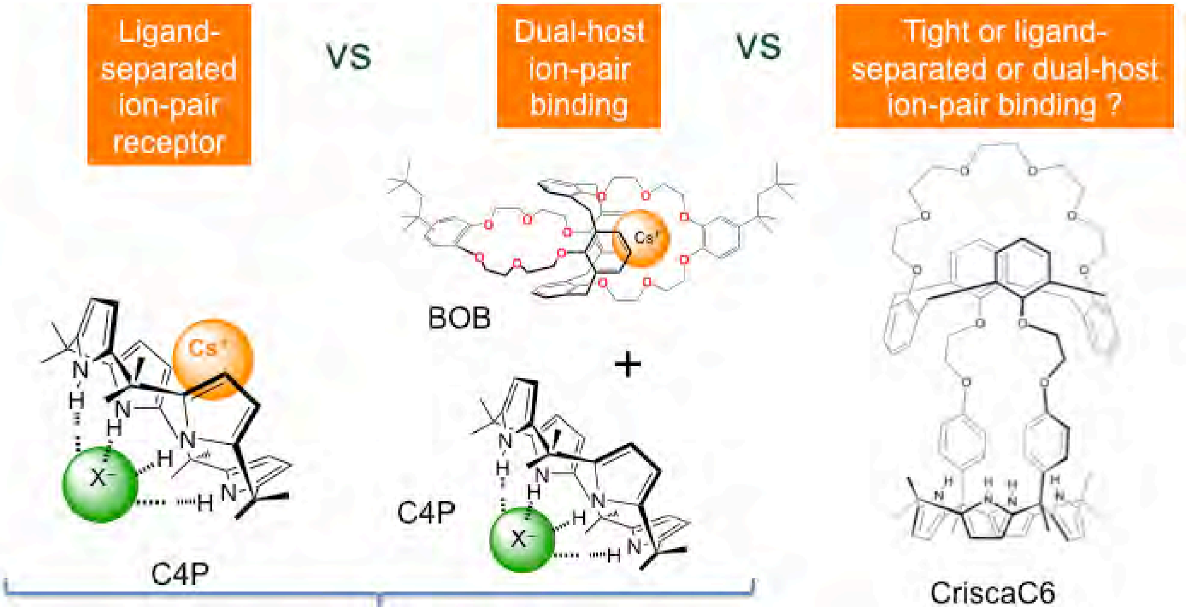
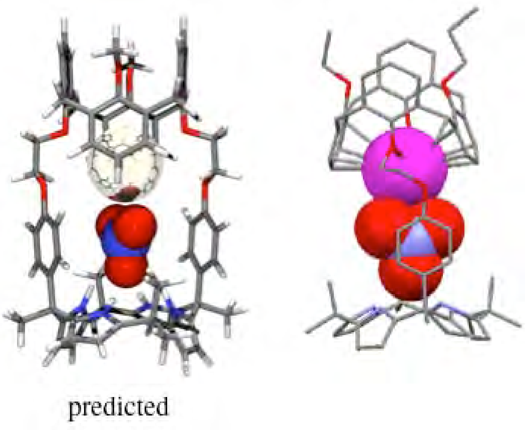


Figure 1. Extraction mechanism comparison

A key question lies therefore in the required conditions to obtain an ion paired extraction system and whether it can lead to cation and anion recognition. This research led to the study of a molecule that can be seen as the combination of BOB and C4P, the Crown-6-Calix[4]arene Capped Calix[4]pyrrole (CriscaC6). The results revealed that CriscaC6 in nitrobenzene complexed both cesium and the anion (fluoride, bromide, chloride, nitrate) but the cation and the anion were too far apart and the extraction behavior was primarily that of a dissociated system. Two other molecules were considered for comparison, one bearing only a 5 carbon crown ether and another where the crown was replaced by propoxy groups.



Complexation constants in both sites were within a few percents of those obtained with the corresponding dual host system. While CriscaC5 only demonstrated a poorer cesium extraction without shedding more light on the extraction process, the use of Crisca-propoxy revealed some ion pairing. The lack of a crown to accommodate the cesium forced the cation to choose either the spacers environment or the “cup” formed by C4P upon complexation with the anion. Thermodynamic data proved that the location between the spacers is a much better environment for cesium. Cesium proximity to the anion also switches the extraction mode from fully dissociated to ion-paired. Based on the extraction results, a molecular modeling study was developed and showed that cesium and its counter ion could reside in the ditopic receptor as presented in Figure 2. A crystal structure showing this arrangement with nitrate was obtained subsequently. The tetrapropoxy calix[4]arene was synthesized to study the extraction and complexation of cesium. The effect of the length and the nature of the spacers will also be studied. This effort will be done in parallel with molecular modeling predictions regarding the binding site(s) and distance calculations to determine if the thermodynamic modeling of the extraction results is consistent with ion pairing or ion dissociation.

Science objectives for 2011-2013:

- Exploration of the frontiers and inherent advantages of ion-paired extraction vs. dissociated mechanism
- Determination of cooperative effects due to the extraction of a cation and an anion by a ditopic receptor
- Determination of thermodynamics values for all considered systems and elucidation of distance requirements

Publications supported by this project 2009-2011

Kim, S. K.; Sessler, J. L.; Gross, D. E.; Lee, C.-H.; Kim, J. S.; Lynch, V. M.; Delmau, L. H.; Hay, B. P. A Calix[4]arene Strapped Calix[4]pyrrole. An Ion Pair Receptor Displaying Three Different Cesium Cation Recognition Modes. *J. Am. Chem. Soc.* **2010**, 132, 5827-5836.

Moyer, B. A.; Sloop, F. V., Jr.; Fowler, C. J.; Haverlock, T. J.; Kang, H.-A.; Delmau, L. H.; Bau, D. M.; Hossain, A.; Bowman-James, K.; Shriver, J. A.; N. Bill; Gross, D. E.; Marquez, M.; Sessler, J. L. Enhanced Liquid-Liquid Anion Exchange Using Macrocyclic Anion Receptors: Effect of Receptor Structure on Sulfate-Nitrate Exchange Selectivity. *Supramol. Chem.* **2010**, *22*(11), 653–671.

ACTINIDE BORATES

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Prof. W. Depmeier, E. Alekseev, University of Kiel, Germany
Dr. C. Booth, Lawrence Berkeley National Laboratory

Overall research goals: To answer the following questions.

- What are the crystalline structures of An(III, IV, V, VI) (An = U, Np, Pu, Am, Cm) borates?
- How can unusual structural features be related to important physical properties?
- Can disproportionation of the An(V) oxidation state be used as a synthetic strategy for preparing mixed- and intermediate-valent compounds?
- How stable are these materials?

Significant achievements during 2010-2011: We have prepared and structurally characterized more than 50 new actinide borates in oxidation states ranging from +3 to +6. We have prepared an entire family of uranyl borates, many mixed-valent neptunium borates, and several plutonium borates. For the first time, we have developed air-free techniques for manipulating low-oxidation states of plutonium in molten boric acid.

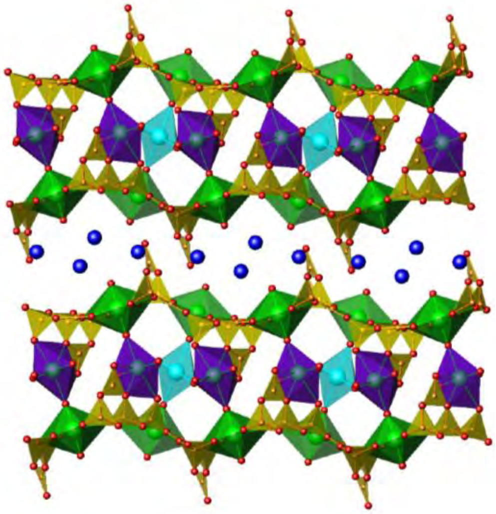

Figure 1. A depiction of the structure of $K_4(NpO_2)_{6.73}B_{20}O_{36}(OH)_2$ or $Ba_2(NpO_2)_{6.59}B_{20}O_{36}(OH)_2 \cdot 0.6H_2O$ showing $Np^{VI}O_8$ (green), $Np^{V}O_7$ (dark blue), and $Np^{IV}O_6$ (light blue) units linked by BO_3 triangles and BO_4 tetrahedra, and by bridging oxo atoms to form 1.6 nm thick slabs that are separated by K^+ or Ba^{2+} cations. Some of the disordered cations between the layers have been omitted for clarity.

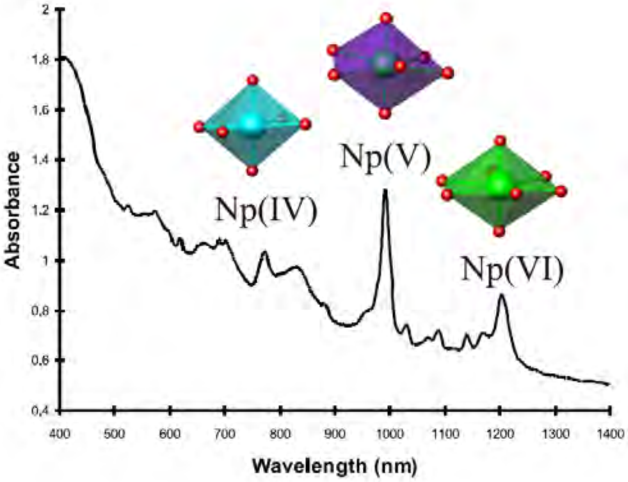

Figure 2. UV-vis-NIR spectrum of $K_4(NpO_2)_{6.73}B_{20}O_{36}(OH)_2$ showing regions of f-f transitions that indicate the presence of Np(IV), Np(V), and Np(VI). Corresponding $Np^{VI}O_8$ (green), $Np^{V}O_7$ (dark blue), and $Np^{IV}O_6$ (light blue) polyhedra are placed above each region of the spectrum.

Science objectives for 2011-2013:

- There are several challenges that remain. These include preparing mixed-valent plutonium and americium borates, microscale synthesis of curium borates.
- Developing calorimetric techniques for measuring the heats of formation of all of the compounds that we have prepared.

Selected Publications supported by this project 2010-2011 (out of ~34)

1. S. Wang, E. V. Alekseev, J. Ling, S. Skanthakumar, L. Soderholm, W. Depmeier, T. E. Albrecht-Schmitt, "Neptunium Diverges Sharply from Uranium and Plutonium in Crystalline Borate Matrixes: Insights into the Complex Behavior of the Early Actinides Relevant to Nuclear Waste Storage," *Angewandte Chemie*, *Int. Ed.*, **2010**, *49*, 1263-1266. *Selected for Cover Art Feature.*
2. S. Wang, E. V. Alekseev, J. Diwu, W. H. Casey, B. L. Phillips, W. Depmeier, T. E. Albrecht-Schmitt, "NDTB-1: A Supertetrahedral Cationic Framework that Removes TcO_4^- from Solution," *Angewandte Chemie*, *Int. Ed.*, **2010**, *49*, 1057-1060. *Featured on the Discovery Channel website. Spread throughout the web, MSNBC, Wired, CNN, Etc.*
3. S. Wang, E. V. Alekseev, J. T. Stritzinger, G. Liu, W. Depmeier, T. E. Albrecht-Schmitt, "Structure-Property Relationships in Lithium, Silver, and Cesium Uranyl Borates," *Chemistry of Materials*, **2010**, *22*, 5983-5991.

Selective Recognition of Heavy Elements by Protein-Based Reagents

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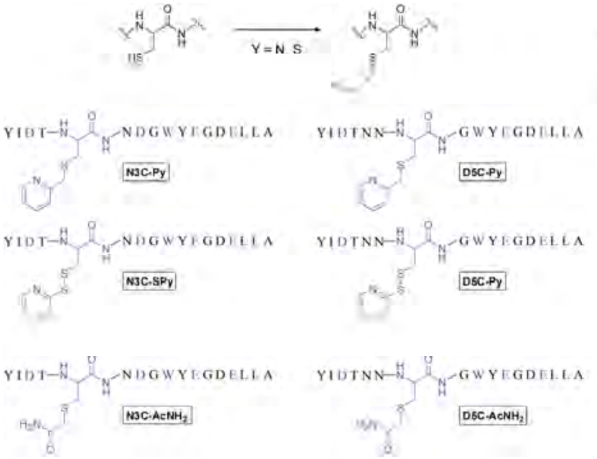
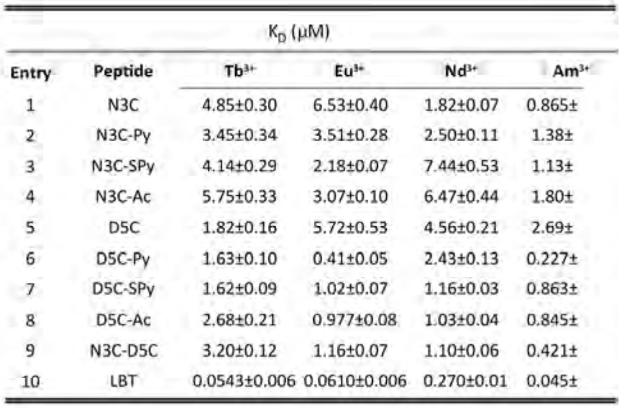
Overall research goals: The objective of this project is to engineer protein-based reagents that can selectively bind heavy elements in aqueous solutions. Our long-term goal is to design and evolve proteins that can bind individual actinide ions tightly and selectively.

Significant achievements during 2009-2011: To date, we have explored three different systems with significant progress made:

1. Unnatural peptides to selectively bind trivalent actinide ions (Fig. 1). We have synthesized a series of modified lanthanide/actinide-binding peptides. The K_d values of these peptides to Tb^{3+}, Eu^{3+}, Nd^{3+}, and Am^{3+} were obtained.





		K_D (μM)			
Entry	Peptide	Tb^{3+}	Eu^{3+}	Nd^{3+}	Am^{3+}
1	N3C	4.85±0.30	6.53±0.40	1.82±0.07	0.865±
2	N3C-Py	3.45±0.34	3.51±0.28	2.50±0.11	1.38±
3	N3C-SPy	4.14±0.29	2.18±0.07	7.44±0.53	1.13±
4	N3C-Ac	5.75±0.33	3.07±0.10	6.47±0.44	1.80±
5	D5C	1.82±0.16	5.72±0.53	4.56±0.21	2.69±
6	D5C-Py	1.63±0.10	0.41±0.05	2.43±0.13	0.227±
7	D5C-SPy	1.62±0.09	1.02±0.07	1.16±0.03	0.863±
8	D5C-Ac	2.68±0.21	0.977±0.08	1.03±0.04	0.845±
9	N3C-D5C	3.20±0.12	1.16±0.07	1.10±0.06	0.421±
10	LBT	0.0543±0.006	0.0610±0.006	0.270±0.01	0.045±

Figure 1. Left: Modified peptides synthesized for binding assays to trivalent lanthanides and actinides. Right: K_d values obtained from the binding asays.

2. Uranyl-selective proteins based on a Protein Data Bank screen. We wrote a computational script and screened all published protein crystal structures in the Protein Data Bank for uranyl-selective binding sites. In this script, we allow mutation of any residue to Asp and Glu in order to dock in a hexagonal or pentagonal bipyramidal coordination geometry for uranyl. We obtained over 4,000 hits. Out of these we elected 10 hits from the top 100, synthesized these genes, expressed the proteins, and tested uranyl binding. Four proteins have been shown to bind uranyl at nM affinity (Figure 2A). We are excited to improve binding affinities through protein engineering.

3. Developing ReO_4^-/TcO_4-binding protein. We engineered a molybdate (MoO_4^{2-})-binding protein from *E. coli* to bind perrhenate ion with high affinity. The best mutant protein can bind perrhenate with a K_d ~104 nM. We obtained a high-resolution crystal structure of the perrhenate-bound protein (Figure 2B) and we hope to engineer a more selective and sensitive protein in the future. We also hope to eventually test pertechnetate binding.

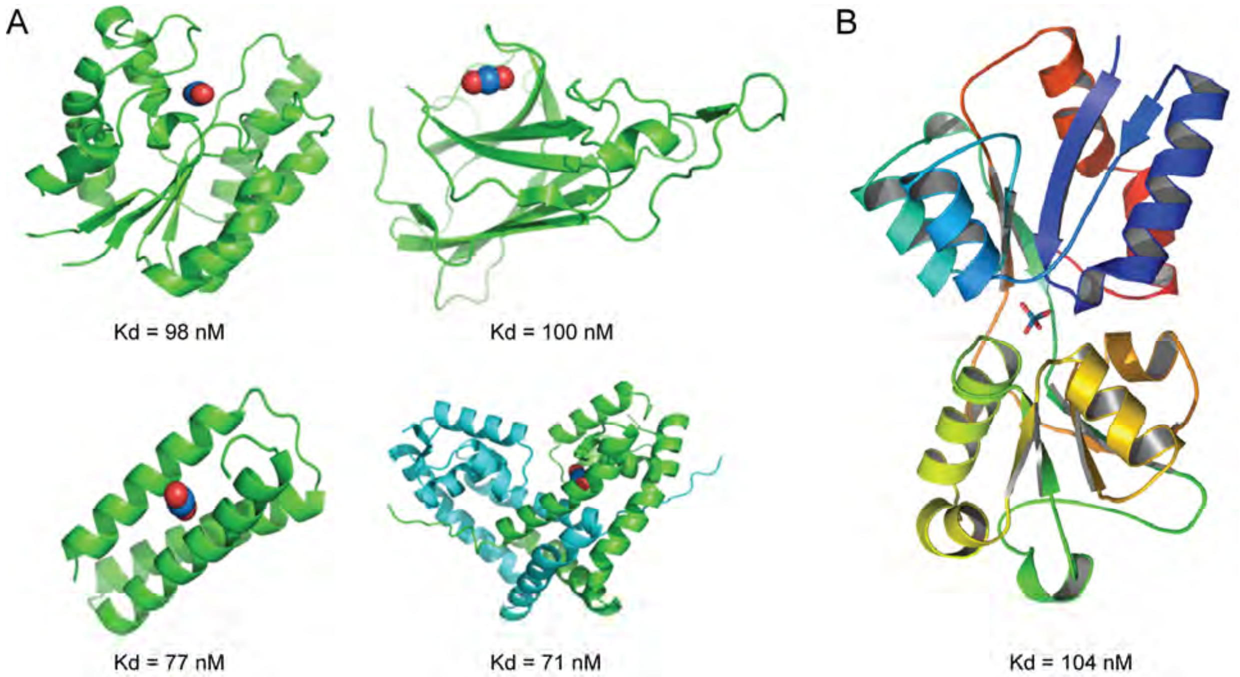


Figure 2. (A) Selective uranyl-binding proteins. Further protein engineering will be conducted to improve uranyl affinity. (B) An engineered protein that binds perrhenate. The crystal structure is shown.

Science objectives for 2011-2013:

- Replace unnatural amino acids in the lanthanide/actinide binding peptide with dithiophosphonate to improve selectivity toward trivalent actinide ions.
- Based on the predicted or experimentally obtained crystal structures of uranyl-bound proteins, we plan to perform protein engineering to significantly improve uranyl-binding affinity.
- Develop highly sensitive and selective perrhenate-binding and pertechnetate-binding ModA.

Publications supported by this project 2009-2011

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Preorganized and Immobilized Ligands for Metal Ion Separations

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Leigh R. Martin (Idaho National Laboratory)

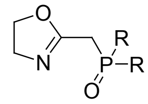
Andrew J. Gaunt (Los Alamos National Laboratory)

Overall Research Goals: Organic ligand synthesis, lanthanide coordination chemistry, spectroscopic and structural analyses and computational molecular design methods are employed to reveal the fundamental and complex interplay between electronic, steric and architectural organizational features that influence the selective recognition of f-element ions by receptor molecules in solution. 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 that includes quantitative solvent extraction analyses, ligand radiation damage analyses and actinide coordination chemistry and spectroscopic analyses.

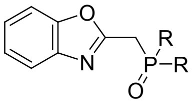
Significant Achievements during 2009-2011:

Ligand design/synthesis/Ln coordination chemistry activities: During this 18-month period our ongoing studies of the generalized ligand architectures illustrated by PO,N (**1**), PO,N **(2**), PO,PO,NO (**3**) and PO,NO,NO (**4**) have continued and several new coordination conditions have been revealed that have guided continuing studies of related ligand targets. This includes the development during the current grant period, of a set of poly-pyridine/pyridine N-oxides, PO,N,N,N **(5**) PO,NO,NO,NO (**6**). The synthesis, characterization and coordination chemistry of these ligands with their hardened and softened coordination fields continues. In addition, development of several new targets and applications have taken place. For example, the syntheses for thiophosphonic acid derivatives (**7**) and (**8**) have been explored and some of the coordination chemistry of **(7**) has been completed. Further modifications of the basic multidonor ligand coordination field of **(3**) also have been accomplished with syntheses of the dissymmetric ligand PO,NO,NH_2 (**9**) and the ligand POPONONH_2 (**10**). The coordination chemistry of these ligands is under study and both are being used to form "switchable"polar/nonpolar extractants.

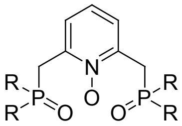
Finally, a new ligand family based upon a dibenzofuran framework (**11**) has been developed and the coordination chemistry of this platform is under study.



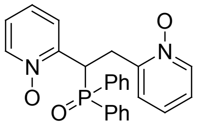
PO,N (**1**)



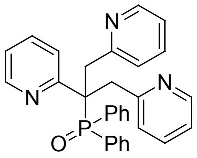
PO,N (**2**)



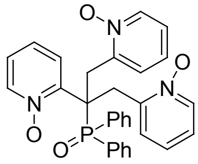
PO,NO,NO (**3**)



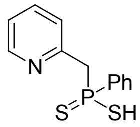
PO,NO,NO (**4**)



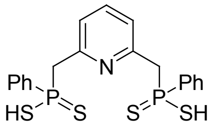
PO,N,N,N (**5**)



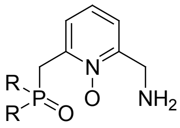
PO,NO,NO,NO (**6**)



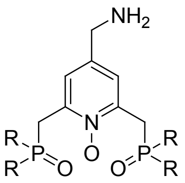
PS,SH,N (**7**)



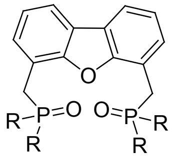
PS,PS,SH,SH,N (**8**)



PO,NO,NH$_2$ (**9**)



PO,PO,NO (**10**)



PO,PO,O (**11**)

<u>Science objectives for 2011-2012</u>: The study program of ligand design, synthesis and lanthanide coordination chemistry will be continued with the major focus on platforms **5-11**. This will include a major effort to characterize the performance of **9** and **10** as switchable solvents using CO_2 as the trigger reagent. These reagents offer the possibility of greatly reduced organic process solvents in practical extraction schemes.

<u>Publications supported by this project 2010-2011</u>:

1. S. Pailloux, C.E. Shirima, K.A. Smith, E.N. Duesler, R.T. Paine, N.J. Williams and R.D. Hancock "Synthesis and Reactivity of (Benzoxazol-2-ylmethyl)phosphonic Acid" *Inorg. Chem.* **2010**, *49*, 9369.
2. J.-M. Camus, S. Pailloux, C.E. Shirima and R.T. Paine "Synthesis of 2,5-bis(phosphinoylmethyl)- and 2,5-bis(thiophosphinoylmethyl) thiophenes" Mai*n Group Chemistry* **2011**, *10*, 25.
3. 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" submitted for publication

Heavy Element Nuclear and Radiochemistry

Heino Nitsche, Principal Investigator, Kenneth E. Gregorich, Co-Principal Investigator
Postdoctoral researcher: Jan Dvorak, Irena Dragojevic
Graduate students: Paul A. Ellison, Oliver R. Gothe, Nicholas E. Esker
Undergraduat students: Joseph P. McLaughlin
Lawrence Berkeley National Laboratory (LBNL), Nuclear Science Division, MS 70R0319, 1 Cyclotron Road, Berkeley, CA 94720-8169
Email:hnitsche@lbl.gov; Web: http://heavyelements.lbl.gov/

Collaborators: Prof. Dr. Christoph Düllmann, University of Mainz and GSI, Institute of Nuclear Chemistry, Fritz-Strassmann-Weg 2, D-55128 Mainz (Germany).

Overall research goals:

We are maintaining a flexible first-rate program which can respond quickly to new research opportunities in heavy element studies, and for a broader range of experiments requiring a) high-intensity beams, b) highly efficient or highly specific separations, and/or c) requiring the most extreme detection sensitivity. These fields of expertise will be essential in the development of apparatus and experiments for the use in existing and planned stable and radioactive beam facilities. The Berkeley Gas-filled Separator (BGS) allows separation and detection of heavy element isotopes produced in compound nucleus reactions. With the combination of high-intensity heavy-ion beams from the 88-Inch Cyclotron and the high efficiency and selectivity of the BGS, the LBNL Heavy Element and Nuclear Radiochemistry Group will continue to make important contributions in the study of the production, nuclear decay properties, and chemistry of the heaviest elements.

These exotic and frontier studies attract many undergraduate and graduate students to nuclear and radiochemistry. This research provides excellent education and training for future contributions and careers in a variety of applied areas, as well as in frontier research.

Significant achievements during 2009-2011:

- **First independent verification of the formation of element 114**. For the past 11 years, there have been numerous reports from Dubna (Russia) on the formation of superheavy elements in the irradiation of actinide targets with ^{48}Ca beams. These fantastic claims went unconfirmed for nearly 10 years. Using the newly completed actinide target irradiation facility at the BGS, ^{242}Pu targets were irradiated with a ^{48}Ca beam to produce element 114 isotopes. One atom each of ^{286}114 and ^{287}114 were produced by the ^{242}Pu(^{48}Ca,4n)^{286}114 and ^{242}Pu(^{48}Ca,3n)^{287}114 reactions. The observed decay modes, decay energies and half-lives of the element 114 isotopes and their daughters agree with values published by the Dubna group.

- **Additional verification of element 114 and discovery of ^{277}Hs.** We actively participated in an international collaboration at the TASCA separator at GSI that independently confirmed two additional isotopes of element 114 using ^{244}Pu targets to produce ^{288}114 and ^{289}114 using the reactions ^{244}Pu(^{48}Ca,4n)^{288}114 and ^{244}Pu(^{48}Ca,3n)^{289}114 reactions. A total of fifteen decay chains were observed and assigned to the decay of ^{288,289}114. A new alpha- decay branch in ^{281}Ds was observed, leading to the new isotope ^{277}Hs.

- **A new isotope of element 114 and five new transactinide isotopes**. We produced a new, neutron-deficient element 114 isotope, ^{285}114, using the ^{48}Ca + ^{242}Pu → ^{285}114 + 5n reaction with the BGS. The decay of ^{285}114 and daughters led to the identification of six new isotopes: ^{285}114, ^{281}Cn, ^{277}Ds, ^{273}Hs, ^{269}Sg, and ^{265}Rf. We also observed the decay of ^{286}114 via the ^{48}Ca + ^{242}Pu → ^{286}114 + 4n reaction, thus re-confirming earlier work, both at the BGS and at Dubna.

- **Chemical studies of elements 114 and 112.** Chemical studies of superheavy elements are ideally suited to probe the influence of relativistic effect on electronic shell structure. Early predictions emphasized the direct relativistic effect, i.e., the strong stabilization of s- and $p_{1/2}$-orbitals, such as the outermost ones occupied in elements copernicium (Cn, element 112) and element 114. These elements were thus predicted to be chemically inert, similar to noble gases. In contrast, more recent, fully-relativistic density functional calculations of these elements and their interaction with metal surfaces predicted a more reactive behavior, e.g., for element 114 with a gold surface. So far, two chemistry experiments were performed with element 114. The first one, carried out by a PSI-led collaboration at the FLNR in Dubna, Russia, reported indications for an inert behavior of 114. Our international collaboration has performed a successful experiment at GSI using the new gas-filled Transactinde Separator and Chemistry Apparatus (TASCA) in the fall of 2009. The clean alpha-spectra obtained through pre-separation in TASCA allowed the unique identification of two decay-chains from 114. This experiment clearly observed the formation of an element 114-Au bond, a result in conflict with the result of the PSI study. The collaboration is now embarking on a new experiment with 114, which goes beyond the scope of previous studies. The chemical behavior of five relevant elements will be compared directly with each other: the rather reactive Pb, less reactive Hg, the noble gas Rn, the superheavy elements Cn (a homolog of Hg) and 114 (a homolog of Pb). The chemistry setup consists of a series of detectors: a first one, covered with inert SiO_2, which will retain only Pb; a second one, covered with Au, kept at room temperature, which will retain Hg; a third one, covered with Au, cooled to low temperature, which will retain the noble gas Rn that reacts very weekly with any surface and is also fairly inert to Cn deposition. This study will answer the question concerning the trend in reactivity among all five studied elements.

