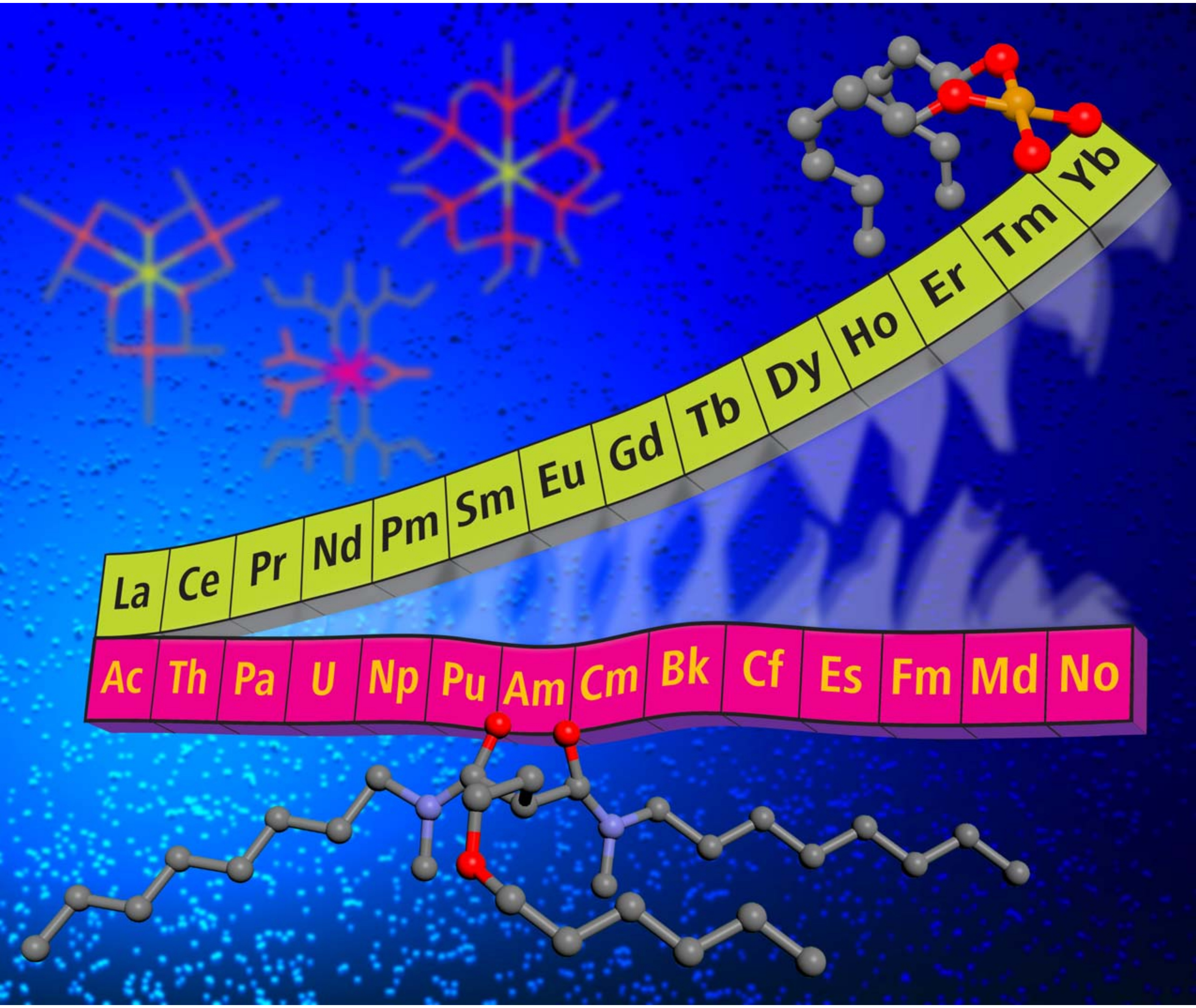
Program and Abstracts

Separations Program
Heavy Element Chemistry Program
Contractors' Meeting

O'Callaghan Annapolis Hotel, Annapolis, MD April 24-27, 2007



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

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Cover Graphics:
The cover artwork is a metaphor of DMDOHEMA dragging down Am^{3+} into the organic layer, while HDHP tugs at Yb^{3+}. The "teeth" illustrate a stretched "adhesive," a metaphor for the difficulty in separating 4f from 5f trivalent ions. For more detail see abstract P1-2, Mark R. Antonio, "Structural Chemistry of Lanthanide and Americium Complexes in Solvent Extraction," p 25. Image reproduced by permission of Mark R. Antonio and The Royal Society of Chemistry from Benoît Gannaz, Mark R. Antonio, Renato Chiarizia, Clément Hill and Gérard Cote, Dalton Trans., 2006, 4553, DOI: 10.1039/b609492a.

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Foreword

This abstract booklet provides a record of the seventh U.S. Department of Energy contractors' meeting in separations sciences and the fourth in heavy element chemistry. The Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences and its predecessors have sponsored research in heavy element chemistry and separations sciences for 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 third 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 keynote talks, oral presentations, and posters, organized so that papers in related disciplines – such as ligand design, theory and bonding, and interfacial science – 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 have the privilege of organizing this joint meeting and 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 hope that all of you will build on your successes and that we will assemble in a very few years for our next joint meeting.

We thank Diane Marceau of the Chemical Sciences, Geosciences and Biosciences Division, and Sophia Kitts and Lois Irwin 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
Larry A. Rahn
Lester R. Morss
Norman Edelstein

DOE Heavy Element Chemistry-Separations Contractors' Meeting
O'Callaghan Annapolis Hotel, Annapolis, MD April 24-27, 2007
Agenda

Tuesday, April 24 2007

5:00 – 6:30	p.m.		Registration
6:30 – 7:30			Dinner

Session 1 – Coordination Chemistry - Richard Bartsch, Chair

7:30 – 7:45	p.m.		Welcome – Lester Morss and Bill Millman
7:45 – 8:10		CC-1	Bruce Moyer - Principles of Chemical Recognition and Transport in Extractive Separations: Liquid-liquid separations of anions
8:10 – 8:35		CC-2	Heino Nitsche - Chemistry of the Heaviest Elements
8:35 – 9:00		CC-3	Jaqueline Kiplinger - Tuning Metal-Ligand Bonding Interactions and Novel Reactivity Patterns in Organometallic Actinide Complexes

Wednesday April 25

7:30 – 8:10	a.m.		Continental Breakfast

Session 2 – Coordination Chemistry - Lynda Soderholm, Chair

8:10 – 8:15	a.m.		Introduction of Invited Speaker
8:15 – 9:00		CC-4	Invited speaker - Tobin Marks - Invention of Highly Selective Organo-f-Element Centered Catalytic Transformations
9:00 – 9:25		CC-5	David Clark - Quantifying Covalency in Actinide Metal-ligand Bonds
9:25 – 9:50		CC-6	Iain May - Probing actinide spectroscopic features and structural motifs through polyoxometalate complexation
9:50 – 10:15		CC-7	Jonathan L. Sessler - Actinide Coordination to Expanded Porphyrins
10:15 – 10:45			Break

Session 3 – Electronic Structure & Bonding of Molecules and Complexes -Corwin Booth, Chair

10:45 – 11:10	a.m.	ESM-1	Richard Martin - Electronic Structure Studies of Actinide Complexes
11:10 – 11:35		ESM-2	Guokui Liu - Orbital Hybridization and Ion-Ligand Interactions in f-Element Compounds
11:35 – 12:00	p.m.	ESM-3	Russ Pitzer - Theoretical Treatment of the Electronic Properties of Heavy Element Complexes
12:00 – 12:25		ESM-4	Michael Heaven - Spectroscopic Studies of Prototype Actinide Compounds
12:25 – 1:20			Working Lunch
1:20 – 1:30			Put up posters for Poster Session 1
1:30 – 5:30			Interaction Time
5:30 – 6:00			Poster Previews
6:00 – 7:00			Working Dinner

Session 4 – DOE Update and Poster Session 1

7:00 – 7:25	p.m.		DOE Program updates – John Miller, Lester Morss, Bill Millman
7:25 – 9:25			Poster Session 1 – with no-host bar

P1-1	Spiro D. Alexandratos - A New Approach to the Design of Ion-Selective Polymer-Supported Reagents: Tuning the Selectivity of Primary Ligands with Auxiliary Groups
P1-2	Mark Antonio - Structural Chemistry of Lanthanide and Americium Complexes in Solvent Extraction
P1-3	Dick Bartsch - New Proton-Ionizable, Calixarene-Based Ligands for Selective Metal Ion Separations
P1-4	Radu Custelcean - Principles of Chemical Recognition and Transport in Extractive Separations: Anion Coordination and Separation with Metal-Organic and Hydrogen-Bonded Frameworks
P1-5	Ben Hay - Principles of Chemical Recognition and Transport in Extractive Separations: Molecular Modeling and Design of Anion Receptors
P1-6	Bruce Bursten - Presented by Michael Mrozik: The Electronic Structure of Heavy Element Complexes
P1-7	Sue Clark - Nuclear and Radiochemistry Summer Schools
P1-8	Rod Ewing - Colloid Transport of Plutonium in the Far-field of the Mayak Production Association
P1-9	Richard Wilson - The Structural Chemistry of Actinide Hydrolysis
P1-10	Corwin H. Booth - Effects of self-irradiation on local crystal structure and 5f localization in $PuCoGa_5$
P1-11	Linfeng Rao - Actinide Solution Chemistry Chemical Thermodynamics and Structure of Actinide Complexes in Solution
P1-12	David Clark - Plutonium in Higher Oxidation States in Alkaline Media
P1-13	Robert T. Paine - Preorganized and Immobilized Ligands for Metal Ion Separations

Thursday April 26

7:30 – 8:10	a.m.		Continental Breakfast

Session 5 – Actinide Compounds – John Gibson, Chair

8:10 – 8:15	a.m.		Introduction of Invited Speaker
8:15 – 9:00		AC-1	Invited speaker – Rod Ewing - Nuclear Waste Forms for Actinides: Design & Selection
9:00 – 9:25		AC-2	Chris Cahill - Hydrothermal chemistry of UO_2^{n+} phases: Formation and stabilization of pentavalent uranium compounds
9:25 – 9:50		AC-3	Peter Dorhout - A Study of New Actinide Zintl Ion Materials
9:50 – 10:15		AC-4	S. Skanthakumar - Understanding the Magnetic Behavior of Actinide Compounds
10:15 – 10:45			Break

Session 6 – Electronic Structure and Bonding of Interfaces and Solids – Sheng Dai, Chair

10:45 – 11:10	a.m.	ESI-1	David Shuh - Soft X-ray Synchrotron Radiation Investigations of Actinide Materials
11:10 – 11:35		ESI-2	Dick Haire - Probing the Changing Role of the5f Electrons through Experiments and Theory
11:35 – 12:00	p.m.	ESI-3	De-en Jiang - Computational Studies of Novel Separation Media
12:00 – 12:25	.	ESI-4	Gus Scuseria - Covalency surprises in the actinide dioxides
12:25 – 1:20			Working Lunch
1:20 – 1:30			Take down Session 1 posters, Put up Session 2 posters
1:30 – 5:30			Interaction Time
5:30 – 6:00			Poster Previews

6:00 – 7:00 Working Dinner

Session 7 – Poster Session 2

7:00 – 9:00 p.m. Poster Session 2 – with no-host bar

P2-1 Sheng Dai - Fundamental Studies of Novel Separations
P2-2 Jeff Davis - Self-assembled Ionophores: New Directions
P2-3 Mark Dietz - Neoteric Solvent Systems for Metal Ion Separations
P2-4 Renato Chiarizia - Third Phase Phenomena in Solvent Extraction
P2-5 Lynda Soderholm - The Correspondence between Solution and Solid-State Structures
P2-6 John Gibson - Gas-Phase Actinide Ion Chemistry Elucidates Fundamental Aspects of f-Element Science
P2-7 Tom Albrecht-Schmitt - Critical Role of Water Content in the Formation and Reactivity of Uranium, Neptunium, and Plutonium Iodates Under Hydrothermal Conditions
P2-8 Dick Haire - Reduction of Actinides in Higher Oxidation States by Hydroquinone-Enriched Humic Derivatives
P2-9 Rod Ewing - Stability of Uranium-(VI) Peroxide Hydrates under Ionizing Radiation
P2-10 Jim Ibers - Actinide Transition-Metal Chalcogenides and Pnictides
P2-11 Steven Conradson - Intrinsic Nanoscience: Nanoscale Heterogeneity and Collective Properties of Complex Materials
P2-12 Asok Ray - A Fully Relativistic Density Functional Study of the Role of 5f Electrons in Chemical Bonding in Transuranium Elements
P2-13 Abraham Clearfield - Synthesis and Characterization of New Families of Inorganic-Organic Ion Exchangers

Friday April 27

7:30 – 8:10 a.m. Continental Breakfast

Session 8 – Complexation and Particles – Rod Ewing, Chair

8:10 – 8:35 a.m. CP-1 Greg Choppin - Research in Actinide Chemistry
8:35 – 9:00 a.m. CP-2 Wibe de Jong - Influence of Solution Phase and Interfacial Structure on the Stability of Actinide Oxidation States: A Computational Chemistry Approach
9:00 – 9:25 CP-3 Don Baer - Reaction Specificity of Nanoparticles in Solution
9:25 – 9:50 CP-4 You Qiang - Monodispersive Iron-Iron Oxide Core-Shell Nanoparticles for Environmental Applications
9:50 – 10:15 CP-5 Sue Clark - Interaction of Fission Product and Transuranium Cations with U(VI) Mineral Phases

10:15 – 10:30 Break

Session 9 – Close Out Session –Lester Morss and Bill Millman, Chairs

10:30 – 12:00 Presentation of program summaries and discussion

12:00 – 1:00 p.m. Working Lunch – box lunch for those who have to leave early

1:00 – 3:00 Open Discussion and take down posters

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Session 5 – Actinide Compounds – John Gibson, Chair

Session 6 – Electronic Structure and Bonding of Interfaces and Solids – Sheng Dai, Chair

Session 7 – Poster Session 2

Session 8 – Complexation and Particles – Rod Ewing, Chair

Principles of Chemical Recognition and Transport in Extractive Separations
Liquid-liquid separations of anions

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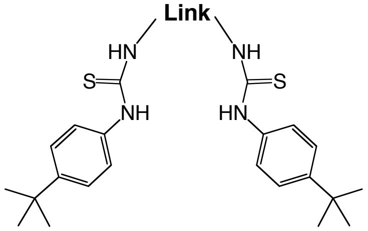
Co-PIs: Peter V. Bonnesen, Radu Custelcean, Laetitia H. Delmau, Benjamin P. Hay, Oak Ridge National Laboratory, Oak Ridge, TN 37831

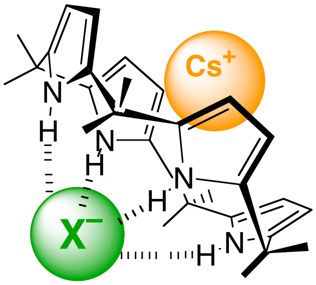
Collaborators: Jonathan L. Sessler, Dept. of Chemistry and Biochemistry, Univ. of Texas, 1 Universtity Station A5300, Austin, TX 78712. Kristin Bowman-James, Dept. of Chemistry and Biochemistry, Univ. of Kansas, Lawrence, KS 66045

Overall research goals: The overarching scientific goal of the program pertains to the central question of selectivity in chemical separations and whether it can be achieved by a molecular-design approach incorporating the principles of ion recognition and transport by novel receptors and extractive materials. Toward elucidating this question, we are proceeding along three lines: *1. Design: How can theoretical methods be employed to arrange hydrogen-bonding (H-bonding) or other donor groups in space within accessible molecular architectures to effect selective binding of target anions? 2. Functionality: Can functionality be incorporated into such structures to harness the selective binding, effecting the extraction of a target anion from competing species? 3. Self-assembly: Can supramolecular structures be assembled from simple molecular building blocks to bind and separate target anions?* This presentation will focus on the second line of investigation dealing with anion binding in liquid-liquid extraction.



Significant achievements in 2005-2007: The linker in bisthiourea tweezers was found to have a definite effect on anion binding, indicating the importance of structural organization of H-bond donor groups. Eleven bisthiourea tweezers and several monothiourea controls were synthesized by the general method of reacting 4-*t*-butylphenyl isothiocyanate with the appropriate amine. Extraction surveys with chloroform solutions established (a) greater extraction of *p*-toluate and tosylate by the tweezers vs their monothiourea controls by factors of up to 58 and 13, respectively, indicating likely bidentate binding by at least some of the tweezers; (b) an influence of the structure of the linker in the tweezers; and (c) an effect of the terminating group. Distribution results using nitrobenzene as a diluent indicated exclusive formation of the anionic complexes $[RX]^-$ and $[R_2X]^-$ in the organic phase, as confirmed by ES-MS. Selectivity followed the expected attenuation of Hofmeister bias with minor perturbation for NO_3^- and Br^-. Divalent anions partially ion pair to monoanionic species in the organic phase.

In collaboration with the Univ. of Kansas and the Univ. of Texas at Austin, we initiated an effort to understand the synergistic effect of added neutral anion receptors on the selectivity of liquid-liquid anion exchange. As expected, the normal Hofmeister selectivity of anion exchange by highly lipophilic long-chain quaternary ammonium salts was perturbed by the binding selectivity of added lipophilic anion receptors. The latter included macrocyclic amides and calixpyrroles. Equilibrium modeling calculations confirmed our hypothesis that the extraction behavior can be explained by the competitive binding behavior of the added receptor toward the two anions in the system.



Extraction data were shown to be consistent with a remarkable binding of Cs halide ion pairs by *meso*-octamethylcalix[4]pyrrole (OMP). In collaboration with the Sessler group, we had puzzled over the exceptionally strong ion-pairing of CsCl and CsBr when extracted by OMP into nitrobenzene. This behavior led us to hypothesize that halide binding organizes OMP into a bowl-shaped, electron-rich Cs^+ receptor, which X-ray crystallography confirmed in the solid state. Analysis of extraction data confirmed the formation of a 1:1:1 Cs(OMP)X complex in solution. The standard Gibbs energies for Cl^- and Br^- binding by free OMP are respectively -20.9 ± 0.1 and –13.9 ± 0.2 kJ/mol. The ion-pairing Gibbs energies between the two OMP-halide complexes and the Cs^+ cation are unusually large and comparable (–29.5 ± 1 kJ/mol). ^{1}H NMR behavior in a variety of solvents was consistent with inclusion of the Cs^+ cation in the complex cavity.

Science objectives for 2007–2009:

- Understand the effect of architecture of multidentate thioureas on anion binding
- Generate candidate tris- and tetrakis(thiourea) anion receptors using HostDesigner, synthsize accessible candidates, and determine thermodynamics of anion extraction
- Investigate question of charge complementarity in mixed anion receptors containing both neutral thiourea and guanidinium H-bond donors

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Chemistry of the Heaviest Elements

Heino Nitsche[1,2], Ken E. Gregorich[2], Darleane C. Hoffman[1,2], Principal Investigators
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Prof. Andy Türler, Technical University Munich, Germany;
Dr. Matthias Schädel , GSI, Darmstadt, Germany;
Prof. Gunnar Skarnemark, Chalmers University, Gothenborg, Sweden.

Overall research goals: Study of the chemical properties of the elements is the most fundamental goal in Chemistry. Our studies of the chemical properties of the transactinide elements (Z=104-108) are unique within the US. We have recently pioneered the use of the Berkeley Gas-filled Separator as a pre-separator for chemical studies, providing an important new resource for the study of superheavy element chemical properties.

Significant achievements in 2004-2006:

Development of selective liquid-liquid extraction systems for Rf (Z=104) and Db (Z=105).

The use of the Berkeley Gas-filled Separator as a preseparator for heavy element chemical studies allows much greater flexibility in the choice of chemical systems for studies of transcatinide elements. This is because the requirement for the chemical system to remove all interfering activities is relaxed, allowing the choice of chemical systems targeted specifically at the chemical properties of interest. In preparation for experiments with rutherfordium (Z=104), we have been measuring the liquid-liquid extraction properties of its homologs, Zr and Hf into crown ethers. We have determined 1) that the metal ions are extracted into the organic phase by forming an ion association complex with the hydronium ion of the crown ether, 2) that the associated equilibria are fast enough for Rf studies, and 3) that we can control the extraction yields by choice of crown ether and acid concentrations.

In the SISAK automated liquid-liquid extraction system used with the BGS to study the extraction of Rf (element 104) isotopes, the contact time between the organic and aqueous phases is relatively short. In the near future, we plan to extend these liquid-liquid extraction experiments to the study of Db (element 105) isotopes. Being in group 5 of the periodic table, Db should have chemical properties similar to Nb and Ta. The aqueous phase chemical properties of these group-5 elements is quite complex because of extreme tendencies to complexation and hydrolysis. We have undertaken exploratory liquid-liquid extraction studies of the Nb and Ta homologs, in search of a suitable extraction system with fast enough kinetics for use in the SISAK system. So far, extraction of Zr and Ta from acidic solutions into bis 2-ethylhexyl phosphoric acid (HDEHP) has been studied. While this system shows an interesting selectivity between Nb and Ta, the extraction kinetics are relatively slow.

Production of long-lived transactinide isotopes with ^{244}Pu targets

Use of ^{244}Pu targets will allow access to isotopes of elements 104-108 with half lives long enough for chemical separations. In addition, if claims of superheavy element production are confirmed, these radioactive targets should allow study of chemical properties up to element 114. Work is progressing on facilities and safety apparatus for use of radioactive ^{242}Pu, ^{244}Pu and possibly ^{248}Cm targets in the Berkeley Gas-filled Separator. To date, a rotating wheel apparatus has been designed, built and tested. Work is progressing on techniques for electroplating large-area Pu targets, and design work for containment enclosures at the BGS is in progress.

Science objectives for 2007-2008:

Production of long-lived transactinide isotopes with ^{244}Pu targets.

A ^{244}Pu target wheel for use in the Berkeley Gas-filled Separator is being built. With appropriate radioactivity containment controls, this target will be used to produce heavy element isotopes for chemical studies. Because of the neutron excess of the ^{244}Pu isotope, heavy element isotopes with relatively long half-lives will be accessible. Based on the cross section systematics from the series of experiments with ^{238}U targets, we anticipate production rates of isotopes of elements from Rf(Z=104) through Hs(Z=108) to be high enough for chemical studies.

Superheavy element search with ^{244}Pu targets.

The claims of superheavy element production with Z >112 by the Dubna Gas-Filled Separator group remain unconfirmed after more than six years. However, these reports are important enough to warrant further confirmation attempts. The ^{244}Pu target will be used with 48Ca beams in a search for superheavy element production in the ^{244}Pu(^{48}Ca,xn)292-x114 reaction. This reaction has been reported to result in the largest superheavy element cross sections. The high beam intensities available at the 88-Inch Cyclotron, together with the highly efficient and selective Berkeley Gas-filled Separator, result in the best facility, worldwide, for such a confirmation attempt.

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Tuning Metal-Ligand Bonding Interactions and Novel Reactivity Patterns in Organometallic Actinide Complexes

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D. E. Morris and P. J. Hay, Co-Principal Investigators
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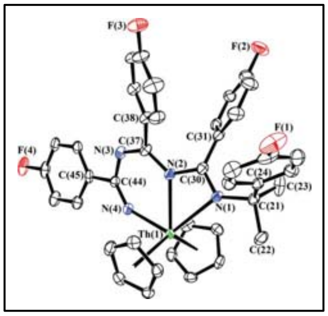
Collaborators: P. B. Duval (U Missouri, Columbia), P. P. Power (UC Davis), B. E. Bursten (U Tennessee), W. W. Lukens (LBNL), J. C. Green (Oxford U.)

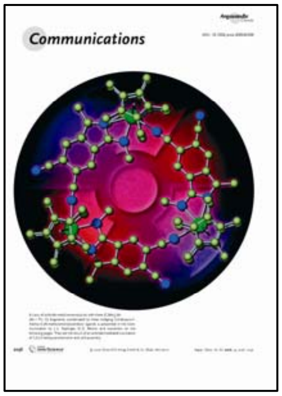
Overall Research Goals: This project explores the existence and manifestations of covalent metal-ligand bonding, including the generation and investigation of actinide-ligand multiple bonds, in complexes of uranium and other light actinides over a broad range of ligand sets and structure types through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

Significant Achievements in 2005-2007:

Actinide-Mediated Nitrile Coupling Reactions. Actinide molecular chemistry continues to generate a variety of novel structural motifs that demonstrate unusual and fascinating reactivity patterns, including activation and coupling of small molecules. Recently, we reported that benzonitrile inserts into the actinide-carbon bonds in complexes of the type $(C_5Me_5)_2AnR_2$ to afford bis(ketimide) complexes $(C_5Me_5)_2An[-N{=}C(Ph)(R)]_2$ (where An = Th, U; R = CH_3, CH_2Ph, Ph), exhibiting physicochemical properties consistent with enhanced covalency in the actinide-ketimide linkages. We have extended this chemistry to include fluorinated nitriles in an effort to tune the relative energies of the metal 5f- and 6d-orbitals by varying the electronic profile of the ketimide ligands. In this work, a new thorium-mediated reaction sequence was discovered involving the coupling of four equivalents of 4-fluorobenzonitrile to yield an unusual eight-membered Th(IV) tetraazametallacycle shown in the Figure. The tetraazamacrocycle is produced by sequential metal-mediated coupling of four equivalents of 4-fluorobenzonitrile; its formation is consistent with the involvement of an imido intermediate, generated from a thorium ketimide complex.

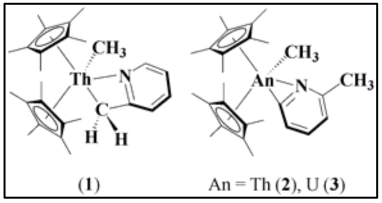


Synthesis and Characterization of Trinuclear Thorium and Uranium Macrocycles. We discovered a new class of actinide metallomacrocycles in which three $(C_5Me_5)_2An$ (An = Th, U) fragments are coordinated by three isoindole bridging groups. The tetravalent actinide centers form an uncommon triangular array in the products obtained through an unprecedented actinide-mediated cyclization of 1,2,4,5-tetracyanobenzene and subsequent self-assembly. Actinide metal centers are uncommon as building blocks in supramolecular multimetallic assemblies due to their flexible and unpredictable coordination behavior, but can clearly support such structures in organometallic chemistry. Metal-metal communication in these systems was ambiguous; electrochemical data are consistent with some interaction, but neither optical nor magnetic data exhibit traditional indications of any significant coupling. Enhanced f-f transition intensities reflect an unusually strong metal-indole interaction in these actinide complexes, which is a likely origin for their formation and a potential springboard for the design of additional new



multimetallic actinide systems tailored for enhanced metal-metal communication. This work was selected by the Editor to be highlighted in the frontispiece at the beginning of the “Communications” section of *Angewandte Chemie*.

C-H Activation of C-H Bond in Pyridine Ring Systems by Organometallic Thorium and Uranium Complexes. We uncovered a remarkably selective hydrocarbon C-H bond activation reaction mediated by 5f-element metal centers. $(C_5Me_5)_2Th(CH_3)_2$ and 2-picoline react to give preferential sp^3 C-H bond activation (to yield **1**) in the presence of a more reactive sp^2 C-H bond (to yield **2**). Transition metal systems demonstrating this sort of unusual selectivity have been shown to involve intermediate alkylidene complexes. Through isotope labeling studies, kinetics, and deuterium isotope effects it was shown that the thorium chemistry occurs by σ-bond metathesis and does not involve an intermediate thorium alkylidene complex. The studies confirmed that **1** is the kinetic product and **2** is the thermodynamic product. This is the opposite of all known C-H σ-bond metathesis reactions. Intriguingly, the analogous uranium complex, $(C_5Me_5)_2U(CH_3)_2$, proceeds through a different mechanism and only reacts with the 2-picoline sp^2 C-H bond, giving $(C_5Me_5)_2U(CH_3)[\eta^2\text{-}(N,C)\text{-}6\text{-}CH_3\text{-}NC_5H_3]$ (**3**) as expected. This observation demonstrates for the first time *different* mechanistic reaction pathways for isostructural uranium and thorium complexes.



(**1**) An = Th (**2**), U (**3**)

We have used density functional theory (DFT) to determine the structures and energies of the products and transition states along the reaction pathways. For the thorium and uranium systems, the relative order of stability for the products sp^2-picolyl (e.g. **2**) < sp^3-picolyl (e.g. **1**) was observed. The sp^3 C-H bond activated species lies 2.8 kcal/mol (Th) and 5.5 kcal/mol (U) higher in energy than the sp^2 C-H bond activated products. These results are in accord with experimental observations. The transitions states were found to have activation energies E_{act} (sp^3) < E_{act} (sp^2) for thorium but with the reverse ordering for uranium.

Specific objectives for 2007-2008:

We will continue our efforts to introduce new members to the family of actinide complexes containing multiply bound ligands (e.g. alkylidenes, alkylidynes, nitrides), either by redox reactions, insertion chemistry, or by ligand transfer methods.

We will pursue the synthesis and investigate the electrochemical and spectroscopic properties of new $(C_5Me_5)_2U(V)$ complexes. This is an exceedingly rare oxidation state for uranium and the chemistry and physical properties of complexes of this metal valence are poorly understood.

We will continue our emission and resonance Raman spectroscopic investigations of actinide metallocene complexes that exhibit molecular-type (e.g., charge-transfer) electronic excited states. The principal target for these studies will be complexes that possess actinide-main group multiple bonds such as oxo and imido complexes. Many such complexes have been prepared previously as part of the LANL BES/HEC effort, but a systematic investigation into their spectral properties was never undertaken. New studies will provide a more fundamental insight into factors governing covalent bonding and the manifestation of such bonding in spectroscopic behavior.

We will employ theoretical tools such as DFT to aid in understanding the bonding, reactivity and spectroscopic properties of organoactinide complexes containing metal-ligand multiple bonds or metal-metal bonds. As the complexes described above are synthesized, we will continue to explore how their chemistry and spectroscopy varies as a function of the ligand electronic properties and the nature of the actinide metal.

INVENTION OF HIGHLY SELECTIVE ORGANO-f-ELEMENT CENTERED CATALYTIC TRANSFORMATIONS

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The lanthanides and actinides offer many intriguing and instructive characteristics for stoichiometric and catalytic transformations, including large and incrementally tunable ionic radii, high electrophilicity, high kinetic lability, predictable and constrained formal oxidation states, polar metal-ligand bonding, built-in paramagnetic probes, relatively high abundance, and relatively low toxicity. This lecture describes recent exploratory synthetic, mechanistic, and thermochemical research aimed at inventing new, unusual, and useful transformations mediated by complexes of these elements. This includes the addition of element-hydrogen bonds to unsaturated hydrocarbons ("hydrofunctionalization") to effect C-N, C-O, C-P, C-Si, and C-B bond forming processes. Our goals are to catalyze and understand highly selective processes involving single additions, cascades of multiple bond fusions, and bond fusions coupled to polymerization processes.

CC-4

Quantifying Covalency in Actinide Metal-ligand Bonds

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Program Scope: 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, optical, and vibrational spectroscopy, coupled with quantum chemical calculations. This represents a new research direction for our program.

Recent Progress: A good deal of debate has centered around covalency arguments for the actinide series, with a common suggestion that low-valent early actinides are expected to display the greatest covalency due more expanded valence orbitals. For the UCl_6^{n-} anions, structural and vibrational data challenge this established dogma. Table 1 compares the U-Cl bond distances and the Raman-active totally symmetric (ν_1, A_{1g}) U-Cl stretching frequencies as a function of oxidation state. From Table 1 it can be seen that as the oxidation state decreases from VI to III, there is a steady increase in U-Cl bond distance from 2.42(1) to 2.81(1) Å, respectively. Since bond length is not always a good measure of bond strength, we also compare the totally symmetric stretching frequencies in Table 1. As with bond length, as the oxidation state decreases from VI to III, we see a steady decrease in ν_1 from 369 to 235 cm^{-1}. Combined, these data clearly indicate that the U-Cl bonds are getting longer and weaker with decreasing oxidation state. The trends in bond length and bond strength clearly suggest that the higher oxidation state metal ion has the greatest covalency, a trend that mirrors that observed elsewhere in the periodic table.

Table 1. Bond length and vibrational frequencies for octahedral UCl_6^{n-} complexes (n = 0, 1, 2, 3).

