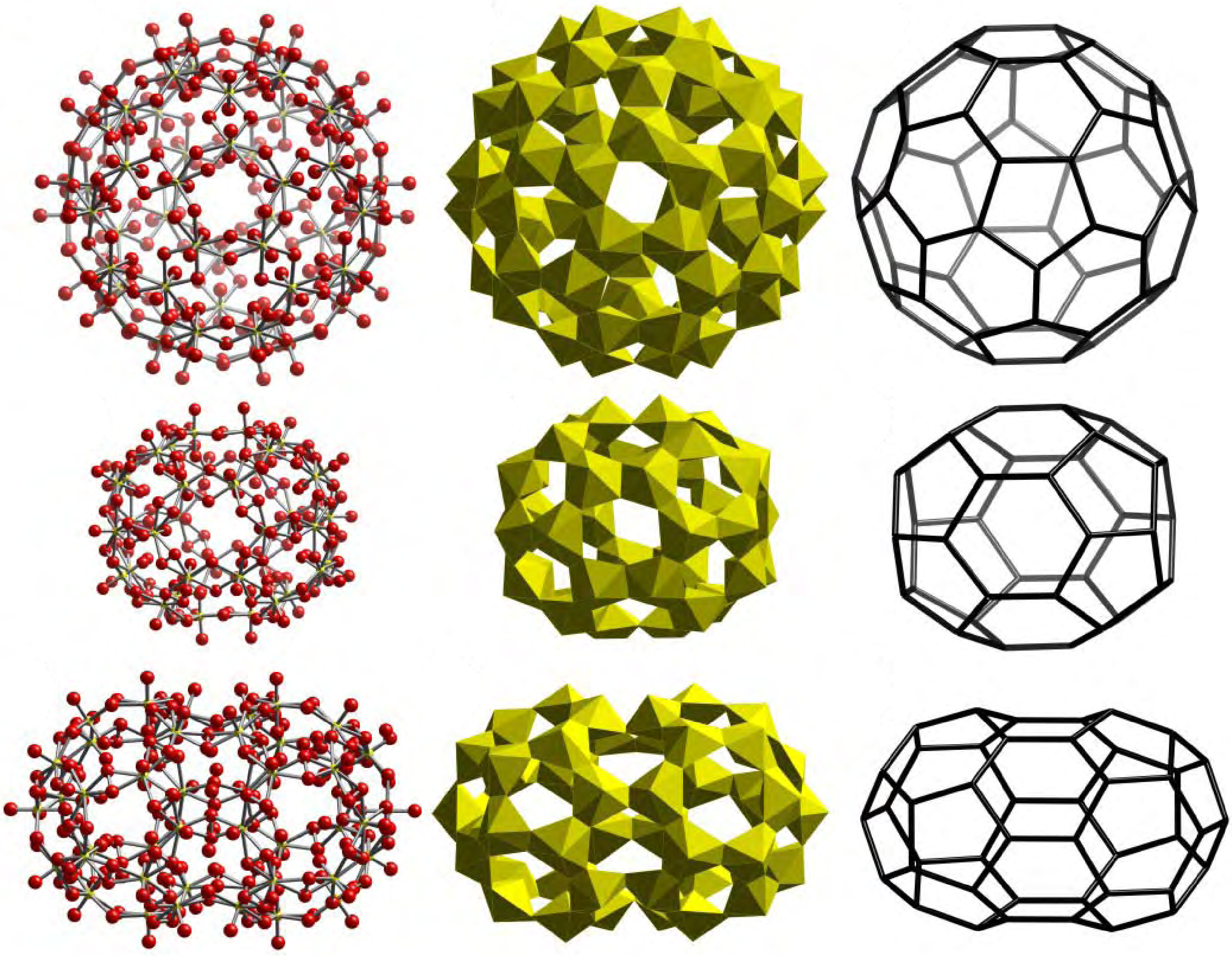
Program and Abstracts

DOE Separations and Heavy Element Chemistry Research Meeting

Airlie Center, Warrenton, Virginia, April 21- 24, 2009



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

Program and Abstracts

Separations Program
Heavy Element Chemistry Program

Contractors' Meeting

Airlie Center
Warrenton, VA
April 21-24, 2009

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Cover Graphics:
The cover artwork is representations of the uranyl peroxide components of the structures (top to bottom) U60, U36, and U44. For more details see abstract by Peter C. Burns on p. 21 of this book. Also see *G. E. Sigmon, et al, Angew.Chem.Int. Ed. 2009,* ***48****, p. 2737* and *Nature, March 20, 2009, p. 262*. Used by permission of Peter C. Burns, University of Notre Dame, Notre Dame, IN 46556.

This document was produced under contract number DE-AC05-06OR23100 between the U.S. Department of Energy and Oak Ridge Associated Universities.

The research grants and contracts described in this document are supported by the U.S. DOE Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division.

Foreword

This abstract booklet provides a record of the ninth U.S. Department of Energy contractors' meeting in separations sciences and the fifth in heavy element chemistry. This year the meeting is co-chaired by Dr. Laetitia Delmau (Oak Ridge National Laboratory) and Professor Michael Heaven (Emory 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 fourth 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 has invited talks, oral presentations, as well as invited and regular posters, organized so that papers in related disciplines are loosely clustered together. With ample time for discussion and interactions, we emphasize that this is an informal meeting for exchange of information and building of collaborations; it is not a review of researchers' achievements or a forum to choose future directions.

We are pleased to collaborate with Laetitia Delmau and Michael Heaven 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 Margaret Lyday 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.

William S. Millman
Lester R. Morss
Norman Edelstein
Larry A. Rahn

Agenda

DOE Separations and Heavy Element Chemistry Research Meeting
Airlie Center, Warrenton, Virginia, April 21- 24, 2009

Tuesday, April 21, 2009

3:00 – 6:00	p.m.	*** Registration ***
6:00 – 7:00		*** Dinner ***

Session 1 – Complexation and Coordination I – David Clark, Chair

7:00 – 7:15	p.m.	Welcome – Lester Morss, Bill Millman, Michael Heaven and Laetitia Delmau
7:15 – 7:40		Spiro D. Alexandratos – Variables in the Design of Ion-Complexing Polymer-Supported Reagents: Hydrogen Bonding as a Switching Mechanism in the Binding of Lanthanide Ions from Highly Acidic Solutions
7:40 – 8:05		Laetitia H. Delmau – Calixarene crown-6 and Calixpyrrole: A Cation and Anion Receptors Combination
8:05 – 8:30		Ben Hay – Principles of Chemical Recognition and Transport in Extractive Separations: Molecular Modelling and Design of Anion Receptors

Wednesday, April 22

7:30 – 8:00	a.m.	*** Breakfast ***

Session 2 – Complexation and Coordination II and DOE Update – Bruce Moyer, Chair

8:10 – 8:35	a.m.	John Miller – DOE Update
8:35 – 9:20		Invited – Terry Todd - Bridging the Gap Between Basic Science and Applied Research and Development for the Advanced Fuel Cycle Initiative Separations and Waste Form Campaign
9:25 – 9:50		Linfeng Rao – Actinide Solution Chemistry: Thermodynamics and Structure of Actinide Complexes in Solution
9:50 – 10:15		Richard Bartsch – New Proton-Ionizable, Calixarene-Based Ligands for Selective Metal Ion Separations
10:15 – 10:45		*** Break ***
10:45 – 11:10	a.m.	Paula Diaconescu – C-H Activation Reactions by Uranium Alkyl Complexes
11:10 – 11:35		Robert T. Paine – Preorganized and Immobilized Ligands for Metal Ion Separations

Invited Poster Introductory Presentations: – Laetitia Delmau, Chair

11:35 – 11:40	p.m.	Sofie Pasilis – Probing the solution chemistry of uranyl complexes using ESI-MS and vibrational spectroscopy
11:40 – 11:45		Mikael Nilsson – Chemical Interactions in the Non-Aqueous Phase for Liquid-Liquid Extraction Systems
11:45 – 11:50		Trevor Hayton – Synthesis, Characterization and Reactivity of a Uranyl(V) Bis(pyridine) Complex
11:50 – 11:55		Ping Yang – Theoretical Studies of Electronic Structure and Reactivity of Actinide Complexes
11:55 – 12:00		Andrew Gaunt – Transuranic Coordination Chemistry and Relative Covalency in An(III)/Ln(III) Complexes
12:00 – 1:00	p.m.	*** Working Lunch ***

Session 3 – Interfacial and Nano – Iain May, Chair

1:00 – 1:25 De-en Jiang – Chemistry of Novel Separation: Molecular Dynamics Simulations of Separation Media
1:25 – 1:50 Abraham Clearfield – Aza Crown Ethers and Porous Metal Phosphonates as Separation Agents
1:50 – 2:15 Peter C. Burns – Topological Structural Relationships, Properties, and Nano-Structures of U(VI), Np(V), Pu(V) and Pu(IV) Materials

2:15 – 5:00 Interaction time and opportunity to put up posters for both poster sessions

Session P1 – Poster Session 1

5:00 – 6:00 p.m.
P1-1 Michael Heaven – Spectroscopic Studies of Prototype Actinide Compounds
P1-2 Invited – Sofie Pasilis – Probing the Solution Chemistry of Uranyl Complexes Using ESI-MS and Vibrational Spectroscopy
P1-5 David K. Shuh – Soft X-ray Synchrotron Radiation Investigations of Actinide Materials
P1-6 Invited - Mikael Nilsson – Chemical Interactions in the Non-Aqueous Phase for Liquid-Liquid Extraction Systems
P1-9 Sheng Dai – Fundamental Studies of Novel Separations
P1-10 Invited - Trevor Hayton – Synthesis, Characterization and Reactivity of a Uranyl(V) Bis(pyridine) Complex
P1-13 David Clark – Quantifying Covalency in Actinide Metal-ligand Bonds
P1-14 Invited - Ping Yang – Theoretical Studies of Electronic Structure and Reactivity of Actinide Complexes
P1-17 Guokui Liu – Ion-Ligand Interactions in Actinide Compounds
P1-18 Invited – Andrew Gaunt – Transuranic Coordination Chemistry and Relative Covalency in An(III)/Ln(III) Complexes
P1-21 Heino Nitsche – The Chemistry and Physics of the Heaviest Elements
P1-22 Gustavo Scuseria – Accurate Theoretical Approaches for Studying the Chemistry of Actinides and Other Heavy Atoms
P1-25 Steven D. Conradson – Structural Studies of UO_{2+x} on Multiple Length and Time Scales
P1-26 Richard Martin – Covalent Interactions in Actinide Oxides

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

Session 4 – Supramolecular Complexes – Sheng Dai, Chair

7:00 – 7:25 p.m. David Morris – Organometallic Uranium Chemistry – New Platforms for the Exploration and Tuning of Electronic Structure and Covalency
7:25 – 7:50 Mark R. Antonio – Structural Aspects of Solution Chemistry in Separations Science
7:50 – 8:15 Jeffery T. Davis – Self-Assembled Ionophores: New Directions

Poster Session 1 (Cont'd)

8:15 – 10:00 p.m. *** No Host Bar ***

Thursday, April 23

7:30 – 8:10 a.m. *** Breakfast ***

Session 5 – Electronic Structure I – Bert de Jong, Chair

8:10 – 8:55 a.m. Invited – Laura Gagliardi – Exploring Actinide Chemistry with Multiconfigurational Quantum Chemical Methods

9:00 – 9:25 John Gibson – Gas-Phase Actinide Ion Chemistry: A Fruitful Interplay between Experiment and Theory

9:25 – 9:50 Eric Bylaska – Influence of Solution Phase and Interfacial Structure on the Stability of Actinide Oxidation States: A Computational Chemistry Approach

9:50 – 10:15 Asok Ray – A Fully Relativistic Density Functional Study of the Role of 5f Electrons in Chemical Bonding in Transuranium Elements

10:15 – 10:45 *** Break ***

Session 6 – Actinides I – Heino Nitsche, Chair

10:45 – 11:10 a.m. Lynne Soderholm – Structures and Stability Constants of Actinide-Halide Complexes in Solution

11:10 – 11:35 Marianne Wilkerson – Near-Infrared Photoluminescence and Ligand K-edge X-ray Absorption Spectroscopies of $AnO_2Cl_4^{2-}$ (An: U, Np, Pu)

11:35 – 12:00 Thomas Albrecht-Schmitt – Toward an Improved Understanding of Structure and Magnetism in Neptunium and Plutonium Phosphonates and Sulfonates

12:00 – 1:00 p.m. *** Working Lunch ***

Session 7 – Electronic Structure II – Gustavo E. Scuseria, Chair

1:00 – 1:25 Corwin Booth – Responding to Magnetic and Structural Disorder in Lanthanide- and Actinide-based Superconductors

1:25 – 1:50 Enrique R. Batista –Theoretical Studies of Actinide-Ligand Bonding Interactions

1:50 – 5:00 Interaction time and opportunity to put up Session 2 posters if not already up

5:00 – 6:00 p.m. *** No Host Bar ***

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

Session P2 – Poster Session 2 *** No Host Bar ***

7:15 – 10:00 p.m.

P2-3 Jonathan L. Sessler – Synthetic Receptors and Sensors for Actinide Cations and the Pertechnetate Anion

P2-4 R. A. Andersen and C. H. Booth – Multiconfigurational Ground States and Open-shell Singlet Formation in Ce- and Yb-based Organometallics

P2-7 Lester Andrews – Matrix Infrared Spectroscopic Investigations of Novel Small Uranium Containing Molecules

P2-8 Bert De Jong – Influence of Solution Phase and Interfacial Structure on the Stability of Actinide Oxidation States: A Computational Chemistry Approach

P2-11 Christopher Cahill – Hydrothermal Chemistry of UO_{2}^{n+} Phases: Formation and Stabilization of Pentavalent Uranium Compounds
P2-12 Sue Clark – Actinide Incorporation and Radiation Effects in U(VI) Solids: Thermodynamic and Mechanistic Study
P2-15 Radu Custelcean – Principles of Chemical Recognition and Transport in Extractive Separations: Anion Recognition and Separation with Self-Assembled Cage Receptors
P2-16 S. Skanthakumar – Understanding Bonding by Studying Magnetic Behavior of Actinide Compounds
P2-19 Rodney Ewing – Actinide Sorption/Incorporation and Radiation Effects in Layered Structures
P2-20 Mark Jensen – Origins of Soft Donor Ligand Selectivity in Actinide(III)/Lanthanide(III) Separations
P2-23 Wayne Lukens – EPR and Magnetic Susceptibility Studies of the Bonding in f^1 and f^3 Organometallic Complexes
P2-24 Iain May – Probing the Structural, Spectroscopic and Magnetic Properties of Actinyl(VI) Cations ($\{UO_2\}^{2+}$, $\{NpO_2\}^{2+}$ and $\{PuO_2\}^{2+}$) through Polyoxmetalate Coordination

Friday, April 24

7:30 – 8:00 a.m. *** Breakfast ***

Session 8 – Actinide II – Christopher L. Cahill, Chair

8:10 – 8:35	a.m.	Jim Ibers – Actinide Transition-Metal Chalcogenides and Pnictides
8:35 – 9:00		Chuan He – Selective Recognition of Heavy Elements by Protein-Based Reagents
9:00 – 9:25		Richard Andersen – The Nature of the Multiple Bonds in Cp'_2UO and Cp'_2UNMe: Experimental and Calculational Results
9:25 – 9:50		Richard E. Wilson – Structural, Optical, and Chemical Properties of Actinide Polynuclear Complexes
9:50 – 10:15		Paul F. Mantica – Nuclear and Radiochemistry Summer Schools

10:15 – 10:30 *** Break ***

Session 9 – Close Out Session – Michael C. Heaven and Laetitia Delmau, 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 7 – Electronic Structure II – Gustavo E. Scuseria, Chair

Session P2 – Poster Session 2

Session 8 – Actinide II – Christopher L. Cahill, Chair

Session 1 – Complexation and Coordination I

Variables in the Design of Ion-Complexing Polymer-Supported Reagents: Hydrogen Bonding as a Switching Mechanism in the Binding of Lanthanide Ions from Highly Acidic Solutions

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Overall Research Goals

The overall goal of this research is the design, synthesis and characterization of ion-selective polymer-supported reagents. The emphasis of current research has been on defining the variables that can be used to design these polymers. Hydrogen bonding has been identified as one such variable. Thus, phosphate ligands have been found to have far greater affinities for metal ions when bound to polystyrene through pentaerythritol because of hydrogen bonding between the hydroxyl groups and the phosphoryl oxygen. This was confirmed with FTIR spectra and other factors, such as a steric effect by the polystyrene backbone, were shown to be inoperative.

Significant Achievements for 2007-2009

The hydrogen bonding effect was extended to a new class of ion-binding ligands: the metal ion affinities of amides were shown to be strongly influenced by hydrogen bonding. Tetramethylmalonamide (TMMA) was immobilized onto polystyrene beads and its affinity determined for lanthanide ions in 0.001 M - 8 M HCl and HNO_3 solutions. In HCl, distribution coefficients are low from 0.001 to 2 M, increase in 4 M and 6 M HCl, then decrease in 8 M HCl. The affinity sequence in 6 M HCl is Tb > Dy > Eu > Gd > Ho > Sm > Er > Tm > Yb > Lu > Nd > Ce > La. The complexation mechanism is ion-pairing: at acid concentrations exceeding 2 M, protonation of the amide occurs at the carbonyl oxygen which is stabilized by hydrogen bonding to the adjacent carbonyl; this then switches on an iminium moiety that becomes the site of electrostatic attraction to the anionic lanthanide chlorocomplex and releases waters of hydration. The TMMA - Ln interaction exemplifies *recognition* since there is a point of maximum affinity rather than a monotonically changing affinity across the series. There are two opposing factors: electrostatic attraction of $Ln(H_2O)_xCl_4^-$ by the protonated TMMA ligand and loss of waters of hydration. The increasing electrostatic attraction parallels the lanthanide contraction. Along with this trend, dehydration becomes increasingly difficult from La to Lu, dominating when the TMMA - Ln interaction passes Tb. The mechanism is also operative in HNO_3.

Objectives for 2009-2011

The iminium site can be generated through ligands other than malonamide. The appropriate polymers will be synthesized and they will be tested for the abilities to bind the lanthanide ions. The emphasis will therefore remain on extending the general principle of hydrogen bonding as a mode of affecting the affinities of immobilized ligands.

Publications (2007 – 2009)

Y. Yang and S. D. Alexandratos, The Affinity of Polymer-Supported Reagents for Lanthanides as a Function of Polarizability, Industrial & Engineering Chemistry Research, submitted (2009)

S. D. Alexandratos, Ion Exchange Resins: A Retrospective from Industrial and Engineering Chemistry Research, Industrial & Engineering Chemistry Research, 48, 388-398 (2009)

S. D. Alexandratos and X. Zhu, Polyols as Scaffolds in the Development of Ion-Selective Polymer-supported Reagents, Inorganic Chemistry, 47, 2831-2836 (2008)

S. D. Alexandratos and X. Zhu, Immobilized Phosphates with Enhanced Ionic Affinity: Supported Ligand Synergistic Interaction, Separation Science and Tech., 43, 1296-1309 (2008)

S. D. Alexandratos and X. Zhu, High-Affinity Ion-Complexing Polymer-Supported Reagents: Affinity for the Uranyl Ion, Reactive and Functional Polymers, 67, 375-382 (2007)

S. D. Alexandratos and X. Zhu, Immobilized Tris(hydroxymethyl)aminomethane as a Scaffold for Ion-Selective Ligands, Inorganic Chemistry, 46, 2139-2147 (2007)

X. Zhu and S. D. Alexandratos, Determination of Mercury in Solutions by ICP-AES: Elimination of the ‘Memory Effect’, Microchemical Journal, 86, 37-41 (2007)

S. D. Alexandratos, New Polymer-Supported Ion-Complexing Agents: Design, Preparation and Metal Ion Affinities, Journal of Hazardous Materials, 139, 467-470 (2007)

Calixarene crown-6 and Calixpyrrole: A Cation and Anion Receptors Combination

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Collaborators: Bruce A. Moyer, Benjamin P. Hay, Peter V. Bonnesen, Radu Custelcean, Oak Ridge National Laboratory, Prof. Jonathan Sessler, Department of Chemistry, University of Texas at Austin, Austin, TX

Overall research goals: The objective of this project is to understand the thermodynamic properties of extraction systems underlying cation, anion, or ion-pair recognition.

Significant achievements during 2007-2009:

- The extraction of CsBr and CsCl using the anion receptor *meso*-octamethylcalix[4]pyrrole (C4P) in nitrobenzene was shown to occur by binding of a CsX ion pair by a single C4P molecule. Nitrobenzene was chosen because it is normally known to keep the ion pair dissociated. Distribution ratios are therefore roughly independent from the initial cesium salt concentration.

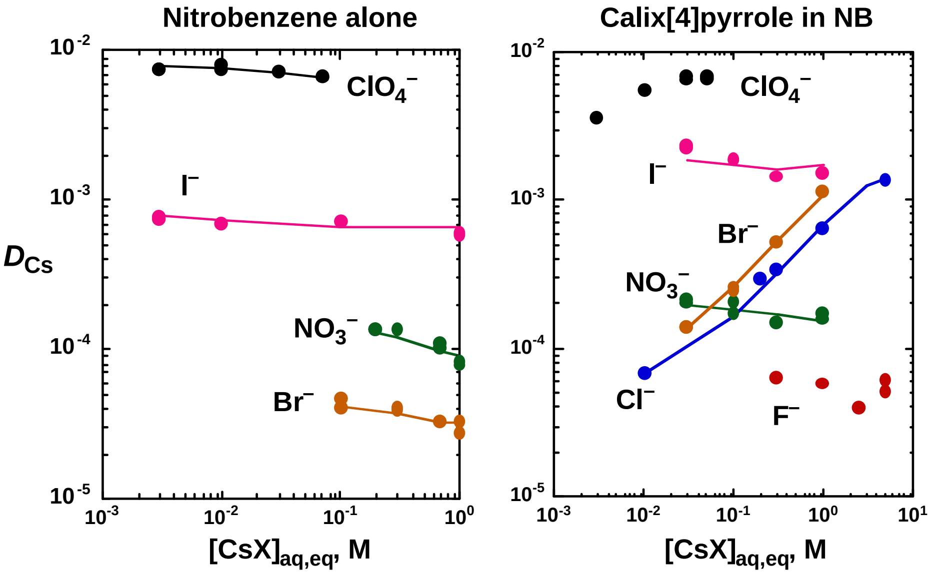
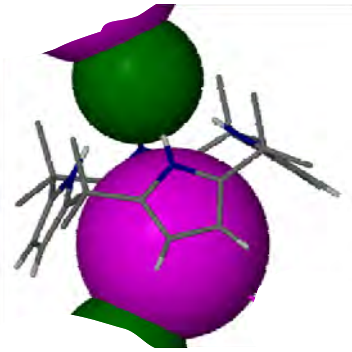
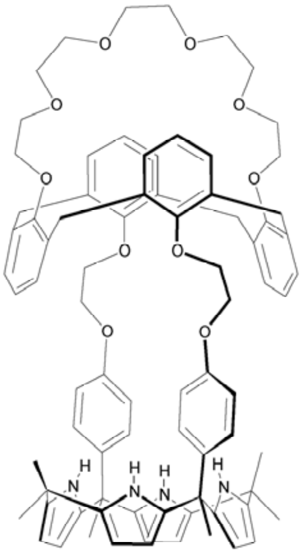


Figure 1. Cesium distribution ratios as a function of the cesium halide concentration

In spite of the strong polarity of the diluent, it was demonstrated that the cation and the complexed anion remain ion-paired. Results have clearly confirmed the formation of an ion-paired 1:1:1 cesium:calix[4]pyrrole:halide complex. In order to investigate the thermodynamic properties of the system, we considered organic phases that contained either the anion receptor exclusively or a combination of cation and anion receptors. The combination of bisoctylbenzo calix[4]arene-crown-6 (BOBCalixC6) as cesium extractant and *meso*-octamethylcalix[4]pyrrole as anion receptor has allowed the determination of the cesium and anion binding



constants of this system. Extraction results were modeled using the program SXLSQI to obtain the thermodynamic values inherent to the solvent extraction system, either with chloride or bromide. The binding Gibbs energy between the halide anion and the calix[4]pyrrole was found to be about 7 kJ/mol larger for cesium chloride than for the cesium bromide. However, the ion pairing Gibbs energies between the calix[4]pyrrole/halide complex and the cesium cation are of the same order of magnitude for either halide, i.e. 29.5±1 kJ/mol, consistent with the structural model involving a ligand-separated ion pair. This value is much larger than expected for CsX ion pairing in nitrobenzene, consistent with coordinative interactions of C4P that "glue" the ion pair together under solvent conditions that normally favor dissociation.



- The extraction of cesium using the Crown-6-Calix[4]arene Capped Calix[4]pyrrole (Crisca4) in nitrobenzene was studied as a natural follow up. This molecule comprises a calix[4]pyrrole and a calix[4]arenecrown-6. Thus, it could be expected to behave at the same time as a cesium and an anion receptor, potentially extracting the cation and the anion as ion pairs. The main objective was to characterize Crisca4, especially to determine the extraction mechanism and its efficiency as dual receptor (cation and anion receptor). Unfortunately, for a wide range of concentrations, and without taking into account the loading effects, the extraction mechanism with Crisca4 showed that the system is dissociated. However, it seems that, at high concentrations, the amount of cesium extracted is higher than predicted with this equilibrium. Further experiments are planned to see if an associated mechanism can occur at these concentrations. It was also determined that BOBCalixC6 is a better receptor for cesium than Crisca4: for the same concentration of CsX, doubling [BOBCalixC6] multiplies D_{Cs} by $\sqrt{2}$, which is what would be expected if BOBCalixC6 were the primary cesium extractant. Plots showing D_{Cs} at different cesium concentrations prove that the extraction of cesium using Crisca4 as an anion receptor is higher than when using C4P. This may lead to significant improvements regarding structure that needs to be developed in the future for high-efficiency dual-hosts receptors.

Science objectives for 2009-2011:

- Elucidate anion binding and ion-pairing phenomena by pyrrole-based derivatives containing crown-ethers in collaboration with Prof. Jonathan L. Sessler (U. Texas, Austin).
- Collect extraction data using tristhioureas and/or guanidinium-based derivatives toward understanding how the linker between functional groups controls affinity and selectivity in anion binding and extraction.

Publications supported by this project 2007-2009

Wintergerst, M. P.; Levitskaia, T. G.; Moyer, B. A.; Sessler, J. L.; Delmau, L. H. Calix[4]pyrrole: A new ion-pair receptor as demonstrated by liquid-liquid extraction. J. Am. Chem. Soc. **2008**, *130*(12), 4129-4139.

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

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Collaborators: Bruce A. Moyer (PI), Peter V. Bonnesen, Laetitia H. Delmau, Radu Custelcean, Oak Ridge National Laboratory, Oak Ridge, TN 37831
Dr. Vyacheslav S. Bryantsev, Caltech, Pasadena, CA 91125
Prof. Alamgir Hossain, Jackson State University, MS 39217
Prof. Stephan Kubik, Technishe Universität Kaiserslauern, Germany
Prof. Darren W. Johnson, University of Oregon, Eugene, OR 97403
Prof. Jonathan L. Sessler, University of Texas, Austin, TX 78712

Overall research goals: The primary objective of this research is ion-recognition through discovery and exploitation of host-guest principles in extractive separations. A major focus is the deliberate design of receptors for anions, 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 2007-2009: De novo structure-based design methods, implemented in HostDesigner (HD) software, enabled the design of novel anion receptors. HD was used to identify the optimal linkage for a biscyclopeptide-based anion receptor. Synthesis and testing confirmed the designer linkage yielded the highest binding affinities for I^- and SO_4^{2-} anions.[2] HD calculations for the design of bis-urea tweezers[7,8] were extended to identify tris- and tetrakis–urea candidates now under investigation at Jackson State University. HD was used to design ligands for a water-soluble metal-organic cage, leading to the preparation of a self-assembled cavity lined with six urea groups. This tetrahedral cage, shown in Figure 1, exhibits an unprecedented aqueous binding affinity for SO_4^{2-} (6×10^6 M^{-1}), far surpassing any synthetic receptor to date.[10]

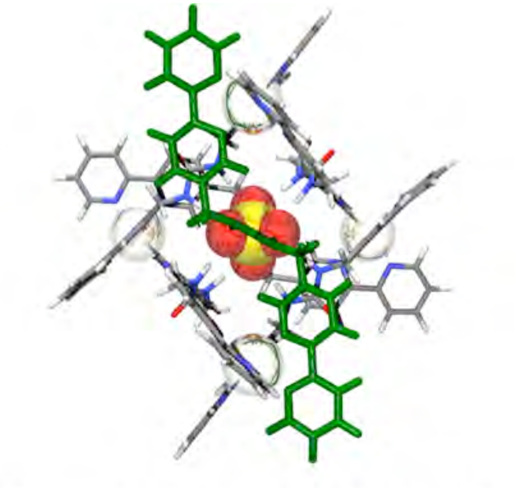

Figure 1. Predicted structure for this M_4L_6 tetrahedral cage, deliberately functionalized to complement SO_4^{2-}, was confirmed by X-ray analysis.[10] One ligand is highlighted in green.

Electronic structure calculations yielded molecular-level understanding of the geometric and energetic aspects of anion interactions with potential binding sites. It was discovered that the hydrocarbon linkages used to connect conventional OH and NH binding sites provide additional binding interactions with unexpectedly strong anion affinities. Several motifs were studied in detail including CH hydrogen bonding, anion-π interactions, and σ bonding interactions with aryl groups (Figure 2),[1,3] and CH hydrogen bonding with aliphatic groups.[9] Experimental corroboration of theoretical predictions was obtained through evaluation of crystal structure data[1,3,6,9,11] and collaboration with university researchers.[4,5]

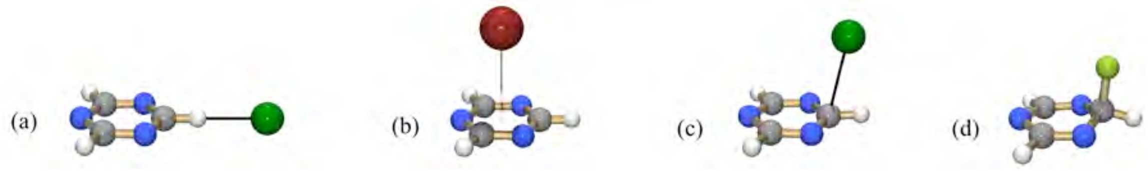

Figure 2. Anion-arene binding motifs include:[3] (a) CH hydrogen bonding with Cl$^-$, (b) anion-π interaction with Br$^-$, (c) weak σ interaction with Cl$^-$, and (d) strong σ interaction with F$^-$. The weak σ interaction, which is the favored binding motif in many cases, had not previously been characterized.

Science objectives for 2009-2011:

- Elucidate the geometric and energetic aspects governing host-guest interactions via electronic structure calculations and graphical representations of electron density.
- Computer-aided design of anion receptor architectures in which the hydrocarbon backbones are organized to provide additional binding sites.
- Computer-aided design of molecular building blocks for the dynamic covalent self-assembly of shape-selective anion receptors.

References of works supported by this project

1. O. B. Berryman, V. S. Bryantsev, D. P. Stay, D. W. Johnson, and B. P. Hay, "Structural Criteria for the Design of Anion Receptors: The Interaction of Halides with Electron-Deficient Arenes," *J. Am. Chem. Soc.* **129**, 48-58 (2007).
2. C. Reyheller, B. P. Hay, and S. Kubik, "Influence of Linker Structure on the Anion Binding Affinity of Biscyclopeptides," *New. J. Chem.* **31**, 2095-2102 (2007).
3. B. P. Hay and V. S. Bryantsev, "Anion-Arene Adducts: C–H Hydrogen Bonding, Anion-π Interaction, and Carbon Bonding Motifs," Invited Feature Article, *Chem. Commun.* 2417-2428 (2008). Highlighted on journal cover.
4. D.-W. Yoon, D. E. Gross, V. M. Lynch, J. L. Sessler, B. P. Hay, C.-H. Lee, "Phenyl-, Pyrrole-, and Furan-containting Diametrically Strapped Calix[4]pyrroles. An Experimental and Theoretical Study of Hydrogen Bonding Effects in Chloride Anion Recognition," *Angew. Chem. Int. Ed.* **47**, 5038-5042 (2008).
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Session 2 – Complexation and Coordination II

Bridging the Gap Between Basic Science and Applied Research and Development for the Advanced Fuel Cycle Initiative Separations and Waste Form Campaign

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Basic research, funded by the DOE Office of Science, and applied research and development activities funded by the DOE Office of Nuclear Energy, have historically not been well integrated. The basic research efforts, often at the discovery or very fundamental stage of research, are inherently long-term, with potential application a decade or two in the future. Applied research programs are focused on near-term solutions to problems and often only have a few years to show progress toward implementation. Basic research tends to be performed more by scientific disciplines, while applied research is often directed by engineers.

The Advanced Fuel Cycle Initiative has until recently been an applied program, focused on the demonstration of technology, often with a very limited fundamental understanding of the chemical and/or physical properties that drive the process. This focus of the program appears to be changing, largely due to two factors: 1) the formation of "Sigma Teams" in the AFCI program, to focus researchers from multiple laboratories on a single separation issue. The team includes researchers spanning fundamental to applied research and development. 2) the new Secretary of Energy, who has a strong scientific background, that will likely result in the AFCI program strategy focusing on a more longer-term science-based R&D approach. These two factors create the opportunity to better integrate the rather small separations and waste form communities, and encourage more interaction and cross-talk between the basic and applied researchers.

An overview of the AFCI Separations and Waste Form research activities will be given, with specific examples of where basic research can support programmatic research.

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

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Dr. S. J. Teat, Advanced Light Source, Lawrence Berkeley National Laboratory
Prof. S. B. Clark, Washington State University
Prof. C. M. Wai, University of Idaho

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 2007-2009:

1. Equilibrium constants and enthalpy of Pu(VI) hydrolysis at 10 - 70°C were determined with multiple techniques including potentiometry, microcalorimetry and spectrophotometry. As previously observed for U(VI) and Np(V), the hydrolysis of Pu(VI) is enhanced by several orders of magnitude when the temperature is increased from 10°C to 70°C. This could have significant implications in the transport behavior of actinides in the waste repository.

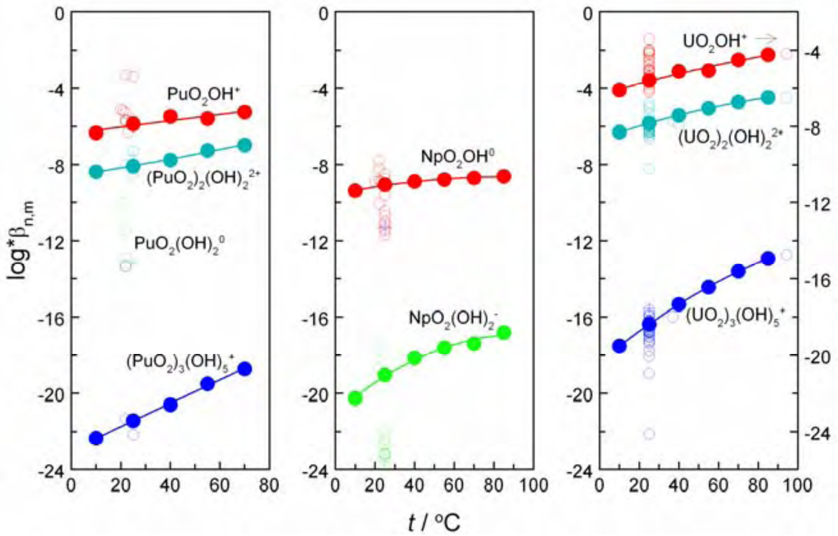

Figure 1. Hydrolysis of Pu(VI), U(VI) and Np(V) at different temperatures
(solid symbol – from this project; open symbol – from NEA database).

2. Thermodynamic trends (stability, enthalpy and entropy) in the complexation of actinides (III, IV, V, VI) with a series of structurally-related amide/carboxylate ligands were determined. Structural parameters were obtained by single-crystal X-ray diffraction, IR, laser-induced luminescence and EXAFS, including the bond lengths and stretching frequencies of O=An=O, C=O and C-O-C bonds. Very good correlations are observed between the thermodynamic trends and structural parameters. Besides, several structures of Np(V) and Pu(VI) complexes provided insight into the nature of f-f transitions and helped to interpret the optical spectra of Np(V) and Pu(VI).

3. New collaborations were initiated with academic researchers, including Prof. C. Wai (U. Idaho) on using environmentally-benign ligands in supercritical fluid CO_2 for actinide separations, Prof. B. Powell (Clemson U.) on thermodynamics of actinide interactions on liquid-solid interfaces, and Prof. Y. Qiang and A. Paszczynski (U. Idaho) on using amide ligands in magnetic separations of actinides. The new collaborations have resulted in a few research proposals for advanced nuclear energy systems and led to the funding of an NERI project for FY08-09.