Science objectives for 2011-2013:

- Continue to make important contributions in the study of the production, nuclear decay properties, and chemistry of the heaviest elements.
- Use the BGS for synthesis, identification, and chemistry studies of new heavy element isotopes.
- Continue international collaboration at GSI, Germany, using TASCA to perform additional chemistry experiments with element 114 that will differentiate between mercury- or lead-like-homologous behavior.

Publications supported by this project 2009-2011

1. L. Stavsetra, K. E. Gregorich, J. Dvorak, P.A. Ellison, I. Dragojević, M.A. Garcia, H. Nitsche,. "Independent verification of element 114 production in the ^{48}Ca + ^{242}Pu reaction," Phys. Rev. Lett. 103. 132502 (2009).
2. Ch.E. Düllmann, M. Schädel,. Yakushev, A. Türler, K. Eberhardt, J.V. Kratz, D. Ackermann, L.-L. Andersson, M. Block, W. Brüchle J. Dvorak, H.G. Essel, P.A. Ellison, J. Even, J.M. Gates, A. Gorshkov, R. Graeger, K.E. Gregorich W. Hartmann, R.-D. Herzberg, F.P. Heßberger, D. Hild, A. Hübner, E. Jäger, J. Khuyagbaatar, B. Kindler, J. Krier, N. Kurz, S. Lahiri, D. Liebe, B. Lommel, M. Maiti, H. Nitsche, J.P. Omtvedt, E. Parr D. Rudolph, J. Runke, B. Schausten, E. Schimpf, A. Semchenkov, J. Steiner, P. Thörle-Pospiech, J. Uusitalo, M. Wegrzecki, N. Wiehl, "Production and decay of element 114: high cross sections and the new nucleus ^{277}Hs," Physical Review Letters, 104, 252701 (2010) DOI: 10.1103/PhysRevLett.104.252701.
3. P.A. Ellison, K.E. Gregorich, J.S. Berryman, D.L. Bleuel, R.M. Clark, I. Dragojević, J. Dvorak, P. Fallon, C. Fineman-Sotomayor, J.M. Gates, O.R. Gothe, I.Y. Lee, W.D. Loveland, J.P. McLaughlin, S. Paschalis, M. Petri, L. Stavsetra, M. Wiedeking, and H. Nitsche, "New Superheavy Element Isotopes: ^{242}Pu(^{48}Ca,5n)^{285}114," Phys. Rev. Lett. 105, 182701, (2010) DOI: 10.1103/PhysRevLett.105.182701.

Reproducible and Reliable Electrochemical Determination of U and TRU Concentrations

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Abstract:

In the pyrochemical treatment of used nuclear fuel, the electrorefining step is used to both dissolve the actinide all species less noble than the actinides while simultaneously depositing either pure uranium or a uranium/transuranic alloy at cathodes. Consequently, in-situ, real-time monitoring the concentration of uranium and transuranics in an electrorefiner is important to ensure that these concentrations are maintained within specified process control limits. We have been investigating the use of voltammetric techniques for measuring uranium and transuranic concentrations in a molten salt electrolyte that contains varying concentrations of uranium, neptunium, and gadolinium. A simple method for determining the effective area of the working electrode will be presented along with data from potential step experiments and a variety of voltammetric techniques. The results will be discussed in the context of how proper electrode pre-treatment (cleaning potential, open circuit rest period, and base potential,) before each measurement affects the reproducibility of the measurements.

Correlations between structure, magnetism, and electronic properties in neptunium compounds

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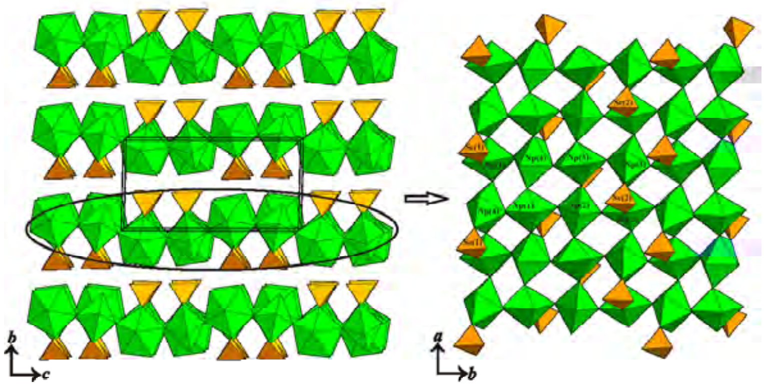
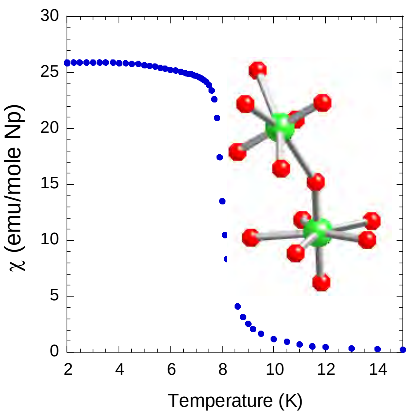
Collaborators: Geng Bang Jin, L. Soderholm, Guokui Liu, Argonne National Laboratory
James Ibers, Department of Chemistry, Northwestern University, Evanston, IL 60208
T.E. Albrecht-Schmitt, CEGS Department, University of Notre Dame, IN 46556

Overall research goals: This research is centered on understanding the influence of crystalline structure on the electronic and magnetic properties of actinide-containing materials. Of particular interest are Np compounds, notably those containing neptunyl(V), because they form structures with variable lattice dimensionality. The presence of cation-cation interactions (CCI)s, the bonding of an –yl oxygen on one Np(V) as an equatorial ligand on a neighboring cation, can enhance local-moment magnetic interactions by providing magnetic superexchange pathways. Using the rich and tunable lattice dimensionality afforded by neptunyl(V) CCIs, we seek a fundamental understanding of the interplay between local f-spins and their ion-ion interactions.

Significant achievements during 2009-2011: Several new neptunium compounds have been synthesized, their structures determined, and their magnetic response determined as a function of temperature. These include lower-valent chalcogenides [1] and several neptunyl structures that all exhibit evidence of magnetic ordering, antiferromagnetic ordering at temperatures below about 35 K for the lower valent Np compounds and ferromagnetic ordering below about 8-12 K for the neptunyl(V) materials.





Our results on neptunyl(V) magnetism complement existing work on magnetic ordering in these CCI materials and point to the important impact of lattice dimensionality on magnetic ordering, while suggesting that the ordered moment, determined largely by single-ion properties, also plays a role. This interplay between spin and lattice dimensionality is central to magnetic properties of metal-ions in general and is not limited to localized f-states in rare-earth and actinide systems.

Science objectives for 2011-2013:

- Focus on the syntheses of new neptunyl(V) materials exhibiting CCIs with reduced lattice dimensionality. Syntheses will focus on the opportunity to tailor the Np-Np interactions from single-ion to 3 D framework structures, including ribbon and chain interactions (fractal lattice dimensionality).

- Detailed optical studies will be undertaken on selected magnetic materials in order to understand the electronic energy level structure within a single-ion intermediate coupling scheme and modifications thereof, including contributions from ion-ion covalent intereactions. Determination of low-lying energy states and their relationships to CCIs will be the central focus of this effort.

Publications supported by this project 2009-2011

1. D.M. Wells, G.B. Jin, S. Skanthakumar, R.G. Haire, L. Soderholm, J.A. Ibers, Quaternary neptunium compounds: Syntheses and characterization of $KCuNpS_3$, $RbCuNpS_3$, $CsCuNpS_3$, $KAgNpS_3$, and $CsAgNpS_3$, *Inorg. Chem. 48* (2009) 11513-11517.
2. D.M. Wells, S. Skanthakumar, L. Soderholm, J.A. Ibers, Neptunium(III) copper(I) diselenide, Acta Cryst. E: Structure Reports Online (2009), E65(3), i14.
3. G.B. Jin, A.D. Raw, S. Skanthakumar, R.G. Haire, L. Soderholm, J.A. Ibers; Single-crystal structures of uranium and neptunium oxychalcogenides AnOQ (An = U, Np; Q = S, Se), *J. Solid State Chem. 183* (2010) 547-550.
4. D.E. Bugaris, D.M. Wells, J. Yao, S. Skanthakumar, R.G. Haire, L. Soderholm, J.A. Ibers, Dichalcogenide bonding in seven alkali-metal actinide chalcogenides of the KTh_2Se_6 structure type, *Inorg. Chem. 49* (2010) 8381-8388.
5. S. Wang, E.V. Alekseev, J. Ling, S. Skanthakumar, L. Soderholm, W. Depmeier, T.E. Albrecht-Schmitt; Neptunium diverges sharply from uranium and plutonium in crystalline borate matrixes: Insights into the complex behavior of the early actinides relevant to nuclear waste storage, *Angew.Chemie 49* (2010) 1263-1266.
6. G.B. Jin, S. Skanthakumar, R.G. Haire, L. Soderholm, J.A. Ibers; Synthesis, structures, and magnetic properties of Np_3S_5 and Np_3Se_5, *Inorg. Chem. 50* (2011) 1084-1088.
7. G.B. Jin, S. Skanthakumar, L. Soderholm; Cation-cation interactions in neptunyl(V) selenate hydrates $(NpO_2)_2(SeO_4)(H_2O)_n$ (n = 1,2 and 4); submitted for publication.
8. G.B. Jin, S. Skanthakumar, L. Soderholm; Two new neptunyl(V) selenites: A novel cation-cation interaction framework in $(NpO_2)_3(OH)(SeO_3)(H_2O)_2{\cdot}H_2O$ and a uranophane-type sheet in $Na(NpO_2)(SeO_3)(H_2O)$; submitted for publication.

Spectroscopy of organometallic radicals

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Overall research goals: The objective of this project is to provide detailed and highly accurate spectroscopic and thermochemical data concerning organometallic radicals and actinide-containing species, concentrating on thorium and uranium compounds that can be safely handled in a university environment.

Significant achievements during 2009-20011: Major efforts during the 2009-2011 period have concentrated on the construction of a cryogenically cooled ion trap photodissociation spectrometer. A schematic diagram of the instrument is shown below, along with a photograph of one of the two-dimensional turning quadrupoles.

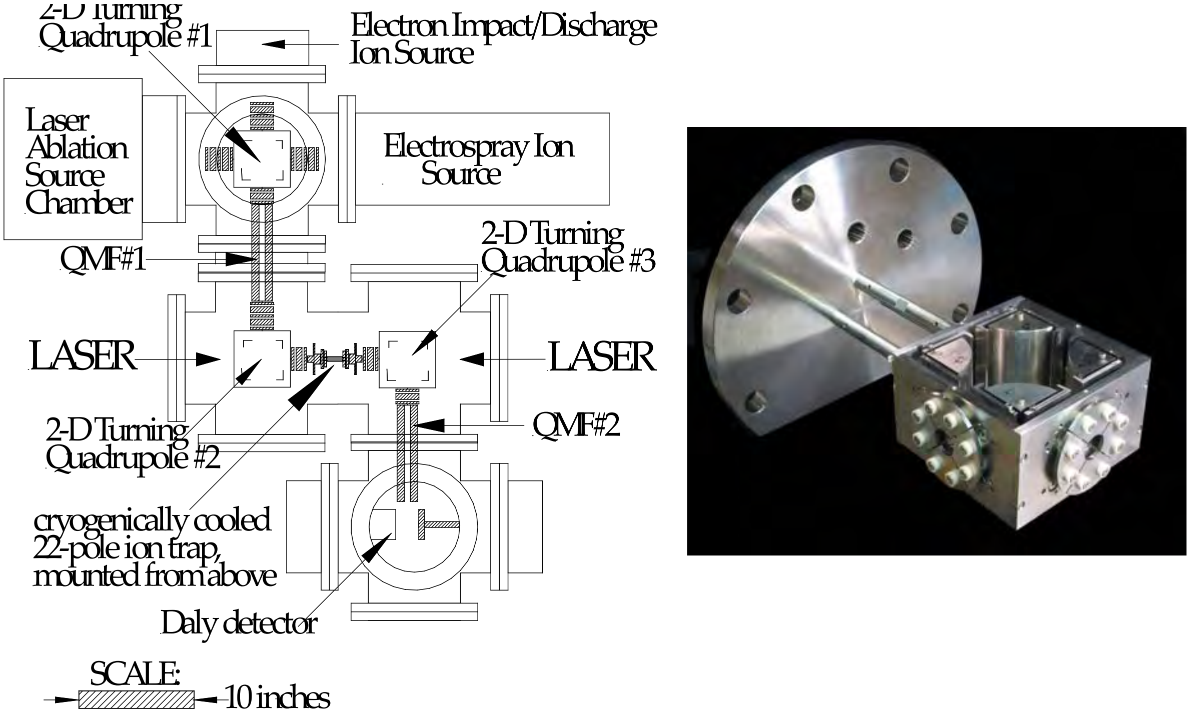

Figure 1. Scheme of the cryo-cooled ion photodissociation spectrometer (left); one of the three turning quadrupoles (right).

During the 2009-2011 time frame, the electron impact ion source, first quadrupole mass filter, two of the turning quadrupoles, and the Daly ion detector have been built and tested. Although much of the ion trap itself has been built, the pieces have not yet been assembled and tested; currently the machine shop is making the heat shield and flanges needed to support the cryostat that will cool the trap to temperatures below 10 K. In addition to turbomolecular pumping, a cryogenic pumping facility will be placed under the second turning quadrupole assembly, just upstream of the ion trap, in order to trap condensable gases before they impinge onto the cold surfaces of the trap. This project is the primary responsibility of my postdoctoral researcher, Sergei Aksyonov.

Other significant achievements during this time frame are the analysis and publication of the spectrum of diatomic CrC (a $^3\Sigma^- \leftarrow X\ ^3\Sigma^-$ band system) and TaC (for which several $^2\Pi_{1/2} \leftarrow X\ ^2\Sigma^+$ transitions were observed and analyzed). These studies represent the first spectroscopic investigations of any kind on these molecules, and provide experimental verification of the ground state electronic symmetries that have been computationally predicted, along with precise measurements of the ground state bond lengths (1.6188 and 1.7490 Å, respectively). Additional achievements are the measurement and analysis of spectra of ZrF and OsN, which will be submitted for publication shortly. Experimental work on the spectrum of CuCCH is nearly complete, as is the analysis of the 1-0 band of the $\tilde{A}\,^6\Sigma^+ \leftarrow \tilde{X}\,^6\Sigma^+$ band system of CrCCH.

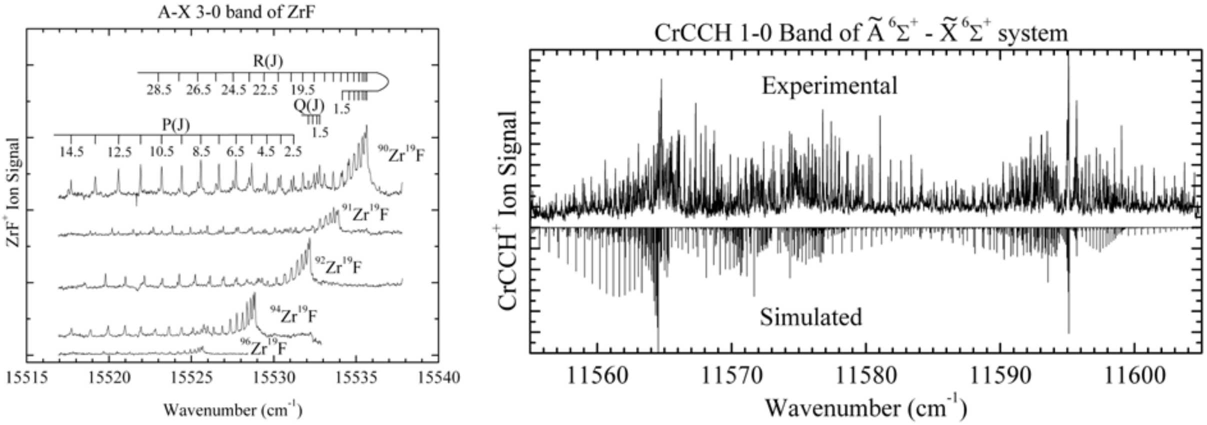

Figure 2. Rotationally resolved spectra of the isotopes of ZrF (left) and of the 1-0 band of the $\tilde{A}\,^6\Sigma^+ \leftarrow \tilde{X}\,^6\Sigma^+$ system of CrCCH (right).

Science objectives for 20011-2013:

- Complete the construction of the 22-pole trap, the second quadrupole mass filter, and the software needed to trap and photodissociate ions. Test and completely debug the system using the electron impact ion source. Collect spectra of simple species that can be generated with this source, particularly those that are fragments of volatile organometallic complexes such as $Fe(CO)_5$, $Co(CO)_3NO$, $Ni(CO)_4$, and $Cr(CO)_6$.

- Integrate the 22-pole ion trap instrument with the laser ablation source, and begin experiments using laser-ablated ion sources, including uranium and thorium. Important goals here are to collect spectra of UO_2^+ and its solvated analogs.

- Design and begin construction of the electrospray ion source, so that multiply-charged ions such as UO_2^{2+} can be investigated, both as a bare ion and as a solvated system.

- Obtain resonant two-photon ionization spectra of ThO_2 and other small thorium and uranium species. The electronic and geometric structure of ThO_2 will be compared to the known isovalent species TiO_2, ZrO_2, and HfO_2.

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2. O. Krechkivska and M. D. Morse, "Resonant two-photon ionization spectroscopy of jet-cooled tantalum carbide, TaC," J. Chem. Phys. **133**, 054309/1-054309/8 (2010).
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4. M. Garcia and M. D. Morse, " Resonant two-photon ionization spectroscopy of jet-cooled OsN," (in preparation for the Journal of Chemical Physics).
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Thermodynamics and Kinetics of Extraction Systems

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Clint Sharrad and Louise Natrajan (The University of Manchester, UK)
Kenneth L. Nash (Washington State University)

Overall research Goals

The objective of this program is to study the fundamental solution phase chemistry of the lanthanides and actinides to gain a mechanistic interpretation of the processes involved in successful solvent extraction separations of these 4*f* and 5*f* ions. Through studying the fundamental thermodynamic parameters ΔG^o, ΔH^o and ΔS^o of complex formation, we seek to provide insight into the thermodynamic driving forces for each of the constituents of the extraction process. Through probing the many facets of chemical kinetics of these complex systems it is also our intent to provide insights into the molecular-atomic scale ordering of solute and solvent species.

Significant achievements 2009-2011

Thermodynamics. We have developed an analytical method for determination of heats of liquid-liquid distribution reactions using isothermal microcalorimetry. The calorimeter employed in this study uses extremely small quantities of reagents, employs a strategy of microliter titrant addition and enables the accurate detection of ΔT of 10^{-6} °C. The measurement of the enthalpy change for the extraction of Am by HDEHP followed the extensive 2-phase calorimetric studies using lanthanides. Figure 1 shows a power compensation trace for the HDEHP-mediated liquid-liquid distribution of Am(III) from mildly acidic aqueous sodium nitrate solution into the immiscible hydrocarbon phase. The experimental trace for the blank titration (titrant addition into a liquid-liquid system less HDEHP) is also included for comparison. The Am(III) titration experiments were investigated in duplicate and yielded an average integrated value of -402 ± 30 μJ (±1σ) as the observed heat of phase partitioning. This net energy is mainly a product of endothermic heat of metal ion dehydration and exothermic heat of complex formation in the organic phase. Figure 2 shows the thermodynamic parameters for the studies Am(III) partitioning, together with the previously determined values for the lanthanide ions.

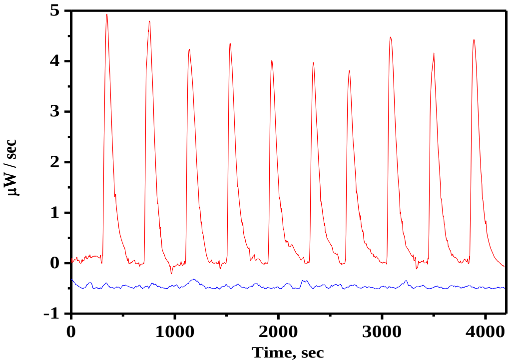

Figure 1. Calorimetric power compensation trace collected for the liquid-liquid distribution of americium ion. Aqueous phase: pH 3.2, 1.0 M $NaNO_3$. Organic phase: 0.2 M HDEHP in *n*-dodecane.

The collected parameters for Am(III) correctly fit into the ΔG_{tr}, ΔH_{tr} and ΔS_{tr} trends at the expected position of Pm(III). The negative entropy term opposes the partitioning of the metal ion into the organic phase due to the ordering effect of complex formation as well as the hydration of three protons, which are exchanged back to the aqueous solution. A favorable exothermic heat of Am(III) / HDEHP compound formation opposes the unfavorable entropy term. The overall free energy of liquid-liquid distribution of Am(III) is slightly endothermic, matching the light lanthanides characterized by lower charge density relative to the heavier and harder members of this series.

Kinetics. DTPA complexation kinetics have been performed with several lanthanides using Arsenazo(III) as a colorimetric indicator. It was identified that the reaction between the Ln-(AAIII) complex and DTPA exhibited slow complex formation kinetics (over 60 seconds). In addition a simple first order rate equation was not found to adequately describe the data generated by these experiments (Figure 3). Americium showed the same behavior as the lanthanides in these systems although the complexation kinetics were notably faster in this system. Further investigation revealed that AAIII was interfering in the complexation reaction. However, using a double exponential fit to analyze the data we were able to deconvolute preliminary rates for metal ion DTPA complexation kinetics for a range of lanthanides and americium. These rates qualitatively show that Am binds to DTPA significantly faster than lanthanides representative of the whole series (Figure 3 inset).

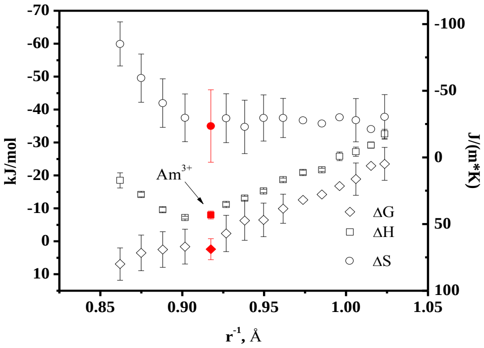

Figure 2. *The comparison of the thermodynamic parameters for the HDEHP-facilitated liquid-liquid partitioning of Am(III) with those reported for the lanthanide series.*

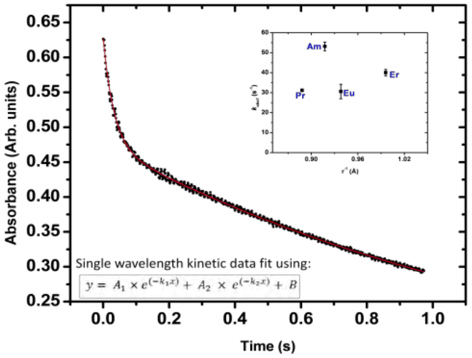

Figure 3. *Sample kinetics trace from the stopped flow spectrophotometer measuting the rate of reaction of Pr with DTPA. Inset: Plot of average k1 for the reaction of DTPA with Pr, Eu, Er and Am as a function of ionic radii.*

Science objectives for 2011-2013

- Continue kinetics investigations for a more direct pathway to measure aminopolycarboxylate complexation kinetics with lanthanide and actinide ions.
- Begin to focus on the thermodynamics of curium chemistry in solvent extraction systems using the methodologies developed with americium.

Publications supported by this project 2008-2010

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Organometallic Chemistry of the f-Block Elements; Intermediate-Valence Ground States, Magnetism, and Chemistry

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Overall research goals: The goal is to prepare organometallic molecules of the empirical composition Cp^*_2Yb(heterocycleamine) that exhibit correlated-electron behavior. The initial focus is to develop a molecular level of understanding of the bulk magnetic behavior of thesecompounds by application of L_{III}-edge XANES measurements and to generate a physical model by quantum mechanical computational studies. After a microscopic model is delineated, the next step is to develop reaction chemistry of these "radical" species that exploits their multi-configurational ground states for breaking and Making specific chemical bonds.

Significant achievements during 2009-2011.

A model that is developed to account for the magnetic properties in the intermediate-valence complexes of the type $(C_5Me_5)_2$Yb(bipy), where bipy is 2,2'-bipyridine and its methyl-substituted bipyridine derivatives, is based upon CASSCF multireference calculations, in which the C_5Me_5-lignad is modeled with C_5H_5. The computations show that the open-shell singlet state is comparable in energy to the open-shell triplet state. The triumph of these computations is that they rationalize why the L_{III}-edge XANES are temperature invarient from about 30 to 500K, ruling out a valence tautomeric equilibrium between valence isomers but consistent with a ground state wave function that is multiconfigurational and temperature independent. Adducts with methyl-substituents in the 4-Me and 5-Me positions and two methyl-substituents in the 3,3'-Me,4,4'-Me_2,and 5,5-Me_2-positions of the bipyridine ligands have temperature dependent L_{III}-edge XANES magnetic susceptibility values that can be fit to a Boltzman distribution from which the thermodynamic constants, ΔH and ΔS, are obtained for the equilibrium between two states, both of which are open-shell singlets that lie lower in energy than the triplet state! These new and challenging experimental results require extending the computations to incorporate these new experimental findings. The new model calculations begin by replacing the model C_5H_5-ligand with the C_5Me_5-ligand used in the experimental studies,by introducing a MP2-contribution into the CASSCF computation and by increasing the active space by including the empty π_1^*, π_2^*, π_3^*, and π_4^*-orbitals of bipyridine. This refined model lowers two open-shell singlet states below the triplet state for the mono-methyl substituted bipyridine complexes, and most importantly, in the unsubstituted derivative, $(C_5Me_5)_2Yb$(bipy), only one open-shell singlet state is lower in energy than the triplet state. Thus, the new model is intellectually satisfying and scholastically rigorous since it accounts for all of the known experimental facts.

Preparation of 1,10-phenanthroline, and their mono- and dimethyl derivatives, adducts of $(C_5Me_5)_2Yb$ will provide experimental tests for the model, since only two unoccupied π_1^* and π_2^*-orbitals are available to house the electron. These derivatives show magnetic and L_{III}-edge XANES data that allow them to be classified into two classes: (a), those whose singlet states are lower in energy than the triplet, *i.e.,* like the bipy derivatives and (b), those in which the triplet state is lower than the singlet, *i.e.,* unlike the bipy derivatives. The challenge is to create a model that fits this divergent set of experimental facts.

Science objectives for 2001-2013:

- Develop a model that accounts for the dependence of the magnetic behavior that depends upon the number of methyl-substituents and their position in the phenanthroline ring when complexed to $(C_5Me_5)_2Yb$.
- Develop and control the radical chemistry that is a consequence of the multi-configurational ground states.

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Nuclear and Radiochemistry Summer Schools

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Overall program goal: The objective of this program is to stimulate career interest in the fields founded in nuclear chemistry and technology. The Nuclear and Radiochemistry Summer Schools (hereafter referred to as "Summer Schools") are a strategic intellectual investment to meet the long-term national need for nuclear chemists and radiochemists at the U.S. DOE National Laboratories. Started in 1984 at San Jose State University (SJSU) and expanded to the Brookhaven National Laboratory (BNL) site in 1989, 24 highly qualified undergraduate chemistry/physics/biochemistry students are provided fundamental training in nuclear and radiochemistry through formal class lectures, laboratories, field trips, and a guest lecture series. Although not all participating students will eventually enter nuclear science fields, the Summer Schools generate awareness and acceptance of basic and applied nuclear science methods.