Compd	Ox. State	R(U-Cl), Å	ν_1(U-Cl), cm^{-1}	Ref
UCl_6	VI	2.42(1)	369	a
UCl_6^-	V	2.513(1)	345	a,b
UCl_6^{2-}	IV	2.626(1)	296	a,b
UCl_6^{3-}	III	2.808(5)	235	b

[a] J. Shamir, *J. Inorg. Nucl. Chem*. **1975**, *37*, 1429, [b] this work

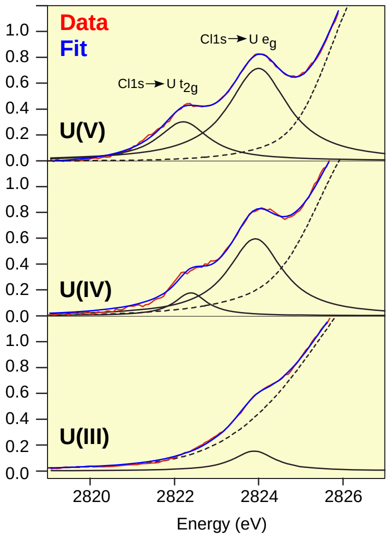

Fig. 1. A comparison of Cl K-edge XAS data on the UCl_6^{n-} series of compounds where the oxidation state varies from U(V) to U(III). Data in red, fit in blue. The Cl 1s transitions are assigned to the U 6d t_{2g} and e_g orbitals, as noted in the figure.

Chlorine K-edge x-ray absorption spectroscopy on UCl_6^{n-} systems indicates that there are covalent interactions between Cl 3*p* and uranium 6*d* orbitals, with no participation from uranium 5*f* orbitals. A comparison of the normalized Cl K-edge spectra for UCl_6^-, UCl_6^{2-}, and UCl_6^{3-} is shown in Fig 1. The UCl_6^{n-} anions show two distinct pre-edge features that show clear differences in intensity as a function of oxidation state, with U(V) > U(IV) > U(III). The decrease in pre-edge intensity reflects a decrease in the covalency of the U-Cl bond as the oxidation state decreases, and ionic radius increases. The relative energy of the rising edge inflection point increases with increasing oxidation state on U, and indicates the overall charge donation by the chloride is greater for U(V), than U(IV), and U(III). Higher charge donation by chloride to U(V) results in a Cl 1s core shift to deeper binding energy.

All published electronic structure calculations for UCl_6 systems indicate that a purely ionic bonding model is an inadequate description of UCl_6, and that appreciable covalency with 6*d* orbitals (t_{tg}, e_g) is present, and only minor interactions are calculated for the 5*f* orbitals (a_{2u}, t_{1u} t_{2u}). The predominant covalent interactions are expected to occur through U-Cl σ- and π-bonding that takes place through t_{2g} and e_g interactions with U 6*d* orbitals. For the Cl K-edge data therefore, we expect bound state transitions from Cl 1s → e_g (σ*) and t_{2g} (π*) orbitals, with the e_g lying highest in energy. Qualitatively, the Cl K-edge data fulfills our expectations, and we assign the lowest energy pre-edge feature to the Cl 1s → t_{2g} (π*) transition, and the higher energy feature to the Cl 1s → e_g (σ*) transition. Since we do not observe any additional features at low energy in these spectra, these data would indicate the absence of 5*f* orbital covalency in these simple chloride systems. Future theoretical analyses will be undertaken over the next review period to assess the validity of this assertion.

The intensity of a ligand pre-edge peak is the intensity of a ligand-centered 1*s*→3*p* transition weighted by the covalent character of the ligand 3*p* orbitals in the antibonding molecular orbitals of primarily 5*f* or 6*d* character. The pre-edge intensities will be proportional to the percent character of ligand *p* contribution to Ψ*. Pre-edge and rising edge features can be modeled by pseudo-Voigt line shapes (1:1 ratio of Lorentzian to Gaussian) and a step function (**Fig 1**). Using D_{2d} Cs_2CuCl_4 as a well-defined reference with 7.5% Cl 3*p* character per Cu-Cl bond, the Cl 3*p* character per U-Cl bond was determined for each of the uranium complexes. For the σ covalency the Cl 3*p* character per U-Cl bond is 34.6, 26.5, and 5.1% for UCl_6^-, UCl_6^{2-} and UCl_6^{3-}, respectively, while π covalency is found to be 8.3, 3.3 and 0%. These preliminary studies, reproduced during two separate experimental runs, using two separate encapsulation approaches, and two different detector types establishes that we can observe pre-edge features in light actinide complexes, that we an extract the percent covalency from these data, and that we can successfully encapsulate actinides for transuranic studies. These and other data comparing octahedral lanthanide and transition metal MCl_6^{n-} ions will be presented.

Science objectives for 2007-2009: Over the next review period we will focus our efforts on three general classes of compounds, chosen for their relative importance in the field of actinide chemistry, their high local symmetry to aid in spectroscopic analysis, and the accessibility of their ligand K-edge XAS at OBES synchrotron light sources. These three general classes include (i) homoleptic octahedral MCl_6^{n-} and $M(SR)_6^{n-}$ complexes of actinide, lanthanide and transition metal ions, (ii) 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, Am), and (iii) metallocene chlorides of general formula Cp_2MCl_2, Cp_2MCl, and Cp_3MCl of light actinides (Th, U, Np, Pu), lanthanides and transition elements. Our research plan is designed to coordinate inorganic synthesis, spectroscopic characterization, and theoretical calculations. For a given class of compounds, we should be able to present data on *f-f* transitions, *d*-orbital ligand interactions, complete vibrational analysis and structural data, all underpinned by a strong theoretical understanding.

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Probing actinide spectroscopic features and structural motifs through polyoxometalate complexation

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Overall research goals: Utilize complexation by polyoxometalate ligands to probe spectroscopic features and structural diversity in actinide chemistry.

Significant achievements prior to 2007: We have been investigating the interaction of heteropolyoxometalate anions with f-element cations. Early achievements included the encapsulation of a trimeric uranyl cationic species, $\{(UO_2)_3(\mu_3\text{-}O)(\mu_2\text{-}H_2O)_3\}^{4+}$, by the anionic phosphotungstate cluster $[P_2W_{15}O_{56}]^{12-}$ and the structural characterization of the neptunyl(V) complex $[Na_2(NpO_2)(PW_9O_{34})_2]^{12-}$. This neptunyl complex represented the first structural transuranic study in the UK for a generation.

Since 2005 our most interesting results have centered on neptunyl V and VI coordination by different heteropolyoxometalate ligands. For $\{NpO_2\}^+$, reaction with the B-type tri-lacunary ligands $[BiW_9O_{33}]^{9-}$ and $[SbW_9O_{33}]^{9-}$ leads to the formation of $[(Np_3W_4O_{15})(H_2O)_3(BiW_9O_{33})_3]^{18-}$ and $[(Np_3W_4O_{15})(H_2O)_3(SbW_9O_{33})_3]^{18-}$, respectively (Figure 1). Each complex anion contains three neptunyl(V) moieties encapsulated within heteropolyoxotungstate frameworks, where axial $\{NpO_2\}^+$ oxygens form one face of a WO_6 octahedron in a central $\{Np_3W_4O_{15}\}^{9+}$ core. The remarkable decrease in energy of the main $\{NpO_2\}^+$ *f-f* transition on encapsulation in these clusters (to 1022 nm from 980 nm for $[NpO_2(H_2O)_5]^+$) is a measure of the change in electronic structure within the f^2 Np centers on complexation by these strong hard-donor ligands.

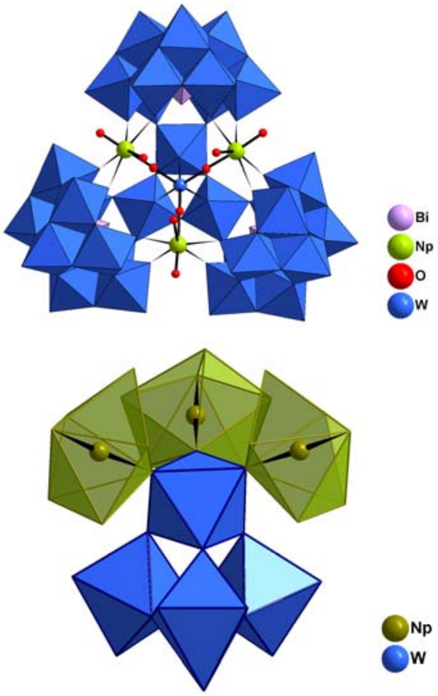

Figure 1. Polyhedral and ball and stick representation of the anion $[(Np_3W_4O_{15})_3(H_2O)_3(BiW_9O_{33})_3]^{18-}$ (top) and the central $[Np_3W_4O_{15}]^{9+}$ group (bottom)

Our initial neptunyl(VI) coordination chemistry studies with POM ligands indicate very similar behavior to known uranyl(VI) chemistry, apart from the tendency for reduction to neptunyl(V). Of more interest is the significant effect that POM complexation has on both the electronic absorption (visible/near infra-red) and emission spectroscopic properties of Np(VI). For example, adding $[GeW_9O_{34}]^{10-}$ to an aqueous $\{NpO_2\}^{2+}$ solution leads to the formation of $[Na_2(Np^{VI}O_2)_2(GeW_9O_{34})_2]^{14-}$, and an associated dramatic color change from pale pink to olive green. The solution vis/nIR spectrum (Figure 2) revealed both distinct high energy fine structure features at the tail of the charge transfer band and the major characteristic 1223 nm transition decreases in intensity and shifts to higher energy (1130 nm). In addition, this complex has been used to probe hitherto unknown solution phase luminescence properties of Np(VI). The coordinated polyoxometalate ligand both prevents inner sphere coordination of O-H oscillators and sensitizes nIR luminescence from the metal centre, both through the LMCT bands of the ion and the abs. bands of a coordinated ligand, thus allowing emission lifetime to be measured (Figure 3).

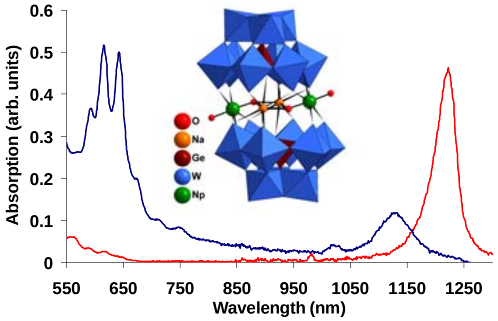

Figure 2. Polyhedral representation of $[Na_2(Np^{VI}O_2)_2(GeW_9O_{34})_2]^{14-}$ and associated aqueous abs. spectrum (blue) vs. the abs. spectrum of $[NpO_2(H_2O)_5]^{2+}$ (red

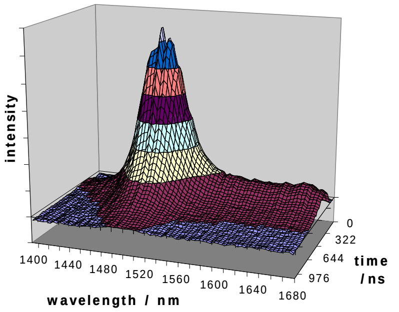

Figure 3. Time resolve luminescence spectrum for $[Na_2(Np^{VI}O_2)_2(GeW_9O_{34})_2]^{14-}$ in D_2O following excitation at 337 nm.

Science objectives for 2007-2008:

- Develop a synthetic plutonium polyoxometalate coordination chemistry capability at LANL, initially with a focus on the preparation of plutonyl(VI) complexes due to their comparative ease of synthesis.
- A luminescence spectroscopic study of neptunyl and plutonyl polyoxometalate complexes in both the solid state and in aqueous solution.
- Attempt to trap uranium and plutonium oxide fragments (as cationic clusters) through encapsulation by polyoxometalate anions.

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Actinide Coordination to Expanded Porphyrins

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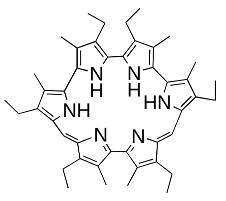
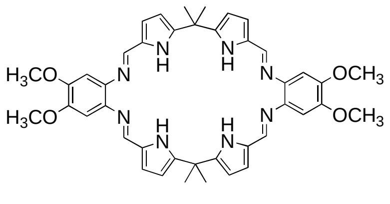
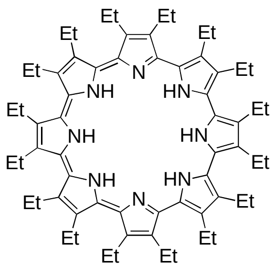
Overall research goals: The primary goal of this project is to generalize the finding that a specific expanded porphyrin, namely isoamethyrin, can coordinate the actinide cations uranyl(VI) and neptunyl(V) and trigger a colorimetric response by i) studying this system further and ii) preparing other expanded porphyrins that allow for the stabilization of complexes derived from these cations, as well as plutonyl(VI). In addition to this, an ancillary project goal is to develop binding agents for the pertechnetate anion and its common surrogate, perrhenate. In the context of these paired objectives, the project is focused on mapping out more fully in a general sense how such classic receptor "variables" as size, shape, donor number, charge, and ease of oxidation/reduction effect the actinide and pertechnetate anion coordination process. In the area of actinide cation recognition, a fundamental understanding of the differences in complexation characteristics (in both a kinetic and thermodynamic sense) displayed by the cations under investigation, U, Np and Pu, and also competing cations, such as the transition metals and lanthanides is necessary to achieve the long-range goal of having a useful optical sensor system that could function under various real-life conditions, including those associated with a response to a terrorist 'dirty bomb' attack. Towards this latter end, a key goal of the project is to develop the synthetic methodology needed to incorporate the receptors in question into so-called "smart materials", either through attachment to a solid support or through creation of cation-responsive liquid crystals. In the pertechnetate recognition area, the key predicates to success are considered to be a codification of the features that lead to effective and selective binding of large, charge diffuse tetrahedral anions, including pertechnetate.



isoamethyrin



huggsiphyrin



cyclo[8]pyrrole

Significant achievements for 2005-2006:

Previous solution-phase studies served to show[8] that isoamethyrin acts as a colorimetric sensor for high-valent oxo-type actinide cations. Considerable effort was thus devoted to the synthesis of a functionalized isoamethyrin that was amenable to attachment to a solid support. One such solid support is an optical fiber and, in collaboration with Dr. Andrew Shaw, it was shown that the resulting systems act as highly effective sensor under interfacial aqueous conditions; field-deployed systems showed stabilities of > 4 months and allowed detection or the uranyl cation at the <500 ppb level. Supporting studies of this ligand and of huggsiphyrin served to show that coordination of the vanadyl cation,[5,6] a potential transition metal analogue of the uranyl, neptunyl, and plutonyl cations, is possible. Other basic analyses were also carried out.[1-3]

On the anion recognition side, several receptors for tetrahedral anions were developed, the most promising of which is cyclo[8]pyrrole; this system was found to be an effective extractant for the pertechnetate anion under mixed aqueous-organic conditions.[7]

Specific Objectives for 2007-2009:

1) Explore further the factors that govern both cation coordination and tetrahedral anion recognition selectivity, as a function of receptor type as the cation or anion is varied.
2) Scale up the synthesis of the functionalize isoamethyrin that has been used successfully to produce a working optical fiber sensor system.
3) Synthesize new actinide-coordinating expanded porphyrins.
4) Prepare additional actinide-containing liquid crystals and study their properties.
5) Extend our coordination studies to the low valent actinides (U(III) and Pu(III)).
6) Prepare new receptors optimized for the binding of pertechnetate anion.
7) Begin exploring combinatorial methods as a way to access receptors more easily.

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LANL Heavy Element Chemistry

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Collaborators: Gustavo Scuseria, Department of Chemistry, Rice University.

Overall research goals:

The aim of this subtask is to develop and apply state-of-the-art theoretical models to understand the electronic structure and properties of actinide species in aqueous and non-aqueous solution, and in solids. Our efforts are tightly coupled with experimental investigations by our colleagues at Los Alamos,.

Significant achievements in 2005-2007:

- **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 .
- **Bonding in novel linear N=U=N and O=U=N linkages.** The chemical bonding and structural properties of uranium bis-imido ($U(NR)_2^{2+}$) and uranium oxo-imido ($OU(NR)^{2+}$) complexes were studied theoretically. The calculated structure and vibrational frequencies are in good agreement with the experimental values for complexes isolated by our experimental colleagues. The linear versus bent structures of N=U=N were compared to their equivalents in the uranyl ion UO_2^{2+}. The bent structure of N=U=N was predicted to be16 kcal/mol higher in energy than the linear linkage, yielding a similar landscape as that of UO_2^{2+} whose bent structure is 18 kcal/mol higher than the linear one. The chemical bonding of $U(NR)_2^{2+}$ and $OU(NR)^{2+}$ are similar to that of UO_2^{2+} involving six bonding molecular orbitals with significant participation of uranium 5f and 6d orbitals. The covalency of the bonds, as measured by the charge on the metal center, was found to increase monotonically along the series $UO_2^{2+} < OU(NR)^{2+} < U(NR)_2^{2+}$.
- **Excited states of Th ketimido complexes**. Time-dependent density functional theory (TD-DFT) calculations on the excited states of $(C_5Me_5)_2Th(N{=}C(CH_3)PhF_n)_2$ fluroketimido complexes have been carried out to complement the synthetic and spectroscopic experimental studies of our colleagues E. Schelter, D. Morris and J. Kiplinger. In particular the electronic withdrawing effects of F substituents on the phenyl rings and the steric effects of nonplanarity of the ketimido pi-electron system with ortho F substituents were examined both for the ketimide complexes and for isolated ketimide ligands. Excellent correlation between the predicted structures and excited state absorption energies was obtained between theory and experiment.
- **Experimental Isolation of Predicted Uranyl Cyanide Complex**. Previous DFT calculations by the Los Alamos group [J. L. Sonnenberg et al., *Inorg. Chem*. **2005**, *44*, 2255-2262] examined the structures of uranyl cyanides and isocyanides, despite the fact that no such species had yet been isolated. The pentacyano complex $[UO_2(CN)_5]^{3-}$ was predicted to be the most stable species in solution with five equatorial ligands having D_{5h} symmetry. Recent experimental studies [J-C. Berthet et al., *Chem. Comm*. **2007**, 604-606] have confirmed the existence of the first actinyl cyanide complex, $[NEt_4]_3[UO_2(CN)_5]$. The geometry of this pentacyano species from the crystal structure agrees well with the theoretical prediction both in the local D_{5h} structure about the uranyl as well as the observed average U-C distances, 2.567(11) Å, compared to the calculated value of

2.653 Å.

- **Theoretical Studies on Actinide Oxides.** We continued our studies in strong correlations in actinide dioxides. Much effort centered on benchmarking the properties of a new density functional (HSE) developed in Gustavo Scuseria's group at Rice University. This new screened hybrid functional allows us to study the properties of the metallic phase in addition to the insulating phase typical of the actinide dioxides. Calculations of the properties of PuO_2 were published, compared with experimental photoemission spectra and other functionals, and the properties of the $PuO_{2:25}$ stoichiometry studied. A study of the evolution of the electronic structure in the entire series of AnO_2 was undertaken, and unexpected behavior observed. In addition, we benchmarked the functional on model, non-actinide, systems where oftentimes more data is available. HSE significantly improves our predictive capability for bandgaps in semiconductors, a long standing problem with DFT. It also yields, unlike conventional DFT, reliable defect energies for various phases of silicon. This suggests it may represent a viable approach to determining point defect energies in actinide solids. Finally, the properties of the Mott metal-insulator transition in the prototype transition metal system MnO were addressed. Our preliminary results, accumulated during a collaboration sponsored by the DOE/OBES materials science CMSN "Predictive Capabilities for Strongly Correlated Electrons" are quite exciting. HSE gives excellent agreement with the critical pressure, and volume collapse from recent experiments.

Specific objectives for 2007-2009:

- In collaboration with our experimental synthesis and characterization efforts, we will employ theoretical tools such as DFT to aid in understanding the bonding, reactivity and spectroscopic properties of organoactinide complexes containing metal-ligand multiple bonds or metal-metal bonds.
- We will investigate models for the interpretation of ligand K-edge XAS probes of covalency in solids containing lanthanide, actinide and transition metal solids.

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Orbital Hybridization and Ion-Ligand Interactions in f-Element Compounds

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Overall research goals:

The objective of this project is to investigate the electronic interactions of lanthanide and actinide ions in compounds and provide a fundamental understanding of orbital hybridization and covalence effects that impact the systemic behavior of chemical bonding and separation.

Significant achievements in 2005-2007:

Orbital hybridization and covalence effects including charge transfer vibronic coupling are studied through optical spectroscopic experiments and theoretical analyses in a framework of crystal field theory and empirical modeling. By directly taking into account the specific contributions from configuration mixing (on site orbital hybridization) and ion-ligand exchange charge interaction, progress has been made in analysis and interpretation of the experimental results that could not be satisfactorily interpreted within the conventional crystal field theory. It is shown that the “free-ion” $5f^n$ states of an actinide ion in complexes can be mixed selectively with the excited states in the $5f^{n-1}6d$ configuration. The impact of the configuration mixing has been investigated in analysis of the absorption spectrum of U^{3+} in $LaCl_3$ and $LaBr_3$, in which the lower energy levels of the $5f^26d$ configuration overlap with that of $5f^3$ in the visible region.

In a related study, we investigated the systematic behavior of ligand-to-ion charge transfer transitions for both lanthanide ions and actinide ions in a soft ligand complex: $M(Et_2dtc)_3(bipy)$ ($M = Ln^{3+}$ or An^{3+}). Our studies present clear evidence that the ligand-Ln^{3+} (An^{3+}) charge transfer transition strongly influences the 4f (5f) states, indicating measurable covalence even in the lanthanide complexes. A comparison between the lanthanide systems and an actinide system (Am^{3+}) indicates that the later has higher charge transfer energies. This comparison suggests that the trivalent actinides are relatively more stabilized in the Et_2dtc complexes.

In order to understand the mechanisms and dynamics of ion-ligand interactions, we have studied uranyl charge transfer vibronic transitions in detail. Inclusion of the anharmonic charge transfer vibronic interaction leads to formation of multiple wells in the excited state potential surface as shown in Fig 1. We have shown that anomalous hot bands, which were previously observed in $Cs_2ZrCl_6:UO_2Cl_4^{2-}$ but not understood, are due to a double-well potential of harmonic charge transfer vibronic excitons (CTVE-I) and anharmonic charge transfer vibronic excitons (CTVE-II) (see Fig. 1 (b)). This work provides a theoretical basis for further analysis of spectroscopic properties of uranyl in different ligand environments.

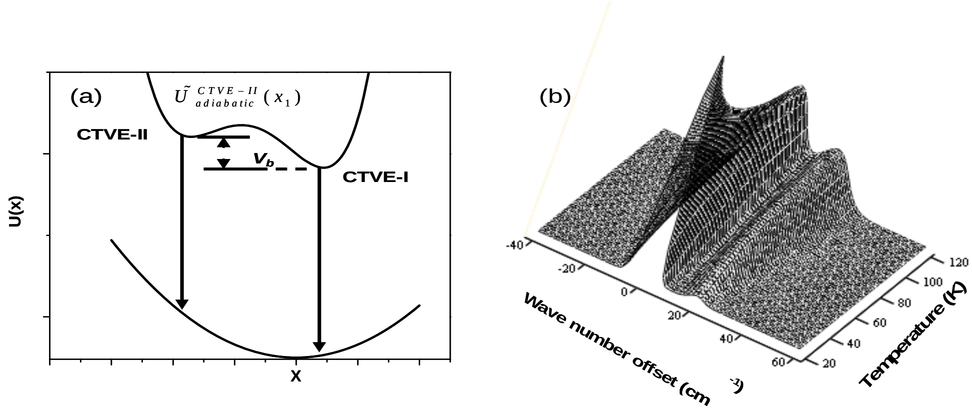

Fig. 1 (a) Potential of uranyl harmonic charge transfer vibronic exciton (CTVE-I) and anharmonic charge transfer vibronic exciton (CTVE-II) with respect to the ground state potential well and expected luminescence emission. (b) Simulated luminescence spectrum of uranyl CTVE-I and CTVE-II as a function of temperature.

<u>Science objectives for 2007-2009</u>:

- *Hybridization and vibronic interactions.* With experimental capabilities in determining energy levels and transition intensities, our investigation will focus on electronic interactions in high-valent systems in which the 5f orbitals are occupied by three or less electrons. The non-bonding contributions are dominantly influenced by on-site hybridization, charge transfer and vibronic interactions. The main objectives include analysis and decoupling of electronic transitions and vibronic transitions, and theoretical modeling of orbital hybridization including evaluation of the odd crystal-field parameters that specifically contribute to the orbital hybridization.

- *Exchange charge interaction and covalence*. Instead of the point charge approximation in the current model for energy level calculations, overlap and exchange charge integrals will be evaluated for specific ion-ligand electron pairs. The nature of this portion of our work is similar to *ab initio* approaches to ion-ligand systems. Some previously determined values, such as the 4f-2p integrals for lanthanide-oxygen bonds, will be used for comparison with our work on evaluation of the anticipated stronger covalence in terms of the 5f-2p overlapping in actinide systems.

<u>References of work that was supported by this project:</u>

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Theoretical Treatment of the Electronic Properties of Heavy Element Complexes

Department of Energy Separations and Heavy Element Chemistry Meeting
Annapolis, MD; April 24-27, 2007

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The theoretical/computational treatment of the electronic structure, and all its related properties, of heavy-element complexes requires additional effort due to relativistic effects and to the high density an complication level of open f-shell states. The plans over the next five years, to install much larger computers in national centers, offer the opportunity to carry out heavy-element studies with much greater computational effort. Although advances in the design and capability of individual central processing units (cpus) are taking place, it is expected that the principal way of building substantially larger computers is to use 10^4 to 10^5 cpus, placing great emphasis on the parallel performance of the available software.

Among the chemistry programs related to electronic structure that are being considered are NWChem (density functional theory, coupled-cluster), Columbus (multireference configuration interaction, MRCI), CPMD (Car-Parinello molecular dynamics), and quantum Monte Carlo programs. We work with the Columbus programs, which are the most flexible in describing complicated electronic coupling, such as for open f shells, but are less efficient in describing electron correlation for large numbers of electrons. A collaborator (Thomas Műller, Jűlich Research Center) has demonstrated that the Columbus programs run efficiently on 10^3 cpus and anticipates no intrinsic problem in using 10^4 cpus.

Recent work has included applications to several types of systems. Work with protactinium systems, in collaboration with J. K. Gibson and coworkers started with the ionization potential of PaO_2^+, a formally f^0 system. Relatively simple calculations gave results that turned out to be surprisingly accurate.[1] The ionization occurs from a σ_u orbital with heavy oxygen 2p character, to give PaO_2^{2+}.

Work on $PaO^{+,}$ with the above collaborators and with B. E. Bursten, was carried out with the objective of understanding its high reactivity compared to other AnO^+ ions. The ground state of PaO^+ is $5f\varphi\ 6d\delta\ ^3H_4$ compared to neighboring ThO^+ $7s\ ^2\Sigma_{1/2}$ and UO^+ $5f\varphi\ 5f\delta\ 5f\pi\ ^4I_{9/2}$. Thus, as the earliest 5f AnO^+ ion, the 5f orbitals of PaO^+ are close in energy to the 7s and 6d orbitals and are therefore more chemically active than those of the later AnO^+ ions. All of the lower PaO^+ excited electronic states involve a substantial 5f orbital population also.[2]

Comparisons with the electronic excitation energies of Pa^{n+} ions are also pertinent to our work, but the available experimental values[3] are often quoted with large error ranges (e.g. $10{,}000 \pm 6000\ \text{cm}^{-1}$), so we are obtaining theoretical values for these energies. Our preliminary results show good agreement with the experimental values, suggesting that the error ranges are probably too large,

We have also collaborated with T. A. Miller and coworkers to study the Jahn-Teller vibrational structure of electronic spectra of Ag_3, which has a D_{3h} e′ $^2E'$ ground state and a D_{3h} e″ $^2E''$ excited state. The spectra are irregular and have been assigned in different ways in previous work. The simplest way to gain confidence in an experimental assignment is to carry out theoretical electronic calculations of the energy surfaces to give reasonably accurate values of the Jahn-Teller constants. This was done and yielded an extensive assignment.[3,4] The electronic theory involved did not use perturbation theory and therefore could be applied to Au_3 and even heavier clusters.

We also completed work on the study of the binding of I^- and Xe to $B_{10}H_{14}$ to compare the known stability of the I^- complex with the possible stability of the Xe complex. We compared a number of theoretical methods. The results[5] are quite functional dependent for DFT calculations, expected to be best for coupled-cluster calculations and not particularly affected by including the spin-orbit interaction. The Xe compound was found to be so weakly bound as to be unlikely to be observable.

We plan to do extensive software work and basis-set development work for relativistic effective core potentials in order to be able to do much more computationally demanding calculations. Among the projects being planned are the electronic spectra of UO_2^+ (with the M. Heaven group) and of hydrated actinyl ions.

DOE supported publications:

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Spectroscopic Studies of Prototype Actinide Compounds

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Overall research goals:

High-level theoretical models of the electronic structures and properties of actinide compounds are currently being developed by several research groups. This is a challenging problem due to the need for explicit treatment of relativistic effects, and the circumstance that many of these molecules exist in states where the *f* and/or *d* orbitals are partially filled. The latest generation of theoretical models must be tested and evaluated through comparisons with experimental results. Gas phase data are most suitable for this purpose, but there have been very few gas phase studies of actinide compounds. In the present project we are carrying out gas phase spectroscopic studies of simple Uranium and Thorium compounds (oxides and halides). To complement the experimental effort we are also investigating the potential for using relativistic *ab initio* calculations and empirically adjusted Ligand Field Theory (LFT) models to predict and interpret the electronic energy level patterns.

Significant achievements in 2005-2007: The ThO^+ cation is of interest as it is a useful prototype for experimental and theoretical studies of bonding in a simple actinide compound. Formally the ground state of ThO^+ has the configuration $Th^{3+}(7s)O^{2-}$, where there is a single unpaired electron associated with a closed-shell Th^{4+} ion core. The first tier of excited states above the $X\ ^2\Sigma^+$ ground state is expected to be $1^2\Delta$, $1^2\Pi$ and $1^2\Sigma^+$ derived from the $Th^{3+}(6d)O^{2-}$ configuration. Spectroscopic observations of ThO^+ using the pulsed field ionization – zero kinetic energy (PFI-ZEKE) photoelectron technique were carried out. Rotationally resolved spectra were recorded for the $X\ ^2\Sigma^+$, $1^2\Delta$ and $1^2\Pi$ states. Extensive vibrational progressions were observed. Accurate values for the ionization energies of ThO (53253.8(2) cm^{-1}) and Th (50868.71(8) cm^{-1}) were determined. These results stimulated new theoretical calculations by Pitzer and Tyagi.

The PFI-ZEKE technique was used to characterize the low-lying states of UO^+. Thirty-three vibronic bands were observed with full rotational resolution. Term energies, vibrational frequencies and rotational constants were determined for nine electronic states. Figure 1 shows the pattern of low-lying states, organized according to the relationship of the molecular states to the energy levels of the $U^{3+}(^4I)$ atomic ion core. We found that the atomic ion spin-orbit coupling strength was preserved in UO^+ to the extent that the atomic spin-orbit interval was recurrent in the energy level structure. This observation, and the demonstration that the pattern of low-lying states can be successfully predicted by LFT,

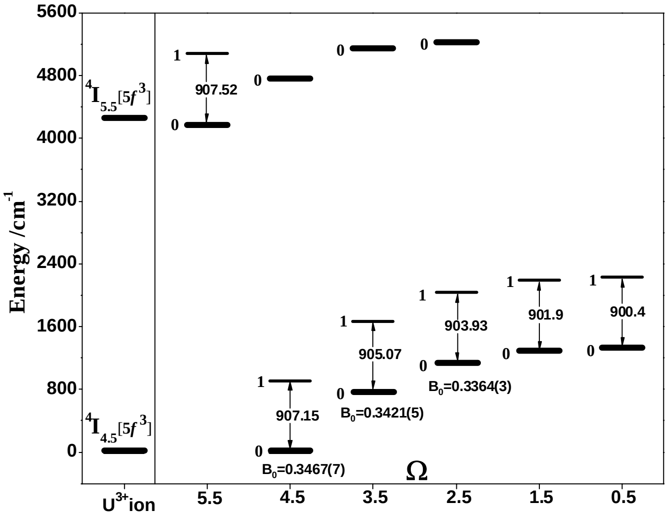

Fig. 1 Observed electronic states (v=0 and 1 levels) for the $U^{3+}(^4I)O^{2-}$ configuration arranged according to energy and η . The atomic spin-orbit splitting is shown on the left.

shows that the 5*f* electrons make a negligible contribution to covalent bond formation in UO^+.