Science objectives for 2009-2011:

- Complete the on-going work on the hydrolysis of Pu(VI) and Th(IV) at elevated temperatures, and extend the thermodynamic studies at elevated temperatures to ligands with different degrees of hydration or coordination ability (e.g., ligands with neutral oxygen and/or nitrogen donors). The effect of temperature on the complexation of actinides with these ligands is expected to be different from those previously studied. Results from this investigation will help to shed light in the nature of f-orbital bonding in actinide complexes.
- Continue the studies on actinide complexation with ligands of importance in advanced actinide separations. On the basis of the thermodynamic and structural information on the complexation of actinides with oxa-diamide ligands and derivatives in single-phase aqueous solutions, we plan to investigate the interactions of actinides with these ligands in more complex systems such as conventional solvent extraction, SCF CO_2 extraction and sorption on liquid-solid interfaces. The solvation effect, expected to play significant roles in the interactions, will be the focus in these studies.

Publications supported by this project (2007-2009)

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

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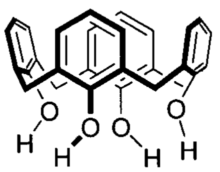
Program Scope: The objective of this project is the design and synthesis of new proton-ionizable, calix[4]arene-based ligands and their evaluation and application in metal ion separation processes.

Recent Progress: The calix[4]arene framework (**1**) provides an unusually versatile scaffold for the construction of new metal ion complexing agents. Attachment of one to four acidic side arms through the lower-rim phenolic oxygens can produce ligands that form electroneutral complexes with mono-, di-, tri- and tetravalent metal ion species, respectively. 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. By selection of appropriate lower-rim substituents, ligands can be prepared in conformationally mobile forms or in conformationally locked cone, partial cone, 1,3-alternate and 1,2-alternate conformations (**1**-**4**, respectively). Further structural modification is possible by variation of upper-rim substituents. In our work, attention has been focused upon carboxylic acid and *N*-(X)sulfonyl carboxamide [-C(O)NHSO$_2$X] groups as the pendent acidic functionality. For the latter, the acidity can be "tuned" by variation of the electron-withdrawing properties of X.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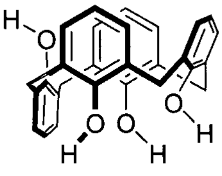
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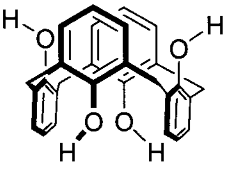
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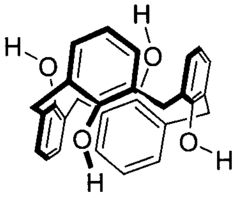
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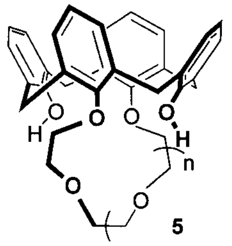
Connection of two phenolic oxygens of the calix[4]arene scaffold with a polyether chain gives calixarene-crown ether ligands, also called calixcrowns. Attachment of two distal oxygens results in a calix[4]arene-1,3-crown ether ligand **5**; whereas linking two proximal oxygens provides a calix[4]arene-1,2-crown ether analogue **6**. (Both structures are shown with the calix[4]arene unit in the cone conformation.)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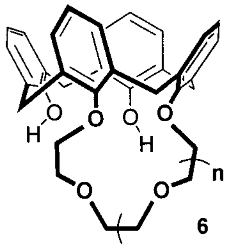
◄— Calix[4]arene-1,3-crown Ether

Calix[4]arene-1,2-crown Ether —►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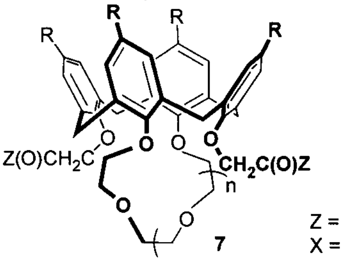
If the remaining two phenolic oxygens bear acidic functionality, the di-ionizable calix[4]arene-crown ether ligands upon ionization can form electroneutral complexes with divalent metal ions. We have prepared di-ionizable calix[4]arene-1,3-crown compounds **7** (with n = 1-3; R = H and *tert*-butyl) in cone conformations and evaluated their divalent metal ion complexation behavior by competitive solvent extraction of four alkaline earth metal ion species and by single-species extractions of lead(II) and mercury(II) from aqueous solutions into chloroform. With n = 2 and 3, analogues with the calix[4]arene scaffold in the partial cone and 1,3-alternate conformations were also synthesized and evaluated. The results provide excellent insight into the effect of extractant structure upon the extraction efficiency/selectivity. In contrast with scattered literature reports for metal ion complexation by non-ionizable calix[4]arene-1,2-crown ether ligands, we have discovered that di-ionizable calix[4]arene-1,2-

crown ligands **8** may exhibit unexpectedly high metal ion extraction selectivity. We have prepared ligands **8** with n = 0-3 and evaluated them in solvent extraction experiments to probe the influence upon metal ion complexation of changing the attachment site for the polyether unit.



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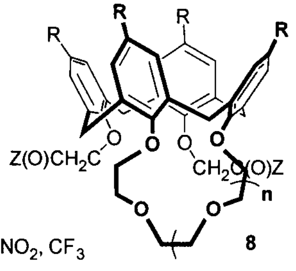
Z = OH, $NHSO_2X$
X = CH_3, Ph, C_6H_4-NO_2, CF_3



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Science Objectives for 2009-20011: Our investigations of metal ion separations by di-ionizable calix[4]arene ligands and calix[4]arene-crown analogues will be continued. This will include conformationally mobile, di-ionizable calix[4]arenes and conformationally locked, di-ionizable calix[4]arene-crown compounds. Also, we will initiate the study of ligands with ionizable groups attached to the para positions on the aromatic rings in di-ionizable calix[4]arenes and calix[4]arene-crown compounds. As before, our primary method for probing the selectivity and efficiency of metal ion separations will be solvent extraction from aqueous solutions into an organic diluent.

Publications Supported by This Project in 2007-2009:

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9. "Heavy Metal Separation with Polymer Inclusion Membranes," C. Sgarlata, G. Arena, E. Longo, D. Zhang, Y. Yang and R. A. Bartsch, *Journal of Membrane Science*, **2008**, *323*, 444-451.
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C-H Activation Reactions by Uranium Alkyl Complexes

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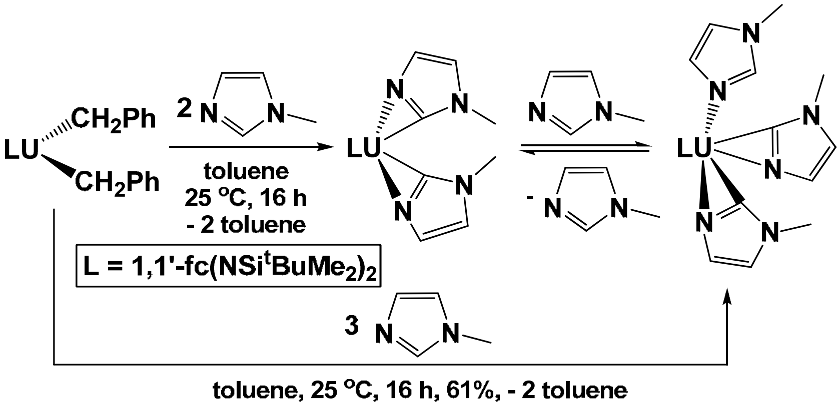
Overall research goals: The objective of this project is to study C-H activation reactions specific to uranium alkyl complexes supported by ferrocene diamide ligands. Specifically, the reactivity of these uranium complexes with aromatic heterocycles is investigated.

Significant achievements during 2008-2009: To date, we have explored the reactions of aromatic N-heterocycles with $LU(CH_2Ph)_2$ (L = 1,1'- $fc(NSi^tBuMe_2)_2$). Two significant results have emerged:

1. The double C–H activation reaction of imidazoles (Scheme 1 and Figure 1). The ability to undergo two C−H activation reactions is unique to uranium.



Scheme 1. The C-H activation reaction of 1-methylimidazole mediated by the uranium dibenzyl complex $LU(CH_2Ph)_2$.

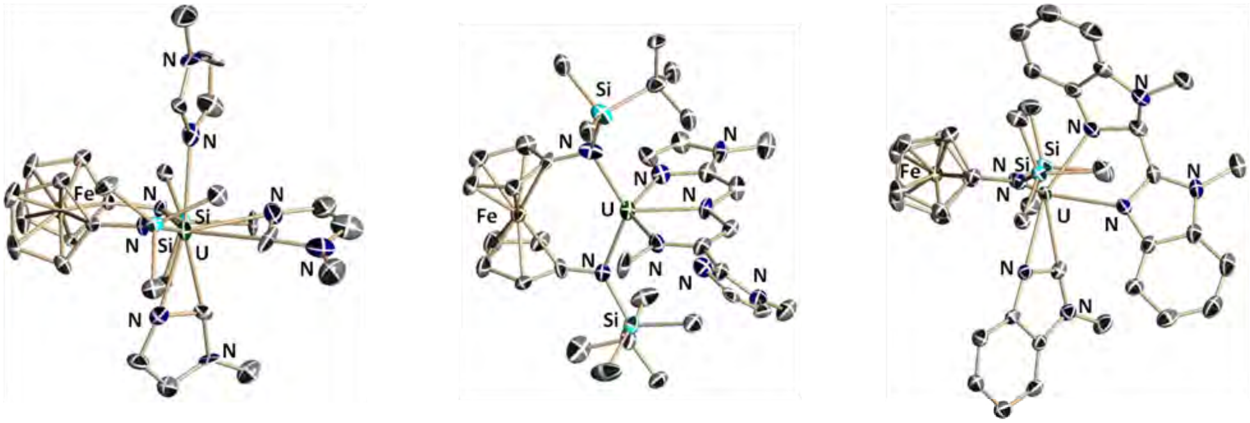
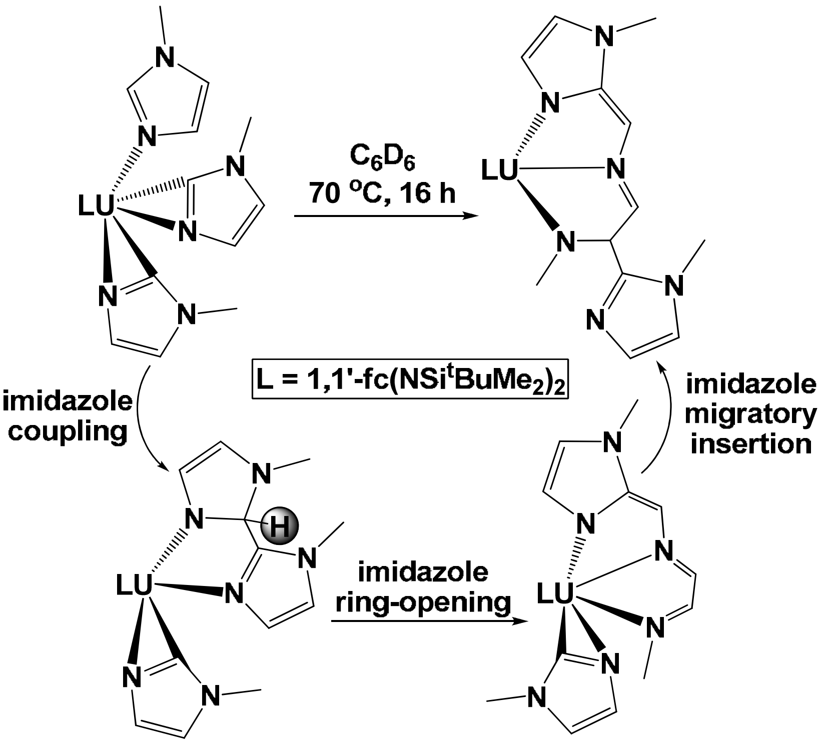


Figure 1. Molecular structures for the complexes drawn in Schemes 1 and 2.

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. The C–C coupling, ring-opening, and migratory insertion of imidazole (Figure 1 and Scheme 2). This sequence of reactions has no precedent in the organometallic chemistry of transition metals.



Scheme 2. Ring-opening of 1-methylimidazole mediated by the uranium dibenzyl complex LU(CH_2Ph)$_2$.

The cleaved ligand in the final product was the coordinated imidazole ligand in LU(η^2-N,C-imidazole)$_2$(imidazole), indicating that LU(CH_2Ph)$_2$ might be powerful enough to be used in the ring-opening of other heterocycles. This observation differentiates the uranium chemistry from that reported earlier for scandium, because a scandium imidazolyl complex analogous to LU(η^2-N,C-imidazole)$_2$ cannot be generated base free and only coordination of Lewis bases stronger than 1-methylimidazole may be anticipated.

Science objectives for 2009-2011:

- Investigate the reactions of LU(CH_2Ph)$_2$ with other aromatic heterocycles to explore the scope of the double C-H activation process.
- Investigate the reactions of LU(η^2-N,C-imidazole)$_2$ with other Lewis bases, in particular aromatic heterocycles, to determine whether their cleavage occurs.
- Investigate the possibility of transforming the stoichiometric reactions into catalytic ones. The use of silanes has established catalytic cycles when amides of group IV were involved.

Publications supported by this project 2008-2009

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2. Monreal, M. J. and Diaconescu, P. L., “Reversible C-C Coupling in a Uranium Biimidazole Complex”; in preparation for Organometallics.

Preorganized and Immobilized Ligands for Metal Ion Separations

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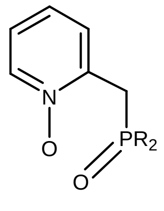
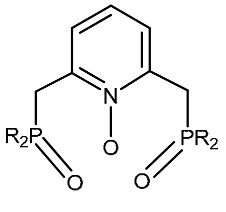
Overall research goals: This project, through systematic computational molecular design, organic ligand synthesis and coordination chemistry activities, attempts to reveal the fundamental interplay of steric, electronic and architectural organization features that impact and modify selective recognition and binding of robust multi-functional receptors to f-element ions, e.g. Ln(III), Th(IV) and UO_2^{2+}. This scope is expanded via collaboration studies to include transuranic ion chemistry pertinent to the development of practical reagents for nuclear material separations in the DoE complex. Those collaborations provide quantitative solvent extraction characterizations, thermodynamics of solution complexation data, ligand radiation damage analyses, actinide ion coordination chemistry and actinide spectroscopic analyses.

Significant Achievements during 2007-2009:

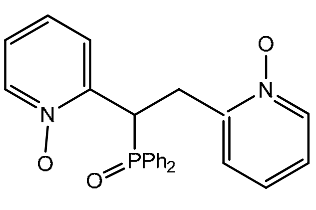
Ligand design/synthesis/coordination chemistry activities.
Based upon successes outlined in prior published studies, we have continued to develop robust multi-functional hybrid ligands that carry donor centers with inequivalent polarizability characteristics distributed on organic backbones that provide variable degrees of preorganization and chelation potential on Ln and An ions. Through variation of donor atom polarizability and steric/architectural features we aim to define ligands that selectively bind with these ions. The specific activities in this time period include the continued development of NO,PO (**1**), NO,PO,PO (**2**) and NO,NO,PO (**3**) ligands and new efforts to develop PO,N (**4**, **5**), PO,PO,S (**6**), PS,PS,S (**7**), NO,CO (**8**, **9**) and NO,CO,CO (**10**, **11**) hybrid ligands. The synthetic protocols and spectroscopic characterization for these ligands have been completed and coordination chemistry



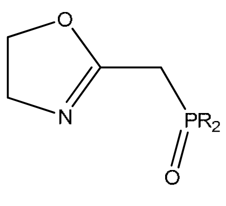
NO,PO (**1**)



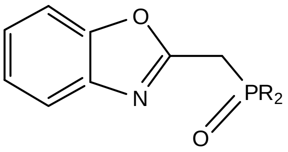
NO,PO,PO (**2**)



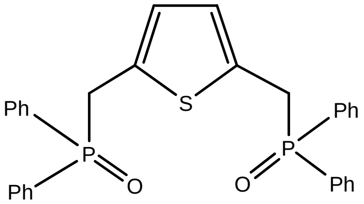
NO,NO,PO (**3**)



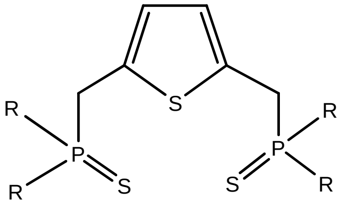
PO,N (**4**)



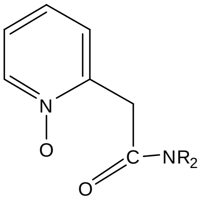
PO,N (**5**)



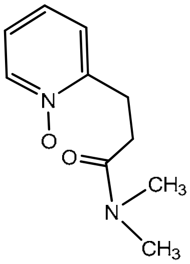
PO,PO,S (**6**)



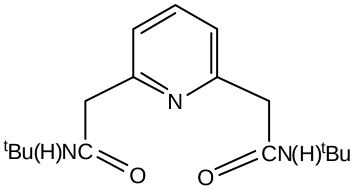
PS,PS,S (**7**)



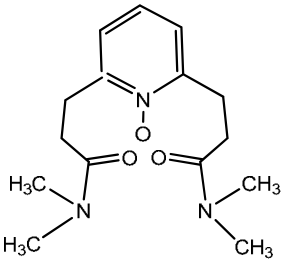
NO,CO (**8**)



NOCO (**9**)



NOCOCO (**10**)



NOCOCO (**11**)

with Ln(III) ions surveyed. X-ray crystal structure determinations suggest that several ligands adopt hemi-labile coordination environments and efforts are underway to determine if these types of interactions are responsible for the unique extraction behavior displayed by CMPO, NO,PO and NO,PO,PO ligands.

Science objectives for 2010-2011:

- Undertake collaborative mass spectroscopic studies to determine gas phase nucleophilicities of representative ligands from the groups **1**, **5**, **8** and **9** with R varied in order to assess the impact of electronic effects on PO and CO donor ability.
- Continue the development of the "CHNO"-type ligands **8**, **9**, **10** and **11** in order to obtain derivatives appropriate for solvent extraction analyses.
- Explore routes to ligand platforms containing higher degrees of preorganization of NO,PO- and NOCO-like ligands.

Publications supported by this project 2007-2009

1. S. Pailloux, I. Binyamin, S. Kim, L.M. Deck, B.M. Rapko, B.P. Hay, E.N. Duesler, and R.T. Paine "Oxidation Reactivity Channels for 2-(Pyridin-2-yl)-N,N-diphenyl acetamide *J. Org. Chem. 72*, 9195 (2007).
2. S. Pailloux, C.E. Shirima, A.D. Ray, E.N. Duesler, R.T. Paine, J.R. Klaehn, M.E. McIlwain and B.P. Hay "Synthesis and Coordination Chemistry of Trifluoromethyl Decorated Derivatives of 2,6-Bis[(diphenylphosphinoyl)methyl]pyridine N-Oxide Ligands with Lanthanide Ions" *Inorg. Chem.*, in press.

Session 3 – Interfacial and Nano

Chemistry of Novel Separation: Molecular Dynamics Simulations of Separation Media

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Collaborator: Prof. Adri C. T. van Duin, Department of Mechanical and Nuclear Engineering, the Pennsylvania State University, University Park, PA 16802.

Overall research goals: The objective of this project is to understand (1) the transport mechanism of olefin molecules in advanced ionic liquids via first principles molecular dynamics simulations and (2) the formation of porous carbons from polymeric precursors via reactive force field-based molecular dynamics simulations.

Significant achievements during 2007-2009: We made significant progresses in employing molecular dynamics simulations to understand the chemistry of two classes of novel separation media explored in parallel experimental efforts: Ag-complex based ionic liquids and porous carbons.

1. Using state-of-the-art first principles molecular dynamics techniques, we examined the $[\mathrm{Ag(C_2H_4)_2}^{+}][\mathrm{BF4}^{-}]$ ionic liquid which represents a class of novel task-specific ionic liquids synthesized in our group for olefin/paraffin separation. A mechanism of ethylene transfer similar to the Grotthuss type of proton transfer in water is identified, where a silver cation accepts one ethylene molecule and donates another to a neighboring silver cation (Figure 1). This mechanism may contribute to fast transport of olefins through ionic liquid membranes based on silver complexes for olefin/paraffin separation, which our group has observed.

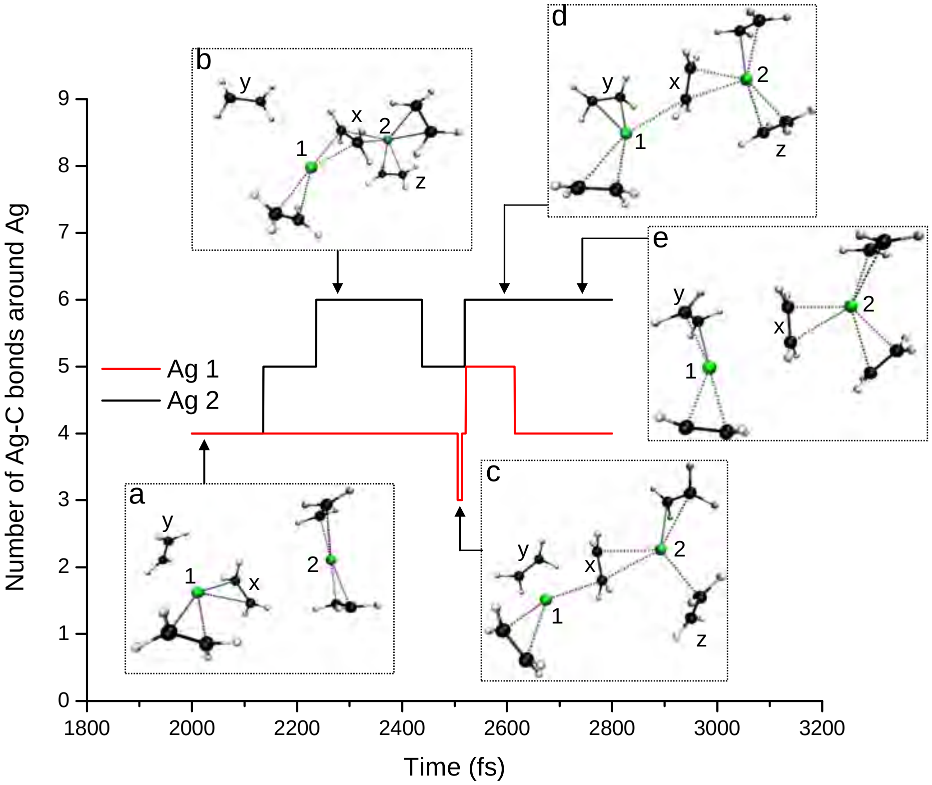
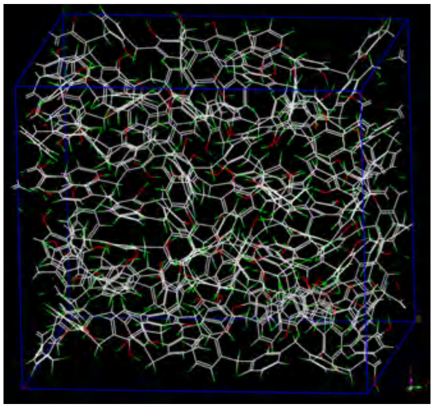


Figure 1. Change of number of Ag−C bonds for Ag 1 and Ag 2 versus time at 617 K, together with five snapshots.

2. The soft-template method developed in our group for synthesis of porous carbons involves a critical step of pyrolysis of phenolic resins which leads to carbon formation. Simulating this resin-to-carbon process atomistically is a daunting task. Collaborating with Prof. Adri van Dui of Penn State, we modeled the initial stage of this process by using the ReaxFF reactive force field which bridges electronic-structure and classical force-field methods. We ran molecular dynamics simulations to examine evolution of small molecules at different temperatures. Main small-molecule products found include H_2O, H_2, CO, and C_2H_2. We find multiple pathways leading to H_2O formation, including a frequent channel via β-hydrogen elimination which has not been proposed before.



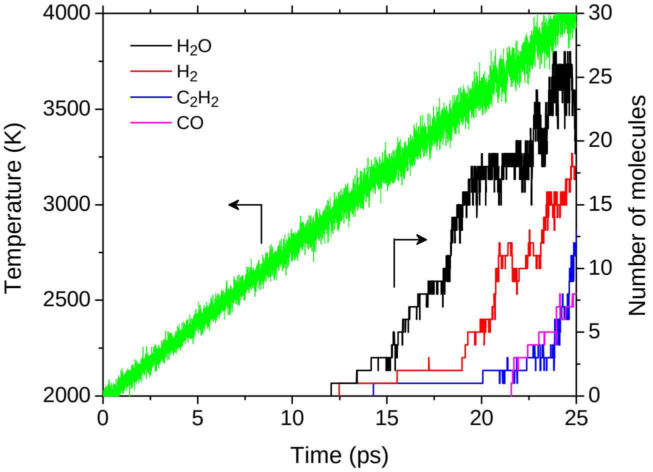


Figure 2. Left: the formaldehyde-phenolic-resin polymer equilibrated at 300 K for 20 ps. Right: Evolution of small-molecule products with time during temperature ramping from 2000 to 4000 K.

Science objectives for 2009-2011:

- Explore olefin transport in newly designed and synthesized ionic liquids in our group via first principles molecular dynamics simulations.
- Perform multiple cooling/heating cycles in the reactive-force-field molecular dynamics simulations to explore formation of carbon structures.

Publications supported by this project 2007-2009

1. Jiang, D. E., van Duin, A. C. T., Goddard, W. A. and Dai, S., "Simulating the Initial Stage of Phenolic-resin Carbonization via the Reactive Force Field," *J. Phys. Chem. A*, in preparation.
2. Jiang, D. E. and Dai, S., "First principles molecular dynamics simulation of a task-specific ionic liquid based on silver-olefin complex: Atomistic insights into a separation process," *J. Phys. Chem. B*, **112**, 10202 (2008).
3. Jiang, D. E.; Tiago, M. L.; Luo, W. D.; Dai, S. "The 'Staple' Motif: A Key to Stability of Thiolate-Protected Gold Nanoclusters." J. Am. Chem. Soc., **130**, 2777 (2008).
4. Jiang, D. E. and Dai, S., "Spin states of zigzag-edged Möbius graphene nanoribbons from first principles," *J. Phys. Chem. C*, **112**, 5348 (2008).
5. Jiang, D. E. and Dai, S., "Electronic ground state of higher acenes," *J. Phys. Chem. A*, **112**, 332 (2008).
6. Jiang, D. E., Sumpter, B. G. and Dai, S., "Unique chemical reactivity of a graphene nanoribbon's zigzag edge," *J. Chem. Phys.*, **126** (2007).
7. Jiang, D. E., Sumpter, B. G. and Dai, S., "First principles study of magnetism in nanographenes," *J. Chem. Phys.*, **127** (2007).

Aza Crown Ethers and Porous Metal Phosphonates as Separation Agents

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Overall Research Goals

1. To provide a system of large ring aza and aza-oxo crown ether rings and determine their usefulness in complexing metals
2. To provide robust inorganic ion exchangers for ion exchange separations of lanthanides and actinides.
3. To provide a robust family of organic-inorganic hybrids that can be engineered to provide separations of ions and molecules based on size, charge and hydrophobic – hydrophilic differences

Significant achievements during 2007-2009:

I. The original intent was to synthesize a number of large pore aza-crown ethers and to examine their structure and uptake of cations to use in separations Chemistry. We succeeded in synthesizing 7 such compounds with ring sizes of 24, 26, 30 atoms. The rings consisted of 6 or 8 aza groups and for one compounds 4 aza and two oxo groups. All of them were converted to phosphonic acids by bonding of – $CH_2PO_3H_2$ groups to the ring nitrogen atoms for additional complexing ability. The crystal structures of four of the phosphonic acid compounds were determined and exhibit conformations in which 4 phosphonic acid groups (in the 6-aza compounds) extend away from the ring and two turn inward towards the center of the ring one above and one below. Extensive hydrogen bonding with water and between rings occurs to form chains. The chains are separated from each other by a layer of water molecules. Several complexes with Cu and Mn were prepared. These studies have not yet been published due to loss of my post-doc to an industrial position.

II. Inorganic Ion exchangers for Lanthanide and Actinide Exchange: We have prepared a series of M(IV) tri-silicates of general formula $Na_2MSi_3O_9\bullet H_20$ where M=Ti, Sn, Zr, Sn/Zr, Zr/Ge. These compounds are zeolitic in nature with two types of cavities – one with a 16-ring another with a 12-ring cavity and connected to each other by a 14-ring opening. The variation in unit cell volume from the small Ti unit cell, 915Å^3 , to the ZrGe cell is 1053Å^3. The selectivity for lanthanide ions of the $K_2SnSi_3O_9\bullet H_2O$ phase was La > Pr > Sn > Gd > Er. This series is in the order of increasing selectivity for increasing unhydrated ionic radii. This is in accord with the earlier selectivity series for alkali cations $Cs^+ = Rb^+ > K^+ > Na^+ > Li^+$. In mixtures of ions the selectivity was $Th^{4+} > Gd^{3+} > Ca^{2+} > Na^+$. Since all these ions have about the same ionic radius (~1Å), charge appears to be the most important factor.

III. Organic-Inorganic Hybrid Ion Exchangers: We have prepared both layered compounds of Zr and Sn (IV) phosphonates with aryl and alkyl groups. The Zr compounds are non-porous but the Sn compounds are porous. For the latter compounds the porosity arises from the very small (nano) size of the particles that form "house of cards" type inter particle pores. However, by cross linking the layers with α, ω- type alkyl and aryl phosphonic acids internal porosity is obtained. Preparing mixed derivatives with phosphonic acid imparts ion exchange capability to the mixed derivative. Such compounds have shown a distinct preference for lanthanide ions over alkali and alkaline earth cations. We have now prepared compounds with increased amounts of carboxylic acid and sulfonic acid interspersed between the pillars. Determination of selectivities is in progress.

Science objectives for 2009-2011:

In the next grant period we will concentrate primarily on synthesizing pillared layered ion exchangers. Emphasis will be placed upon design of materials with specific pore sizes using flexible pillars, $H_2O_3P(CH_2)_n\ PO_3H_2$, n = 2-12, rigid pillars $H_2PO_3(C_6H_4)_n$-PO_3H_2 n = 1-3 and mixed alkyl-aryl pillars. These pillars will be spaced by incorporation of –COOH, P-OH, -PO_3H_2 and –SO_3H groups as weak, medium and strong acid groups. Hydrophobic-hydrophilic character will be moderated by using phosphates rather than phosphonates or pyridyl, oxo and imino chains.

In the case of the tin phosphonates of composition $Sn(O_3CH_2COOH)_2$ porosity (~150m^2/g) already exists. By addition of NH_3 the nanoparticles exfoliate. Addition of complexes such as$Co(NH)_{3_4}^{2+}$, $Ru(Bipy)_3^{2+}$ results in entrapment of the complex as the layers enclose the complex. This type of reaction may have a size-charge effect that can be used to separate complexes on this basis. Neutral compounds may be separated by the pillared porous materials based upon pore size and hydrophobic-hydrophilic character.

Further efforts will be made to complete the crown ether study and to publish the results.

Publications supported by this project 2007-2009

1. Fewox, Christopher S.; Clearfield, Abraham. Synthesis and characterization of protonated zirconium tri silicate and its exchange phases with strontium. The Journal of physical chemistry (2008), 112(12), 2589-97
2. Celestian, Aaron J.: Clearfield, Abraham. The origin of ion exchange selectivity in a porous framework titanium silicate. J. Mater. Chem. (2007), 17(46), 4839-4842.
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4. Christopher S. Fewox, Sharath R. Kirumakki, and Abraham Clearfield, Structural and Mechanistic Investigation of Rubidium Ion Exchange in Potassium Zirconium Trisilicate, Chem, Mater., 19, 384-392 (2007).
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Topological Structural Relationships, Properties, and Nano-Structures of U(VI), Np(V), Pu(V) and Pu(IV) Materials

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Overall research goals: The Project Objectives are: (1) A systematic examination of the crystal chemistry of uranyl peroxide compounds that form from near-neutral to alkaline solutions. (2) To synthesize and determine the structures of a chemically diverse suite of Np(V) and Pu(V) compounds, to develop topological relationships within this group of structures and those of U(VI), and the study of magnetic properties of well-characterized Np(V) compounds. (3) A detailed assessment of the structures of actinyl peroxide nanoclusters, the exchange of cations with such clusters, their precipitation with and incorporation of organic ligands, and their catalytic properties. (4) Determination of the compositions, structures, and formation mechanisms of Pu(IV), Th(IV) and Zr(IV) nano-scale clusters. (5) The training of two Ph.D. graduate students in actinide chemistry and mineralogy.

Significant achievements during 2007-2009: We reported earlier that incorporation of peroxide into uranyl hexagonal bipyramids caused the formation of nano-scale spherical clusters containing 24, 28 and 32 polyhedra (Burns et al. 2005, Angew. Chemie Int. Ed. 44, 2135-2139). In order to more fully explore the chemistry and structures of such nano-clusters, we have adopted a combinatorial synthesis approach. To date, uranyl peroxide clusters containing 16, 20 (3 clusters), 24 (2 clusters), 28 (2 clusters), 30, 32, 36, 40, 44 (2 clusters), 50 and 60 polyhedra have been crystallized and structurally characterized. Those containing 40 and 50 polyhedra were reported in Forbes et al. (2008), and details of those with 36, 44 and 60 polyhedra are in Sigmon et al. (2009).

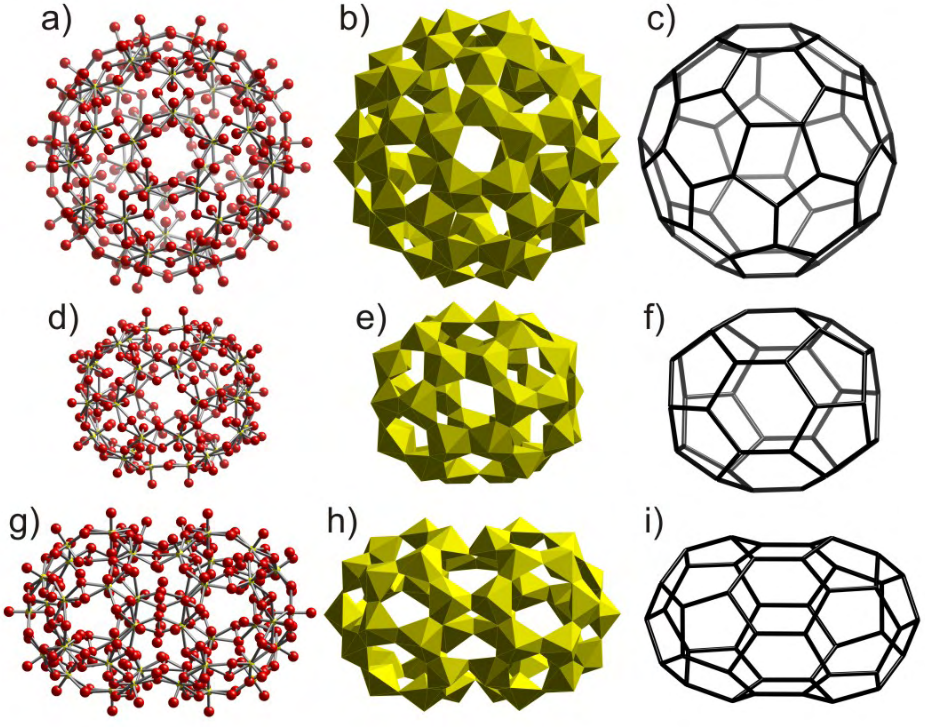

Figure 1. Ball-and-stick, polyhedral, and topological connectivity representations of the structures of U_{60} (a-c), U_{36} (d-f) and U_{44} (g-i). From Sigmon et al. (2009).

The structures of the U_{36}, U_{44} and U_{60} clusters are shown in Figure 1. Each of these is based upon a fullerene topology with 12 pentagons and several hexagons. The U_{60} cluster topology is identical to C_{60} Bucky ball and contains 12 isolated pentagons and 20 hexagons. Five clusters of uranyl polyhedra are now known that are based upon fullerene topologies, and it appears that those isomers with maximum symmetry are favored.

In addition to creation of nano-scale uranyl peroxide clusters, we have synthesized several new uranyl peroxide compounds that have more conventional structures. These include the first actinide compound found to contain a μ-η^2:η^1 peroxide coordination (Unruh et al. 2009).

Progress has also been made in creation of new Np(V) compounds. One manuscript has been published concerning the first Np(V) neptunyl silicates (Forbes and Burns 2007). We also published a structural hierarchy of inorganic Np(V) and Np(VI) compounds known to date, where we drew extensive comparisons between the structures of Np and U(VI) compounds (Forbes et al. 2008).