Significant achievements during 2009-2011: The Summer Schools are held during a six-week period starting in mid-June. Twelve students are selected by the National Director, in consultation with four members of the ACS Division of Nuclear Chemistry and Technology, to participate at each of the two sites. Prof. Herbert B. Silber is Site Director at SJSU. Dr. Louis Pena serves the same role at BNL. Students may earn transferable college credits for both the lecture and laboratory portions of the Summer Schools. The lecture syllabus includes the following topics: atomic nucleus, decay modes, decay kinetics, interaction of radiation with matter, radiation detection, nuclear forces, nuclear structure and models, nuclear reactions and fission, and applied nuclear science including selected topics in actinide chemistry, environmental radiochemistry, nuclear medicine, and nuclear power. Laboratory modules cover topics in radiation counting and statistics, radiochemical separations (including solvent and column extractions), half-life determination, radiation shielding, radioimmunoassay, radiopharmaceutical synthesis, and neutron activation analysis.

The Summer Schools are greatly enhanced by extracurricular activities that include guest lectureships and special symposia on nuclear medicine, environmental remediation, and graduate and employment opportunities in nuclear science and technology. Field trips to basic and applied nuclear science laboratories near the school locale provide participating students with real-life nuclear science experiences. Students at SJSU have visited Lawrence Berkeley National Laboratory, Lawrence Livermore National Laboratory, the Stanford Synchrotron Light Source and the PET Center at the University of California, San Francisco. The BNL participants have had the opportunity to visit the Relativistic Heavy Ion Collider, the Brookhaven Linac Isotope Producer, the National Synchrotron Light Source, Memorial Sloan-Kettering Cancer Center, and the Nuclear Structure Laboratory at SUNY-Stony Brook.

Of the 48 students who participated in the 2008 and 2009 Summer Schools program, 33 of the students were known to have enrolled in advanced degree programs, and 22 of those students elected a program with a significant nuclear science component. In addition, 16 Summer Schools alumni received an advanced degree over the 2009-2010 academic year.

The demographics of the student participants at the last three Summer Schools are given in Table I.

Table 1. Demographics of Nuclear and Radiochemistry Summer Schools Participants.

	Class of 2008	Class of 2009	Class of 2010
Gender (male/female)	16/7	12/12	18/6
Average GPA (maximum 4.00)	3.63	3.76	3.81
College Type (small college/research university)	13/10	10/14	6/18
Undergraduate Major			
Chemistry	17	19	16
Physics	1	1	1
Dual Chemistry/Physics	0	1	3
Chemical/Nuclear Engineering	4	2	2
Biochemistry/Biophysics	1	1	2
Completed Applications	55	80	119

Program objectives for 2011-2013:

- Provide an optimal Summer Schools experience for participating undergraduates. It is crucial to provide a quality educational program, while at the same time generating excitement and espousing the long-term prospects for career pathways in nuclear science and technology.
- Continue to disseminate Summer Schools recruiting materials to a broad undergraduate audience. Information regarding the program was distributed electronically this year to NUCL members, reference writers for former Summer School applicants, chemistry and physics department administrators, and ACS student affiliate chapters and advisors. Announcements of the program were also distributed to undergraduate list servers. Competition with other summer programs is increasing, and it is imperative to reach as many interested and accomplished students as possible.
- Maintain the alumni database that is posted on the Summer Schools website. The students who attended the 2010 Summer Schools and ultimately decide to pursue a career in nuclear chemistry or technology will not appear in the U.S. DOE workforce for 7-10 years. Career tracking is important to judge the success of the program.
- Transition program leadership. Prof. Dave Robertson (University of Missouri, Columbia) will assume the National Director position with the completion of the 2011 Summer Schools. This will also be Dr. Louis Pena's first year as Site Director at Brookhaven National Laboratory. The Summer Schools program is a shared responsibility among many individuals, and keeping all participants informed, engaged, and focused on program goals is critical to its continued success.

Publications supported by this project 2009-2011

None to report

Session 5 – Forensics and Characterization

The Science Behind Modern Day Nuclear Forensic Analysis: Definition, Importance, and Example

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The first portion of this presentation will be spent defining terms and describing the application of nuclear forensic analysis as a tool for combating nuclear proliferation and terrorism. The latter half of this talk will focus on developments in the science behind modern day nuclear forensics using a real world sample of opportunity. During World War II, the Hanford Site in Washington became the location for U.S. plutonium production. In 2004, a bottle containing a sample of plutonium was recovered from a Hanford waste trench. Here, state-of-the-art instrumental analyses, reactor model simulations, and investigative science techniques were used to provide insights as to the origin of this unknown sample, a process collectively termed as nuclear archeology. Isotopic age dating conducted on the sample in 2007 indicated the sample was separated from the spent fuel roughly 60 years earlier. The isotope ^{22}Na, a detectable product of a secondary nuclear reaction, proved useful as a powerful tool for nuclear forensic analysis as (1) an easily detectable signifier of the presence of alpha emitting actinides, (2) an indicator of sample splitting, and (3) a measure of the time since sample splitting. Analytical results of minor actinide isotopes and reactor model simulations confirmed the material originated from the X-10 reactor in Oak Ridge, TN. Corroborated by historical documents, we concluded this sample was part of the first batch of Pu separated at T-Plant, Hanford, the world's first industrial-scale reprocessing facility, on December 9, 1944. This sample represents the oldest known collection of reactor-produced Pu in the world.

Matrix Infrared Spectroscopic and Computational Investigations of Novel Small Uranium Containing Molecules

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Overall research goals: Matrix infrared spectroscopic and density functional computational investigations on new small molecules containing uranium, thorium and lanthanide atoms.

Significant achievements during 2009-2011: Laser evaporation of carbon rich uranium/carbon alloy targets into condensing argon or neon matrix samples gives weak infrared absorptions that increase on annealing, which can be assigned to new uranium carbon bearing species. New bands at 827.6 cm^{-1} in solid argon or 871.7 cm^{-1} in neon become doublets with mixed carbon 12 and 13 isotopes and exhibit the 1.0381 carbon isotopic frequency ratio for the UC diatomic molecule. Another new band at 891.4 cm^{-1} in argon gives a three-band mixed isotopic spectrum with the 1.0366 carbon isotopic frequency ratio, which is characteristic of the anti-symmetric stretching vibration of a linear CUC molecule. No evidence was found for the more stable cyclic U(CC) isomer. Other bands at 798.6 and 544.0 cm^{-1} are identified as UCH, which has a uranium-carbon triple bond similar to that in UC. Evidence is found for bicyclic $U(CC)_2$. This work shows that U and C atoms react spontaneously to form the uranium carbide U≡C and C≡U≡C molecules with uranium-carbon triple bonds.

Laser-ablated lanthanide metal atoms were condensed with CH_2F_2 in excess argon at 6 K or neon at 4 K. New infrared absorption bands are assigned to the oxidative addition product methylene lanthanide difluorides on the basis of deuterium substitution and vibrational frequency calculations with density functional theory (DFT). Two dominant absorptions in the 500 cm^{-1} region are identified as lanthanide-fluoride stretching modes for this very strong infrared absorption. The predominantly lanthanide–carbon stretching modes follow a similar trend of increasing with metal size and have characteristic 30 cm^{-1} deuterium and 14 cm^{-1} ^{13}C isotopic shifts. The electronic structure calculations show that these CH_2LnF_2 complexes are not analogous to the simple transition and actinide metal methylidenes with metal–carbon double bonds that have been investigated previously: the lanthanide metals (in the +2 or +3 oxidation state) do not appear to form a π-type bond with the CH_2 group. The DFT and *ab initio* correlated molecular orbital theory calculations predict that these complexes exist as multi-radicals, with a Ln-C σ bond and a single electron on C-2p weakly coupled with f^x (x = 1 (Ce), 2 (Pr), 3(Nd), etc.) electrons in the adjacent Ln-4f orbitals. The Ln-C σ bond is composed of about 15% Ln-5d,6s and 85% C-sp^2 hybrid orbital. The Ln-F bonds are almost purely ionic. Accordingly, the argon-neon matrix shifts are large (13-16 cm^{-1}) for the ionic Ln-F bond stretching modes and small (~1 cm^{-1}) for the more covalent Ln-C bond stretching modes.

Reactions of laser-ablated U atoms with N_2 and H_2 mixtures upon co-deposition in excess argon at 5 K gave strong NUN and weak UN infrared absorptions and new bands at 3349.7, 966.9, 752.4, and 433.0 cm^{-1} for the unusual new U(V) molecule N≡U=N−H, uranimine nitride, containing both triple and double bonds. This identification is based on D and ^{15}N isotopic substitution and comparison with frequencies computed by density functional theory for the $^2\Delta$ ground state NUNH. Calculated bond lengths are compared to those of the $^1\Sigma_g^+$ ground state of U(VI) uranium dinitride N≡U≡N, the $^2\Phi$ ground state of the isoelectronic nitride oxide N≡U=O, and the ^{3}A ground state of the U(IV) uranimine dihydride HN=UH_2 molecule, which have all been prepared in solid argon matrices. Mulliken bond orders based on the CASSCF orbitals for N≡U=N−H are 2.91, 2.19, and 1.05, respectively. Here the terminal nitride is effectively a triple bond just as found for N≡U≡N. The solid argon matrix is a convenient medium to isolate reactive terminal uranium nitrides for examination of their spectroscopic properties.

Objectives for 2011-2012. Complete the reactions of U, Th and Ln metal atoms with methanol and dimethyl ether. The $CH_3U(O)H$ and $(CH_3)_2UO$ molecules will be prepared and compared to the H_2UO product from the water reaction.

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Spectroscopic Studies of Prototype Actinide Compounds

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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 2009-2011: Ionization of both ThO and HfO reduces the bond energies. Paradoxically, the vibrational frequencies increase and the bond lengths shorten. We have further explored this trend by applying pulsed field ionization - zero electron kinetic energy (PFI-ZEKE) spectroscopy to characterize HfS^+. Data for the $X^2\Sigma^+$ ground state defined an ionization energy (IE) of 61934 cm^{-1}, vibrational constants ω_e=555.0, $\omega_e x_e$=1.415 cm^{-1} and a rotational constant of B_0=0.13 cm^{-1}. Ionization reduced the bond energy by 6886 cm^{-1}, whereas the vibrational and rotational constants both increased, following the behavior of HfO and ThO. High-level theoretical calculations (CCSD(T) with QZ quality basis sets) yielded predictions for HfS^+ that were in reasonably good agreement with the measurements. Data were also obtained for the low-lying $^2\Delta_{3/2}$ state (T_e=5267, ω_e=529.4 and $\omega_e x_e$=1.579 cm^{-1}). The characteristics of this state are consistent with the ligand field theory prediction that the first electronically excited state correlates with $Hf^{2+}(6d\delta)S^{2-}$.

It has been recognized that the low-lying $^3\Delta_1$ state of HfF^+ is suitable for investigation of the electric dipole moment of the electron (eEDM, a manifestation of CP-violation). Experimental data for HfF^+ have not been reported previously, and we have obtained the first spectroscopic constants for this ion. Rotationally resolved spectra were obtained for the $X^1\Sigma^+$, $^3\Delta_1$, $^3\Delta_2$ and $^3\Delta_3$ states. The IE was found to be 59464 cm^{-1}, indicative of a weakening of the bond by 4416 cm^{-1} on ionization. Molecular constants for HfF^+ are listed in Table 1.

Table 1. Molecular constants for HfF^+

	$X^1\Sigma^+$	$^3\Delta_1$	$^3\Delta_2$	$^3\Delta_3$
T_0	0.0	978.0(10)	2151.7(10)	3935.9(10)
ω_e	791.2(5)	761.3(10)	762.3(10)	[761.5(5)]
$\omega_e x_e$	2.95(10)	2.18(25)	2.88(25)	-
B_0	0.304(5)	0.301(5)	0.300(5)	0.308(5)

The isoelectonic actinide

molecule ThF^+ is of interest from the perspectives of its bonding and potential for eEDM studies. Prior to the work repoted here, there were no spectrocopic observations of ThF or ThF^+. As a first step towards charaterizing both species, we have recorded laser induced fluorescence and multiphoton ionization spectra for ThF. Several electronic tarnsitions have been identified in the 19200-20500 cm^{-1} range. Fig. 1 shows the rotational structure for one of the stronger feaures. The ground state is identified as X $^2\Delta_{3/2}$, as expected by analogy with HfF, with a rotational constant of B_0=0.2304 cm^{-1}. Measurements for the ion are in progress.

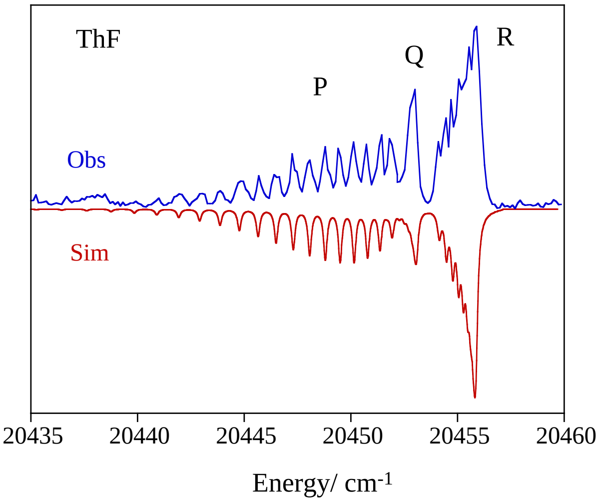

Fig. 1 Laser induced fluorescence spectrum of ThF

In collaboration with Prof. Steimle we used the optical Stark spectrum of the $E(0^+)–X^1\Sigma^+$ (1,0) band of thorium monoxide, ThO, to determine the permanent electric dipole moments for the $E(0^+)$ (v=1) and $X^1\Sigma^+$(v=0) states. Values of 2.782±0.012 D (X) and 3.534±0.010 D (E) were obtained. The experimental results were used to assess the quality of recent electronic structure calculations for the $X^1\Sigma^+$ (v=0) state.

Science objectives for 2011-2013: Over the next two years we will characterize the diatomic species MX and MX^+ for M=Th, U and X=F, H. These data are important for the evaluation of relativistic basis sets and ligand field theory models. Photodetachment spectroscopy of mass selected anions will be the second major focus. We are currently developing a system that will achieve sub-wavenumber resolution using the technique of slow electron velocity map imaging. This instrument will be used to characterize actinide metal dimers, clusters, and organo-metallic complexes.

Publications supported by this project

[1] F. Wang, A. Le, T. C. Steimle, and M. C. Heaven, J. Chem. Phys. 134, 031102/1 (2011). *"Communication: The permanent electric dipole moment of thorium monoxide, ThO"*

[2] M. C. Heaven, J. K. Gibson, and J. Marcalo, in The chemistry of the actinide and transactinide elements, edited by L. R. Morss, N. M. Edelstein, and J. Fuger (Springer, 2010), Vol. 6, pp. 4079. *" Molecular spectroscopy and reactions of the actinides in the gas phase and cryogenic matrices "*

[3] H. Stoll, K. A. Peterson, J. M. Merritt, and M. C. Heaven, J. Phys. Chem. A 113, 12353 (2009). *"On the Ionization Energy of HfO"*

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Session 6 – Electronic Structure, Characterization

X-ray Studies of Liquid-Liquid Interfaces as Model Solvent Extraction Systems

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Overall research goals: The objective of this project is to use x-ray surface scattering, surface sensitive x-ray fluorescence, and other relevant techniques to determine the interfacial structure at liquid-liquid interfaces under conditions that provide insight into the process of solvent extraction.

Significant achievements during 2009-2011: We have used x-ray reflectivity, x-ray fluorescence, and interfacial tensiometry to probe the aqueous-organic (liquid-liquid) interface between aqueous solutions (with and without $ErCl_3$) and dodecane solutions (with and without an extractant – HDEHP – or a surfactant – DHDP – that have similar phosphate headgroups). HDEHP is bis(2-ethylhexyl)-phosphate and DHDP is di-hexadecyl-phosphate. Two significant results have emerged:

1. We have developed a method to quantitatively measure and analyze x-ray fluorescence from the liquid-liquid interface for the purpose of quantifying the presence of specific ions at the liquid-liquid interface.

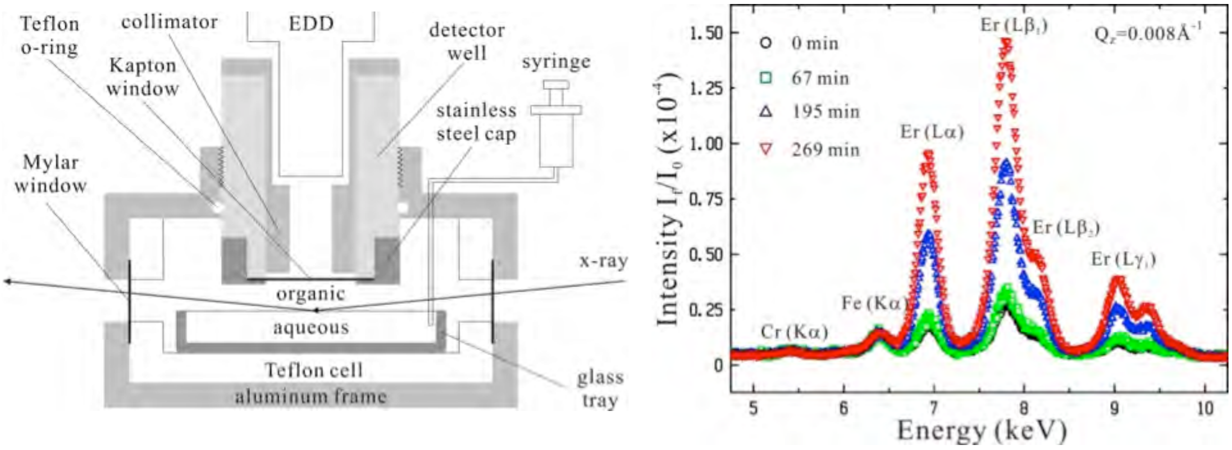

Figure 1. Left: New sample cell for the quantitative measurement of x-ray fluorescence from liquid-liquid interfaces (EDD is the energy dispersive detector). Right: Example of fluorescence data from the dodecane-water interface with $ErCl_3$ in the water and HDEHP extractant in the dodecane that shows the time dependence of crud formation at the interface.

2. Preliminary x-ray reflectivity and fluorescence results indicate that a monolayer of DHDP forms at the liquid-liquid interface between pure water and a dodecane solution of DHDP, but addition of $ErCl_3$ to the water will stabilize the formation of an inverted bilayer of DHDP at the liquid-liquid interface (see Figure 2). If confirmed, this unexpected result provides insight into the mechanism of Er^{3+} ion transfer across the aqueous-organic interface.

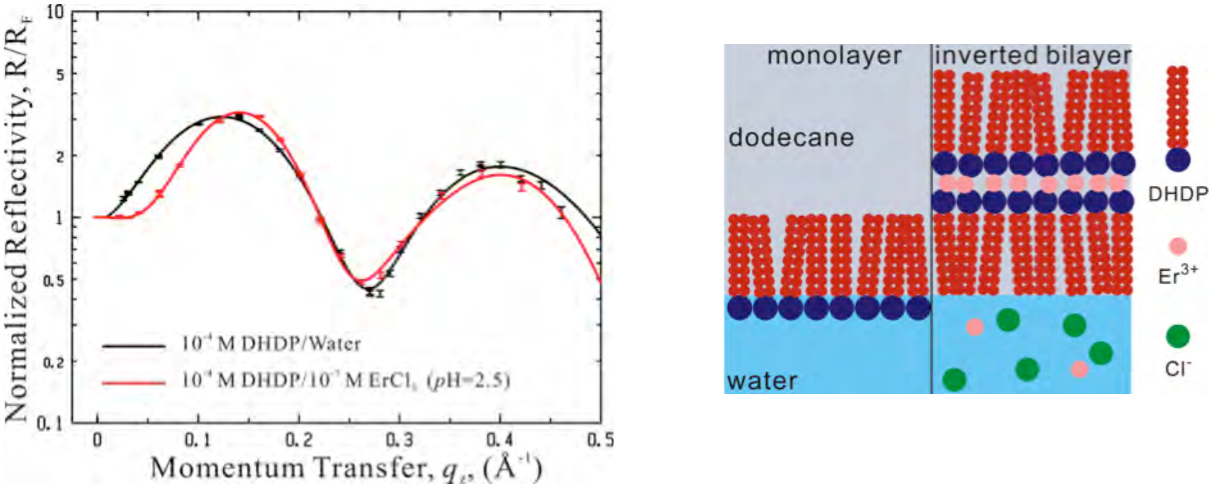

Figure 2. Left: X-ray reflectivity that indicates the formation of a monolayer (black line, without $ErCl_3$) and an inverted bilayer (red line, with $ErCl_3$). Right: cartoon of the monolayer and inverted bilayer structure.

Science objectives for 2011-2013:

- Confirm formation of inverted bilayer of DHDP. Test for inverted bilayer formation in shorter chain analogs of DHDP that approach a size that is typical of industrially relevant extractants with phosphate headgroups (such as HDEHP).
- Determine if DHDP acts as an extractant above its adsorption transition temperature. If so, measure the variation of the interfacial structure with temperature as the system undergoes a transition from surfactant to extractant behavior.
- Characterize the ionic composition in the headgroup region of the inverted bilayer. Experiments with $ErBr_3$, instead of $ErCl_3$, will determine if the anion is also in the headgroup region of the inverted bilayer.

Publications supported by this project 2009-2011

1. Wei Bu, Binyang Hou, Miroslav Mihaylov, Ivan Kuzmenko, Binhua Lin, Mati Meron, L. Soderholm, Guangming Luo, and Mark L. Schlossman, *X-ray fluorescence from a model liquid/liquid solvent extraction system*, submitted to the Journal of Applied Physics (2011).

Trends in Orbital Mixing for Actinide-Ligand Bonds.

Presenting; Stosh A. Kozimor
Principal Investigator; David Clark;
Co-authors; Kevin S. Boland, Enrique R. Batista; Steven D. Conradson, Scott R. Daly, Andrew J. Gaunt, Jason M. Keith, Richard L. Martin, Iain May, Stefan G. Minasian, Gregory L. Wagner, Marianne P. Wilkerson.

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Abstract. This presentation will focus on quantifying orbital mixing in metal-ligand bonding in transition metal, lanthanide, and actinide complexes. Theoretical and spectroscopic studies indicate that variations in orbital character and differing contributions of metal *d*- or *f*-orbital covalency are connected with changes in chemical reactivity. Of the experimental approaches to determine covalency, ligand K-edge X-ray Absorption Spectroscopy (XAS) has emerged as a powerful measure of the amount of ligand orbital mixing with metal-based orbitals. On the low energy side of the ligand K-edge are bound state transitions of ligand 1*s* electrons into metal-based orbitals that contain ligand *p* character due to covalent mixing. The intensity of these pre-edge features is directly related to the metal-ligand mixing coefficient, and provides a direct experimental probe of covalency in bonding.

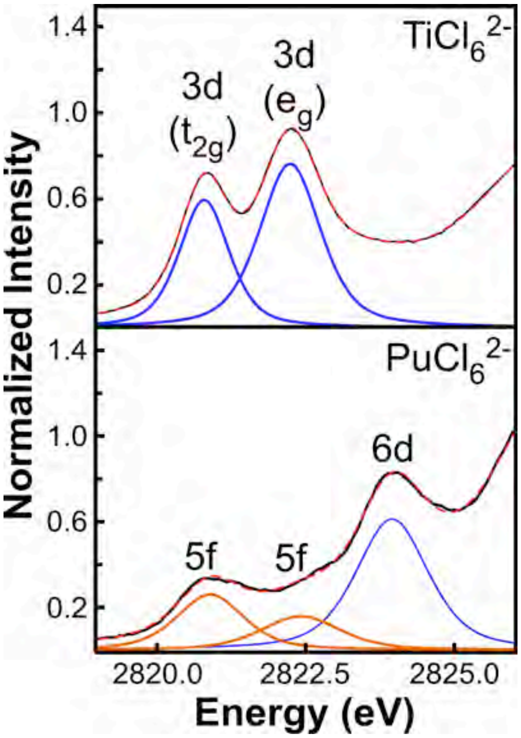

Fig 1. Cl K-edge XAS spectra for $MCl_6(PPh_4)_2$ (M = Ti, *top*; Pu *bottom*).

Preliminary efforts have involved developing the use of ligand K-edge XAS spectroscopy and hybrid density functional theory (DFT) calculations to evaluate orbital mixing and electronic structure in a series of simple octahedral transition metal (Ti, Zr, Hf) salts, MCl_6^{2-}. These studies have focused on assessing the relative trends in orbital mixing between 3*d*, 4*d*, and 5*d* elements. Expectations from group theory and electronic structure calculations indicate the predominant covalent interactions will occur through M-Cl bonding via t_{2g} and e_g interactions with M n*d* orbitals. For the Cl K-edge data, Fig 1, we find bound state transitions from Cl 1s to e_g (σ^*), and t_{2g} (π^*) orbitals that fulfill these expectations. Analyses of these highly symmetric d^0-complexes provide a foundation for evaluating actinide systems, $AnCl_6^{2-}$ (An = Th, U, Np, and Pu), where more complicated spectra were obtained due to significant contributions to orbital mixing from both 5*f*- and 6*d*-orbitals.

Presented here are results from a new effort to expand the use of ligand K-edge XAS spectroscopy and electronic structure calculations in evaluating systems that contain actinide bonds for ligands other than Cl. Specifically, we use an analogous "build-up approach" to interpret An-O K-edge XAS spectra, which involves using highly symmetric d^0-complexes to provide insight for actinide compounds. In summary, this contribution expands on our the initial Cl K-edge XAS work and focuses on understanding how orbital mixing varies in actinide-chloride vs. oxo ligand bonding.

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

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-chalcogen vs actinide-chlorine 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 2009-2011

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Computational studies of NMR chemical shifts in open-shell actinide and lanthanide systems

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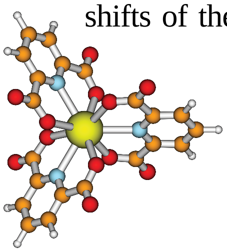
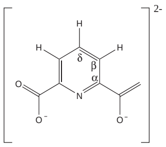
Overall research goals: The main objective of this project is to develop and apply new theoretical methods for the computation of ligand paramagnetic NMR (pNMR) chemical shifts in lanthanide and actinide complexes with unpaired electrons using a density functional theory (DFT) framework. The project goals include developments to enable relativistic DFT computations of all required pNMR spectroscopic parameters with the NWChem quantum chemistry package (now open source), along with additional developments using the Amsterdam Density Functional (ADF) package. Both codes are widely used for computations on lanthanide and actinide species.

Significant achievements during 2009-2011: The project took off in late autumn of 2009 after the hire of Dr. Aquino (Nov. 2009) and the recruitment of graduate student Ben Pritchard (Jan 2010). During the course of the past 15 months we have gained experience with the challenges of accurately modeling pNMR chemical shifts in systems with heavy atoms, and we have laid the foundations for the method developments in NWChem. Specifically,

1. To a first approximation, two of the 'ingredients' for pNMR ligand shifts are the *g*-tensor and the ligand hyperfine tensor (*A*-tensor) (Patchkovskii, 2003). We performed calculations of *g*-tensors in AnX_6 (An=U,Np, X=F,Cl) systems with one unpaired electron which showed that an available first-order derivative spin-orbit method in ADF has difficulties assigning the sign of the *g*-tensor components. This, and the lack of hybrid functional support in the first-order method prompted us to develop an alternative second-derivative hybrid DFT approach starting from a spin-free reference. We showed that for NpF_6 this method predicts the accepted negative sign of *g* [1]. In a follow-up publication [2] it was shown that hybrid DFT offers significant improvements for the fluorine hyperfine coupling in this system and several other members of our benchmark set of molecules with light and heavy atoms. The *A*-tensor code incorporates a finite nucleus model.

2. The new methods developed for *g*- and *A*-tensors [1,2] were used to calculate pNMR chemical shifts of the Ce(III) DPA complex shown on the left [1]. Comparison with calculated and experimental data for analogous La and Ce systems showed that the approach is able to discern the paramagnetic effects on the ligand NMR shifts for such systems where the spin density is well localized on the metal center. We also investigated pNMR contact and pseudo-contact shifts in a set of Ru(III) benchmark systems [2] to further validate the methods.

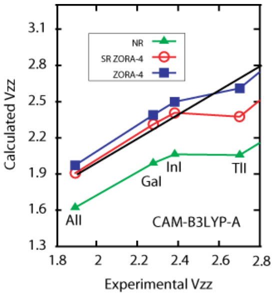




3. All-electron scalar relativistic NMR chemical shift DFT computations using the ZORA relativistic Hamiltonian have been implemented in NWChem. The code is ready for production as of Jan. 2011. A corresponding ZORA method for *g*-tensors has been implemented and is currently in the debugging stage. A manuscript is in preparation [3].