The dipole moments and magnetic *g*-factors for UO are fundamental properties that are valuable for benchmarking theoretical calculations. They also provide insights concerning the electronic structure. These properties were determined from optical Stark and Zeeman spectra recorded at near the natural linewidth limit spectral resolution. For the electronic ground state these data yielded a dipole moment of 3.363(26) D and a magnetic *g*-factor of 2.562(12). These values were consistent with results from ab initio and LFT calculations. These results further support the notion that the early actinide compounds are sufficiently ionic for the meaningful application of LFT models. Dipole moments and magnetic *g*-factors were determined for the two electronically excited states.

Science objectives for 2007-2009:

We have obtained preliminary PFI-ZEKE spectra for UO_2^+. This is a technically significant result as UO_2 exhibits delayed ionization. The spectra recorded so far show the vibrational structure of the electronic ground state. In the coming months we will characterize the states arising from the $U^{4+}(5f)O_2^{4-}$ configuration. REMPI studies of UF and UH will be carried out for comparison with the UO^+ as all three are prototypical $5f^3$ ion core species. Ionization and bond dissociation energy measurements will be made for the metal dimers Th_2 and U_2.

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A New Approach to the Design of Ion-Selective Polymer-Supported Reagents: Tuning the Selectivity of Primary Ligands with Auxiliary Groups

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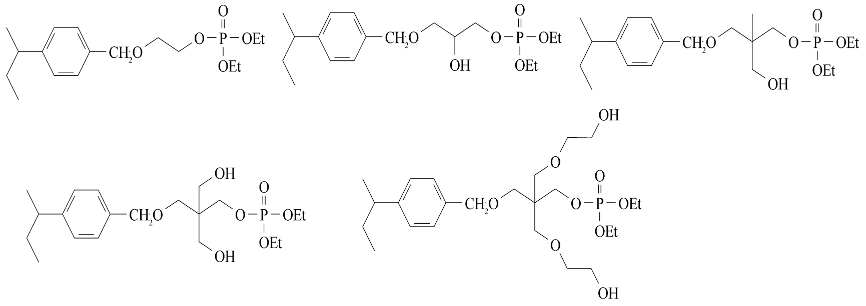
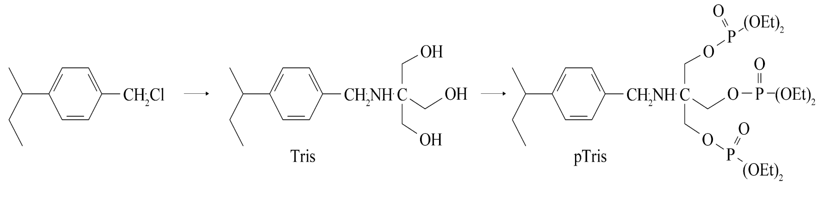
Program Scope: This research centers on the design and development of ion-selective polymer-supported reagents. The objective is to understand the mechanisms through which immobilized ligands interact selectively with metal ions. This understanding will lead to the synthesis of polymers capable of the energy-efficient removal of targeted metal ions from groundwater, wastewater, and process water.

Progress in 2005-2007: A series of polymers has been prepared wherein auxiliary groups are placed in known stereochemical arrangements around a primary ligand in order to probe the ligand - ion interactions. In the first series, phosphate is the ligand to which the metal ions bind and hydroxy groups are the auxiliary groups. The polymers are phosphorylated glycol, glycerol, tris(hydroxymethyl)ethane, pentaerythritol, and pentaerythritol triethoxylate. The metal ion affinities of Pb(II), Cd(II), Cu(II), Ni(II) and Zn(II) were determined from 10^{-4} N solutions in a background of 0.01M nitric acid and the results show that the ionic affinity of a ligand changes when placed proximate to auxiliary groups capable of interacting with the ligand. For example, the percent Pb(II) complexed for the phosphorylated pentaerythritol, glycerol, pentaerythritol triethoxylate, tris(hydroxymethyl)ethane, and glycol is 96.1%, 89.9%, 90.7%, 76.1%, and 9%, respectively. The distribution coefficients for each of the five ions correlate linearly with their polarizability, as measured by the Misono softness parameter (0.40, 0.30, 0.28, 0.25, and 0.24, for Pb, Cd, Cu, Ni, and Zn, respectively). The slope of the correlation, S, quantifies the selectivity of the polymer (the larger the value, the more selective the polymer). The selectivities for the pentaerythritol, glycerol, pentaerythritol triethoxylate, tris(hydroxymethyl)ethane, and glycol polymers are 3811, 1344, 1483, 474, and 21, respectively. The correlation between the distribution coefficients and the softness parameter allows us to propose that the polarizability of the divalent ions is the dominant variable in determining the affinity and selectivity of a bifunctional coordinating polymer. With the current set of polymers, the -OH groups activate the phosphoryl oxygen by increasing its softness and the resulting differences in polarizability affect binding to the divalent ion. It is further proposed that the phosphoryl oxygen gains electron density and becomes more polarizable by hydrogen bonding from the -OH group to the phosphoryl oxygen which draws electron density from the phosphoryl oxygen and decreases back-donation of the pi-electrons into the phosphorus.



The studies have been extended to the synthesis of a coordinating polymer with immobilized tris(hydroxymethyl)-aminomethane which, after phosphorylation of the three -OH groups, shows the effect of -NH- as



the auxiliary group. The affinity with the divalent ions is similar to that found with tris(hydroxymethyl)ethane (with a selectivity of 229). The most significant difference relative to the phosphorylated polyols is that the -NH- group results in a high affinity for trivalent ions and this may be due to a stronger hydrogen bond interaction between the -NH- and P=O ligand. The strength of the hydrogen bond is determined through an analysis of FTIR spectra. The auxiliary group effect may be enhanced by a scaffold effect in which the three neighboring phosphate ligands cooperate in the binding of a single metal ion.

Objectives for 2007-2009: New polymers will be prepared with different primary ligands and auxiliary groups. Their interaction will be probed with FTIR spectra and their metal affinities determined for divalent and trivalent ions. The mechanisms of ion-binding will be probed by correlating the distribution coefficients with parameters quantifying the electronic properties of the metal ions. The primary ligands will include phosphonate monoesters (which will require the development of a synthesis that gives exclusive hydrolysis of the diester to the monoester) and carboxylates.

Publications of research supported by DE-FG02-02ER15287 during 2005-2007

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Meeting Abstracts

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Alexandratos, S. D.; Pustam, A. N. Ligand-modified polymeric sorbents for the remediation of drinking water: an overview and future directions. Preprints of Extended Abstracts presented at the ACS National Meeting, Division of Environmental Chemistry 2007, 47, 1539-1542.

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Structural Chemistry of Lanthanide and Americium Complexes in Solvent Extraction

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Prof. Gérard Cote, Ecole Nationale Supérieure de Chimie de Paris, Université Pierre et Marie Curie-Paris6, Laboratoire d'Electrochimie et de Chimie Analytique-UMR7575-CNRS-ENSCP-Paris6, 75231 Paris, France

Program scope: Effective separation of the trivalent actinide ions—An(III), especially Am(III)—from the trivalent lanthanide ions, Ln(III), through use of liquid-liquid extraction processes is a long-standing challenge in heavy element chemistry; we are employing a multifaceted approach to disentangle the effects of structure hierarchy on selectivity and control, synergism and antagonism in An(III)/Ln(III) separations science.

Recent progress: Contemporary research in the field of nuclear and hydrometallurgical process technologies concerns the separation of long-lived radionuclides, specifically An(III), from Ln(III) by solvent extraction, wherein An(III) ions are preferentially moved out of an aqueous cocktail of actinides/lanthanides and into an organic phase via complexation with an extractant molecule. A new liquid-liquid extraction process dubbed DIAMEX (Diamide Extraction)—SANEX (Selective Actinide Extraction), developed at the Commissariat à l'Energie Atomique (CEA, France), has been found to be particularly effective for An(III)/Ln(III) separation because it utilizes a combination of two extractants. One is *N*,*N*′-dimethyl-*N*,*N*′-dioctyl-hexylethoxymalonamide (DMDOHEMA) and the other is di-*n*-hexylphosphoric acid (HDHP). Their structures are illustrated to scale in Figure 1.

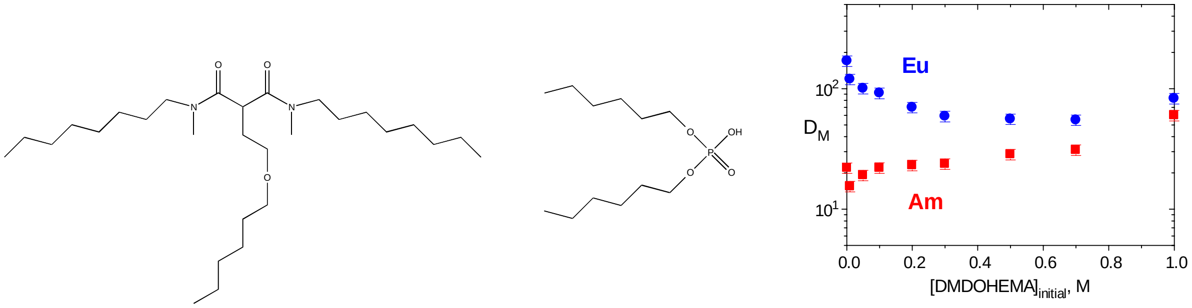


Figure 1. (left) DMDOHEMA; (middle) HDHP; (right) DMDOHEMA concentration dependencies of the Eu(III) and Am(III) distribution ratios, D_M, in the presence of constant 0.1 M HDHP in *n*-dodecane with 0.10 M HNO_3 and 3 M $NaNO_3$ in the aqueous phase at 25 °C.

Because the chemical behavior of this system is complicated, liquid-liquid extraction results, such as shown in Figure 1, are not easily interpreted due to the dearth of information about the stoichiometries and structures of the molecular An(III)- and Ln(III)-complexant species in organic diluents. A Franco-American collaboration involving scientists in the Heavy Elements and Separation Science Group at Argonne, the CEA, and Ecole Nationale Supérieure de Chimie de Paris, France, has succeeded in obtaining structural information about the solution complexes of Ln(III) and Am(III) with the two extractants as well as for mixtures of the two using synchrotron and neutron measurements obtained under the auspices of the Actinide Facility. Through systematic variations of extraction combinations and conditions, EXAFS (extended X-ray absorption fine structure) results, together with ancillary extraction data and infrared spectra, indicate that the HDHP complexes with Nd(III), Eu(III), Yb(III), and Am(III)—abbreviated collectively as M(III)—involve M-O_6 coordination and distant M-P interactions, whereas the DMDOHEMA complexes with M(III) involve M-O_8 coordination. The M(III) coordination with HDHP alone results in two molecular species—one for Am(III) and Eu(III), and a different one for Nd(III) and Yb(III). As shown in Figure 2 (left and middle, respectively), both have the same O coordination number (6) and differ only in the number of distant P atoms (3 and 6).

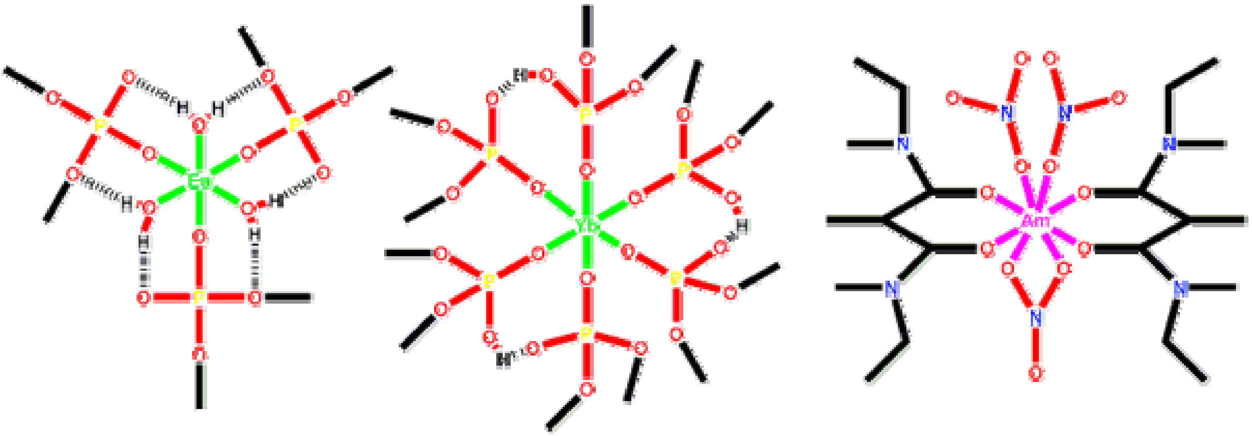


Figure 2. Structures of complexes formed with M(III) upon solvent extraction for (left) Eu(III) and Am(III) with HDHP; (middle) Nd(III) and Yb(III) with HDHP; (right) M(III) with DMDOHEMA.

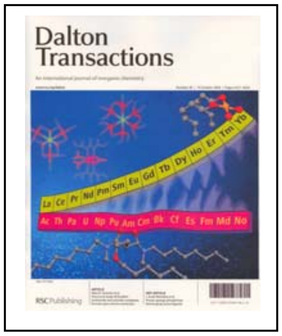
The M(III) coordination with DMDOHEMA alone results in one molecular species, shown in Figure 2 (right). This structure precisely accounts for the EXAFS response of 8 O about all M(III), and the infrared results, which suggest a combination of monodentate and bidentate O coordination of the nitrate ions. The M EXAFS data for the three binary extractant systems were shown to be linear combinations of the M EXAFS for the single extractant complexes with HDHP and DMDOHEMA. The results suggest that the partioning of Am(III) in the DIAMEX—SANEX process is due to the conformational flexibility afforded by the simultaneous presence of both extractants in the binding of M(III) ions and the subsequent supramolecular organization of the M(III)–extractant complexes in the organic phase.

Science objectives for 2007-2009:

- Little is known about the aggregation chemistry taking place in DMDOHEMA-HDHP extractant mixtures. We will determine whether the two extractants act independently or, alternatively, if they form aggregated species that act in concert. Toward this end, small-angle X-ray and neutron scattering data will be used to provide information on the morphology of the polar M(III) core structure and the hydrophobic shell, respectively, of the extractant aggregates.
- We plan to extend our studies on solute organization to heteropoly acids in tri-*n*-butyl phosphate (TBP) to determine if highly charged anions of Lindqvist, Keggin, Wells-Dawson, and Preyssler polyoxometalates can be driven into aggregation behaviors, including third-phase formation.

Publications supported by the HEC program:

This Franco-American research program was featured on the cover of the 14 October 2006 (No. 38) issue of *Dalton Trans.*, which was voted the best cover artwork for 2006 (http://www.rsc.org/Publishing/Journals/Cover_Competition06.asp), and was highlighted in the October 2006, Issue 11, of *Chemical Technology*.


Dalton Transactions

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

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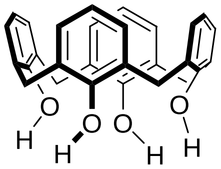
Program Scope: The objective of this project is the design and synthesis of new proton-ionizable, calix[4]arene-based ligands and their evaluation and application in metal ion separation processes.

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 is 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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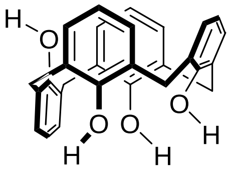

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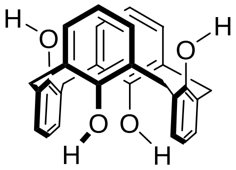

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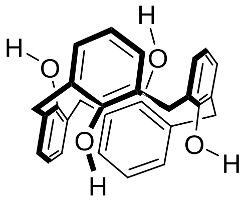

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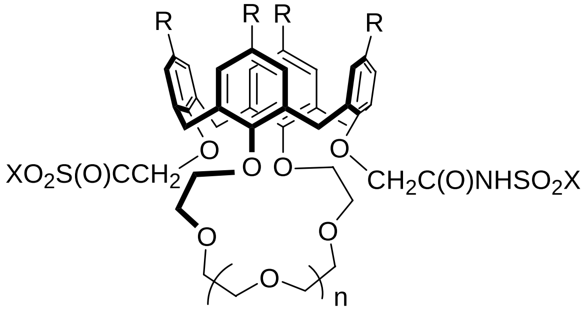
Connection of two phenolic oxygens of the calix[4]arene scaffold with a polyether chain gives calixarene-crown ether ligands, also called calixcrowns. Attachment of two distal oxygens results in a calix[4]arene-1,3-crown ether ligand; whereas linking two proximal oxygens provides a calix[4]arene-1,2-crown ether compound. 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-5 and -crown-6 compounds (n =1 and 2; R = H and *tert*-butyl; X = methyl, phenyl, *p*-nitrophenyl and trifluoromethyl) in cone (**5**), partial cone and 1,3-alternate 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. The results provide valuable insight into the effect



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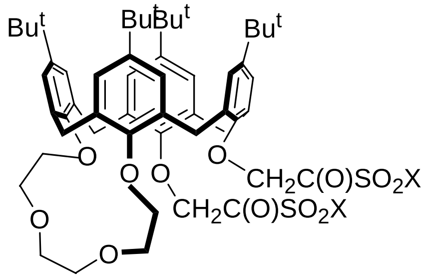

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extractant structure upon the extraction efficiency/selectivity. In contrast with scattered literature reports for metal ion complexation by non-ionizable calix[4]arene-1,2-crown ether ligands, we have discovered that di-ionizable calix[4]arene-1,2-crown-4 ligands **6** (X = methyl, phenyl, *p*-nitrophenyl and trifluoromethyl) exhibit outstanding barium(II) selectivity and efficiency in competitive extraction of alkaline earth metal cations. Since the barium ion is too large to be accommodated within the polyether ring cavity, it must be sandwiched between a polyether "wall" on one side and the two ionized groups on the other. Why such an unusual coordination geometry produces the observed high barium(II) extraction selectivity and efficiency is currently under investigation.

Science Objectives for 2007-2009: During the next two-year period, we will continue our investigations of metal ion separations by di-ionizable calix[4]arene-1,3-crown ether ligands and analogous 1,2-crown ether 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 ethers.

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7. "Di-ionizable *p-tert*-Butylcalix[4]arene-1,2-crown-4 Ligands: Synthesis and High Divalent Metal Ion Extraction Selectivity," C. Tu, K. Surowiec and R. A. Bartsch, *Tetrahedron Letters*, **2006**, *47*, 3443-3446.
8. "Di-ionizable *p-tert*-Butylcalix[4]arene-1,2-crown-5 and -crown-6 Compounds in the Cone Conformation: Synthesis and Alkaline Earth Metal Cation Extraction," C. Tu, D. Liu, K. Surowiec, D. W. Purkiss and R. A. Bartsch, *Organic & Biomolecular Chemistry*, **2006**, *4*, 2983-2944.
9. "Effect of *para*-Substituents on Alkaline Earth Metal Ion Extraction by Proton Di-ionizable Calix[4]arene-crown-6 Ligands in Cone, Partial-cone and 1,3-Alternate Conformations," H. Zhou, D. Liu, J. Gega, K. Surowiec, D. W. Purkiss and R. A. Bartsch, *Organic & Biomolecular Chemistry*, **2007**, *5*, 324-332.
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Principles of Chemical Recognition and Transport in Extractive Separations:

Anion Coordination and Separation with Metal-Organic and Hydrogen-Bonded Frameworks

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Overall research goals: The main scope of this project is to explore the possibility of using crystalline coordination and hydrogen-bonded solids for anion recognition and separation. The metal-organic frameworks (MOFs) previously involved in anion separation showed almost exclusively solvation-controlled Hofmeister selectivity as a result of the hydrophobic nature of the organic linkers typically employed for the synthesis of these materials.[5] We hypothesized that the functionalization of MOFs with hydrogen-bonding groups for specific anion coordination would result in anion selectivities that depart from the typical Hofmeister behavior, and ideally lead to peak selectivities based on shape recognition.

Significant achievements in 2005-2007: We demonstrated a new concept for anion separation involving selective crystallization of MOFs functionalized with hydrogen-bonding groups for complementary anion complexation.[1,4,6] In this strategy, the MOFs are competitively crystallized from an aqueous mixture of anions, a process that results in the selective inclusion of certain anions (or group of anions) depending on their size, shape, symmetry, and specific interactions with the network. The MOFs may thus be essentially considered 'infinite' anion-binding hosts self-assembled *in situ* via metal-ligand coordination.

Strategic functionalization of MOFs with urea hydrogen-bonding groups resulted in specific coordination of various anions in the solid state.[3] Competitive crystallization of Zn^{2+} coordination networks containing a mono-urea linker, from aqueous mixtures of Cl^-, Br^-, I^-, NO_3^-, ClO_4-, and SO_4^{2-}, resulted in total exclusion of the oxoanions and selective inclusion of the halides with an anti-Hofmeister selectivity ($Cl^- > Br^- > I^-$).[4] In order to achieve higher selectivity for oxoanions, we employed more elaborate linkers, containing multiple urea groups positioned complementarily around the anion. Thus, the self-assembly of a bis-urea linker with Ni^{2+} led to an MOF that displayed exclusive selectivity for sulfate from an aqueous environment containing equivalent amounts of Cl^-, Br^-, I^-, NO_3^-, and ClO_4- as competing anions.[6] Furthermore, sulfate was selectively separated from a twenty-fold excess of nitrate, albeit in only 27% yield. Single-crystal X-ray structural analysis revealed that the sulfate is intercalated between Ni^{+2}-coordination layers, and is hydrogen-bonded by four urea groups, two from each layer, in a total of 8 hydrogen bonds (Figure 1).[6]

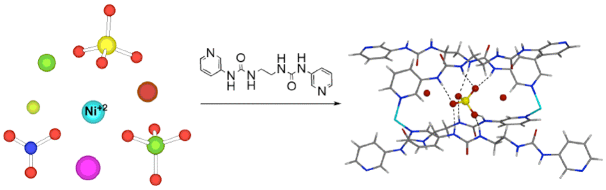

Figure 1. Separation of sulfate by competitive crystallization of a urea-functionalized MOF.

Although the complementarity of this coordination framework for sulfate was very high, it was not ideal, as two water molecules were additionally included to complete the sulfate coordination. Molecular modeling suggested that sulfate ideally accommodates 6 urea groups, each binding to one of the 6 O-S-O edges of the tetrahedral SO_4^{2-} in a total of 12 hydrogen bonds. A tris-urea linker built from tren seemed ideal for this purpose, as indicated by molecular modeling, which showed that sulfate can accommodate two such linkers. Indeed, single-crystal X-ray diffraction analysis showed that the MOF obtained from this linker and Ag_2SO_4 encapsulates the sulfate with 6 urea groups, thereby saturating the anion by 12 hydrogen bonds.[2]

Preliminary results showed that hydrogen-bonded frameworks can be alternatively employed for anion coordination and separation. Thus, monoprotonation of a bis-pyridine-urea linker with one equivalent of HX (X = Cl, Br, I, NO_3, ClO_4) led to the formation of an isostructural series of hydrogen-bonded helices held together by pyridinium---pyridine hydrogen bonding, with the urea acting as an anion-binding group. Competitive crystallization experiments indicated small perturbations from the Hofmeister selectivity. We anticipate that the employment of more complementary linkers will result in higher selectivity for targeted anions.

Science objectives for 2007-2009:

- Investigate anion separation using urea-functionalized MOFs with the goal of better understanding the factors that control anion selectivities. In particular, we will probe the role of complementarity and organizational rigidity of the frameworks on selectivity.
- Explore the concept of anion coordination and separation with hydrogen-bonded frameworks.
- Initiate a new thrust on anion recognition and separation using self-assembled cage receptors.

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

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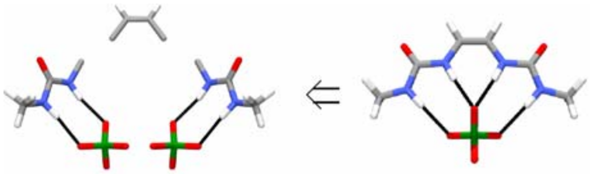
Overall research goals: Ion-recognition through discovery and exploitation of host-guest principles in extractive separations constitutes the primary objective of this research.. A major focus is the deliberate design of receptors for anions, both to learn how to enhance salt extraction and to understand factors determining anion selectivity. Research centers on the use of molecular modeling to address fundamental questions concerning the design of superior extractants and resins for chemical separations in support of environmental and other needs of the USDOE. 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 2005-2007: Molecular-level understanding of the geometric and energetic aspects of anion interactions with potential binding sites provide structural design criteria for shape-selective anionophores. High level electronic structure calculations, which provide a convenient tool for studying such interactions, have been applied to several systems yielding to new insights into the nature of weak interactions. Others had shown that electron-deficient arenes (EDA) can bind anions via non-covalent interactions in which the anion is centered above the arene π-system. We established that EDA are capable of alternative binding motifs that are often more stable than the anion-pi interaction. First, EDA are unexpectedly strong C–H hydrogen bond donor groups, forming bonds that exceed the strength of conventional N–H and O–H donors.[4,6] In collaboration with the University of Oregon, we discovered the presence of a novel third EDA bonding motif involving charge-transfer from the anion to the arene π-system yielding a geometry in which the anion lies above the periphery of the ring, displaced up to 2 Å from the arene centroid.[11]

Electronic structure methods also were employed to study anion complexation with bidentate hydrogen bond donor groups. Differences and similarities in the optimal placement of urea about spherical, trigonal planar, and tetrahedral anions were studied to ascertain instances where host architecture might be exploited to achieve recognition on the basis of anion shape.[1] Exhaustive analysis of the structure and potential-energy surfaces (PES) of simple urea[2,8] and thiourea[10] derivatives provided a basis for understanding and predicting the geometries of receptors containing these functional groups. Molecular structure and PES from these studies were used to validate and improve the Merck Molecular Force Field, providing a rapid and accurate model for testing host architectures containing two or more bidentate hydrogen bond donor groups.[2,5,10]

Using computer-aided molecular design methods, implemented in HostDesigner (HD) software, we have completed a first-of-a-kind study in which de novo structure-based design and high-throughput screening methods were deployed to identify promising anion host architectures prior to synthesis and binding-affinity measurements.[9] The purpose of this study was the design of bisurea "tweezers" structurally organized for binding tetrahedral oxoanions. The basis for the design process derived from preceding electronic structure calculations (vide supra), which provided information needed to define HD input geometries. Over a billion structures were built and evaluated, 12,000 binding energies were calculated, and 3000 conformational analyses were performed to yield a short list of the 30 best candidate architectures. Selected candidates were synthesized and are being tested at ORNL.



Anion receptors were generated by connecting urea groups with hydrocarbon spacers. In this example, a cis-ethene spacer yields an architecture that accommodates tetrahedral anions.

Science objectives for 2007-2009:

- Perform electronic structure studies to understand the geometric and energetic aspects governing anion interactions with charged donor groups such as guanidinium cations.
- Deliberate design of higher denticity podand, tripod, and macrocycle architectures organized for anion selective complexation.
- Evolve design methodologies for application to more complicated supramolecular structures, such as capsules and extended crystalline frameworks, that are formed via self-assembly of complementary component molecules.

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The Electronic Structure of Heavy Element Complexes P1-6

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Overall Research Goals: Principal objective of the research is to understand the electronic structure and bonding of actinides in both small and large complexes through the use of existing theoretical/computational methods.

Significant Achievements 2005-2007: In the efforts to increase understanding of actinide structure and bonding, presentations were given at the 38th Midwest Theoretical Chemistry Conference and at the 2006 Pu Futures–The Science conference in July, 2006. At the latter conference, this work resulted in a Best Student Presentation award for M. Mrozik for excited state investigation of the PaO$^+$ molecule. Mr. Mrozik was also selected to attend the 4th Summer School on Actinide Science and Applications in Karlsruhe, Germany this upcoming summer as acknowledgement for his work in the actinide sciences.

As part of an investigation with J. L. Kiplinger, Th(IV) bis-η^5-pentamethylcylcopentadienyl (Cp*) sandwich complexes were investigated to further understand the coordination of picoline-N-oxide ligands and the nature of the linear Cp*–Th–Cp* conformation. The implementation of hybrid density functional theory (B3PW91) has led to characterization of numerous sets of 2 to 5 equatorial ligands, such as chloride (Cl^-) (Fig. 1) and nitrite ($[NO_2]^-$). Development of fast and efficient methodologies for a larger number of atoms has also allowed for examination of full Cp* complexes as well as simplistic model groups, such as the cyclopentadienyl ligands (Cp).

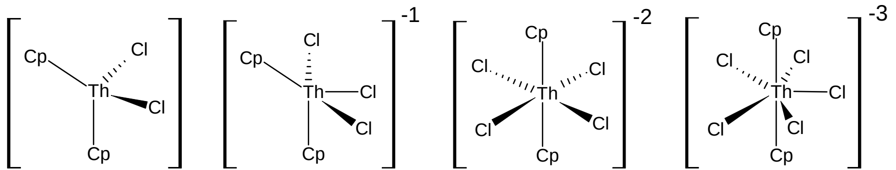

Figure 1: Geometries for ground state structures for the $[ThCp_2Cl_{n=2-5}]^{+2-n}$ complexes were completed using B3PW91 functional and a 68-electron RECP for the central Th atom. The electronically simple chloride ligands are able to generate the same bending phenomenon as the larger picoline-n-oxide complexes and further examination could lead to the origins of the linear Cp–Th–Cp conformations.

Studies involving nitrite and chloride ligands demonstrate similar coordination behavior and an apparent saturation of the equatorial plane. Identification of electronic ground states and molecular orbital contributions, from both the actinide atom and the ligands, across the spectro-chemical series, have also been completed in an effort to elucidate the nature interactions of the Cp(*)–Th–Cp(*) bending.

Specific Objectives 2007-2008: Completion of analysis for actinide sandwich complexes with additional ligands will tease out the properties behind the bent angles. The combination of substitutions will identify whether ligand size or σ/π donating/withdrawing characteristics of the ligands can straighten the Cp–Th–Cp angle without saturation of the equatorial plane. Expanding the set of molecules through substitution of the examined Cp ligands for most complexes to the full Cp* will complete the treatment of the Th sandwich systems.

Continued work with modeling small actinyl molecule solvation through examination of the interactions with rare gas atoms or explicit water molecules to further expand the understanding the growing aspects of actinide solvation chemistry.

Recent Publications:

J. K. Gibson, R. G. Haire, J. Marçalo, M. Santos, A. P. de Matos, M. K. Mrozik, R. M. Pitzer, B. E. Bursten, "Gas-phase Reactions of Hydrocarbons with An^+ and AnO^+ (An = Th, Pa, U, Np, Pu, Am, Cm): The Active Role of 5f Electrons in Organoprotactinium Chemistry," submitted for publication.

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H. P. Hratchian, J. L. Sonnenberg, P. J. Hay, R. L. Martin, B. E. Bursten, and H. B. Schlegel, "Theoretical Investigation of Uranyl Dihydroxide: Oxo Ligand Exchange, Water Catalysis, and Vibrational Spectra," *J. Phys. Chem. A*, **109**, 8579-8586 (2005).

J. L. Sonnenberg, P. J. Hay, R. L. Martin, and B. E. Bursten, "Theoretical Investigations of Uranyl-Ligand Bonding: Four- and Five-Coodinate Uranyl Cyanide, Isocyanide, Carbonyl, and Hydroxide Complexes," *Inorg. Chem.*, **44**, 2255-2262 (2005).

B. Liang, R. D. Hunt, G. P. Kushko, L. Andrews, J. Li, and B. E. Bursten, "Reactions of Laser-Ablated Uranium Atoms with H_2O in Excess Argon: A Matrix Infrared and Relativistic DFT Investigation of Novel Uranium Oxyhydrides," *Inorg. Chem.*, **44**, 2159-2168 (2005).

Nuclear and Radiochemistry Summer Schools

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American Chemical Society, Division of Nuclear Chemistry and Technology

Program Scope: 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 to stimulate interest in future career opportunities in fields founded in nuclear chemistry and technology. 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.

Recent Progress: 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 4 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 experiences 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 visit 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 an 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 participants at the last three Summer Schools are given in Table I. The applicant pool was significantly enhanced following the allotment of student stipends to the Class of 2002, and over the last three years the number of completed applications has averaged above 60 per year. The average overall GPA of accepted students is 3.8/4.0, and we have continued to attract some of the best undergraduate science majors in the country.