Tori Forbes received her Ph.D. in 2008, and Daniel Unruh and Ginger Sigmon are Ph.D. students who are contributing significantly to this project. Several undergraduates have also been involved.

Science objectives for 2009-2011:

- Continue to expand the complex family of actinyl peroxide nanostructures through combinatorial synthesis.
- Develop a “road map” of synthesis conditions that result in specific uranyl peroxide clusters.
- Begin to examine the relative stabilities and solubilities of different uranyl peroxide nanoclusters.
- Continue to synthesize and structurally characterize Np(V) compounds.

Publications supported by this project 2007-2009:

1. Unruh, D., Burtner, A. and Burns, P.C. (2009): Expanding the Crystal Chemistry of Actinyl Peroxides: μ-η^2:η^1 Peroxide Coordination in Trimers of U^{6+} polyhedra. *Inorganic Chemistry* DOI: 10.1021/ic8024217
2. Sigmon, G., Unruh, D.K., Ling, J., Weaver, B., Ward, M., Pressprich, L. and Burns, P.C. (2009): Symmetry vs. minimal pentagonal adjacencies in uranium-based polyoxometalate fullerene topologies. *Angewandte Chemie International Edition* (In press, VIP). DOI: 10.1002/anie.200805870
3. Ling, Jie and Burns, P.C. (2009) Syntheses, structures and characterizations of novel amino-templated uranyl selenates. *Journal of Solid State Chemistry* 182, 402-408.
4. Forbes, T.Z., McAlpin, G., Murphy, R. and Burns, P.C. (2008): Metal-oxygen isopolyhedra assembled into fullerene topologies. *Angewandte Chemie International Edition* 47, 2824-2827. (VIP)
5. Forbes, T.Z., Wallace, C. and Burns, P.C. (2008): Neptunyl compounds: Polyhedral geometries, bond-valence parameters, and structural hierarchy. *Canadian Mineralogist* 46, 1623-1645.
6. Soderholm, L., Almond, P.M., Skanthakumar, S., Wilson, R.E. and Burns, P.C. (2007): The structure of a 38-plutonium oxide nanocluster: $[Pu_{38}O_{56}Cl_{54}(H_2O)_8]^{14-}$. *Angewandte Chemie International Edition* 47, 298-302. (VIP)
7. Forbes, T.Z. and Burns, P.C. (2007): Synthesis, structure, and infrared spectroscopy of the first neptunyl silicates, $Li_4(NpO_2)_4(H_2Si_2O_7)(H_2SiO_4)_2(H_2O)_4$ and $K_3(NpO_2)_3(Si_2O_7)$. *Inorganic Chemistry* 47, 705-712.
8. Forbes. T.Z., Goss, V., Jain, M. and Burns, P.C. (2007): Structure determination and infrared spectroscopy of $K(UO_2)(SO_4)(OH)(H_2O)$ and $K(UO_2)(SO_4)(OH)$. *Inorganic Chemistry* 46, 7163-7168.

Session P1 – Poster Session 1

Spectroscopic Studies of Prototype Actinide Compounds

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Overall research goals: Understanding the influence of electrons in partially filled *f*-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 is particularly valuable for the evaluation of theoretical models. This information is not compromised by the local perturbations that are inescapable in a condensed phase environment. Furthermore, when rotationally resolved spectra can be obtained, these data yield unambiguous identification of state symmetries, and insights concerning electronic configurations. 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 2007-2009: The electronic ground state of the UO_2^+ cation has been examined in the gas phase using pulsed field ionization – zero kinetic energy (PFI-ZEKE) photoelectron spectroscopy. Extensive vibrational progressions were observed and these were assigned to excitation of the symmetric stretch and bending modes of UO_2^+. The vibrational numbering was confirmed by recording spectra for the $U^{18}O_2^+$ isotopomer. Harmonic vibrational constants of 919 cm^{-1} and 145 cm^{-1} were determined for $U^{16}O_2^+$. Data were obtained for levels that were up to 4700 cm^{-1} above the ground state zero-point level. The congestion of the spectrum increased dramatically with increasing energy. The first electronically excited state was found at 2678 cm^{-1}. Progressions in the bending and symmetric stretch levels of this state were also observed. The ionization energy derived from the PFI-ZEKE spectrum was 6.127(1) eV.

The photoionization kinetics of UO_2^+ proved to be of interest in their own right. At the energetic threshold the electrons were ejected from the molecule with a characteristic appearance time of 189 ns. This value decreased with increasing energy above the ionization limit. Delayed ionization of this kind has been observed for metal clusters, but the case of UO_2 is the first example of this phenomenon for a triatomic molecule.

PFI-ZEKE spectra were recorded for HfO to examine the effect that ionization has on this molecule. Our previous studies of isoelectronic ThO motivated this investigation. For ThO it was found that ionization weakens the bond by 0.3 eV. However, counter to intuitive expectations, the equilibrium bond length shortens and the vibrational frequency increases on ionization. Theoretical calculations for HfO and HfO^+ predicted a similar anomaly.

Pulsed laser vaporization was used to generate gas phase HfO. This experiment was also used in the process of developing a nozzle source that is suitable for the production of

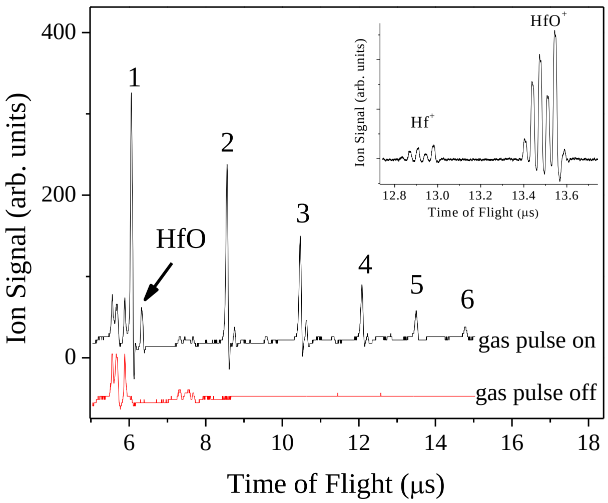

Figure 1. Time of flight mass spectra recorded for the pulsed laser vaporization and free jet expansion source utilizing a Hf metal target and He carrier gas. Expanded scale shows isotopes.

small metal clusters. The mass spectrum in Fig. 1 shows that HfO and bare metal clusters (Hf_n, n=1-6) were generated by our current nozzle system. The one-color excitation spectrum of HfO was recorded as a preliminary to making PFI-ZEKE measurements. Several new band systems of the neutral molecule were discovered in this phase of the project. Spectra for HfO^+ revealed a progression in the stretch vibration up to $v^+ = 4$, allowing for determination of the ground electronic state vibrational frequency of $\omega_e = 1017.7(10)$ cm^{-1} and anharmonicity of $\omega_e x_e = 3.2(2)$ cm^{-1}. The zero-point rotational constant of HfO^+ was determined to be 0.403(5) cm^{-1}. As for ThO^+/ThO, the bond length of HfO^+ is shorter than that of HfO, and the vibrational frequency is higher. The trend for the bond energy is also the same, with HfO^+ being 1.1 eV *less* deeply bound than HfO. The ionization energy of HfO was determined to be 7.91687(10) eV, which is 0.37 eV higher than the value reported from electron impact measurements. Underestimation of the IE in the previous studies is attributed to ionization of thermally excited states. Benchmark theoretical *ab initio* calculations were carried out in order to explore the effects of electron correlation on the predicted molecular properties.

Science objectives for 2007-2009: We will continue efforts to characterize di- and tri-atomic actinide species, with an emphasis on molecules that have been studied theoretically, and where new spectra can advance our understanding of the bonding and reactivity of *f*-element compounds. Species to be examined include UH, UF, ThH, ThF, CUO and UO_2. Metal-metal bonding will be explored through studies of the metal dimers Th_2, U_2 and ThU.

References of publications that were supported by this project

J. M. Merritt, J. Han, and M. C. Heaven, J. Chem. Phys. **128**, 084304/1-084304/8 (2008)

"Spectroscopy of the UO_2^+ cation and the delayed ionization of UO_2"

J. M. Merritt, V. E, Bondybey and M. C. Heaven, J. Chem. Phys. accepted Feb 2009 (A09.01.0095)

"Ionization measurements and spectroscopy of HfO and HfO^+"

M. C. Heaven, J. K. Gibson and J. Marçalo in Chemistry of the Actinide and Transactinide Elements, Chapter 39

"Molecular spectroscopy and reactions of actinides in the gas phase and cryogenic matrices"

Probing the solution chemistry of uranyl complexes using ESI-MS and vibrational spectroscopy

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Overall research goals: The immediate goal of this research is to develop vibrational spectroscopic and mass spectrometric methods to elucidate interactions between actinide metals, especially uranium, and organic complexing agents, including biomolecules. Other goals include determining the factors affecting the detection of uranyl(VI)-ligand complexes in electrospray ionization mass spectrometry (ESI-MS), and investigating uranyl-amino acid, peptide and protein binding interactions.

Significant achievements: In past work, I have used Raman and attenuated total reflectance FTIR (ATR-FTIR) spectroscopies and ESI-MS to investigate how citric acid, a small organic ligand, affects uranyl(VI) solution speciation and surface interactions with model mineral oxides.[1, 4] This combination of techniques allowed me to gain a more detailed understanding of the pH-dependent behavior of the uranyl(VI)-citrate system in aqueous solution than that previously available in the literature. A clear picture of solution speciation facilitated characterization of surface complexes formed upon coadsorption of uranyl(VI) and citrate to an alumina substrate.

ESI-MS has been used successfully to examine metal ion speciation and uranyl(VI)-ligand stoichiometry and structure. However, the relationship between detected ions and uranyl(VI) solution chemistry is not always clear. Factors affecting the detection of uranyl-ligand solution species and the formation of gas-phase uranyl(VI)-ligand complexes have not been thoroughly examined.

I am currently investigating the relationship between the known uranyl(VI)–ligand solution species and the complexes detected using ESI-MS for three aminopolycarboxlate ligands: nitrilotriacetic acid (NTA), ethelyenediaminetetraacetic acid (EDTA), and diethylenetrinitrilopentaacetic acid (DTPA).

In the case of NTA and DTPA, complexes of the form $(UO_2)L$ and $(UO_2)L_2$, where L= NTA or DTPA, are detected using ESI-MS. Both NTA and DTPA are known to form 1:1 complexes with the uranyl dication. For both ligands, complexes of the form $(UO_2)L_2$ are far more predominant in the mass spectrum at pH 3.5 than at the higher pH values. The $(UO_2)L_2$ complexes likely result from the formation of gas-phase adducts with excess NTA or EDTA present in solution.

Raman spectra acquired from a solution of uranyl and EDTA show pH-dependent shifts in the $\nu_s(UO_2)$ mode, indicating the presence of at least three distinct uranyl-EDTA complexes over the pH range from 4 to 10 (Figure 1). Critically selected stability constants are available for five uranyl-EDTA complexes: (UO_2)EDTA, $(UO_2)_2$EDTA, $(UO_2)_2(EDTA)_2$, $(UO_2)_4(OH)_4(EDTA)_2$, and $(UO_2)_4(OH)_4(EDTA)_3$. Uranyl-EDTA complexes detected using ESI-MS include (UO_2)EDTA, $(UO_2)(EDTA)_2$ and $(UO_2)_2(EDTA)_2$. The (UO_2)EDTA complex is the predominate species in the mass spectrum at all pH values examined. There are no significant differences in ESI-MS spectra acquired from solutions 1 mM in UO_2^{2+} and EDTA at pH 3.8, 7.2, and 8.8.

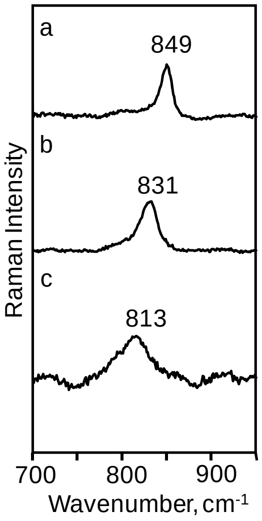

Figure 1. Raman spectra showing the pH dependence of $\nu_s(UO_2)$ for a solution 5 mM in uranyl(VI) and 5 mM in EDTA at a) pH 4.0, b) pH 7.0, and c) pH 10.0

Science objectives for 2009-2011:

- Investigate uranyl-amino acid, peptide and protein binding interactions, and how small ligands, such as phosphate and citrate, can effectively compete with uranyl-binding proteins for uranyl. This research will provide a basis in understanding how the chemical reactions uranium undergoes in the body affect its chemical toxicity and potential for long-term harm. In addition, a better understanding of the biological chemistry of uranium may help guide the development of sequestering agents for chelation therapy in the case of accidental contamination.
- Continue to explore the factors affecting the detection of uranyl(VI)-ligand complexes in electrospray ionization mass spectrometry (ESI-MS). Examine the effect of the electrospray and desolvation processes on the species distribution of uranyl/ligand complexes.

Publications related to this project

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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 optimization of soft X-ray SR techniques for actinide investigations.

Significant achievements in 2007-2009: The soft x-ray emission spectroscopy (XES), resonant inelastic x-ray scattering (RIXS), and near-edge x-ray absorption fine structure (NEXAFS) investigations of actinides at the Advanced Light (ALS) continue. The RIXS spectra from curium oxide were collected as a function of excitation energy corresponding to the Cm 5d features in the NEXAFS spectrum. The experimental RIXS spectrum and those calculated for free Cm(III) and Cm(IV) ions are shown in Fig. 1 (left). The inelastic scattering features, which are attributed to 5f-5f intra-atomic transitions (f-f excitations), appear at energies 1 eV to 4 eV (loss features) below the excitation energy (the elastic line). The energy differences between the inelastic scattering features and the elastic peak in the calculated spectra, when compared the experimental spectra, yield strong evidence for trivalent Cm. This conclusion is supported by the agreement between the energy dependence of the five main RIXS features in the Cm(III) calculations and the observed experimental spectra that were collected from 115 eV to 135 eV. The results of this investigation show that the atomic multiplet approach complements experimental RIXS investigations and that the physical/electronic properties of radioactive materials can be successfully elucidated from microgram quantities in the soft X-ray region.

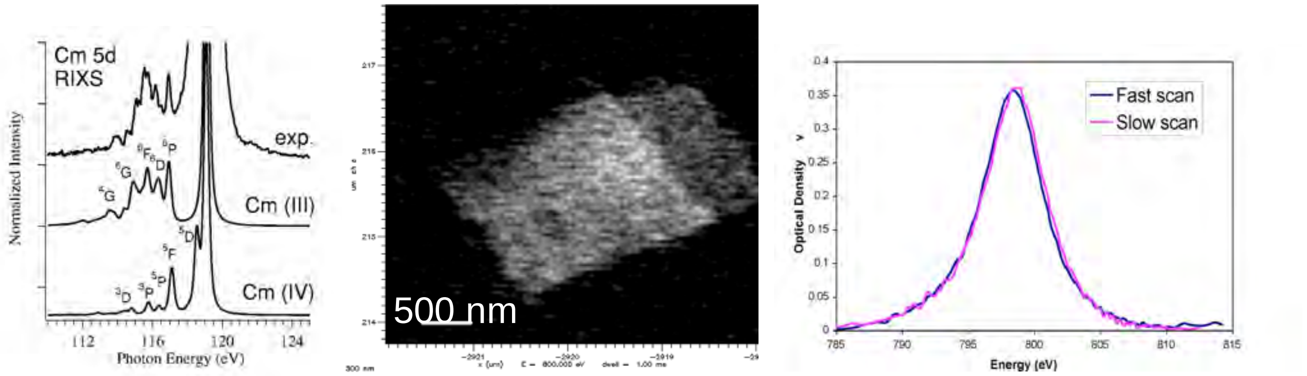

Figure 1. Left: Cm 5d RIXS spectra from curium oxide recorded at ALS BL-7.0.1 with an excitation energy of 119.0 eV compared to the theoretical spectra calculated for Cm(III) and Cm(IV) ions; Center: Elemental Pu map obtained at ~800 eV from a hydrated Pu(III) oxalate crystal; Right: Pu $4d_{5/2}$ NEXAFS with the blue (dark) spectra are from the pristine Pu(III) oxalate, whereas the pink (light) spectra are from the radiation-damaged complex.

Trivalent Pu has been characterized by examining small single crystals of oxalate precipitated from a Pu(III) solution. Fig.1(center) shows an element-specific image of the hydrated $Pu(C_2O_4)_2$ crystal from which the NEXAFS at the Pu $4d_{5/2}$ edge was collected in two different modes (Fig. 1 right; blue trace-fast scan, pink trace-slow scan]. The pink (light) trace shows a slight signature of radiation alteration induced by the soft x-rays and a slight charge state shift towards higher energy is noticeable. This result reinforces that radiation damage from soft x-ray techniques can be severe in some materials and that the ALS-MES STXM provides a unique method to mitigate beam-induced damage for sensitive materials.

Science objectives for 2009-20011:

- STXM investigations will continue to be performed on transuranic materials, reference materials, and complexes with Raymond ligands. This will be complemented by theoretical calculations and structural studies of the same complexes with the ALS small molecule diffractometer. Emphasis will be on transuranic materials and materials produced from within the ACG.
- XES/RIXS will continue to examine actinide reference materials, oxides, and complexes relevant to trivalent separations. A Pu(III) reference material will be investigated.
- The design of the actinide generation II end station, connection section, and actinide materials preparation glove box will be advanced towards construction as components permit.
- The next stage of ACG laboratory improvements will follow the final implementation of the instrument systems currently being commissioned.
- References to work supported by this project 2007-2009:

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Chemical Interactions in the Non-Aqueous Phase for Liquid-Liquid Extraction Systems

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Overall Research Goals:

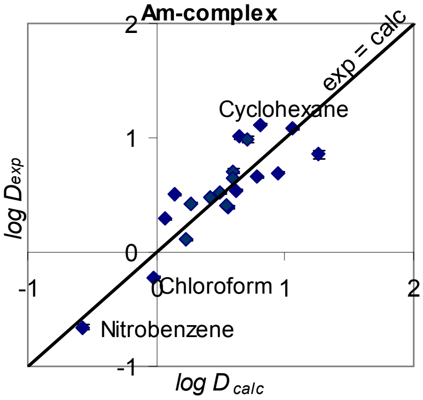
The objective of this research is to increase the understanding of the organic phase properties in a 2-phase extraction system. By combining experimental observations with thorough thermodynamic theoretical treatment we hope to some degree overcome and avoid the use of simplifications and assumptions regarding the theoretical modeling of the organic phase.

Previous significant achievements and observations:

Chalmers University of Technology, 2001-2005:

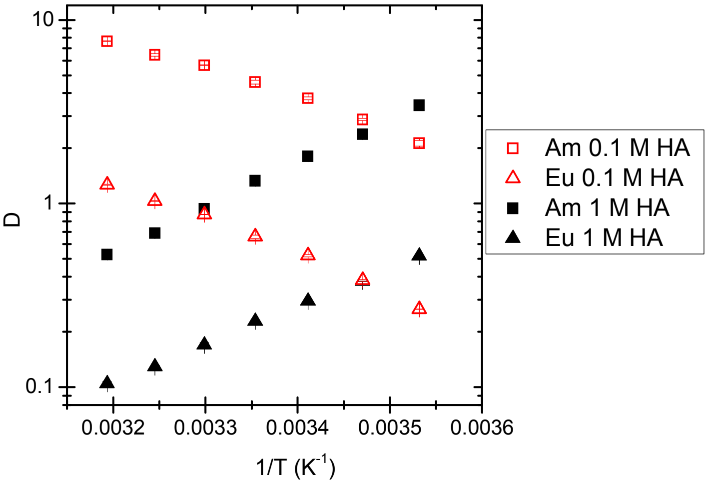
Several observations were made indicating the need for describing the organic phase interactions in actinide/lanthanide separation systems. In addition, some work was done to try to model the interactions using simple models. For instance, a model was suggested based on Hansen's solubility parameters that could be used to calculate distribution ratios for a synergic extraction systems using 2,2':6',2''-terpyridine (terpy) and 2-bromodecanoic acid (HA) [1]. The model was applied to extraction data for americium, curium and promethium using different organic diluents and validated using mixtures of several diluents. The comparison between experimental and calculated values was reasonably good, see figure 1, but limitations in the Hansen solubility parameters to describe strong polar interactions require a need for a more detailed model. Furthermore, assumptions still had to be made for the stoichiometry of the extracted complex.

Figure 1. Experimental and calculated distribution ratios of Am using different organic diluents [1].



The temperature dependence of the same synergic extraction system was investigated by Å. Enarsson [2] and it was noticed that by changing the concentration from 0.1 M HA to 1 M the extraction dependency switched from endothermic to exothermic, see figure 2, suggesting a switch in extraction mechanism. The reason for this switch in mechanism is not entirely clear but an increase in 2-bromodecanic acid concentration would most likely only affect the organic phase since the organic acid is lipophilic with a distribution ratio around 800 [3].

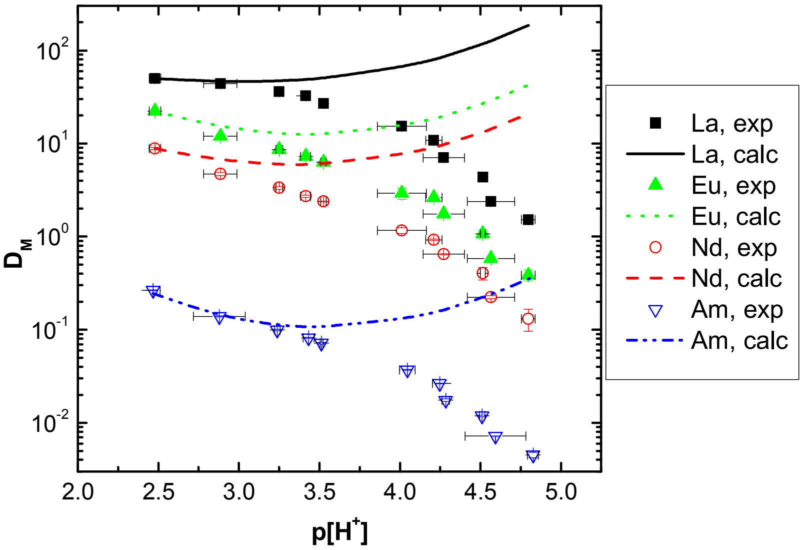
Figure 2. Temperature dependence of Am and Eu extraction using 0.02 M terpy and 0.1 or 1 M HA. Data collected by Enarsson [2].



Washington State University, 2006-2008:

A number of extraction studies were carried out to investigate different aspects of the TALSPEAK extraction system. This extraction system relies on a single organic extraction molecule, bis-2-diethylhexylphosphoric acid (HDEHP), potentially simplifying the theoretical treatment of the organic phase. However, with 2 complexing agents present in the aqueous phase, diethylenetriamine pentaacetic acid (DTPA) and lactic acid (HL), the 2-phase extraction system is complicated. By using a set of thermodynamic data to describe the speciation in the aqueous phase and previously defined extraction constants for HDEHP a set of theoretical distribution ratios as a function of aqueous acidity can be calculated. Results show that these calculated values very poorly describe the experimental observations, see figure 3. The interactions in the aqueous phase are reasonably well established (although this has been debated and is currently under investigation) which may suggest that the organic phase is poorly described in this model. Changes in the organic phase composition could result in unpredicted experimental observation as shown above.

Figure 3. Distribution ratios of Am, Nd, Eu and La using TALSPEAK chemistry, compared to calculated trends. Data from Nilsson and Nash [4].



Future research plan and goals:

To use analytical tools to determine certain parameters of the organic phase in an extraction system and coupled with distribution ratios see if any trends can be observed. Potential tools to characterize the organic solvent worth investigating may be vapor pressure osmometry, water content titrations, IR-spectroscopy to name a few. Theories based on solubility parameters could be used as a starting point with the goal of trying to expand the theories to use variables that are more accessible. One very useful but challenging and potentially time consuming task would be to successfully determine activity coefficients in an organic mixture.

References:

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Fundamental Studies of Novel Separations

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Overall research goals: The objective of this project is to investigate fundamental issues in designing chemical architectures that selectively bind target species through tailored interactions. Currently, the systems of study include novel nanoporous materials and ionic liquids.

Significant achievements during 2008-2009:

(1) A strategy to assemble phenolic resins for making highly ordered mesoporous carbons via an $I^+X^-S^+$ mechanism was developed. The effect of phenol reactivities with formaldehyde on the formation of ordered mesoporous carbons has also been investigated. The carbon material obtained exhibits highly ordered hexagonal mesostructure and high thermal stability; it can be graphitized at 2600 °C while considerable mesoporosity is maintained.

(2) The size-sieving properties of a mesoporous carbon membrane were studied via molecular permeation and cyclic voltammetry experiments. Two phenomena, simple diffusion and electrochemically aided diffusion, were investigated. The diffusion of molecules transported through the membrane was characterized by the values of permeability and apparent diffusion coefficient in the membrane. Because larger molecules are more restricted in terms of penetrating the pores, the size-based selectivity of the mesoporous carbon membrane could be readily observed.

(3) Ordered mesoporous carbons (OMCs) are ideal for many applications in separation. The surface modification of OMCs is crucial for controlling the interfacial properties of these materials in molecular separation. Prato's reaction, which is based on the 1, 3-dipolar cycloaddition of azomethine ylides, has been applied to organic modification of fullerenes, carbon nanotubes, and carbon nanohorns. We for the first time report the functionalization of OMCs via 1, 3-dipolar cycloaddition of azomethine ylides, generated by thermal condensation of an amino acid and an aldehyde. The cycloaddition reaction leads to the formation of pyrrolidines attached on the surfaces of OMCs. The effect of carbon wall characteristic (amorphous or graphitic) of OMCs on the efficiency of functionalization was investigated both experimentally and computationally.

(4) Vaporization enthalpies for two series of ionic liquids (ILs) composed of 1-N-alkyl-3-methylimidazolium cations, $[\mathrm{Im}_m^{1+}]$ (m = 2, 3, 4, 6, 8, or 10), paired with either the bis(trifluoromethanesulfonyl)amide, $[\mathrm{Tf_2N^-}]$, or the bis(perfluoroethylsulfonyl)amide anion, [beti-], were determined using a highly reproducible thermogravimetric approach and from these values, Hildebrand solubility parameters were estimated. Our results reveal two interesting and unanticipated outcomes: (i) methylation at the C2 position of $[\mathrm{Im}_m^{1+}]$ affords a significantly higher vaporization enthalpy; (ii) in all cases, the [beti-] anion served to lower the enthalpy of vaporization relative to $[\mathrm{Tf_2N^-}]$.

(5) A novel series of ionic liquids containing cationic silver complexes have been synthesized via a new methodology. The essence of this methodology is to form the cations of ionic liquids through the complexation reaction of neutral organic ligands with silver ion, followed by the metathesis reaction of the resulting salts with a hydrophobic anion donor. Olefin, amide, and amine compounds have been demonstrated to be effective neutral organic ligands to use in forming these silver-based ionic liquids. These novel ionic liquids, in which silver ion is an integrated component of the corresponding cations, give rise to the efficient transport of olefins through (a) the fast molecular

diffusion of the silver-olefin complexes and (b) the hopping motion of the olefin ligands among neighboring cationic silver sites. This dual-transport mechanism entails the olefin-transport modes of both liquid and polymer membranes, leading to significantly improved transport efficiencies and energy savings for separation of olefins from paraffins via silver complexation.

(6) We made a significant progress along the line of simulating dynamic processes relevant to our parallel experimental endeavors. Our group found that Ag^+-complex based ionic liquids demonstrate superior permeance and selectivity of olefin over paraffin when supported as a liquid membrane. To understand this membrane transport process, we used first principles molecular dynamics simulations to examine the binding-unbinding events between ligands and the cation for a simplified ionic liquid whose cations and anions are silver-ethylene complex $[Ag(C_2H_4)_2{}^+]$ and BF_4^-, respectively. We identified a mechanism of ethylene transfer similar to the Grotthus type of proton transfer in water, where a silver cation accepts one ethylene molecule and donates another to a neighboring silver cation. This mechanism may contribute to fast transport of olefins through ionic liquid membranes based on silver complexes.

Science objectives for 2009-2011:

- We investigate the preparation and characterization of mesoporous carbon membranes by direct carbonization of polymeric composite films for molecular separation.
- The synthesis of new classes of ionic liquids based on superbases will be pursued for gas separation.
- We will examine dynamics of Ag ionic liquids with different ligands experimentally and computationally.
- We will use the reactive force field (ReaxFF) to model the process of carbonization of our porous carbons.

Selected publications supported by this project 2008-2009

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Synthesis, Characterization and Reactivity of a Uranyl(V) Bis(pyridine) Complex

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We are exploring the ligand design requirements for stabilizing the reactive pentavalent uranyl ion (UO_2^+). We have found that the Ar_2nacnac ligand (Ar_2nacnac = (2,6-$^iPr_2C_6H_3$)*N*C(Me)CHC(Me)*N*(2,6-$^iPr_2C_6H_3$)) can stabilize UO_2^+, in part because its two bulky aryl substitutents effectively protect the metal center. Thus reduction of [(Ar_2nacnac)UO_2(OTf)$]_2$ with Cp_2Co in the presence of pyridine provides (Ar_2nacnac)UO_2(py)$_2$ (**1**), a rare example of isolable uranyl(V) complex. Complex **1** undergoes facile ligand exchange with several N-donor ligands, such as methylimidazole and 2,2'-bipyridine, generating (Ar_2nacnac)UO_2(MeIm)$_2$ (**2**) and (Ar_2nacnac)UO_2(bipy) (**3**), respectively. Complexes **1** (Figure 1), **2**, and **3** have all been structurally characterized. We are also exploring the reactivity of **1** with a variety of O- and S-donors in an attempt to determine the ligand preferences for the UO_2^+ fragment. Preliminary results suggest that, unlike UO_2^{2+}, uranyl(V) prefers soft donors which is consistent with its lower ionic charge.

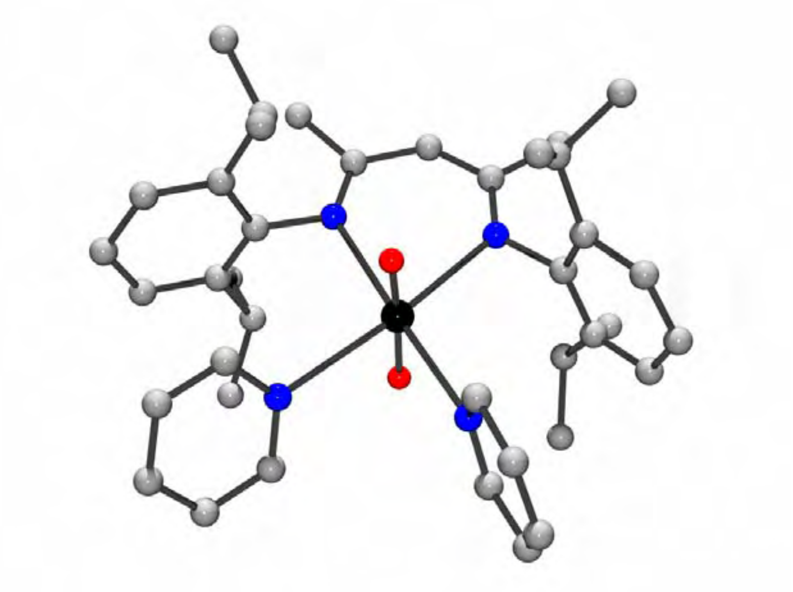

Figure 1. Solid-state molecular structure of (Ar_2nacnac)UO_2(py)$_2$ (**1**).

Quantifying Covalency in Actinide Metal-ligand Bonds

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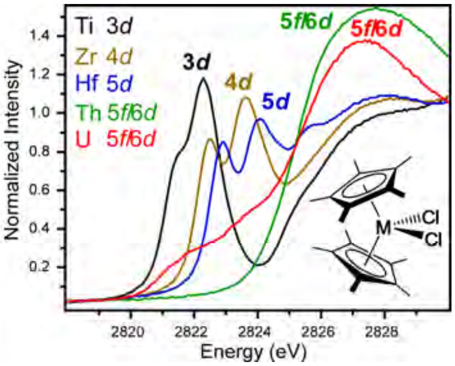
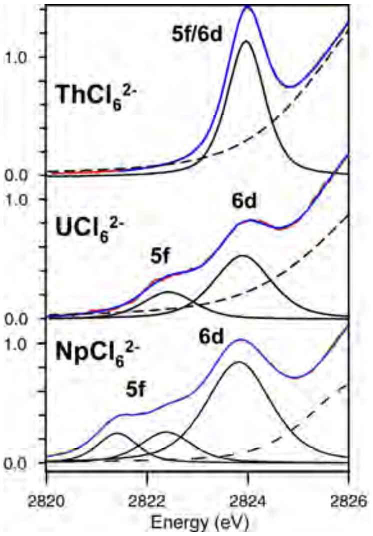
Overall Research Goals: The goal of this subtask is to understand the nature of chemical bonding, the relative roles of valence 5*f* and 6*d* orbitals, and the degree of covalency in light actinide compounds through the use of modern synthetic methodologies, ligand K-edge x-ray absorption spectroscopy (XAS), optical, and vibrational spectroscopy, coupled with quantum chemical calculations. This represents a new research direction for our program initiated in 2007.

Significant achievements in 2007-2009:.



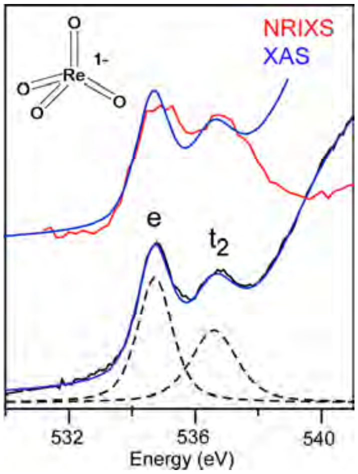
Experimental Cl K-edge XAS for $(C_5Me_5)_2MCl_2$ (M = Ti, black, Zr, brown; Hf, blue; Th, green; U, red).

Chlorine K-edge XAS studies of Metallocene dichlorides. We completed studies of the amount of Cl 3*p* involvement in M-Cl bonding as a function of 3*d*, 4*d*, 5*d*, and 6*d*/5*f* metal orbitals in a series of structurally similar $(C_5Me_5)_2MCl_2$ (M = Ti, Zr, Hf, Th, and U) complexes using Cl K-edge XAS and electronic structure calculations. The results demonstrate that the % Cl 3*p* character in the M-Cl bond in the structurally similar $(C_5Me_5)_2MCl_2$ system follows the order 3*d* > 4*d* > 5*d* > 6*d/*5*f*. From the molecular orbital description and simple perturbation theory this trend is well-understood. For a common ligand such as Cl, the energy gap between Cl 3*p* and metal n*d* orbitals increases as we progress the series 3*d*, 4*d*, 5*d*, 6*d* because the metal based orbitals rise in energy with increasing principal quantum number. What is striking from the experimental data is that we find relatively smooth trend within the *d*-block elements with covalency decreasing from 25, to 23 to 22 % Cl 3*p* character for Ti, Zr and Hf, respectively. For the actinides, we find a large (roughly 50%) drop in covalency to 9% for U. This is consistent with greater M-Cl bond polarity for the actinide system.



Experimental Cl K-edge XAS for MCl_6^{2-} (Th, U, and Np; red), curve fits (blue) and individual peak contributions to the fit (black).

Chlorine K-edge XAS studies of Octahedral MCl_6^{n-} Complexes. We have continued the studies of Cl K-edge XAS and hybrid density functional theory calculations on a series of simple octahedral chloride salts MCl_6^{n-} (M = Zr, Hf, W, Ce, Th, U, Np, Pu; n = 1, 2, 3 depending on the metal) in order to assess the relative roles of the valence nf and (n+1)d orbitals in these systems. These studies, reproduced during three separate experimental runs, using two separate encapsulation approaches, and two different detector types establishes that we can observe pre-edge features in Cl K-edge XAS of light actinide and lanthanide octahedral MCl_6^{n-} complexes. Using ground state and transition dipole calculations in modern density functional theory as a guide, we conclude that covalent M-Cl bonding interactions take place with both 5*f* and 6*d* orbitals on Th, U, and Np. The dominate M-Cl bonding takes place via 6d orbitals, and for U, 5*f* orbital contribution decreases with decreasing oxidation state, and is essentially nonexistent in U(III). For Ce, we find a similar result in the Ce(IV) appears to utilize both 4*f* and 5*d* orbitals in M-Cl bonding, while Ce(III) shows no evidence for 4*f* interaction, and only a weak 5*d* interaction. The magnitude of n*f* and (n+1)*d* interactions are remarkably small, when compared to transition metal chloride systems which have been found to contain between 10-30% Cl depending on oxidation state and position in the periodic table. The higher oxidation states for U were found to contain only 10% covalency, while U(III) and Ce(III) were found to contain closer to only 5%. We are encouraged by these results, and efforts to extend the series to transuranic octahedral MCl_6^{n-} systems are in progress.