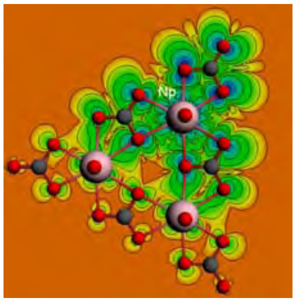
4. ZORA relativistic DFT calculations of magnetic shielding, *g*-, and *A*-tensors with ZORA require accurate numerical integration of the perturbation operator matrix elements. The numerical integral code is the foundation of such calculations and therefore we validated it carefully. For this purpose,

we conducted a relativistic DFT benchmark study [4] of heavy atom electric field gradients (EFGs). The EFG is a first-order property for which the operators have an inverse nuclear distance dependence similar to the operators relevant to NMR. A particular focus of this work have been effects from spin-orbit coupling (shown on the right for group 13 iodides), and localized orbital analyses of EFGs aimed at rationalizing ligand effects on uranium EFGs in uranyl complexes. Computed EFGs are also needed in later stages of the project in order to estimate NMR line broadening effects due to nuclear quadrupole coupling.



Science objectives for 2011-2013:

From the experience gained so far in the project, thermal averaging over low lying excited states appears to be crucial for a successful modeling of pNMR ligand shifts in actinide species. Testing of 'average-of-configurations' approaches will commence after the methods reported in [1,2] are extended to handle fractional orbital occupations (currently under development). Over the last months we have developed a DFT based spin-orbit ZORA complete active space (CAS) type program along the lines of DFT-CI work by Grimme & Waletzke and Marian & Fleig. Significant additional developments are needed to obtain the *g*- and *A*-tensors from this approach; in particular we need to pay attention to describing spin polarization on the ligands. The figure shows a plot of the calculated ground state noncollinear spin density for a mixed 2:1 uranyl neptunyl carbonate complex studied by our experimental collaborator Bruce McNamara (view along the O-An-O directions). The relative spin density magnitudes clearly support the experimental assignment of the carbon shifts. For accurate predictions of these shifts we need to consider the spin density distribution at finite temperatures.



Graduate student K. Sutter has just completed an implementation for Madelung potentials in ADF. We will use this method to set up embedded cluster models for La and Ce monazite crystals and calculate pNMR effects for the ^{31}P chemical shifts in these systems using the methods described in [1,2]. Thibault Charpentier (CEA, France) uses such systems as non-radioactive substitutes to study nuclear waste forms by NMR, but little is known about how to interpret paramagnetic effects in the NMR spectra of these systems.

Relativistic DFT developments in NWChem for *A*-tensors and nuclear shielding tensor calculations with spin-orbit coupling are needed to be able to employ the newest density functionals available in NWChem for the project. We will also develop localized orbital analysis methods for these properties, similar to those developed for the EFG study [4], to help interpreting the results in chemically intuitive terms.

Publications supported by this project 2009-2011

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SISGR: Understanding Actinide Aggregation

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Overall research goals: The objective of this research is to develop a fundamental understanding of actinide-aggregate formation under conditions that promote hydrolysis. Specifically, we are developing a molecular-level comprehension of nanoaggregate species in terms of their structures, stabilities, formation reactions, and surface reactivities. Inspiring this work is the need to develop new separations strategies for next generation nuclear fuels that are better able to remove stable metal aggregates without the need for extreme solution conditions.

Significant achievements during 2009-2011: Efforts are well underway to probe clusters forming under solution conditions that favor hydrolysis. Synthetic studies in aqueous Th solutions have resulted in a variety of interesting structures that point to a competition between oxalation reactions (M-OH + OH-M → M-O-M + H_2O) leading to the direct formation of Th-O-Th bonds, and olation reactions (M-OH + M-(H_2O) → M-OH-M + H_2O), the condensation of Th hydroxide species to yield hydroxo bridged Th oligomers. In addition, a condensation reaction is possible in which two H_2O molecules are eliminated. Among the results is the crystal structure of a hexanuclear $[Th_6(OH)_4O_4]^{12+}$ core decorated by twelve monochloroacetate ligands, as shown in Figure 1. Extensive modeling studies are underway of the core Th_6 polyhedron for a broad range of possible terminations at the Th and for different protonation states of the Th-O-Th bridges. The proton nmr shifts of the bridging OH have been calculated to aid in experimental design as have vibrational frequencies. The acidities of the model $Th_6(OH)_4O_4O_6$ complex have been calculated and these complexes are predicted to be very strong gas phase acids with acidities in the range of 250 to 270 kcal/mol.

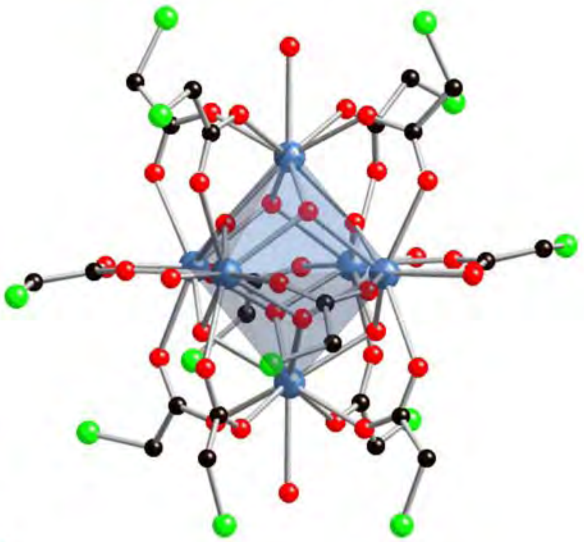

Figure 1. $[Th_6(OH)_4O_4]^{12+}$ core (blue polyhedron) decorated by twelve monochloroacetate ligands in **2**. Blue spheres are Th(IV) atoms. Red, black and green spheres represent the oxygen, carbon and chlorine atoms, respectively, of the R-COO$^-$ ligands (R = CH_2Cl)

The initial reactions for all three types have been studied using density functional theory and self consistent reaction field approaches for the metal cations Be^{2+}, Mg^{+2}, Ca^{2+}, Sr^{2+}, Zn^{+2}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, and Mn^{2+}, as well as UO_2^{2+} as a precursor to studying the Th reactions. Many different types of structures were found as internal proton transfer reactions, water transfer among ions and movement of water into the second solvation shell were all found in the optimized structures. In very few cases was the actual simple structure expected from simple bonding ideas found. The types of reactions that are most favored thermodynamically also change as the cation size changes.

The condensation of ThO_2 to form $(ThO_2)_n$ nanoclusters has been studied for up to n = 6 as have the initial hydrolysis reactions of the clusters. This effort builds on our work on the structure and energetics of nanoclusters of the group 4 and group 6 transition metal dioxides $(MO_2)_n$ for M = Ti, Zr, and Hf and trioxides $(MO_3)_n$ for M = Cr, Mo, and W sponsored by DOE BES in the catalysis program. The heats of formation of the clusters have been reliably calculated based on normalized clustering energies and the energy of ThO_2 which has been validated from CCDS(T) calculations with a large basis set. These are first reliable thermodynamic predictions for these species. The clustering energies are converging slowly to the bulk value than do the transition metal oxides. The average water binding energy for physisorption is ~ 18 kcal/mol for thorium oxide clusters. On the basis of our work on water binding to $(TiO_2)_n$ nanoclusters, this provides the first good estimate for the physisorption energy of water onto thorium oxide surfaces. An approach to the accurate prediction of the energetics of actinide compounds has been developed on the basis of CCSD(T) calculations with large basis sets and pseudo isodesomic reactions using the energies of transition metal oxides.

Science objectives for 2011-2013:

- Hypothesizing that the increasing metal-ion hardness seen with increasing atomic number, resulting from the actinide contraction, will be sufficient to demonstrably favor oxolation reactions for the heavier ions, we will extend the current work on Th to heavier tetravalent actinides, notably Pu^{4+}.
- Study oxolation, olation, and condensation reactions for An^{4+} for An = Th, U, and Pu.
- Study AnO_2 clusters and hydrolysis reactions for An = U and Pu.
- Support experimental efforts in terms of modeling larger clusters with counterions.

Publications supported by this project 2010-2011

1. "Thorium(IV) Molecular Clusters with a Hexanuclear Core," K E. Knope, R E. Wilson, L. Soderholm, M. Vasiliu, and D. A. Dixon, in preparation for *Inorg. Chem.*
2. "Reliable Predictions of the Thermodynamic Properties of Actinide Oxides and Fluorides," K. S. Thanthiriwatte, S. Li, and D. A. Dixon, in preparation for *J. Phys. Chem. A*
3. "Clustering and Hydrolysis Reactions of $(ThO_2)_n$ Nanoclusters," V. E. Jackson, R. Flamerich, N. Corbin, D. A. Dixon, and L. Soderholm, in preparation for *Inorg. Chem.*
4. "Oxolation, Olation, and Condensation Reactions of Group IIB Metal Cations," V. E. Jackson, S. Walker, D. A. Dixon, and L. Soderholm, in preparation for *Inorg. Chem.*
5. "Oxolation, Olation, and Condensation Reactions of Transition Metal Cations," V. E. Jackson, S. Walker, D. A. Dixon, and L. Soderholm, in preparation for *Inorg. Chem.*

Session 7 – Theory and Characterization

Actinide Coordination Chemistry: From Solution to the Gas Phase

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Collaborators: M. C. Michelini (U. Calabria, Italy); J. Marçalo (Instituto Tecnológico e Nuclear, Portugal); C. J. Marsden (U. Paul Sabatier, France); M. J. Van Stipdonk (Wichita State U.)

Overall Research Goals: To explore actinide chemistry at a fundamental level in the gas phase by ion reactivity and dissociation; to elucidate condensed phase actinide chemistry by transfer of species from solution to gas; to provide a basis to develop/validate actinide molecular theory.

Significant achievements during 2009-2011

- Electrospray ionization mass spectrometry (ESI/MS) of PuO_2^{2+} produced $Pu^{VI}O_2^{2+}(L)_n(g)$ (L = acetone or acetonitrile; n = 4-6). Collision induced dissociation (CID) gas-phase chemistry included hydrolysis of $Pu^{VI}O_2^{2+}$ to $Pu^{IV}(OH)_3^+$ (Figure 1), providing a probe of mechanisms.

- Kinetics and terminal degree of gas-phase hydration of lanthanide hydroxide/halide cations, LnX_2^+, $LnX(OH)^+$ and $Ln(OH)_2^+$, correlate with DFT computed hydrate structures/energetics.

- Hydration of AnO_2^+ and $AnO_2(OH)^+$ ions produced $AnO_2^+(H_2O)_x$ and $AnO_2(OH)^+(H_2O)_y$ (An = U, Np, Pu). DFT indicated that x = 4 and y = 3 correspond to terminal inner-shell hydrates: disparities between gas and solution hydration reveal secondary coordination effects.

- Anionic lanthanide chloride clusters, $Ln_nCl_{(3n+1)}^-$, exhibited high-stability compositions, n = 4, 5 or 6; stability variations across the series were correlated with DFT structures and energetics.

- Gas-phase thermochemistry of elementary actinide monosulfides, AnS where An = Th, Pa, U, Np, Pu, Am or Cm, were investigated by experiment and theory to elucidate actinide bonding.

- Reactions of Th^{2+} and U^{2+} with small alkanes were studied in detail by experiment and theory, revealing that DFT is capable of providing reliable potential energy pathways for such reactions.

- Bare US_2^{2+} was synthesized as potential "thio-uranyl". DFT is being employed to determine if this species does indeed correspond to linear $\{S{=}U{=}S\}^{2+}$, "thio-uranyl".

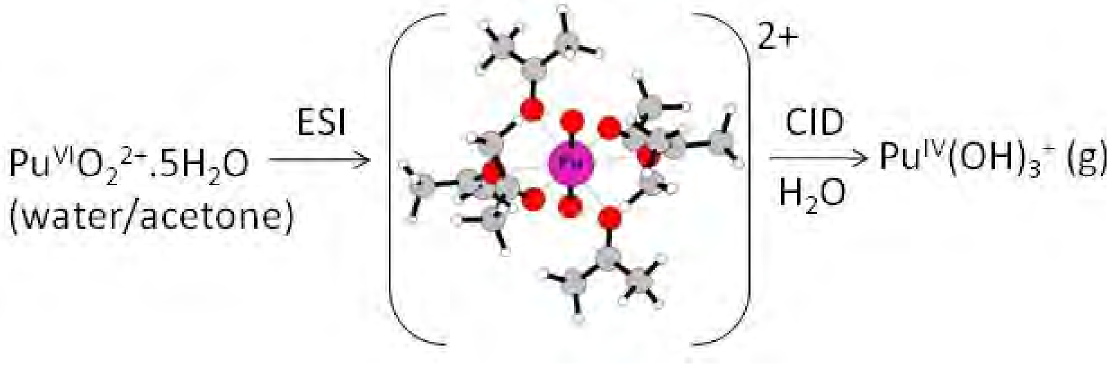

Figure 1. Solution $Pu^{VI}O_2^{2+}\cdot 5H_2O$ to gas $Pu^{VI}O_2^{2+}\cdot 6[CH_3COCH_3]$; ensuing gas hydrolysis to $Pu^{IV}(OH)_3^+$.

Science objectives for 2011-2013

• Transfer of actinyl ions from solution to gas as coordinated $AnO_2^{2+}(L)_n$ and $AnO^+(L)_n$; and gas-phase ligand-exchange: $AnO_2^{+/2+}(L)_n + L' \rightarrow AnO_2^{+/2+}(L)_{n-1}(L') + L$. Probe actinyl ion-ligand interactions as a function of ligand basicity, dipole moment, polarizability, ionization energy, etc.

• Reactions and DFT of uranium oxide clusters, $U_nO_m^-$ (n = 2-14; m = 6-35) with model reaction substrates, such as methanol, to probe the transition from molecular to interfacial chemistry.

• Multiply-charged actinide complexes from solution to gas; characterization by reactivity, dissociation and electron capture. Focus on actinide ions which exist in solution, such as AnO_2^{2+} and $Th(OH)_n^{(4-n)+}$. Goals include understanding solution speciation and reaction mechanisms.

• Explore actinide-transition metal (An-M) bonding: gaseous AnM^+ bimetallic ions will be synthesized, and characterized by reactivity and dissociation.

• Actinyl oxygen exchange and activation of An=O bonds in the gas phase: effects of hydroxyl ligands; weakening of the An=O bonds from U to Np to Pu; non-covalent coordination; etc.

• ESI/MS and MALDI/MS to study growth of U, Np and Pu oxide/hydroxide clusters; also, examine cluster structures and chemistry in the gas phase by CID and reactivity.

Publications supported by this project 2009-2011

1. D. Rios, P.X. Rutkowski, M.J. Van Stipdonk, J.K. Gibson “Gas-Phase Coordination Complexes of Dipositive Plutonyl and Uranyl Ions”, Submitted to Inorg. Chem. (2011).
2. P.X. Rutkowski, M.C. Michelini, T.H. Bray, N.Russo, J. Marçalo, J.K. Gibson “Hydration of gas-phase ytterbium ion complexes studied by experiment and theory”, Theor. Chem. Acc., In press (2011).
3. E. Di Santo, M. Santos, M.C. Michelini, J. Marçalo, N. Russo, J.K. Gibson, “Gas-phase reactions of the bare Th^{2+} and U^{2+} ions with small alkanes, CH_4, C_2H_6 and C_3H_8: An experimental and theoretical study of elementary organoactinide chemistry”, J. Am. Chem. Soc., ASAP online 01/25/2011.
4. T. H. Bray, R. Copping, D. K. Shuh, J. K. Gibson “Electrospray ionization mass spectrometry of a cerium(III) phosphomolybdate complex: Condensed and gas-phase cluster chemistry”, Int. J. Mass Spectrom. 299 (2010) 35-46.
5. C. Pereira, J. Marçalo, J.K. Gibson, “Thermochemistry of Elementary Actinide Sulfide Molecules: A Gas-Phase Study of Curium Sulfide” In MRS Symposium Series vol. 1264 (2010), pp. 37-42.
6. T.H. Bray, R. Copping, D.K. Shuh, J.K. Gibson, “Electrospray Ionization Mass Spectrometry of the Cerium(III)-Phosphomolybdate Complex $(NH_4)_{11}Ce(PMo_{11}O_{39})_2$” ibid, pp. 29-35.
7. I. Infante, A. Kovacs, G. La Macchia, A. R. M. Shahi, J.K. Gibson, L. Gagliardi, “Ionization energies along the actinide oxides series, from thorium to curium: theory versus experiment”, J. Phys. Chem. A 114 (2010) 6007-6015.
8. M.C. Michelini, J. Marçalo, N. Russo, J.K. Gibson, “Gas-phase reactions of uranate ions, UO_2^-, UO_3^-, UO_4^- and UO_4H^-, with methanol: A convergence of experiment and theory”, Inorg. Chem. 49 (2010) 3836-3850.
9. M.C. Heaven, J.K. Gibson, J. Marçalo, “Molecular spectroscopy and reactions of actinides in the gas phase and cryogenic matrices”, Chemistry of the Actinide and Transactinide Elements, 4th edition, L. Morss, N.M. Edelstein, J. Fuger, Eds., 2010, Springer: Dordrecht.
10. J. Marçalo, J.K. Gibson, “Gas-phase thermodynamics of actinide oxides-an assessment of neutral and cationic monoxides and dioxides from thorium to curium”, J. Phys. Chem. A 113 (2009) 12599-12606
11. J. Marçalo, M. Santos, A. Pires de Matos, J.K. Gibson "Molecular uranates - laser synthesis of uranium oxide anions in the gas phase", Inorg. Chem. 48 (2009) 5055-5057.

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

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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

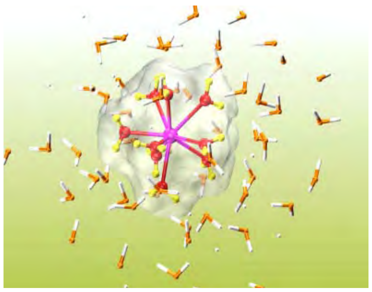
Overall research goals: The goal of our program is to develop a fundamental understanding of the influence of the local molecular environment on the oxidation state of actinides, on the speciation of actinides in solution environments, and the adsorption and reduction of these actinides on mineral surfaces, 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 2009-2011: The project has made significant progress in modeling actinides in solution and interacting with surfaces, and multiple collaborations have been developed.

1. The adsorption and energetics of microsolvated uranyl dication species, $UO_2(H_2O)_n^{2+}$, were determined on fully hydroxylated and proton-deficient α-alumina(0001)-like finite cluster models. Energetics computed from the difference between the optimized structures and the appropriate reference states point to a preference for an inner-sphere type complex. Based on these observations, we can say that in acidic environments (low pH) the inner-sphere sorption mechanism will be more favorable. In neutral or more basic environments, the inner-sphere mechanism is also the prevalent one, although monodentate complexes are likely to yield outer-sphere complexes of uranium trioxide. This work appeared on the cover of JPCA. We also performed full *ab-initio* dynamics simulations using periodic systems and potential of mean force simulations, and the results are generally consistent with the findings of the cluster simulations.

JPCA (2011) cover.

2. The solvent shell structure of the trivalent Curium ion (Cm^{3+}) in aqueous solution was studied using three simulation protocols: *ab initio*, classical molecular dynamics, and quantum mechanics/molecular mechanics. The results indicated that the first hydration sphere of Cm^{3+} contains 8 water molecules arranged in a square antiprism geometry or 9 water molecules arranged in a tricapped trigonal geometry and are close in energy. The simulated EXAFS were in good agreement with recent experimental data from Soderholm et al. From the long-time classical molecular dynamics trajectories we elucidated the water exchange mechanism between the first and second shell and predicted mean first shell residence time to be on the nanosecond time scale. The computed diffusion coefficient of Cm^{3+} agreed well with experimental data. In addition, the effect of



Snap shot of dynamics simulation of Cm^{3+} in solution counter ions on the coordination of curium has been studied and a manuscript detailing the results is in preparation.

3. We're continuing our work on assessing the strengths and weaknesses of density functional theory methods for open-shell uranyl species by comparing theory with gas-phase experiments from Gibson (LBL) and Groenewold (INL). These collaborative efforts have been very productive and our computational methods were able to demonstrate that carboxylates were observed to bind simultaneously in a bi- and mono-dentate fashion, which was also observed earlier by Rao et al. (LNBL) in solution experiments.

4. We have been investigating U reduction at mineral/aqua interfaces via AIMD simulations of fully-solvated UO_2^{2+} on the FeS(001) surface. The simulations predicted reduction from U(VI) to U(V) accompanied by a slight lengthening of the uranyl bonds and conversion to a four-coordinated ion (loss of water ligand). Thermodynamic measurements of U molecules suggest certain U(IV) species, e.g. $U(OH)_4$, are viable prompting a detailed theoretical investigation into the energetics of U(IV) and U(V) molecules. Energies were calculated for an array of U molecules, varying the oxidation state and the number of oxo-, hydroxo-, and hydro-ligands. If reduced to U (IV), the $U(OH)_4$ molecule again looks to be a favorable conformation. To obtain accurate ΔH_f for this species we have performed CCSD(T) calculations, which predict a higher ΔH_f compared with tabulated experimental values. We have started a collaboration with Dr. Jeff Terry from the Illinois Institute of Technology who performed experiments and has EXAFS data that suggest the formation of U (V) species.

Science objectives for 2011-2013:

- Understand the role of ligands, counter-ions and oxidation state in aqueous solution on the formation and stability of mono- and multimeric actinide species.
- Model the structure, thermodynamics, and redox chemistry of solvated actinide ions on reducing mineral surfaces will be simulated for ambient conditions.

Publications supported by this project 2009-2011

1. F. Aubriet, J.J. Gaumet, W.A. de Jong, G.S. Groenewold, A.K. Gianotto, M.E. McIlwain, M.J. Van Stipdonk, and C.M. Leavitt, "Cerium Oxyhydroxide Clusters: Formation, Structure and Reactivity." J. Phys. Chem. A 113, 6239 (2009)
2. G.E. Schoendorff, T.L. Windus, and W.A. de Jong, "Density Functional Studies on the Complexation and Spectroscopy of Uranyl Ligated with Acetonitrile and Acetone Derivatives J. Phys. Chem. A 113, 12525 (2009)
3. C.M. Leavitt, V.S. Bryantsev, W.A. de Jong, M.S. Diallo, W.A. Goddard III, G.S. Groenewold, and M.J. Van Stipdonk. 2009. "Addition of H2O and O-2 to Acetone and Dimethylsulfoxide Ligated Uranyl(V) Dioxocations." J. Phys. Chem. A 113, 2350 (2009)
4. G.S. Groenewold, M.J. Van Stipdonk, J. Oomens, W.A. de Jong, G.L. Gresham, and M. McIlwain, "Vibrational Spectra of Discrete UO_2^{2+} Halide Complexes in the Gas Phase." Int. J. Mass Spec. 297, 67 (2010)
5. G.S. Groenewold, W.A. de Jong, J. Oomens, and M.J. Van Stipdonk, "Variable Denticity in Carboxylate Binding to the Uranyl Coordination Complexes." J. Am. Soc. Mass Spec. 21, 719 (2010)
6. V.A. Glezakou and W.A. de Jong, "Cluster-models for Uranyl(VI) adsorption on α-alumina." J. Phys. Chem. A 2011, 115, 1257 (2011), **Cover**
7. R. Atta-Fynn, E.J. Bylaska, G.K. Schenter, and W.A. de Jong, "Hydration Shell Structure and Dynamics of Curium(III) in Aqueous Solution: First Principles and Empirical Studies.", submitted to J. Phys. Chem. A (2011)

Four additional publications in preparation, with subjects ranging from counter ion effect on curium solvation, uranium(V) solvation, thermodynamics of $U(OH)_4$, and ab initio dynamics simulations of uranyl(aq) on alumina.

Origin of Actinide Partitioning in Biphasic Systems

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Overall research goals: The goal of the work is to provide a chemical description of the multiple forces that contribute to heterogeneous solvent organization and ion extraction at length scales accessible by quantum mechanical and statistical mechanical methods. A fundamental understanding of ion extraction mechanisms will enable the exploitation of "phase phenomena" to achieve more efficient, predictable, and controllable separation processes. We utilize a synergistic approach composed of simultaneous density functional theory (DFT) calculations and molecular dynamics (MD) simulations that respectively provide electronic structure and ensemble correlations of molecular systems. These studies are engaged in a feedback loop to yield a self-consistent description of prototypical actinide ions (e.g., Np) and their chelates (acetylacetate ion) in aqueous and organic media as well as at the liquid:liquid phase boundary.

Significant achievements during 2009-2011: The following objectives have been pursued since 2009:

- Characterize the supramolecular chemistry of exemplary spherical (trivalent) and linear di-oxo (hexavalent) Np ions in pure water and alkane solvents, including solvent exchange and complexation reactions with prototypical acetylacetone (acac) ligands substituted with hydrophobic and hydrophilic substituents.
- Determine the interfacial structure of water:alkane mixtures as a function of alkane packing, varying concentrations of extracting acac ligands, and proximity of solutes to the interface.
- Describe the transport process of Np(III) and Np(VI)O_2^{2+} and their acac complexes across water:alkane interfaces, and determine the influence of 1) interfacial order and packing of the alkane, and of 2) hydrophobic and hydrophilic solvation characteristics on transport properties.

To date significant achievements have been made on each objective. 1) Density functional theory studies were first performed so as to benchmark the interaction potentials of the ion with water and organic solvents against more highly accurate MP2 and DF-LPM2 methods. DFT studies were then performed examine the solvation of Np(III) and NpO_2^{2+} in both aqueous and organic media. Significant charge polarization is observed across aqueous solvation shells for both metal ions, which is absent in organic media, however the conformational flexibility of the alkane solvent significantly impacts its solvation structure. The benchmarked DFT data (along with MP2) is currently being used to fit classical polarizable interaction potentials using the ForceFit program. 2) Similar computational benchmarking (but including CCSD(T) methods) has been performed for the interaction potentials of water with pentane and neopentane organic solvent molecules. In this context dispersion corrected density functionals have been very successful in correctly describing the weak attractive interaction and thus have been used to examine the solvation of single water molecules by organic solvents and vice versa. This has allowed us to determine thermodynamic properties of solvation that are relevant at a dynamic oil:water interface. These DFT methods will be used in further periodic boundary DFT calculations. In parallel, classical molecular dynamics simulations are being performed to further explore the dynamical features of the oil:water interface as a function of the conformational flexibility of the organic solvent (chain pentane vs. neopentane). In particular, we are focusing upon the calculation of radial distribution functions, density profiles, diffusion coefficients, the surface tension at the interface, and the free energy of permeation across an interfacial boundary of both water and organic solvents. 3) Initial DFT calculations have been performed that examine the thermodynamic and structural features of Np(III) and NpO_2^{2+} complexes with extracting acetylacetate ligands. Very good agreement has been obtained with available experimental data and is being used to ascertain the most likely metal-complexes in aqueous and organic solutions. 4) The upcoming scientific accomplishment made on the project rely heavily on analyses of data from molecular dynamics simulation. We have developed a method for post-processing that uses the tools of graph theory and network analysis to explore and characterize the H-bond network of liquid water. By treating individual molecules as vertices and H-bonds as edges, we obtain information about connectivity and supramolecular structure of water in the bulk, around solutes, and at interfaces.

Science objectives for this project 2011-2013: Our science objectives for the next biennium include extensive DFT and MD study of oil:water interfaces in the presence of metal ion, extracting acac ligands, and metal-acac complexes. The physical-chemical properties of the acac ligand will be modulated through substitution of the bridging carbon with hydrophobic and hydrophilic units to examine the effects of changing the binding strength and modifying the hydrophobic interaction of the ligand with water of hydration. Finally, we will examine transport processes for Np(III) and $Np(VI)O_2^{2+}$, their acac chelates, and combined solvent-chelate cations from the aqueous to organic phase (and vice versa). Potential of mean force MD simulations will provide energetic and interfacial structural information as bare and chelated metal ions are manually steered across the phase boundary. Electronic structure information will be obtained from DFT under varying solvation environments as the exchange occurs between polar and nonpolar solvent molecules coordinating the solute.

Publications for this project 2009-2011:

Y. Ghadarghadr, A. E. Clark “DFT, DF-LMP2, MP2, and CCSD(T) Examination of the Energetic and Structural Features of Hydrophobic Solvation” J. Phys. Chem. A, submitted 2011).