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

	Class of 2005	Class of 2006	Class of 2007
Gender (male/female)	15/9	11/13	14/10
Average GPA (maximum 4.00)	3.72	3.84	3.78
College Type (small college/research university)	14/10	11/13	15/9
Undergraduate Major			
Chemistry	14	18	17
Physics	5	1	1
Dual Chemistry/Physics	3	3	2
Chemical Engineering	1	1	1
Biochemistry/Biophysics	1	1	3
Completed Applications	57	67	61

Objectives for 2007-2009:

- 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. The success of the Summer Schools program has been driven in part by the high quality of undergraduate applicants. Competition with other summer programs is increasing, and it is imperative to reach as many interested and accomplished students as possible.
- Foster continued engagement of Summer Schools participants in the nuclear science field by awarding fellowships for a second summer of research. Advice regarding potential summer research opportunities has been provided to all successful students of past Summer Schools programs. We have proposed a more formal fellowship program through the U.S. DOE Science Undergraduate Laboratory Internships (SULI) program, where four of these internships would be earmarked for former Summer School participants.
- Enhance methods for tracking the career pathways of former Summer Schools participants. The Summer Schools are a long-term investment by the U.S. DOE to maintain a critical knowledge base of nuclear chemistry and radiochemical methods required to meet future national needs. The students who attend the 2007 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.
- Raise awareness of nuclear science opportunities beyond the undergraduate experience for all Summer Schools applicants. There are a number of qualified students who do not have the opportunity to participate in the Summer Schools due to limitations on enrollment (currently 12 students each at BNL and SJSU). These students have expressed interest in the field of nuclear science, and ways to encourage their pursuit of the field should be explored.

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Colloid Transport of Plutonium in the Far-field of the Mayak Production Association, Russia

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Overall research goals: The objective of this research program is to understand the form of plutonium and the other actinides on colloids transported to the “far-field” based on the analyses of the groundwater colloids from highly contaminated area in Mayak Production Association, Russia

Significant achievements in 2005-2006:

We have completed systematic analyses of the composition and redox state of groundwaters and filtered samples, and characterization of the actinides associated with the colloids. The Pu-activity is ~1000 Bq/l at the source, while it is still 0.16 Bq/l at 3 km distance, where 70-90 mol% of the Pu is sorbed onto colloids, confirming that colloids are responsible for the long distance transport of Pu. Nano-SIMS elemental maps reveal that amorphous Fe-oxide colloids adsorb Pu(IV)-hydroxides or -carbonates along with U-carbonates.

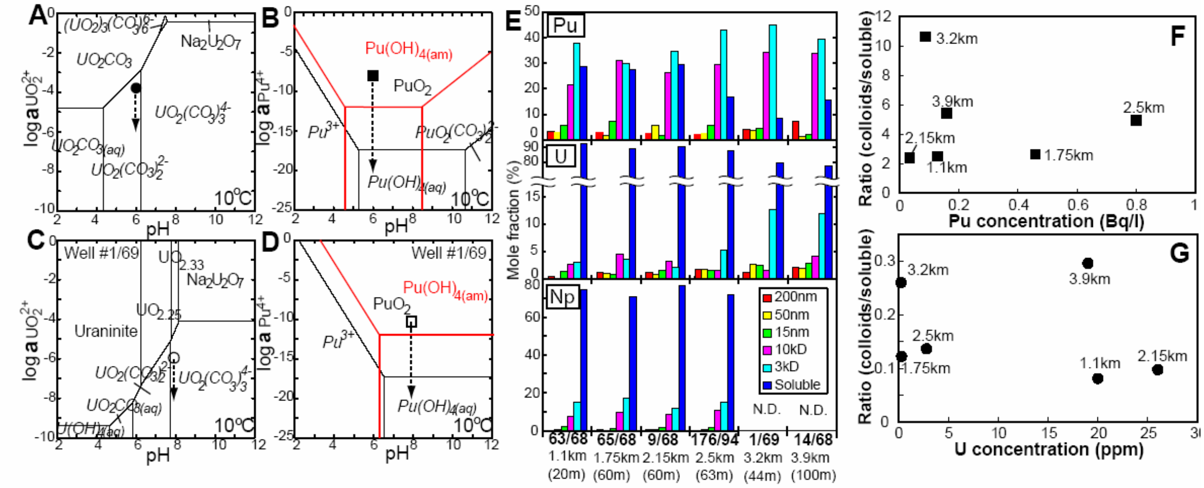

Fig. 1. Stable species of actinides and evidence of actinides bound to colloids. (A, B), Thermodynamic stability diagrams of U and Pu species under the conditions near Karachai lake (well #41/77), respectively. **(C, D)** Thermodynamic stability diagram of U and Pu species under the conditions at well 1/69 located 3.9 km from the source at 44 m depth. Total U and Pu concentrations in the groundwater are plotted as circles and squares in **(A-D)**. Filled symbols are for data near the source, and open symbols are for the data at well #1/69. Plain and italic texts represent solid and aqueous species, respectively. The arrows in **(A-D)** indicate a transition of solution composition for the case that Pu-precipitates as intrinsic or aquatic colloids, or is sorbed onto psuedo-colloids. For these thermodynamic calculations, Act-2 application in Geochemist’s Workbench was used with the database of “thermo.com.v8.r6+”. Solubility data of $Pu(OH)_{4(aq)}$ are updated. In illustrating the stability fields (in red) of $Pu(OH)_{4(am)}$ in **(B, D)**, the temperature was set to 25 °C because of the limited solubility data. **(E),** Mole fraction of actinides (i.e., Pu, U, and Np) bound to colloids as a function of the size. In the legend, 10 kD and 3kD correspond

to approximately 1.5 nm and 1.0 nm, respectively. **(F, G),** Ratios between actinides bound to colloids and as a soluble form for Pu and U, respectively. Pu concentration is a total in the groundwaters.

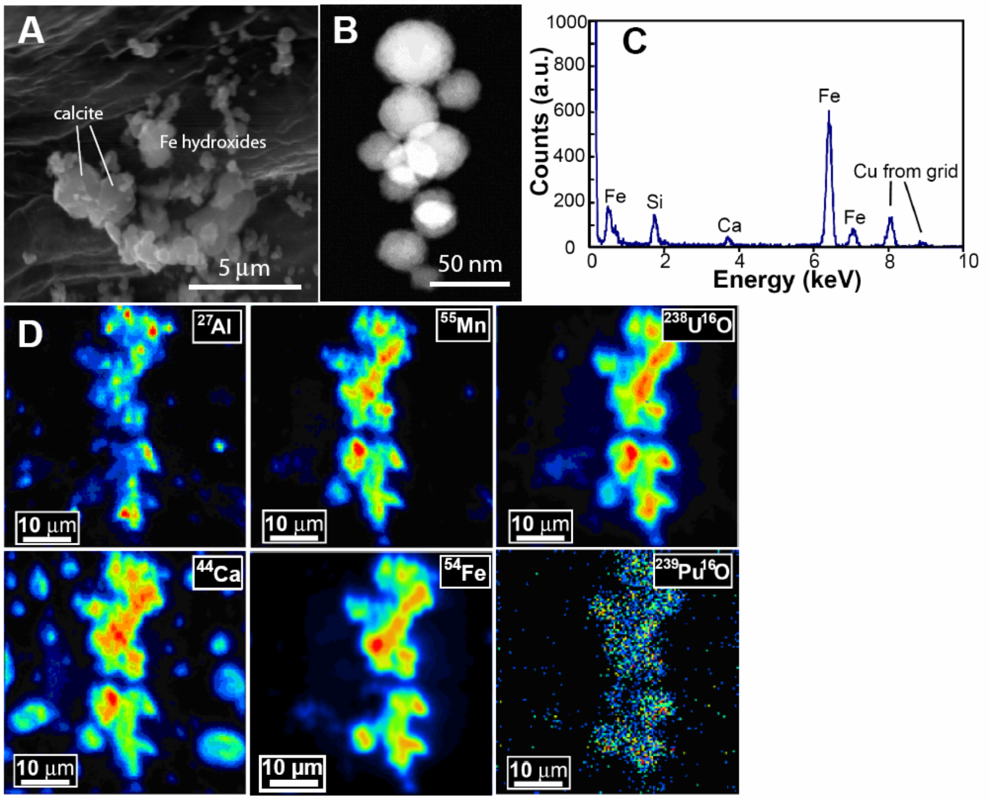

Fig. 2. Direct evidence of Pu-adsorption onto amorphous Fe (hydro-) oxide. (A), SEM micrograph of typical colloids from well #1/69. Many spherical particles were observed with a size of < 1 µm. **(B),** HAADF-STEM (high-angle annular dark-field scanning TEM) image of the spherical colloids. Electron diffraction patterns from these particles indicate that they are amorphous. **(C),** EDS (Energy dispersive X-ray spectrum) from the spherical particles show that Fe is a major constituent associated with trace amounts of Si and Ca. **(D),** Nano-SIMS elemental maps. The contrast of these maps has been enhanced to show the distribution clearly. Thus, the intensity of the color in the chemical maps does not correspond to the concentrations of the different elements.

Science objectives for 2007-2008:

- To understand the transformation of the actinide species bound to colloids during transported as a function of distance, aging, gradient of physico-chemical condition of the groundwater.
- To expand the current understanding to the migration of radionuclides in the other groundwater systems, such as in Nevada Test Site.

References of works that was supported by this project

1. Alexander P. Novikov, Stepan N. Kalmykov, Satoshi Utsunomiya, Rodney C. Ewing, François Horreard, Alex Merkulov, Sue B. Clark, Vladimir V. Tkachev, Boris F. Myasoedov “Colloid Transport of Plutonium in the Far-field of the Mayak Production Association, Russia” *Science,* **240,** 521-528(2005).

The Structural Chemistry of Actinide Hydrolysis

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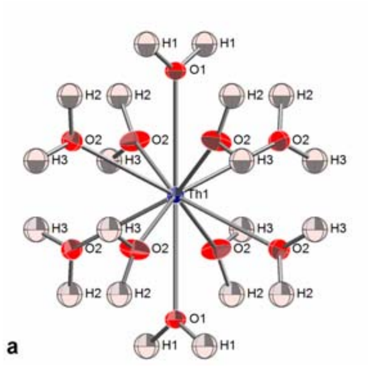
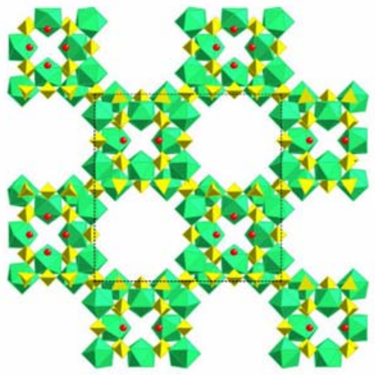
Overall research goals: Our research focuses on the structures of actinide aqua complexes and hydrolysis products, both in solution and in the solid state. The origin of the complexes is probed in the solution state to understand the relative role of electrostatic, bonding, and packing interactions on the coordination environment of actinide ions.

Significant Achievements in 2005-2007: Synthetic efforts focused on the aqua ions and hydrolysis products of the actinides have produced several new structures providing valuable insight into their behaviors in aqueous solution. Beginning with thorium, we have discovered two new hydroxo-bridged dimers of Th(IV) crystallized from both nitrate and chloride media and have demonstrated their existence in solution using x-ray scattering. Insight gained from this work lead to the preparation and the first crystal structure of the thorium aqua ion $[Th(H_2O)_{10}]Br_4$, and indeed the first fully hydrated tetravalent-cation structure ever to be determined. Exploring the thorium system further, multiple oligomeric hydroxo-complexes consisting of infinite chains, hydroxo-linked clusters, and nanoporous materials have been discovered. The preliminary work with thorium has been extended to uranium, resulting in the discovery of a new hydroxo-bridged dimer of uranium. Efforts focused on the aqueous chemistry of plutonium demonstrated the preparation of three new trivalent plutonium chloride compounds isolated from aqueous solution. We also prepared the first triflate salt of Cm(III) in support of efforts to more fully understand the coordination and structure of trivalent actinides in aqueous solution.



$[Th(H_2O)_{10}]Br_4$: The crystal structure of the thorium aqua ion.



A nanoporous material of thorium with neutrally charged 1.1 nm channels.

Science objectives for 2007-2009:

- *Focused efforts on tetravalent transuranium ions:* The success of our efforts with thorium necessitate the expansion of the synthetic efforts into the tetravalent transuranium ions, Np(IV) and Pu(IV). We argue that it is differences in the ion acidities between Th, U, Np and Pu that explain subtle but significant differences in their chemistries, particularly as it relates to the formation of polymeric species (dimers and hexamers). No guidance from thermodynamic models exists for oligomeric complexes of the tetravalent transuranium ions. Whereas we were able to target complexes of thorium based on available thermodynamic models, we are charting new territory into the solution chemistry of the transuranium ions in the study of these solution species.

References of work that was supported by this project (2005-2007)

S. Skanthakumar, M. R. Antonio, R. E. Wilson, L. Soderholm. *The curium aqua ion. Inorganic Chemistry* (2007) in the press.

Richard E. Wilson, S. Skanthakumar, Ginger Sigmon, Peter C. Burns, L. Soderholm. *Structures of Dimeric Hydrolysis Products of Thorium. Inorganic Chemistry,* 46, 2368-2372, (2007) **Cover Article**

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Effects of self-irradiation on local crystal structure and 5f localization in PuCoGa5

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Overall research goals: The objective of this project is to measure and explain magnetic, electronic and structural properties in f-electron intermetallics.

Significant achievements in 2003-2005: The 18.5 K superconductor $PuCoGa_5$ has a propensity to self-damage due to the radioactive nature of the plutonium atoms. Most of the damage is due to the recoiling U nucleus after a Pu alpha decay. This nucleus can precipitate the development of thousands of defect-hole pairs, although many are expected to recombine after a few picoseconds. The amount of damage should be directly related not only to this material's high critical current densities and high upper critical magnetic field, but also to the observed decrease in T_c with time (-0.22 K/month). Since no atomic-scale measurements of lattice disorder and defects due to radiation damage exist for this material, or even on Pu metal, researchers have long relied on theoretical calculations of defect concentrations to provide the necessary structural details. We have collected local structure extended x-ray absorption fine-structure (EXAFS) and x-ray absorption near-edge structure (XANES) data as a function of total self-irradiated dose in samples of $PuCoGa_5$ that show the amount of damage in $PuCoGa_5$ develops much more quickly that expected from such calculations, at least over the first year or two after synthesis. The EXAFS, however, also include any lattice distortions as damaged material. Our fitting model divides the sample into three regions: undamaged material, strongly damaged material and weakly damaged material. The results are consistent with all or nearly all of the atoms in a damage cascade as distorted, with smaller distortions near the edges of the cascade. These results will be directly comparable to a molecular dynamics simulation when one becomes available. Interestingly, the damage accumulates most quickly in the first year, leveling off considerably thereafter, presumably due to annealing of the damage as the samples are stored at room temperature. Moreover, we have observed not only a shift toward a more local f-moment character in the Pu L_{III} XANES compared to, say, α-Pu, but a shift that grows slowly with damage, consistent with a model where the f orbital is more strongly localized in the damaged regions.

These data are significant for a number of reasons. First, they help explain the reduction of T_c in $PuCoGa_5$ with time. More importantly, they provide a way to directly test molecular dynamics calculations of the crystal structure in radiation damaged regions at the atomic scale. Such experimental confirmation has eluded theorists for over 50 years, and has implications for reactor fuel cladding, waste forms, and the nuclear stockpile.

Science objectives for 2005-2006:

- Explore aspects of atomic species and lattice in the development of radiation damage. New materials include PuGa3 and PuAl2, but we also want to look at other Pu115 materials as they become available from our Los Alamos colleagues.
- We continue to explore doping of atoms into the superconducting planes in 115 compounds. In anticipation of an eventual PuCoGa5-xInx, we will explore such behavior in $CeRhIn_{5-x}Hg_x$, as well as in $CeCoIn_{5-x}Cd_x$ from Zach Fisk's group at UC Irvine

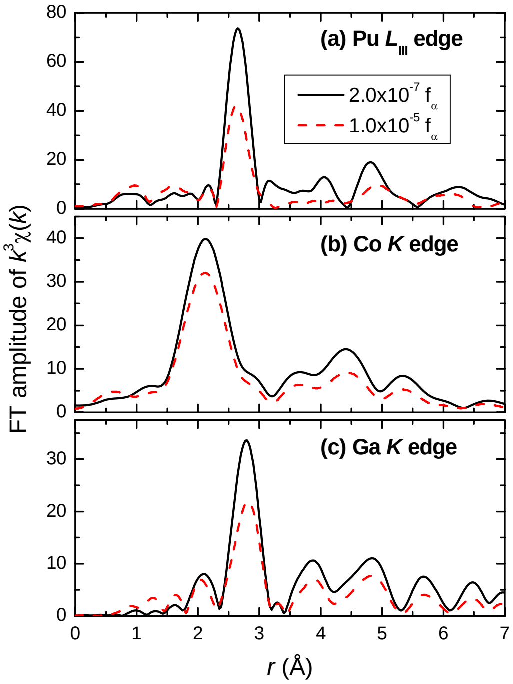

Figure 1. EXAFS spectrum showing strong suppression of local crystalline order around Pu, Co and Ga over time. Sample age is given in alpha decays per atom (f_α), corresponding to about 2 years for the older sample.

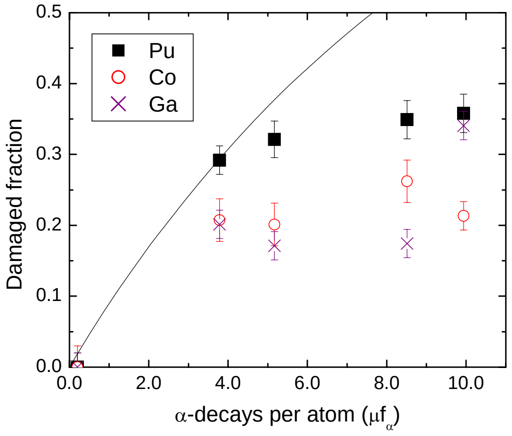

Figure 2. Estimated total fraction of damaged sample from EXAFS fits. The solid line is a percolation model forced to go through the earliest aged data point at $4\mu f_\alpha$. Simple calculations are an order of magnitude lower.

(formatting note: End of two-column section)

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

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Program Scope: To measure the thermodynamic properties and characterize the structures of actinide complexes in solution and improve the fundamental understanding of the thermodynamic principles and structural factors governing the chemical behavior of actinides in solution.

Recent Progress:

- Continued the studies on thermodynamics of actinide complexation in solution at elevated temperatures. Two studies, U(VI)/thiodiacetate (10-85°C) and Th(IV)/malonate (10-70°C), have been completed and published. A few studies are in progress: Pu(VI)/OH (10-85°C), Th(IV)/OH (10-85°C), U(VI)/oxalate (10-85°C), Np(V)/oxydiacetate (25-70°C).
- Continued the thermodynamic and structural studies of actinide complexation with a series of oxa-diamides and related ligands. Thermodynamic trends (ΔH, ΔS) of complexation were determined as the functional groups of ligands change from carboxylate (in oxydiacetate) to amide (in tetramethyl-3-oxa-glutaramide). Structures of a few actinide/lanthanide complexes have been determined (Ln(III), Th(IV), U(VI) and Np(V)). Data are being summarized and manuscripts in preparation.
- Completed collaborative studies with Prof. S. Clark of Washington State University (WSU) on the complexation of actinides/lanthanides with gluconic acid. These studies are a part of the dissertation work of Zhicheng Zhang, a graduate student at WSU. Ph.D. was awarded to Z. Zhang in 2006. Two papers have been published. Another two are in preparation.
- Completed a collaborative study with the Raymond's group on the thermodynamics and structure of the Np(V) complex with 5-LIO(Me-3,2-HOPO), a potential sequestering agent. The formation constant (β) of the 1:1 complex was determined spectrophotometrically to be $10^{11.47}$. The crystal structure of this complex has been determined using the small-molecule X-ray crystallography beamline at the ALS. The structure shows that the NpO_2^+ is coordinated by four oxygen atoms of the ligand and one oxygen from a water molecule in the equatorial plane. A manuscript is in preparation.

Science objectives for 2007-2009:

- Complete the Pu(VI)/OH (10-85°C) study and extend the series of hydrolysis studies to Np(VI)/OH. Thermodynamic trends in the temperature effect on the hydrolysis of U(VI), Np(VI) and Pu(VI) will provide interesting fundamental information on the actinide series.
- Complete the Th(IV)/OH (10-85°C) study. This system is difficult because several models can interpret the results equally well and few spectroscopic techniques are applicable to this system to help identify the species. Efforts (e.g., using ESI-MS, EXAFS) will be made to characterize the hydrolysis species to help select the best hydrolysis model.
- Continue the studies on the complexation of actinides with oxa-diamides and related ligands. Based on the thermodynamic and structural data that have been obtained for these systems, the substitution groups on these ligands will be systematically changed with the aim to improve the complexation and extraction of these ligands for actinides.

Publications supported by this program since the 2005 Contractor Meeting:

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Plutonium in Higher Oxidation States in Alkaline Media

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Program Scope: The goal of this work was to study the highest possible oxidation states of plutonium in alkaline media.

Recent Progress: In 2004 we reported that during oxidation of Pu(VI) with ozone in NaOH solutions to prepare Pu(VII), the electronic absorption spectra revealed time-dependent oscillations in the measured optical density of nearly 30%. Pu(VII) in alkaline solution is characterized by a blue-black color and a distinct electronic absorption spectrum with a maximum at 635 nm. The extinction coefficient is known to vary from 530 – 600 L mol^{-1} cm^{-1}, and this was historically attributable to experimental differences from different laboratories. Changes in extinction coefficient reaching 30% had never been reported, and were likely due to the strong and vigorous ozonolysis conditions employed. Additional experiments employing strong ozonolysis conditions led to the conclusion that during Pu(VI) oxidation with ozone in alkaline solution, Pu(VII) is formed as the major product, and that a minor amount of Pu(VIII) is also produced. In our most recent work, we provide a series of new chemical and electrochemical experiments that more reliably support the proposal that Pu(VIII) can be prepared in small quantities during the preparation of Pu(VII) in alkaline solution.

Ozone and Electrochemical oxidation of Pu(VI). A 3.5 vol.% O_3/O_2 gas mixture was added via bubbling to a pure solution of 2.9 mM Pu(VI) in 1.5M NaOH at 20^{o}C over a 30 min. period. This produces a blue-black alkaline solution of nominal oxidation state Pu(VII) with a characteristic electronic absorption spectrum (λ_{max} = 607 and 635 nm) as reported previously. Stepwise addition of equimolar aliquots of the starting Pu(VI) solution in 1.5M NaOH to an ozonized [colored, Pu(VII)] solution results in an immediate decrease in optical density of the blue-black solution. The decrease in Pu(VII) is not 1:1 based on the amount of added Pu(VI)! One possible explanation for this unusual observation is that the ozonolysis of Pu(VI) in 1-3M NaOH produces a mixture of Pu in two different oxidation states; of the previously known Pu(VII) and a small amount of hypothetical Pu(VIII). To account for the decrease in optical density with addition of Pu(VI), the proposed Pu(VIII) could react with Pu(VI) according to the stoichiometry of equation 1 as described previously.

$$\text{Pu(VIII)} + \text{Pu(VI)} \rightarrow 2\text{Pu(VII)} \qquad (1).$$

Alternative explanations of the observed data include the possible formation of a mixed-valent Pu(VI)–Pu(VII) compound, or the formation of either ozonide or peroxy-complexes of Pu(VII), which can interact with the initial Pu(VI) under the stated conditions. To test for these possibilities, we prepared oxidized Pu(VI) solutions under a variety of chemical and electrochemical conditions, all in the absence of ozone.

Identical reactions between Pu(VI) and oxidized blue-black Pu solutions were carried out in 2M NaOH solution, with the exception that the oxidation of Pu(VI) was performed electrochemically. The data obtained from both ozonolysis and electrochemical oxidation experiments support our original conclusion regarding the possibility of Pu(VIII) formation in oxidized alkaline solutions of Pu(VI), and allow us to determine a probable value of the molar extinction coefficient (ε) of Pu(VIII) as ~2600 ± 400 M$^{-1\cdot}$cm^{-1}. The extinction coefficient of Pu(VII) in the 500-550 nm was then found to be ~100 M$^{1\cdot}$cm^{-1}. From these data the yield of presumed Pu(VIII) in the experimental solution was estimated to be ~(15±5)%.

Chemical redox reactions. Addition of equal molar quantities of freshly ozonized Pu(VI) to Np(VI) solutions results in the appearance of an electronic absorption spectrum typical for Np(VII) solutions. Knowing the concentration of Pu in the added aliquot, and the concentration of Np(VII) in the test solution, it was possible to calculate the ratio of Np : Pu ~ 1.2 ± 0.1 (the results of three parallel experiments). If only Pu(VII) were present in ozonized 2M LiOH solution, the resulting ratio of Np(VII) : Pu(VI) in the experiments above must be 1:1 as indicated in equation 2.

$$\mathrm{Np(VI)} + \mathrm{Pu(VII)} \rightleftharpoons \mathrm{Np(VII)} + \mathrm{Pu(VI)} \quad (2).$$

The fact that the observed Np(VII) : Pu(VI) ratio was found to be 1.2 ± 0.1 (20% greater than the expected ratio of 1:1) suggests that there must be ~20±10% of an unknown complementary oxidizing agent in the ozonized Pu(VI) solution. This closely mirrors the results of spectrophotometric titration of ozonized and non-ozonized solutions of Pu(VI) in alkaline media which suggested approximately 15±5 % of an unknown oxidizing agent (see above). Similar results are obtained through chemical reduction of Fe(VI), oxidation of Fe(III), and oxidation of Mn(VI). In all these chemical redox experiments, we find evidence for approximately 20% of another Pu oxidation state. Finally, chronopotentiometry was used to show that there were two oxidized forms of Pu in oxidized alkaline solutions.

These series of chemical and electrochemical experiments are consistent with the existence of two oxidation states of plutonium after chemical oxidation of Pu(VI) by ozone, or electrochemical oxidation of Pu(VI) in alkaline media. We submit that these data further support our original proposal that oxidation of Pu(VI) in NaOH solution produces predominantly Pu(VII) and a small but significant concentration of Pu(VIII). The values of the molar extinction coefficients (ε) of Pu(VIII) at 635 nm, and Pu(VII) at 500-550 nm, were estimated as ~2600 ± 400 and ~100 $M^{1}\cdot cm^{-1}$, respectively. The yield of the assumed Pu(VIII) in the experimental solution is estimated to be ~(15±5)%. Finally, we admit that it is impossible to completely exclude the possibility of formation of Pu(VII) peroxy-complexes during Pu(VI) oxidation by ozone or electrochemically.

Science objectives for 2007-2009: This work was supported by the Office of Basic Energy Sciences, through the Heavy Element Chemistry Program under a grant that ended in 2006. We will continue the fruitful collaboration between Los Alamos and the Vernadsky Institute as time and funding permits.

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Preorganized and Immobilized Ligands for Metal Ion Separations

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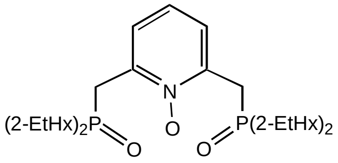
Overall Research Goals: The objective of this project is the exploration of geometric and electronic factors that control the binding of f-block element ions to multifunctional receptor molecules. Coordination responses revealed in the studies are used to design new receptor molecules with properties appropriate for practical separations objectives in the DOE complex.

Significant Achievements 2005-2006:

A. Design and Synthesis of Phosphinopyridine Platforms

The synthetic development of phosphinopyridine based ligands has continued in this time period. Initial studies showed that ligands such as **1** act as strong chelating ligands toward Ln(III) and An(III) ions and lipophillic examples display very favorable solvent extraction performance such as illustrated in Figure 1. Solvent extraction characterization of **1** continued during the early part of the current grant period and the positive features formed the basis for a successful application for funding from the DOE AFCI NERI program where further synthetic development, stability characterization and separations process modeling is being studied.



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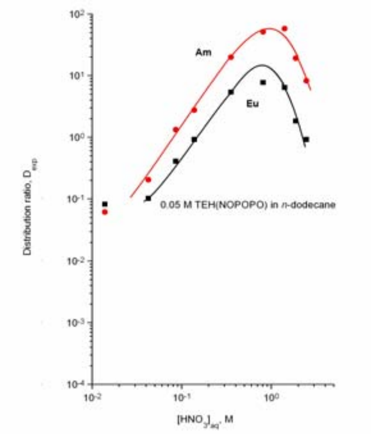
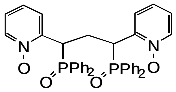


Figure 1. Dependence of the Am and Eu distribution ratios on HNO_3 concentration into dodecane solutions of **1**.

At the end of the prior grant period, we reported initial attempts to prepare a series of related phosphinopyridine chelators that offered geometric platform variations on the theme first explored with **1**. Work continued on the synthetic development of **2** – **7** and on the structural analysis of coordination compounds of **2** – **4**. Each of these ligands forms Ln•L complexes and work continues exploring the variations provided by structural modifications.

In addition to extensions of the phosphinopyridines we have continued to develop amido functionalized pyridine platforms. Here we expect to be able to “soften” the ligand coordination field. The coordination chemistry has proven to be fruitful. In addition, aspects of the oxidation of the pyridine platforms to pyridine N-oxides has proven to be very interesting and unexpectedly complex.



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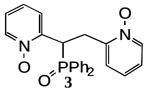

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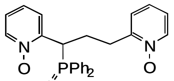

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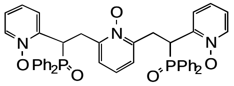

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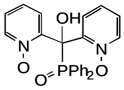

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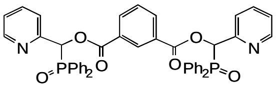

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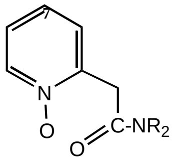
Finally, we have begun development of oxazoline based ligands and the first examples of ligands of the general types **10** and **11** have been prepared and coordination chemistry shows that these ligands also can act as bidentate chelates.



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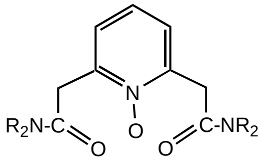

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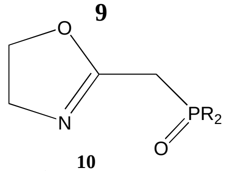

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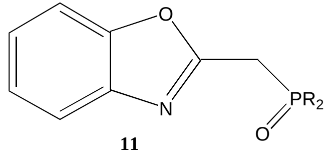

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Specific Objectives for 2007-2008:

- The design and synthesis development of the new families of ligands of types **2 – 11** will be continued. Through the studies of coordination interactions with Ln(III) ions we will be able to further define electronic and geometric factors that impact coordination sphere constructs on Ln(III) ions and indirectly An(III) ions. This work will lead to identification of additional platforms suitable for extraction analysis.

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Nuclear Waste Forms for Actinides: Design & Selection

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Plutonium has been produced in significant enough quantities that it is a source of energy in fission reactions, a source of fissile material for nuclear weapons, and of environmental concern because of its long-half life and radiotoxicity. During the past fifty years, approximately 1,800 metric tonnes of plutonium and substantial quantities of the “minor” actinides, such as Np, Am and Cm, have been generated in nuclear reactors. There are two basic strategies for the disposition of these transuranium elements: 1.) to “burn” or transmute the actinides using nuclear reactors or accelerators; 2.) to “sequester” the actinides in chemically durable, radiation-resistant materials that are suitable for geologic disposal. Primary candidates for the immobilization of actinides include silicates (zircon), phosphates (monazite and apatite) and oxides (pyrochlore, zirconolite and muratiate). Recently, there has been substantial interest in the use of isometric pyrochlore, $A_2B_2O_7$, for the immobilization of actinides, particularly plutonium. Systematic studies of rare-earth actinides in which the B-site may be occupied by Ti, Zr, Sn or Hf, have lead to the discovery that certain compositions (Zr, Hf) are stable to very high doses of alpha-decay event damage. The radiation stability of these compositions is closely related to the structural distortions that occur for specific pyrochlore compositions and the electronic structure of the B-site cation. This understanding provides the basis for designing materials for the safe, long-term immobilization and sequestration of actinides.