O K-edge XAS (blue) and NRIXS (red) of ReO_4^- (top). Curve fit results (black) and peak assignments (bottom).

Oxygen K-edge XAS and NRIXS studies of MO_4^{n-} ions. At the extremely low energies of the first row atoms (N, O), XAS suffers from x-ray self-absorption effects, making it extremely difficult to obtain accurate intensity data for covalency determation. Another way to obtain the same information is through non-resonant inelastic x-ray scattering (NRIXS). The x-ray scattering is not subject to self-absorption, but does suffer from lower resolution and longer data acquisition time. By combining the intensity data from NRIXS with the energy resolution of XAS, we can push our covalency studies into light elements such as O, N and F. We have employed soft x-ray UHV synchrotron techniques to obtain oxygen K-edge XAS measured by total electron and fluorescence yield on a series of transition metal MO_4^{n-} complexes, and compared these with hard x-ray NRIXS data on the same compounds. We started with the T_d MO_4^{n-} series (Cr, Mo, W, Re) Since their electronic structure is relatively well understood. Our studies indicate that fluorescence yield gives reliable intensities with our radiological containment approach, and compares well with NRIXS data. Furthermore, these studies indicate that ReO4- may serve as a reliable O K-edge intensity standard for use with actinides. Comparisons between these data and analogous measurements and calculations conducted on uranium containing compounds, like $UO_2Cl_4^{2-}$, and $UOCl_5^-$ will be discussed in an effort to determine the relative percentage of oxygen 2*p* character per U=O bond. These preliminary comparisons will be presented as a basis for quantifying covalency of the $(AnO_2)^{2+}$ cation (An = U, Np, Pu) and provide insight into the relative roles of *d*- and *f*-orbitals in actinide bonding.

Science objectives for 2009-2011: Over the next review period we will focus our efforts on extending Cl K-edge studies to transuranic $AnCl_6^{n-}$ (Pu, Am), $AnO_2Cl_4^{2-}$ (Np, Pu), and $(C_5Me_5)_2AnCl_2$ (Np, and perhaps Pu) systems. Additional metallocenes Cp_2MCl and Cp_3MCl of light actinides (Th, U, Np, Pu), lanthanides and transition elements (Ti, Zr, Hf) will be studied along with linear trans dioxo, diimido and oxo-imido $AnO_2Cl_4^{n-}$, $An(NR)_2Cl_4^{n-}$ (n = 2, 3), $AnO(NR)Cl_4^{n-}$, $AnO_2Cl_2L_x$, and $An(NR)_2Cl_2L_x$ (x = 2, 3) complexes of light actinide elements (An = U, Np, Pu). Soft x-ray and NRIXS studies will focus on the O and N K edges of these latter systems. Time permitting, we plan to examine the octahedral AnF_6^{n-} series (Th, U, Np, Pu) via F K-edge XAS. Our research plan is designed to coordinate inorganic synthesis, spectroscopic characterization, and theoretical calculations for a more comprehensive understanding of covalency and electronic structure.

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2. S. A. Kozimor, P. Yang, E. R. Batista, K. S. Boland, C. J. Burns, C. N. Christensen, D. L. Clark, S. D. Conradson, P. J. Hay, J. S. Lezama, R. L. Martin, D. E. Schwarz, M. P. Wilkerson, L. E. Wolfsberg, *Inorg. Chem.*, **2008**, *47*(12), 5365-5371.

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Theoretical studies of electronic structure and reactivity of actinide complexes

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KEYWORDS: covalency, density functional theory, DFT, TDDFT, UV-absorption spectroscopy, magnetism

The actinide series marks the emergence of 5f electrons in the valence shell. Theoretical and spectroscopic studies indicate that variations in orbital character and metal *d*-and *f*-covalency are connected with differences in chemical reactivity and magnetic properties. Quantum chemical simulations are able to provide a first-principle description of the metal-ligand bonding. We have applied this analysis to the series of complexes in order to understand the participation of *d*-*f* electrons as a function of ligand type, oxidation state, and symmetry of actinide complexes. This includes the bonding motif of U-oxygen, U-nitrogen, and U-chloride. In this study, density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations reproduce the experimental observations including ligand K-edge X-ray Absorption Spectra, UV-absorption spectra, and chemical reactivity in a quantitative manner. I will present our recent theoretical studies to understand these covalent interactions. Our results provide the basis towards a fundamental understanding of the physico-chemical interactions that drive the rational design of chelating ligands for separation and remediation technologies.

Ion-Ligand Interactions in Actinide Compounds

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Overall research goals:

This research provides a fundamental understanding of electronic interactions of actinides in compounds. Our efforts focus on the consequences of the interplay between ions and their complex environments. Spectroscopic experimental studies and theoretical modeling development are aimed at establishing correlations between electronic properties and the aspects of coordination and separation. The basic electronic properties addressed in this research include 1) the influence of orbital hybridization and ion-ligand exchange charge interactions on bonding and coordination and 2) dynamics of ion-ligand interactions interpreted through quantitative analysis and simulation of multiphonon vibronic transitions.

Significant achievements during 2007-2009:

1. Theoretical modeling of crystal-field induced orbital hybridization (5f-6d configuration mixing) and analysis of absorption spectrum of trivalent uranium in crystals with hexagonal structures was performed. We investigated vibronic coupling in the electronic transitions. By combining orbital hybridization, crystal field interaction and vibronic coupling, we simulated the experimental spectra and determined the energy level structure and transitions intensities in these systems (Fig. 1). This work demonstrates the potential of a theoretical framework we developed for actinide spectra that conventional crystal-field theory fails to interpret.

2. Progress has been made in quantitative interpretation of charge transfer vibronic coupling and its effects on the progressive multiphonon bands of uranyl in $(UO_2)(C_7H_3NO_4)$ and similar systems of uranium coordination polymers. We have further developed the theoretical model of charge transfer vibronic excitons (CTVE) for interpreting a novel excited state splitting observed in these systems (Fig. 2).

Science objectives for 2009-2011

We plan to extend our ongoing effort in modeling hybridization and covalence. With experimental capabilities in determining energy levels and transition intensities, our focus for the non-bonding contributions to electronic interactions is on high-valent systems in which the 5f orbitals are occupied by up to four electrons. We will use a new theoretical framework we developed for evaluating the effect of orbital hybridization and ligand-ion charge exchange, the non-bonding contributions are influenced by on-site hybridization (p-, d-, and f-state mixing). We will continue our investigation on the influence of orbital hybridization and covalence on energy levels and electronic transitions in Np and Pu systems in which 5f-6d configuration coupling is strong.

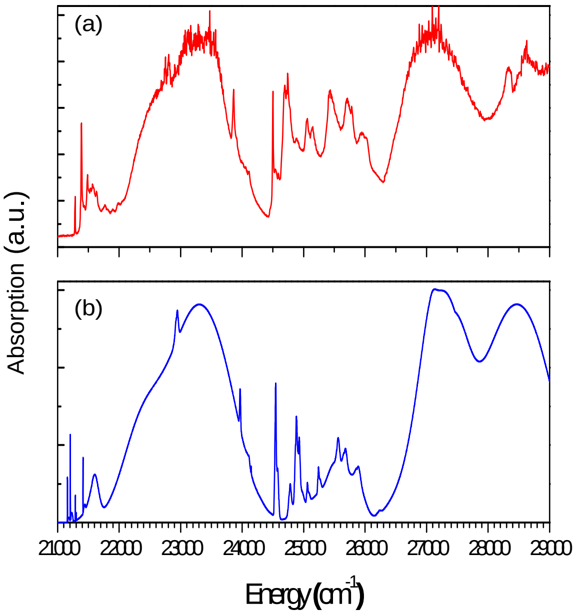

Fig. 1 Absorption spectrum (a) and theoretical simulation (b) for U^{3+}:$LaCl_3$ at 4 K. Mixing of the $5f^3$ and $5f^26d$ states and vibronic coupling must be counted in order to simulate the experimental spectrum.

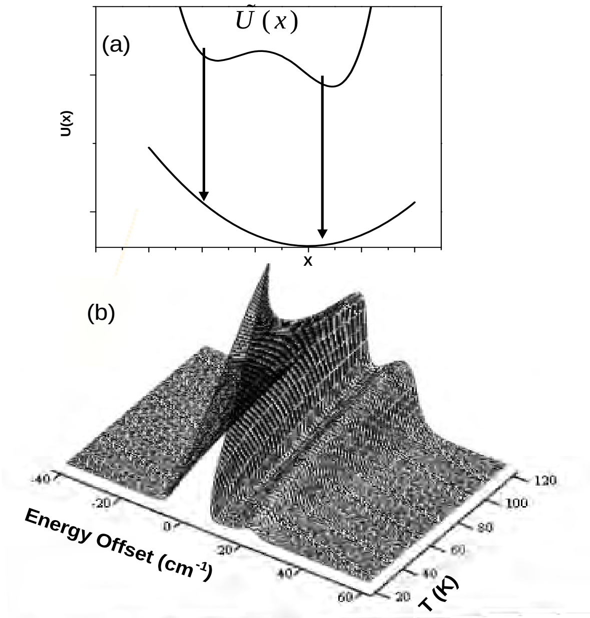

Fig. 2 Charge transfer vabronic exciton model of uranyl luminescence (a) and simulated luminescence dynamics (b) where a hot band appears in the low energy side of zero-phonon line.

We believe that electronic interactions alone do not remove certain degeneracies in uranyl excited states. Both electronic interactions and the collective effects of vibronic exciton dynamics in charge transfer states contribute. To better understand the electronic properties of actinyl systems, the influence of ligands on the excited states through charge transfer and vibronic coupling must be evaluated. This means orbital hybridization, charge transfer, and vibronic coupling must be addressed at the same time. Building on our previous work, we will continue experimental studies and theoretical modeling of the problematic excited state splitting on the $[UO_2Cl_4](C_nH_mN_x)$ series using different approaches including an anharmonic model of charge transfer vibronic exciton interaction and cation-cation coupling.

Publications supported by this project 2007-2009

1. Anharmonic charge transfer vibronic states and luminescence dynamics of uranyl compounds
   G. K. Liu and V. S. Vikhnin, Chem. Phys. Lett. 437, 56-60 (2007).
2. A few mistakes in widely used data files for f^n configurations calculations
   Xueyuan Chen, Guokui Liu, Jean Margerie and Michael F. Reid, J. Luminescence 128, 421-427(2008)
3. Enhancement of Phosphor Efficiency via Composition Modification
   Y. X. Pan and G. K. Liu, Optics Letters 33, 1816-1820(2008)
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   Wei Wang, Hong Zhang, Guokui Liu, MRS Proceedings 1104, NN04-08(2008)
5. Configuration interaction of trivalent uranium in crystals of hexagonal symmetry
   W. Wang and G. K. Liu, in prep for Phys. Rev. B.

Transuranic Coordination Chemistry and Relative Covalency in An(III)/Ln(III) Complexes

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Proposed Collaborators: Enrique Batista, Stosh Kozimor, Iain May (all LANL) & Robert T. Paine (UNM)

(i) Overall Research Goals.

- Employ coordination chemistry to probe actinide-ligand bonding and elucidate the fundamental important bonding principles that can be manipulated in the future design of separations for Advanced Nuclear Fuel Cycles, especially An(III)/Ln(III).
- Understand the extent to which covalency is important and determine covalency differences between actinide-ligand and lanthanide-ligand bonding.
- Judiciously select soft donor ligand types designed to invoke a greater degree of covalency in An-L bonds relative to Ln-L bonds.
- Develop the syntheses of transuranic non-aqueous precursors as a platform to allow a wide range of soft donor and other covalency inducing ligands to be studied.
- Assess the effect of the An and Ln contractions (i.e. changes in orbital energies and polarizability) upon covalent interactions in the bonding. This approach is designed to develop bonding trends across the series and study the transuranic elements (Np-Cm) directly.

(ii) Significant Achievements.

We have prepared and structurally characterized molecular Pu(III), Pu(IV) and Pu(VI) complexes to serve as vital synthons in the development of non-aqueous plutonium coordination chemistry (for example, see Figure 1). These complexes lay the foundation for an in-depth probe of the electronic structure and bonding with our carefully selected ligands designed to promote orbital mixing.

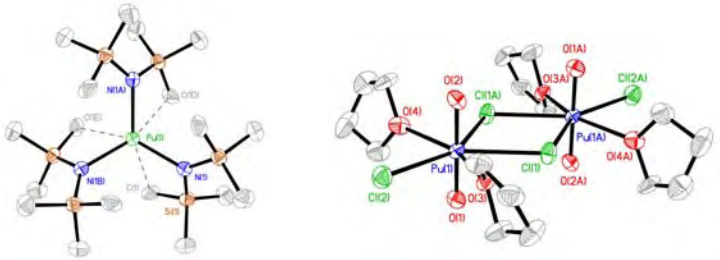

Figure 1. Crystal structure of the Pu(III) synthon, $Pu[N(SiMe_3)_2]_3$ (left). Crystal structure of $[PuO_2Cl_2(thf)_2]_2$ (right), providing entry into non-aqueous plutonyl(VI) chemistry.

We have prepared complexes with N, S, Se and Te donor ligands to examine for bonding differences between trivalent 4*f* and 5*f* ions of similar ionic radii. Homoleptic trivalent Pu, U, La and Ce complexes with $[N(EPR_2)_2]^-$ ligands (E = S, Se, Te; R = Ph, *i*Pr) allow systematic variation of the ‘softness’ of the donor atom, and also the ‘hardness’ of the metal ion, in isostructural compounds (Figure 2). We find enhancement of covalency in An(III) ‘soft’ donor complexes compared to Ln(III), reflected by shorter An-E than Ln-E bonds. Similar bonding differences are observed both between U(III)/La(III) and also Pu(III)/Ce(III), which has the implication that covalency may be an important factor in extraction behaviour as far across the series as Am(III) and Cm(III). The computational calculations are consistent with, and accurately model trends from the experimental data. This is the first study of a series of An(III) and Ln(III) complexes, with differing donor atoms, that conclusively shows a clear trend in bond distance differences (with low esd values) in molceular structures as an indication of covalency differences.

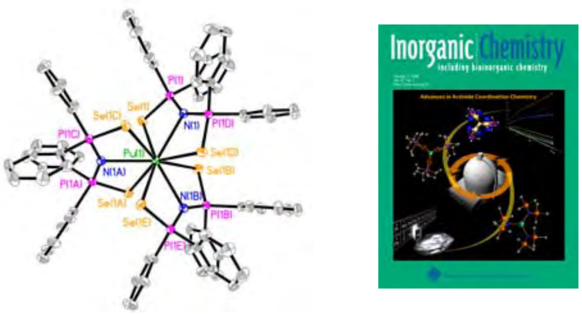

Figure 2. Crystal structure of $Pu[N(SePPh_2)_2]_3$, one of the complexes used to study bonding differences between An(III) and Ln(III) ions with soft donor atoms.

(iii) Science Objectives for 2009-2012 (with May, Kozimor and Batista).

- Assemble a multi-disciplinary team with a unique capability to address the scientific challenge of understanding covalency with an integrated and comprehensive approach.
- Advance the syntheses of transuranic complexes with soft donor ligands chosen to push the boundaries of hard-soft metal-ligand interactions to optimize covalent interactions and maximise differences between An(III) and Ln(III) bonding.
- Conduct ligand K-edge XAS measurements to quantify the covalent mixing between ligand σ- and π- orbitals with An and Ln *f*- and *d*-orbitals.
- Perform thermochemical measurements on the soft donor systems that we have studied.
- Combine variable temperature competition experiments and kinetic data with the structural, K-edge XAS, and thermodynamic data to begin to rationally develop novel separation strategies.

(iv) Selected References Supported by this Project:

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[3] *“Structural Characterization of* $Pu[N(SiMe_3)_2]_3$*: a Synthetically Useful Plutonium(III) Precursor”* Andrew J. Gaunt, Sean D. Reilly, Alejandro E. Enriquez, Brian L. Scott, Mary P. Neu *Inorganic Chemistry*, **2008**, 47, 26 (***article featured on front cover***).

[4] *“Covalency in the f-element–chalcogen bond. Computational studies of* $M[N(EPR_2)_2]_3$ *(M = La, Ce, Pr, Pm, Eu, U, Np, Pu, Am, Cm; E = O, S, Se, Te; R = H,* ^{i}*Pr, Ph)”* Kieran I. M. Ingram, Matthew J. Tassell, Andrew J. Gaunt, Nikolas Kaltsoyannis *Inorganic Chemistry*, **2008**, *47*, 7824.

[5] *“Covalency in the f-element-chalcogen bond. Computational studies of* $[M(N(EPH_2)_2)_3]$ *(M = La, U, Pu; E = O, S, Se, Te)”* Kieran I. M. Ingram, Nikolas Kaltsoyannis, Andrew J. Gaunt, Mary P. Neu *Journal of Alloys and Compounds*, **2007**, 444-445, 369.

[6] *“An Entry Route into Non-Aqueous Plutonyl Coordination Chemistry”*Andrew J. Gaunt, Sean D. Reilly, Trevor W. Hayton, Brian L. Scott, Mary P. Neu *Chemical Communications*, **2007**, 1659.

The Chemistry and Physics of the Heaviest Elements

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Overall research goals: Study the chemistry and physics of the heaviest elements/transactinide elements.

Significant achievements during 2007-2009:

1. Transactinide gas phase organometallic chemistry.
Gas chemical methods have proven powerful for the investigation of the transactinide elements (TAN, Z≥104) which are produced in heavy-ion-induced fusion reactions. Chemical systems with transactinides and organic molecules have not been accessible so far due to the plasma caused by the intense heavy-ion beam. The Berkeley Gas-filled Separator (BGS) separates the nuclei of interest from fission and transfer reaction products. The heavy element nuclei of interest pass through a thin Mylar window and stopped in the gas-filled Recoil transfer Chamber (RTC)). In the RTC the volatile organic molecules are reacted with the separated nuclei and sent by gas-jet to our chmical separation/alpha-detection system. To prepare for an experiment with Rf, a new detection system allowing for the use of even shorter-lived α-decaying nuclides was constructed. The detector wheel facilitates detection of alpha emitting particles, but can also be coupled to a gamma detector to study the physics of transactinides in near background-free conditions. The new apparatus was tested at the 88-inch cyclotron using a beam of ^{40}Ar that was accelerated to 180 MeV on a target of ^{169}Tm for the nuclear reaction: ^{169}Tm(^{40}Ar, 4n)^{205}Fr. Francium-205 is an excellent model nuclide for testing the apparatus. It has a comparable half-life to some long-lived transactinide nuclides ($t_{1/2}$ = 3.85 s) and decays by high-energy alpha-decay (E = 6.915 MeV). We determined with this experiment that 80% of the Fr atoms were transported to the alpha-detector wheel within 0-4 s, and the remaining 20% came within the next 4-8 s. Thus the alpha-detector wheel is well suited to detecting transactinides with half-lives on the order of a few seconds to minutes.

2. Identification of two new isotopes of element 108.
One of the final experiments in our systematic study of "cold fusion" between ^{208}Pb and ^{209}Bi targets with medium mass beams (from ^{48}Ca through ^{65}Cu) was the comparison of element 108 production cross sections in the ^{208}Pb(^{58}Fe,n)^{265}Hs and ^{208}Pb(^{56}Fe,n)^{263}Hs reactions. In the latter reaction, six atoms of the new isotope ^{263}Hs were identified. The alpha decay energies of ^{263}Hs provide information on the strength shell effects near the N=152 deformed shell. The N=152 shell is strongest near Z=100. Comparison of the alpha decay energies for ^{263}Hs with those of heavier Hs isotopes show that the N=152 shell is still significant at Z=108. We extended this experiment with a search for the next-lighter Hs isotope, ^{262}Hs produced in the ^{207}Pb(^{56}Fe,n)^{262}Hs reaction. Four spontaneous fission decays with a very short half life were observed. As is true in Z=104-107 isotopes near N=152, the deformed shall seems to stabilize against alpha decay, but not spontaneous fission.

Objectives for 2009-2011:

With the versatile and reliable LBNL 88-Inch Cyclotron, together with world-leading ECR ion source development, and the highly efficient and selective BGS, the LBNL Heavy Element Nuclear and Radiochemistry program is ideally situated to take full advantage of new experimental opportunities in the study of the nuclear physics and chemistry of the heaviest elements. Experimental directions for the next several years will include:

Use of the BGS for synthesis, identification, and chemistry of new heavy element isotopes.
The Berkeley Gas-filled Separator (BGS) allows separation and detection of heavy element isotopes produced in compound nucleus reactions. Studies of the production and decay of these heaviest isotopes provide important information on nuclear masses, heavy element production reaction mechanisms, and nuclear structure and stability at the high-Z limit. Exciting results on the production and decay of superheavy elements near Z=114 and N=180 have been reported by the Russian group at the Flerov Laboratory for Nuclear Research in Dubna. 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 and nuclear decay properties of the heaviest elements.

New organometallic compounds of transactinides

The new on-line alpha detection system enables us to use of even shorter-lived α-decaying nuclides. To prepare for an experiment with Rf, an. experiments is scheduled for spring 2009 to produce ^{158}Hf ($T_{1/2}$=2.6 s).for an optimization of the detection system for this time-scale. The main goal of this study is an experiment on the formation of Rf-cyclooctatetraene complexes using pre-separated ^{257}Rf ($T_{1/2}$ = 4.3 s). Future work will utilize the nuclear reaction ^{22}Ne(^{244}Pu, 5n)^{261m}Rf to examine the organometallic chemistry of rutherfordium-261m.

Publications supported by this project 2007-2009

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J. M. Gates, L. Stavsetra, R. Sudowe, M. N. Ali, M. G. Calvert, I. Dragojević, J. Dvořák, Z. Dvořáková, P. A.Ellison, M. A. Garcia, K. E. Gregorich, S. L. Nelson, T. Parsons-Moss, and H. Nitsche, “Extraction of niobium and tantalum isotopes using organophosphorus compounds – Part II – Extraction of ‘carrier-free’ metal concentrations from HCl/LiCl solutions,” Radiochim. Acta, 97, 1-4 (2009), DOI 10.1524/ract.2009.1583. LBNL -

J. M. Gates, M. A. Garcia, K. E. Gregorich, Ch. E. Düllmann, I. Dragojević, J. Dvořák, R. Eichler, C. M. Folden III, W. Loveland, S. L. Nelson, G. K. Pang, L. Stavsetra, R. Sudowe, A. Türler, and H. Nitsche, “Synthesis of rutherfordium isotopes in the ^{238}U$^{(26}$Mg,*xn*)$^{264\text{-}x}$Rf reaction and study of their decay properties,” Phys. Rev. C 77, 034603 (2008). LBNL – 90E.

J. M. Gates, S. L. Nelson, K. E. Gregorich, I. Dragojević, Ch. E. Düllmann, P. A. Ellison, C. M. Folden III, M. A. Garcia, L. S. Stavsetra, R. Sudowe, D. C. Hoffman, H. Nitsche, “Comparison of reactions for the production of ^{258,257}Db: ^{208}Pb(^{51}V,x*n*) and ^{209} Bi(^{50}Ti, x*n*),” Phys. Rev. C78, 034604 (2008). LBNL – 1158E.

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

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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 2007-2009

1. Methodological and computational developments

We continue to develop and improve the methodological and computational tools that enable our more focused appliactions on actinide systems During this grant period, there were 3 papers specifically dealing with this area (CTRL-click on hyperlink to see the paper):

23. Analytical infrared intensities for periodic systems with local basis sets, A. F. Izmaylov and G. E. Scuseria, Phys. Rev. B **77**, 165131 (2008).

25. Resolution of the identity atomic orbital Laplace transformed second order Moller-Plesset theory for nonconducting periodic systems, A. F. Izmaylov and G. E. Scuseria, Phys. Chem. Chem. Phys. **10**, 3421-3429 (2008).

28. Why are time-dependent density functional theory excitations in solids equal to band structure energy gaps for semilocal functionals, and how does nonlocal Hartree-Fock type exchange introduce excitonic effects?, A. F. Izmaylov and G. E. Scuseria, J. Chem. Phys. **129**, 034101 (2008).

2. Development and assessment of novel exchange-correlation functionals

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:

24. Generalized gradient approximation model exchange holes for range-separated hybrids, T. M. Henderson, B. G. Janesko and G. E. Scuseria, J. Chem. Phys. **128**, 194105 (2008).

26. Accurate solid-state band gaps via screened hybrid electronic structure calculations, E. N. Brothers, A. F. Izmaylov, J. O. Normand, V. Barone, and G. E. Scuseria, J. Chem. Phys. **129**, 011102 (2008).

30. Assessment of a middle-range hybrid functional, T. M. Henderson, A. F. Izmaylov, G. E. Scuseria, and A. Savin, J. Chem. Theory Comp. 4, 1254-1262 (2008).

31. Range separation and local hybridization in density functional theory, T. M. Henderson, B. G. Janesko, and G. E. Scuseria, J. Phys. Chem. **A 112**, 12530-12542 (2008) (Centennial Feature Article).

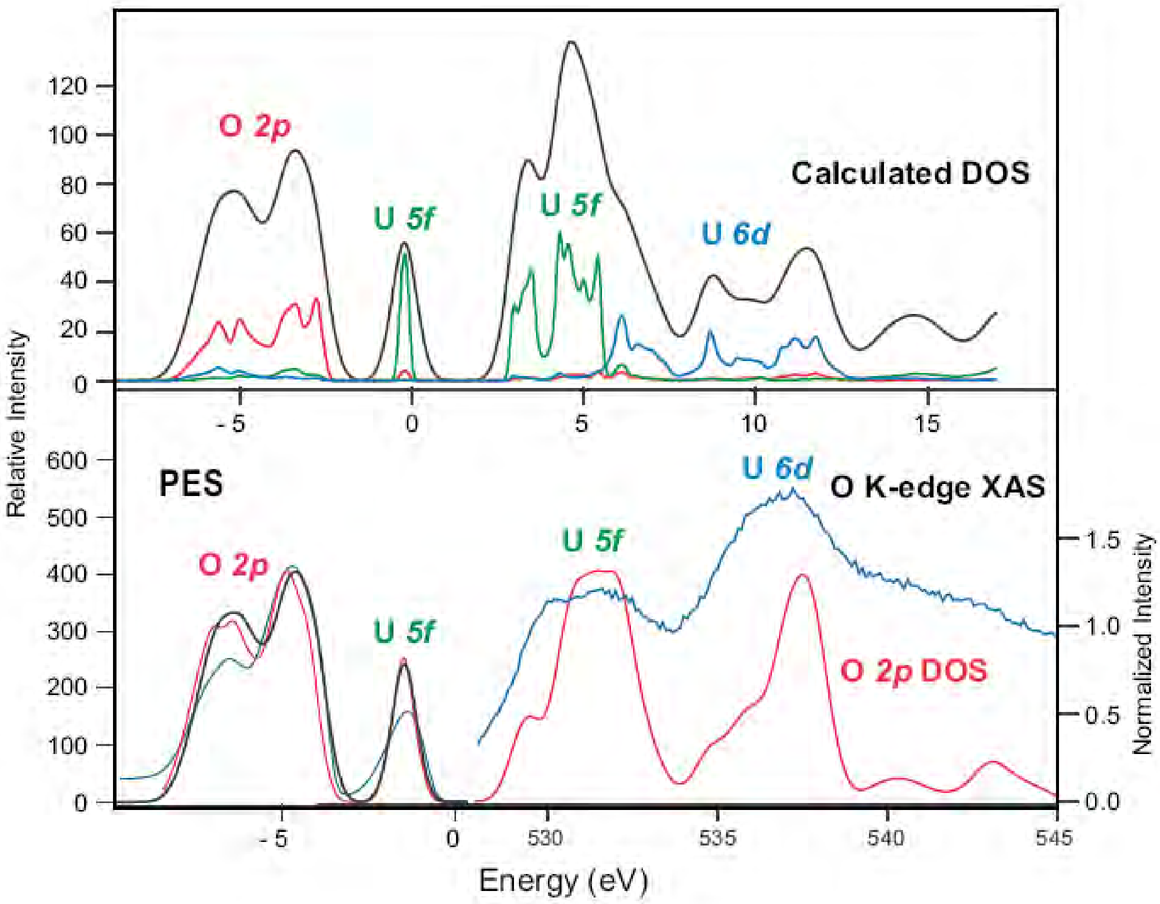
3. **Focused applications on actinide systems**

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. The two papers below report our detailed efforts in this area:

27. A screened hybrid density functional study of metallic thorium carbide, I. S Lim and G. E. Scuseria, Chem. Phys. Lett. **460**, 137-140 (2008).

29. Dispersion in the Mott insulator UO_2: A comparison of photoemission spectroscopy and screened hybrid density functional theory, L. E. Roy, T. Durakiewicz, R. L. Martin, J. E. Peralta, G. E. Scuseria, C. G. Olson, J. J. Joyce, and E. Guziewicz, J. Comp. Chem. **29**, 2288-2294 (2008).

4. **Solid UO_2 : HSE predictions versus experiment (John Joyce, LANL) -Excellent agreement!**



Structural Studies of UO_{2+x} on Multiple Length and Time Scales

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Overall Research Goals: The goal of this subtask is to understand the nature of chemical bonding in mixed-valent actinide oxides AnO_{2+x} at different length and time scales. A major goal is to understand how structural defects interact, and how the resulting collective effects including nanoscale heterogeneity determine many of their structural and chemical properties.

Significant achievements in 2007-2009:.

Variable temperature EXAFS on UO_{2+x} materials. The U L_3 EXAFS at 50, 100, and 200 K, which was originally performed to determine if the U-oxo Debye-Waller factor was typical or unusual despite its normal bond length, gave a surprising result. Although UO_2 EXAFS spectra and structural details were invariant with temperature, except for the expected increase in the Debye-Waller factor, the nearest neighbor O distributions around the U atoms in U_4O_9 and U_3O_7 underwent substantial changes over this temperature range. This is the same temperature range where crystallographic studies had always shown only a single unchanging phase (Fig. 1). Displacements of the O atoms for mixed-valent materials were therefore occurring at low temperatures that did not affect the diffraction patterns. The implications of these data will be discussed.

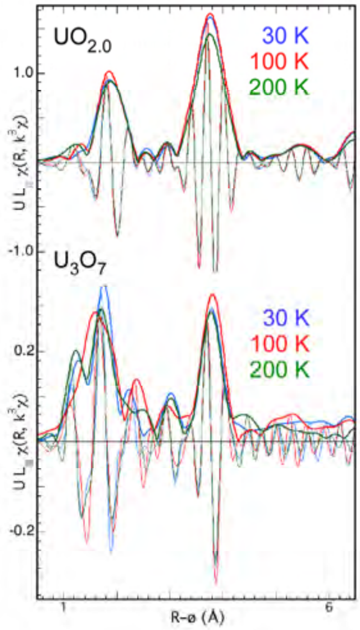

Fig 1. U L_3 EXAFS (Fourier transform representation showing the moduli and real components) of $UO_{2.00}$ (top) and U_3O_7 (bottom) at 30, 100, and 200 K. The highly disordered U and O environments and the sensitivity to temperature of the O nearest neighbor distribution in U_3O_7 relative to $UO_{2.00}$ over this range are evident.

X-ray and neutron PDF studies on UO_{2+x} materials. The comparison of the neutron and x-ray pair distribution functions (PDFs) was studied for the same suite of compounds, UO_2, U_4O_9 and U_3O_7. The same batch of material was studied by both x-ray and neutron techniques. It was expected that structures measured with neutrons and x-rays would be identical except for the differences in the scattering factors between the two probes. These are clearly not the case (Fig 2). What is most interesting is that the neutron data is very similar to that derived directly from the crystal structure whereas the x-ray PDF displays the same deviations from the crystal structure – the very broad nearest neighbor O distribution extending to 1.7 Å and the glassy component underlying the Gaussian portion of the U nearest neighbor distribution – found in the EXAFS. X-rays thus give a structure that differs from that obtained by conventional crystallographic analysis of the diffraction pattern whereas neutrons give a different one that matches the diffraction. Multiple structures are found, but in this case it is not between long range average and local structure probes but rather between x-rays and neutrons.

Fortunately, our prior experience with cuprate superconductors had shown that the critical factor was not the length scale but the time scale of the respective measurements. The practice of setting a window with a finite width for the neutrons to increase the sensitivity of the measurement allows a range of inelastically scattered neutrons to be counted that turns the neutron experiment into a slow probe. The femtosecond response of x-ray scattering and absorption means that these are fast, taking snapshots of the system averaged over all of the atoms in the x-ray beam.

If the PDFs are dependent on the time scale of the measurement, then their differences originate in dynamic processes in the material. The PDF measured by the slow probe typically differs by exhibiting lower resolution so that a two site distribution occurs as a single peak that is broadened to include both sites, conserving the overall width. In these experiments on U_3O_7 the peaks containing the distributions for many of the pairs are not only simpler for the neutrons than for the x-rays but also substantially narrower. The origin of this effect is currently being pursued, but in our earlier modeling of cuprates such radical rearrangements were not needed nor considered.

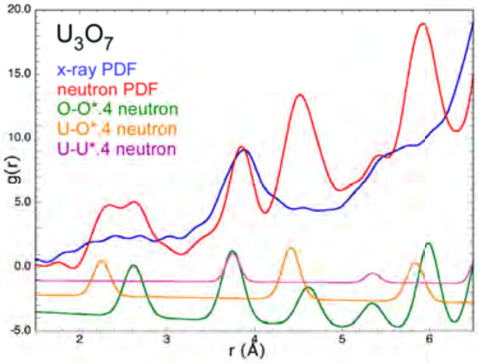

Fig 2. X-ray and neutron PDFs (upper traces) of U_3O_7 at ambient temperature. The lower traces show the separate partial PDFs of the three types of pairs, O-O, U-O, and U-U, calculated from UO_2 which is very similar to U_3O_7 over this range in terms of the positions of the peaks but is less ordered.

Oxygen K-edge XAS studies of UO_{2+x}. We have performed complementary O K edge X-ray Absorption Spectroscopy (XAS) or NEXAFS measurements that probe the unoccupied states above the Fermi level on the same suite of UO_{2+x} materials. These show that, electronically, U_4O_9 and especially U_3O_7 are not superpositions of the UO_2 and a second spectrum from the U(VI)-oxo sites, as would be expected if the system was highly ionic. The spectra of the mixed-valence compounds actually appear somewhat simpler or at least certainly no more complicated than that of $UO_{2.00}$, implying that the electrons are shared and the electronic states are hybridized across the different sites. The differentiated atom positions of the various species, although extreme, may thus be electronically comparable in energy and separated by a relatively small and easily crossed energy barrier. A corollary to this is that such mixing would create unique electronic structure and resultant properties so that the final compound will exhibit reactivity substantially different from both $UO_{2.00}$ and UO_2^{2+} compounds.

Science objectives for 2009-2011: Over the next review period we will focus on completing the detailed analyses on the oxide work, and extension to heavier actinides and alkali metal actinide oxides. This includes a collaborative paper with Stepan Kalmykov (Moscow State U) who has independently observed the same EXAFS features as ours. We will continue to develop methodology for O K-edge XAS and non-resonant inelastic x-ray scattering (NRIXS) on oxides and a means to obtain spectra on transuranic oxides.

References supported by this project:

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4. Mustre de Leon, J.; Acosta-Alejandro, M.; Conradson, S. D.; Bishop, A. R. "Change of the in-plane Cu-O bond distribution in $La_2CuO_{4.1}$ across T_c"**.** *J. Phys. Chem. Solids*, **2008**, 69(9), 2288-2291.
5. Andersson, D. A.; Lezama, J.; Uberuaga, B. P.; Deo, C.; Conradson, S. D. "Cooperativity among defect sites in AO_{2+x} and A_4O_9 (A=U,Np,Pu): Density functional calculations," *Phys. Rev. B: Condens. Matt. Mat. Phys.*, **2009**, 79(2), 024110/1-024110/12.

Covalent Interactions in Actinide Oxides

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Overall research goals:

The goal of our subtask is to develop and apply theoretical tools for the study of properties of actinide species. Our approach is based on electronic structure calculations focusing on molecular and solid state complexes. Our research is tightly connected with the experimental efforts of our co-investigators at LANL.

Significant achievements in 2007-2009:

We continued our studies of the strong correlations and covalency effects in actinide dioxides.