L.R. Corrales, "Statistical Mechanics of Graph-Based Hydrogen Bond Networks", J. Chem. Phys. (submitted 2011).

Accurate Theoretical Approaches for Studying the Chemistry of Actinides and Other Heavy Atoms

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Dr. Donghyung Lee, Postdoctoral Research Associate (partial support)
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Collaborator (Theory): Dr. Richard L. Martin, Group T-1, LANL

Overall research goals: The methodological development and computational implementation of quantum chemistry methods for the accurate calculation of electronic structure and properties of molecules, solids, and surfaces, which contain actinides and other heavy atoms.

Significant achievements during 2010-2011

Our support under the HEC program is now in its 10th year. During this time, 37 publications have acknowledged DOE-HEC support under grant No. DE-FG02-04ER15523. This abstract corresponds to the first year of the grant renewed in 2010. During this period (15-APR-2010 to present), we have continued to focus our attention on three main areas described below. There were four papers published during this grant period and several others are currently under preparation. This research project remains an active collaboration with Richard L. Martin and his experimental collaborators at LANL.

1. Methodological and computational developments

We continue to develop and improve methodological and computational tools that enable our focused applications on actinide systems. During this grant period, we have developed a new electronic structure method capable of dealing with the strong correlations ubiquitous in heavy element compounds and solids (CTRL-click on hyperlink to see the paper):

34. Constrained-Pairing Mean-Field Theory. II. Exact treatment of dissociations to non-degenerate orbitals, G. E. Scuseria and T. Tsuchimochi, *J. Chem. Phys.* **131**, 164119 (2009).

We have also continued to develop a stochastic full CI method with the objective of using it for benchmark calculations in small actinide molecules. This effort was lead by Dr. Miguel Morales whom after a one-year postdoctoral stay in our research group has now joined the Lawrence Livermore National Laboratory as permanent staff. We continue to collaborate with him on this front but have no papers to report yet.

2. **Development and assessment of novel exchange-correlation functionals and other electronic structure methods that deal with strong correlations**

Most (if not practically all) electronic structure calculations on actinide systems are carried out with density functional theory (DFT). The accuracy of these calculations depends on the accuracy of the exchange-correlation functionals employed. During this grant period, the following papers described in detail our progress in this area:

36. Many-electron self-interaction and spin polarization errors in local hybrid density functionals, R. Haunschild, T. M. Henderson, C. A. Jimenez-Hoyos and G. E. Scuseria, *J. Chem. Phys.* **133**, 134116 (2010).

37. Accurate treatment of solids with the HSE screened hybrid, T. M. Henderson, J. Paier, and G. E. Scuseria, *Phys. Status Solidi* **B** **online**

3. **Focused applications on actinide systems**

The main thrust of our research effort is more accurate simulations of actinides and derivatives in solid state, interpretation of data, and collaborations with experimentalists. During this grant period, there were no papers published in this area but there are currently several manuscripts in preparation. We will report details once they are published. They are:

- First Principles Predictive Capabilities for Transuranic Materials: Mott Insulators to Correlated Metals, Eve Bauer et al., *Actinide Research Quarterly*, in preparation.
- Experimental Confirmation of Unexpected Covalency in PuO_2, J. Joyce, et al., *Science*, in preparation.
- Synthesis, Characterization, and Theory of thin films of U_3O_8, A.K. Burrell et al., *Adv. Materials*, in preparation.
- Evolution of Electronic Structure and Covalency in Single-crystal Quality Thin Films of UO_2, NpO_2, and PuO_2, T. M. McCleksey, *J. Am. Chem. Soc.*, in preparation.
- Hybrid Density Functional Theory Study of Actinide Nitrides, AnN (An=U, Np, Pu), X. Wen et al., *Phys. Rev.* **B,** in preparation.

Session P2 – Poster Session 2

The Synthesis, Structures and Chemical Properties of Macrocyclic Ligands Covalently Bonded into Layered Arrays, DE-FG02-03ER15420

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Collaborator: Donald T. Reed, Team Leader, Actinide Chemistry and Repository Science, Los Alamos National Laboratory, Carlsbad, NM 88220, dreed@lanl.gov

Overall Research Goals:

To utilize mixed metal phosphonate phosphates for the separation of lanthanides as a group from actinides and further separate individual actinides.

Significant Achievements during 2009-2011:

1. We have discovered that the selectivities for 3+ and 4+ ions, recorded as Kd values, are greatly enhanced by synthesizing materials using Na_3PO_4 in place of H_3PO_4 in the synthesis of the mixed ligand phosphonates of Sn(IV) and Zr(IV). It appears that these new compounds are structurally distinct from the former compounds prepared with H_3PO_4 i.e. basic solution versus acidic conditions.

2. The actinides follow the same selectivity sequence as the lanthanides in that the selectivity sequence is $An^{4+} = An^{3+} > AnO_2^{2+} >> AnO_2^{+}$.

3. The highest selectivity for Ln^{3+} is at pH 3 whereas for An^{3+}, An^{4+} it is approximately pH 1.9. This may be a basis for separation of lanthanides from actinides.

4. Our ability to work with Pu, Np, Am, Cm is due to the collaboration with Don Reed who has graciously allowed Jon Burns to spend time at the Carlsbad, Los Alamos Laboratory.

Objectives for 2011-2013:

1. To quantify the separation of lanthanides as a group from monovalent and divalent ions.

2. To examine the separation of Ce^{2+} from Ce^{3+} and similarly for Sm, Eu and Yb as 2+ and 3+ ions.

3. To manipulate the oxidation status of Pu, Np and possibly Am so that they may be further separated from 3+ lanthanides and from each other. That is PuO_2^{+} would easily separate from other trivalent species.

4. These mixed ligand phosphonates of composition $M(IV)(O_3PC_6H_4PO_3)_{1-x/2}(HPO_4)_x$ or Na^+ derivatives are amorphous or at best weakly crystalline. A schematic representation is provided in Figure 1 and X-ray pattern in Figure 2. We intend to obtain structural

information from EXAFS and atomic pair distribution studies of both the proton and Na phases and their lanthanide loaded analogues.

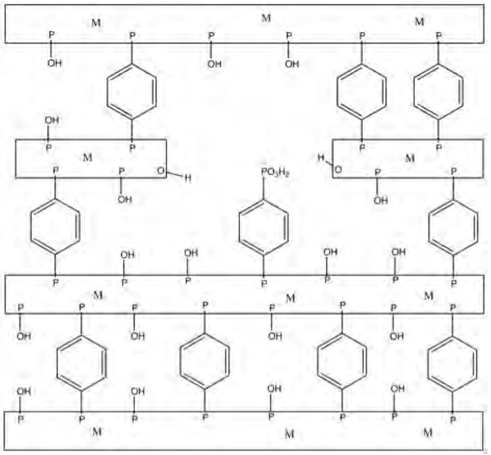

Figure 1. Schematic diagram of M(IV) monophenyldiphosphonate phosphate with defects creating porosity as well as effect of OH spacer group

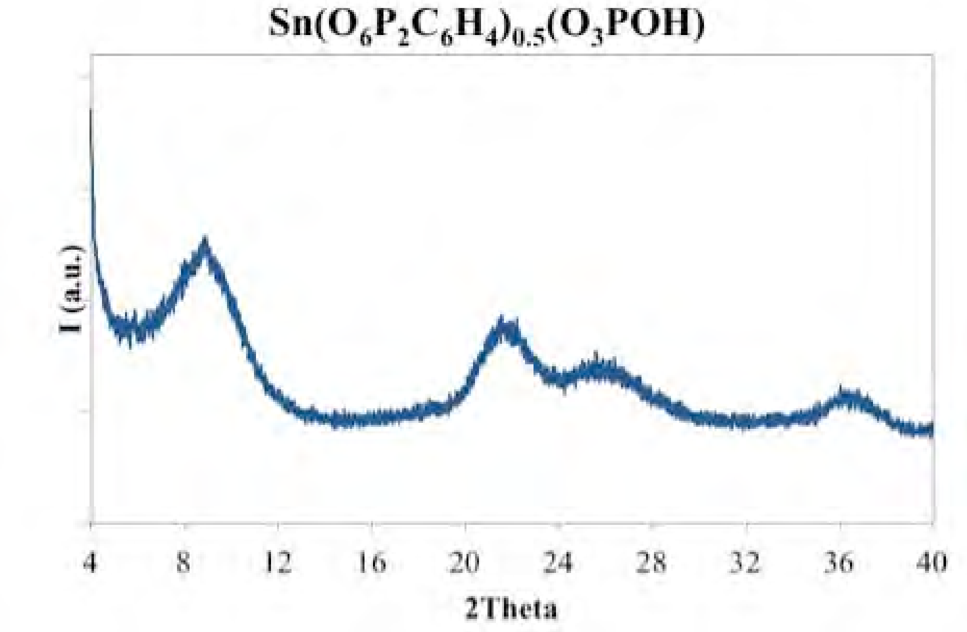

Figure 2. Typical X-ray pattern of M(IV) phosphate phosphonate.

Publications:

1. Christopher S. Fewox, Abraham Clearfield and Aaron J. Celestian, In situ X-ray Diffraction Study of Cesium Exchange in Synthetic Umbite, Inorg. Chem., in press.

2. T. Moller, N. Bestaoui, M. Wierzbicki, T. Adams and A. Clearfield, Separation of lanthanum, hafnium barium and radiotracers yittrium-88, barium-133 for Ra – 223 radioisotope generator, Applied Radiation and Isotopes, in press, proofs on line.

3. Jonathan D. Burns and Abraham Clearfield, Pillared Metal(IV) Phosphate Phosphonates for Extraction of Lanthanides, Solvent Extraction and Ion Exchange, Submitted.

Structural Aspects of Solution Chemistry in Solvent Extraction (SX)

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Overall research goals: The various associations of solutes in solvents that are driven by ion-ion and dipole-dipole forces as well as by ion-dipole ones, and the influences of the solvent itself on solute interactions impact a number of issues in separations science, possibly none more important than solvent extraction (SX). This research is designed to lead to a fundamental understanding of self-assembly and supramolecular behaviors, such as ion-pairing, micellization, and third-phase formation, in bulk media—aqueous and organic alike—and to correlate the structural aspects of microemulsions in advanced SX system chemistry with solute partitioning.

Significant achievements during 2009-2011: We have tested the limits of the micellar interaction model for third phase formation depicted in Figure 1 by extending our SX studies to a variety of extractants, including organophosphorus esters having different basicities and alkyl groups, and also to a host of aqueous phase species ranging from actinide nitrate salts to several common inorganic acids to 12-phosphotungstic acid. The results show that the physico-chemical model of the mechanism and energetics of third phase formation based on van der Waals interactions between the polar cores of reverse micelles, which contain water and polar solutes in their core domain, is

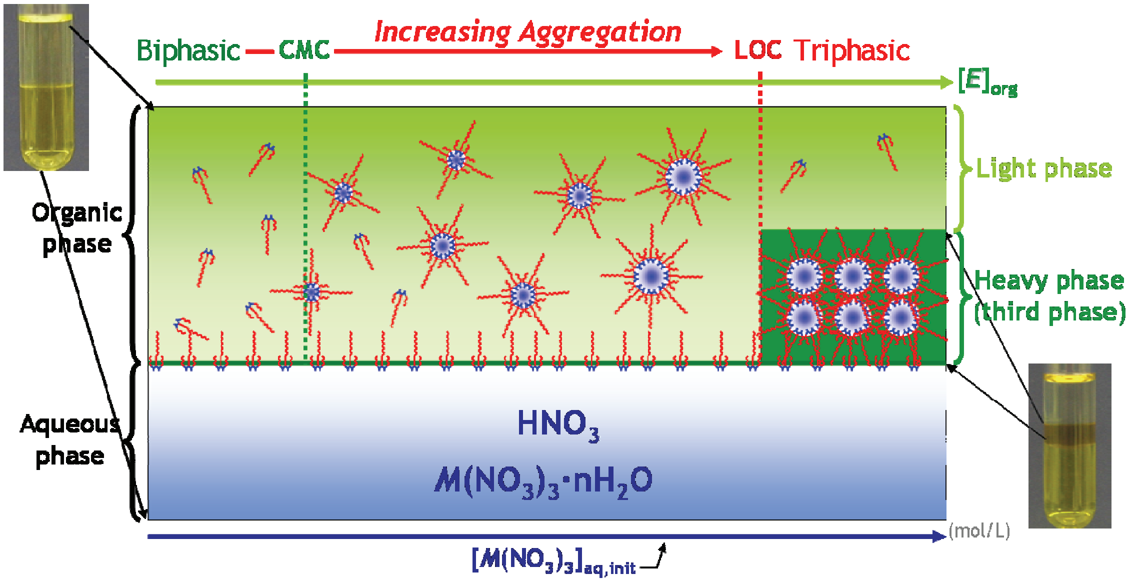

Figure 1. Schematic view of structural aspects of solution chemistry in SX showing, on going from left to right, increasing aggregation from unassociated solutes to reverse micelle formation at the CMC (critical micelle concentration) and, with increasing loading of the nonpolar organic phase (green) containing a neutral amphiphilic extractant molecule (E), third phase formation at the LOC (limiting organic concentration) of solutes extracted from an aqueous phase (blue) containing HNO_3 and $M(NO_3)_3{\cdot}nH_2O$. The organized organic media beyond the CMC contains supramolecular aggregates of $(E_x{\cdot}yHNO_3{\cdot}nH_2O{\cdot}zM(NO_3)_3)$.

valid for all systems investigated except for the heteropolyacid, $H_3PW_{12}O_{40}$, one. Organic phase splitting in normal systems occurs when the intermicellar attractions reach energies of about twice the average thermal energy, $2k_BT$ where k_B is the Boltzmann constant and T is temperature. In contrast, the micellar interaction model does not apply in the case of the extraction of phosphotungstic acid by tri-*n*-butyl phosphate (TBP). The formation of a third phase in this extraction system is distinguished from the others by the highest known attraction energy ($3.2k_BT$), an extremely low initial concentration of $H_3PW_{12}O_{40}$ at the LOC condition, and a third phase that is denser than water. The organic phase splitting of phosphotungstic acid–TBP system is driven by the limited solubility of the heavy and highly polar $H_3PW_{12}O_{40}$-extractant species in *n*-alkane diluents.

Science objectives for 2011-2013:

Despite significant research in SX, a systems wide, solvent-centric correlation of solution structure with solute partitioning has not been realized. The objective is to develop a comprehensive description of the basic mechanisms and energetics of SX processes. The overarching goal is to relate solvent organization and supramolecular solution structures, especially those that exhibit correlation in terms of intermediate-range order, with 4f-/5f-ion distribution ratios and separation factors. Whereas it is known that separation factors generally improve by preorganizing chelating groups of ligands onto molecular (macrocyclic) platforms, such as calixarenes, cavitands, cryptands, trityls, dendrimers, nanoparticles (creating a polydentate extractant), it is our contention that the preorganization of extractants in non-polar diluents mediates the distribution of target solutes between liquid phases in ways that are not fully understood. We are moving forward to fundamental advances in the understanding of heavy element chemistry and separations science in an approach that centers on quantifying atomic- and molecular-scale as well as electrochemical phenomena as they relate to supramolecular organizations of extractant molecules and their complexes with solutes.

Publications supported by this project 2009-2011:

1. Antonio, M. R., Chiarizia, R. and Jaffrennou, F., “Third phase formation in the extraction of phosphotungstic acid by TBP in *n*-octane” Sep. Sci. Technol. 45 (12), 1689-1698 (2010)
2. Chiarizia, R., Stepinski, D. and Antonio, M. R., “SANS study of HCl extraction by selected neutral organophosphorus compounds in *n*-octane” Sep. Sci. Technol. 45 (12), 1668-1678 (2010)
3. Antonio, M. R., Jing, J., Burton-Pye, B. P. and Francesconi, L. C., “Series behavior of lanthanoid(III) complexes with the α-1-Wells-Dawson heteropolyoxoanion in acetonitrile: Electrochemistry and Ln coordination” Dalton Trans. 39, 7980-7992 (2010)
4. Pigga, J. M., Teprovich, Jr., J. A., Flowers, II, R. A., Antonio, M. R. and Liu, T., “Selective monovalent cation association and exchange around Keplerate polyoxometalate macroanions in dilute aqueous solutions” Langmuir 26 (12), 9449-9456 (2010)
5. Meridiano, Y., Berthon, L., Crozes, X., Sorel, C., Dannus, P., Antonio, M. R., Chiarizia, R. and Zemb, T., “Aggregation in organic solutions of malonamides: Consequences for water extraction” Solvent Extr. Ion Exch. 27 (5-6), 607-637 (2009)
6. Pigga, J. M., Kistler, M. L., Shew, C.-Y., Antonio, M. R. and Liu, T., “Counter-ion distribution around hydrophilic molecular macroanions: The source of the attractive force in self-assembly” Angew. Chem., Int. Ed. 48 (35), 6538-6542 (2009)
7. Antonio, M. R., Nyman, M. and Anderson, T. M., “Direct observation of contact ion-pair formation in aqueous solution” Angew. Chem., Int. Ed. 48 (33), 6136-6140 (2009)
8. Antonio, M. R., Chiang, M.-H., Seifert, S., Tiede, D. M. and Thiyagarajan, P., “*In situ* measurement of the Preyssler polyoxometalate morphology upon electrochemical reduction: A redox system with Born electrostatic ion solvation” J. Electroanal. Chem. 626 (1-2), 103-110 (2009)

Local Structure and f-Orbital Localization in Fresh and Aged Uranium and Plutonium Intermetallics

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Overall research goals: The objective of this project is to understand the relationship between the electronic and magnetic properties of actinide (An) intermetallic compounds and their local electronic and crystal structures. Of particular interest is the degree of f-orbital localization and structural disorder in both fresh and aged compounds that undergo significant self-irradiation.

Significant achievements during 2009-2011:

1. A breakthrough occurred over the last year whereby observed shifts between the Pu L_{III} whiteline x-ray absorption energies, which we first observed a few years ago between -Pu, Δ-Pu, and $PuCoGa_5$, have now been observed in a much wider array of materials (Fig. 1). These shifts correlate with the linear coefficient of the specific heat, which, within the Anderson Impurity Model, is a rough measure of f-orbital occupation. Although the correlation is clear, within this strict interpretation, these data imply an f-occupancy for all the measured compounds that is less than that in $PuSb_2$, which we believe to be close to f^5. This interpretation is at odds with at least one other spectroscopic measurement and the current prevailing theories. Another possible interpretation is that a covalent-like delocalization occurs whereby the energy shift is primarily due to a change in the f-orbital extension, which in turn drives the magnetic and electronic properties of these materials.

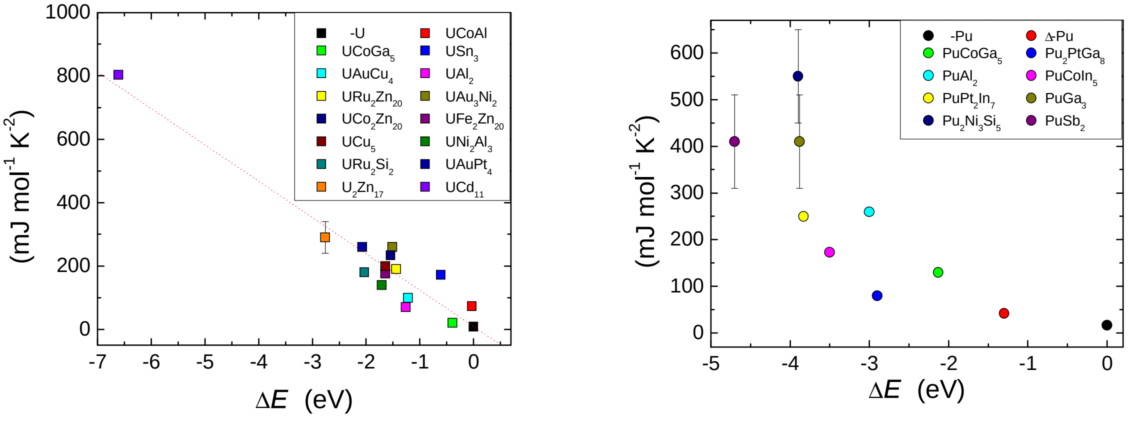

Figure 1. The linear coefficient of the specific heat, , as a function of the shift of the actinide L_{III} x-ray absorption whiteline energy, Δ*E* , of the -form of the actinide. Left: uranium intermetallics, Right: plutonium intermetallics.

2. One ultimate goal for understanding self-irradiation damage in these compounds is to make a direct comparison between experimental and calculational measures of the damage. Molecular Dynamics (MD) calculations have been performed on elemental Pu, and can be compared to extended x-ray absorption fine-structure (EXAFS) measurements of the local structural effects of the damage. Some data have been obtained on samples of Δ-Pu with

1.8at% Ga, but other disorder, potentially due to martensitic transformations to the ´-phase may be increasing the measured damage. In any case, comparisons between actual data and a damage calculation using a 20 keV recoil nucleus are consistent with the observed magnitude of the damage, although differences in the details of the local structure exist that still need to be understood. We are also attempting to understand damage formation and subsequent annealing in other compounds in terms of bond strength.

Science objectives for 2011-2013:

- Although preliminary high-resolution partial fluorescence yield spectra have been collected, better data on a wider variety of compounds will be obtained that should help determine any intermediate-valence nature of the ground state in the An intermetallics.
- An L_{III} x-ray absorption data collected as a function of pressure will be obtained that will also help interpret whiteline edge shifts and how they relate to the electronic structure.
- Exploring radiation damage in Δ–Pu has demonstrated Pu's ability to self-heal at and above room temperature. We therefore must measure at lower temperatures. Through a collaboration with LLNL, we will hold an appropriate sample below 30 K for a several month period and make periodic measurements of the damage.
- MD simulations will focus on $PuGa_3$ to make direct comparisons to EXAFS data. $PuGa_3$ has the advantage of displaying more damage when stored at room temperature.

Publications supported by this project 2009-2011

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2. Booth, C. H. and Hu, Y.-H., "Confirmation of standard error analysis techniques applied to EXAFS using simulations." Submitted to X-Ray Absorption Fine Structure – XAFS14: 14th International Conference, July 26-31, 2009. J. Phys.: Conf. Ser. 190, 012028 (2009).
3. Hu, Y.-H. and Booth, C.H., "Predetermining acceptable noise limits in EXAFS spectra in the limit of stochastic noise." Submitted to X-Ray Absorption Fine Structure – XAFS14: 14th International Conference, July 26-31, 2009. J. Phys.: Conf. Ser. 190, 012029 (2009).
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6. Bondino, F., Magnano, E., Panaccione, G., Offi, F., Malvestuto, M., Parmigiani, F., Booth, C. H., Singh, D., Mandrus, D., Paolicelli, G., Simonelli, L., and Mannella,N., "Electronic structure of $CeFeAsO_{1-x}F_x$ (x=0, 0.11(2)) compounds," Phys. Rev. B 82, 014529 (2010).
7. Tobash, P.H., Jiang, Y., Ronning, F., Booth, C.H. Thompson, J.D., Scott, B.L., and Bauer, E.D., "Synthesis, Structure, and Physical Properties of $YbNi_3Al_{9.23}$." J. Phys.: Condens. Matter, in press.
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Actinide Solution Speciation: Implications for Complex Stability and Separations Chemistry

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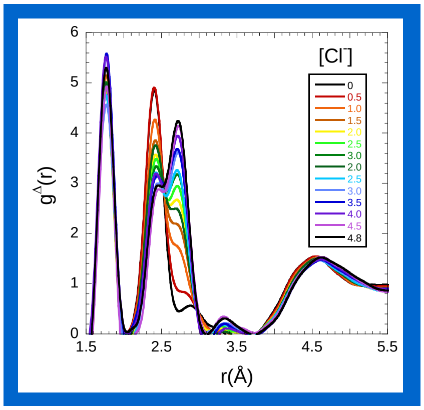
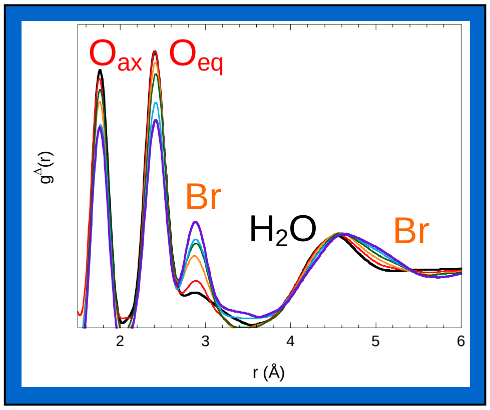
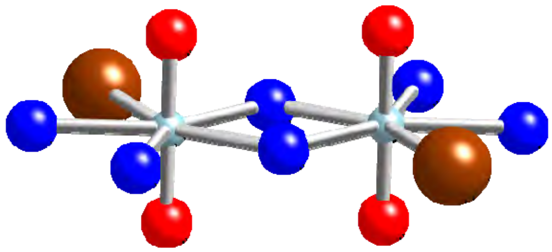
Overall research goals: This research is centered on identifying actinide complexes that form in solution, and quantifying their structures, their stabilities and their energetics. Correspondence is sought between stable correlations that develop in solution and the building units comprising solid state structures with predictive materials synthesis as a long-term goal. Relationships are sought between the structural correlations and complexes that form in solution and the metal-ions behavior in solvent extraction systems of relevance to fission product separations and the nuclear fuel cycle.

Significant achievements during 2009-2011: The focus has centered on halide correlations with hexavalent actindes. Known to form weak complexes, high-energy x-ray scattering (HEXS) data from a series of solution with increasing anion concentration show that both Cl^- and Br^- form only inner-complexes. This is in contrast to Er^{3+},[1] which shows both inner and outer-sphere complexation with chloride ions, and Th^{4+}, which forms only outer-sphere complexes with bromide. Regardless of whether the halide coordinates to the actinide to form an inner- or outer-sphere complex, there is excellent agreement in the stability constants determined from scattering data and those obtained by more classical, solvent extraction techniques.





Complementing structural data on uranyl halide correlations in solution provided by HEXS experiments are several single-crystal x-ray structures of uranyl halide complexes. These crystal studies provide confidence in the peak assignments determined for solution HEXS data analysis and confidence in the coordination numbers and bond lengths determined from these analyses. Comparisons of solution and solid-state coordination environments are providing insight into how to influence metal-ion solubility and solution reactivity.



Science objectives for 2011-2013:

- Continue to probe actinide-ion solution speciation, moving to more complex anions such as sulfate, selenate and thiocynate. Probe metal-ion coordination environments with specific focus on inner- versus outer-sphere anion coordination. Provide metical information in systems amenable to calculations that will provide predictive insight into metal-ion solution stability and reactivity.
- Expand solvent systems beyond aqueous solutions, with specific focus on simple non-polar solvents such as dodecane that are of relevance to solvent extraction protocols. Systems will be chosen that have interest and relevance to our independent program on structural aspects of solution chemistry in solvent extraction.
- Seek molecular level information on metal-ion speciation under conditions of relevance to actinide and fission-product separations. Complementary structural information on lanthanide and actinides are of particular importance as insight is sought into new science-based separations strategies.

Publications supported by this project 2009-2011

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2. Soderholm, L.; Skanthakumar, S.; Wilson, R.E.; Structural correspondence between uranyl chloride complexes in solution and their stability constants, J. Phys. Chem. A. (in the press).
3. R. E. Wilson, S. Skanthakumar, C. L. Cahill, and L. Soderholm. Structural studies coupling X-ray diffraction and high-energy X-ray scattering in the UO_2^{2+}- HBr_{aq} system. *Inorganic Chemistry*. (submitted for publication).

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

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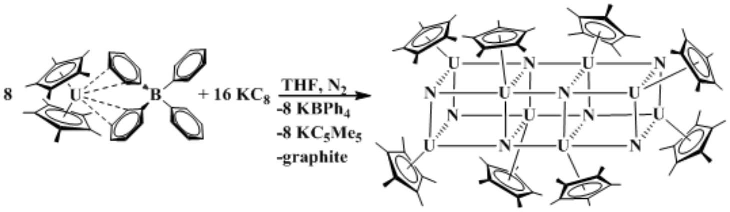
Overall research goals: The objective of this research is to expand knowledge of actinide chemistry to provide fundamental information on actinide metal-ligand bonds that may be useful in the development of advanced nuclear fuel cycles. Recent studies of the reaction chemistry of An-H and An-C bonds (An = U, Th) have shown that surprising new structures and reactivity patterns are available from well-established classes of actinide complexes, some of which have been known for decades. This project will attempt to expand similarly the limits with other donor atoms and especially nitrogen.