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

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Program Scope: The objective of this project is to synthesize pentavalent uranium species under hydrothermal conditions. More generally, we are exploring the redox chemistry of U-containing hydrothermal systems.

Recent Progress: Project came up to speed in July 2006 with hire of Dr. Nebebech Belai. To date, we have explored the use of various reducing agents (organic amines, hydrazine, Mo(V), Zn metal, etc.) to produce reduced valent U phases from the hexavalent uranyl cation, UO_2^{2+}. Two significant results have emerged:

1. The synthesis, crystal structure and XPS characterization of $U^V(H_2O)_2(U^{VI}O_2)_2O_4(OH)$, (Fig. 1). Synthesis involved the reduction of $[UO_2]^{2+}$ at 120 °C in the presence of hydrazine. XPS data suggest some U(IV) may be present as well.

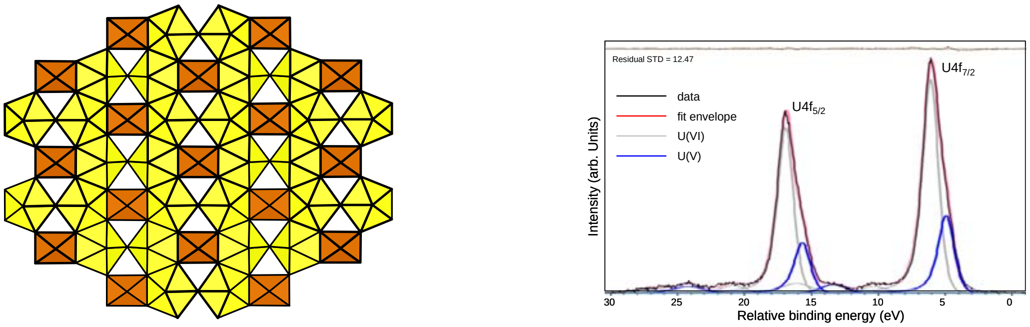

Figure 1. Left: Sheet structure of $U^V(H_2O)_2)(U^{VI}O_2)_2O_4(OH)$, where darker polyhedra are U(V) sites. Right: XPS data of the U(V)-U(VI) synthetic product.

2. The synthesis of $Na_7H[U^{IV}Mo_{12}O_{42}]\cdot 6H_2O$ (Figure 2) via multiple hydro/solvothermal routes. Co-crystallizing with the latter compound is Mo_2O_4, a mixed Mo(II)/Mo(VI) phase that is a novel composition for the wulfenite structure type. The $[UMo_{12}O_{42}]^{8-}$ anion has been known for some time, yet all previously reported syntheses begin with U(IV) and Mo(VI) and demonstrate no redox activity. Our results are significant in that we have delineated reaction conditions to promote reduction of the uranyl cation in aqueous solution by Mo(V). A preliminary redox scheme is given as:

$$16H_2O + 7[Mo_2^VO_4]^{2+} + [U^{VI}O_2]^{2+} \rightarrow [U^{IV}Mo_{12}^{VI}O_{42}]^{8-} + Mo^{II}Mo^{VI}O_4 + 32H^+$$

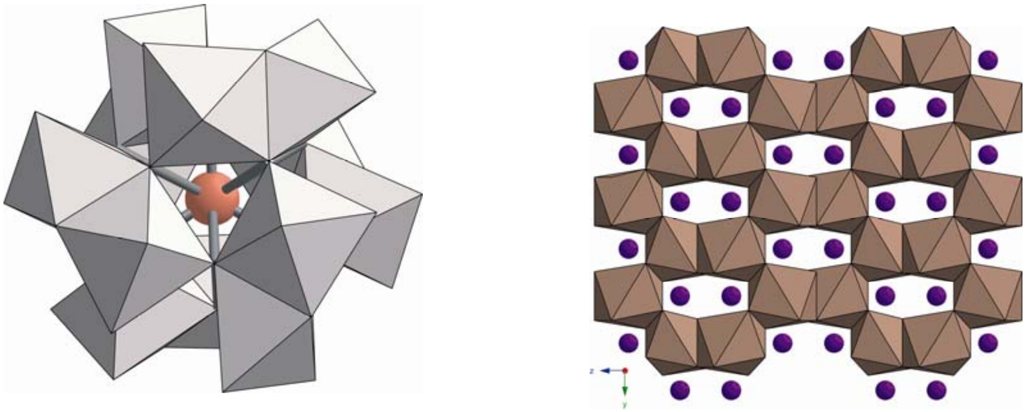

Figure 2. Left: the $[UMo_{12}O_{42}]^{8-}$ anion, where the central U(IV) cation is shown as a sphere. Right: a portion of the $Mo^{II}Mo^{VI}O_4$ structure, where the Mo(II) sites (in tetrahedral coordination) are shown as spheres.

Stabilization of pentavalent U, as opposed to tetravalent U, is proving elusive. It is apparent that a number of synergistic factors are at work and enhanced control of redox processes is necessary. We are confident that subtle adjustments to these reaction conditions will ultimately promote the formation of U(V).

Science Objectives for 2007-2009: Explore the use of complexing anions such as perchlorate, carbonate and benzene-carboxylates in an effort to minimize U(V)-U(V) interactions and ultimately thwart disproportionation.

Explore mixed hydro/solvothermal media such as H_2O/acetonitrile and H_2O/DMF as these combinations have been shown to influence redox in other systems.

Expand XPS efforts to systematically characterize all phases regardless of oxidation state. Analyses of unique local geometries for U^{n+} provide data for collaborative modeling efforts.

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A Study of New Actinide Zintl Ion Materials

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Patrick Feng (BS, 2004 – graduate student at UC-San Diego)
Zeric Hulvey (Summer undergraduate 2004 - graduate student at Notre Dame)
Amy Gray (BS, 2004 – geologist, USGS)

Postdoctoral Fellows supported 2004-06:
Dr. Benny Chan – Faculty member, The State University of New Jersey (Fall, 2006)
Dr. Hugh Selby – Staff member, Los Alamos (Summer, 2006)

Overall research goals: The objective of this project is to synthesize, characterize, and understand the structural chemistry of thorium, uranium, and plutonium solid state materials prepared with main group metal building blocks.

Work Completed 2004-2006: Besides its key role in high temperature superconductors, copper is an interesting element in a number of chalcogenide-based phases. The lower chalcogenides (S-Te) can stabilize the Cu^+ ion because of lower oxidizing power relative to oxygen. The soft d^{10} ion electronic nature of Cu^+ allows flexible structural and coordination environments including potential Cu^+-Cu^+ interaction (~2.7 Å). Cu(I) quaternary compounds offers a remarkable number of new complex structure types; however, no obvious systematic correlation between compounds exist. Fortunately, quaternary systems can be readily mapped and structure/property relationships can be systematically examined. We have worked to complete a study of the K/Cu/An/S (An = Th, U, Pu) quaternary systems.

Thorium containing phases are less well studied than their uranium counterparts. Our early exploration of the K/Th/Cu/S system has yielded three new semiconducting, layered phases, $KCuThS_3$, $K_2Cu_2ThS_4$, and $K_3Cu_3Th_2S_7$ (*Inorg. Chem.*) The compounds vary in their color from colorless ($KCuThS_3$), red ($K_2Cu_2ThS_4$), and yellow ($K_3Cu_3Th_2S_7$), which correlate to their respective band gaps of 3.0 eV, 2.0 eV, and 2.4 eV. The band gaps are direct transitions from the narrow Cu/S valence bands to sulfur-based conduction-band states, as seen in the lanthanide and transition metal analogs.

Three new quaternary U^{4+} compounds were synthesized in a similar region of phase-space as the Th compounds described above. $KCuUS_3$ and $K_2Cu_2US_4$ are isostructural with $KCuThS_3$ and $K_2Cu_2ThS_4$, Figures 1a, c. The third, $K_3Cu_4US_6$, Figure 1d, features layers of isolated U^{4+} octahedra surrounded by distorted CuS_4 tetrahedra separated by K^+ cations. The charge of $K_3Cu_4US_6$ does not balance as written (assuming Cu^+ and U^{4+}), however, EDS microprobe and single crystal diffraction data support the empirical formula. Oxidation states of the metals were confirmed by XPS to be only Cu^+ and U^{4+}. Charge balance is likely achieved by placing "holes" in the sulfur valence bands, making the material a likely p-type conductor. Crystallography could not distinguish differences between potential S^{1-}/S^{2-} species.

As expected, all three uranium-containing compounds display paramagnetic behavior at room temperature and are described in terms of the relative closeness of the U^{4+} octahedra. In $K_3Cu_4US_6$, there would be no expected coupling between uranium cations due to the separation of the uranium octahedra by the CuS_x moieties. In $K_2Cu_2US_4$, there are no interactions between adjacent uranium cations in the linear chains of edge-shared uranium octahedral. $KCuUS_3$ displays an antiferromagnetic transition at $T_n = 61$ K. In the paramagnetic region above 60 K, the compound exhibits Curie-Weiss behavior with a Weiss constant of –58.4 K indicating a net long range antiferromagnetic behavior. The magnetic moment was calculated to be 2.61 μB, which is similar to the theoretical spin only contribution.

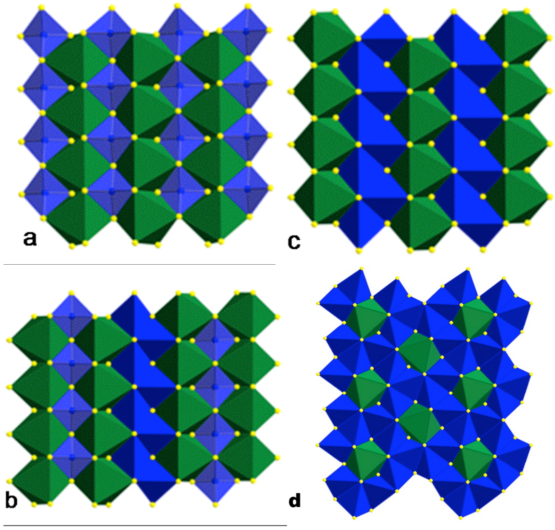
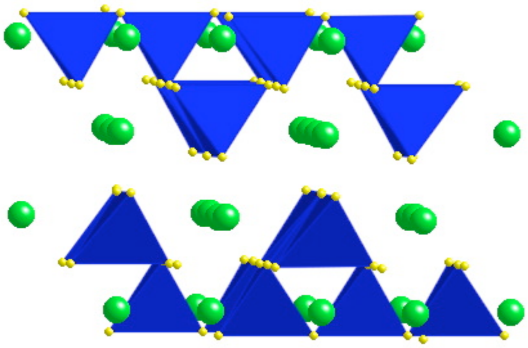


Fig. 1. The actinide chalcocuprates layers are shown, (a) $KCuAnS_3$, (b) $K_3Cu_3Th_2S_7$, (c) $K_2Cu_2AnS_4$, (d) $K_3Cu_4US_6$, where An = U, Th.

Metathesis Reactions to Prepare New Materials

We attempted to prepare new and known materials with new Zintl ion salts as metathesis reaction precursors ase well as using Cu/$CuCl_2$ as a reactants. We prepared and characterized 5 new ternary "starting material" compounds: $K_2P_2Se_6$, $K_4P_2Se_6$, K_3PSe_4, $Cs_4Si_2Se_8$, and $Cs_4Si_4Se_{10}$ (see referenced work, below). These phases were reacted with uranium and plutonium chloride salts to demonstrate that reactions with specific tetrahedral phosphate and silicate building blocks could be preformed with actinide halide starting materials rather than the metals (all other previous reactions were run with U and Th metals). We used a halide scavenger (Tl) to try to help the reactions proceed to completion. However, in the case of Pu, a new Pu-doped thallium salt was isolated and characterized: Pu-$TlCuS_2$, right. While this is a known structure type, this demonstrated for the first time the ability to utilize preformed salts as reactants to with $PuCl_3$.



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Understanding the Magnetic Behavior of Actinide Compounds

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Collaborators: Prof. Thomas Albrecht-Schmitt (Auburn University), Dr. Philip Almond (University of Notre Dame and Argonne National Laboratory, Post-doc), Prof. Peter Burns (University of Notre Dame and Argonne National Lab), Tori Forbes (Graduate student, University of Notre Dame), Prof. James Ibers (Northwestern University)

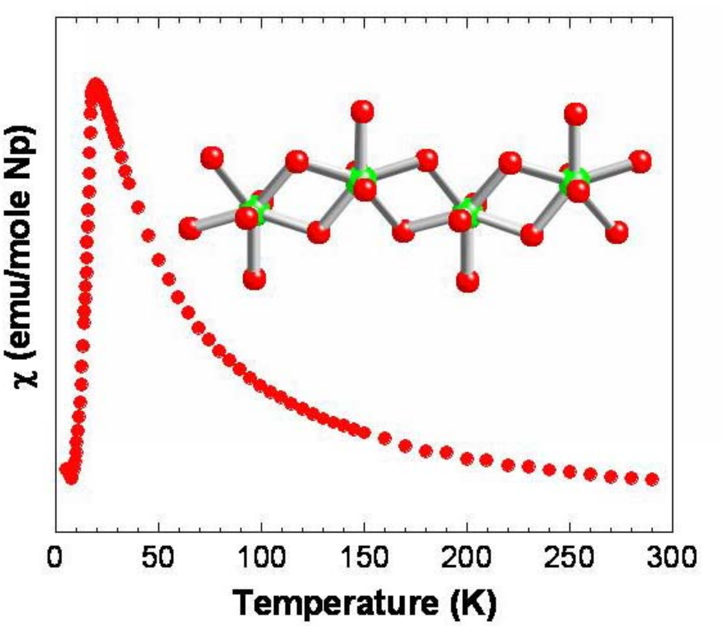
Overall research goals: The goal of this research effort is an understanding of how the structure and bonding in a wide variety of actinide compounds (excluding alloys and metals) influence electronic behavior and magnetic ordering. The 5f actinide ions, with more radially-extended valence orbitals than their 4f lanthanide counterparts, exhibit more varied evidence for electron 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, and magnetic behaviors.

Significant achievements in 2005-2007: As part of ongoing collaborations with Prof. Peter Burns and his group at the University of Notre Dame, as well as Prof. Thomas Albrecht-Schmitt at Auburn University, we have been focusing on Np^{5+} compounds and their magnetic properties. Pentavalent Np, which has a $5f^2$ configuration, is incorporated into oxide-based compounds as the neptunyl NpO_2^+ moiety. Unlike uranyl(VI), neptunyl(V) has unusual propensity to form cation-cation interactions, in which the oxo ligand on one metal center bonds as an equatorial ligand on a neighboring metal center. The result is a short Np-Np interaction compared to standard oxo or hydroxo ligand bridging that, given the right symmetry, can enhance superexchange mediated magnetic interactions between the two metal centers. As neptunyl(V) compounds are synthesized by our collaborators, we are measuring the bulk, averaged magnetic properties as a function of temperature. Interesting systematics are emerging from these studies: (1) if there are no cation-cation interactions, the neptunyl moments do not order magnetically above 5 K, our lowest measured temperature, (2) if there are cation-cation interactions in the structure, the moments order either ferromagnetically or antiferromagnetically, (3) there is a strong bifurcation to the observed ordering temperatures, with the ferromagnetically ordered compounds exhibiting transitions in the 8-10 K range while the antiferromagnetically ordered materials are showing anomalies in the 18-22 K range. Of particular interest are the materials that exhibit ferromagnetic ordering, which represent more than 75% of the materials measured to date. Ferromagnetism is thought to be mediated by RKKY interactions (polarization of the conduction electrons), which would not occur in the materials that we are measuring because they are insulators.

Science objectives for 2007-2009:

- *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)$_2$]:* This compound 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.



Antiferromagnetic ordering seen at 19.5 K for Na[NpO$_2$(OH)$_2$]. Np are connected into chains via bridging OH$^-$ groups along the b direction, and by cation-cation interactions along the c direction.

<u>References of work that was supported by this project (2005-2007)</u>

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T.Z. Forbes, P.C. Burns, S. Skanthakumar, and L. Soderholm, “Synthesis, Structure, and Magnetism in Np$_2$O$_5$,” *J. Amer. Chem. Soc.*, ASAP (2007).

Soft X-ray Synchrotron Radiation Investigations of Actinide Materials

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Dr. Kenneth Raymond, UC Berkeley/LBNL, Berkeley, CA
Dr. Tsuyoshi Yaita, Actinide Coordination Chemistry Group, JAEA, Japan

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 2005-2007: 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 results from NEXAFS and resonant XES of the common uranium oxides found that UO_3 exhibited a significant excitation energy dependence which differed from that of UO_2 and U_3O_8. This is attributed to the differences in the oxygen-uranium hybridization. The XES spectra were successfully compared to electronic structure calculations available in the literature. The first XES/RIXS results from a Cm oxide reference material measured on Beamline 7.0.1 have been successfully simulated. XES/RIXS spectroscopic data were also collected from rare earth materials relevant to trivalent separations prior to the actual actinide investigations. Lastly, an XES study examined nanoscale phenomena in metal oxides to gain further experience as a prelude to future work along the same lines with actinide nanoscale oxides.

The ALS-Molecular Environmental Science (ALS-MES) scanning transmission X-ray microscope (STXM) continues to be used as a characterization tool for actinide materials utilizing NEXAFS spectral and 25 nm spatial resolution imaging capabilities. The first NEXAFS spectra at the 4d edges of Cm, from a ^{248}Cm complex, were obtained. STXM results from U(VI) within uranyl nitrate ($UO_2(NO_3)_2{\cdot}6H_2O$) and perovskite (Ba_2ZnUO_6) yielded structural and electronic properties in agreement with simulations/quantum chemical calculations. The first study STXM investigations of small Pu complexes (Raymond ligands and Pu-maltol series ligands) were successfully performed and examined the K-edges of the light element constituents as well as the Pu 4d's. This complements the structural work being done on the same compounds at the ALS small molecule diffractometer Beamline 11.3.1.

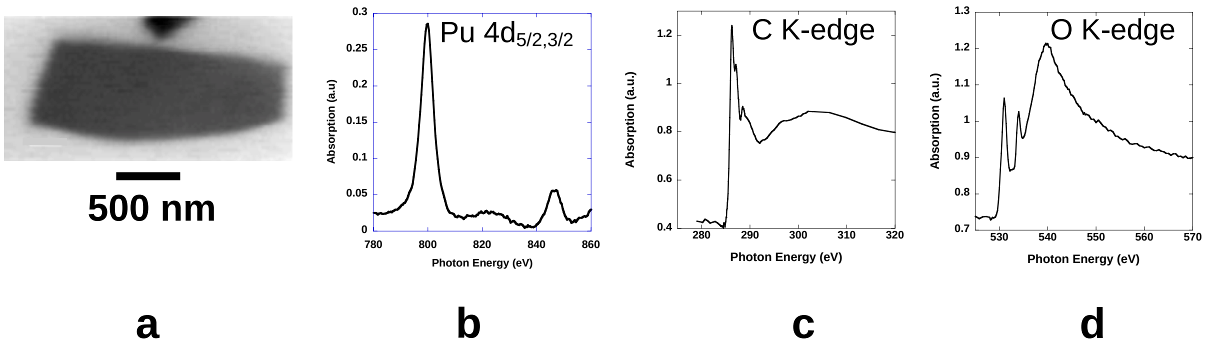

Figure 1. NEXAFS spectra collected with the ALS STXM from a Pu(IV)-bromomaltol complex: (a) The normal contrast transmission image of a Pu bromomaltol particle at 800 eV showing that it is a single crystal; b) Pu $4d_{5/2,3/2}$-edge spectrum; c) C K-edge spectrum; and d) O K-edge spectrum.

Science objectives for 2007-2008:

- 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.
- XES/RIXS will continue to examine actinide reference materials, oxides, and complexes relevant to trivalent separations.
- The conceptual designs of the actinide generation II end station, connection section, and actinide materials preparation glove box will be developed.

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Probing the Changing Role of the5f Electrons through Experiments and Theory

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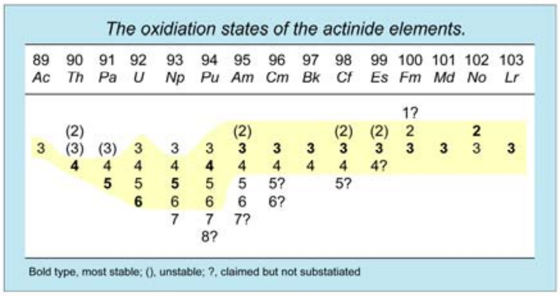
Program Scope: The primary goal to perform fundamental research with the actinide elements and compounds, which generates important information for fundamental insights and the role of electronic configurations and interactions and/or energy levels in determining the chemistry and physics of these materials. A special facet is the changing role of the 5f electrons across the series and whether these are involved in or influence bonding, especially in the condensed state. Collaborations with domestic and international laboratories and universities are stressed and undertaken. The present effort is in full accord with the charges coming out of the recent DOE Workshop, *Basic Research Needs for Advanced Nuclear Energy Systems*, held July 31-Aug.2, 2006. Through constructive interplay between experiment and theory, the aim is to understand the complex correlated basics of actinide materials.

The efforts involve syntheses and characterization of the critical properties of the actinides, their alloys and compounds as a function of temperature and pressure (e.g., "extreme conditions, as expressed as a Workshop goal). These finding are correlated with recent advances in theory to provide a consistent fundamental understand of actinide science. This is in accord with the pronounced shift in recent times to realizing the need for a strong interaction between experimental findings and basic theory and modeling.

Recent Progress: The roles of the 5f electrons in metals, alloys and compounds have been investigated by different techniques to acquire an in-depth understanding of the effects of electronic configurations and bonding, changes occurring with specific configurations and how variables, including composition, can alter these. Our success with understanding curium metal, with regard to its magical $5f^7$ state where seven unpaired electrons maximize spin polarization, stability and generate a magnetically stabilized structure is one example. This was accomplished by a combined experimental and theoretical effort. Given the impact of our original work on americium, there has been a large flux of theoretical efforts on the actinides, not only for the lighter members, but a shift out to the higher members. It became obvious to many scientists that to fully understand the 5f electrons required a total picture effort, not just a few selected elements.

Recent thrusts involve considering compounds as the actinide pnictides, where an unusual volume behavior is encountered that is resembles the famous atomic volume behavior with Z as found with the metals. For the metals, energy loss-spectroscopy together with calculations have examined the electronic and magnetic structural behavior of americium and curium, in relationship to thorium, uranium and plutonium to develop an in-depth view of LS and intermediate coupling behaviors. Studies of alloys have probed the extent of an element's electronic configuration of properties, and when dilution "turns off" these effects. Finally, the role of promotion energies for the actinides has been examined in relationship to their many properties and behaviors. The oxidation states of the actinides can be correlated with 5f electron promotion energies and, in the case of the earlier actinides, with the number of 5f electrons in the hybride bands at the Fermi level in the metallic state.



The oxidiation states of the actinide elements.

89 *Ac*	90 *Th*	91 *Pa*	92 *U*	93 *Np*	94 *Pu*	95 *Am*	96 *Cm*	97 *Bk*	98 *Cf*	99 *Es*	100 *Fm*	101 *Md*	102 *No*	103 *Lr*
											1?			
	(2)					(2)			(2)	(2)	2		**2**	
3	(3)	(3)	3	3	3	**3**	**3**	**3**	**3**	**3**	**3**	**3**	3	**3**
	4	4	4	4	**4**	4	4	4	4	4?				
		5	5	**5**	5	5	5?		5?					
			6	6	6	6	6?							
				7	7	7?								
					8?									

Bold type, most stable; (), unstable; ?, claimed but not substatiated

Selected Scientific Objectives for 2007-2009: Additional studies incorporating experiment and theory will be carried out, when possible developing new first principle approaches to solve the 5f electron complexities, and hopefully a parameter free theory for actinides. Efforts are expected in compounds that are relevant and important in ANES systems. As funding priorities have changed, much of this future work will be performed at other laboratories and with a different funding base.

Publications supported by this program in the last two years:

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Computational Studies of Novel Separation Media

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Overall research goals: The objective of this project is to use computer modelling to understand fundamental chemistry during synthesis, functionalization, and utilization of novel separations media.

Significant achievements in 2005-2007: In the past, our group has successfully developed mesoporous silica based molecular imprinting system for highly selective ion extraction. We are interested in how mesoporous silicas function as adsorbent supports. Recent work by others indicates that silver salts supported on mesoporous silica display excellent adsorption selectivities of ethylene over ethane and propylene over propane. What we intended to find out with quantum mechanical (QM) tools was how surface silanol groups interact with silver salts and how the Ag^+ counter anion affects the binding with olefins. We employed a state-of-the-art density functional theory (DFT) method in our studies. Computationally inexpensive yet reliable, this method is well suited to study adsorption of small molecules on extended surfaces. One major result from our study is that surface silanols are very flexible, ready to re-organize to form multiple hydrogen bonds with the anion (Figure 1). Another conclusion is that although the interaction between Ag 4d and olefin π states dominates the Ag-olefin π complexation, the anion affects the strength of the complexation by changing the interaction between Ag 5s and olefin π states (Table 2 and Figure 2). These results indicate a way to improve the sorbent selectivity for olefins, which may help our design of sorbents and ionic liquids for olefin/paraffin separation.[1]

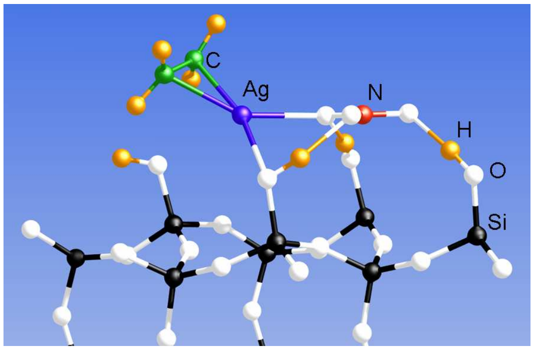


Figure 1. C_2H_4 adsorption on SiO_2-supported $AgNO_3$.

The same QM method was also employed to address surface functionalization of mesoporous carbons and metallic materials.[2, 3] Aryl groups can be covalently attached to porous carbons via reduction of aryl diazonium salts. Here, the intriguing question is where and how the aryl groups are bonded to porous carbon. To address this problem, we started with a simple model for our carbon, a graphene sheet. First, we examined the interaction between the phenyl group (C_6H_5) and a graphene sheet. Isolated C_6H_5 groups were found to be weakly bonded to the basal plane, comparable to physisorption, whereas a pair of C_6H_5 molecules, located at the para-positions of the same six-membered ring, were found to be significantly more stable (Table 2 and Figure 3). We then introduced edges to the graphene model and demonstrated the high reactivity of edge sites for aryl attachments, especially the zig-zag edge for the first aryl attachment due to its edge states (Figure 4). Our calculations support the experimental observation that edge sites of graphite are more reactive during the aryl diazonium-grafting process. Furthermore, we demonstrated the reactivity of zigzag edges in greater detail by computing the dissociation energies of bonds between the zigzag edge and common radicals.[4]

Science objectives for 2007-2009:

- Examine molecular building blocks for porous carbons and their chemical reactivity by using quantum mechanical methods; these building blocks include nanographenes with pentagon and heptagon defects and complex curvatures.
- Develop a force field for Ag^+-complex based ionic liquids from *ab initio* quantum chemistry calculations; investigate olefin transport through these ionic liquids using classical molecular dynamics simulations with the developed force field.

Table 1. Adsorption Geometry and Energetics for C_2H_4 on Various Silica-Supported Silver Salts

Ag salt	Ag^+	$AgNO_3$	$AgClO_4$	$AgBF_4$
Ag charge	0.68	0.77	0.78	0.79
C-C (Å)	1.376	1.377	1.372	1.365
Ag-C (Å)	2.219 2.225	2.235 2.257	2.250 2.301	2.337 2.345
E_{ad} (eV)	–0.80	–0.70	–0.69	–0.64

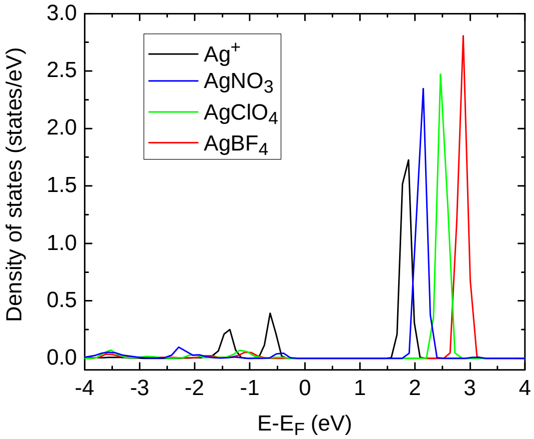
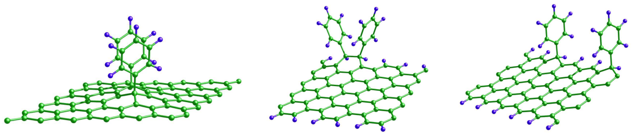


Figure 2. Orbtial-projected density of states for the Ag 5s states of various Ag-salt/SiO_2 at their static-adsorption configuration.

Table 2. Energetics (eV) of the Phenyl Group (C_6H_5) on a Graphene Basal Plane, Armchair Edge, and Zigzag Edge.

Attachment	Graphene basal plane	Armchair edge	Zigzag edge
first	–0.25	–1.11	–2.75
second	–1.27	–2.74	–2.17



basal plane armchair edge zigzag edge

Figure 3. Phenyl interaction with graphenes.

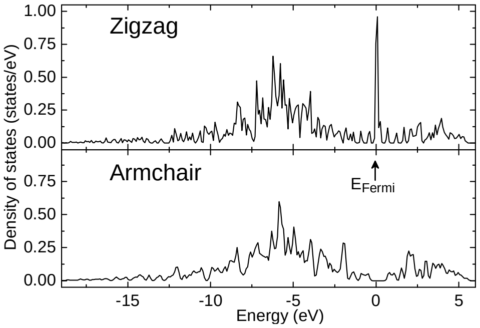


Figure 4. Local density of states of carbon atoms on the graphene edge.

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Covalency surprises in the actinide dioxides

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Overall research goals:

The methodological development and computational implementation of quantum chemistry methods for the accurate calculation of properties of solids and surfaces containing actinides and other heavy atoms. Here, we discuss the first systematic study of the electronic properties of the AnO_2 series, An = Th–Es, using the HSE (Heyd-Scuseria-Ernzerhof) screened exchange hybrid density functional.

Significant achievements in 2005-2007:

Actinide-based materials are challenging for both experiment and theory. These materials have partially occupied *f* orbitals, with electrons that can exhibit competition between itineracy and localization. This leads to multiple competing low energy states and phases in the elemental solids, with localized behavior gaining importance as Z increases in the actinide series and the effective 5*f* orbital radius decreases. A strong electron correlation manifests in the compounds of the actinides; in particular, the early members of the actinide dioxides (e.g. UO_2) are Mott insulators, and the electrons occupying the 5*f* orbital are strongly localized at the actinide site. In analogy with the elemental solids, one would expect the remaining members of the series to show increasingly localized characteristics. The screened hybrid density functional[a] (HSE) calculations reported here suggest that this is not the case. Figure 1 displays the calculated lattice parameters for antiferromagnetic AnO2, together with the measured values.[b-d] Experiment shows a monotonic decrease in lattice constant with increasing Z, with a deviation in the general trend at Cm. The experimental values are generally closely reproduced by theory, with the exception of the region near half-filling [Cm^{4+} (f^6), Bk^{4+} (f^7)]. Note that theory captures, but overdramatizes, the increase in lattice constant at CmO_2 relative to the general trend.

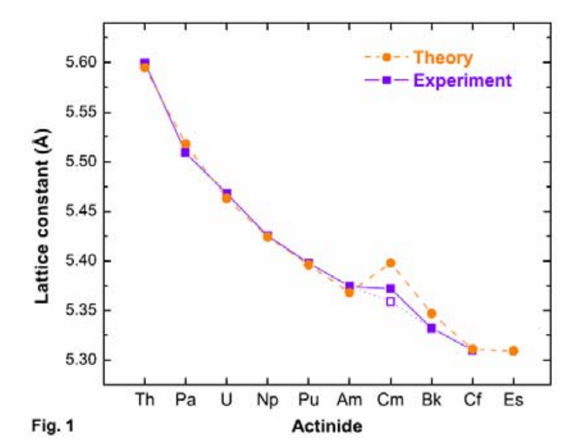

Fig. 1

Figure 1: Optimal lattice constants calculated with HSE for AnO_2 (An = Pa-Es). Predictions are compared to known experimental data from Ref. b. The measured lattice constants for CmO_2 are for isotopes ^{244}Cm (solid square [Ref. c]) and for the longer-lived ^{248}Cm (open square [Ref. d]).