1. **Band dispersion in UO_2:** We have generated the band structure for UO_2.. In contrast to popular approximations such as the LDA+U, which artificially constrains the *f*-bands to be completely localized with no dispersion, our screened hybrid DFT calculations find a small, but measurable, dispersion in the *f*-manifold. The overall dispersion in the *f*-band was computed to be some 300meV. In the past year, our experimental colleagues Tomasz Durakiewicz and John Joyce have measured the dispersion in the direction ☝ to X in the Brillouin zone in single crystal UO_2 using angle-resolved photoemission. The dispersion in this direction is measured to be 130meV, compared with our theoretical prediction of 190meV. We were also able to quantify the computed 5*f*-*2p* hybridization as 0.52 electrons used for covalent mixing. This value is in good agreement with a previous experimental estimate of ~0.6. This work was published in an invited contribution to a special edition of J. Computational Chemistry focusing on computational solid-state chemistry.

2. **Covalency in UO_2:** Our colleagues David Clark, Steven Conradson, and Stosh Kozimor have measured the X-ray absorption near-edge structure for the oxygen K-edge in UO_2. The presence of peaks reflects structure in the unoccupied density of states at the leading edge of the conduction band; their intensities map the O2p character in the empty levels, and hence the amount of orbital mixing, or covalency, between metal and ligand. We find that the O K-edge structure of UO_2 is in excellent agreement with the partial O2*p* density of states arising from our previous calculation. The combination of theory and experiment confirms the characterization of UO_2 as a Mott insulator with the unoccupied 5*f* states lying below the empty 6*d* band. Earlier optical spectra assignments placed the 6*d* below below the 5*f* in the conduction band.

3. **Dispersion in PuO_2:** Continuing on the theme of covalency, earlier calculations found unexpectedly large covalency in some of the later actinide oxides. In particular, while UO_2 looks relatively ionic in character, with easily distinguished 5*f* and O2*p* bands, that was not the case in PuO_2, where the levels at the Fermi energy were nearly a 50:50 mix

of metal and ligand. This prediction can be tested via both angle-resolved photoemission probes of the occupied states, and O K-edge x-ray absorption edge measurements. Greater covalency implies greater band dispersion, and so we have computed the band structure and dispersion in PuO_2 in the screened hybrid approximation, in hopes of future experimental measurements. Our earlier predictions of strong dispersion in light of the large orbital mixing observed are born out in the explicit band structure.

4. **Spin-orbit coupling in AnO_2:** We have extended our earlier work on the series AnO_2, by including the spin-orbit operator. The band gaps adjustments are not dramatic. As expected, they become larger with increasing Z. The largest correction to the band gap (0.7eV) is found for the ferromagnetic phase of BkO_2, but most others are of the order of 0.1 -- 0.2eV.

Specific goals for 2009-2011:

We have begun examining non-stoichiometric actinide oxides with calculations on U_3O_8. We have also investigated defect energies for He incorporated into UO_2 and U_3O_8. We hope to extend these to U_4O_9 in the near future. We will continue our collaboration with Gustavo Scuseria (Rice) and our experimental colleagues to study covalency in actinide compounds through photoemission and x-ray absorption spectroscopy. We plan to investigate further the performance of screened hybrid functionals for actinide compounds in the metallic phase.

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3. Lindsay E. Roy, Tomasz Durakiewicz, Richard L. Martin, Juan E. Peralta, Gustavo E. Scuseria, Cliff G. Olson, John J. Joyce, Ela Guziewicz, *J. Comp. Chem.* **2008**, 29, 2288-2294.

Session 4 – Supramolecular Complexes

Organometallic Uranium Chemistry – New Platforms for the Exploration and Tuning of Electronic Structure and Covalency

David E. Morris, Jaqueline L. Kiplinger, P. Jeffrey Hay, Richard L. Martin, Enrique R. Batista,
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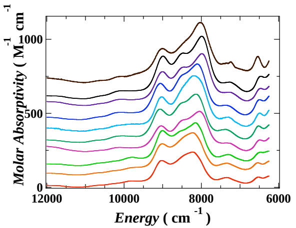
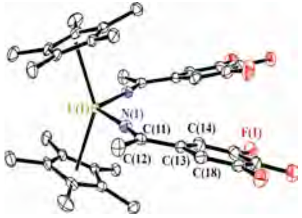
Overall research goals: The work described here is one element of a broader HEC program at Los Alamos (Organometallic Actinide Chemistry – Tuning Covalency and Reactivity). The focus here is on the synthesis, spectroscopic and electrochemical characterization, and theoretical studies of molecular and electronic structure in organometallic uranium and thorium complexes. The exquisite control and variability in molecular structure and metal oxidation state enabled by the synthetic chemistry have provided a suite of new uranium complexes possessing nominal valence electronic configurations from $5f^0$ [U(VI)] through $5f^3$ [U(III)] and metal-ligand bonding interactions spanning the continuum from simple dative interactions through strongly covalent metal-ligand multiple bonds. This has enabled a systematic examination of the factors underlying metal-ligand covalency and elucidation of the signatures of covalency in electronic structural data including electronic and vibrational spectroscopy and electrochemistry.

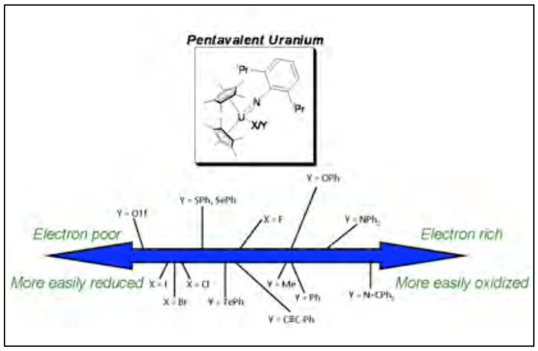
Significant achievements during 2007-2009:





Tetravalent Uranium Chemistry. A series of fluorinated uranium(IV) bis(ketimide) complexes $(C_5Me_5)_2U[-N{=}C(CH_3)(Ar_F)]_2$ (where Ar_F = 2-F-C_6H_4 (**4**), 3-F-C_6H_4 (**5**), 4-F-C_6H_4 (**6**), 2,6-F_2-C_6H_3 (**7**), 3,5-F_2-C_6H_3 (**8**), 2,4,6-F_3-C_6H_2 (**9**), 3,4,5-F_3-C_6H_2 (**10**), and C_6F_5 (**11**)) were prepared by nitrile insertion chemistry and characterized by X-ray diffraction, ^1H and ^{19}F NMR, cyclic voltammetry, electronic spectroscopy, and magnetic susceptibility. The most significant structural perturbation imparted by the fluorine substitution is a rotation of the fluorinated aryl (Ar_F) group out of the plane defined by the $N{=}C(C_{CH_3})(C_{ipso})$ fragment in complexes **7**, **9**, and **11** when the Ar_F group possesses two ortho fluorine atoms. Excellent agreement is obtained between the optimized ground state DFT calculated and experimental crystal structures for **11**, which displays the distortion, as well as **6**, which does not. All complexes exhibit U^V/U^{IV} and U^{IV}/U^{III} redox couples, although the sterically induced distortion in **7**, **9**, and **11** renders the U^{IV}/U^{III} couple irreversible. The separation between these metal-based couples remains constant at 2.15 V. The electronic spectra are dominated by unusually intense f-f transitions in the near IR that retain nearly identical band energies but vary in intensity as a function of the fluorinated ketimide ligand, and visible and near UV bands assigned to metal(5f)-to-ligand($\pi*$) charge transfer (MLCT) and interconfiguration transitions, respectively. The MLCT excited states and large f-f intensities are engendered by the unusually strong metal-ligand bonding interactions.

Pentavalent Uranium Chemistry. While tri-, tetra- and hexavalent complexes have dominated uranium chemistry, the pentavalent ($5f^1$) systems are comparatively rare, yet provide fertile ground for advancing our understanding of electronic structure, reactivity and bonding. Over the past year, we have prepared a variety of pentavalent uranium organometallic complexes $(C_5Me_5)_2U({=}N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(X/Y)$ (where X = F, Cl, Br, I; Y = OTf, SPh, SePh, TePh, NPh_2, OPh, Me, Ph, C≡CPh, N=CPh_2). This series was examined using structural analyses, magnetic susceptibility, electrochemistry, and spectroscopy. The electrochemical data shows that the ligand framework can stabilize both the U^{IV} and U^{VI} oxidation states. An excellent linear



correlation was observed between the ^{1}H NMR chemical shift values of C_5Me_5 ligand protons and the metal oxidation potentials suggests a common origin - overall σ- and π-donation from the ancillary X/Y ligand to the metal - contributing to both observables. From these data the overall donating ability of the X/Y ligand to the U^V metal center is established: OTf < I < Br < Cl < [SPh ~ SePh] < TePh < C≡CPh < F < [OPh ~ Me ~ Ph] << NPh_2 < $N{=}CPh_2$. The absorption spectroscopic data provide a focus on the contribution of the X/Y ancillary ligand to the splitting of the f-f states. The complexes can be divided into two classes based on these data, one includes X/Y = OTf, I, Br, Cl, SPh, C≡CPh, Me, Ph, and $N{=}CPh_2$, which are strong σ-donors and weaker π-donors, and the other includes X/Y = F, NPh_2, and OPh, which interact strongly with the U^V metal center by both σ- and π-donation leading to a larger splitting of the $5f^1$ levels. The signatures of covalency include stabilization of multiple metal oxidations states [U^{IV}, U^V, and U^{VI}] and enhanced intensities in the intraconfiguration (f-f) transitions, such as the more than 20-fold enhancement in the f-f intensities observed for Y = C≡CPh and $N{=}CPh_2$.

Science objectives for 2009-2011:

- Synthesis and characterization of multimetallic actinide systems to examine longer range coupling between metal centers through the agency of covalently bound bridging ligands.
- Electronic and resonance Raman spectroscopic investigations complexes having molecular-type (e.g., charge-transfer) electronic excited states to provide a more fundamental insight into factors governing covalent bonding and the manifestation of such bonding in spectroscopic behavior.

Publications supported by this project 2008-2009: (pertinent to this project element)

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2. “*Organometallic Uranium(V)-Imido Halide Complexes: From Synthesis to Electronic Structure and Bonding*,” C. R. Graves, P. Yang, S. A. Kozimor, A. E. Vaughn, D. L. Clark, S. D. Conradson, E. J. Schelter, B. L. Scott, J. D. Thompson, P. J. Hay, D. E. Morris, and J. L. Kiplinger, *J. Am. Chem. Soc.* **2008**, *130*, 5272-5285.
3. “*Ultrafast Spectroscopy of the Uranium(IV) and Thorium(IV) Bis(Ketimide) Complexes* $(C_5Me_5)_2An[-N{=}C(Ph)(CH_2Ph)]_2$ *(An = Th, U)*,” D. J. Hilton, R. P. Prasankumar, E. J. Schelter, V. K. Thorsmølle, S. A. Trugman, A. P. Shreve, J. L. Kiplinger, D. E. Morris, and A. J. Taylor, *J. Phys. Chem. A* **2008**, *112*, 7840-7847.
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6. “*Probing the Chemistry, Electronic Structure and Redox Energetics in Pentavalent Organometallic Actinide Complexes*,” C. R. Graves, A. E. Vaughn, B. L. Scott, E. J. Schelter, J. D. Thompson, D. E. Morris, and J. L. Kiplinger, *Inorg. Chem.* **2008**, *47*, 11879-11891.
7. “*Evidence for the Involvement of 5f-Orbitals in the Bonding and Reactivity of Organometallic Actinide Compounds: Thorium(IV) and Uranium(IV) Bis(hydrazonato) Complexes*,” T. Cantat, C. R. Graves, K. C. Jantunen, B. L. Scott, E. J. Schelter, C. J. Burns, P. J. Hay, D. E. Morris, and J. L. Kiplinger, *J. Am. Chem. Soc.* **2008**, *130*, 17537-17551.
8. “*Selenate and Tellurate Complexes of Pentavalent Uranium*,” C. R. Graves, B. L. Scott, D. E. Morris, and J. L. Kiplinger, *Chem. Commun.* **2009**, 776-778.

Structural Aspects of Solution Chemistry in Separations Science

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Overall research goals: The various associations of solutes in solvents impact a number of issues in heavy element chemistry and separations science, possibly none more important than ion exchange (IX) and solvent extraction (SX). This research is designed to lead to a fundamental understanding of self-assembly and -organization behaviors, such as ion-pairing, micellization, and third-phase formation, in bulk media—aqueous and organic alike—and to correlate the structural chemistry of complex formation in IX and SX processes with solute partitioning.

Significant achievements during 2007-2009: Highly charged, inorganic anions with appropriate topologies for binding metal-cations in aqueous solutions are important for consideration in the removal of ^{137}Cs from alkaline, high-level radioactive waste streams. We applied small-angle X-ray scattering and electrochemical methods to show that the Born model of electrostatic ion solvation applies to the 146-atom Preyssler heteropolyoxoanion (Figure 1), wherein the electrochemical potential difference between the first redox couples that differ by a unit charge has an inverse dependence on the Born radius. Moreover, electrostatic, contact ion-pairing interactions were shown to figure prominently in the self-association of Cs^+ ions with the 25-atom Lindqvist isopolyoxoanion. This evidence of structural hierarchy in solution provides a glimpse into the incipient crystallization of molecular clusters whose structures observed in solid-state salts also prevail under selected solution conditions. Metrical information about the morphology of ion-ion interactions is relevant to a predictive understanding of a number of basic properties, including kinetics and thermodynamics of electron- and ion-exchange processes.

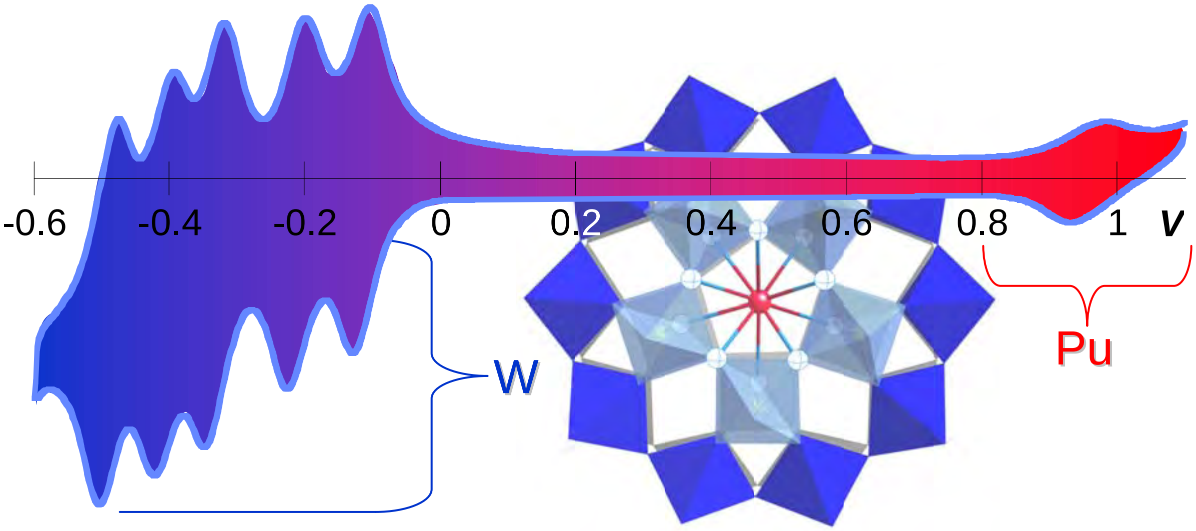

Figure 1. The *trans*-uranium chemistry of the Preyssler heteropolyanion was extended to include the synthesis of the Pu(III) complex, $[PuP_5W_{30}O_{110}]^{12-}$, whose electroanalytical characterization reveals dual redox activity involving the 1-electron Pu(III)/Pu(IV) couple of the guest ion at +0.96 V vs. Ag/AgCl and the 5 × 2-electron reductive electrochemistry of the P-W-O host framework at potentials between -0.6 and 0 V, and electrostatic ion solvation behavior.

A long-standing Franco-American collaboration between scientists at Argonne and at the Commissariat à l'Energie Atomique has succeeded in obtaining structural information about the solution complexes of trivalent lanthanide ions and Am(III) with a mixture of malonamide and di-*n*-alkylphosphoric acid extractants using synchrotron and neutron measurements as well as mass spectrometry and vapor pressure osmometry. The picture that emerges shows a progressive aggregation of solutes into mixed reverse micelles in nonpolar diluents, wherein the separation factor in the DIAMEX—SANEX process is attributed to, in part, supramolecular organization.

Science objectives for 2009-2011:

- We will correlate the morphology of self-assembled reverse micelles that form upon dissolution amphiphilic extractants in *n*-alkanes diluents with metal extraction properties. A bottom up approach is planned, beginning with studies of the extractants alone, then with low-loadings of f-cations (*R*) and, finally, to dense, highly-*R*-loaded third phases. The hierarchical, metrical descriptions of the solution structures will provide new insights into complex, multifunctional systems for 4f and 5f element separations processes.
- We will probe the electrochemical behaviors of trivalent *R* ions in third phases formed deliberately upon their extraction with a selection of malonamides. Our hypothesis is that the structural organization in the third phase will have a pronounced effect on the kinetics of electron transfer in ways that are totally different from that in conventional, nonaqueous solvent systems, thereby providing a unique entry into valence-controls of metal-ion extraction.

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Self-Assembled Ionophores: New Directions

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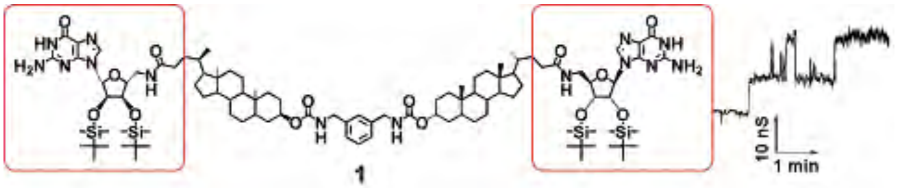
Prof. Gang Wu, Queen's University, Canada
Prof. Marco Colombini, University of Maryland

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. Lipophilic guanosine nucleosides hydrogen bond to give G-quadruplexes that selectively bind cations. Our goals include: 1) learning how to control structure & dynamics of nucleoside self-association and ion binding; 2) design self-assembled ionophores that selectively bind various ions and 3) construct supramolecular structures that function as synthetic ion channels.

Significant achievements During 2007-2009: 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 "Large and Stable Transmembrane Pores from Guanosine-Bile Acid Conjugates" *J. Am. Chem. Soc.* **2008**, *130*, 2938-2939.

New Cl^- Anion Receptors/Membrane Transporters. In the past grant period we extended our use of self-assembly to prepare compounds that transport Cl^- anions across bilayer membranes. Using various assays with liposomes we compared the H^+/Cl^- co-transport activity of a series of calixarene amides, pyrrole natural products and synthetic isophthalamides. These compounds' ability to transport Cl^- at uM 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 (Jan 2007-Feb. 2009):

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2. "Conformational Control of Transmembrane Cl- Transport." Paul V. Santacroce, Jeffery T. Davis, Mark E. Light, Philip A. Gale, José Carlos Iglesias-Sánchez, Pilar Prados and Roberto Quesada *J. Am.Chem. Soc.* **2007**, *129*, 1886-1887.

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

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

11. "Membrane Active Nucleobases." Ling Ma and Jeffery T. Davis, **2009**, in preparation as Feature Article for *Chemical Communications.*

Session 5 – Electronic Structure I

Exploring actinide chemistry with multiconfigurational quantum chemical methods

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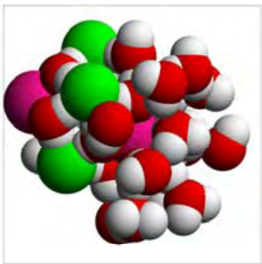
Quantum chemistry is a mature science that can be applied to the study of systems containing any atom in the periodic table. In this lecture I will discuss our latest results in actinide chemistry. I will present the study on Pu-oxides [1] that has allowed us to resolve the controversy between different experiments concerning the value of the ionization potential of PuO_2 and some recent results on Np-oxides.

Since in nature most of heavy element chemistry occurs in a condensed phase, we try to understand the behavior of highly charged ions in solution by combining *ab initio* quantum chemistry with classical molecular dynamics simulations. I will report the results of our recent studies on curium(III) [2] and various lanthanide(III) salts [3] in water.

[1] G. La Macchia, I. Infante, J. Raab, J. K. Gibson, L. Gagliardi *A theoretical study of the ground state and lowest excited states of* $PuO^{0/+/+2}$ *and* $PuO_2^{0/+/+2}$ Phys. Chem. Chem. Phys., 2008, 10, 7278

[2] D. Hagberg, E. Bednarz, N. M. Edelstein and L. Gagliardi *A quantum chemical and molecular dynamics study of the coordination of Cm(III) in water* J. Am. Chem. Soc. 2007, 129, 14136

[3] C. Beuchat, D. Hagberg L. Gagliardi and N. Edelstein in preparation



Gas-Phase Actinide Ion Chemistry: A Fruitful Interplay between Experiment and Theory

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Dr. David K. Shuh, Lawrence Berkeley National Laboratory
Prof. Laura Gagliardi, University of Minnesota
Prof. Colin Marsden, U. Paul Sabatier, Toulouse, France
Dr. Marinella Mazzanti, CEA-Grenoble, France

Overall Goals: The goals of the project are to explore fundamental aspects of molecular actinide chemistry by gas-phase studies of chemical and physical properties of actinide complexes, from molecules to clusters. A key component is to work closely with theoreticians to better understand and optimize the experimental component of the work, as well as to enable the development and validation of advanced theoretical methodologies.

Significant achievements during 2007-2009:

1. Thermodynamic properties of the elementary CmO molecule were determined. Among the properties determined were the first and second ionization energies, and the bond dissociation energy, for CmO.

2. Reactions of dipostive lanthanide ions, Ln^{2+}, with alkanes and alkenes were studied. Different accessibilities of d^1 electronic configurations and the range of electron affinities of the Ln^{2+} revealed conditions for bond activation, and electron, hydride or methide ion transfer.

3. Reactions of An^{2+} ions with alkanes and alkenes provided insights into the effects of actinide electronic configurations on these organometallic reactions, suggesting a special role for the 5f electrons in Pa^{2+}.

4. Reactions of UO_x^- anions with methanol were studied both experimentally and theoretically. Experiments using isotopic labeling, as in Figure 1, clearly confirmed computed DFT mechanisms.

Science objectives for 2009-2011:

- Electrospray ionization quadrupole ion trap mass spectrometry (ESI/QIT-MS) investigations of clusters grown in solution and the gas phase. Initial studies will focus on cerium polyoxometalate (Ce-POM) aggregates, which will provide a groundwork for planned actinide studies, particularly of Pu-POMs. These and other types of clusters, such as thorium and plutonium hydrolysis products, will be studied in the QIT-MS by collision induced dissociation and chemical reactivity.

- Kinetics of hydration of elementary lanthanide and actinide species will be studied in the QIT. The measured sequential hydration rates will be evaluated in a collaborative DFT study of the hydration processes. Initial model studies will compare hydration of $Yb(OH)_2^+$, $YbCl_2^+$, and $Yb(OH)Cl^+$.

- An online electrochemical (EC) cell will be incorporated into the ESI/QIT-MS. We will employ this novel actinide EC/ESI/QIT-MS capability to investigate several aspects of actinide chemistry, including mechanisms and speciation during disproportionation of pentavalent actinyl ions; and the structure and reactivity of multivalent uranium oxo clusters, while varying the compositions and oxidation state distributions in the clusters.

- Gas-phase FTICR/MS experiments will be performed to study reactions of neutral molecules with $AnM[nd]^+$ and AnX^+ ions (M[nd] = d-block transition metal; X = p-block element). The $AnM[nd]^+$ will be produced by LDI of alloys or intermetallics, while the AnX^+ will be generated either by reactions in the gas phase or by LDI of AnX(n) solids. We will gain insight into the role of 5f electrons in the bonding and chemistry, and perform thermochemical studies to determine bond energies and ionization energies. The concept of autogenic isolobality will be explored by comparing $AnM[nd]^+$ and corresponding AnX^+.

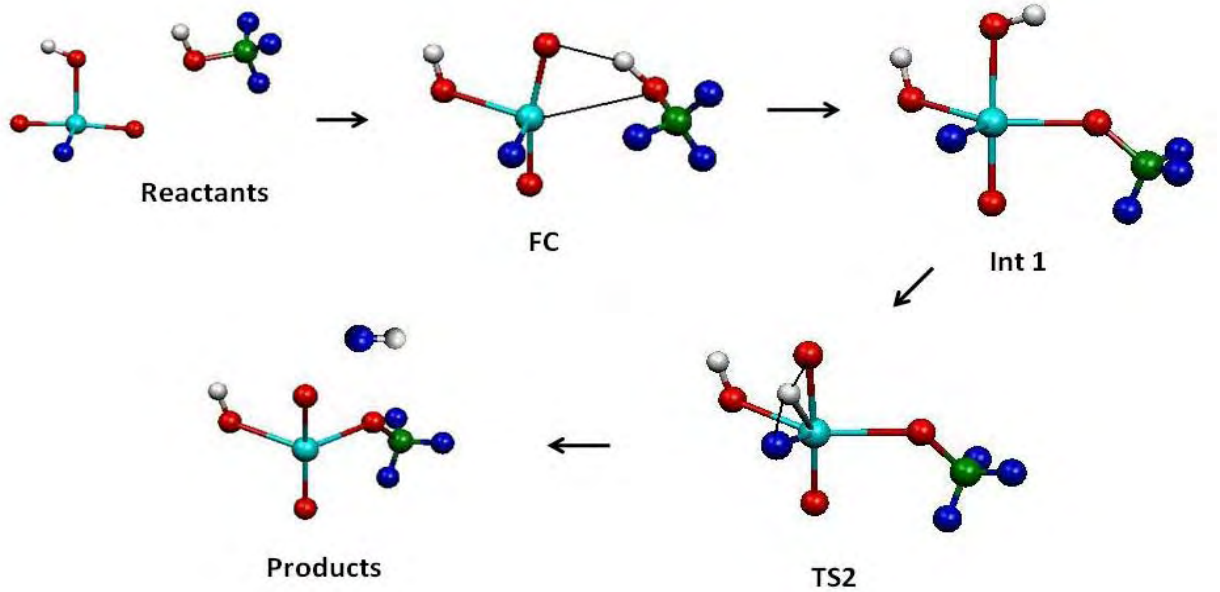

Figure 1. Computed (and also observed) mechanism for the reaction of UO_3HD^- with CD_3OH. Turquoise = uranium; red = oxygen; green = carbon; grey = hydrogen; dark blue = deuterium.

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

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Overall research goals: The goal of the 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 surface imperfections, to accurately portray actinide redox chemistry under real-world conditions using a combination of statistical and quantum mechanical methods.

Significant achievements during 2007-2009: Progress started in late 2006 with hire of Dr. Patrick Nichols. To date, we have developed the essential spin-orbit zeroth order regular approximation (ZORA) in NWChem, assessed the accuracy of density functional methods, modeled the dynamic behavior of actinides in solution, and developed an adsorption model for uranyl on a mineral surface:

1. Assessment studies have been performed on the accuracy of relativistic density functional theory methods for open-shell uranyl species by comparing theory with gas-phase molecule infrared multiple photon dissociation experiments done by researchers from Idaho National Laboratory and Wichita State University. This collaborative effort probes the competitive formation and reactivity of uranium (VI) ($5f^0$)- and (V) ($5f^1$)-ligand species in the gas-phase, and has provided a successful proving ground for computational methods.
2. *Ab initio* density functional theory Car-Parrinello Molecular Dynamics simulations of uranyl (UO_2^{2+}) in aqueous solution have provided unique insights into the dynamic behavior of water molecules around the actinide ion not seen in previous work. The calculated EXAFS spectrum and found that the simulation results are in excellent agreement with experimental information obtained from extended x-ray absorption fine structure experiments (see Figure 1). Following the successful simulations of uranyl in solution we are currently completing dynamics

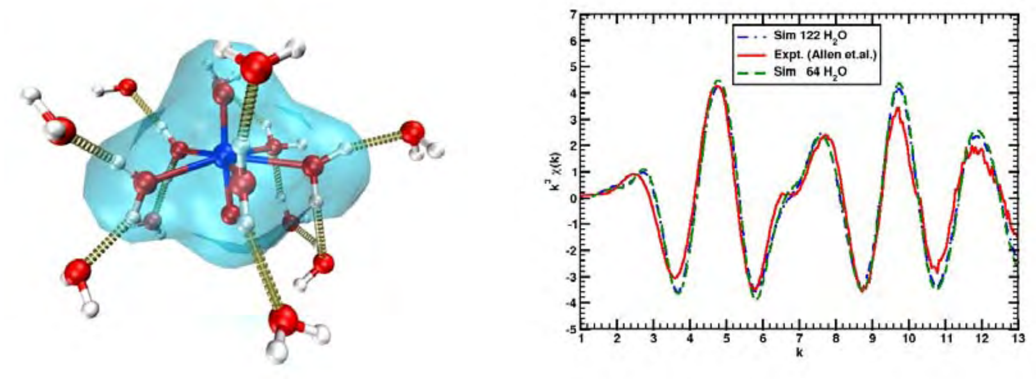

Figure 1. Left: A snapshot of the two inner solvation shells of five-coordinate UO_2^{2+} are shown. The blue surface identifies the inner-coordination spheres and golden lines show the array of hydrogen bonds that are formed in the structure. Right: The experimental and simulated extended x-ray absorption fine structure spectra of UO_2^{2+} in water are in perfect agreement. The results shown are from NWChem Car-Parrinello Molecular Dynamics of UO_2^{2+} and 122 H_2O molecules with a simulation time of 10 ps.

simulations of Cm^{3+} in aqueous solution. In contrast to uranyl, curium has an occupied half-filled $5f^7$ shell that requires the inclusion of spin-orbit coupling effects.

3. As a first step towards modeling the dynamic behavior of complex actinide species in solution interacting with mineral surfaces, we studied the adsorption of uranyl on a hydroxylated (0001) α-Al_2O_3 surface. Uranyl has been shown experimentally to adsorb to this surface, but does not reduce the actinide as it would on an iron oxide surface. We observed that the hydrogens at the uranyl binding site on the hydroxylated surface do not leave the surface but are clearly displaced from the uranyl bonding site. This may be due to the lack of solvation in this model, which we are currently investigating. We also find exothermic adsorption of about 55 kcal/mol, this in contrast to the 78 kcal/mol endothermic interaction found by the Rösch group. We are currently studying the system with uranyl surrounded by water molecules to probe the binding mechanisms of the actinide to the surface.

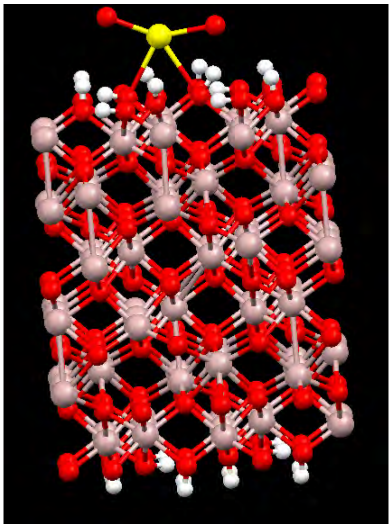

Figure 2: Optimized structure of uranyl interacting with the α-Al_2O_3 surface. The results shown are from NWChem plane-wave calculations.

4. A unique set of relativistic density functional theory capabilities were developed within the spin-orbit zeroth order regular approximation (ZORA) framework in NWChem. Within the Gaussian framework we utilize the atomic approximation of van Lenthe et al. to reduce gauge invariance, which also avoids the need separate gradient or second derivative terms of the relativistic contributions. Our plane-wave framework has exact exchange and uses spin-orbit pseudopotentials that are directly generated from the atomic ZORA-Kohn-Sham wavefunctions.

Science objectives for 2009-2011:

- Understand the role of ligands, counter-ions and oxidation state in aqueous solution on the formation and stability of mono- and multimeric uranium and plutonium species.
- Model the structure, thermodynamics, and redox chemistry of solvated uranyl and plutonyl ions on mineral surfaces will be simulated for ambient conditions.
- Develop non-collinear spin-orbit density functional theory for open-shell systems within the NWChem software, and integrate into the time-dependent DFT capability.

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A Fully Relativistic Density Functional Study of the Role of *5f* Electrons in Chemical Bonding in Transuranium Elements

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Overall research goals: The objective of this project is a fundamental, complete, and detailed understanding of transuranium actinide surfaces and atomic and molecular adsorptions on these surfaces.

Significant achievements during 2007-2009: During the years of 2007-2009, we have completed a number of studies, including atomic and molecular adsorption studies on α – and δ – Pu surfaces and dhcp Am (0001) surface, as also bulk electronic structure studies of δ – Pu and dhcp Am. As an example, we found that in molecular state, water is physisorbed in an almost flat-lying orientation at a one-fold coordinated on-top site. The interaction of the water $1b_1$ orbital and the Pu-6*d* orbital provides the stability of water on the surface, implying that the Pu-5*f* electrons remain chemically inert. The co-adsorption cases of partially dissociated and fully dissociated products at the three-fold hollow sites yield chemisorption, coupled with rumpling of the surface layer and delocalization of the Pu-5*f* electrons and formation of strong ionic bonds. Use of hybrid density functional theory yields non-magnetic ground states for δ – Pu and dhcp Am (Figs. a, b, and c). Specifically, the results for dhcp Am are in very good agreement with all aspects of experimental data

Figure a

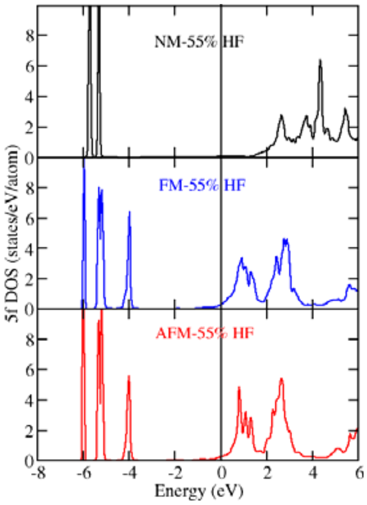


Figure b

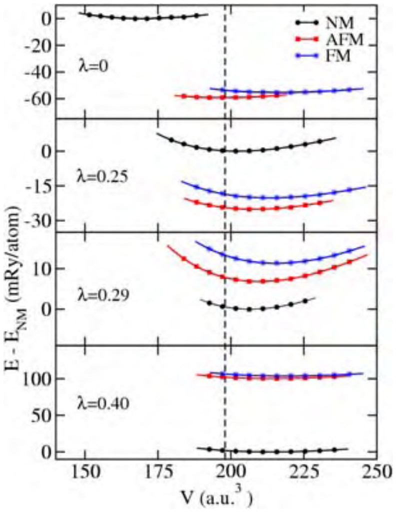
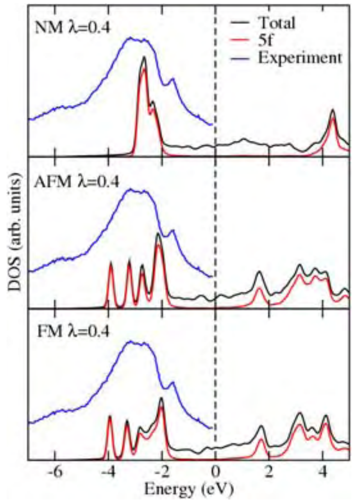


Figure c



Science objectives for 2009-2011:

- Density functional, hybrid density functional, and LDA+*U* studies of the high-symmetry surfaces of α –Pu, δ – Pu, dhcp Am, fcc Am, and dhcp Cm.
- Density functional, hybrid density functional, and LDA+*U* studies of molecular adsorptions, for example, H_2, O_2, H_2O, and CO_2, among others on the high-symmetry surfaces of α –Pu, δ – Pu, dhcp Am, and fcc Am,
- Search for a “universal” theory and/or a “universal” functional to properly describe actinide surfaces and atomic and molecular adsorptions on such surfaces.

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Session 6 – Actinides I

Structures and Stability Constants of Actinide-Halide Complexes in Solution

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Overall research goals: We are focused on correlating an actinide-ion's coordination in solution with its solubility, reactivity and energetics. Using high-energy x-ray scattering (HEXS) to obtain structural information as a function of solution conditions, we are probing complexation details and how they are manifested in properties such as stability constants and free energies. These results, when coupled with independent experiments such as liquid-liquid separations, are providing new molecular-level insights into how solution conditions influence solute behaviors.

Significant achievements during 2007-2009:

- A detailed study of the curium coordination in aqueous solution was undertaken to complement a theoretical study by Bursten et al. (Inorg. Chem. 46 (2007) 4917-25) By combining HEXS results with EXAFS data it was demonstrated that the Cm^{3+} ion in a 1 M $HClO_4$ solution is coordinated by nine water ions in trigonal prismatic geometry. This environment is very similar to that seen in the solid-state structure of the Cm triflate, although the splitting of the water distances corresponding to the six short and three long Cm – H_2O correlations is larger in solution.
- Initial structural studies of Er in acidic aqueous solution have verified that there are eight waters in the first coordination sphere of the metal ion. Further experiments probing Er coordination as a function of chloride ion concentration, done at constant ionic strength, have been coupled with liquid-liquid separations data to provide metrical information about the anion coordination to Er, which bind as both inner- and outer-sphere complexants under the same solution conditions. This combination of physiochemical probes has allowed the determination of stability constants for the addition of Cl^- to the Er aqua coordination sphere and to separate the role of inner- and outer-sphere association on the energetics of complex formation.