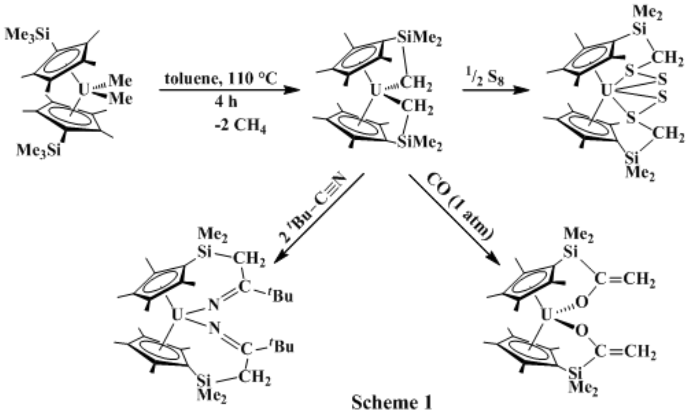
Significant achievements during 2010-2011:

1. A collaborative calculational study with Professor Laura Gagliardi [ref 1] showed that the X-ray crystal data on $[(C_5Me_5)UX]_8$ was reasonable for X = N, eq 1. Since this complex is a molecular species dense in U and N, it could be a possible molecular precursor to uranium nitride. Accordingly, an improved synthesis of this compound and related species are being pursued.



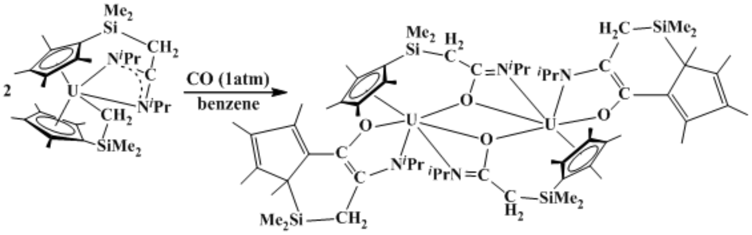
(1)

2. Attempts to make a more soluble version of $[(C_5Me_5)UN]_8$ in eq 1 with $(C_5Me_4SiMe_3)^{1-}$ ligands led to the isolation of the double tether complex, $(\eta^5\text{-}C_5Me_4SiMe_2CH_2\text{-}\kappa C)_2U$, Scheme 1 [2]. Exploration of the reaction chemistry of this species led to a variety of tethered U−N, U−O, and U-S bound species, Scheme 1 [3-5]. The reaction chemistry of these uranium-element linkages can now be explored in tethered form.



Scheme 1

3. Preliminary studies of a tethered nitrogen-ligated uranium amidinate led to the unusual cascade reaction, eq 2, which includes amidinate C−N bond cleavage, alkyl or silyl migration, and U−O, C−C, and C−N bond formation.



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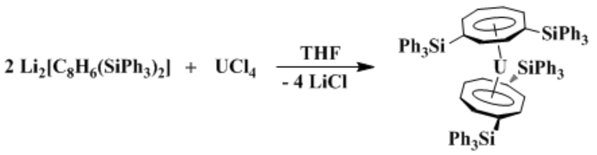
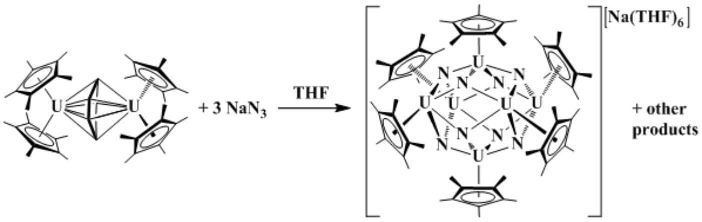
4. A collaboration with Professor Frank Edelmann in Magdeburg led to the first simple uranocene with non-parallel rings, eq 3.



(3)

Science objectives for 2011-2013.

1. Better synthetic routes to clusters like $[(C_5Me_5)UN]_8$ above and the recently identified $\{[(C_5Me_5)U]_6N_8\}\{Na(THF)_6\}$, eq 4, and their analogs will be pursued.



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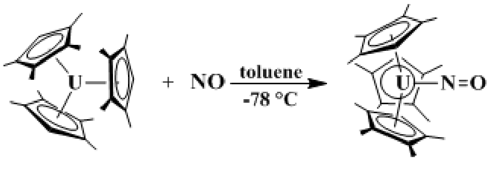
2. As part of this project, radical chemistry of organoactinides will be studied. Preliminary studies of one of the reagents being investigated, NO, has provided the first f element $(NO)^{1-}$ complex, eq 5. The reaction chemistry of the UNO linkage will be studied for the first time with this complex.



(5)

3. The reactivity of tethered U–N, U–O, and U–S linkages shown in Scheme 1 vs traditional ligands will be studied.

Publications supported by this project 2010-2011:

1. "DFT and CASPT2 Analysis of Polymetallic Uranium Nitride and Oxide Complexes: The Power of Theory When X-ray Analysis is Inadequate" Tanya K. Todorova, Laura Gagliardi, Justin R. Walensky, Kevin A. Miller, and William J. Evans *J. Am. Chem. Soc.* **2010**, *132*, 12397-12403.

2. "Synthesis and Reactivity of a Silylalkyl Double Tuck-in Uranium Metallocene, $(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2CH_2)_2U$, and Its Conversion to Bis(tethered) Metallocenes" William J. Evans, Nathan A. Siladke, and Joseph W. Ziller, *Chem., Eur. J.* **2010**, *16*, 796-800.

3. "Reactivity of the Tethered Alkyl Uranium Bonds of $(\eta^5{:}\kappa^1\text{-}C_5Me_4SiMe_2CH_2)_2U$" William J. Evans, Nathan A. Siladke, and Joseph W. Ziller *Compt. Rend. Chim.* **2010***, 13,* 775-780.

4. "Importance of Energy Level Matching for Bonding in Th^{3+}-Am^{3+} Actinide Metallocene Amidinates, $(C_5Me_5)_2[^iPrNC(Me)N^iPr]An$" Justin R. Walensky, Richard L. Martin, Joseph W. Ziller, and William J. Evans, *Inorganic Chemistry* **2010**, 49, 10007-10012.

5. "Insertion, Isomerization, and Cascade Reactivity of the Tethered Silylalkyl Uranium Metallocene $(\eta^5\text{-}C_5Me_4SiMe_2CH_2\text{-}\kappa C)_2U$" Nathan A. Siladke, Joseph W. Ziller, and William J. Evans, *J. Am. Chem. Soc.* **2011**, *133*, 3507-3516.

6. "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.

7. "Importance of Energy Level Matching for Bonding in Th^{3+}-Am^{3+} Actinide Metallocene Amidinates, $(C_5Me_5)_2[^iPrNC(Me)N^iPr]An$" Justin R. Walensky, Richard L. Martin, Joseph W. Ziller, and William J. Evans, *Inorganic Chemistry* **2010**, 49, 10007-10012.

Actinide Transition-Metal Chalcogenides and Pnictides

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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 2009-2011: Most of these achievements are embodied in the publications listed below. Here we discuss some unpublished results.

The compounds $Tl_3Cu_4USe_6$ and $Tl_2Ag_2USe_4$ have been synthesized and structurally characterized by Daniel Bugaris (Thesis, Northwestern University, 2009). In addition, they have been characterized by means of magnetic measurements (Eun Sang Choi, National High Magnetic Field Laboratory, Florida State University) and XANES measurements (David K. Shuh and coworkers, Lawrence Berkeley National Laboratory and Advanced Light Source). These compounds were synthesized by the reactions of the elements in excess TlCl at 1123 K. Both compounds crystallize in new structure types (Figs. 1 and 2), in space groups $P2_1/c$ and $C2/m$, respectively, of the monoclinic system. Each compound contains layers of USe_6 octahedra and MSe_4 (M = Cu, Ag) tetrahedra, separated by Tl^+ cations. The packing of the octahedra and the tetrahedra within the layers is *oct tet tet oct*.

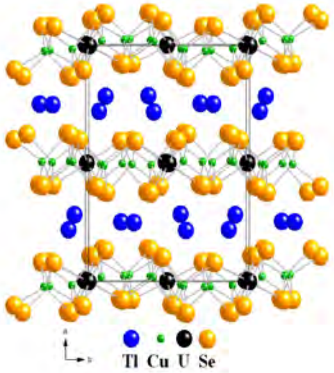

Fig. 1. The crystal structure of $Tl_3Cu_4USe_6$, viewed down *c**.

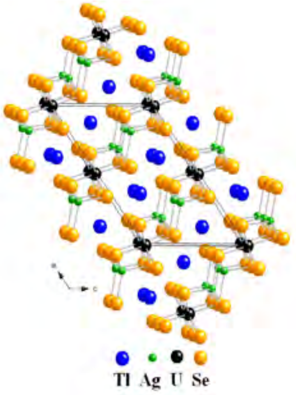

Fig. 2. The crystal structure of $Tl_2Ag_2USe_4$, viewed down [010].

$Tl_3Cu_4USe_6$ displays antiferromagnetic transitions at 5 K and 70 K, with an effective magnetic moment of 1.58(1) μ_B in the temperature range 85−230 K whereas $Tl_2Ag_2USe_4$ exhibits modified Curie-Weiss paramagnetic behavior with μ_{eff} = 3.4(1) μ_B in the temperature range 100−300 K X-ray absorption near-edge structure (XANES) results from scanning transmission X-ray spectromicroscopy confirm that $Tl_3Cu_4USe_6$ has Se bonding characteristic of discrete Se^{2-} units, Cu bonding generally representative of Cu^+, and U bonding consistent with a U^{4+} or U^{5+} species. On the basis of these measurements, as well as bonding arguments, the formal oxidation states for U are assigned as +5 in $Tl_3Cu_4USe_6$ and +4 in $Tl_2Ag_2USe_4$

Science objectives for 20011-2013: We will test our speculation that syntheses that make use of U, Cu, and halide salts may provide additional U^{5+} compounds. Such U^{5+} systems are rare but are of particular interest because of the $5f^1$ electronic configuration of U. The study of such systems allows for a better understanding of what contribution the 5f orbitals make to structure, bonding, and physical properties of solid-state actinide compounds.

We will continue our syntheses of new Np-containing chalcogenides and pnictides and compare their structures and properties to those of related U and Np compounds.

Publications supported by this project 2009-2011

1. Wells, D. M.; Skanthakumar, S.; Soderholm, L.; Ibers, J. A. *Acta Crystallogr.* **2009**, *E65*, i14. Neptunium(III) copper(I) diselenide.
2. Bugaris, D. E.; Wells, D. M.; Ibers, J. A. *J. Solid State Chem.* **2009**, *182*, 1017-1020. Synthesis, structure, and magnetic and electronic properties of $Cs_2Hg_2USe_5$.
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5. Bugaris, D. E.; Ibers, J. A. *J. Solid State Chem.* **2009**, *182*, 2587-2590. $RbAuUSe_3$, $CsAuUSe_3$, $RbAuUTe_3$, and $CsAuUTe_3$: Syntheses and structure; magnetic properties of $RbAuUSe_3$.
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Self-Assembled Ionophores: New Directions

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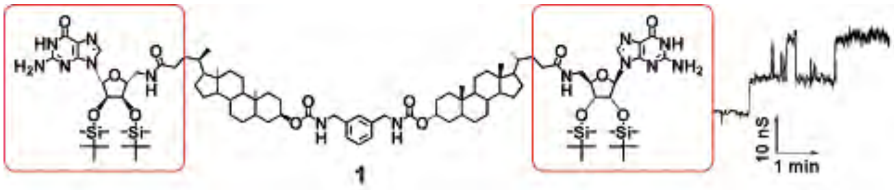
Prof. Gang Wu, Queen's University, Canada
Prof. Marco Colombini, University of Maryland

Overall research goals: Our goal is to build "self-assembled" ionophores that selectively bind and transport ions. 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 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 2009-2011: 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 (**Scheme 1**). 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 mechanism of ion transport and also develop more improved analogs.



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Scheme 1. The structure of a compound that forms a synthetic ion channel. The data on the right shows the transmembrane conductance that is occurs upon addition of this compound to a planar bilayer membrane. This work has been described in the paper "Stabilizing Guanosine-Sterol Ion Channels with a Bis-Urea Linker Unit." Ling Ma, William A. Harrell, Jr. and Jeffery T. Davis, *Organic Letters* **2009**, *11*, 1599-1602.

New Cl^- Anion Receptors/Membrane Transporters. In the past grant period we extended our use of self-assembly to prepare compounds that transport Cl^- and HCO_3^- anions across bilayer membranes. Using various assays with liposomes we compared the H^+/Cl^- co-transport activity and the Cl^-/HCO_3^- anion exchange properties of a series of synthetic molecules and natural products (including prodigiosins and ceramides). These compounds' ability to transport Cl^- and HCO_3^- at micromolar concentrations, their low molecular weight and simple preparation make them valuable leads in drug development for diseases caused by Cl^- transport malfunction.

Science Objectives for 2009-2011:

In addition to continuing our fundamental studies of self-assembled ionophores, continued emphasis in the coming budget years will be placed on developing self-assembled compounds that can form large pores and channels in phospholipid membranes. We also plan to use self-assembly of these lipophilic nucleosides to make other complex and functional nanostructures.

Papers supported by this DOE Grant (2009-2011):

1. "Catechols as Transmembrane Anion Transporters." Sofya K. Berezin and Jeffery T. Davis, *J. Am. Chem. Soc.* **2009**, *131*, 2458-2459.

2. "Using "Small" Molecules to Facilitate Exchange of Bicarbonate and Chloride Anions Across Liposomal Membranes." J. T. Davis, P. A. Gale et al. *Nature Chemistry* **2009**, *1*, 138-144.

3. "Probing the Na^+ Binding Site in a Calix[4]arene-Guanosine Conjugate Dimer by Solid-State ^{23}Na NMR and Quantum Chemical Calculation." Alan Wong, Frank W. Kotch, Irene C. M. Kwan, Jeffery T. Davis and Gang Wu, *Chem. Commun.* **2009**, 2154-2156.

4. "Stabilizing Guanosine-Sterol Ion Channels with a Bis-Urea Linker Unit." Ling Ma, William A. Harrell, Jr. and Jeffery T. Davis, *Organic Letters* **2009**, 11, 1599-1602.

5. "Ceramide-Mediated Transport of Chloride and Bicarbonate Across Phospholipid Membranes." William A. Harrell, Jr., Marie Liesel Bergmeyer, Peter Y. Zavalij and Jeffery T. Davis, *Chem. Commun.* **2010**, *46*, 3950-3952.

6. "Recent Advances in the Transmembrane Transport of Anions." Jeffery T. Davis, Oluyomi Okunola and Roberto Quesada, *Chem. Soc. Rev.* **2010**, *39*, 3843-3862.

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8. "Tripodal Transmembrane Transporters for Bicarbonate." Nathalie Busschaert, Philip A. Gale, Cally J.E. Haynes, Mark E. Light, Stephen J. Moore, Christine C. Tong, Jeffery T. Davis and William A. Harrell, *Chem. Commun.* **2010**, *46*, 6252-6254.

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Article for *Chemical Communications.*

Multiconfigurational quantum chemical study of actinide and lanthanide containing systems

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Overall research goals: The objective of this project is to 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 solution. More specifically, we are exploring the following areas:

a) Actinide containing molecules in the gas phase and in a matrix. (Project in collaboration with Profs. Lester Andrews, Michael Duncan and John Gibson)

b) Polymetallic uranium nitride and oxide complexes and organoactinide systems (Project in collaboration with Prof. William Evans)

c) The maximum coordination in lanthanide and actinide aminodiboranate complexes. (Project in collaboration with Prof. Gregory Girolami)

d) Actinide and lanthanide ions in solution: a combined quantum and classical study

Significant achievements during 2009-20011:

The grant was awarded in the fall of 2009. Since then a PhD student, Ms Bess Vlaisavljevich, has started working on the project. In the summer of 2010 the two postdocs, Daniel Grant and Danylo Zherebetskyy, joined the project.

To date, we have completed the following projects:

1) We have explored actinide mono- and di-oxides series, from Th to Cm. We have computed their first and second ionization energies and compared with experimental values, when available. We have performed quantum chemical calculations on uranium and uranium dioxide carbonyl cations. These systems have been produced by laser vaporization and have been studied with mass-selected ion infrared spectroscopy in the C-O stretching region in the group of Professor Duncan. Our calculations, together with dissociation patterns and spectra, established that the fully coordinated ions are $U(CO)^+$ and $UO_2(CO)^+$, with D_{4d} square antiprism and D_{5h} pentagonal bipyramid structures. In collaboration with Professor Andrews, we have studied complexes of UO_2 and noble gases in order to investigate the effect of noble gases on the electronic structure of UO_2.

2) We have analyzed the structure of polyuranium molecules containing $(N)^{3-}$ and $(O)^{2-}$ ligands, namely $[(C_5Me_5)U(\mu\text{-}I)_2]_3(\mu3\text{-}N)$, $[(C_5Me_5)U(\mu\text{-}I)_2]3(\mu3\text{-} O)$, and chair and boat conformations of $[(C_5Me_5)_2U(\mu\text{-}N)U(\mu\text{-}N_3)(C_5Me_5)_2]_4$, recently synthesized in the laboratory of Professor Evans. We have been able to differentiate nitride versus oxide in molecules for which the crystallographic data were not definitive and to provide insight into the electronic structure and unique chemical bonding of these polymetallic compounds.

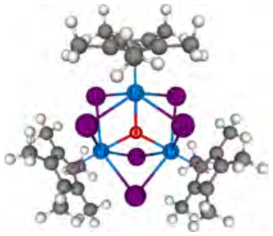

Figure 1: the structure of $[(C_5Me_5)U(\mu\text{-}I)_2]_3(\mu3\text{-} O)$

3) We have performed quantum chemical calculation on the first 15-coordinate complex with formula $[Th(H_3BNMe_2BH_3)_4]$, recently synthesized in the group of Professor Girolami. This compound extends the recent studies of a new class of chelating borohydride ligands, developed in the Girolami's lab, some of which form highly volatile complexes that are useful as precursors for the chemical vapor deposition of thin films. Our calculations have been indispensable for the rationalization of the structure of the Th compound.

4) We have studied with a combined quantum chemical and classical molecular dynamics simulation approach solutions containing chloride salts of La^{3+}, Gd^{3+}, and Er^{3+} at various concentrations (from 0.05 to 5 M), with the purpose of understanding their structure and dynamics and analyzing how the coordination varies along the lanthanide series.

Science objectives for 2011-2013:

- Explore actinide-containing molecular species present in the gas phase in collaboration with Profs. Andrews, Duncan and Gibson, like, for example, thorium and uranium carbides, which show unexpected abundances. Understand the mechanism of CO_2 insertion into U-C bonds.
- Expand the quantum chemical and classical study of actinide ions in solution. We will study Th^{4+} in the near future and then pentavalent actinide ions. In a second stage we will also address the problem of electronically excited states of actinides in solution.
- Study the reactivity of organoactinide hydride complexes of actinides, as multielectron reductants and the reactivity of actinides as catalysts.
- Explore actinide- and lanthanide-metal bonds in heterobimetallic compounds with the aim of a better understanding of the possibility of actinide-actinide homobimetallic multiple bond.

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7. A. M. Ricks, L. Gagliardi, M. A. Duncan *Infrared Spectroscopy of Extreme Coordination: The Carbonyls of* U^+ *and* UO_2^+ J. Am. Chem. Soc. 132, 15905-15907 (2010)
8. B. B. Averkiev, M. Mantina, R. Valero, I. Infante, A. Kovacs, D. G. Truhlar, L. Gagliardi *How accurate are electronic structure methods for actinoid chemistry?* Theor. Chem. Acc., in press (2011)
9. L. Andrews, W. Xuefeng, L. Gagliardi, B. Vlaisavljevich Combined triple and double bonds to uranium: the N≡U=N−H uranimine nitride molecule prepared in solid argon. Inorg. Chem., in press (2011)

Topological Structural Relationships, Cation-Cation Interactions, and Properties of U(VI), Np(V) and Th(IV) Compounds

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Overall research goals:

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 well-characterized 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 structural stability.

3: Crystallization of Th oxide nano-scale clusters (polymers), guided by small-angle X-ray scattering studies of mother solutions, and studies of the crystal-chemistry of Th.

Significant achievements during 2009-2011:

Considerable success has been achieved on several research fronts during the past two years:

Research concerning nano-scale actinide clusters published under this grant (Burns, 2010; Burns et al., 2010; Sigmon et al., 2009a; Sigmon et al., 2009b) has now been transitioned to the EFRC Materials Science of Actinides program.

Our studies of uranyl germanates have been provided several novel materials with interesting structures that have been published (Ling et al., 2010). An article in press reports the synthesis and structures of four uranyl germanates that include U^{6+} cation-cation interactions in their framework structures (Morrison et al., 2011).

New structural topologies have been reported in novel uranyl tellurate compounds (Ling et al., 2011).

A finite cluster of uranyl peroxide polyhedra with a novel uranyl-peroxide configuration has been reported (Unruh et al., 2009).

We have explored the complex crystal-chemistry of the beta-U_3O_8-type sheet topology, and argued that it stabilizes unusual U^{6+} coordination environments, such as a tetraoxido core (Unruh et al., 2010).

We have studied the dissolution of several important uranyl minerals, with detailed characterization of their XPS spectra (Schindler et al., 2009a; Schindler et al., 2009b; Schindler et al., 2009c).

Complex thorium borates and sulfates have been synthesized and characterized, with publication of the results pending (Lipp & Burns, 2011; Albrecht et al. 2011). Development of a structural hierarchy for Th compounds is nearing completion.

Science objectives for 2011-2013:

Emphasis will be placed on the synthesis of U^{6+} compounds with cation-cation interactions at high temperatures, creation and characterization of Np^{5+} compounds, and comparison of cation-cation interactions in Np^{5+} compounds with those obtained in U^{6+} materials.

Publications supported by this project 2009-2011

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-. (2009c) XPS spectra of uranyl minerals and synthetic uranyl compounds. II: The O 1s spectrum. Geochimica Et Cosmochimica Acta, 73(9), 2488-2509.

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Unruh, D.K., Burtner, A., and Burns, P.C. (2009) Expanding the Crystal Chemistry of Actinyl Peroxides: mu-eta(2):eta(1) Peroxide Coordination in Trimers of U6+ Polyhedra. Inorganic Chemistry, 48(6), 2346-2348.

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

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Overall research goals: The primary objective of this research 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. A major focus is the deliberate design of anion receptors, both to learn how to enhance salt extraction and to understand factors determining anion selectivity. The theoretical objectives are (1) to develop sufficient structural criteria to allow the deliberate design of candidate host structures with maximum organization for coordination to targeted ionic species and (2) to generalize the design process computationally. Ultimately, we hope to design molecular architectures in which anion– and cation–receptor functions are combined into a single ditopic host for the recognition of complete ion pairs.

Significant achievements in 2009-2011: Structural and energetic aspects of anion interactions with potential binding sites were studied to gain structural design criteria for shape-selective anionophores. We unexpectedly discovered that the hydrocarbon linkages used to connect traditional bonding sites often augment anion binding. Some C-H groups provide surprisingly strong interactions. An example occurs with 1,2,3-triazole, which binds Cl^- (–18.5 kcal/mol) with a strength approaching that of pyrrole (–22.5 kcal/mol).[8] When attached to polarizing substituents, even aliphatic C-H groups can exhibit interaction energies comparable to those obtained with O-H and N-H groups.[2] A critical survey of the Cambridge Structural Database revealed C-H hydrogen bonds with anions to be the dominant binding motif involving electron-deficient π systems, refuting prior claims of the widespread occurrence of anion-π interactions in the solid state.[3]

Fundamental studies of ion binding interactions also provide a basis for extending traditional force field models to treat ionophores and their ion complexes. Such models enable the rapid prediction and quantitative evaluation of molecular structure in host-guest complexes, as illustrated in studies of lanthanide complexes with N-oxide, phosphine oxide, and amide ligands.[5,6] Application of an extended MMFF94 model correctly predicted that a ditopic ligand, formed at UT-Austin by linking calix[4]pyrrole and calix[4]crown[6], would encapsulate $CsNO_3$ as a contact ion-pair (Figure 1).[7]

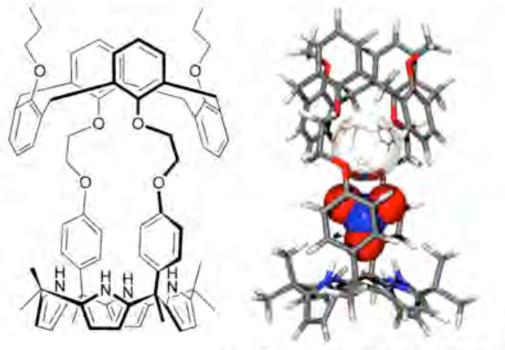

Figure 1. Ditopic ligand (left) and calculated structure (right) with $CsNO_3$ encapsulated as contact ion pair. Model was later confirmed at UT-Austin by x-ray crystallography.

De novo structure-based design methods, implemented in HostDesigner (HD) software, use data from the fundamental studies to construct novel receptor structures by combining molecular fragments.[1] Application of these methods to urea-based anion receptors, summarized in an invited review article,[9] culminated in the design of molecular building blocks that promote the self-assembly of a urea-lined M_4L_6 tetrahedral cage, leading to one of the strongest known sulfate receptors in aqueous solution.[4]

Science objectives for 2011-2013:

- 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 anion receptor architectures using H-bond donors that do not self-associate (pyrroles, acidic C-H groups, and electron-deficient π systems).
- Computer-aided design of molecular building blocks for shape-selective anion receptors that form via self-assembly.

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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 solid, and help to understand the thermodynamic trends as well as the nature of f-orbital bonding in actinide complexes.

Significant achievements during 2009-2011:

1. The studies on the Np(V) complexes with a series of structurally related diacetic acids and oxa-diamides have revealed the relationship between the optical properties and the symmetry of the complex species (Figure 1) [3,5,6,8].

2. Spectroscopic properties and hydration state of Cm^{3+} in solution at 10-85°C were studied. For the first time, quantum yields and a set of correlations between the luminescence lifetime and the hydration number of Cm^{3+} in solution at different temperatures were obtained (Figure 2) [1].

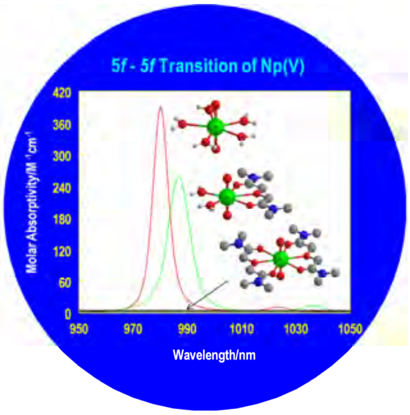

Fig. 1. The f-f transitions of Np(V) are governed by the symmetry of the NpO_2^+ species [6].

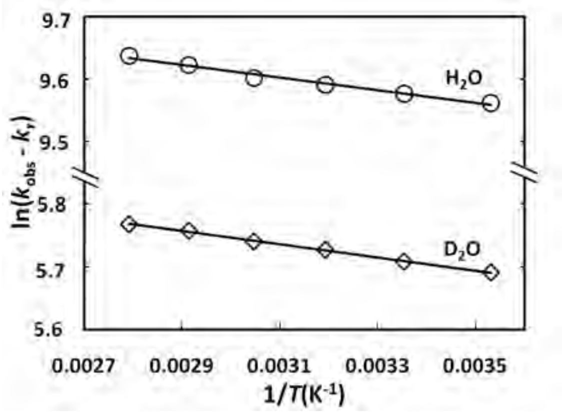

Fig. 2. The non-radiative luminescence decay rate constant ($k_{nr} = k_{obs} - k_r$) of Cm^{3+} increases as the temperature is increased, probably due to the thermal population of the second (A_2) and higher levels of the metastable $^6D'_{7/2}$ multiplet [1].