Figure 2 shows the calculated 5*f* orbital spin density which is defined as the difference between the alpha and beta electron densities according to a Mulliken population analysis. For comparison, the spin density expected for formal An^{4+} ions is also plotted, and it is evident that the formal expectations are encountered only for the lighter actinide dioxides. The situation changes at AmO_2 and especially at CmO_2, where significant depletion of oxygen beta spin occurs (see Figure 2B). These spin densities (and the covalency they imply) reflect a tendency towards An^{3+} character as the energy of the 5*f* orbital drops with increasing Z. Another important feature observed in our calculations is the degeneracy of the 5*f* and O2*p* orbitals beginning with PuO_2 which can be observed from the evolution of the partial density of states for the series.

Therefore, we emphasize here two main results:
1. An orbital energy near-degeneracy for $PuO_2 – CmO_2$
2. Deviations from the canonical formal charge, An^{4+}

The near degeneracy leads to unexpected orbital mixing for the intermediate members of the series, and in contrast to the pure elemental forms, generates an evolution from localized to delocalized *f* electron character as Z increases. Another consequence of the 5*f* stabilization with increasing nuclear charge is a driving force toward An^{3+} valences. This, combined with strong on-site exchange interaction, leads to a magnetic ground state in the nominally non-magnetic CmO_2.

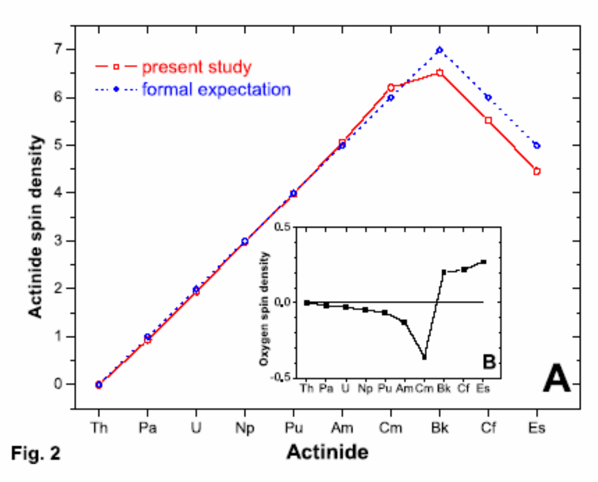

Fig. 2

Figure 2: (**A**) Theoretical prediction for the absolute value of the spin density for the An 5*f* orbitals in AnO_2 (An = Th-Es) at their respective equilibrium geometries. The expectations from formal An^{4+} charges and Hund's first rule are plotted with a dashed line. The inset (**B**) shows the corresponding spin density at the oxygen sites, for the ferromagnetic case.

Specific objectives for 2007-2009:

- Extend our all-electron and pseudopotential periodic codes to include the spin-orbit interaction self-consistently.
- Incorporate the calculation of UV and optical spectra via time dependent density functional theory.
- Apply these new tools to the study of electronic properties and lattice distortions of AnO_2 and solid An.

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Fundamental Studies of Novel Separations

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Overall research goals: The overall goal 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 Experimental Achievements in 2005-2006:
(1) ***High-Yield Functionalization of Nanoporous Carbon Materials***. A new functionalization methodology for porous carbon materials was developed to tailor the separation properties of nanoporous carbon materials. The surfaces of various ordered mesoporous carbons were chemically functionalized by employing an approach, in which the selected diazonium compounds were in-situ generated and reacted with the carbon frameworks of mesoporous carbons. The aromatic organic molecules containing chlorine, ester and alkyl groups were covalently attached to the surfaces of these ordered mesoporous carbons. A grafting density of 0.9-1.5x10^{-6} mol/m^2 was achieved.[1,2]

(2) ***Self-Assembly Synthesis of Nanoporous Carbon Materials***. A new methodology has been developed for the synthesis of ordered mesoporous carbon materials. The essence of this methodology is the self-assembly of block copolymers and carbon precursors through multiple hydrogen bonding. Carbon precursors with monodentate, bidentate, and tridentate hydroxyl groups have been systematically investigated for the self-assembly of highly ordered mesoporous carbon structures. Our results showed that the strong hydrogen bonding between the templates and the carbon precursors plays a key role in self-assembly synthesis of ordered mesoporous carbon materials. The pore size of the mesoporous carbon can be adjusted in a continuous manner by using block copolymers of various molecular weights. Through this self-assembly method, various forms of the mesoporous carbons (e.g., monolith, fine particles, thin films, and fibers) can be fabricated to meet the material needs of various separation techniques.[3]

(3) ***Immobilization of Ionic Liquids for Separation***. A new methodology to immobilize ionic liquids through the use of a bridged silsesquioxane N-(3-triethoxysilylpropyl), N(3)-(3-trimethoxysilylpropyl-4,5-dihydroimidazolium iodide that incorporates an ionic functionality for the assembly of novel period mesoporous organosilica (PMO) materials has been developed. The resulting PMO materials were investigated for use as novel anion-exchange resins for the separation of perrhenate anions in aqueous solution. As compared with cetyltrimethylammonium chloride, 1-hexadecane-3-methylimidazolium bromide has been demonstrated to be a more efficient surfactant template for generation of mesopores and surface areas for such PMO materials.[4]

(4) ***Dendrimer-Based Ionic Liquids***. Dendrimers are a new class of molecules with great potentials for novel separation. We have developed a new method to synthesize dendrimer-based ionic liquids. The essence of our methodology for the formation of the dendrimer cations is through the acid-base reaction of the neutral amine and amide groups on a dendrimer with a Bronsted acid, followed by the metathesis reaction of the resulting aqueous salt solution with an anion donor.[5] Another class of protic ionic liquids with unique cationic structures explored by us is based on protonated amides. A simple, one-pot strategy to form a novel class of proton-transfer room-temperature ionic liquids (RTILs) whose Bronsted bases were composed of N,N-dimethylformamide (DMF) and a series of analogs all containing an acyclic amide was developed. The proton-accepting groups of this unique class of protic RTILs are a significant departure from the amine, pyridine, or imidazole groups. Due to a tautomerization process, the protons

are more weakly bound, leading to a series of RTILs with improved proton conductivity. A successful proton-pumping experiment demonstrated the potential of these protic RTILs in separation of gases.[6]

(5) ***Metal-Containing Task-Specific Ionic Liquids***: A novel series of ionic liquids whose cations consist of metal cations instead of organic cations have been synthesized with a new methodology. The conventional formation of ionic liquids can be regarded as the complexation reactions of simple anionic species by neutral compounds. The essence of our new methodology is to form the cations of ionic liquids through the complexation reactions of neutral organic ligands with metal ions, followed by the subsequent metathesis reactions of the resulting salts with appropriate anion donors. Metal ions demonstrated include Ag(I), Cu(II), and Zn(II). Given their immiscibility with water, tunable sorption site density, and non-existing vapor pressure, such TSILs are especially well-suited for gas separations.[7]

(6) ***Gas Separation Based on Microporous Metal-organic Frameworks (MOFs)***. A MOF material has been synthesized and used as separation media for gas chromatography. Both size and shape selectivities of this MOF material for alkanes have been demonstrated. The MOF material utilized in our experiments exhibits a unique dynamic pore structure. The pore size can be tuned, to an extent, according to the adsorbate. The organic moieties of the framework also contribute to the selectivity because of the various interactions between the frameworks and the adsorbates. This research opens up a new dimension in applications of MOF materials in separation sciences.[8]

Specific experimental objectives for 2007-2008: The methodologies to synthesize ordered carbon materials with controlled pore sizes by varying block copolymer templates with different molecular weights will be explored. These porous carbon materials will provide unique opportunities to investigate the effects of pore sizes on selectivities for various carbon-based separation systems. The new synthesis strategy recently developed by our group will be used to synthesize new RTILs whose cations are composed of coordination complexes of silver ions and olefins for selective transport of olefins.

Selected References of work that were supported by this project (selected publications from +40)

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(8) Chen, B. L.; Liang, C. D.; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yaghi, O. M.; Dai, S. "A microporous metal-organic framework for gas-chromatographic separation of alkanes," *Angew. Chem.-Int. Edit.* **2006**, *45*, 1390-1393.

Self-Assembled Ionophores: New Directions

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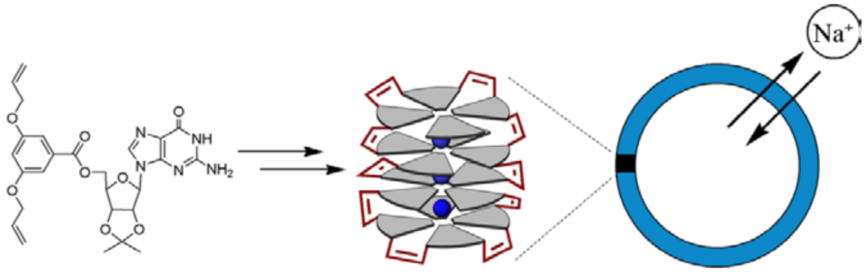
Overall research goals: Our goal is to build "self-assembled" ionophores that selectively bind and transport ions and/or ion pairs. We have used non-covalent interactions to synthesize such receptors. Like DNA, we lipophilic guanosine nucleosides also hydrogen bond to give G-quadruplexes that selectively 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 in 2005-2006: Supramolecular Assemblies that Transport Na^+ across Phospholipid Bilayer Membranes. We recently prepared a novel synthetic assembly that can move Na^+ cations across phospholipid bilayer membranes (Scheme 1). Such transporters could eventually serve as intracellular sensors or antimicrobial agents. We achieved the desired properties by adding polymerizable groups—allyl ethers—to the nucleoside's sugar sidechain. When templated by K^+, 16 monomers of the guanosine derivative form a noncovalent assembly that consists of four layers of hydrogen bonded G-quartets. The entire structure is then stitched together by olefin metathesis to give a single compound that functions as a membrane transporter. 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.



Scheme 1. A Lipophilic Guanosine Nucleoside that Forms a Transmembrane Ion Transporter.
"A Unimolecular G-Quadruplex that Functions as a Synthetic Transmembrane Na^+ Transporter." M. S. Kaucher, W. A. Harrell, J. T. Davis, *J. Am. Chem. Soc*. **2006**, *128*, 38-39.

New Cl^- Anion Receptors/ Membrane Transporters. In the past grant period we have continued to extend our use of strategy of self-assembly to prepare a series of compounds that can transport Cl^- anions across bilayer membranes. Using various assays with synthetic EYPC liposomes we compared the H^+/Cl^- co-transport activity of a series of calixarene amides, acyclic butylamides, pyrrole natural products and synthetic and isophthalamide analogs. These compounds' ability to transport Cl^-, to maintain a transmembrane potential, along with high activity at _M concentrations, low molecular weight and simple preparation make them all valuable leads in drug development for diseases caused by Cl^- transport malfunction. In addition to such applications these compounds also provide a framework on which to build other functional supramolecular structures.

Science objectives for 2007-2008:

In addition to continuing our fundamental studies of self-assembled ionophores, continued emphasis in the coming budget year 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 2005-Feb. 2007):

1. "Using Diffusion NMR to Characterize Guanosine Self-Association. Insights into Structure and Mechanism." M. Kaucher, Y. Lam, S. Pierraccini, G. Gottarelli, J. T. Davis, *Chemistry-A European Journal*, **2005**, *11*, 164-173.

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8. "A Transmembrane Anion Transporter Selective for Nitrate over Chloride." Paul V. Santacroce, Oluyomi A. Okunola, Peter Zavalij and Jeffery T. Davis, *Chemical Communications*, **2006**, 3246-3248.

9. "N2, C8-Disubstituted Guanosine Derivatives Can Form G-Quartets. " Mark S. Kaucher and Jeffery T. Davis, *Tetrahedron Lett.* **2006**, *47*, 6381-6384.

10. "Cation Exchange in Lipophilic G-Quadruplexes: Not All Ion Binding Sites are Equal." Ling Ma, Maura A. Iezzi, Mark S. Kaucher, Yiu-Fai Lam and Jeffery T. Davis, *J. Am. Chem. Soc.* **2006**, *128*, 15269-15277.

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12. "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.

13. " Self-Assembled Ionophores from Isoguanosine: Diffusion NMR Clarifies Cation's and Anion's Influence on Supramolecular Structure." Tamar Evan-Salem, Limor Frish, Fijs W. B. van Leeuwen, David N. Reinhoudt, Willem Verboom, Mark S. Kaucher, Jeffery T. Davis and Yoram Cohen, *Chemistry: A European Journal*, **2007**, *13*, 1969-1977.

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15. " The G-Quartet in Supramolecular Chemistry and Nanoscience." Mark S. Kaucher, William A. Harrell, Jr and Jeffery T. Davis, **Quadruplex Nucleic Acids**, S. Neidle, S. Balasubramanian (Ed.), Royal Society of Chemistry, Cambridge, U.K., **2006**, 253-296.

Neoteric Solvent Systems for Metal Ion Separations

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Program scope: Increasing awareness of the adverse environmental impact of the use of conventional organic solvents in chemical separations has led to growing interest in the application of potentially more environmentally benign alternatives, in particular, supercritical fluids and ionic liquids (ILs). Our recent work with these "neoteric" solvents has focused primarily on obtaining an improved understanding of the fundamental aspects of metal ion transfer into ILs in the presence of various types of extractants, with the ultimate objective of developing guiding principles for the rational design of IL-based separation systems.

Recent progress: In prior work under this program, we showed that unlike conventional solvent systems in which neutral complex partitioning is observed, the transfer of Sr^{2+} from aqueous nitrate solution into the ionic liquid (IL) 1-pentyl-3-methylimidazolium *bis*[(trifluoromethyl)sulfonyl]imide ($C_5mim^+Tf_2N^-$) containing a macrocyclic polyether (CE) proceeds *via* exchange of the cationic 1:1 strontium:CE complex for the cationic component of the IL. In subsequent studies, we demonstrated that the predominant mode of strontium ion transfer shifts from this cation-exchange process to conventional neutral nitrato complex partitioning as the length of the appended alkyl chain (and thus, the IL cation hydrophobicity) is increased. In more recent work, we have evaluated the effect of alkyl side chain fluorination on the mode of strontium ion transfer into a series of 1-fluoroalkyl-3-methylimidazolium salts, finding that fluoroalkyl substituents are only slightly more effective in inducing a shift from cation-exchange to neutral complex partitioning than their non-fluorous analogs. At the same time, fluorinated ILs yield distribution ratios as much as an order of magnitude lower than the corresponding 1-alkyl-3-methylimidazolium (C_nmim^+) salts, indicating that fluorous ILs are unlikely to offer compelling advantages over C_nmim^+ ILs as extraction solvents. In related studies of sodium ion partitioning between aqueous nitrate media and $C_nmim^+Tf_2N^-$ ILs in the presence of CEs, we have uncovered evidence of a second type of ion-exchange process by which metal ion partitioning may occur, one whose prevalence is determined not by the alkyl chain length of the IL cation, but by the ease of extractant protonation (Figure 1). Thus, contrary to our earlier expectations, increasing the hydrophobicity of the IL cation is not, by itself, sufficient to ensure the predominance of neutral complex partitioning as a path for metal ion transfer into an ionic liquid. Just as important is the fact that the formation of a protonated extractant, if followed by its exchange for the IL cation, may lead to significant and undesirable solubilization of the IL in the aqueous phase.

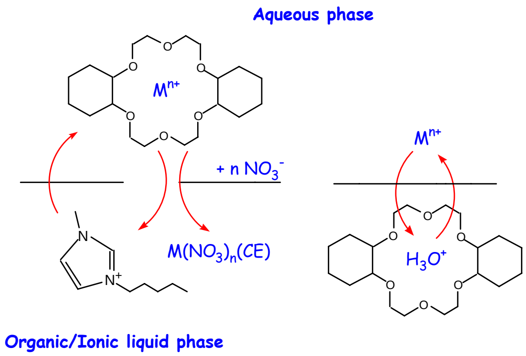

Figure 1. Modes of metal ion transfer into an IL in the presence of a neutral extractant

<u>Science objectives for 2007-2009:</u> Our systematic investigation of the influence of IL cation and anion structure, the properties of the metal ion and extractant, and the aqueous phase conditions on the mode of metal ion partitioning into various families of ionic liquids will continue, with emphasis on actinide and fission product ions.

<u>Publications supported by this program:</u>

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2. M.L. Dietz, "Ionic Liquids as Extraction Solvents: Where do we Stand?", *Sep. Sci. Technol.* **41**, 2047-2063 (2006).
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5. M.L. Dietz, J.A. Dzielawa, M.P. Jensen, J.V. Beitz, M. Borkowski, "The Road to Partition: Mechanisms of Metal Ion Transfer into Ionic Liquids (ILs) and their Implications for the Application of ILs as Extraction Solvents" in *Ionic Liquids IIIB: Fundamentals, Progress, Challenges, and Opportunities*, R.D. Rogers and K.R. Seddon, Eds., American Chemical Society, Washington, DC, 2005, pp. 2-18.
6. M.L. Dietz, D.C. Stepinski, "A Ternary Mechanism for the Facilitated Transfer of Metal Ions into Room-Temperature Ionic Liquids (RTILs): Implications for the "Greenness" of RTILs as Extraction Solvents", *Green Chem.* **7**, 747-750 (2005).
7. M.A. Firestone, M.L. Dietz, S. Seifert, S. Trasobares, D.J. Miller, N.J. Zaluzec, "Ionogel-templated Synthesis and Organization of Anisotropic Gold Nanoparticles", *Small* **1**, 754-760 (2005).

Third Phase Phenomena in Solvent Extraction

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Program scope:

The objective of this project is to investigate aggregation processes taking place in liquid-liquid, biphasic separation systems. Third phase formation in solvent extraction, a generally unwanted and potentially hazardous phenomenon, is the present main focus of our research, because a comprehensive description of its mechanism and energetics is still lacking.

Recent progress:

Our 2005-2007 studies support our previous conclusion that tri-*n*-butyl phosphate (TBP) in *n*-alkane diluents, in contact with aqueous phases containing nitric acid and uranyl, thorium, zirconium and plutonium nitrates, forms small reverse micelles containing up to four TBP molecules[1,2]. Water, nitric acid and metal nitrates are incorporated into the polar core of the micelles and these interact through van der Waals forces between their polar cores. The separation of most of the solute particles in a new phase takes place when the energy of attraction between the particles in solution becomes about twice the average thermal energy, k_BT (k_B = Boltzmann constant). We have extended our investigations to the extraction of mineral acids with different hydration properties by TBP and its triisobutyl and tri-*sec*-butyl isomers[3-5]. The series of effectiveness with respect to third phase formation ($HClO_4 > H_2SO_4 > HCl > H_3PO_4 > HNO_3$) correlates with the amount of water present into the organic phase at the point of phase splitting. This result, reported for the first time in the literature, reinforces the validity of our reverse micellar model for third phase formation. Figure 1 shows, as an example, the simplified phase diagram and small-angle neutron scattering (SANS) data for the $HClO_4$-TBP system. The analysis of the SANS data allowed us to conclude that also for the extraction of acids, organic phase splitting occurs when the intermicellar attraction energy reaches $-2\ k_BT$.

In a related study, we investigated the solvent extraction and structural properties of the mixture of two extractants, di-*n*-hexyl phosphoric acid (HDHP) and N,N'-dimethyl-N,N'-dioctyl-hexylethoxymalonamide (DMDOHEMA), a system that is currently under consideration for the partitioning of trivalent actinides from lanthanides[6,7]. Distribution measurements provided evidence for the formation of mixed extractant species[7] that we are currently investigating through physical measurements. In another study, we investigated the conditions for aggregate formation in the organic phase of the biphasic system HNO_3 - tetraalkyldiglycolamide in the presence of lanthanide ions[8].

Science objectives for 2007-2009:

Our future program consists in testing the generality of the solute interaction model that we are developing by investigating third phase formation in systems involving:

- extraction by TBP of other acids ranging from small, weak organic acids (e.g., formic and acetic) to large, complex, multicharged, strong acids (e.g., polyoxometalates in acid form)

- extractants with increasing basicities of the donor groups (e.g., phosphates vs. phosphonates vs. phosphine oxides)
- extractants with different alkyl groups, linear and branched, to test the effect of the stickiness of the reverse micelles on third phase formation
- multidentate extractants (e.g., of the carbamoylphosphine oxide (CMPO) type)
- different media, diluents and temperatures.

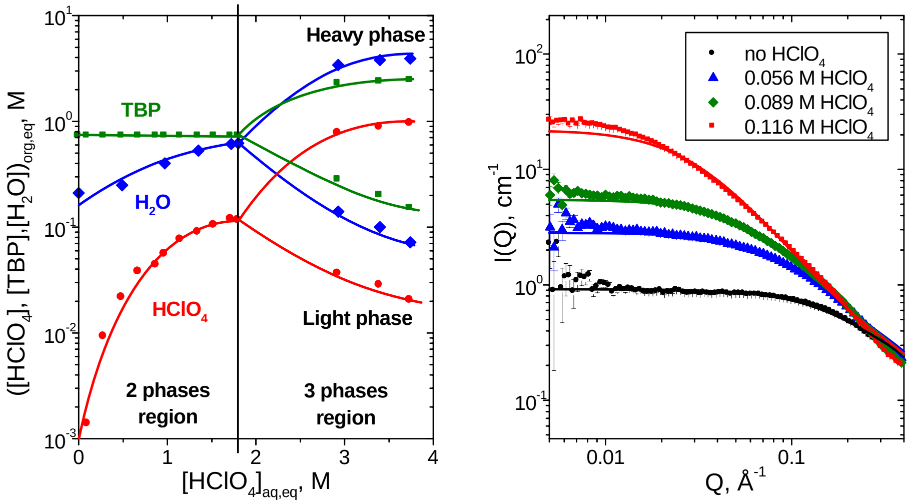

Figure 1. Left: Simplified phase diagram for the $HClO_4$ - 0.73 M TBP in *n*-octane system. Right: SANS data for 0.73 M TBP in *n*-octane after extraction of increasing amounts of $HClO_4$.

References of work that was supported by this project:

1. R. Chiarizia, M. P. Jensen, M. Borkowski and K. L. Nash. A New Interpretation of Third Phase Formation in the Solvent Extraction of Actinides by TBP. In *Separations for the Nuclear Fuel Cycle in the 21st Century*, G. J. Lumetta, K. L. Nash, S. B. Clark and J. I. Friese, Eds., ACS Symposium Series 933, American Chemical Society, Washington, DC, 2006, 135-150.
2. J. Plaue, A. Gelis, K. Czerwinski, P. Thiyagarajan and R. Chiarizia. Small-Angle Neutron Scattering Study of Plutonium Third Phase Formation in 30% TBP/HNO_3/Alkane Diluent Systems. *Solvent Extr. Ion Exch.*, **2006**, *24*, 283-298.
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4. R. Chiarizia, D. C. Stepinski and P. Thiyagarajan. SANS Study of Third Phase Formation in the Extraction of HCl by TBP Isomers in *n*-Octane. *Sep. Sci. Technol.*, **2006**, *41*, 2075-2095.
5. R. Chiarizia and A. Briand. Third Phase Formation in the Extraction of Inorganic Acids by TBP in *n*-Octane. *Solvent Extr. Ion Exch.*, **2007**, *25*(3), *in press.*
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The Correspondence between Solution and Solid-State Structures

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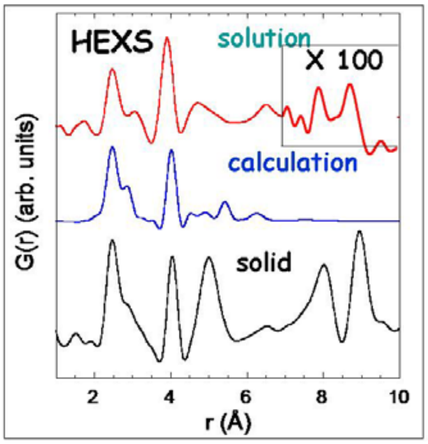
Overall research goals: A fundamental understanding is sought of the structure and bonding patterns of actinide ions and their correspondence between solution and the solid state. Our work is focused on quantifying the energetics driving complex stability and chemical reactivity with the focus of a predictive knowledge of actinide solution complexation and aggregate formation under a wide range of chemical conditions.

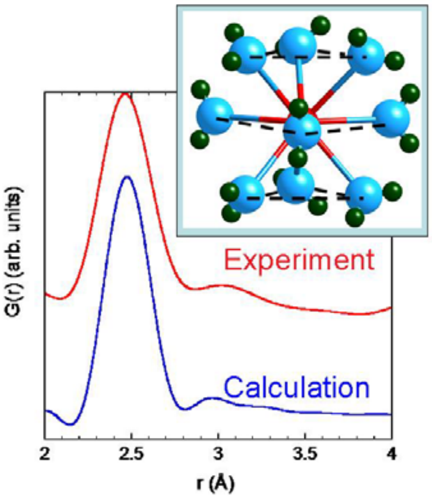
Significant achievements in 2005-2007: The application of high-energy X-ray scattering (HEXS) to solutions containing dissolved actinide ions is yielding detailed information about solute-solvent correlations, including the number and distances of ligands associated with the metal for the first, second, and sometimes more distant coordination shells. By combining these solution data with X-ray diffraction analyses of single-crystals that precipitate from solution, we are able to obtain unprecedented information about solution coordination environment. For example, HEXS experiments were used to determine that, under select solution conditions, the uranyl ion has an average coordination environment between four and five. Assuming an equilibrium, it was possible to determine that about 1 kcal was necessary to add a H_2O ligand to $UO_2(H_2O)_4^{2+}$. This is the first experimental determination of such an hydration energy and the results are being used by theorists to test their calculations. In another study, HEXS was used to test the correspondence of structure between a Th-Cl dimer in solution and in the solid state. The crystal structure was critical to the analysis of the solution data, the latter of which clearly showed evidence of the same type of dimer-dimer correlations seen in the crystal structure.



A comparison of HEXS data obtained from a Th-Cl solution with data obtained from the precipitate. The dimer structure obtained from analysis of X-ray diffraction data is used to obtain the calculated PDF also shown in the figure.

Science objectives for 2007-2009:

- *Quantify actinide homoleptic aqua coordination:* Where possible, provide a detailed description of $An(H_2O)_x^{n+}$ for the trivalent and tetravalent (n=3,4) actinides, for which x represents the most stable coordination number in acidic solution. In addition, we wish to study AnO_2^{2+} cations for An = Np, Pu to complement the uranyl work and to determine if there is a shift in the proposed 4-5 equilibrium for equatorial H_2O coordination toward the lower number. Such a shift would support the hypothesis of steric crowding as the driving force for the non-integral coordination number. The same hypothesis has been used to explain the splitting of the first shell water coordination in the lanthanide triflates. We will extend this study to a comparison of the solution and solid-state homoleptic water coordination for the tri- and tetravalent actinides. This work follows on our recent studies of Cm aqua coordination. Data obtained from NpO_2^+ in solution indicate that similar attempts to study homoleptic coordination of pentavalent ions with actinyl coordination will be vitiated by cation-cation interactions. These findings are supported by recent structural studies of NpO_2^+ systems, which show a high propensity to form extended cation-cation networks. In collaboration with Professor David Dixon, our solution studies will be augmented by detailed theoretical calculations aimed at understanding the relative stability of dissolved metal-ion coordination in aqueous solution.



The solution coordination of Cm^{3+} compared with the Cm nonaaqua coordination calculated using the triflate structural parameters.

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*Cover article

Gas-Phase Actinide Ion Chemistry Elucidates Fundamental Aspects of f-Element Science

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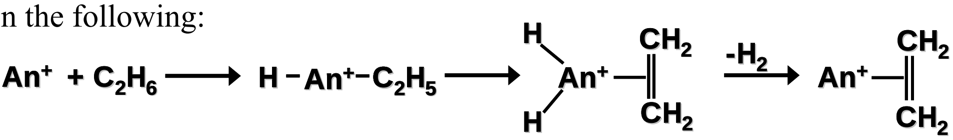
Program Scope: The core objective is to perform basic experimental research to provide information for an overall understanding of the underlying science, properties and behavior of actinides. Gas-phase actinide ion chemistry is a valuable approach for obtaining such fundamental information and insights. The studies focus on experimental molecular actinide chemistry, but close interactions with parallel theoretical efforts are increasingly crucial to effectively interpret the experimental observations. An underlying theme of these efforts is the role of the 5f electrons/orbitals in molecular chemistry.

Recent Progress: Activation of C_1–C_4 hydrocarbons by bare and oxo-ligated actinide cations (Th^+ through Cm^+) was examined. The reactivities of bare Pu^+, Am^+ and Cm^+ correlate with energies for excitation to a $5f^{n-2}6d7s$ configuration, indicating that their 5f electrons are inert in insertion processes such as depicted in the following:



The reactivity trend for the early actinides, $Th^+ > Pa^+ > U^+ > Np^+$ (Table 1), is interpreted to indicate 5f electron participation in σ-type bond activation by Pa^+. Among the AnO^+ ions, only ThO^+, PaO^+ and UO^+ activated hydrocarbons, with the reactivity of PaO^+ being distinctively high (Table 2). Electronic structure calculations for PaO^+ reveal a $Pa(5f6d)O^+$ ground state; all excited states up to 1.8 eV have a 5f-orbital occupancy of ≥0.8. The high reactivity and substantial 5f character of the metal center in PaO^+ indicate participation of its 5f electrons in bond activation. The results for An^+ and AnO^+ reveal that the 5f electrons of Pa play a distinctively active role in σ-type organoprotactinium bonding.

Oxidation reactions of bare and ligated Pa ions were studied using seven oxidants, ranging from the thermodynamically robust oxidant, N_2O, to relatively weak CH_2O—all oxidized Pa^+ to PaO^+, and PaO^+ to PaO_2^+. It was established that $D[Pa^+\text{-}O]$ and $D[OPa^+\text{-}O]$ exceed 751 kJ mol^{-1}; specific estimates were obtained for $D[Pa^+\text{-}O]$, $D[OPa^+\text{-}O]$, IE[PaO] and $IE[PaO_2]$. The seven oxidants reacted with Pa^{2+} to produce PaO^{2+}, indicating that $D[Pa^{2+}\text{-}O] \geq 751$ kJ mol^{-1}. Oxidation of PaO^{2+} by N_2O produced PaO_2^{2+}, a species which contains formally hexavalent Pa. Collision induced dissociation of PaO_2^{2+} resulted in O-atom elimination, suggesting a protactinyl type of connectivity: $\{O\text{-}Pa\text{-}O\}^{2+}$. The experimentally determined $IE[PaO_2^+] \approx 16.6$ eV is in agreement with that obtained from self consistent field and configuration interaction calculations for PaO_2^+ and PaO_2^{2+}. The calculations for PaO_2^{2+} indicate an oxidation state intermediate between Pa(V) and Pa(VI), participation of 5f orbitals in the bonding, and a partial "6p hole".

Theoretical calculations indicate that Ir should behave as a chemical analogue to N—i.e., "autogenic isolobality"—such that $IrUO^+$ was predicted to be a stable species isoelectronic with NUO^+ and UO_2^{2+} [L. Gagliardi, P. Pyykkö, *Angew. Chem., 43* (2004) 1573]. We have recently synthesized $IrUO^+$, the first so-called "metalloactinyl". Furthermore, reactions of UIr^+, UPt^+ and UAu^+ with oxidants and hydrocarbons demonstrated strong actinide-transition metal covalent bonding, and provided direct experimental evidence for "autogenic isolobality". Other $AnPt^+$ (An = Th, Pa, U, Np, Pu, Am, and Cm) were all produced in high abundances by laser desorption ionization of alloys, which is indicative of strong An-Pt covalent bonding throughout the first half of the actinide series.