Science objectives for 2009-2011:

- *Anion coordination to f-ions in solution*: To date we have focused on the homoleptic aqua coordination of f ions in solution to provide a starting point for more complex correlation environments. Recent work has built our capabilities to include simple halide complexants as well. Our studies to date have been on f-ion halide systems that have low stability constants and free energies associated with their formation in aqueous solution. We plan to extend these studies into solution conditions that energetically clearly favor the formation of a metal-ligand complex. Initial efforts will focus on a study of lanthanide and actinide thiocyanate complexes that probes their structural details. Lanthanide and actinide solution correlations will be compared to quantify details of complexation, with specific focus on inner- versus outer-sphere ligation. Such differences were postulated to account for experimental observations of bulk solution behavior. These solution studies will be augmented with structural studies of lanthanide and actinide thiocyanates to support the solution studies.

- *Actinide halide complexes:* Fundamental studies will continue on lanthanide and actinide halide complexes that form in solution. Our interest is the quantification of weak ion-ion interactions, which play an important role in the chemical behavior of dissolved metal ions in aqueous environments. The energetics of these interactions can be small enough to raise questions about the existence of true interactions or ion pairing, despite indirect evidence supporting their formation, including optical spectra and liquid-liquid separations data. By measuring a variety of lanthanide and actinide ions in aqueous chloride solutions, we plan to correlate structural details of their complexes with measured stability constants and with comparable solid-state structures. This study will provide the metrical information necessary to reach a fundamental understanding of structure-bonding relationships in f-ion halides.

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Near-Infrared Photoluminescence and Ligand K-edge X-ray Absorption Spectroscopies of $AnO_2Cl_4^{2-}$ (An: U, Np, Pu)

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Overall research goals: The objective of this project is to investigate electronic structures and metal-ligand bonding of molecular transuranic actinide species using laser-induced photoluminescence spectroscopy and X-ray Absorption spectroscopy.

Significant achievements during 2007-2009:

1. We have reported the first example of photoluminescence from electronically excited states of the plutonyl ion. These studies were carried out on the crystalline system $Cs_2U(Pu)O_2Cl_4$ cooled to 75 K following pulsed laser excitation. Photoluminescence spectra reveal a large number of transitions, which are assumed to be principally due to decay between 5*f* electronic states, and to include numerous vibronic sidebands. Excitation spectra in the region 15,000-16,000 cm^{-1} compared favorably with absorption spectra of $Cs_2U(Pu)O_2Cl_4$ reported by Gorshkov and Mashirov.[1] Analyses of excited-state lifetime data measured from the transitions suggest complicated decay patterns, in which multiple luminescence states are involved.

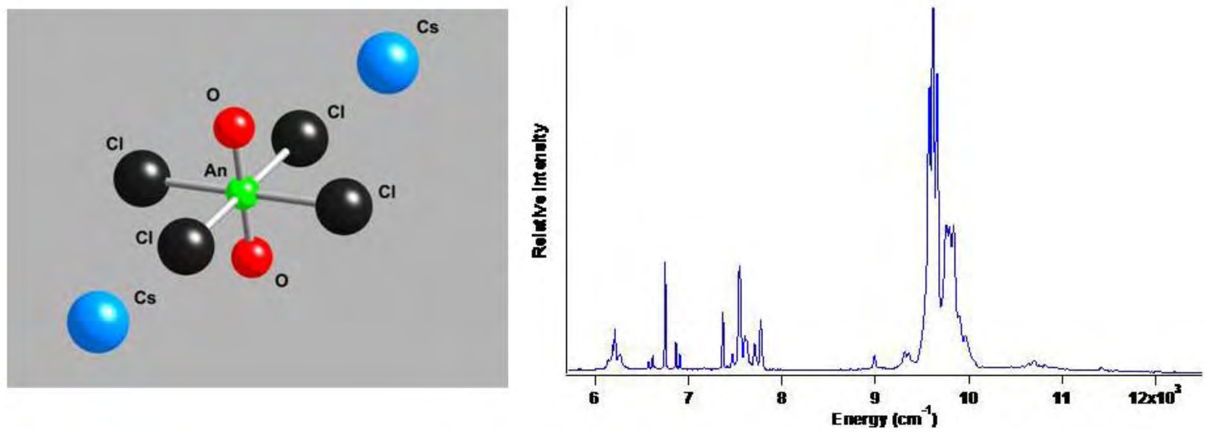
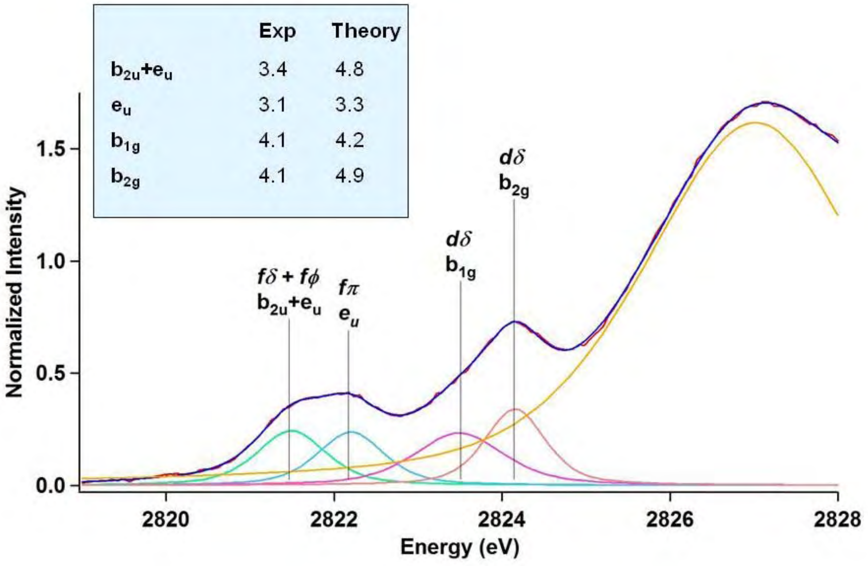


Figure 1. Left: Molecular structure of $Cs_2AnO_2Cl_4$ (An = U, Np, Pu). Right: Photoluminescence spectrum of $Cs_2U(Pu)O_2Cl_4$ at 75 K following pulsed excitation at 628 nm.

[1] Gorshkov, N. G.; Mashirov, L. G. *Radiokhimiya* **1985**, *27*, 552-566.

2. We have employed Cl K-edge X-ray Absorption Spectroscopy to quantify the extent of covalency in actinide-ligand bonding and to measure the energies of the antibonding states in $UO_2Cl_4^{2-}$. The use of ground state and time-dependent hybrid-Density Function Theory provides assignments of these transitions.



	Exp	Theory
b_{2u}+e_u	3.4	4.8
e_u	3.1	3.3
b_{1g}	4.1	4.2
b_{2g}	4.1	4.9

Figure 2. Chlorine K-edge X-ray Absorption spectrum of $UO_2Cl_4^{2-}$. Assignments of the transitions are labelled, and theoretical calculations of the degree of covalency in the metal-ligand bonds are consistent with measurements.

Science objectives for 2009-2011:

- At the beginning of FY09, we purchased a near-infrared detector to extend our detection capability to 2.2 μm in part with funding from the OBES Heavy Element Chemistry program. We have initiated photoluminescence measurements with this detector from $Cs_2U(Np)O_2Cl_4$ and $Cs_2U(Pu)O_2Cl_4$.
- We will expand Chlorine K-edge Absorption measurements to include $Cs_2NpO_2Cl_4$ and $Cs_2PuO_2Cl_4$, and we will carry out Oxygen K-edge X-ray Absorption measurements and Non-Resonant Inelastic X-ray Scattering on $Cs_2AnO_2Cl_4$ (An: U, Np, Pu)

Publications supported by this project 2007-2009

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TOWARD AN IMPROVED UNDERSTANDING OF STRUCTURE AND MAGNETISM IN NEPTUNIUM AND PLUTONIUM PHOSPHONATES AND SULFONATES

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Overall research goals: To answer the following questions.

- Can crystalline An(IV, V, VI) (An = Np, Pu) phosphonates be prepared?
- Will their structures differ from transition metal and lanthanide phosphonates?
- Given that Np and Pu possess 5f electrons, will it be possible to develop magneto-structural correlations? (Is long-range ordering possible?)
- Can we systematically change the structures of actinide phosphonates by changing the nature of R?

Significant achievements during 2007-2009: We have prepared numerous uranyl phosphonates. However, the most exciting results are from transuranium phosphonates that include $Np(CH_3PO_3)(CH_3PO_3H)(NO_3)(H_2O)\cdot H_2O$, $Pu(CH_3PO_3)_2$, $M[CH_2(PO_3)_2](H_2O)_n$ (An = Np, Pu; n = 1, 2), and $UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (An = Np, Pu). The most significant results are as follows.

1. In the $An[CH_2(PO_3)_2](H_2O)_n$ (An = Th, U, Np, Pu; n = 1, 2) series we find that thorium and neptunium adopt the same composition (i.e. $An[CH_2(PO_3)_2](H_2O)_2$) and are isotypic. Whereas uranium and plutonium crystallize as compounds with the same formula (i.e. $An[CH_2(PO_3)_2](H_2O)$), but are not isotypic. Therefore, sequential changes or periodic trends that might occur as a function of the actinide ion, such as ionic radius, are not clearly identified in this system.

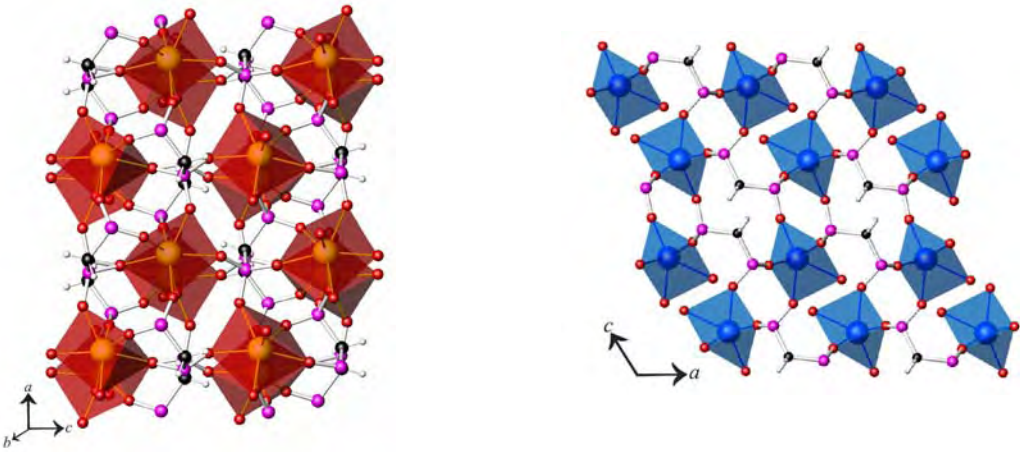

Figure 1. A depiction of the structures of $An[CH_2(PO_3)_2](H_2O)$ (An = U (left), Pu(right)). The AnO_7 units are very rare in actinide chemistry.

2. One of the important discoveries made in the course of this work is that isotypic U(VI)/An(IV) (An = Th, Np, Pu) phosphonates can be prepared and isolated as single crystals. This is surprising because the structure of $UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (An = Th, Np, Pu) is very complex, and since the methylenediphosphonate ligand is partially protonated, the formation of this compound is probably highly pH sensitive. Nevertheless, this is what occurs, and the first U(VI)/Th(IV), U(VI)/Np(IV), and U(VI)/Pu(IV) phosphonates has been isolated and characterized.

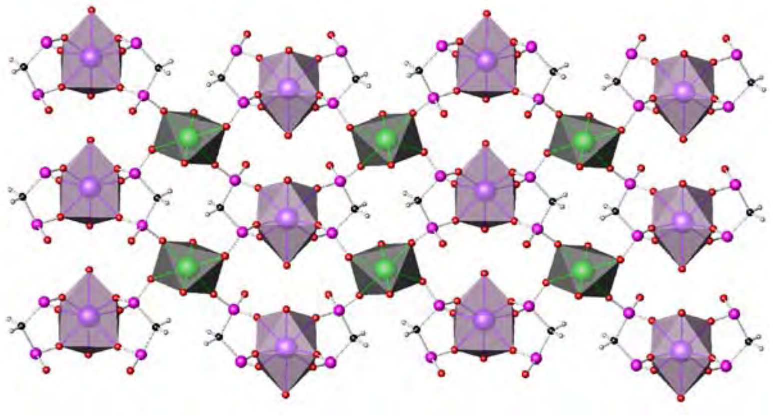

Figure 2. An illustration of the structure of $UO_2An(H_2O)_2[CH_2(PO_3)(PO_3H)]_2$ (An = Th, Np, Pu) consisting of UO_6 tetragonal bipyramids (grey/green) containing an uranyl, UO_2^{2+}, core, and AnO_8 distorted dodecahedra (purple) containing an An(IV) center that are bridged by partially protonated methylenediphosphonate.

Science objectives for 2009-2011:

- The challenge that remains is to isolate a heterobimetallic An(VI)/An(IV) compound where both actinides are transuranium elements possessing 5f electrons. If certain bonding requirements can be met, magnetic coupling between two different actinides with differing numbers of 5f electrons could be investigated.

- We will continue to probe the structural chemistry of actinide phosphonates to address the question: Do these surrogates actually mimic the chemistry of transuranics?

Selected Publications supported by this project 2007-2009 (out of 17)

1. A.-G. D. Nelson, T. H. Bray, F. A. Stanley, and T. E. Albrecht-Schmitt, “Periodic Trends in Actinide Phosphonates: Divergence and Convergence between Thorium, Uranium, Neptunium, and Plutonium Systems,” *Journal of the American Chemical Society*, **2009**, *submitted.*
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Session 7 – Electronic Structure II

Responding to magnetic and structural disorder in lanthanide- and actinide-based superconductors

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Overall research goals: The objective of this project is to understand the properties of heavy-fermion superconductors through chemical substitutions and other perturbations of the crystal structure, including by decreasing the material size to the nanoscale. This research therefore strives to understand the universal relationships between magnetism, electronic properties, and local structure in *f*-electron intermetallics and related materials.

Significant achievements in 2007-2009: While magnetism is anathema to conventional superconductors, many lanthanide- and actinide-based superconductors are believed to derive their unique properties from a magnetically-mediated mechanism to form the superconducting state. In these materials, the interaction between the *f* orbitals and the conduction band causes a drag on the conductivity in the normal state that is typically modeled by an enhanced carrier mass. Such heavy electron (or more generally, heavy fermion) materials paradoxically become superconductors when they are near a magnetic phase boundary, typically tuned with applied pressure or with chemical substitutions.

Recent years have witnessed a strong interest in the so-called “115” materials, especially in $CeCoIn_5$ and $PuCoIn_5$ (Figure 1). This class of materials exhibits some of the highest superconducting transition temperatures, T_c, known for heavy fermion materials, and the $T_c \approx 19$ K for $PuCoIn_5$ remains the highest of any known actinide intermetallic. These large T_cs are thought to be due, in part, to the anisotropic structure, promoting a two-dimensional character to the superconducting state, analogous to the high-temperature superconducting copper oxides. Also in analogy to the oxides, a great deal can be learned about the superconducting state by perturbing the lattice.

We have explored the effect of disorder on the crystal lattice, both in the immediate structure around the lanthanide sites through carefully designed chemical substitutions, and in larger regions of disorder induced by the radioactive decay of the plutonium atoms. In this way, we validate the concept of chemical pressure in the absence of disorder through substitutions onto the Co site [Daniel et al., Phys. Rev. B **71**, 054417], and then consider direct perturbations of the Ce-In(1) planes, where superconductivity is thought to occur. For these studies, we focus on substitutions into indium sites with Sn [Daniel et al., Phys. Rev. Lett, **95**, 016406], Cd, and Hg [1], which can be thought of as electron (Sn) and hole (Cd and Hg) dopants. Such dopants not only change the local electronic

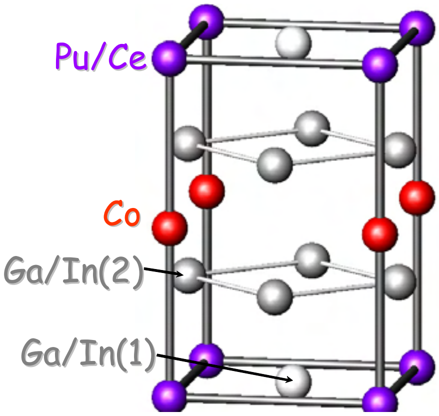

Figure 1. Tetragonal crystal structure of $CeCoIn_5$ and $PuCoGa_5$.

density of states around a cerium atom, but also affect the local magnetic properties due to changes in the hybridization of the *p* and *f* orbitals, potentially generating magnetic scattering centers that affect the superconducting state. Complicating this picture, local structure measurements show that these substituents prefer the less-constrained In(1) site, sometimes causing local distortions to occur. These structural and electronic distortions together with the sensitive electronic structure of the 115s conspire to make the properties of these materials remarkably sensitive to such substitutions. For instance, superconductivity is destroyed after less than 1.5% Hg for In in $CeCoIn_5$.

Similar chemical substitution studies have not yet been performed for $PuCoIn_5$. The Pu superconductors are, however, intrinsically disordered after the first radioactive decay of a Pu atom occurs, and many of the interesting properties of this system derive from self-irradiation damage. Local structure measurements demonstrate [2,3] that a surprising amount of damage occurs for each α-decay, with about 20% of the atoms displaced from their equilibrium positions after only one year in a sample dominated by ^{239}Pu. This amount of damage is actually far more than expected from the simple Frenkel-defect generation typically used to described such damage, and is therefore interesting in its own right and in relation to other situations where self-irradiation damage occurs, such as in metallic Pu, nuclear power generation, and high-level waste disposal. Despite this extreme amount of damage, however, superconductivity persists in this material even after several years where nearly half of the sample is damaged. This persistence of superconductivity in radiation-damaged $PuCoGa_5$ is in stark contrast to the destruction of superconductivity in chemically-substituted $CeCoIn_5$ with only percent-level substitution of Sn, Cd, or Hg.

These results will be discussed in terms of the superconducting coherence length as the minimum length scale where disorder needs to occur to affect the superconducting state, as well as putting these results in the context of their electronic structure.

Science objectives for 2009-2011

- Explore other Pu115 materials as they become available from our Los Alamos colleagues, especially materials substituted onto the Ga site.
- Extend these studies to include applied pressures up to 20 GPa.

Publications supported by this project 2007-2009

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4. L. Downward, C. H. Booth, W. W. Lukens, F. Bridges, "A variation of the F-test for determining statistical relevance for particular parameters in EXAFS analysis." In *X-Ray Absorption Fine Structure – XAFS13: 13th International Conference, July 9-13, 2006*. AIP Conference Proceedings **882**, 129 (2007). LBNL-62566
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6. A. L. Lima, X. Zhang, A. Misra, C. H. Booth, E. D. Bauer, and M. F. Hundley, "Length scale effects on the electronic transport properties of nanometric Cu/Nb multilayers." Thin Solid Films **515**, 3574-3579 (2007). LBNL-62632

Theoretical Studies of Actinide-Ligand Bonding Interactions

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Overall research goals:

The goal of our subtask is to develop and apply theoretical tools for the study of properties of actinide species. Our approach is based on electronic structure calculations and the physical systems are molecular and solid state complexes. Our research is tightly connected with the experimental efforts of our co-investigators at LANL.

Significant achievements in 2007-2009:

- **Thermochemistry of C-H activation by Th and U**. Previous experimental work at Los Alamos has shown that the complexes $(C_5Me_5)_2An(CH_3)_2$ (An=Th and U) exhibit different C-H insertion chemistry with N-heterocycles depending on whether ring C-H bonds (sp^2) or methyl substituents (sp^3 bonds) are involved. We have used density functional theory (DFT) to study the reactions of these complexes with 2-methylpyridine to determine the structures and energies of the products and transition states along the reaction pathways. For both Th and U the thermodynamically preferred product is the result of insertion into the ring sp^2 C-H bond and a calculated exothermicity of 18 kcal/mol. The product corresponding to insertion into the ortho methyl C-H group is about 2 kcal/mol higher in energy. The transitions states are found to have activation energies E_{act} (sp^3) < E_{act} (sp^2) for Th but with the reverse ordering for U. This is consistent with the observation of the kinetic sp^3 product for Th but no such observation in the case of U.
- **Covalent interaction in Group IV metallocene dichloride bonds**. Experimental work at LANL used core k-edge spectroscopy to probe the low lying virtual electronic states on metallocene dichloride complexes. The advantage of this technique resides in using highly localized initial electronic states, the Cl core electrons, yielding a clean picture of the metal-ligand bond. We used linear response density functional theory to simulate the experimental data and give an interpretation of the measured spectra. The good agreement between measured and calculated spectra validated the computational technique employed. The DFT calculations lead to the understanding of the pre-edge features yielding a bonding picture that involves the 5f and 6d electrons in the covalent An-ligand bond.
- **Uranium bis(imido) reaction pathways**. This is work aimed at the understanding of the chemistry of uranium bis(imido) complexes, that were discovered at LANL. The work of our experimental collaborators at LANL indicated that the reaction of $[U(NPh)(N^tBu)(I)_2(OPPh_3)_2]$ with PhNCO does not yield the exchange expected of one of the $U{=}N^tBu$ bonds by the stronger U=O but instead the reaction proceeds replacing the $U{=}N^tBu$ by U=NPh. We used hybrid density functional theory calculations to study the reaction path way as well as the thermochemistry of the possible reactions. It was found that the predicted product, the replacement by a U=O bond, is indeed lower in energy

than the observed one, U=NPh by 13kcal/mol. However, in order to reach the more stable product the activation barrier is higher by almost 10kcal/mol than the reaction path way leading to the imido product. Therefore, according to the DFT calculations the reaction proceeds in the way it does due to a kinetic barrier that blocks the expected, more stable, product from forming.

Specific goals for 2009-2011:

We will, in collaboration with the synthesis and characterization effort at LANL, use computational tools to aid in the understanding of chemical bonding, reactivity and spectroscopic signatures of metal-ligand interactions of organoactinide complexes. We have begun examining non-stoichiometric actinide oxides with calculations on U_3O_8. We have also investigated defect energies for He incorporated into UO_2 and U_3O_8. We hope to extend these to U_4O_9 in the near future. We will continue our collaboration with Gustavo Scuseria (Rice) and our experimental colleagues to study covalency in actinide compounds through photoemission and x-ray absorption spectroscopy. We plan to investigate further the performance of screened hybrid functionals for actinide compounds in the metallic phase.

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Session P2 – Poster Session 2

Synthetic Receptors and Sensors for Actinide Cations and the Pertechnetate Anion

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Overall research goals: The objective of this project is to generate receptors that will allow for the sensing, complexation, and extraction of actinide cations and the pertechnetate anion.

Significant achievements during 2007-2009: Functionalization of isoamethyrin, a hexaaza macrocyclic system was achieved. This allowed tethering to preexisting supports and the demonstration of selective uranyl sensing under conditions mimicking those that might be seen in the field. Concurrent with this work, receptors were created that were found to interact with the pertechnetate anion. Efforts to develop receptor-containing polymers were also advanced, and a new hexadentate receptor for the uranyl cation was discovered. The most significant results are summarized below; other accomplishments will be detailed in the poster proper.

1. Isoamethyrin (**1**; Figure 1) is an expanded porphyrin that undergoes a dramatic change in color and intensity when exposed to high valent actinide cations as the result of concurrent oxidation and aromatization upon formation of the corresponding actinide complex (cf., e.g., **2**; Figure 1) that has been shown to be quite selective for these cations over all other tested species except Cu(II). This has led to consideration that it could function as an actinide-specific colorimetric sensor. To realize this promise, the isoamethyrin core was modified (giving **3** and **4**) and appended to a solid support, either a a tentagel amino resin bead or an optical fiber. Studies carried out in collaboration with Prof. John T. McDevitt and Andrew Shaw, respectively, illustrated a strong response in the presence of the uranyl cation, a test actinide cation (Figure 2).

2. Two cyclo[n]pyrroles, compounds **5** and **6** (Figure 1), first developed with NSF funding, have been found to have properties of potential interest in the area of actinide complexation and pertechnetate binding. In particular, cyclo[8]pyrrole, **5**, was found to bind the perrhenate anion in the solid state as a 1:2 complex (receptor to anion) and extract pertechnetate anion from aqueous media. Meanwhile, cyclo[6]pyrrole, **6**, was found to form a stable complex with the uranyl cation after oxidation to a formally antiaromatic 20 π-electron form.

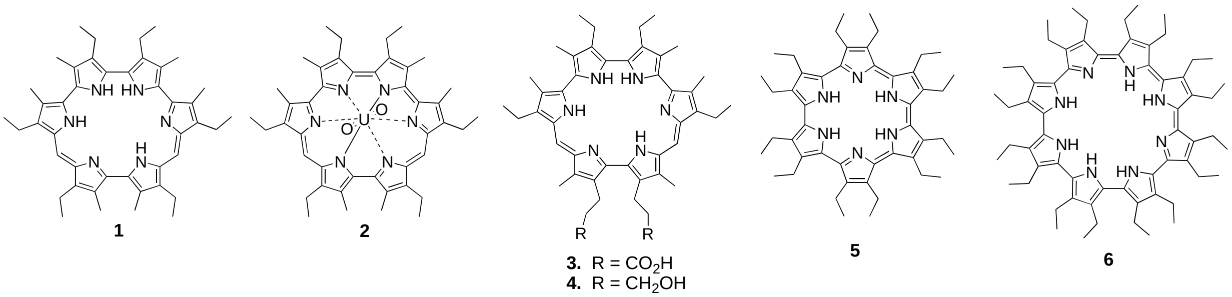

Figure 1. Structures of metal-free isoamethyrin (**1**), the oxidized uranyl complex (**2**), and the new functionalized derivatives (**3** and **4**) used to effect attachment to solid supports. Also shown are cyclo[8]- and cyclo[6]pyrrole (**5** and **6**).

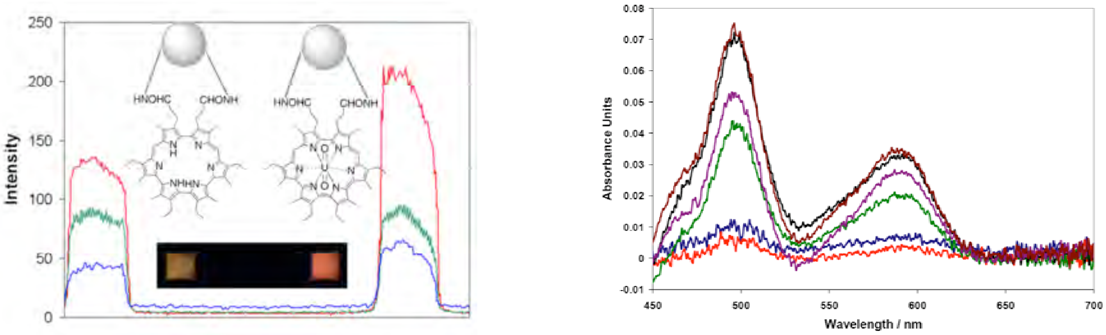

Figure 2. Left: Intensity values in the red (red line), green (green line) and blue (blue line) channels for a tentagel bead containing isoamethyrin (left side, 6.4% amine coverage) and a bead exposed to 0.0024 M uranyl acetate for nine days (right side). Right: Change in absorbance seen in the presence of increasing aqueous uranyl cation concentrations (– 10 ppb, – 100 ppb, – 500 ppb, – 1 ppm, – 5 ppm, – 10 ppm) for an optical fiber modified with isoamethyrin.

Science objectives for 2009-2011:

- Develop new ligands for various actinide cations, including those based on imidazolium centers.
- Generate polymers based on isoamethyrin and test their ability as actinide cation extractants.
- Explore combinatorial approaches to the post-synthetic functionalization of modified polymers.
- Complete studies of cyclo[8]pyrrole as a pertechnetate anion receptor; explore other ligands for this purpose.

Publications supported in whole (original papers) or part (reviews) by this project 2007-2009

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Multiconfigurational ground states and open-shell singlet formation in Ce- and Yb-based organometallics

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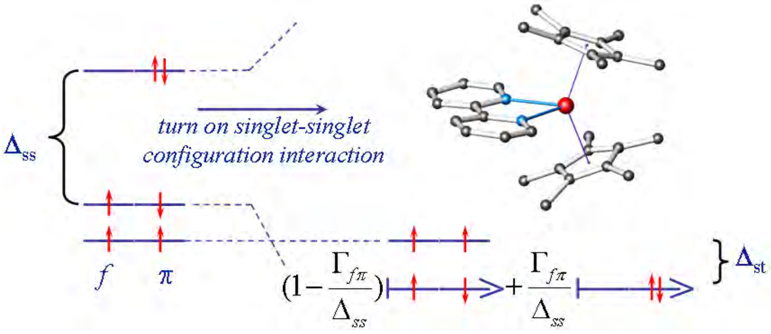
Overall research goals: The objective of this project is to understand the properties of *f*-element organometallic molecules that are in a multiconfigurational state describe by intermediate valence of the *f*-element.

Significant achievements in 2007-2009: The canonical view of magnetism and bonding in lanthanide organometallic compounds is that of localized *f* orbitals split by interactions with ligand orbitals, but not participating in bonding. This rule, of course, has some well known exceptions, particularly in solid-state intermetallics. Two features of *f*-orbital bonding in these intermetallic systems are noteworthy. First, a reduced magnetic moment at low temperatures is often observed, and second, a theoretical understanding cannot be obtained without including higher-order (many-body) interactions than are typically provided by a molecular theoretical method such as Density Functional Theory (DFT). Recently, several N-heterocyclic base adducts of ytterbocene of the form $Cp^*_2Yb(L)$, where Cp* = pentamethylcyclopentadienyl = C_5Me_5 and *L* is one of several bipy (bipy = 2,2′-bipyridine), dad (dad = 1,4-diazabutadiene), and related adducts, have been shown to display unusual magnetic properties involving an apparently reduced magnetic moment of the complex, corresponding to an extremely strong antiferromagnetic coupling constant. The origin of the reduced moment in these molecules has been controversial. The heart of the controversy has been whether the reduced moment is caused by some type of antiferromagnetic coupling (mostly intramolecular, as shown by correlating solid-state magnetism and solution ^1H NMR chemical shifts), or is due to the electronic structure on the metal center or the molecule.

Over the past several years, we have synthesized and characterized a number of Yb-based organometallics that display such behavior in their valence and magnetism. We have recently completed a longer work on the ytterbocenes to complement our previous work on Ce(cot)2, otherwise known as cerocene where cot=cyclooctatetraene, and $Cp^*_2Yb(bipy)$ [Booth et al., Phys. Rev. Lett. **95**, 267202 (2005)]. In particular, partial ytterbium *f*-orbital occupancy (*i.e.* intermediate valence) and open-shell singlet formation are established for a variety of bipyridine and



diazabutadiene adducts with decamethylytterbocene, $(C_5Me_5)_2Yb$, abbreviated as $Cp*_2Yb$. Data used to support this claim include ytterbium valence measurements using Yb L_{III}-edge X-ray absorption near-edge structure (XANES) spectroscopy, magnetic susceptibility and Complete Active Space Self-Consistent Field (CASSCF) multiconfigurational calculations, as well as structural measurements compared to density-functional theory (DFT) calculations. The CASSCF calculations indicate that the intermediate valence is the result of a multiconfigurational ground state wave function that has both an open-shell singlet $f^{13}(\pi^*)^1$, where π^* is the LUMO of the bipyridine or diazabutadiene ligands, and a closed-shell singlet f^{14} component. A number of other competing theories for the unusual magnetism in these materials are ruled out by the presence and lack of temperature dependence of intermediate valence.

These results will be presented together with our previous work on cerocene, a study extending to interconversion between cerocene and the triple decker $Ce_2(cot)_3$, as well as our recent work on the Pn_2*Ce that we have found, together with Dermot O'Hare's group at Oxford, to be another example of a multiconfigurational ground state in a cerium organometallic. Together with the above ytterbocene results, we are beginning to understand the ubiquity of such behavior and the importance of configuration interactions in lanthanide organometallics. These results have implications for understanding chemical bonding not only in organolanthanide complexes, but also for *f*-element chemistry in general, as well as understanding magnetic interactions in nanoparticles and devices.

Science objectives for 2009-2011

- Explore related adducts that demonstrate significant temperature dependence in the Yb valence
- Expand toward other lanthanide and non-Cp-based organometallics
- Expand toward actinide organometallics

Publications supported by this project 2007-2009

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Matrix Infrared Spectroscopic Investigations of Novel Small Uranium Containing Molecules

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Overall research goals: The objective of this project is to synthesize new uranium species under matrix isolation conditions, to obtain their infrared spectra, and to perform density functional calculations of these product structures and vibrational frequencies.

Significant achievements during 2008-2009: DOE funding for this research became available in September 2008. Our first project is the reaction of U and SO_2 to form SUO_2, which is an analog of UO_3.

Reactions of laser-ablated U atoms with SO_2 molecules gave the very stable U (VI) molecule, SUO_2, as the major product. Infrared absorptions for two new U=O stretching modes were observed in solid argon (891.2, 821.7 cm^{-1}) and neon (904.5, 835.5 cm^{-1}). The band assignments were confirmed by appropriate $^{34}SO_2$, $S^{18}O_2$ and $S^{16,18}O_2$ isotopic shifts. B3LYP and PW91 density functional calculations were performed to determine molecular structure, vibrational frequencies, and isotopic shifts. The C_{2v} structure of SUO_2 is analogous to those computed for UO_3 and US_3. Minor products were identified as the SUO_2^+ cation (987.5 cm^{-1}) the $(SO_2)(SUO_2)$ adduct (1211, 927, 847 cm^{-1}), and the SUO molecule (857.0 cm^{-1}). Part of the matrix infrared spectrum is shown in Figure 1, which is amplified to feature the weaker bands.

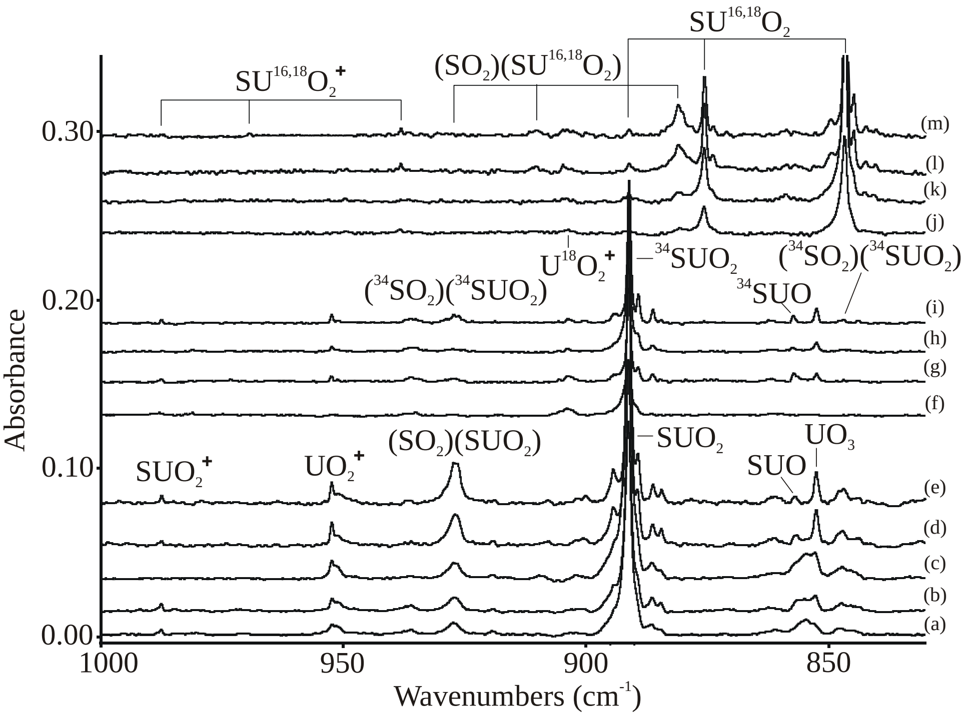

Figure 1. Infrared spectra in the 1000-830 cm^{-1} region for products formed in the laser-ablated uranium atom reaction with sulfur dioxide during condensation in excess argon at 5 K. (a) normal isotopic $^{32}SO_2$ isotopic sample at 0.4 % in argon co-deposited for 60 min, (b) after annealing to 20 K, (c) after > 220 nm irradiation, (d) after annealing to 30 K, (e) after annealing to 35 K, (f) $^{34}SO_2$ isotopic sample at 0.2 % in argon co-deposited, (g) after annealing to 30 K, (h) after > 220 nm irradiation, (i) after annealing to 35 K, (j) $S^{18}O_2$ and $S^{16,18}O_2$ isotopic mixture at 0.4 % total co-deposited, (k) after > 220 nm irradiation, (l) after annealing to 30 K, (m) after annealing to 35 K.