3. Studies on the complexation of actinides with a number of ligands at elevated temperatures have been completed, including the complexation of Np(V) with acetate, and Cm(III) with nitrate. The results have been published in peer-reviewed journals. These ligands may exist in moderate to high concentrations in nuclear wastes or used nuclear fuel reprocessing processes. Thermodynamic data on their complexation with actinides at elevated temperatures are very few. Results from our studies

have revealed the effect of temperature on the complexation, the thermodynamic driving force in the complexation, and the coordination modes in the complexes [2,4,9,10].

Science objectives for 2011-2013:

- Continue the studies on actinide complexation with ligands of importance in advanced actinide separations. The studies will expand 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.
- Complete and publish the results on the hydrolysis of Pu(VI) at elevated temperatures with multiple techniques including potentiometry, microcalorimetry and spectrophotometry. Data on the hydrolysis of U(VI), Np(V) and Pu(VI) at elevated temperatures will be compared and summarized. Various theoretical models for predicting the effect of temperature will be evaluated with these experimental data. A journal article will be published based on these results.
- Study the effect of temperature on the hydration state and luminescence properties (including quantum yields) of Eu(III) in comparison with Cm(III). The luminescence properties of Eu(III) in aqueous solutions (pure H_2O, pure D_2O, and mixtures of H_2O/D_2O) and at different temperatures (up to 85°C) will be investigated, including the quantum yield and the lifetimes of radiative and non-radiative decays.

Publications supported by this project in the last two years:

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2. L. Rao, G. Tian, Effect of Temperature on the Complexation of Cm(III) with Nitrate in Aqueous Solutions, *Dalton Trans*. 40 (4), 914 – 918 (2010).
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6. L. Rao, G. Tian, Symmetry, Optical Properties and Thermodynamics of Neptunium(V) Complexes, *Symmetry*, 2(1), 1-14 (2010).
7. S. Vermote, C. Wagemans, O. Serot, J. Heyse, J. Van Gils, T. Soldner, P. Geltenbort, I. AlMahamid, G. Tian, L. Rao, Ternary particle emission in spontaneous fission of ^{250}Cf and ^{252}Cf and in neutron induced fission of ^{249}Cf and ^{251}Cf**,** *Nucl. Phys. A* 837 176-194 **(**2010).
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10. P. Di Bernardo, P. Zanonato, G. Tian, M. Tolazzi, L. Rao; Thermodynamics of the complexation of Uranium(VI) with oxalate in aqueous solution at 10-70°C, *J. Chem. Soc. Dalton Trans*. 23, 4450-4457 (2009).
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12. G. Tian, L. Rao, S. J. Teat, G. Liu; Quest for Environmentally-Benign Ligands for Actinide Separations: Thermodynamic, Spectroscopic, and Structural Characterization of U(VI) Complexes with Oxa-Diamide and Related Ligands, *Chemistry, a European Journal*, 15, 4172-4181 (2009).

Collective and Cooperative Phenomena in Actinide-Based Materials: Intrinsic Dynamical Processes in Hypervalent Urania

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Overall research goals: This project characterizes the atomic and electronic structures of complex actinide-based and related materials and the phenomena underlying their special properties. Most recently it is investigating the intrinsic dynamics of charge inhomogeneities in UO_{2+x} and modeling the affects of inhomogeneity domains on the crystal and electronic structures of their hosts.

Significant achievements during 2009-2011: The structural measurements on UO_2, U_4O_9, and U_3O_7 that demonstrated the intrinsic dynamics and the analysis of the data were completed. Ultrafast, pump-probe optical reflectivity measurements elucidating the behavior of the optically induced charge-separated state and its associated polaron were performed, perhaps the first experiments probing the excited state dynamics of an actinide compound.

The comparison of the complete set of XAFS and x-ray and neutron pdfs (Figure 1) demonstrates the U-O multisite distributions for the x-ray and simple distribution for the neutron measurements that are indicative of the dynamical character of the "super" polaron in urania that is much more radical than the analogous one in cuprates and other first row transition metal compounds. Analysis of the widths and areas of the peaks indicates the presence of both static and dynamic anharmonic components.

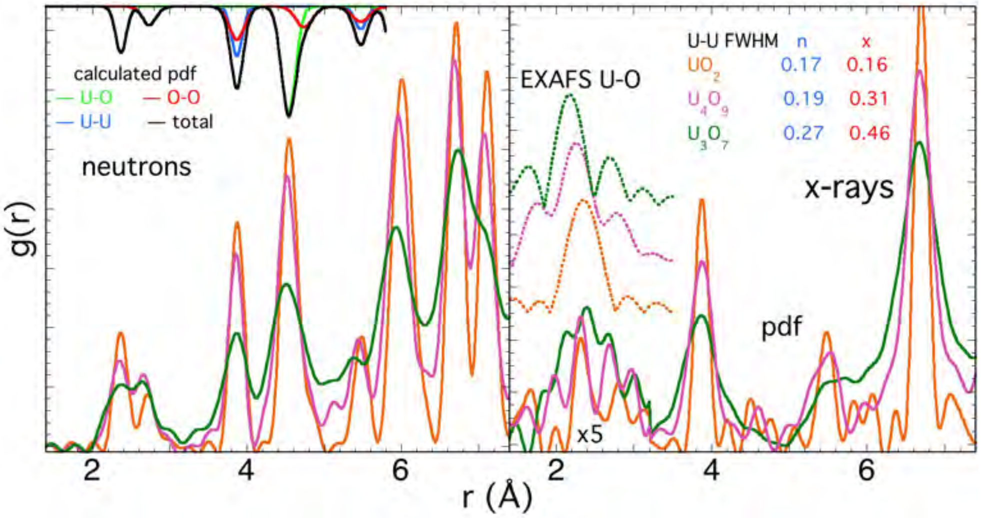

Figure 1. Neutron (left) and x-ray pdfs and phase corrected U-O contributions to the EXAFS (right) of indicated compounds.

Ultrafast pump-probe optical reflectivity measurements (Figure 2) above and within the Mott gap demonstrated that, whereas the initial metal-to-metal charge transfer excitation is normal, the relaxation is not. Within 10-20 picoseconds relaxation to a mid-gap state occurs, consistent with polaron formation. Two relaxation from this state are observed, one on the order of 100 psec and the other of 1 –2 μ sec. The fast relaxation has an anomaly at the AFM transition, the slow one an anomaly of unknown origin at higher temperature. Although both accelerate with increasing temperature, the temperature dependence differs from a standard thermally activated process. Furthermore, the increase in the lifetime with increased pump power is consistent with self-interaction, i.e., clustering of these mobile optically induced polarons.

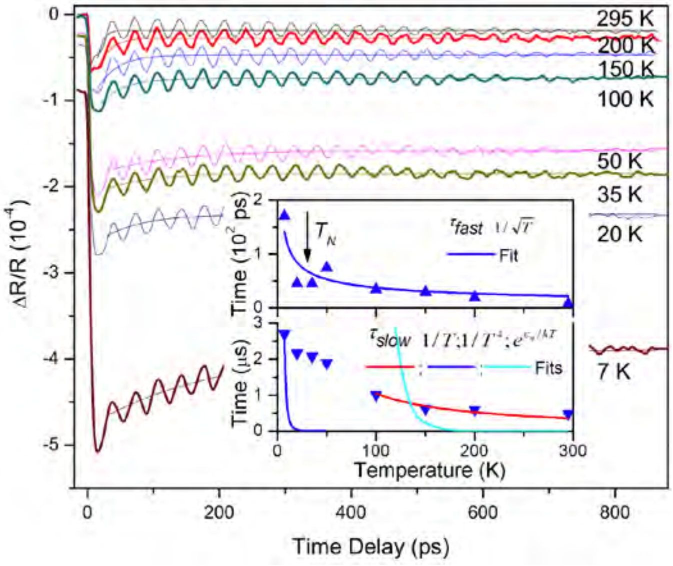

Figure 2. Results of pump-probe time resolved optical reflectivity measurements.

The relevance to the current HEC them of covalency is that in addressing the goal of determining covalency in solid state materials to complement measurements in molecular ones it was discovered that hypervalent urania displays these highly unusual properties associated with intrinsic dynamics, as occur in other complex correlated materials. This includes the unique finding in O K edge XAS measurements of homogeneous type electronic structures that occur despite the very large degree of disorder in the crystal structures, which may result from the breakdown of the Born-Oppeheimer approximation in polarons with tunneling, although this particular manifestation was not predicted in the original examination of this phenomenon. However, the model system was cuprates that have a much less radical polaron. We are therefore pursuing these effects because of their novel physics related to the distinct electronic structure of actinides and their relevance to polaron physics in general.

Science objectives for 2011-2013:

- Expand advanced optical measurements that probe the excited state behavior and other transport properties.
- Reinstate our solid state synthesis capabilities that have been lost to produce single crystals of UO_{2+x} with known stoichiometries. These may also be synthesized in collaboration with the CEA lab in Cadarache, which would be faster but would not allow us to extend this capability to transuranics.
- Use these crystals in further optical and other studies, including inelastic neutron scattering and resonant inelastic x-ray scattering to probe the soft modes associated with the dynamics and the transformation of the electronic states as they are pinned by the adventitious O atoms.
- Continue to develop the real state modeling approach for application to these materials and also the polaron model to elucidate the role of dynamics on electronic structure.
- Use these results as input to determination of the structure and electronic structure calculations.

Facilitating Experiments at a Synchrotron

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Collaborators: P. Fenter (ANL-CSE), M. Schmitt (CSE Postdoc), Meimei Li (ANL-NE), J. Almer (APS), B. Lai (APS), S. Vogt (APS), P. Eng (U Chicago), J. Stubbs (U Chicago), M. Schlossman (UIC), W. Bu (UIC Postdoc), T. Paunesku (Northwestern), G. Woloschak (Northwestern)

Overall research goals: Over the last two decades synchrotron experiments have revolutionized our understanding of actinide chemistry. Our goal is to facilitate this continued revolution by (1) assisting experimenters with actinide samples access to synchrotron radiation, and (2) developing and adapting new techniques targeted specifically at problems of current interest to the actinide and separations sciences communities.

Significant achievements during 2009-2011: The last two years have been largely focused on scattering techniques. Building on our development of high-energy x-ray scattering for probing actinide speciation in solution, we have combined results from pdf analysis of coordination environments with independent solvent extraction experiments to provide structural information about metal complexes targeted for separation.

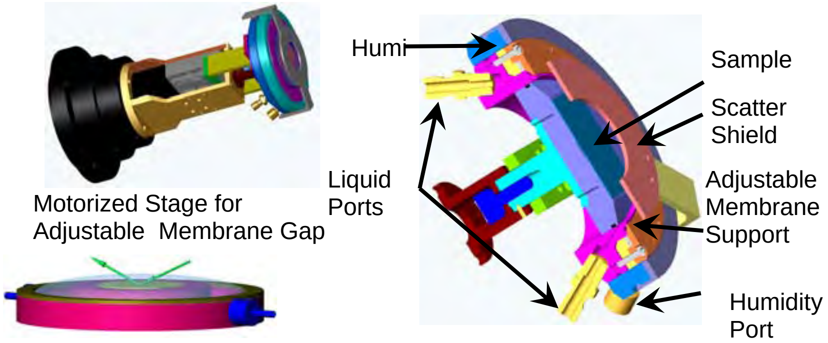
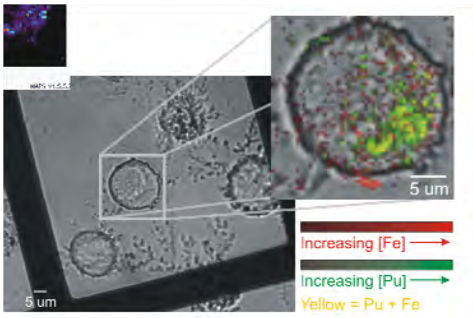


Figure 1: Solid-liquid surface cell for *in situ* x-ray scattering

Our structural efforts have extended from simple solutions to solid-liquid interfaces. Structural characterization of metal-ion adsorption to single-crystal surfaces is providing new insight into catalytic and environmental processes. Responding to community needs, we have brought together scientific and technical expertise to address complex experimental requirements associated with running in-situ experiments with actinide substrates and/or adsorbates. The result is a purpose-built flow cell, as shown in Figure 1, that can accommodate the complex geometrical requirements associated with surface-scattering experiments. Tested on Pu solutions in contact with a muscovite surface, [1] this cell design is available to the general community. [2]



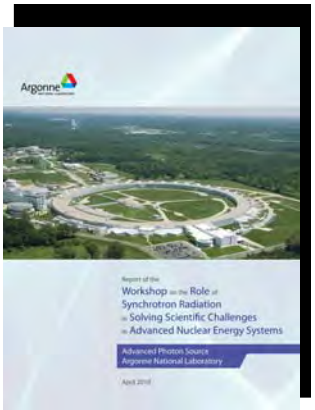
Efforts to extend our capabilities into x-ray imaging have begun with experiments centered on probing Pu uptake by mammalian cells. Low-level actinide concentrations in light matrices make this an ideal project to begin such studies. Encapsulation and sample handling have been the predominant problems to overcome. Although low energies currently limit encapsulation options, planned availability of high-energy imaging beamlines should be of importance to this community.

Science objectives for 2011-2013:

- Develop in-situ heating capabilities for solution experiments with application centered on teasing entropic contributions from metal-ligand complex free energies determined by HEXS. Also planned are *in situ* studies of solvothermal reactions to provide here-to-fore unavailable kinetic and structural information of relevance to mechanistic modeling.
- Extend solid-liquid interfacial scattering opportunities to liquid-liquid interfaces. Working with Professor Schlossman (UIC), scattering experiments involving aqueous-organic, liquid-liquid interfaces will be undertaken, with an initial focus on rare-earth systems. Extension to actinide-containing samples will proceed as appropriate cell designs are developed. Systems will be chosen based on current issues in lanthanide/actinide separations.
- In collaboration with Office of Nuclear Energy funded experimenters, the design of synchrotron imaging experiments is currently underway. The issues concern limiting external radiation dose, different from our experiences to date, which have centered on hazards associated with sample activity. The focus is on quantifying stress cracking of reactor components under *in situ* conditions, with the goal of a mechanistic understanding of radiation damage to components of critical interest to nuclear reactor applications.

Publications supported by this project 2009-2011

1. L. Soderholm, S. Skanthakumar, R.E. Wilson; Structures and energetics of erbium chloride complexes in aqueous solution, *J. Phys.Chem. A 113* (2009) 6391-6397.
2. P. Fenter, S.S. Lee, C. Park, L. Soderholm, R.E. Wilson, O. Schwindt; Interaction of muscovite (001) with Pu^{3+} bearing solutions at pH 3 through ex-situ observations, *Geochim. Cosmochim. Acta, 74* (2010) 6984-6995.
3. M. Schmidt, P. Eng, J. Stubbs, P. Fenter, L. Soderholm,; On a new X-ray reflectivity environmental cell design for in situ studies of radioactive and atmosphere-sensitive samples (submitted).
4. W. Bu, B. Hou, M. Mihaylov, I. Kuzmenko, B. Lin, M. Meron, L. Soderholm, G. Luo, M. L. Schlossman; X-ray fluorescence from a model liquid/liquid solvent extraction system (in press).
5. M. P. Jensen, D. Gorman-Lewis, B. Aryal, T. Paunesku, S. Vogt, P. G. Rickert, S. Seifert, B. Lai, G. E. Woloschak, L. Soderholm; Solution Conformations of Plutonium-bearing Transferrins Reveal a Mechanism for Cellular Uptake of Plutonium. *Nature Chemical Biology* (in press).



6. L. Soderholm, Workshop report, *Role of Synchrotron Radiation in Solving Scientific Challenges in Advanced Nuclear Energy Systems,* www.aps.anl.gov/News/Conferences/2010/RAD/RAD-Workshop-Report.pdf

Experimentally Characterizing the Electronic Structures of f-Electron Systems Using Advanced High Resolution Fourier Transform Microwave Spectroscopies

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Overall research goals: The objective of this project is to develop Fourier transform microwave spectroscopy techniques for the study of prototypical actinide-containing molecules in order to provide fundamental, and tractable, new data for use in the theoretical treatment of f- electron systems.

Significant achievements during 2010-2011: The Project was initiated in the summer of 2010 and one graduate student, Miss Brittany Long is currently working supported on this contract. To date, we have been doing preliminary studies in order to optimize our instrumentation for the planned study of principally U - and Th-species. In this regard good progress has been made. The instrumentation developed consists of a traditional Balle-Flygare Fourier transform microwave spectrometer operating between 6 and 26 GHz, a chirped-pulse Fourier transform microwave spectrometer operating between 8 and 18 GHz, and a novel high frequency instrument operating between 70 and 110 GHz. All instruments are equipped with laser ablation sources.

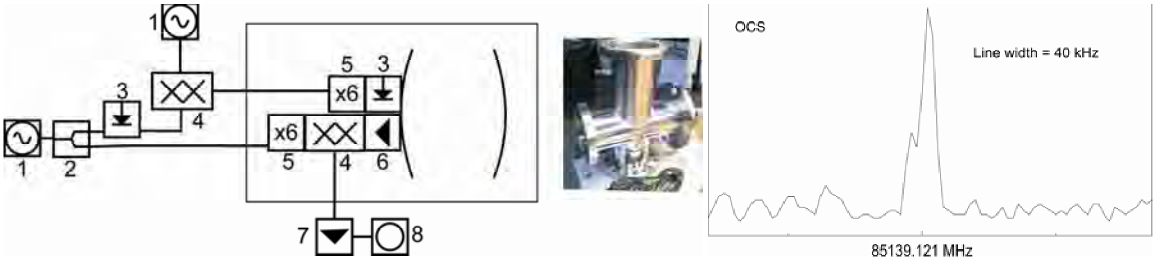

Figure 1. Our newly constructed W-band FTMW spectrometer

With instrumentation developed with have been pursuing pure rotational spectroscopic from a variety of heavy element species, XY, where X =Ba, Hf, Nd, Lu, Pb; Y=O,F,S,Cl, and Br. Data from these studies will be presented.

Science objectives for 2011-2013:

- We will fully transition to the study of the primary target species, i.e. simple U- and Th-systems.
- Analyses of spectral data will be performed.
- Computational approaches will be explored, in collaboration, to identify successful methodologies that support the data collected.

Publications supported by this project 2010-2011

None at this time. But several manuscripts have been planned based upon the work performed in this time frame.

Session 8 – Separations

Selectivity Principles in Anion Separation by Self-Assembled Cage Receptors

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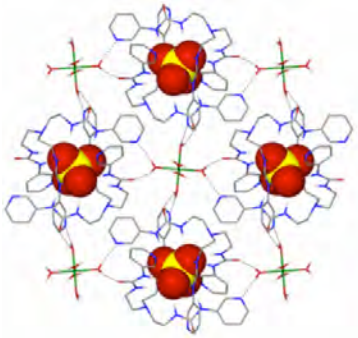
Collaborators: Benjamin P. Hay, Peter V. Bonnesen, Bruce A. Moyer, Oak Ridge National Laboratory

Overall research goals: We seek to understand the factors underlying selectivity in anion binding and separation by self-assembled cage receptors. Encapsulation inside molecular or crystalline cages, which ensures complete isolation of the anion from its competitive aqueous environment, is targeted to maximize the anion recognition and separation efficiency. We employ a self-assembly approach towards these cage receptors, which allows their quick and efficient construction from relatively simple building blocks, unlike the laborious multi-step organic synthesis of traditional receptors. Finally, exquisite anion selectivity is achieved by introduction of molecular recognition elements into the building units, and through precise spatial organization of binding groups guided by computer-aided design.

Significant achievements during 2009-2011: The fundamental principles governing anion selectivity in crystallization of urea-functionalized cages (Figure 1) have been elucidated in a comprehensive study including a detailed analysis of thermodynamic, kinetic, structural, and solvation factors. Crystallization of the cages was found to be highly exothermic, with the most favorable enthalpy of crystallization corresponding to SO_4^{2-} and SeO_4^{2-}, in agreement with the X-ray structural data showing shape complementarity between these tetrahedral anions and the urea-lined cavities of the capsules. Sulfite, on the other hand, has a significantly less favorable enthalpy of crystallization, which may be attributed to its poor fit inside the capsules, involving repulsive interactions. An interesting enthalpy-entropy interplay was observed to take place, in which the enthalpically favored selenate lost to the entropically more favored sulfate. On the other hand, sulfite, which was enthalpically least favored, remained competitive against selenate due to its favorable entropy of crystallization.



	ΔH ($kJmol^{-1}$)	TΔS ($kJmol^{-1}$)
SO_4^{2-}	-99.1	-3.8
SeO_4^{2-}	-108.5	-21.4
SO_3^{2-}	-64.6	+22

Figure 1. Sulfate separation by selective crystallization of urea-functionalized hydrogen-bonding cages. The X-ray structure shows sulfate-binding cages interlinked by $Mg(H_2O)_6^{2+}$ cations into an extended hydrogen-bonded framework.

In a complementary approach, an M_4L_6 coordination cage receptor complementary to tetrahedral oxoanions was developed with the help of computer-aided design (Figure 2). A detailed study was conducted, including solution NMR and ESI-MS analyses, X-ray structural determination, electronic-structure calculations, and MD simulations, to understand the self-assembly, anion binding, and solution dynamics of this promising new class of anion receptors. Anion-exchange experiments in competitive aqueous solutions indicated preferential encapsulation of tetrahedral oxoanions with a charge of –2 or higher, such as SO_4^{2-}, SeO_4^{2-}, CrO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, or PO_4^{3-}.

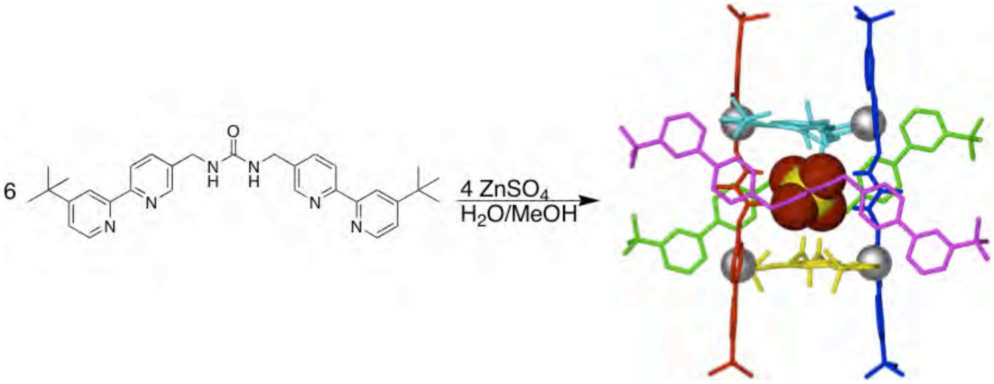


Figure 2. Self-assembly of a sulfate-encapsulating Zn_4L_6 tetrahedral cage receptor.

Science objectives for 2011-2013:

- Study the structure-selectivity relationships in anion separation by selective crystallization of self-assembled cages.
- Investigate the mechanism of anion exchange by self-assembled M_4L_6 cages in aqueous solutions, to better understand the factors governing the anion recognition and separation in this novel class of receptors.
- Employ dynamic covalent chemistry for the self-assembly of more robust anion-binding receptors and materials (e.g., dynamic covalent cages, covalent organic frameworks) with designed selectivity.

Publications supported by this project 2009-2011:

1. Custelcean, R. “Anions in Crystal Engineering”, *Chem. Soc. Rev.*, **2010**, *39*, 3675 (invited review).
2. Custelcean, R.; Bock, A.; Moyer, B. A. "Selectivity Principles in Anion Separation by Crystallization of Hydrogen-Bonding Capsules", *J. Am. Chem. Soc.* **2010**, *132*, 7177.
3. Custelcean, R., “Ion Separation by Selective Crystallization of Organic Frameworks”, *Curr. Opin. Solid State Mater. Sci.* **2009**, *13*, 68 (invited review).
4. Custelcean, R.; Bosano, J.; Bonnesen, P. V.; Kertesz, V.; Hay, B. P., “Computer-Aided Design of a Sulfate Encapsulating Receptor”, *Angew. Chem. Int. Ed.* **2009**, *48*, 4025.
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Binding and Releasing Anions with CH Hydrogen-Bonded Receptors

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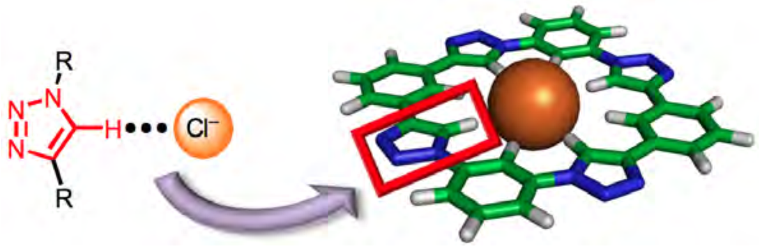
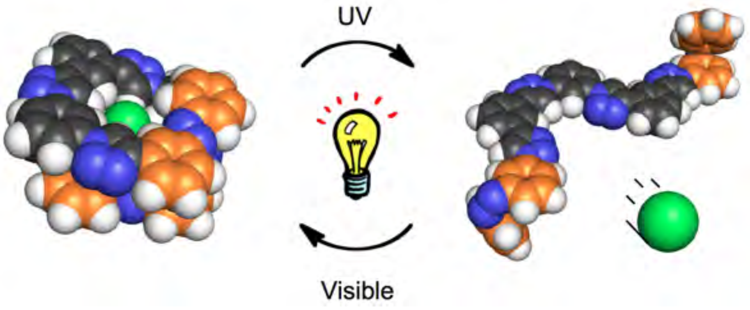
Overall research goals: Design of receptors employing CH hydrogen bonds to bind anions and then to release them using light

Significant achievements during 2009-2001: Project started in 2009. To principle developments have emerged.

1. Understanding the factors that control anion binding in aryl-triazole receptors. The macrocyclic receptors, termed triazolophanes, demonstrate extremely high anion affinities arising from the inherent pre-organization of eight CH hydrogen bond donors. The anions are stabilized in the binding pocket by surprisingly strong triazole CH hydrogen bonding.



2. After quantifying these interactions with the help of theory and experiment, inspiration from biology led us to design light-activated, anion-binding foldamers bearing azobenzene units. Taking advantage of the *cis*/*trans* photoisomerization of azobenzene, we demonstrate control over the stability of the folded structure providing a means to start regulating chloride concentrations in solution.



Science objectives for 2011-2013:

- Expand the size of the receptor cavities to be able include tetrahedral oxyanions
- Increase the hydrophobicity for anion extraction regimes
- Investigate pH swing receptors

Publications supported by this project 2009-2011

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.
2. Hua, Y.; Flood, A. H., Flipping the switch on chloride concentrations with a light-active foldamer, *J. Am. Chem. Soc.* **2010**, *132*, 12838-12840
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Controlling Actinide Hydration in Mixed Solvent Systems: Towards Tunable Solvent Systems to Close the Nuclear Fuel Cycle

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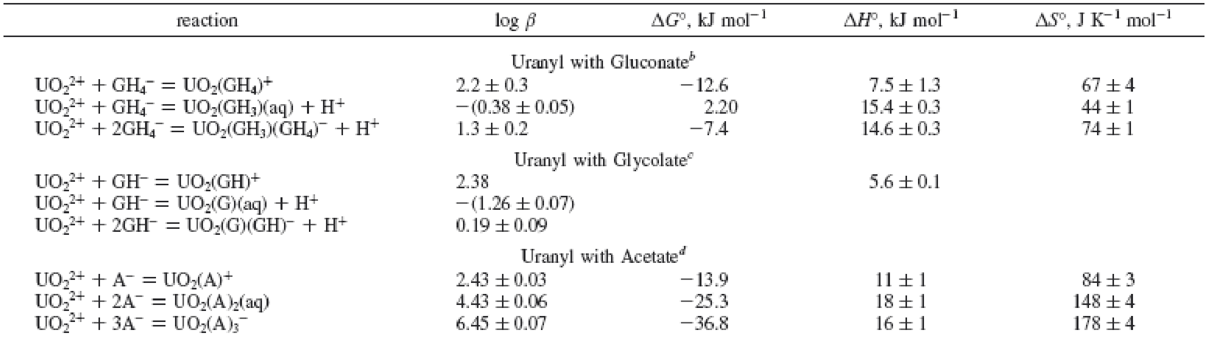
Overall research goals: The overall goal of this project is to integrate experimental methods to directly probe the hydration and covalency of the f-element cations in aqueous and mixed solvent electrolyte systems. We will accomplish this goal using traditional thermodynamic methods and advanced spectroscopic tools to explore the effect of solvent properties, cationic radius, and covalency for the f-element cations on solubility, hydration, and coordination chemistry for solution species.