Table 1. Reactions of M^+ with n-C_4H_{10}

M^+	Products	k / k_{COLL}
$Ta^+(5d^36s)$	$TaC_4H_4^+ + 3H_2$	0.22
$Th^+(6d^27s)$	$ThC_4H_6^+ + 2H_2$	0.18
$Pa^+(5f^27s^2)$	$PaC_4H_6^+ + 2H_2$	0.10
$U^+(5f^37s^2)$	$UC_4H_6^+ + 2H_2$	0.08
$Np^+(5f^46d7s)$	$NpC_4H_6^+ + 2H_2$	0.01
$Pu^+(5f^67s)$ $Am^+(5f^77s)$ $Cm^+(5f^77s^2)$	N/A	<0.001

Table 2. Reactions of MO^+ with 1-C_4H_8

MO^+	Products	k / k_{COLL}
$Ta(5d6s)O^+$	$TaOC_4H_4^+ + 2H_2$	0.36
$Th(7s)O^{+\ (a)}$	$ThOC_3H_5^+ + \bullet CH_3$	0.16
$Pa(5f6d)O^+$	$PaOC_4H_6^+ + H_2$	0.43
$U(5f^3)O^{+\ (b)}$	$UOC_4H_6^+ + H_2$	0.01
$Np(5f^4)O^+$ $Pu(5f^5)O^+$ $Am(5f^6)O^+$ $Cm(5f^7)O^+$	N/A	<0.001

(a) Goncharov & Heaven, *JCP, 124* (2006) 064312.
(b) Goncharov, et al., *JCP, 125* (2006) 133202.

Selected science objectives for 2007-2009:

- Reactions of $U_xO_y^-$ molecular (x = 1) and cluster (x > 1) anions with model neutral molecules, such as CH_3OH, will be examined by FTICR/MS. The experimental effort will be pursued in parallel with collaborative DFT calculations of energies and structures for reaction intermediates. The results will illuminate the nature and chemistry of uranium oxide nanostructures, surfaces and other interfaces.
- Electrospray ionization mass spectrometry (ESI/MS) studies of actinides will be initiated. Two broadly defined areas of inquiry are identification and characterization of species present in solutions under a variety of conditions; and chemical and physical properties of gas-phase species. Specific topics which will be explored include actinide aggregation, solvation, and complexation.
- As the initial results for the UM_{5d}^+ (M_{5d} = Ir, Pt, Au) ions have shown promise for elucidating intermetallic bonding, this line of inquiry will be extended to other actinides (An = Th, Pa, Np, Pu, etc.), to lanthanides, LnM_{5d}^+, and to 3d- and 4d-block transition metals, AnM_{3d}^+ and AnM_{4d}^+. The overall goal is to systematically examine covalent bonding between f-elements and d-block metals.

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Critical Role of Water Content in the Formation and Reactivity of Uranium, Neptunium, and Plutonium Iodates Under Hydrothermal Conditions

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Overall research goals: The objective of this research program is to investigate the hydrothermal crystal growth of novel actinide solids, to elucidate the crystal structures of these compounds, and to measure their physical properties.

Significant achievements in 2005-2007: The reactions of $^{237}NpO_2$ with excess iodate under acidic hydrothermal conditions result in the isolation of the Np(IV), Np(V), and Np(VI) iodates depending on both the pH and the amount of water present in the reactions. Reactions with less water and lower pH favor reduced products. While the initial redox processes involved in the reactions between $^{237}NpO_2$ or $^{242}PuO_2$ and iodate are similar, the low solubility of $Pu(IO_3)_4$ dominates product formation in Pu iodate reactions to a much greater extent than $Np(IO_3)_4$ does in the Np iodate system. UO_2 reacts with iodate under these conditions to yield U(VI) iodates solely. The isotypic structures of the An(IV) iodates, $An(IO_3)_4$ (An = Np, Pu) are reported and consist of one-dimensional chains of dodecahedral An(IV) cations bridged by iodate anions. The structure of $Np(IO_3)_4 \cdot nH_2O \cdot nHIO_3$ is constructed from NpO_9 tricapped trigonal prisms that are bridged by iodate into a polar three-dimensional framework structure. Second-harmonic generation measurements on a polycrystalline sample of the Th-analog of $Np(IO_3)_4 \cdot nH_2O \cdot nHIO_3$ reveals a response of approximately 12× α-SiO_2. Single crystal magnetic susceptibility measurements of $Np(IO_3)_4$ show magnetically isolated Np(IV) ions.

Science Objectives for 2007-2009: The new goals of this research program are to:

- Prepare pure samples of novel Np(IV), Np(V), and Pu(IV) phosphonates and sulfonates.
- Structurally characterize these compounds using single crystal and powder X-ray diffraction.
- Measure the magnetic susceptibility of these compounds, especially on oriented single crystals.
- Determine their magnetic structure using neutron diffraction.

- Develop a theoretical model that explains both the antiferromagnetic and ferromagnetic ordering in Np(V) compounds with cation-cation interactions.

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Reduction of Actinides in Higher Oxidation States by Hydroquinone-Enriched Humic Derivatives

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Program Scope: The project was part of the U. S. Department of Energy –Russian Academy of Sciences Program for Basic Actinide Chemistry.

Recent progress: Recent progress of the project involved syntheses of several humic acid materials with hydroquinone groups having reducing properties. The goal was to obtain humic materials that would bring about reduction of penta- and hexavalent neptunium and/or plutonium. The objective was to generate actinide species less prone to transport and/or migration in the environment. These “designer” humic materials have multiple applications for remedial operations and control of actinides in the environment.

Natural humic materials are known to cause a reduction of penta- and hexavalent plutonium; however, contradicting results are reported for neptunium. The study was to prove if incorporation of additional reducing centers into humic structure would yield materials with enhanced reducing performance with respect to higher valence actinides; nominally, Pu(V, VI) and Np(V). Hydroquinone-moieties were used as redox centers, which were incorporated into humic structure using a formaldehyde condensation process. Variable monomer to humic ratios produced materials of different reducing performance.

Reduction of actinides by the hydroquinone-enriched humic materials was studied both under anoxic and oxic conditions and at acidic and neutral conditions. Redox speciation of plutonium and neptunium was monitored using solvent extraction technique and liquid scintillation counting. It was shown that both non-modified leonardite humic acid plus all obtained derivatives reduced Pu(V) quantitatively both at neutral and acidic pH and under anoxic and oxic conditions. The reduction rate increased with the increased modification of the humic material, reaching a maximum with the HQ500 derivative. For neptunium, reduction was observed only under anoxic conditions at acidic pH. The hydroquinone-modified derivatives had much higher reducing performance compared to non-modified leonardite humic acid. From the results it was concluded that good prospects existed for hydroquinone-modified humic materials as reactive agents for remediation of actinide contaminated aquifers.

The properties of humic materials used in this study are listed in Table 1. The reduction capacity increased with an increase in hydroquinone content, and the derivatives were put in the following ascending order of capacity. CHP < HQ100 < HQ250 < HQ500.

The kinetics of Pu(V) reduction in the presence of parent leonardite HA under oxic and anoxic conditions was significantly higher compared to aerobic conditions. Under anoxic conditions, almost complete Pu(V) reduction occurred within 3-4 hours, while under atmospheric conditions, it took 120 hours for completion. The slower reduction kinetics of Pu(V) was evidently caused by competitive interaction of redox centers of CHP with air dissolved in test solutions.

The kinetics of Pu(V) reduction in the presence of different hydroquinone-enriched derivatives under anoxic conditions at pH 7.5 was studied. Complete Pu(V) reduction was observed in the presence of all derivatives but the rate increased with an increase in modification of the humic. Thus, the order was: CHP < HQ100 ≤ HQ250 < HQ500. For HQ500, equilibrium was reached within four hours; for HQ100 and HQ250 - within twelve hours; and for CHP within 22 hours.

In contrast, reduction of Np(V) in the presence of the humic derivatives was much slower. Comparative results on Pu(V) and Np(V) reduction under anoxic conditions at pH 4.5 are presented in Table 2. At 2 hours of exposure time reduction of Np(V) is negligible compared to Pu(V) (~complete reduction of Pu(V). As it can be seen, only partial reduction of Np(V) was taking place in the presence of CHP, HQ100,and HQ250 and complete reduction was observed with the HQ500 derivatives after 144 hours. Contrary to Pu(V), there was no reduction of Np(V) observed under oxic conditions for all humic derivatives tested.

Table 1

Sample	**Description**	**-COOH[a], mmol/g**	**-ArOH[b], mmol/g**	**Reduction capacity, mmol/g**
CHP	Leonardite HA	4.2±0.2	1.1	0.6±0.1
HQ100	HQ:CHP ratio of 100:1000 mg	4.3±0.3	4.0	1.2±0.2
HQ250	HQ:CHP ratio of 250:1000 mg	3.6±0.1	4.4	2.9±0.1
HQ500	HQ:CHP ratio of 500:1000 mg	3.1±0.2	4.3	4.0±0.1

Publications:

1. N. S. Shcherbina, et al, *Reduction of Actinides in Higher Oxidation States by Hydroquione-Enriched Humic Drativiatives, J. Alloys and Cmpds (in press, 2007)*
2. N. S. Scherbina et al*, Reduction of Neptunium by Hydroquinone-Enriched Humic Derivatives,* Environmental Scinece and technology, (in press, 2007). ,

Stability of Uranium-(VI) Peroxide Hydrates under Ionizing Radiation

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Overall research goals: The objective of this research program is to evaluate the stability of uranium-(VI) phases that are expected to form as secondary alteration products during the corrosion of spent nuclear fuel under oxidizing conditions. In this presentation, we focus on the radiation stability of select U(VI)-phases.

Significant achievements in 2005-2006: The uranyl peroxides, studtite, $UO_4\cdot4H_2O$ ($C2/c$, Z=4) and metastudtite, $UO_4\cdot2H_2O$ ($Immm$, Z= 2) were successfully synthesized at UPC. As shown in Figure 1, except for a small volume of impurity phase detected with a ~7Å of *d*-spacing, both synthetic studtite and metastudtite are almost pure with a degree of high crystallinity. The effect of ionizing radiation on uranyl peroxides was examined by electron beam irradiation experiments on both of the uranyl peroxides. All experiments were completed using transmission electron microscopy (TEM) with an acceleration voltage of 200 kV at room temperature. For the studtite samples, the complete amorphization occurred at an electron fluence of 0.51×10^{17} e/cm^2, which is equivalent to an absorbed doses of 0.73×10^{7} Gy. The synthetic metastudtite becomes amorphous at a higher dose (1.31×10^{7} Gy) than synthetic studtite, most likely because of the fewer number of water molecules in the structure. All uranyl peroxides become partially amorphous even at much lower doses (> ten times less) than the amorphization doses. During further irradiation, uraninite nanocrystals form that are a few nanometers in diameter for all of the uranyl peroxides at the doses of 4-20×10^{10} Gy (Fig. 2). These results suggests that uranyl peroxide phases that form in high radiation environments (e.g., due to the radiolytic decomposition of water) may be less stable, due to radiation damage, than predicted based on their thermodynamic stability.

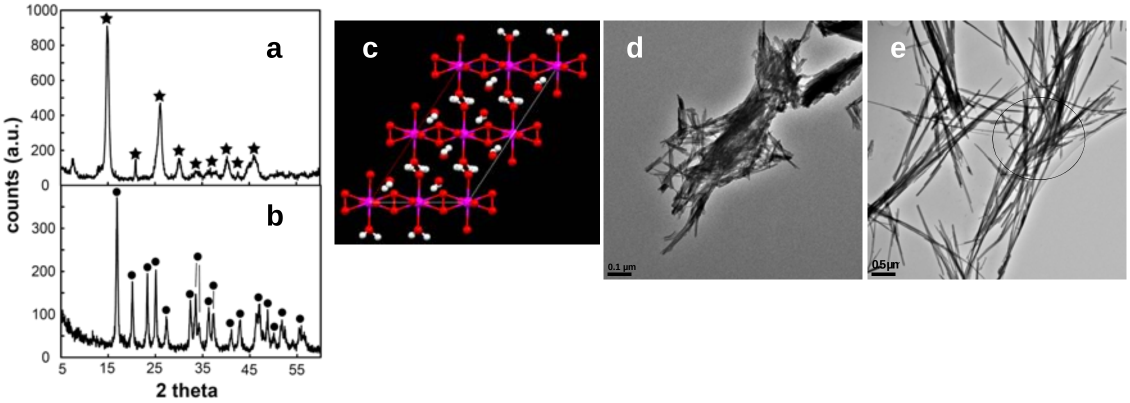

Figure 1. Powder X-ray diffraction pattern of synthesized uranyl peroxides; (a) studtite and (b) metastudtite. (c) The schematic illustration of the structure of studtite viewed along the *b*-axis. (d) Bright-field TEM image of studtite. (e) BFTEM image of metastudtite.

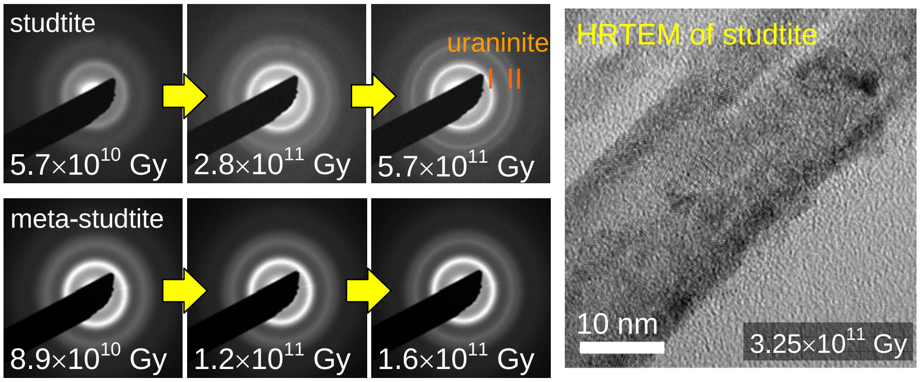

Figure 2. Transition of selected area electron diffraction pattern (SAED) during further electron irradiation after complete amorphization of uranyl peroxides. High-resolution TEM (HRTEM) image of former studtite after an irradiation of 3.25×10^{11} Gy on the left plate reveals the formation of randomly oriented uraninite nanocrystals a few nanometers in size.

Science objectives for 2007-2008:

- Utilizing the IVEM Tandem facility at Argonne National Laboratory, ion-beam irradiation experiments will be performed on uranyl peroxides and the other U(VI) minerals to simulate ballistic collision processes due to alpha particle and the recoil nuclei interactions.
- Examination of the stability of uranyl peroxides at elevated temperatures up to ~800 ^{o}C as a function of aging. The heating experiments will be carried out *in situ* in a transmission electron microscope, an include *ex situ* characterization with X-ray powder diffraction in collaboration with A. Rey at Universitat Politecnica de Catalunya (UPC).

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P2-10

Actinide Transition-Metal Chalcogenides and Pnictides

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Program Scope: 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.

Recent Progress:

We have made significant progress in addition to the results reported in the Publications below.

1. We have developed new mounting techniques so that electrical conductivity measurements can be made on a Quantum Design Physical Property Measurement System, PPMS, on a single crystal with a long axis of only about 300 μm. The leads are constructed of 15 μm diameter copper wire and 8 μm graphite fibers. These are attached to the crystal with DOW 4929N silver paint. Crystals slightly longer in length will be required for the measurement of thermal conductivities because larger diameter leads are needed for thermal input.

2. In our first Np reaction we have made KNp_2Se_6. In the study of $K_{0.91}U_{1.79}S_6$ and KU_2Se_6, which is summarized in Reference 2 below, we found that in KU_2Se_6 there are two alternating Se−Se distances of 2.703(2) Å and 2.855(2) Å, both much longer than an Se−Se single bond, whereas in $K_{0.91}U_{1.79}S_6$ there are alternating normal S_2^{2-} pairs 2.097(5) Å in length. The Se−Se distances in KNp_2Se_6 are 2.682(1) Å and 2.845(1) Å; hence KNp_2Se_6 and KU_2Se_6 are isostructural and both contain An^{4+} (An = U or Np). We offered the explanation in the U paper that the electron responsible for the reduction of the Se−Se single bond in KU_2Se_6 cannot reduce the stronger S−S single bond in $K_{0.91}U_{1.79}S_6$ because of the relatively higher position of the S 3*p* σ* orbital compared to the Se 4*p* σ* orbital. Although the necessary charge balance could have been achieved through reduction of U to an average oxidation state of 3.5+ metal deficiencies occurred instead. The result is $K_{0.91}U_{1.79}S_6$ in which the formal oxidation state of U is again 4+.

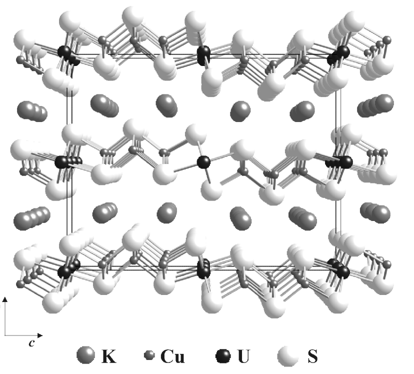

Figure 1

3. The compound $K_2Cu_3US_5$ was obtained from K_2S, UCl_4, CuCl, and S at 973 K by taking advantage of a newly developed metathesis reaction. $K_2Cu_3US_5$ crystallizes in a new structure type. The structure (Fig.1) contains layers of CuS_4 tetrahedra and US_6 octahedra that are separated by K^+ cations. There are no S−S bonds in the structure, the shortest S···S interaction being 3.645 Å. Therefore, the formal oxidation state of S in $K_2Cu_3US_5$ is 2−. Thus, the combined formal oxidation states of three Cu atoms and one U atom must be 8+ to achieve charge balance. This can be accomplished with three Cu^+ and one U^{5+} or two Cu^+, one

Cu^{2+}, and one U^{4+} cations. The Cu^{2+} oxidation state is very rare or perhaps unknown in sulfides, which makes it more likely that $K_2Cu_3US_5$ is a very rare example of a non-oxide solid-state compound that contains U^{5+}. Further indirect evidence for this comes from the bond distances and bond valence calculations. Moreover, EPR measurements on a single crystal by Dr. Hans-Albrecht Krug in the laboratory of Prof. Alois Loidl at the Lehrstuhl für Experimentalphysik V, Universität Augsburg show no signal from Cu^{2+}. The magnetic properties of what is almost certainly a U^{5+}compound should be extremely interesting. Such measurements are currently being conducted by Dr. Lynne Soderholm at Argonne National Laboratory.

4. In our search for new thermoelectrics in order to reduce thermal conductivity we have concentrated on the synthesis of compounds that contain U and other heavy metals. We have synthesized in low yield the compounds $UTa_2S_6OCl_6$, $[Ta_4(Se_2)_8][UI_6]$, $Cs_2UHg_2Se_5$, and $[Hg_3Te_2][UCl_6]$.

Objectives 2007-2009

Note the caveat that solid-state syntheses are characterized by frequent failures and occasional surprises.

1. Measure the conductivity and magnetic susceptibility of KNp_2Se_6.
2. Synthesize, characterize, and measure the physical properties of KNp_2S_6. Will it be a non-stoichiometric compound of Np^{4+}?
3. Synthesize $K_2Cu_3NpS_5$ and compare its structure and physical properties with those of $K_2Cu_3US_5$. Although a Np^{5+} chalcogenide would not be as unusual as is a U^{5+} chalcogenide, the comparison, especially of magnetic properties, should be valuable.
4. Find higher-yield syntheses for $UTa_2S_6OCl_6$, $[Ta_4(Se_2)_8][UI_6]$, $Cs_2UHg_2Se_5$, and $[Hg_3Te_2][UCl_6]$. Measure their physical properties, especially thermopower. Attempt to make related and analogous compounds in which Np is substituted for U, Te is substituted for S or Se, and I is substituted for Cl.
5. Continue the search for new *An*/*M*/*T* and *An*/*T*/*Q* compounds, where *An* is U or Np, *M* is a transition metal, and *T* is As, Sb, or Bi. In all instances, the synthesis of a Np compound will be attempted only after the successful synthesis of the related U compound. Physical property measurements, including thermopower, will be made on compounds synthesized.

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2. Mizoguchi, H. Gray, D.; Huang, F. Q.; Ibers, J. A. *Inorg. Chem.* **2006**, *45*, 3307-3311.
Structures and Bonding in $K_{0.91}U_{1.79}S_6$ and KU_2Se_6.

3. Chan, G. H.; Deng, B.; Bertoni, M.; Ireland, J. R.; Hersam, M. C.; Mason, T. O.; Van Duyne, R. P.; Ibers, J. A. *Inorg. Chem.* **2006**, *45*, 8264-8272. Syntheses, Structures, Physical Properties, and Theoretical Studies of CeM_xOS (M = Cu, Ag; $x \approx 0.8$) and CeAgOS.

4. Kim, J.-Y.; Gray, D. L.; Ibers, J. A. *Acta Crystallogr.* **2006**, *E62*, i124-i125.Caesium zirconium uranium pentatelluride, $CsZrUTe_5$.

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6. Gray, D. L; Ibers, J. A. *J. Alloys Compd.* In press. Corrected proof available online 13 October 2006. Synthesis and structure of $CsTi_5Te_8$: relation to the TlV_5S_8, $TlCr_3S_5$, and similar channel structures.

7. Gray, D. L.; Mitchell, K.; Huang, F. Q.; Ibers, J. A. *J. Alloys Compd.* In press. Corrected proof available online 26 January 2007. Synthesis and characterization of $Ln_4Yb_{11}Se_{22}$ (*Ln* = Ce, Sm, Gd).

P2-11

Intrinsic Nanoscience: Nanoscale Heterogeneity and Collective Properties of Complex Materials

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Project objective: This project will determine the structural chemistry, i.e., the arrangements of atoms, the bonding modes, and the reactivity, of the $AnO_{2\pm x}$ compounds of the light actinides, related materials such as actinates, and selected model systems via novel synthetic methods, multiscale structural measurements, and calculations and computer experiments including the development of new modeling approaches designed specifically for complex and heterogeneous materials that lack periodicity and that may be dominated by local effects.

Recent Progress. A common structural motif for many $AnX_{2\pm x}$ compounds (even hydrides) of the light actinides Pa-Cf is the relatively open fluorite structure, consisting of intertwined fcc An and cubic X sublattices with the cubic holes alternately containing a cation and empty. This cation sublattice is remarkably resilient crystallographically and chemically, changing slightly in size with x while exhibiting minimal distortions even at x=0.5 and across phase transitions. The robustness of the An sublattice explains a notable characteristic of $AnX_{2\pm x}$, their tendency to display a continuous range of stoichiometries. This complicates the structural chemistry of the oxides of U-Am for x>0 because of the domination in molecular complexes of the trans dioxo moiety for An(V/VI), whose rigid oblate geometry is incompatible with the spherically symmetric cation sites. The response to this problem is element specific; U displays 16 distinct crystallographic phases by the $UO_{3.0}$ endpoint, Np terminates at Np_2O_5 with no reported intermediates, and Pu shows only the Fm3m pattern with smoothly increasing lattice constant through its maximum x of 0.25. In contrast, the ternary actinates display a complete range of cation geometries for these higher valences that includes both the trans dioxo and spherical extremes. This conundrum has fomented a disagreement between the Willis group that has interpreted x-ray/neutron scattering and ion channeling results as showing that the adventitious O in UO_{2+x} resides (off center) within sites in a related U_4O_9-like cuboctahedral structure that are equivalent to the cubic holes, whereas our group finds that XAFS of samples prepared by both conventional and novel methods indicates that it is incorporated as Pu(V) and U(VI) oxo groups as part of a multisite near neighbor O distribution around Pu and U (Fig. 1). The basis for the oxo groups is apparent even in the raw data, the peak near R=1.4 Å in $\chi(R)$ – even in an aged UO_2 sample – that is fit by an O near 1.75 Å and is completely absent from the EXAFS calculated from the U_4O_9 crystal structure.

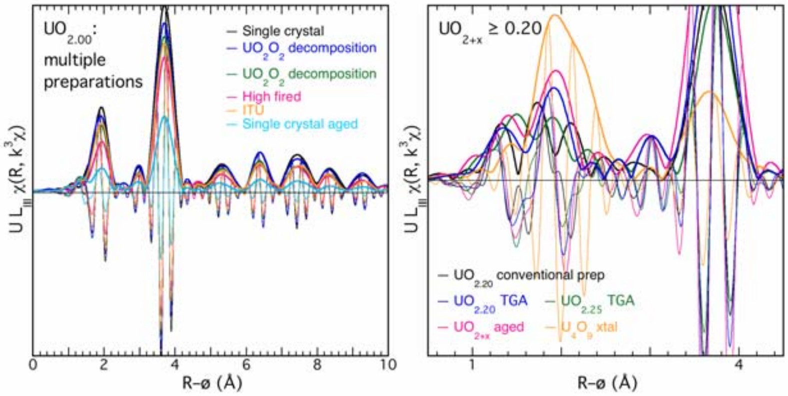

Figure 1. (Left) EXAFS of UO_{2+x} samples prepared by thermogravimetric method. (Right) Magnified O near neighbors plus U contribution to EXAFS of nominal $UO_{2.2}$ samples, aged single crystal, and U_4O_9 calculated from the crystal structure .

There is, however, also an area of agreement that is even more important. Both groups find strong evidence that the O atoms do not add randomly but rather collectively to form O enriched domains while leaving the UO_2 regions of the materials intact, which in the EXAFS causes the high R peaks to diminish evenly with x (Fig. 1). Thus, the adventitious O atoms facilitate the placement of additional ones in proximity to themselves, most likely into an ordered, U_4O_9-like structure. The chemical potentials of the atoms are thus not homogeneous but vary throughout the material depending on the local environment in terms of the proximity of adventitious O atoms. As with Pu, this explains the non-thermodynamic nature of the oxidation, first that it occurs at all despite (IV) being the lowest energy valence under these conditions, and second that it does not go to completion but ceases at a point determined by the H_2O activity.

Science Objectives for 2007-2009. The five papers on Pu/UO_{2+x} published during this last period posed far more questions than they answered and are thus obviously only the inception of our goal of elucidating the structural chemistry of $AnO_{2\pm x}$. Experimentally, we will continue to perform multiscale structural measurements including EXAFS, high resolution XRD, and x-ray and neutron pdf, on samples prepared by better methods than calcinations that especially for PuO_2 but even for UO_2 produce materials with varying degrees of disorder (Fig. 1). Thermal decomposition of U(VI)-peroxide complexes initially purified by chromatography give reproducible EXAFS spectra very close to that of single crystal material. The thermogravimetic approach to oxidation is also a breakthrough in that the control of x is greatly facilitated so that more samples can be prepared more quickly and accurately. The syntheses and measurements are therefore almost routine, and we anticipate expansion to other actinides and compounds.

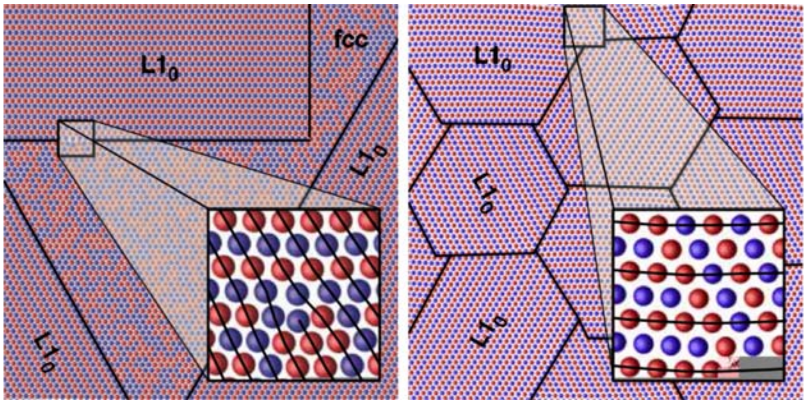

Figure 2. (Left) Dislocations and possibly other defects at the interface between two domains focus the stress at the defect sites, allowing the two structures to develop fully. (Right) Coherency between the domains distributes the stress as displacement of the atoms evenly throughout the entire structure.

What is not is the use of these results to construct a model with of the order of 10^6 atoms (a crystal 100 atoms on each side) that includes all of the significant attributes of the real systems including the collective behaviors and its subsequent use in calculating the properties of importance. As demonstrated by the listed (and unlisted) references, we have, however also been making substantial progress in modeling complex materials with nanoscale heterogeneity. Using a simple AB system with tetragonal and cubic endpoints, we have been able to identify some directly relevant phenomena occurring at the interfaces between the domains (Fig. 2). In this system we have found that defects at the domain interfaces act as foci for the strain and allow the structures to develop fully within the domains giving crystallographic phase separation. In contrast, coherency has the opposite effect and the diffraction pattern is that of the average structure but with broadened lines that may contain information on the organization. What is of most interest from the chemical perspective is that, in the former case, the atoms at the defect sites will be much more reactive than normal. This effect could be the origin of the oxidation behavior described above. In addition, the heterogeneity could also stabilize other defects, such as those originating in radiation damage. We will continue to develop and exploit this type of modeling for $AnX_{2\pm x}$.

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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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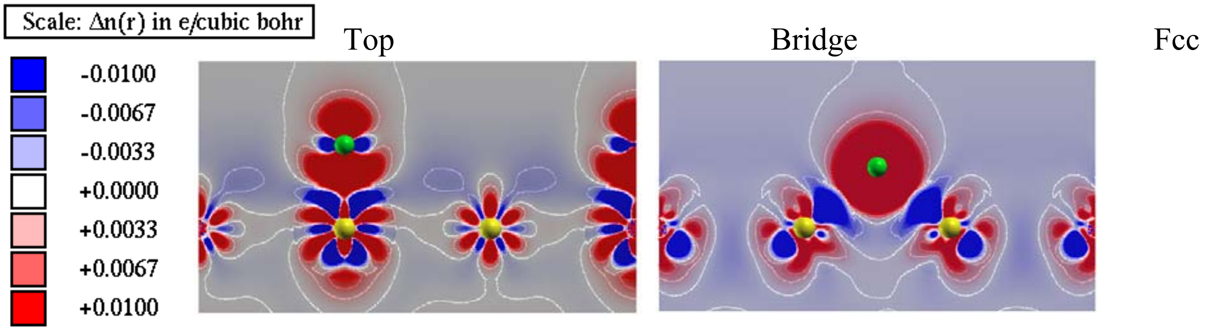
Program Scope: The various goals in the project are: a) Electronic structure studies of transuranium surfaces, including surface relaxations, reconstructions, and magnetic phase transitions; b) Studies of atomic and molecular adsorptions on these surfaces; c) Understanding and establishing the extent of the validity of density functional theory (DFT) in regards to surface chemistry processes.

Recent Progress: We have completed the following studies: a) *Electronic structure studies of the δ-Pu (111), (001), and (110) surfaces:* FP-LAPW calculations for δ-Pu films up to seven layers at the AFM-SO ground state indicate that the surface energy rapidly converges and the semi-infinite surface energy is predicted to be 1.16, 1.21, and 1.42 J/m^2 for δ-Pu (111), (001), and (110) films, respectively. In addition, the work functions are predicted to be 3.41, 3.11, and 2.99 eV for the three surfaces. b) *Electronic structure studies of the Am monolayer, dhcp Am (0001) and fcc Am (111) and (001) surfaces;* The work function of dhcp Am (0001) 7-layer surface at the ground state is predicted to be 2.90 eV. The surface energy for dhcp Am (0001) semi-infinite surface energy at the ground state is predicted to be 0.84 J/m^2. c) *First-principles FP-LAPW studies of atomic carbon, nitrogen, and oxygen chemisorptions on the (111) and the (001) surfaces of δ-Pu:* Chemisorption energies were optimized with respect the distance of the adatom from the surface for four adsorption sites, namely the top, bridge, hollow fcc, and hollow hcp sites. Computations were carried out at two theoretical levels, one with no spin-orbit coupling (NSOC) and one with spin-orbit coupling (SOC). For NSOC calculations, the hollow fcc adsorption site was found to be the most stable site for C and N with chemisorption energies of 6.272 eV and 6.504 eV respectively, while the hollow hcp adsorption site was found to be the most stable site for O with a chemisorption energy of 8.025 eV. For SOC calculations, hollow fcc adsorption site was found to be the most stable site in all cases with the chemisorption energies for C, N, and O, being 6.539 eV, 6.714 eV, and 8.2 eV respectively. For all chemisorption processes on the (100) surface, the center adsorption site was found to be the most preferred site with chemisorption energies of 7.964 eV, 7.665 eV, and 8.335 eV for the C, N, and O adatoms, respectively. The respective distances of the C, N, and O adatoms from the surface were found to be 0.26 Å, 0.35 Å, and 0.48 Å. The work functions and the net magnet moments respectively increased and decreased in all cases compared with the bare δ-Pu (100) surface; d) *Relaxation studies of Pu and Am surface;.* For the δ-Pu (111) surface, a 5-layer slab with 4 atoms per layer was considered; the central layer was fixed and the outermost layers were relaxed; Δd_{12} was found to be 7.1% and Δd_{23} is 0.4%, with a relaxation energy of 0.052 mRy/atom. For the (0001) surface of dhcp-Am, a 6-layer slab with 4 atoms per layer was considered; the 2 central layers were fixed and the outermost layers were relaxed; Δd_{12} was found to be 2.0% and Δd_{23} is 0.0%, with a relaxation energy of 0.091 mRy/atom.