It is interesting the compare harmonic frequencies calculated for the SUO_2 molecule using the B3LYP hybrid density functional and the PW91 pure density functional. Typically the hybrid functional predicts slightly higher frequencies than the pure density functional. The O=U=O stretching frequencies for the SUO_2 molecule are predicted about 30 cm^{-1} higher with the hybrid functional. The gaseous molecule is not known, but extrapolating from argon to neon to gas phase predicts these two modes near 925 and 855 cm^{-1}, which are very close to the B3LYP values. The lower PW91 frequencies are within 5 cm^{-1} of the argon matrix values. So here the PW91 functional clearly underestimates the O=U=O stretching frequencies and the B3LYP functional predicts frequencies very close to extrapolated gas phase values for the SUO_2 molecule.

The SUO_2 molecule is formed directly in concerted highly exothermic reaction (1), and this reaction energy is computed as – 196 kcal/mol at the B3LYP level of theory in the absence of spin orbit coupling. The clear increase of the major SUO_2 absorptions in solid argon and neon on annealing indicates that reaction (1) is spontaneous and requires no activation energy. The matrix soaks up the reaction energy and allows the SUO_2 molecule to be trapped. In the gas phase, reaction (1) would give primarily the UO and SO diatomic molecules as products.

$$U + SO_2 \rightarrow SUO_2 \qquad (1)$$

Science objectives for 2009-2011:

- Laser ablation of UB_x, UN_x, UP_x, and US_x samples to form new binary uranium-main group transients. [This work will be done in collaboration with John Gibson at LBNL, who will examine mass spectra of the ablated materials.]
- Reactions of U atoms and NF_3, PF_3, AsF_3, SbF_3. We have started this investigation and $N{\equiv}UF_3$ is the major product. The U≡N triple bond is strong, and we wish to investigate how effective P, As, and Sb will be at forming triple bonds to uranium and thus stabilizing the U(VI) oxidation state. Parallel work will be done with thorium for comparison.
- Reactions of U atoms with BF_3 and BCl_3. In order to complete our first row triple bond series, we will prepare the $B{\equiv}UF_3$ molecule. We will investigate the development of the E≡U triple bond in the $B{\equiv}UF_3$, $HC{\equiv}UF_3$, and $N{\equiv}UF_3$ molecules.
- Complementary reactions with lanthanide metal atoms. We wish to investigate the reactions of the lanthanide metal atoms with CH_4, CH_3F, CCl_4 and CF_4 in order to compare the effect of 4*f* orbitals, which typically have core-like character, on the bonding and structure with the analogous reaction products formed by actinides with 5*f* orbitals and with early transition metal atoms.

Hydrothermal chemistry of UO_2^{n+} phases: Formation and stabilization of pentavalent uranium compounds.

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I. Program Scope: The objective of this project is to synthesize pentavalent uranium species under hydrothermal conditions. More generally however, we are exploring the redox chemistry of U-containing hydrothermal systems. This approach includes investigation of *in situ* ligand synthesis pathways as well as controlling hydrolysis to 'select' desired coordination geometries.

II. Significant Achievements 2007-2009

1. Synthesis and characterization of pentavalent U oxide phases.

We have developed a reproducible hydrothermal route to $[U^V(H_2O)_2(U^{VI}O_2)_2O_4(OH)](H_2O)_4$, a mixed valent U(V)/U(VI) material produced via the reduction of the uranyl cation. Large single crystals (Figure 1) can be obtained from a three day reaction of uranyl oxyacetate, Zn metal and hydrazine dichloride in a 1:1 H_2O-acetonitrile mixture at 120 °C.

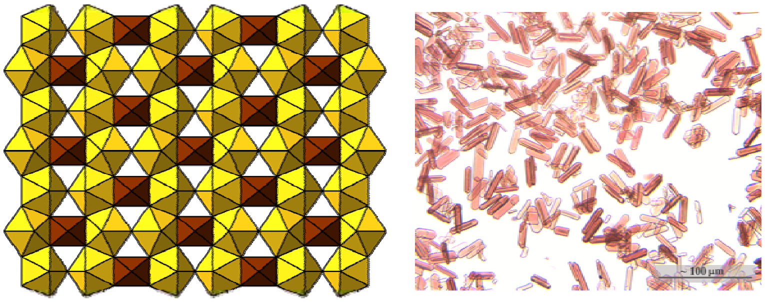


Figure 1. Left: A single layer of $[U^V(H_2O)_2(U^{VI}O_2)_2O_4(OH)](H_2O)_4$. Yellow polyhedra are U(VI) sites whereas brown are U(V). Right: A photograph of single crystals of this compound.

Oxidation state assignments have been confirmed through a combination of crystallographic (i.e. bond-valence summations) and spectroscopic (XPS and EXAFS) investigations.

2. PF_6^- hydrolysis as a route to novel uranyl phosphate materials

Accidental, or undesired hydrolysis of PF_6^- anions to form PO_4^{3-} groups has been known for some time. We have capitalized on this observation to utilize PF_6^- as a precursor to the formation of novel uranyl phosphates. The reasoning here is that 'gradual' introduction of PO_4^{3-} anions (as opposed to using preformed phosphate building units such as H_3PO_4) will avoid formation of highly insoluble dense phases. As such, we have produced $[(UO_2)_5(HPO_4)_3(PO_4)F_4]$ $(H_9C_{10}N_2)_3$ (Figure 2), via hydrothermal treatment of uranyl nitrate, tetrabutylammonium hexafluorophosphate (TBA-PF_6) and 4,4'-bipyridine at 180 °C over

14 days. This structure represents not only a novel uranyl phosphate sheet type, but also contains an unprecedented pentameric, secondary building unit.

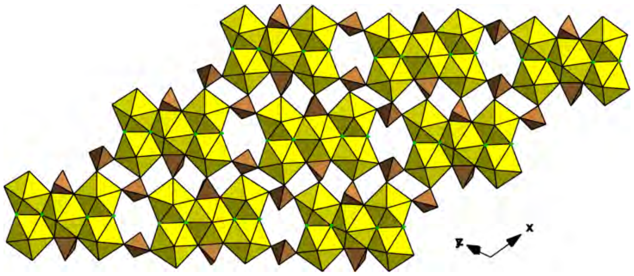


Figure 2. A single layer of $[(UO_2)_5(HPO_4)_3(PO_4)F_4](H_9C_{10}N_2)_3$. Brown polyhedra are PO_4^{3-} anions formed from the in situ hydrolysis of PF_6^- starting materials. Protonated bipyridine molecules are not shown.

III. Science Objectives for 2009-2011

Specific objectives for 2009-2011 include an new focus on solution phase reactivity prior to and during hydrothermal formation of hybrid materials. *In situ* reactions, such at the redox and hydrolysis mentioned above and ligand syntheses referenced below, can be viewed as new routes to materials unobtainable via other means. As such, mechanistic information is critical for understanding known reactions as well as exploiting new possibilities. We intend to use *in situ* NMR combined with GC-MS to closely monitor speciation profiles under hydrothermal conditions. Further, we intend to exploit new reaction types, such as disulfide bond formation, to promote assembly of novel uranyl structure types, a preliminary result of which is shown in Figure 3.

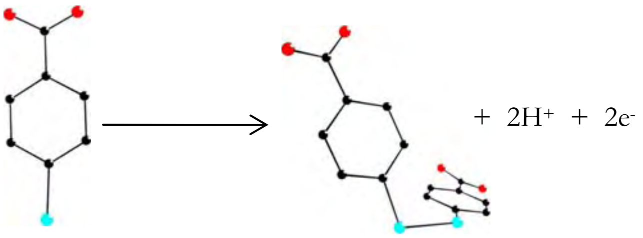
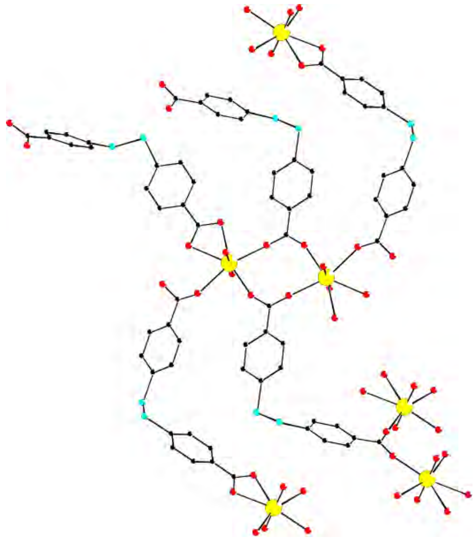


Figure 3. Top: Oxidation of 4-mercaptobenzoic acid to form disulfide bridged dimers. Promotion of this reaction in the presence of $[UO_2]^{2+}$ under hydrothermal conditions yields the $UO_2(C_{21}H_{12}O_6S_3)$ coordination polymer at right.



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Actinide Incorporation and Radiation Effects in U(VI) Solids: Thermodynamic and Mechanistic Study

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Collaborators: Prof. Rod Ewing, Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109-21204.

Overall research goals: The objective of this project is to understand the structural characteristics of U(VI) solids, their thermodynamic stability, and their ability to partition and/or sorb transuranium cations. In collaboration with Rod Ewing at University of Michigan, the radiation effects of these solids are also investigated.

Significant achievements during 2007-2009: During this time period, we have focused our efforts on (1) investigation of U(VI) silicate minerals, e.g., uranophane $(Ca[(UO_2)(SiO_3OH)]_2 (H_2O)_5)$, Na-boltwoodite $(Na[(UO_2)(SiO_3OH)](H_2O)_S)$, sklodowskite $(Mg[(UO_2)(SiO_3OH)]_2(H_2O)_6)$, as sorbents for the transactinide cations, and (2) determining vibrational bands for the U(VI) solids that we can relate to structural characteristics of the solid.

1. The U(VI) silicate minerals are important sinks for U in the natural environment, and have been observed as the solubility-controlling solids in subsurface disposal areas. Uranophane, boltwoodite, and sklowdowskite are U(VI) silicates with similar structural characteristics. They are layered structures that in many ways are analogous to clay minerals (Fig. 1).

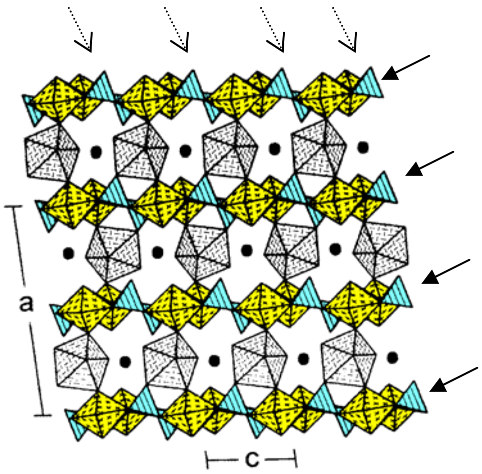

Figure 1: The structure of uranophane, a 1:1 layered U(VI) silicate with Ca^{2+} cations located in the interlayer spaces. Yellow polyhedra indicate the location of the uranyl cations; light blue tetrahedral signify silicate anions. The grey polyhedra located between the sheets are the calcium cations, and the black dots signify water molecules.

The dashed, grey arrows across the top of the drawing denote possible cation adsorption sites to the single oxygen atoms of the silicate tetrahedral that project up from the top of the U(VI):silicate sheet. The dark arrows down the right hand side of the structure are pointing to a different type of site for cation adsorption. These are the silicate tetrahedra located along the edge of the sheets where two oxygen atoms are available for interaction with a sorbing cation.

Because of the net negative structural charge associated with the 1:1 U(VI):silicate sheets, these solids have a strong tendency to sorb cations from solution. We have measured sorption curves for the trivalent, pentavalent, and hexavalent f-elements as a function of pH, and developed an equilibrium model to describe our observations.

2. In the second part of our work, we have been investigating vibrational spectroscopy as a tool for identifying structural characteristics of U(VI) solids, and quantifying the amount and role of water

in these materials. Often, mineral identification based primarily on powder x-ray diffraction, is not unequivocal; Raman and infrared (IR) spectroscopy are additional tools. Furthermore, powder diffraction patterns provide no specific data on the quantity of water in the solid, and only limited information about the structural role of water in the solid.

An example of our studies in this area is below (Fig. 2). In this case, a U(VI) phosphate solid called triuranyl diphosphate tetrahydrate (TDT, $[(UO_2)_3(PO_4)_2]\cdot 4H_2O$) is shown. Interestingly, this solid has uranyl cations both the two-dimensional sheet and in the interlayer area. We are working to resolve vibrational bands observed by Raman and IR, and quantifying the amounts of water associated with various parts of the structure.

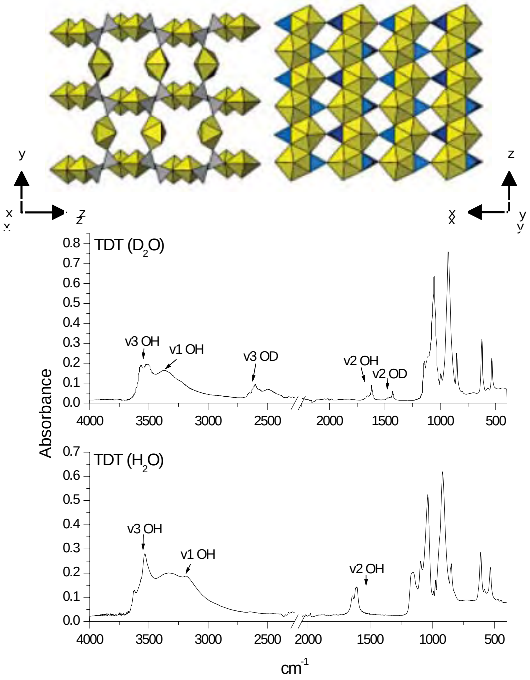

Figure 2: The structure of triuranyl diphosphate tetrahydrate (TDT) and the observed vibrational bands by infrared (IR). The drawing on the left shows the three-dimensional structure of the solid, while the drawing on the right shows the structure of the two-dimensional sheet. Note that although this is a phosphate solid and uranophane is a silicate solid, the sheet structures for both are very similar. Also, the uranyl cation plays two roles in this structure: it is bound within the sheet, and also is an interlayer cation. Water molecules are also located in the interlayer spaces; the role of water in this region is not well understood.

The IR data show are for the solid produced in D_2O (top spectrum), and water (bottom structure). These two spectra can be used to identify the bands arising for vibrations with OH and H_2O moieties in the solid.

Science objectives for 2009-2011:

- Continue to collaborate with Prof. Rod Ewing on the radiation stability of these solids.
- Collaborate with Prof. A. Clark at WSU, a computational actinide chemist, to develop a computational model describing actinide sorption onto U(VI) solid surfaces.
- Continue to pursue spectroscopic approaches for structural characterization of U(VI) solids. We will collaborate with Nancy Hess of PNNL to use neutron diffraction to verify the locations and role of water in U(VI) solids.

Partial List of Publications supported by this project 2007-2009

1. S. B. Clark and M. Douglas (2009). “Transuranium and fission product cation partitioning into U(VI) silicate solid phases”, Proceedings of the Nuclear and Radiochemistry Symposium, January 7-10, 2009, Mumbai, India.
2. Z. Wang, J. M. Zachara, C. Liu, P. L. Gassman, A. R. Felmy, and S. B. Clark (2008). “A cryogenic fluorescence spectroscopic study of uranyl carbonate, phosphate, and oxyhydroxide minerals”, Radiochimica Acta, 96(9-11): 591-598.
3. S. Serkiz, W. Johnson, L. Wile, and S. B. Clark (2007). “Environmental availability of uranium in an acidic acid plume at the Savannah River Site”, Vadose Zone Journal, 6(2): 354-362.

Principles of Chemical Recognition and Transport in Extractive Separations:

Anion Recognition and Separation with Self-Assembled Cage Receptors

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

Overall research goals: The main objective of this project is to explore the ability of self-assembled cages to recognize anions in solution or in the solid state. The cages are functionalized with complementary hydrogen-bonding groups for size and shape recognition of the encapsulated anion from competitive aqueous media. Once the anion is selectively encapsulated, the separation can be achieved either by selective crystallization, or by extraction into an organic solvent.

Significant achievements during 2007-2009: We demonstrated that crystallization of self-assembled capsules functionalized with urea hydrogen-bonding groups can be exploited for selective separation of sulfate anion (Figure 1). The high complementarity and the rigid environment found in such crystalline systems impart strong discrimination between anions of different shape, like sulfate and sulfite, or anions of the same shape but slightly different size, like sulfate and selenate, with selectivity that exceeds that observed in sulfate-binding protein. Similar to natural receptors, these crystalline capsules completely isolate the anions from the aqueous solvent by encapsulating them inside rigid cavities lined with complementary hydrogen-bonding groups. Furthermore, the capsules are made from flexible building blocks, whose structure and relative orientation in the crystal can be allosterically regulated to fine-tune the anion selectivity. These characteristics suggest that crystallization of such urea-functionalized capsules from simple and flexible components represents a particularly promising approach for selective anion separation from highly competitive aqueous environments.[1,2]

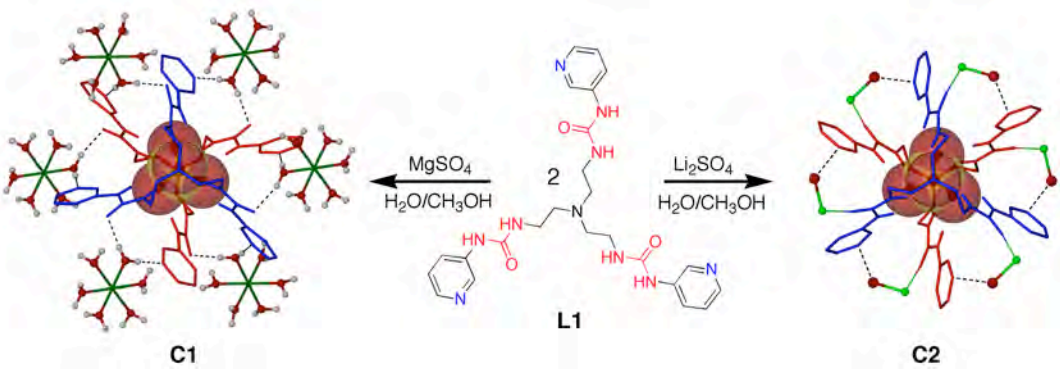

Figure 1. Sulfate encapsulation by self-assembled cages in the crystalline state. Two molecules of **L1** are held together by six $Mg(H_2O)_6^{2+}$ (left) or six $Li(H_2O)^+$ (right).

As an alternative approach, we designed using *de novo* structure-based methods, a discrete, soluble metal-organic cage functionalized with urea H-bond donors for ideal complementarity to SO_4^{2-}. The X-ray structural analysis (Figure 2) revealed, as designed, a self-assembled tetrahedral cage that encapsulates sulfate by 12 hydrogen bonds (Figure 2). ESI-MS provided evidence that the cage persists in water. Competition experiments with Sr^{2+} and Ba^{2+} indicated that the cage binds sulfate very strongly in H_2O, ($K = 6 \times 10^6$ mol^{-1} L), surpassing any synthetic receptor known to date and rivaling the sulfate-binding protein.[3]

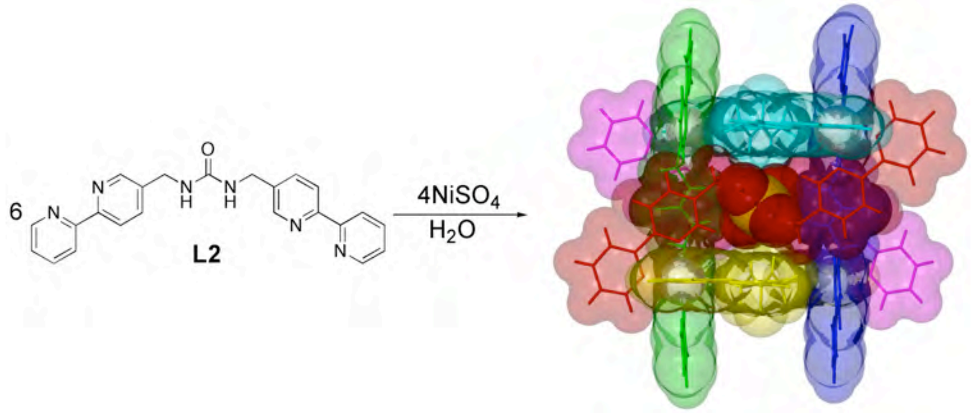

Figure 2. Self-assembly of a metal-organic cage encapsulating SO_4^{2-}. Right: crystal structure of the tetrahedral cage, with each of the 6 edges depicted in a different color.

Science objectives for 2009-2011:

- Study the anion selectivity of the soluble self-assembled cages and investigate the possibility of using them in extractive separations.
- Continue to explore anion separation by selective crystallization of self-assembled cages, with an emphasis on controlling the selectivity of the countercation. Ultimately, we seek ion-pair selectivity in the solid state, by design.
- Explore covalent self-assembled cages for anion recognition and separation.

Publications supported by this project 2007-2009:

1. Custelcean, R.; Remy, P.; Bonnesen, P. V.; Jiang, D.-E.; Moyer, B. A. “Sulfate Recognition by Persistent Crystalline Capsules with Rigidified Hydrogen Bonding Cavities”, *Angew. Chem. Int. Ed.* **2008**, 47, 1866.
2. Custelcean, R.; Remy, P., “*Selective Crystallization of Urea-Functionalized Capsules with Tunable Anion-Binding Cavities*”, *Cryst. Growth Des*., **2009**, in press.
3. Custelcean, R.; Bosano, J.; Bonnesen, P. V.; Kertesz, V.; Hay, B. P., “*Self-Assembled Cages Made to Order: Deliberate Design of a Sulfate Encapsulating Receptor*”, *Angew. Chem. Int. Ed.* **2009**, submitted.
4. Custelcean, R.; Jiang, D.; Hay, B. P.; Luo, W.; Gu, B. “*Hydrogen-Bonded Helices for Anion Binding and Separation*”, *Cryst. Growth Des*. **2008**, *8*, 1909, featured on the cover.
5. Custelcean, R. “*Crystal Engineering with Urea and Thiourea Hydrogen-Bonding Groups*”, *Chem. Commun*. **2008**, 295 (invited Feature Article).
6. Custelcean, R.; Engle, N. L.; Bonnesen, P. V. “*Crystalline Hydrogen-Bonded Nanocolumns of Cyclic Thiourea Octamers*”, *CrystEngComm* **2007**, *9*, 452 (invited paper for the special issue: “*Crystal Engineering in the Design of New Materials”)*

Understanding Bonding by Studying Magnetic Behavior of Actinide Compounds

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Overall research goals: This research is focused on obtaining an understanding of how structure and bonding interact to influence electronic behavior and magnetic ordering in a wide variety of actinide compounds. The 5f ions, with more radially-extended valence orbitals than their 4f lanthanide counterparts, exhibit more varied evidence for electronic coupling, including correlated-electron effects and magnetic ordering. We are interested in how electronic behavior is able to couple with structural dimensionality to result in novel bonding, electronic properties, and magnetism.

Significant achievements during 2007-2009:

- The neptunyl (V) propensity for cation-cation interactions (CCI)s was probed by x-ray scattering studies from solution samples with varying cation concentration. This study revealed that CCIs are present in solution with the same Np-Np distance seen in a variety of solid-state structural studies, a result arguing in favor of electronic structure driving bonding interaction. We were able to quantify the energetics of the CCI by determining a stability constant of 0.74(9) M^{-1} from the scattering data. Similar studies with neptunyl (VI) revealed no evidence of CCIs, consistent with solid-state structural studies. This work was published in Inorganic Chemistry.
- Preliminary x-ray scattering studies from solutions with varying plutonyl (VI) concentrations revealed no evidence of CCIs, even to high Pu concentrations. This result is similar to those seen with neptunyl (VI) solutions. From this work we predict that Pu (VI) solid state structures will not show a preponderance of CCIs.

Science objectives for 2009-2011:

- *Quantify further NpO_2^+ magnetic properties as additional samples become available*: Our particular focus is to establish a correlation between the lattice dimensionality, as determined by the crystal structure, and the characteristics (symmetry and temperature) of the magnetic ordering. Cation-cation interactions are forming 1-dimensional chains, 2-dimensional sheets, and even 3-dimensional frameworks of short Np-Np interactions. Our interest is to correlate superexchange pathways for magnetic exchange with details of the ordering. Such correlations have previously been established for 4f lanthanide compounds, where the magnetic interactions are expected to be more short ranged.
- *Determine the magnetic structure of $Na[NpO_2(OH)_2]$:* Originally planned for last year, this project was delayed by the precipitous closure of the Intense Pulsed Neutron Source. The safety plans were completed, the beamtime was acquired and the experiment was expected to run in the spring of 2008. We are now making plans to do this work at the SNS but do not yet have approved beamtime. Our interest in this project continues because the Np hydroxide is ideal for probing superexchange pathways and their contribution to the symmetry of magnetic ordering. It has only one Np per asymmetric unit in the structure, which has recently been determined.

Np(V) ions are linked by hydroxyl bridges along the crystallographic b-direction and through cation-cation interactions along c. The compound orders antiferromagnetically at about 20 K. Our interest is a detailed understanding of the magnetic structure, which may exhibit several different symmetries and could include both ferro- and antiferromagnetic interactions along different directions in the crystal. These results may give us our first indications of the molecular level magnetic interaction pathways and their role in ordering.

- *Magnetic Properties of PuO nanophases:* Studies on Pu polymer have produced single crystals of monodisperse Pu oxide clusters ranging in sizes from 6 to 90 Pu atoms arranged in structures only slightly distorted from the fluorite structure. Preliminary magnetic measurements reveal temperature dependent paramagnetism that is very different from the temperature independent paramagnetism (TIP) seen for the bulk dioxide. Instead the magnetism is very similar to that seen for $Pu(SeO_3)_2$, the structure of which contains isolated Pu ions. We plan to further investigate the magnetism of our clusters and probe for an evolution of electronic behavior from magnetic for the isolated ions to TIP for the infinite lattice.

Publications supported by this project 2007-2009

1. P.M. Almond, S. Skanthakumar, L. Soderholm, and P.C. Burns, "Cation-Cation interactions and antiferromagnetism $Na[Np(V)O_2(OH)_2]$: Synthesis, structure, and magnetic properties"; Chem. Mater. 19 (2007) 280-285.
2. T.Y. Shvareva, S. Skanthakumar, L. Soderholm, A. Clearfield, and T.E. Albrecht-Schmitt, "Cs^+-Selective Ion-Exchange and Magnetic Ordering in a Three-Dimensional Framework Uranyl Vanadium(IV) Phosphate"; Chemistry of Materials, 19 (2007) 132-134.
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4. T. Z. Forbes, P. C. Burns, L. Soderholm and S. Skanthakumar, "Hydrothermal Synthesis and Structure of Neptunium(V) Oxide"; Mat. Res. Soc. Symp. Proc. 985 (2007) 401-406.
5. D. L. Gray, L. A. Backus, H-A. Krug von Nidda, S. Skanthakumar, A. Loidl, L. Soderholm and J. A. Ibers, "A U(V) chalcogenide: synthesis, structure, and characterization of $K_2Cu_3US_5$ "; Inorg. Chem. 46 (2007) 6992-6996.
6. T. H. Bray, S. Skanthakumar, L. Soderholm, R. E. Sykora, R. G. Haire, and T. E. Albrecht-Schmitt, "Hydrothermal Synthesis, Structure, and Magnetic Properties of $Pu(SeO_3)_2$"; J. Solid. State Chem. 181 (2008) 493-498.
7. L. Soderholm, P.M. Almond, S. Skanthakumar, R.E. Wilson, P.C. Burns, "The Structure of the Plutonium Oxide Nanocluster $Pu_{38}O_{56}Cl_{54}(H_2O)_8]^{14-}$"; Angew. Chem. Inter. Ed. (VIP, Frontespice Article) 47 (2008) 298-302.
8. S. Skanthakumar, M.R. Antonio, L. Soderholm, "A Comparison of Neptunyl(V) and Neptunyl(VI) Solution Coordination: The Stability of Cation-Cation Interactions"; Inorg. Chem. 47 (2008) 4591-4595.

Actinide Sorption/Incorporation and Radiation Effects in Layered Structures

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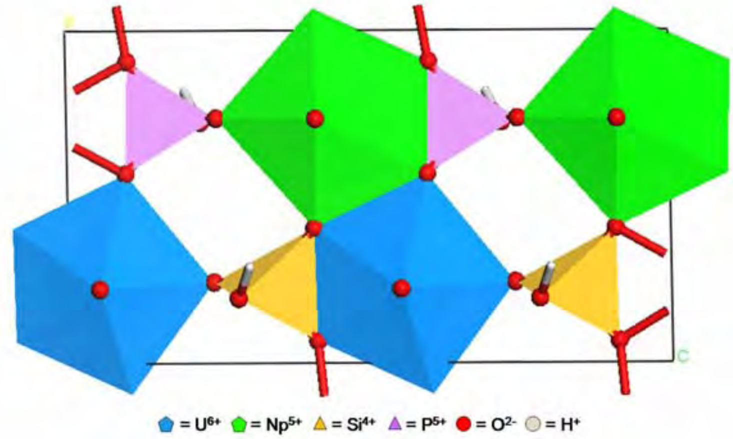
Overall research goals:

1. Develop a fundamental understanding of the interactions between actinides and layered-structures, mainly uranyl phases, sheet silicates and iron oxyhydroxides.
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.

Significant achievements during 2007-2009: Completed extensive studies of the environmentally important U-phase, coffinite ($USiO_4$). Lindsay Shuller initiated systematic computational studies of Np-incorporation into uranyl phases (summarized below). This is the only work on actinide incorporation into uranyl phases using quantum-mechanical calculations. The preliminary calculations on actinide sorption onto hematite (001) were presented as a poster at the annual Goldschmidt Conference this past July.

Np-incorporation into uranyl phases: In order to substitute Np(V) for U(VI), a charge-balance mechanism is necessary. Several charge-balance mechanisms were compared for Np(V)-incorporation into studtite $[(UO_2)O_2(H_2O)_4]$ and boltwoodite $[K(UO_2)(SiO_3OH)(H_2O)_{1.5}]$. For example, coupled-substitution of Np(V) and P(V) for U(VI) and Si(IV) in boltwoodite results in an incorporation energy of 1.24 eV, whereas the incorporation energy for coupled-substitution of Np(V) and H(I) for U(VI) is 1.40 eV. Solid-solution calculations have been completed for the P-coupled substitution mechanism to predict the thermodynamically stable limit of Np-incorporation, which are on the same order of magnitude as experimental results (Figure 1).



T (°C)	Np-incorporation limit
25	1 ppm
100	11 ppm
200	120 ppm
300	580 ppm

Figure 1. **Left:** Np-modified boltwoodite with 50 % substitution of Np(V) and P(V) for U(VI) and Si(IV), respectively. **Right:** Calculated thermodynamically stable limit of Np-incorporaiton into boltwoodite for the P-coupled substitution mechanism.

Actinide sorption onto hematite (001): Quantum-mechanical calculations have been used to systematically compare the sorption energies of different actinide species onto the (001) surface of hematite. Due to the nature of the calculations, adsorption models are simpler than actual actinide-mineral behavior in natural systems. For example, the simplified approach models the aqueous ion in a pure H_2O system, where 4-6 equatorial hydroxyl and/or water molecules complex with the linear actinyl ion. Preliminary results of linear actinyl adsorption onto hematite (001) indicate the actinide species with lower atomic number favor adsorption distances that are closer to the hematite surface. The initial geometry for the adsorption model used in this study describes inner-sphere adsorption, in which the adsorbed actinide is situated in the position of the next hematite-Fe^{3+} layer. The chemical reaction that describes this uranyl(VI) hexagonal bipyramid adsorption onto hematite (001) is: $Fe_4O_6 + 2\cdot[UO_2(OH)_2(H_2O)_4] \rightarrow Fe_4O_6(UO_2(OH)_2)_2(H_2O)_8$, where the product is the hematite slab with uranium(VI), two oxygen, and hydroxyl molecules adsorbed onto the top and bottom surfaces and four water molecules filling both sides of the vacuum gap of the periodic structure. The adsorption energy is half of the difference between the energy of the product and the sum of the energy of the reactants. The adsorption energies were analyzed as a function of adsorbate speciation (i.e., element and oxidation state). Hydration energies for the adsorbates are also included in the calculation to more accurately depict aqueous systems.

<u>Science objectives for 2009-2011:</u>

- Validate computational methodology for determining Np-incorporation into uranyl phases by systematic comparison with experimental and theoretical techniques.
- Determine the effect of electron and charge transfer between the adsorbate and the substrate on the strength of adsorption.
- Investigate the impact of co-adsorbing a reducing species (i.e., H_2S) with the actinide adsorbate, focusing on possible enhanced actinide reduction.

<u>Publications supported by this project 2007-2009</u>

1. A.P. Deditius, S. Utsunomiya and R.C. Ewing (2008) The chemical stability of $USiO_4nH_2O$): 0<n<2 associated with organic matter: A case study from Grants uranium region, New Mexico, USA. <u>Chemical Geology</u>, vol. 251, 33-49.
2. Alexandra Rey, Satoshi Utsunomiya, Javier Giménez, Ignasi Casa, Joan de Pablo and Rodney C. Ewing (2009) Stability of uranium(VI) peroxide hydrates under ionizing radiation. <u>American Mineralogist</u>, **94**, 229-235
3. A.P. Deditius, S. Utsunomiya, M.A. Wall, V. Pointeau, and R.C. Ewing (**in press**) Structure and chemical composition of P-coffinite from natural fission reactor at Bangombé, Gabon, <u>American Mineralogist</u>.
4. S. Utsunomiya, A. Kersting and R.C. Ewing (**in press**) Groundwater nanoparticles in the far-field at the Nevada Test Site: Mechanism for radionuclide transport. <u>Environmental Science & Technology</u>.
5. L.C. Shuller, J. Poling, R.C. Ewing, and U. Becker (2008) Actinide sorption onto hematite (001) surface. <u>Geochimica et Cosmochimica Acta</u> 72: A864.
6. L.C. Shuller, R.C. Ewing, and U. Becker (**in preparation**) Np-incorporation into studtite: a quantum-mechanical evaluation. <u>Journal of Nuclear Materials</u>.
7. L.C. Shuller, R.C. Ewing, and U. Becker (**in preparation**) Quantum-mechanical investigation of Np^{5+}-incorporation into boltwoodite. <u>American Mineralogist</u>.

Origins of Soft Donor Ligand Selectivity in Actinide(III)/Lanthanide(III) Separations

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Overall research goals: This program focuses on understanding the specific origins of the greater affinity of ligands containing donor atoms softer than oxygen for actinide ions as compared to equivalent lanthanide ions. This chemistry is critical to separating trivalent lanthanide and actinide ions. Using experimental measurements of the molecular structure, thermodynamics, and electronic properties, we seek to test the hypothesized electronic origins of this effect using equivalent complexes of trivalent lanthanide and transuranic actinide ions. Our objective is to link thermodynamic, structural, and spectroscopic information into a predictive picture of bonding in actinide-soft donor complexes.

Significant achievements during 2007-2009: To probe the relationship of thermodynamic selectivity to the structure and electronic properties of actinide complexes, we have been focusing on a series of π-accepting aromatic nitrogen donor ligands, each of which is known to favor complexation of trivalent actinides over lanthanides. Using the strong σ-donating soft donor ligand *N*,*N*-diethyldithiocarbamate as the anion, but changing the identity of the nitrogen donor ligand required to complete the coordination sphere, produced a series of crystalline lanthanide (Nd(III)

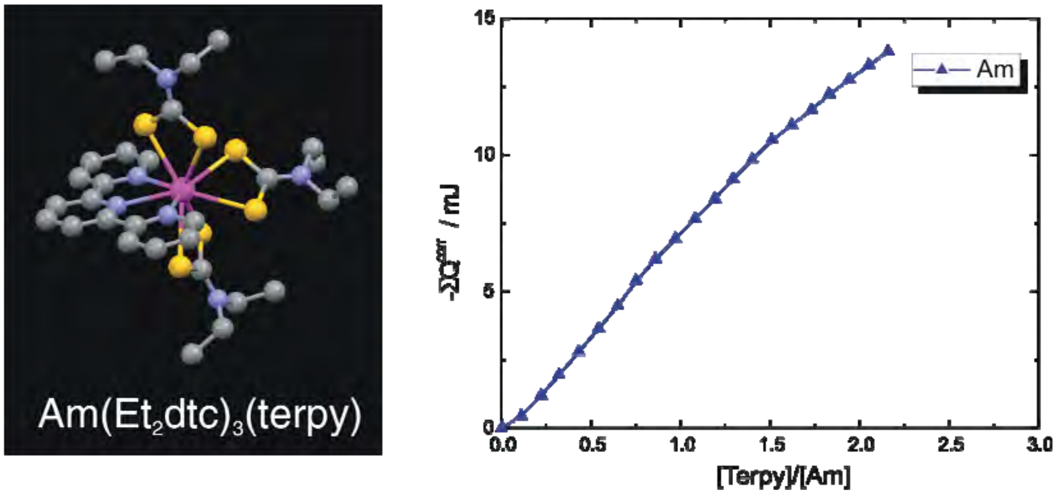

Figure 1. Left: Structure of americium–tris *N*,*N*-diethyldithiocarbamate–terpyridine complex determined by crystallography. Right: Cumulative heats for americium-terpyridine complexation measured by calorimetric titration in acetonitrile at 25 °C.

and Sm(III)) and actinide (Am(III)) complexes with identical structures within each ligand set. However, no significant differences in the metal-ligand bond lengths are observed. Despite obvious differences in the electronic properties of the complexes as indicated by their optical spectra, there was no correlation between the structural differences and the observed differences in the thermodynamic selectivity of the ligands for americium over the trivalent lanthanides.