Significant achievements during 2009-20011: During this time frame, this project has undergone a significant redirection away from the chemistry of U(VI) mineral phases into a study of the solution chemistry of f-element complexation in mixed solvent systems. Thus, the publications listed below reflect the completion of the U(VI) mineral work, and the start-up of the new studies.

Our initial work on the solution chemistry studies has involved investigation of gluconate as a common polycarboxylate ligand. It is a degradation product resulting from the oxidation of glucose, and it has been used in the processing of defense nuclear materials to increase the solubilities of major elements such as iron and aluminum. It is also a strong complexant of the f-element cations, as shown in the Table below. Prior to our studies, no accurate thermodynamic data existed for aqueous or mixed solvent systems.

Table 1. Thermodynamic Parameters of Uranyl Complexation with Carboxylic Acid Ligands[a]



reaction	log β	$\Delta G°$, kJ mol^{-1}	$\Delta H°$, kJ mol^{-1}	$\Delta S°$, J K^{-1} mol^{-1}
		Uranyl with Gluconate[b]		
$UO_2^{2+} + GH_4^- = UO_2(GH_4)^+$	2.2 ± 0.3	−12.6	7.5 ± 1.3	67 ± 4
$UO_2^{2+} + GH_4^- = UO_2(GH_3)(aq) + H^+$	−(0.38 ± 0.05)	2.20	15.4 ± 0.3	44 ± 1
$UO_2^{2+} + 2GH_4^- = UO_2(GH_3)(GH_4)^- + H^+$	1.3 ± 0.2	−7.4	14.6 ± 0.3	74 ± 1
		Uranyl with Glycolate[c]		
$UO_2^{2+} + GH^- = UO_2(GH)^+$	2.38		5.6 ± 0.1	
$UO_2^{2+} + GH^- = UO_2(G)(aq) + H^+$	−(1.26 ± 0.07)			
$UO_2^{2+} + 2GH^- = UO_2(G)(GH)^- + H^+$	0.19 ± 0.09			
		Uranyl with Acetate[d]		
$UO_2^{2+} + A^- = UO_2(A)^+$	2.43 ± 0.03	−13.9	11 ± 1	84 ± 3
$UO_2^{2+} + 2A^- = UO_2(A)_2(aq)$	4.43 ± 0.06	−25.3	18 ± 1	148 ± 4
$UO_2^{2+} + 3A^- = UO_2(A)_3^-$	6.45 ± 0.07	−36.8	16 ± 1	178 ± 4

[a] $I = 1.0$ M $NaClO_4$ and $t = 25$ °C. [b] The error limits represent three standard deviations (3σ) as obtained from the computerized programs. [c] The stability constants and enthalpy of uranyl complexation with glycolate are from refs 33 and, 35, respectively. [d] The thermodynamic parameters of uranyl complexation with acetate are taken from ref 34.

Our data determined to date is summarized in the figure below (next page). Complexation appears to follow an electrostatic trend for divalent, pentavalent, and trivalent cations. For hexavalent cations, however, complexation is much smaller than predicted. This observation is explained by the difference in coordination chemistry for the dioxo hexavalent cations.

In addition, we have observed some interesting photochemistry between the uranyl cation and gluconate. These observations will be described, along with our plans for translating this work into mixed solvent systems.

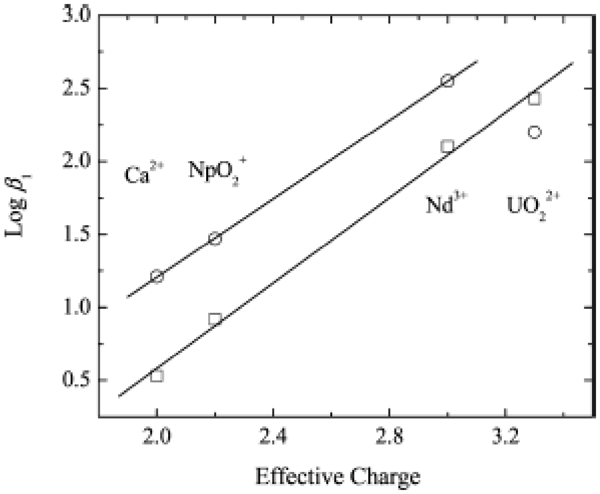


Fig 1 1. Log β_1 versus effective cationic charge plot. Symbol (□): Data of acetate complexation with those cations at $I = 1.0$ M and $t = 25$ °C, ref 34; (○): Data of gluconate complexation with those cations at $I = 1.0$ M $NaClO_4$ and $t = 25$ °C, this group.

Science objectives for 2011-2013:

- Develop thermodynamic data for the complexation of the f-elements with ligands of interest in methanol:water systems
- Develop microcalorimetric capabilities for measuring enthalpies and entropies of complexation of the actinides and lanthanides by polycarboxylate ligands
- Develop ESI-MS as a tool for studying lanthanide and actinide coordination chemistry.

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

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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. A specific aim entails understanding the contribution of coulombic or ion-pairing interactions to the selectivity of anion receptors and how can these effects be harnessed in cooperation with other donor interactions. Recognition in extractive separations can be viewed in terms of cooperative binding and partitioning processes. A consideration of the eleven ways that these processes can be combined to achieve a selective separation of ions has led to the identification of synergistic anion exchange (SAE) as a previously unexplored type of extraction method for selective anion extraction. SAE consists of combining a neutral lipophilic anion receptor with an anion-exchange vehicle such as a lipophilic quaternary ammonium salt. Since the anion-exchanger has a selectivity of its own that follows the well-known Hofmeister order favoring charge-diffuse anions, the addition of an anion receptor to the organic phase is expected to modulate selectivity via structured hydrogen-bond donor (HBD) interactions, leading to non-Hofmeister selectivity. 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 in 2009–2011:

Strong SAE of sulfate from an aqueous sodium nitrate solution in opposition to the Hofmeister bias was observed upon addition of certain macrocyclic anion receptors to a chloroform solution of the nitrate form of a lipophilic quaternary ammonium salt (methyltri-$C_{8,10}$-ammonium nitrate, Aliquat 336N).[2] Eight macrocycles were surveyed, including two derivatives of a tetraamide macrocycle, five derivatives of calix[4]pyrrole (C4P), and β-decafluorocalix[5]pyrrole. Under the hypothesis that the enhancement, up to 1000-fold under the conditions surveyed, originates from sulfate binding by the anion receptors in the chloroform phase, it was possible to show the formation of 1:1 and 2:1 receptor:sulfate complexes, with apparent 1:1 sulfate-binding constants falling in the range 2.1–4.8. Comparison of the results for the various anion receptors included in this study reveals that sulfate binding is sensitive to the nature of the substituents on the parent macrocycle scaffolds in a way that does not follow straightforwardly from simple chemical expectations, such as electron-withdrawing effects on HBD strength.

Extraction results indicated that the lipophilic cation plays a key role in the selectivity of SAE using lipophilic anion receptors. The effect is apparently strong enough for the anion receptor calix[4]pyrrole (C4P) to reverse the enhancement selectivity from Hofmeister nitrate selectivity to anti-Hofmeister sulfate selectivity upon switching the quaternary ammonium cation from tetraheptyl to methyltri-$C_{8,10}$. The reversal was hypothesized to occur from the insertion of the methyl group of the latter quaternary ammonium cation into the cup of C4P cone conformation upon sulfate binding. This hypothesis is supported by DFT calculations and a crystal structure (Fig. 1), the first for a calixpyrrole binding sulfate, showing methyl insertion into the C4P cup and H-bonding of C4P to one O-atom of the sulfate anion. Such anti-Hofmeister selectivity is also seen among competing univalent anions in which chloride is favored vs nitrate, strongly enough that the chloride separation factor vs nitrate exceeds unity, that is, a real "uphill" separation of chloride from nitrate. By contrast, little synergism is observed with a bisthiourea tweezer anion receptor, suggesting a structural basis for cooperativity between the anion receptor and exchanger. Two manuscripts are in preparation.

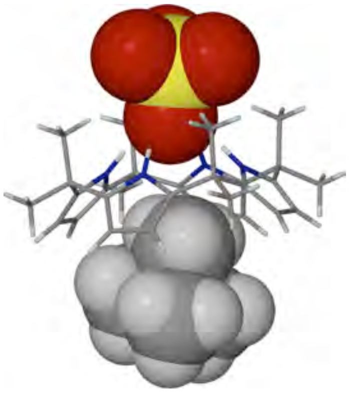

Figure 1. Crystal structure showing insertion of methyl group of the tetramethylammonium (TMA) cation into the cavity of C4P and pyrrolic H-bonding to sulfate.

Science objectives for 2011–2013:

- Through equilibrium modeling, determine the mechanism of SAE involving sulfate extraction by lipophilic quaternary ammonium salts in combination with selected anion receptors. Clarify the cooperative role of the cation in controlling selectivity and elucidate competitive anion binding.
- Investigate the effect of less "innocent" anion exchangers, such as alkylated guanidiniums, that can interact directly with anions and thereby form mixed HBD complexes with anions.
- Begin examining self-assembly of MOF-based anion receptors in ionic liquids. Since self-assembled capsules for anion inclusion may be highly charged yet lipophilic, ionic liquids present themselves as potentially ideal charge-compensating media for anion separations. Experiments employ an ionic liquid to self-assemble our previously designed tetrahedral sulfate-binding cage based on simple linkers each bearing a central urea between terminal 2,2'-bipyridines and Ni^{2+} metal centers. The goal is to test the hypothesis that the ionic-liquid matrix will facilitate an effective liquid-liquid separation of sulfate via encapsulation analogous to the selective crystallization obtained earlier.

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Abstracts Not Presented

Functionalized Scaffolds as a New Approach to the Design of

Ion-Selective Polymer-Supported Complexants

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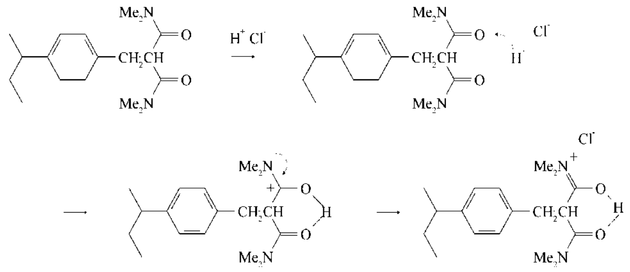
Overall research goals

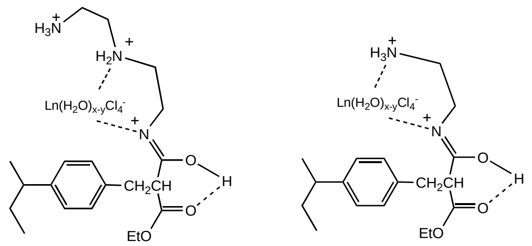
The objective of this research is to define the parameters under which ion-selective polymer-supported complexants can be designed and synthesized. During the current period (2009 – 2011), a review was published tracking the development of ion exchange resins to show how selectivity is influenced by the pK_a of a ligand capable of interacting with metal ions through ion exchange This was followed by a review of polymers with high affinities for lanthanide ions which showed that complexation was influenced by the polarizability of the donor atom on the immobilized ligand; the phosphonic acid ligand was found to be an important ligand affecting the selectivity for lanthanide ions. The same principles were also found for the complexation of transition metal ions.

Significant achievements during 2009-2011

Research during the current period focused on polyamides, with tetramethylmalonamide (TMMA) being studied first. The polymer was contacted with lanthanide ions in 0.001 − 8 M HCl and HNO_3 solutions. The mechanism of complexation was elucidated by first noting that the distribution coefficients were low in 0.001 to 2 M acid, increased in 4 and 6 M, and then decreased in 8 M acid. In low-acid, the metal ion remains in solution. As the acid concentration exceeds 2 M, the amide is protonated to form an iminium moiety that ion-exchanges the anionic lanthanide complex resulting in partial release of waters of hydration. At high acid concentration, the affinity decreases due to competition by the large excess of counterions for the ion-exchange sites. The affinity sequence in 6 M HCl is Tb > Dy > Eu > Gd > Ho > Sm > Er > Tm > Yb > Lu > Nd > Ce > La. The TMMA−Ln interaction is due to recognition since there is a point of maximum affinity across the series rather than a monotonic trend. The two opposing modes are electrostatic attraction of the $Ln(H_2O)_xX_4^-$ complex by the protonated TMMA ligand and loss of waters of hydration as the iminium binds the Ln.

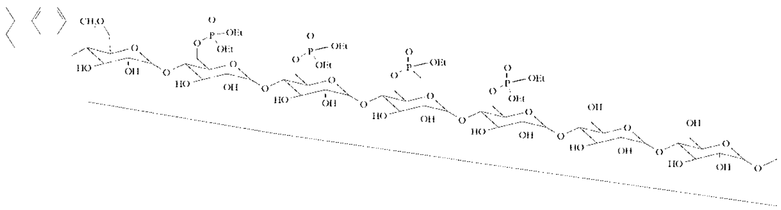


A subsequent study with polystyrene-bound malonate ligands modified with diethylenetriamine showed the same mechanism. The affinities for lanthanide ions were again due to protonation of the carbonyl oxygen triggering formation of an iminium ion. Electrostatic attraction of $[Ln(H_2O)_xX_4]^-$ by the protonated ligand and (partial) loss of the waters of hydration are the two competing reactions that determine the distribution coefficients. Affinity and selectivity are affected by substituents on the iminium ion. Higher affinities of malonate monoamidated with ethylenediamine suggest that the protonated –NH– stabilizes the lanthanide chlorocomplex.



In a different study of designing ion-selective polymers, a silicate-selective polymer-supported complexant was developed that utilizes the reactivity of silicate to generate polyanionic Keggin structures. Heptamolybdate anions were immobilized onto trimethylammonium ligands bound to polystyrene. The heptamolybdate complexed >90% of the silicate from a 20 ppm solution at pH 7. Complexation by the heptamolybdate remained high throughout the pH range 3.8–10.7. Sorption was unaffected by the presence of chloride, sulfate, and nitrate ions. The rate-limiting step was accessibility of the silicate to the heptamolybdate rather than the rate of reaction to form the silicomolybdate. FTIR spectra confirmed silicomolybdate formation.

Earlier research established that polystyrene-bound polyols were effective scaffolds onto which phosphate ligands could be attached. This was extended to the synthesis of phosphorylated polystyrene-bound cyclodextrin. The polymer had a very high affinity for the uranyl ion from acidic solutions.



Objectives for 2011-2013

The synergistic cooperation of groups within a given ligand offers an important pathway in the design of ion-selective ligands. This will be followed during the upcoming period with a series of polymer-bound aminophosphonates. The target interaction will be between the amine and phosphoryl sites in the ligand and the affinities then determined for a wide array of divalent and trivalent metal ions, including the lanthanide and uranyl ions.

Publications supported by this project during 2009-2011

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Zhu, X.; Alexandratos, S. D. *Effect of Hydrogen Bonding: Polymer-Bound Phosphorylated Cyclodextrin, Journal of Applied Polymer Science*, in press (January 2011)

New Proton-Ionizable, Calixarene-Based Ligands for Selective Metal Ion Separations

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Overall research goals: The objective of this project is the design and synthesis of new proton-ionizable calix[4]arene-based ligands and their evaluation and application in metal ion separation processes.

Scientific achievements during 2009-2011: The calix[4]arene framework provides an unusually versatile scaffold for the construction of new metal ion complexing agents. Attachment of two acidic side arms via the lower-rim phenolic oxygens produces ligands that form electroneutral complexes with divalent metal ion species. By avoiding the requirement for concomitant extraction of an aqueous phase anion into an organic medium with the metal ion in a separation process, such 'charge matching' markedly enhances the propensity for metal ion transfer into the organic medium in a solvent extraction or liquid membrane transport process compared to non-ionizable analogues.

In our work, attention has been focused upon ionizable groups of carboxylic acid and *N*-(X)sulfonyl carboxamide [$-C(O)NHSO_2X$] with X = $-CH_3$, $-C_6H_5$, $-C_6H_4$-4-NO_2 and –CF_3. In the latter, X variation serves to 'tune' the acidity over about three pK units.

Appropriate choices for non-ionizable groups attached to the remaining two lower-rim phenolic oxygens controls the conformation of the ligand among the possibilities of conformationally flexible or locked in a cone, partial cone, 1,3-alternate or 1,2-alternate conformation.

Connection of the two remaining phenolic oxygens of the calix[4]arene scaffold with a polyether chain gives di-ionizable calixarene-crown ethers, also called calixcrowns. Attachment of two distal oxygens results in a di-ionizable calix[4]arene-1,3-crown ether ligand; whereas linking two proximal oxygens provides a di-ionizable calix[4]arene-1,2-crown ether analogue.

A further structural variation is the presence of substituents on the para positions of the aromatic rings. The most frequently encountered upper-rim substituent is the *tert*-butyl group.

In this project, the selectivity and efficiency with which new di-ionizable calix[4]arenes complex divalent metal ion species are being probed by solvent extraction of alkaline earth metal cations, lead(II) and mercury(II) from aqueous solutions into chloroform. The effects of systematic structural variations within the di-ionizable calix[4]arene ligands upon their divalent metal ion extraction behavior are providing important insight that is being used in the design of new and improved divalent metal ion complexing agents.

Science objectives for 2011: During the remain months of the final year of this grant, attention will be focused upon ligands with ionizable groups on the para positions of the aromatic rings (upper rims) in di-ionizable calix[4]arenes and calix[4]arene-crown compounds. As before, our primary method for probing separation selectivity and efficiency will be solvent extraction of divalent metal ions from aqueous solutions into an organic diluent.

Publications supported by this project 2009-2011

1. "Metal Ion Complexation in Acetonitrile by Di-ionized Calix[4]arenes Bearing Two Dansyl Fluorophores," Ű. Ocak, M. Ocak, K. Surowiec, R. A. Bartsch, M. G. Gorbunova, C. Tu and M. Surowiec, *Journal of Inclusion Phenomena and Macrocyclic Chemistry,* **2009**, *63*, 131-139.
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12. "Tri-ionizable Calix[4]arene Ligands: Synthesis and Lanthanide Ion Complexation," F. A. Fernandez, R. A. Bartsch, F. Arnaud-Neu, V. Hubscher-Bruder and Sylvie Michel, *ARKIVOC*, **2010** *vii*, 191-202.
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Interfaces in Separations Science

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Overall research goals: As practiced for separations, the solvent extraction process involves transport of targeted molecular species across a liquid-liquid interface. Although ripe with speculation, there is little metrical information currently available that addresses atomic-scale mechanisms at play during ion or complex transfer across an interface. Our goal is to utilize newly developing x-ray scattering methodology to probe aqueous/organic and solution/air interfaces in a quantified approach. Our efforts are expected to provide fundamental knowledge for the development of advanced approaches in metal separations relevant to nuclear-energy systems.

Significant achievements during 2009-2011:

1. $ErCl_3$ (aq.) / dodecane interfaces were studied with x-ray reflectivity. The interfacial adsorption of Er^{3+} ions increases with $ErCl_3$ concentration. This effect is the result of the difference between interfacial and bulk interactions of the ion with neighboring solvent molecules and other ions. For multivalent ions, this effect is enhanced.

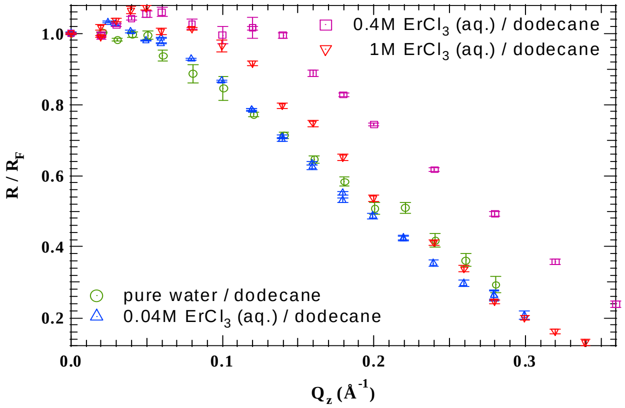

Figure 1. R/R_F from water/dodecane interface as a function of moment transfer, Q (Å^{-1}), with $ErCl_3$ concentrations of 0, 0.04 M, 0.4 M and 1 M. R_F is the calculated Fresnel reflection from sharp interface.

2. Total-reflection x-ray fluorescence (TRXF) was first applied to the study of a liquid-liquid interface. The x-ray penetration depth across the interface with incident angle below or around critical angle is found to be about 50~100 Å. With this technique, the concentration of Er^{3+} was measured at a 10^{-5} M $ErCl_3$ (aq.) / 10^{-3}M HDEHP (dodecane) interface. The result shows there to be less than 1 Er^{3+} per 1000 Å^2, too low to be quantified with this technique. However, for a 0.1 M $ErCl_3$ (aq.) / 10^{-3} M HDEHP (dodecane) interface, TXRF measurement shows Er^{3+} was significantly adsorbed by HDEHP at the interface. The interfacial concentration was seen to increase with time during the experiment, a result consistent with visual observation of Er^{3+} - HDEHP crud formation at the interface.

3. In a collaborative effort with the Actinide Facility and Professor Schlossman, we have begun to design a sample cell for liquid-liquid scattering from acidic samples containing radionuclides. To begin this process we have constructed a coated sample cell for use on non-radioactive samples, as sketched in Figure 2.

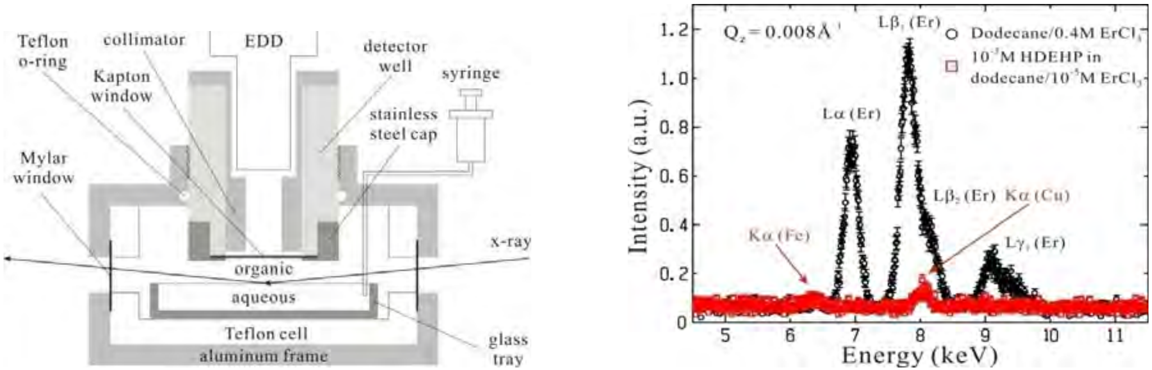

Figure 2. Left: Cross-sectional view of the sample cell for TRXF. EDD refers to the energy dispersive detector. Right: a comparison of x-ray fluorescence (XRF) spectra measured from 0.4M $ErCl_3$ (aq.) / dodecane and 10^{-5}M $ErCl_3$ (aq.) / 10^{-3} M HDEHP (dodecane) interfaces. Er^{3+} emission lines were too weak to be measured for the latter interface.

Science objectives for 2011-2013:

- Study aqueous/organic interfaces with surfactants/extractants with varying hydrophobic chain length but the same headgroup as HDEHP, in order to understand the interaction of the phosphate headgroup with target ions and the influence of hydrophobic-chain length on the formation of the ion/extractant (or surfactant) complexes at the interface.
- Study aqueous/air interfaces with and without extractants present in order to quantify the interfacial structure and to probe interactions between species. In x-ray studies of aqueous/organic interfaces, the scattering from top phase contributes significantly to the detected signal as background. To enhance signal-to-noise and thus spatial resolution, we will begin studies with our new, customized trough (sample cell) by performing experiments at aqueous-air interfaces. In a typical x-ray reflectivity measurement from the aqueous/organic interface Q_z is limited to about 0.3 $Å^{-1}$, but this maximum increases to 0.8 $Å^{-1}$ at the aqueous/vapor interface. We will probe the metal surface concentration with and without the extractant as well as the extractant structure at the surface. These experiments will provide the preliminary information necessary to extend our studies to aqueous/organic interfaces with the same metal and extractant present.

Publications supported by this project 2009-2011

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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 2009-2011: Soft X-ray investigations focused on near-edge X-ray absorption fine structure (NEXAFS) with the Advanced Light Source-Molecular Environmental Science (ALS-MES) Beamline Scanning Transmission X-ray Microscope (STXM) to obtain electronic structure information from actinide materials. NEXAFS spectra were used to understand the novel materials $(CpSiMe_3)_3U$-AlCp* with Arnold[1], $La_2U_2Se_9$ with Ibers[4], and ReO_4^- with Kozimor[8]. The molecular structure and NEXAFS spectra from $(CpSiMe_3)_3U$-AlCp* establishing the trivalent U oxidation state are shown in Fig. 1. Similarly, the U oxidation state in $La_2U_2Se_9$ was found to be tetravalent. O K-edge spectra collected at ALS-MES STXM from ReO_4^- were used to validate the approaches for corresponding studies of complex actinide materials containing oxygen. O K-edge spectra recorded from isoelectronic uranyl species were interpreted using DFT with Den Auwer[11]. STXM was Soft X-ray emission spectroscopy (XES) was employed to probe the filled states of bare trivalent separations ligands based on phenanthroline-derivatives developed by Yaita and the resultant f-element complexes. A spectral signature from the bare trivalent separations ligands alone, indicating whether the ligand is suitable, was identified in the N K-edge (N2p) XES spectra.

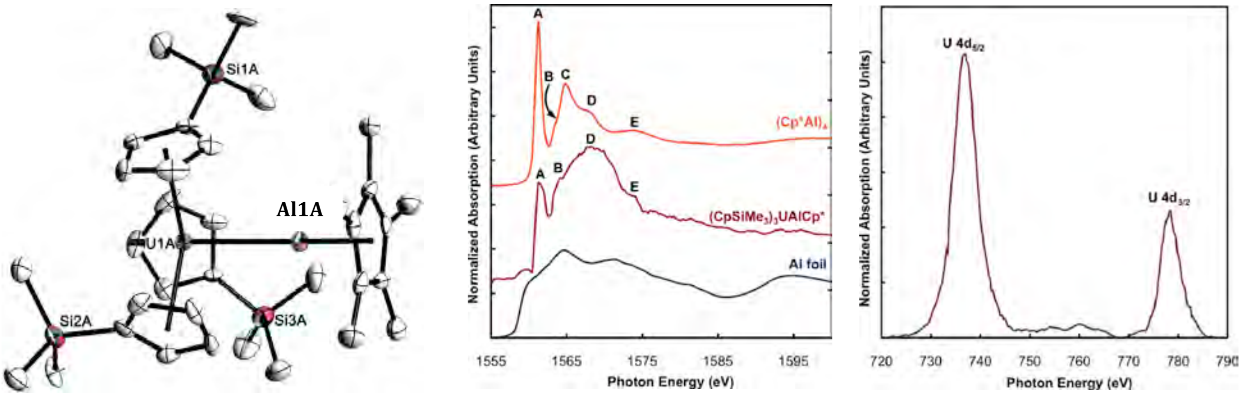

Figure 1. Left: Molecular structure of $(CpSiMe_3)_3U$-AlCp* and thermal ellipsoids at the 50% probability level with the hydrogen atoms removed for clarity; Center: Al K-edge near-edge spectra obtained from a particle of starting material $(Cp^*Al)_4$ (top), $(CpSiMe_3)_3U$-AlCp* (middle), and a slightly oxidized Al thin film (bottom); and the U $4d_{5/2,3/2}$ absorption spectrum collected from the $(CpSiMe_3)_3U$-AlCp* particle.[1]

Science objectives for 2011-2013:

- Actinide STXM investigations will continue to be performed on transuranic materials, reference materials, and complexes. This will be complemented by theoretical calculations and structural studies of the same complexes with the ALS small molecule diffractometer. As materials preparation capabilities mature, more transuranic materials produced from LBNL will be examined.
- XES/RIXS will continue to examine actinide reference materials, oxides, and complexes relevant to trivalent separations. An effort will be made to develop new capabilities for XAS and XES/RIXS at intermediate X-ray energies.
- The efforts in the LBNL laboratory will focus on the implementation of new growth systems, glove boxes, and infrastructure. The development of the actinide generation II end station, initially as a laboratory-based device, will be initiated.

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