Science Objectives for 2007-2009: a) Relativistic electronic structure studies of the adsorptions of CO and H_2O on the (111) and (100) surfaces of δ – Pu; b) Relativistic electronic structure studies of the high-symmetry surfaces of α – Pu and possibilities of surface relaxations, reconstructions and magnetic phase transitions. c) Studies of atomic and molecular adsorptions, specifically H, H_2, O, O_2, C, CO, and H_2O on the high-symmetry surfaces of α – Pu; d) Relativistic electronic structure studies of the high-symmetry surfaces of dhcp Am I and possibilities of surface relaxations, reconstructions and magnetic phase transitions. e) Studies of adsorptions, specifically of H, H_2, O, O_2, C, CO, and H_2O on the high-symmetry surfaces of dhcp and fcc Am; f) Fully-relativistic electronic structure studies of the high-symmetry surfaces of Cm I and Cm II and possibilities of surface relaxations, reconstructions and magnetic phase transitions.

Adsorption sites

Difference charge densities for oxygen on δ-Pu(111)



Two year publication list of work supported by this project

1. M. N. Huda and A. K. Ray, "*A Density Functional Study of O_2 Adsorption on the (100) Surface of γ - Uranium,"* International Journal of Quantum Chemistry, **102,** 98-105 (2005).

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9. D. Gao and A. K. Ray, "*The 5f Localization – Delocalization in Square and Hexagonal Americium Monolayers – A FP-LAPW Electronic Structure Study,"* European Physical Journal B, **50**, 497-503 (2006).

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14. R. Atta-Fynn and A. K. Ray, "*A Full Potential–Linearized Augmented Plane Wave (FP-LAPW) Study of Atomic Carbon, Nitrogen, and Oxygen Chemisorption on the (100) Surface of δ-Pu,*" Physica B, **392**, 112-126 (2007).

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16. P. Dholabhai and A. K. Ray, "*A Density Functional Study of Carbon Monoxide Adsorption on the (100) Surface of γ-Uranium*," Journal of Alloys and Compounds, in press.

17. D. Gao and A. K. Ray, "*A First-Principles Electronic Structure Study of the High-Symmetry Surfaces of FCC Americium*," Journal of Alloys and Compounds, in press.

18. D. Gao and A. K. Ray, "*Quantum Size Effects in the (0001) Surface of Double Hexagonal Close Packed Americium*," European Physical Journal B, in press.

P2_13

Synthesis and Characterization of New Families of Inorganic-Organic Ion Exchangers

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Significant achievements in 2003-2005: We have prepared a series of inorganic-organic hybrids that are porous nanoparticles. They are constructed by reaction of aryl diphosphonic acids with zirconium(IV) compounds in hydrothermal processes. To impart ion exchange capability mixed derivatives with phosphoric acid, which adds -O3POH groups containing exchangeable protons, have been prepared. The reaction of an aryl phosphonic acid with Zr(IV) produces a layered zirconium arylphosphonate. Use of a diphosphonic acid such as H2O3PC6H4PO3H2 results in cross-linking of the layers into three dimensional frameworks and these pillars are spaced by insertion of small -POH groups. Two series of compounds have been prepared utilizing monophenyl and biphenyl diphosphonic acids with increasing amounts of phosphoric acid. The results of preliminary ion exchange data show a high level of selectivity for lanthanide ions. The ability to shape the pore sizes, the hydrophobic and hydrophilic character and the nature of the ion exchange and complexing groups utilized as spacers, will be described. Similar compounds with Sn(IV), Ti(IV) and Aℓ(III) will also be mentioned. These materials have the potential of providing substrates for the separation of compounds as well as ions.

In Figure 1, is presented an idealized version of the pillared zirconium biphenyl-diphosphonate with spacer monohydrogen phosphate groups.

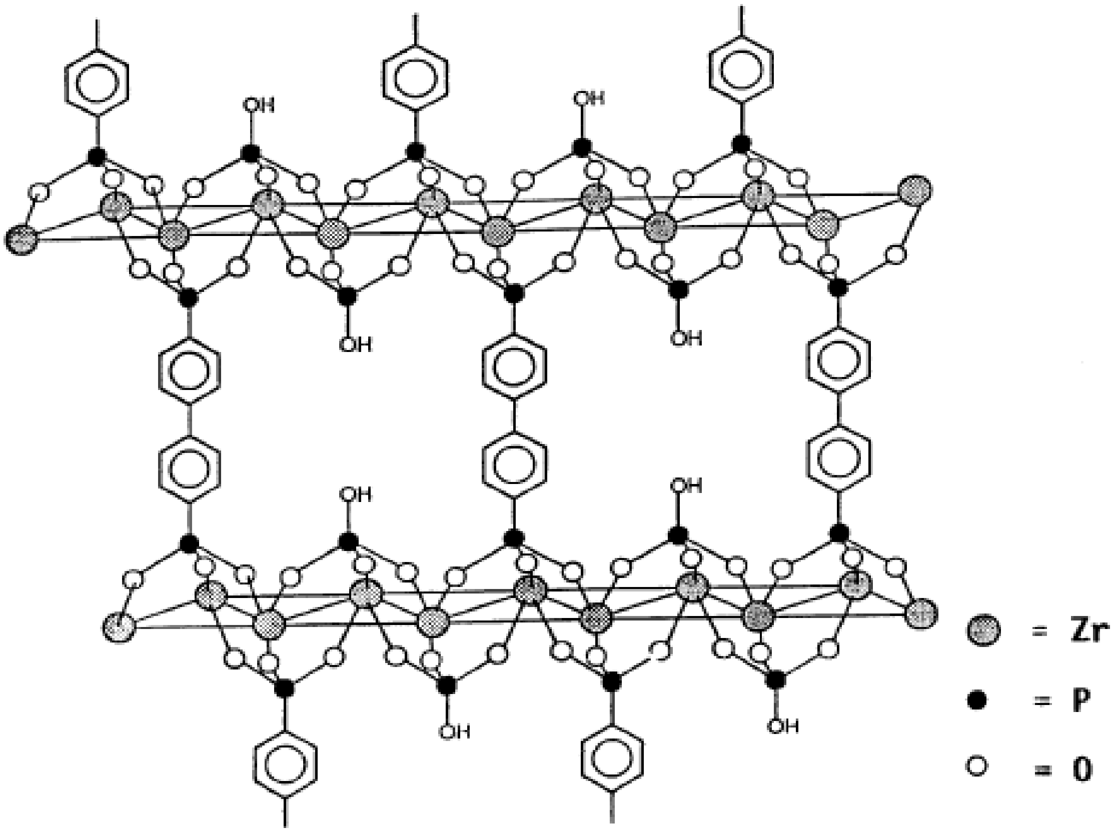

Figure 1. Idealized representation of α-zirconium phosphonate type layers pillared by biphenyl groups. The pillars are spaced 10.6 Å apart by monohydrogen phosphate groups to create microporosity.

However, by using solvothermal methods and an excess of Zr, porous materials are obtained without addition of spacer molecules. A typical isotherm is shown in Figure 2, in which the surface area is ~400 m2/g.

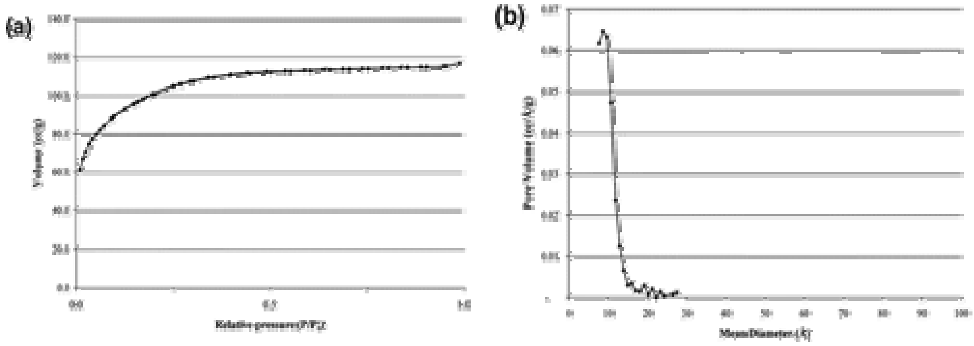

Figure 2 (a). N_2 sorption-desorption isotherm for Zr(IV) phenylphophonate and (b). Pore Size distribution derived from the isotherm.

The use of alkyldiphosphonic acids also yields porous pillared materials. At high levels of spacer group contents the layers contract upon removing solvent and extend when taking up solvent. The use of these materials for separations will be presented.

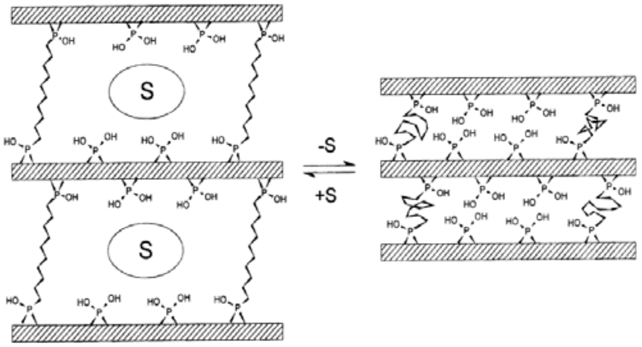

Figure 3. Schematic of the accordion-effect for a zirconium 1,10'-decanediphosphonate derivative with 12% pillaring. The change in interlayer spacing results from the presence or absence of solvents.

Research In Actinide Chemistry

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I. Program Scope: This research program is directed to development and evalution of separation technique of value in processing spent fuel for recovery isolation of unburnt uranium and plutonium for recycle and further buring . To better understand 5f-element behavior, we study the related 4f- elements (lanthanides). Systems chosen for investigation can provide data of value in environmental and waste management modeling.

Much of our research has been directed to expansion of the thermodynamic data base on complexation of actinides by organic ligands which are present in nature or in the wastes (e.g., OH^-, CO_3^{2-}, PO_4^{3-}, SiO_4^{4-}, organics used in separation, humates, etc.) as modeling the environmental behavior requires an understanding of such factors.

II. Recent Progress: Studies have involved the effects of organic chelate complexation on the speciation and solubility of trivalent actinides under strongly basic, high pH conditions, similar to those present in the high level waste (HLW) tanks at the U.S. DOE storage sites. The research has focused on the measurement of complexation of Am(III), Cm(III) and Eu(III) by EDTA, citrate (cit), oxalate (ox), nitrilotriacetate (NTA), trans-1,2-diamino N,N,N', N'-tetraacetate (CDTA) and diethylenetriaminepentaacetate (DTPA) and mixtures of EDTA and cit, NTA, ox, and IDA at high ionic strength (5 m $NaClO_4$), pcH 3.60 over the temperatures range of 0 to 60 °C using solvent extraction and potentiometric titration methods. In addtion, the formatiomn and the binding modes of these mixed lignad complexes of Eu(III) with EDTA+cit, NTA, ox, CDTA+IDA, NTA and ox and DTPA+IDA and ox in solutions were determined by TRLFS (Time Resolved Laser Fluorescence), NMR (^1H and ^{13}C) and EXAFS (Extended X-ray Absorption Fine Structure) spectral studies. These are used to develop models for HLW tank conditions.

CDTA, DTPA, NTA, IDA form 1:1 complexes while cit and ox form both 1:1 and 1:2 complexes with Am(III), Cm(III) and Eu(III) at T= 0-60°C and an ionic strength ($NaClO_4$) of 2-5 M. The positive values of ΔH and ΔS for the complexation thermodynamics reflect extensive dehydration of metal ions at this ionic strength. TRLFS and lifetime measurements have confirmed the formation of these complexes. With mixtures of EDTA+IDA, NTA and ox, these metal ions form ternary complexes. The enthalpies of ternary complexation are large and positive.

Similar studies were done for actinides with taci (1,3,5-triamino 2,4,6-trihydroxy cyclohexane and thci (1,3,5-Trideoxy-1,3,5-tris((2-hydroxybenzyl)amino)-cis-inositol. taci forms trimetallic polymeric complexes with the trivalent lanthanides, while thci forms simple 1:1 and 1:2 species. Both systems are strong complexes and our intrest now is attaching taci to the Rebek ligand as the result should be a very strong complex (as found with Ca^{2+} and Ga^{3+}) which could ne somewhat specific for the Am^{3+} and Ln^{3+} cations.

III. Scientific Objectives for 2007-2009: These years will be the final period of this program. In this period, research will be directed to development and evalution of separation techniques which may be of value in the processing of spent fuel for purification and isolation of unburnt uranium and plutonium for recycle for further burning in a reactor. The research in 2005-2007 will be continued in 2007-2009.In addition, to the TRLFS, NMR and EXAFS techniques. The current research uses DFT calculations with the Gaussian -03 package to better define the coordination chemistry of the actinides.

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13. EXAFS studies and Gaussian View energy calculations of the complexation of Eu(III) with 1,3,5-trideoxy-1,3,5-tris((2-hydroxybenzyl)amino-cis-inositol, D. P. Taylor, C. J. Dodge, A.J. Francis and G. R. Choppin, Inorg. Chim. Acta (In press)
14. Thermodynamics and the Structure of Binary and Ternary Complexation of Am^{3+} Cm^{3+} and Eu^{3+} with DTPA and DTPA+IDA, G.R. Choppin, P. Thakur and J. N. Mathur , Comptes Rendus-Chimie (In press)
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18. Complexation thermodyamics and the formation of the binary and the ternary complexes of tetravalent plutonium with carboxylate and aminocarboxylate ligands in aqueous solution of high ionic strength, P. Thakur, P.N. Pathak and G.R. Choppin, Inorg. Chim. Acta (Submitted)

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 objective of this project is to study the influence of local molecular environments on redox mechanisms and oxidation state stability of actinides in solution and at solution/solid interfaces.

Significant achievements in 2004-2006:

Initial funding was received mid 2006. Postdoctoral fellow was hired and development of Gaussian based and plane-wave based spin-orbit ZORA DFT in NWChem was started.

Science objectives for 2006-2007:

- Develop initial Gaussian based spin-orbit ZORA DFT capability; work mainly done by postdoctoral fellow supervised by Dr. Bylaska.
- Develop initial plane-wave based spin-orbit ZORA DFT and Car-Parinello capability.
- Perform initial test runs for uranyl in solution and at interfaces and publish the results.

Figure 1. Snap-shot of a 0.8 ps plane-wave DFT Car-Parinello simulation of a $[UO_2]^{2+}$ molecule solvated by 64 water molecules. Periodic boundary conditions were used.

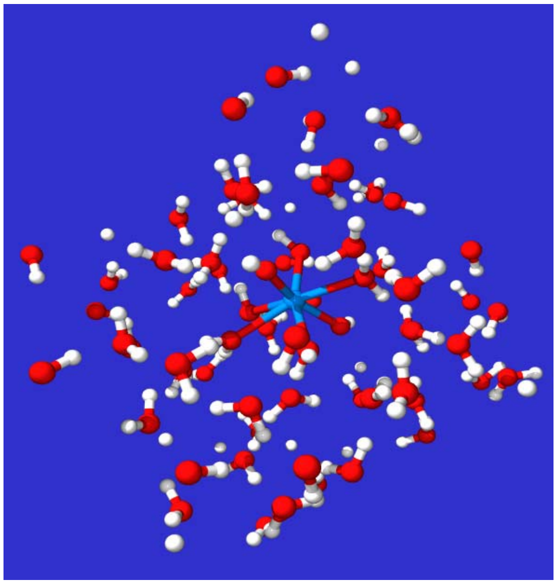
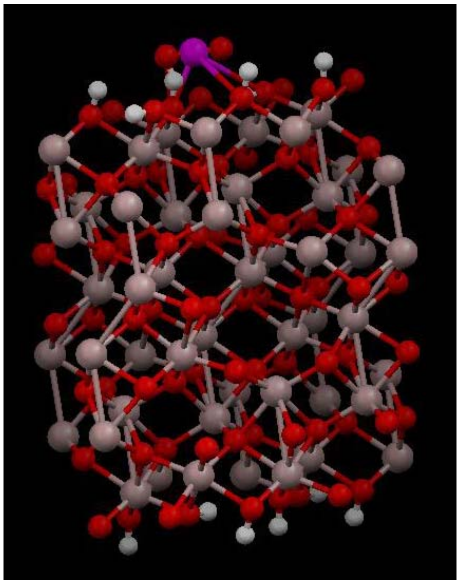


Figure 2. Uranyl on a hydroxylated (0001) Al_2O_3 surface. The surface has been optimized, and simulations with the $[UO_2]^{2+}$ molecule are underway.



References of works that was supported by this project

No peer reviewed publications have been generated to date.

CP-3

Reaction Specificity of Nanoparticles in Solution

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Overall research goals: The objective of this project is to develop a fundamental understanding of the mechanism(s) responsible for the overall particle reactivity and reaction selectivity of iron-based metallic, bimetallic, and oxide nanoparticles.

Significant achievements in 2005-2006: We have demonstrated that the nature of the coating for core-shell iron nanoparticles can significantly change the production of toxic versus non-toxic products during reduction of carbon tetrachloride. In particular, for one type of nanoparticle formed by hydrogen reduction of the iron oxide, the production of CF was 25% or less of that formed for micron-sized iron and many other types of nanoparticles. Because the chemical behavior of iron nanoparticles depends on the specific character of the particles, our studies are conducted on carefully prepared and analyzed particles.

Measurements of particles at different stages of reaction with pure or contaminant-bearing water show that the processes that control contaminant degradation evolve with time. Coordinated particle characterization and reaction studies (batch and electrochemical) show that both the reactivity and reaction pathway change as the particle ages in solution. An example of changes in the oxide shell around the nanoparticles is shown in Figure 1.

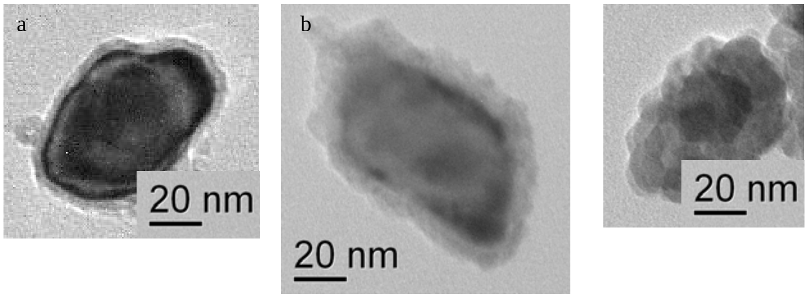

Figure 1. TEM images of nanoparticles in as received condition (a) and after exposure to water for 1 day (b) and 5 days (c). The initial particles have an intact crystalline oxide shell that is broken down upon exposure to solution.

We have developed strategies based on ab initio electronic structure methods for estimating thermochemical and kinetic properties of reactions with chlorinated hydrocarbons. Emphasis is placed on strategies that are computationally fast and can be used for large organochlorine compounds such as 4,4'-DDT. We have applied this approach to the dechlorination of chlorinated ethylenes. Reaction barriers were calculated using ab initio electronic structure methods for the reductive dechlorination of the polychlorinated ethylenes: C_2Cl_4, C_2HCl_3, trans -1,2-$C_2H_2Cl_2$, cis -1,2-$C_2H_2Cl_2$, 1,1-$C_2H_2Cl_2$ and C_2HCl_3. Both concerted and stepwise cleavages of R-Cl bonds were considered. Stepwise cleavages yielded lower activation barriers than concerted cleavages for the reduction of C_2Cl_4, C_2HCl_3, and trans -1,2-$C_2H_2Cl_2$ via strong reducing agents. However, for typical ranges of reducing strength, concerted cleavages were found to be favored.

Science objectives for 2007-2008: This combined BER/BES program involves model-system experiments, theoretical calculations, nanoparticle synthesis and characterization, and nanoparticle reactivity studies.

- The time dependent reaction properties of nanoparticles are being examined in greater detail along with the impact of particle doping and surface contaminants on particle reaction properties and time evolution.
- Theoretical and model systems studies are examining in detail the reaction products form as iron atoms and clusters interact with carbon tetrachloride. A new approach to self-interaction corrected density functional theory is being applied to iron oxides to understand localization and mobility of charge within the oxide shells.

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Monodispersive Iron-Iron Oxide Core-Shell Nanoparticles for Environmental Applications

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Overall research goals: The objective of this project is to develop a fundamental understanding of the mechanism(s) responsible for contaminant reduction and the overall reactivity, reaction selectivity and life cycle of iron-based metallic, bimetallic, and oxide nanoparticles with the intent of optimizing particle size, formulation and structure for reduction of environmental contaminants. This report summarizes results obtained during year one of a three year project supported by DOE-BES.

Significant achievements in 2005-2006:

1. Synthesis of Monodispersive Iron-Iron Oxide Core-Shell Nanoparticles

We successfully prepared monodispersive stable iron-iron oxide core-shell nanoparticles by a technique that is the combination of magnetron sputtering and gas-aggregation. The size of nanoparticles can be controlled from 2 to 100 nm (Fig.1b). Various types of measurements, such as TEM, HRTEM, XRD, XPS, EELS and chemical reactions confirmed the presence of a metallic Fe(0) core and an iron oxide shell (Fig.1).

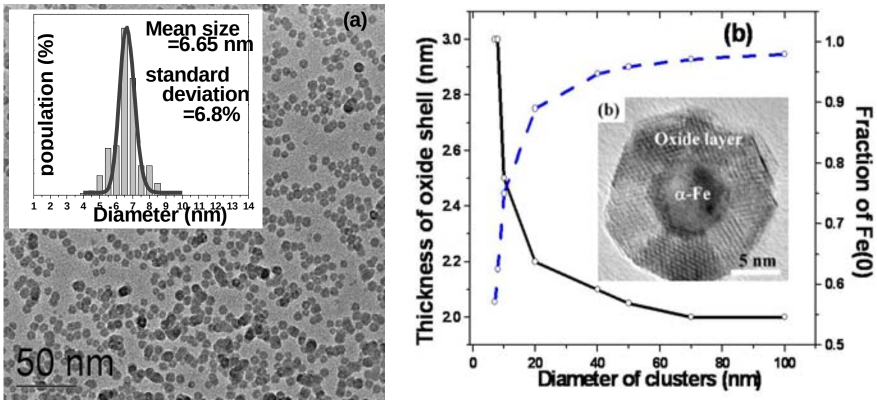

Fig. 1: (a) TEM image of the iron-iron oxide core-shell nanoparticles and the size distribution; (b) The solid curve shows the shell thickness vs diameter of NPs and the dashed curve denotes the fraction of metallic iron core vs NP diameter.

2. Nanoparticle Aging

We have taken an aging process on the core-shell nanoparticles in water by XRD in comparing with Toda's nanoparticles. In particular the Toda particles are 50 nm and the Idaho particles are 12 nm in diameter with a 2.5 nm oxide shell. The corrosion rates are 0.11 nm/hr for Toda's NPs and 0.0067 nm/hr for Idaho's NPs. The results show our core-shell NPs are changing 15 times slower than that of the Toda NPs.

3. Magnetic Nanoparticle-Enzyme Conjugates

One of the major concerns in environmental and other applications of enzymes is their short lifetime. Enzymes lose their activity due to oxidation or other processes which results in less stability and a shorter lifetime thereby rendering them less efficient. An effective way to increase the stability, longevity, and reusability of the enzymes is to attach them to magnetic iron nanoparticles. With this aim, two different catabolic enzymes, trypsin and peroxidase, were attached to uniform magnetic core-shell iron nanoparticles (MNP's) we produced. Our study indicates that the lifetime of enzymes increases dramatically from a few hours to weeks (Fig. 2) and that MNP-Enzyme conjugates are more stable, efficient, and economical. We predict that MNP's shield the enzymes preventing them from getting oxidized or self-digested. This results in an increased lifetime of the enzymes. The magnetization of our nanoparticles being higher, (~140 emu/g) nanoparticle-enzyme conjugates could efficiently be reused making the enzymes more productive. We also found that the enzyme structure plays a major role in efficient attachment of MNP's.

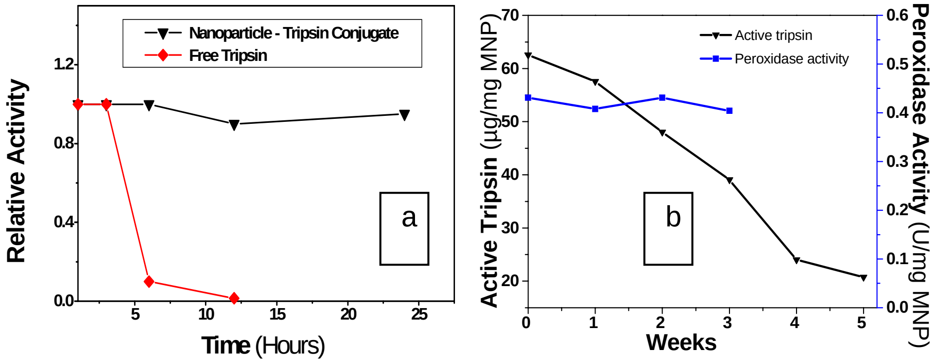

Fig. 2:

a) Activity of MNP-trypsin at pH=7 at 5 °C.

b) Stability of MNP-Es in weeks.

Science objectives for 2007-2008: Current studies of the time dependence of the reaction properties of nanoparticles will be extended to longer times. We are planning to do:

- Particle size dependence on the reduction of nuclear waste of CCl_4.
- Synthesis of metal (Ni, Cu or Pd) doped Fe nanoparticles with variable size and dopant concentration.
- The time dependent reaction properties of nanoparticles are being examined in greater detail along with the impact of particle doping and surface contaminants on particle reaction properties and time evolution.

Publications supported by this project (2005 and 2006)

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Interaction of Fission Product and Transuranium Cations with U(VI) Mineral Phases

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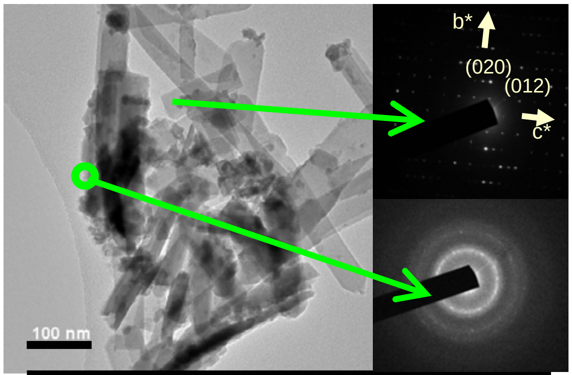
Overall research goals: The objective of this research program is to investigate the interaction of fission product and transuranic cations with U(VI) solid phases. The mechanism of interaction for Np, Pu, and Am is under investigation, and equilibrium expressions with thermodynamic constants for the interactions will be defined.

Significant achievements in 2005-2006: The partitioning of the fission product cations Cs^+, Sr^{2+}, NpO_2^+, and Am^{3+} to U(VI) silicates, oxide hydrates, and peroxides have been investigated. Examples of this work are shown in Figure 1, below. On the left, the partitioning of Sr^{2+} into uranophane ($Ca[(UO_2)(SiO_3OH)]_2{\cdot}5H_2O$) is shown. The uranophane was synthesized in the presence of Sr^{2+} (25% of the Ca^{2+} typically used in the synthesis of uranophane was replaced with Sr^{2+}). The bulk solid was identified as uranophane by powder x-ray diffraction (data not shown). TEM images of the solid (Fig. 1) show that the solid is composed of both the needle-like solids expected for uranophane and that are identified as such by selected area electron diffraction, and finely divided material that is not consistent with uranophane. Furthermore, the Sr^{2+} appears to be preferentially partitioned into the finely divided material as opposed to the uranophane needles. The data on the right is for NpO_2^+ partitioned into metastudtite ($UO_4{\cdot}4H_2O$) that was then allowed to recrystallize with time. The solid formed when NpO_2^+ was included in the metastudtite synthesis was identified as metastudtite by powder x-ray diffraction (data not shown), and 100% of the NpO_2^+ was partitioned into the solid. Upon recrystallization, however, NpO_2^+ is released from the solid at a rate that exceeds congruent dissolution of the solid.



Atomic %	Sr	Ca	U	Si
Single crystal	1.5 ± 0.2	12.3 ± 1.2	55.2 ± 5.5	31.0 ± 3.1
polycrystals	8.6 ± 0.9	10.7 ± 1.1	63.5 ± 6.4	17.2 ± 1.7

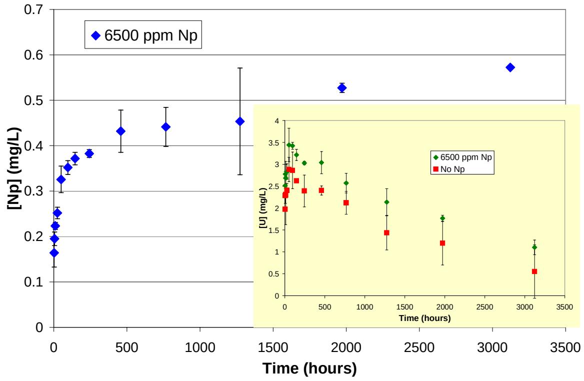


Figure 1: Partitioning of non-U cations to U(VI) minerals. On the left, uranophane was synthesized in the presence of Sr^{2+} to produce the solids imaged by TEM. The needle-like crystallites are uranophane, and additional finely divided U(VI) silicates are shown. On the right, metastudtite was synthesized in the presence of NpO_2^+, and then allowed to aged. Upon aging, the NpO_2^+ cation is released from the solid.

Because sorption of the non-U cations to the U mineral phases is controlled in part by the electrostatics of the surface, we are also interested in the surface charging properties of the U(VI) minerals. We are completing surface titration experiments to determine the points of zero charge for the U(VI) silicates, oxide hydrates, and peroxides. This parameter will be essential for defining linear free energy relationships for fission product and actinide cation adsorption to these solids.

Most of the U(VI) minerals are layered sheet structures, much like clay minerals as shown in Figure 2. In this case, uranophane is shown, which is composed of 1:1 sheets of uranyl cations coordinated to silicate tetrahedral, and calcium cations with water molecules located between the sheets to balance the structural charge of the sheets. For surface sites, the silicate tetrahedral located within the two-dimensional sheets have oxygen atoms that can be protonated or deprotonated (see orange circles). In addition, each sheet terminates with a silicate tetrahedron that has similar oxygen atoms that can be protonated/deprotonated. Like with clay minerals, a two site model of surface sites and edge sites will be considered in our data treatment.

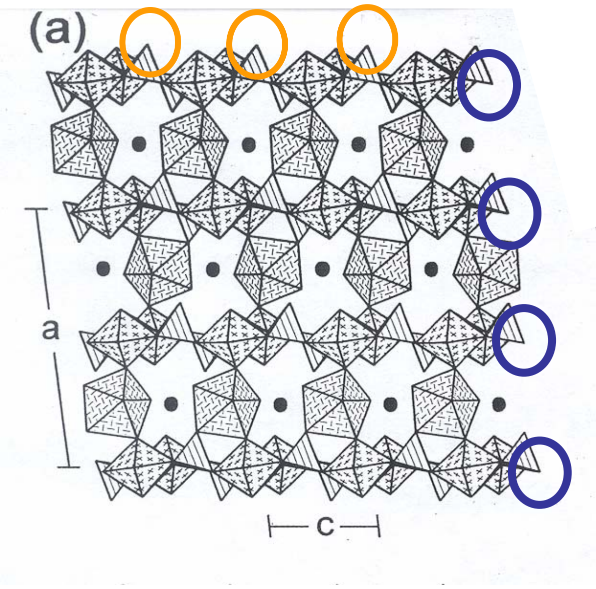


Figure 2: Structure of uranophane ($Ca[(UO_2)(SiO_3OH)]_2 \cdot 5H_2O$). The orange circles show the surface silicate sites and the blue circles show the edge silicate sites. See text for more details.

Science objectives for 2007-2008:

- Elucidate and quantify the importance of polycrystalline phases in the partitioning of the non-U actinide cation, including consideration of the radiation stability of these phases;
- Elucidate and quantify the release of the non-U actinide cation upon dissolution of the U(VI) solid, including consideration of a radiation environment on dissolution and release; and
- Quantify the role of surface complexation of non-U actinide cations to the surfaces of U(VI) mineral surfaces.
- Define linear free energy relationships for the various mechanisms of cation partitioning to U(VI) solid phases, and include radiation damage in the relationship.

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