Our previous work with soft donor ligands for actinide/lanthanide separation has shown a general relationship between enhanced selectivity for actinide(III) cations and an increased number of coordinated soft donor atoms. It has been unclear how much of this thermodynamic enhancement arises from specific electronic effects and how much arises from the simple increase in the number of soft donors. Our lanthanide and americium complexes with bi- and tridentate nitrogen donor ligands indicate that the increase in the number of donors has a substantially larger effect than differences in the electronic structure of the ligands with more soft donors.

Science objectives for 2009-2011:

- Integrate our existing structural and spectroscopic information with additional complexation thermodynamics information on the series of americium-nitrogen ligand complexes to understand the details of actinide selectivity in this group of materials.
- Examine the effect of systematically altering the degree of electron donation from the sulfur donor ligands on the electronic properties of the f-element complexes.
- Explore, in collaboration with Prof. Chuan He, the suitability of soft donor containing peptides or proteins as systematic scaffolds for varying ligand softness in our future studies.

Publications supported by this project 2007-2009

1. Hannel, T. S.; Otu, E. O.; Jensen, M. P., Thermochemistry of the Extraction of Bismuth(III) with Bis(2-ethylhexyl) Phosphoric and 2-Ethyhexyl-Phenylphosphonic Acids. *Solv. Extr. Ion Exch.* **25**, (2007), 241-256.
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EPR and magnetic susceptibility studies of the bonding in f^1 and f^3 organometallic complexes

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Overall research goals: The objective of this project is to understand the role of f-orbitals in bonding in a variety of organometallic systems.

Significant achievements during 2007-2009:

1. f^1 systems: The EPR spectra of anionic $(cot)_2Ce^-$ and neutral $(cot)_3Ce_2$ were analyzed to determine which f-orbitals are occupied by the unpaired electron. This analysis also yields the degree of orbital reduction (covalence) required to obtain a good fit to the observed EPR spectrum. The magnetic susceptibility of $(cot)_2Ce^-$ was used to model the susceptibility of $(cot)_3Ce_2$ so that the coupling between the two f^1 centers could be quantified.

2. f^3 systems: The EPR spectra and magnetic susceptibility of Cp''_3M and Cp''_3ML where, Cp" is 1,3-bis-trimethylsilylcyclopentadienyl, M is Nd or U, and L is either t-butylisocyanide or cyclohexylisocyanide, were analyzed to determine which f-orbitals are occupied by the three unpaired electrons. In the case of the Nd complexes, the assignment of the EPR spectra is straightforward; however, in the case of the U complexes, the assignment is somewhat ambiguous. Russell-Saunders coupling is assumed for the three f-electrons, which is a good assumption for Nd, but possibly not for U.

Science objectives for 2009-2011:

- Extend the EPR investigations to other f^1 and f^3 systems with axial symmetry, especially U(III) complexes to better understand the which f-orbitals are occupied in the ground state.
- Quantify the exchange coupling in other binuclear homometallic lanthanide and actinide systems.
- Quantify the exchange coupling in other binuclear lanthanide and actinide systems containing a radical or transition metal.

Publications supported by this project 2007-2009

1. Walter, M.D.; Booth, C.H.; Lukens, W.L.; Andersen, R.A..; "Cerocene Revisited: The Electronic Structure of and Interconversion Between $Ce_2(C_8H_8)_3$ and $Ce(C_8H_8)_2$." Inorganic Chemistry, *in press*.
2. Lukens, W.L.; Edelstein, N.M.; Andersen, R.A., "EPR spectra, magntetic susceptiblities, and electronic structures of Cp''_3Nd and its complexes with isocyanide ligands., where Cp" is 1,3-bis-trimethylsilylcyclopentadienyl." In prep for Inorganic Chemistry.

Probing the Structural, Spectroscopic and Magnetic Properties of Actinyl(VI) Cations ($\{UO_2\}^{2+}$, $\{NpO_2\}^{2+}$ and $\{PuO_2\}^{2+}$) through Polyoxmetalate Coordination

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Overall research goals: The objective of this project is to gain deeper insight into the electronic structure of actinyl cations through their encapsulation within tungsten-oxygen-heteroatom based polyoxometalate frameworks. Actinide polyoxometalate chemistry had previously been a fruitful area of research for I. May and co-workers at The University of Manchester and The UK national Nuclear Laboratory (pre-2007), with the subsequent effort now focusing on utilizing the specialist facilities now available at LANL. These facilities relate to transuranic synthesis and structural studies (particularly for plutonium), spectroscopy (including luminescence spectroscopy) and magnetism (at the National High Magnetic Field Laboratory).

Significant achievements during 2007-2009: Progress has been made in several areas with three main achievements: -

1. *Plutonyl(VI)*. We have structurally and spectroscopically characterized the first plutonyl polyoxometalate complex, $K_{11}[K_3(PuO_2)_3(A\text{-}\alpha\text{-}GeW_9O_{34})_2]$. The development of containment strategies have allowed us to undertake preliminary magnetic measurements, a very rare example of a molecular plutonium magnetic measurement Finally, spectroscopic studies into the interaction of $[PuO_2\}^{2+}$ with three tri-lacunary A-type ligands, $[\alpha\text{-}PW_9O_{34}]^{9-}$, $[\alpha\text{-}GeW_9O_{34}]^{10-}$ and $[\beta\text{-}SiW_9O_{34}]^{10-}$ indicate complex solution speciation. Figs. 1 and 2 illustrate some of these results.

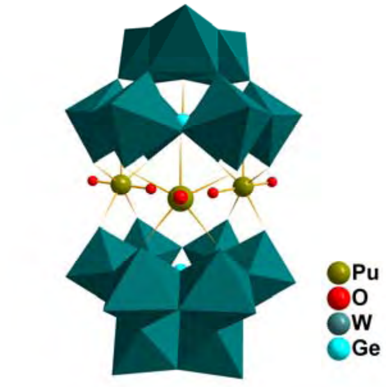

Figure 1 (above). Polyhedral and ball and stick representation of $[K_3(PuO_2)_3(GeW_9O_{34})_2]^{11-}$, with the potassium atoms removed for clarity.

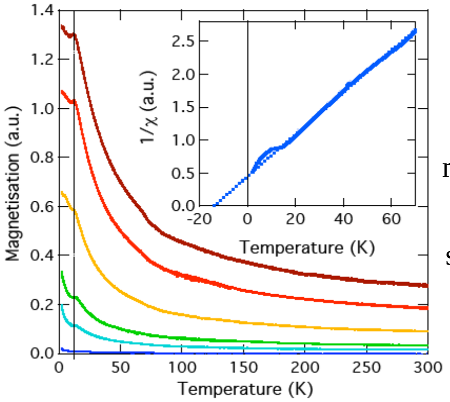

Figure 2 (left). The magnetisation of $K_{11}[K_3(PuO_2)_3(GeW_9O_{34})_2]\bullet 12H_2O$ between 2 and 300 K at magnetic fields of 0.1, 1, 2, 5, 10 and 14 T (lower to upper curves). The cusp at 12 K is indicative of the energy scale of the exchange interaction between Pu-centres. Inset: the inversion magnetic susceptibility. The solid line denotes the data and the dashed line a linear fit over the temperature range 20 – 70 K. The negative temperature intercept of the fit (-14.(3) K) is consistent with antiferromagnetic exchange coupling between the Pu moments.

2. Neptunyl(VI). We have previously observed that polyoxometalate complexation leads to very distinctive changes in the UV/vis/nIR spectra of Np(VI) and enhances the near IR luminescence of this $5f^1$ actinide species in the solution state. Focusing on the $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ ligand, we have probed the absorption spectroscopy of $[Na_2(NpO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{12-}$, both in the solid state (as the hydrated sodium salt) and in solution (see Fig. 3). Luminescence was observed from this compound

in the solid state at 930 nm (10,750 cm^{-1}) following excitation at 600 nm (16,670 cm^{-1}). The decay curve could be fitted to two exponentials with lifetimes of 3.2 and 33 μs respectively with the excitation spectra matching the absorption spectra fine structure centered at 607 nm.

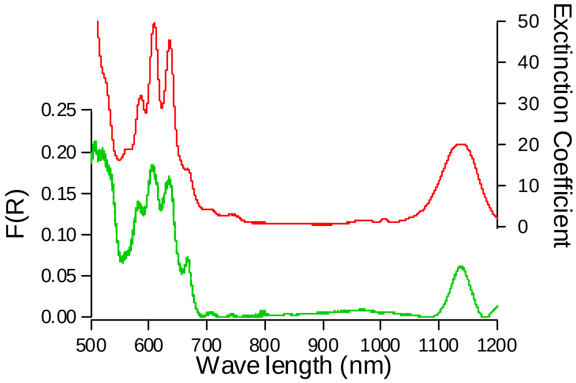

Figure 3 (right). Vis/nIR absorption spectrum of $[Na_2(NpO_2)_2(PW_9O_{34})_2]^{12-}$ in solution (red trace, extinction coefficient) and in the solid state (green trace, F(R)).

3. *Uranyl(VI).* We have recently initiated an investigation into the effect of polyoxometalate complexation on the luminescence properties of $\{UO_2\}^{2+}$. Preliminary investigations into the $[(X)_2(UO_2)_2(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{12-}$ series of complexes (where X = Na^+, K^+ and NH_4^+) reveal that an emission spectra can be obtained from exciting both the uranyl fine structure and the U/W ← O charge transfer regions of the UV/vis absorption spectra, with the greatest emission intensity observed from excitation of the charge transfer region (see Fig. 4) .

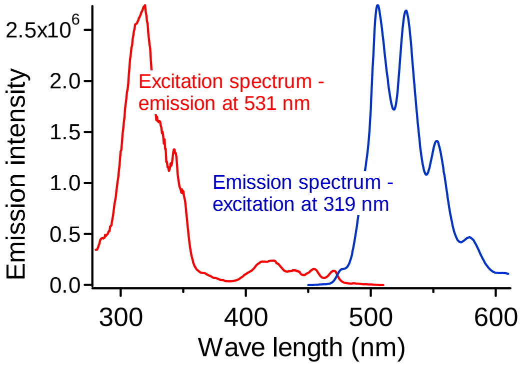

Figure 4 (left). Solution state luminescence spectroscopy of $[K_2(UO_2)_2(PW_9O_{34})_2]^{12-}$.

Science objectives for 2009-2011:

- A complete magnetization study of $K_{11}[K_3(PuO_2)_3(GeW_9O_{34})_2]$ and an exploration into the structural diversity of $\{PuO_2\}^{2+}$ - A-type tri-lacunary heteropolyoxotungstate chemistry .
- Further structural and spectroscopic characterization of neptunyl polyoxometalate complexes and undertake magnetic measurements (*i.e.* a comparison between 5*f*^{2} Pu(VI) and 5*f*^{1} Np(VI).
- A systematic investigation into how subtle variation in polyoxometalate coordination environment effects uranyl luminescence, yielding insight into this fundamental U(VI) property.

All publications supported through BES-HEC funding, 2007-2009

1. S. M. Cornet, L. J. L. Häller, M. J. Sarsfield, D. Collison, M. Helliwell, I. May and N. Kaltsoyannis, "Neptunium(VI) chain and neptunium(VI/V) mixed valence cluster complexes," *Chem. Commun*., **2009**, 917-919.
2. S. M. Cornet, I. May, M. P. Redmond, A. J. Selvage, C. A. Sharrad and O. Rosnel, "Coordination of bistriflimide and triflate to the uranyl bis(diphenylphosphino)methane dication, $\{UO_2(DPPMO_2)_2\}^{2+}$," *Polyhedron*, **2009**, *28*, 363-369.
3. R. Copping, L. Jonasson, A. J. Gaunt, D. Drennan, D. Collison, M. Helliwell, R. J. Pirttijarvi, C. J. Jones, A. Huguet, D. C. Apperley, N. Kaltsoyannis and I. May, "Tetravalent metal complexation by Keggin and lacunary phosphomolybdate anions," *Inorg. Chem*., **2008**, *47*, 5787-5798.
4. R. Copping, C. Talbot-Eeckelaers, D. Collison, S. Faulkner, M. Helliwell, A. J. Gaunt, I. May, S. D. Reilly, B. L. Scott, R. D. McDonald, O. A. Valenzula, C. J. Jones and M. J. Sarsfield, "Probing the 5*f* electrons in a plutonyl(VI) cluster complex," *submitted for publication, Chem. Commun.*

Session 8 – Actinide II

Actinide Transition-Metal Chalcogenides and Pnictides

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Overall research goals: The syntheses of new metal chalcogenides and pnictides of U and Np, the determination of their crystal structures, the measurement of their physical properties, and the development of theoretical insights into these properties.

Significant achievements during 2007-2009: We have made significant progress in addition to the results reported in the Publications below.

1. We have synthesized the isostructural compounds UCuOP and NpCuOP and determined their structure (Fig.1). UCuOP displays antiferromagnetic ordering at 222 K with no evidence of previously proposed spin canting The electrical resistivities of single crystals of UCuOP and NpCiOP differ markedly (Fig.2). The resistivity maximum displayed by UCuOP is often seen in antiferromagnetic compounds where the ordered magnetic unit cell is larger than the crystallographic unit cell. DFT computational studies of a 2x2x2 supercell for both compounds indicate ordering of neighboring actinide sheets in an antiferromagnetic + + − − manner for UCuOP and complex ferromagnetic ordering for NpCuOP. The density of state analysis for both compounds shows increased covalent interactions between the AnO and CuP layers of the structure and dominant contributions from 5*f*-actinide orbitals at the Fermi level.

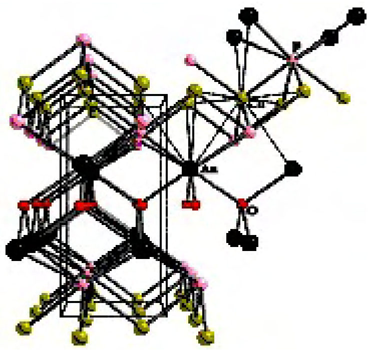

Fig. 1 The structure of *An*CuOP.(*An* = U. Np)

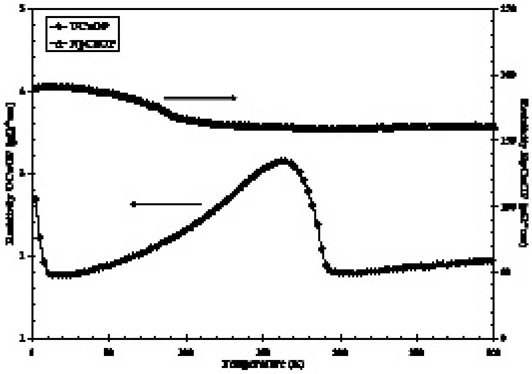

Fig. 2. Electrical resistivities of AnCuOP

2. The compound $La_2U_2Se_9$ has been synthesized and characterized structurally (Fig.3). It appears to be the first mixed lanthanide/actinide chalcogenide with ordered metal sites

3. Among several Np compounds we have synthesized are Np_3Q_5, NpOS, NpOSe, $Np(PS_4)$, and $Np(PO_4)$. The last compound appears to be a genuine example of a Np(III) phosphate.

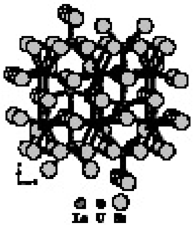

Fig. 3 The structure of $La_2U_2Se_9$.

Science objectives for 2009-2011

Note the caveats: Solid-state syntheses involve frequent failures and occasional surprises. High yields are the exception. It is very difficult to separate mixtures of Np-containing single crystals.

- Measure the magnetic susceptibility of NpCuOP.
- “126" phases: $Rb_{0.85}U_{1.77}S_6$, RbU_2Se_6, KNp_2Se_6, and $CsNp_2Se_6$ have been synthesized and characterized structurally. Re-synthesize KTh_2Se_6 to determine a better structure.
- “1113" phases: $A\mathrm{AuU}Q_3$ (A = Rb, Cs; Q = Se, Te), KCuNpS3, KAgNpS3, CsCuNpS3, CsAgNpS3. Collect magnetic data on $RbAuUSe_3$. Carry out DFT calculations on a 1113 supercell so that magnetization within the layers is not constrained (see Reference 4 below).
- Develop rational, high-yield syntheses of $La_2U_2Se_9$ and $Ba_8Hg_3U_3S_{18}$ to determine magnetic properties and possibly obtain XANES data (ANL) because the formal oxidation state of U is in doubt in both compounds.
- $A_6Cu_{12}U_2S_{15}$ (A = K, Rb, Cs). Measure electrical conductivities. Finish a friendly duel with Kanatzidis as to whether these compounds contain U(V) (mk) or U(VI) (jai).
- Carry out magnetic measurements on the Np chalcogenides and pnictides we have synthesized.
- Continue the search for new $An/M/T$ and $An/T/Q$ compounds (An = U or Np; M = transition metal; T = As, Sb, or Bi). Make physical-property measurements, possibly including thermopower.

.

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Selective Recognition of Heavy Elements by Protein-Based Reagents

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Overall research goals: The objective of this project is to develop protein-based reagents that can selectively bind heavy elements in aqueous solutions. We hope to eventually design and evolve proteins that can bind individual actinide ion tightly and selectively.

Significant achievements during 2007-2009: We have made breakthroughs in engineering a protein that selectively recognizes UO_2^{2+}. We are also designing small proteins that can selectively recognize actinides. These are two major directions we are currently pursuing:

1. The first uranyl-selective DNA-binding protein is designed and engineered using the *E. coli* nickel(II)-responsive NikR as the template (Figure 1). The resulting NikR' protein binds uranyl with a dissociate constant K_d = 53 nM and selectively binds to DNA in the presence of uranyl. The coordination geometry was characterized by uranium L_3 edge EXAFS.

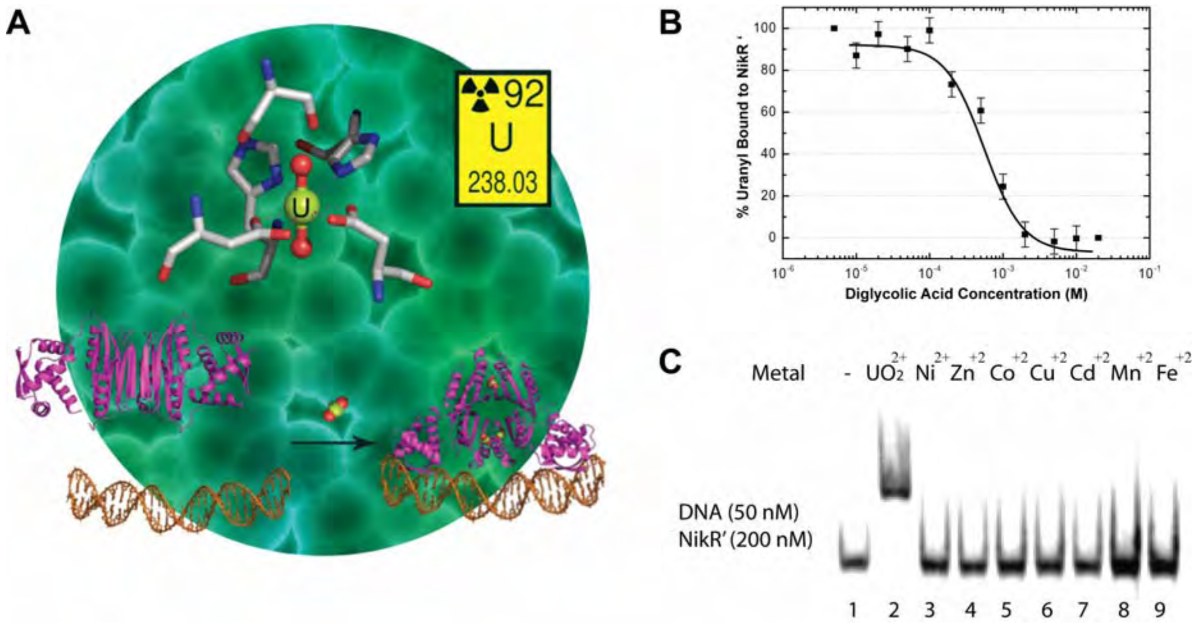

Figure 1. (A) NikR' selective responds to uranyl. (B) K_d measurement obtained from competition of uranyl binding to NikR' and diglycolic acid. (C) NikR' binds promoter DNA in the presence of uranyl.

2. Engineering actinide binding small proteins. Previous work from Barbara Imperiali (MIT) and others have led to design and preparation of lanthanide-binding tags that are small proteins which selectively bind lanthanide ions with high affinities (Figure 2A). We have started redesigning these small peptides with nitrogen- and sulfur-based ligands. Pre-organization of these ligands by the peptide scaffold provides actinide binding affinity. We plan to systematically screen ligand types and geometries to achieve selective binding of actinides over lanthanides. These pre-organized ligand templates provide ideal systems to study the long stranding questions of how to separate actinides from lanthanides. We have synthesized several such peptides and binding experiments are

currently ongoing. More peptides will be prepared and evaluated and structures of these miniature proteins will be characterized.

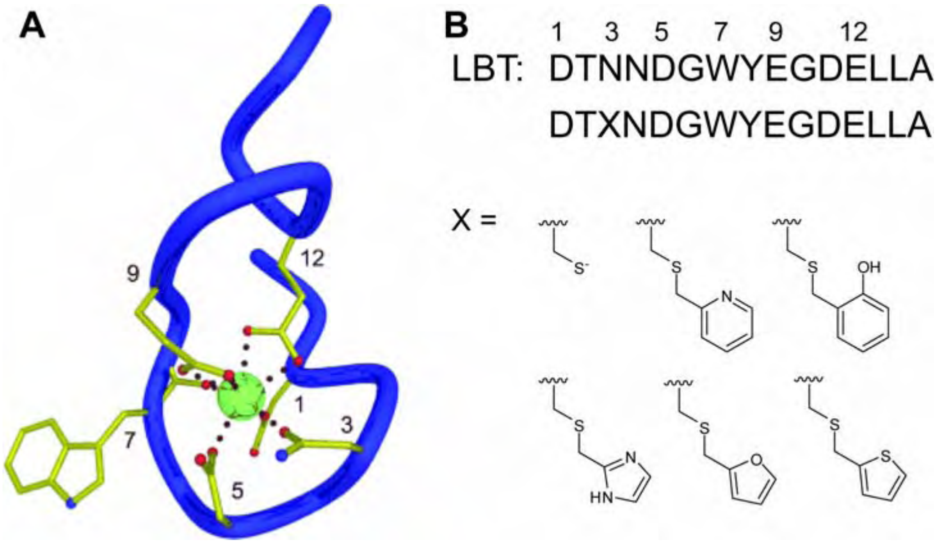

Figure 2. (A) The structure of a lanthanide-binding tag (LBT) with a bound Tb^{3+} (adopted from *Angew. Chem. Int. Ed.* **2004**, *42*, 3682). (B) Newly designed and synthesized peptides for selective actinide binding.

Science objectives for 2009-2011:

- Enhance the affinity of NikR' to uranyl to achieve potential uranyl sensing inside *E. coli*.
- Determine binding constants of the modified LBTs to actinide and lanthanide ions. Further design and prepare other LBTs with additional nitrogen- or sulfur-based ligands.
- Structurally and spectroscopically characterize these actinide-binding proteins.

Publications supported by this project 2007-2009

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The Nature of the Multiple Bonds in Cp’$_2$UO and Cp’$_2$UNMe: Experimental and Calculational Results

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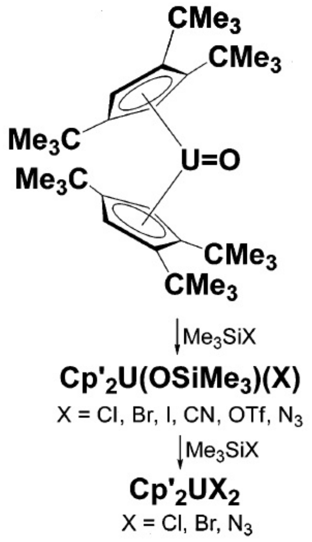
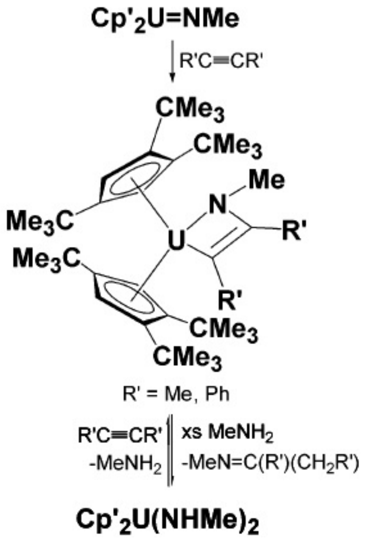
Overall research goals: The focus of my research program is to prepare molecular organometallic compounds of the f-block metals that change the way the chemical community thinks about these elements and their compounds. The strategy is to study the chemical and physical properties of the molecules with the long term goal of providing an answer to the vexing question about the role the electons in f and d orbitals play in their properties.

Significant achievements during 2007-2009: In two publications in 2005, we outlined the synthesis and reactions of two important metallocene derivatives of uranium (IV), Cp’$_2$UO(py) and Cp’$_2$UNMe, where the Cp’ is the 1,2,4-tri-t-butylcyclopentadienyl ligand.





These metallocene derivatives are monomeric and soluble in hydrocarbon solution and they contain the isoelectronic functional groups O and NMe. These two groups are sterically similar and the bonds to the Cp’$_2$U fragment are generally written as double bonds: Cp’$_2$U=O and Cp’$_2$U=NMe. The chemical reactions of these metallocene derivatives provide the results from which a bond model is developed on the nature of the multiple bonds in these compounds, which may have utility in understanding the multiple bonds in the 5f-block metals in general.

As shown in the Figure, the reactivity between these two metallocene derivatives is dramatically different. Thus, Cp'$_2$UO reacts with Me_3SiX but not with acetylenes, whereas the reactions of Cp'$_2$UNMe are exactly opposite; it reacts with acetylenes but not with Me_3SiX.

DFT calculations show that the reactions of Cp'$_2$UO with MeC≡CMe is endoergic in agreement with experiment. In contrast, the reaction of Cp'$_2$UNMe with MeC≡CMe is exoergic and proceeds with a low activation barrier. The origin of the thermodynamic difference is the nature of the UO and UNMe bonds in their initial and final states. The U-O bond is a σ bond that is created from an oxygen 2p orbital (80%) and a U orbital (20%) that is largely 5f in character with about 8% 6d character. The other electrons on oxygen are lone pairs that are essentially non-bonding, as they transfer only 0.2e to the uranium, resulting in a strongly polarized U^+-O^- σ bond. The UNMe bond, on the other hand, is constructed from a σ and π bond; the σ bond is 51% N 2p and 49% U (97% 5f) and the π bond is 80% N 2p and 20% U (78% 5f). The lone pair on N is 62% s-character and it can interact with an empty orbital on U. These calculational studies rationalize the contrasting behavior of Cp'$_2$UO and Cp'$_2$UNMe with acetylenes: the π bond in Cp'$_2$U=NMe can participate in the cycloaddition reaction whereas the lone pairs in Cp'$_2U^+$-O^- cannot.

Additional calculational results on the nature of the bond between CO and Cp'$_3$U in the adduct Cp'$_3$U(CO) show that the electrons used to backbond to CO originate from the U-Cp' bonding molecular orbitals of π symmetry.

Science objectives for 2009-2011

- Prepare for publication the magnetic, XANES, and calculational studies on $(C_5Me_5)Yb(Me_2bipy)$ that show multi-configurational ground states and open shell singlet configuration.
- Explore the equilibrium reaction between Cp'$_3$U(L) and L' by experimental and calculational studies.
- Begin a systematic study of the magnetic properties of Cp'$_2$U(bipy) and related compounds.

Publications supported by this project 2007-2009

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Structural, Optical, and Chemical Properties of Actinide Polynuclear Complexes

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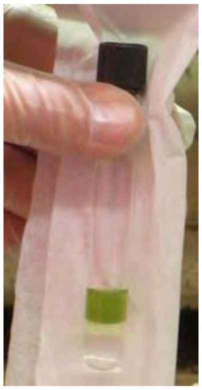
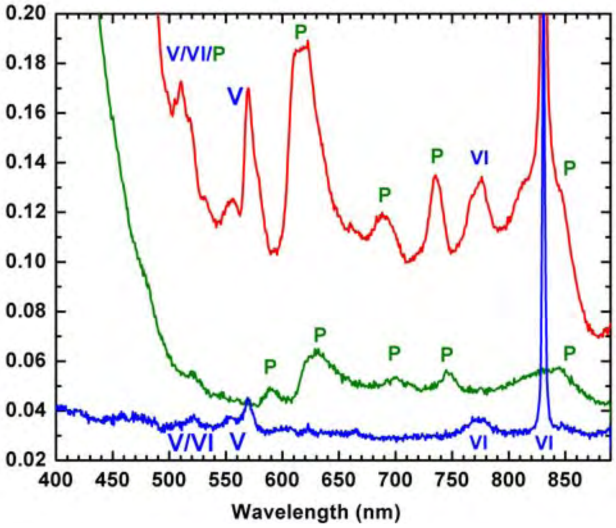
Overall research goals: Our research focuses on the structural chemistry of tetravalent actinide ion hydrolysis in the solid state. A hierarchy of these complexes builds through the aqua complexes of the ions through successive hydrolytic products and ending in large polynuclear molecular clusters. The goal of this research is to understand the role that the periodicity imposed by the actinide contraction has on the resulting chemical and structural properties of actinide ion hydrolysis.

Significant achievements during 2007-2009: Synthetic efforts in the study of tetravalent actinide ion hydrolysis building upon our previous studies with thorium and our collaboration with Professor Burns at the University of Notre Dame have provided significant new insight into the chemical properties of actinide polynuclear complexes resulting from hydrolytic reactions. The structural characterization of nanoscale plutonium oxide clusters with the formula $Li_{14}(H_2O)_x[Pu_{38}O_{56}Cl_{54}(H_2O)_8]$, resulting from the slow hydrolytic condensation of Pu(IV) demonstrated that the hydrolysis of plutonium occurs via an oxolation type reaction in contrast to the multitude of hydroxo-bridged complexes previously isolated for thorium.

Experimentation with the solution chemistry of these plutonium clusters demonstrated that the optical spectra of the clusters, when dissolved directly in water had a one-to-one correspondence with the well known optical spectrum for plutonium polymer. It was subsequently determined that the properties of the optical spectrum were dependent upon the acidity and ionic strength of the supporting electrolyte. Recrystallization of the nanoclusters from these modified solutions provided the same plutonium oxide core, $[Pu_{38}O_{56}]^{40+}$, but with a different surface anion stoichiometry resulting in a different charge to the cluster isolated in the solid state.





The changing optical properties and the different anion stoichiometries found on the surface of the clusters suggests that the surface of the clusters, and by extension the surface of plutonium polymer is reactive, and that the anions populating the surface are labile. Such chemistry has been alluded to in previous studies of plutonium polymer resulting from nitrate solutions where flocculation and aggregation of the polymer was demonstrated to be highly dependent not on acidity but on the ionic strength of the background electrolyte.

Exploiting these observations of surface reactivity has resulted in the demonstration of a selective solvent extraction method targeting these clusters. The observation that the surfaces of these clusters are reactive suggests that the proper selection of anion may be used to probe the chemical properties of the surface towards an understanding of the surface acidity, reactivity, and the underlying role the cluster terminating anions have on the underlying electronic properties of these cluster complexes.

Science objectives for 2009-2011:

- Extend our studies of tetravalent actinide ion hydrolysis to include U(IV) and Np(IV) in order to reveal the chemical effects of periodicity across the early actinide series as it relates to their hydrolysis chemistry.
- Continue our studies of the plutonium polynuclear complexes and the role of anion chemistry on the ultimate size, stoichiometry, and electronic properties of the resulting cluster complexes.
- Exploit our newly developed solvent extraction method in order to quantify, thermodynamically, the interactions of ligands at the surfaces of these nanoclusters.

Publications supported by this project 2007-2009

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2. Richard E. Wilson, S. Skanthakumar, Karah Knope, Christopher Cahill, and L. Soderholm. *A Thorium Sulfate Hydrate with 11.5 Å Framework Voids. Inorganic Chemistry*. 47(20) 9321-9326, 2008.

3. L. Soderholm, P. M. Almond, S. Skanthakumar, Richard E. Wilson, Peter C. Burns. *The structure of a Pu-38 oxide nanocluster. Angewandte Chemie Int. Ed.* 47 298-302, (2008).(VIP Article and Frontispiece)

4. R. E. Wilson, S. Skanthakumar, P. C. Burns, L. Soderholm. *Structure of the homoleptic thorium(IV) aqua ion:* $[Th(H_2O)_{10}]Br_4$. *Angewandte Chemie Int. Ed..* 46, 8043-8045, (2007).

5. Richard E. Wilson, S. Skanthakumar, Ginger Sigmon, Peter C. Burns, L. Soderholm. *Structures of Dimeric Hydrolysis Products of Thorium. Inorganic Chemistry* 46(7) 2368-2372. (**Cover Article)**

6. Richard E. Wilson, S. Skanthakumar, L. Soderholm. *The structures of polynuclear Th(IV) hydrolysis products.* in *Actinides 2006 – Basic Science, Applications and Technology,* ed. K.J.M.. Blobaum, E. Chandler, L. Havela, M.B. Maple, M. Neu., Materials Research Society Proceedings. 986 (2007).

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 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 2007-2009: 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. Richard A. Ferrieri 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 BNL Center for Translational Imaging, the National Synchrotron Light Source, Memorial Sloan-Kettering Cancer Center, and the Nuclear Structure Laboratory at SUNY-Stony Brook.

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

A Symposium to recognize the 25th Anniversary of the Summer Schools was held during the 236th National Meeting of the American Chemical Society in Philadelphia, PA August 17-21, 2008. Frank Kinard, Professor at the College of Charleston and principal lecturer at the SJSU, organized the 1.5 day symposium. The program included talks from 27 alumni of the Summer Schools.

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

	Class of 2007	Class of 2008	Class of 2009
Gender (male/female)	14/10	16/7	12/12
Average GPA (maximum 4.00)	3.78	3.63	3.76
College Type (small college/research university)	15/9	13/10	10/14
Undergraduate Major			
Chemistry	17	17	19
Physics	1	1	1
Dual Chemistry/Physics	2	0	1
Chemical/Nuclear Engineering	1	4	2
Biochemistry/Biophysics	3	1	1
Completed Applications	61	55	80

The Nuclear and Radiochemistry Summer School program and its alumni were also highlighted in the September 8, 2008 issue of Chemical & Engineering News:

http://pubs.acs.org/cen/education/86/8636education4.html

The article focused on nuclear science education, the need to train the next generation of nuclear and radiochemists, and the role of the Summer Schools program in identifying future contributors to the field.

Program objectives for 2009-2011:

- 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 recruit materials to a broad undergraduate audience. Efforts this year focused on email distributions to DNCT members, reference writers for former Summer School applicants, chemistry department administrators, and ACS student affiliate chapters and advisors. Announcements of the program have also been distributed to undergraduate list servers and the ACS newsletter “FANmail”. 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 now is posted on the Summer Schools website. The students who attend the 2009 Summer Schools and 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.
- Improve the Summer Schools website. The website serves as the first “point of contact” for interested students. The goal is to make navigation to and through the site more manageable for potential applicants, and to highlight the successes of the program.

Publications supported by this project 2007-2009

None to report.

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*****The page number in **bold** font is the abstract of the presentation (in session indicated) by this participant, while other page numbers refer to collaborations with this participant cited by other PIs.