

Thursday Afternoon, October 25, 2018

Actinides and Rare Earths Focus Topic

Room 202C - Session AC-ThA

Early Career Scientists

Moderators: Tomasz Durakiewicz, National Science Foundation, David Shuh, Lawrence Berkeley National Laboratory

2:20pm AC-ThA-1 Complexation, Characterization and Separation of the Lanthanides and Actinides: Shedding Light to Subtle Differences within the f-element Series, Gauthier Deblonde, C Booth, Lawrence Berkeley National Laboratory; **M Kelley, J Su, E Batista, P Yang,** Los Alamos National Laboratory; **A Müller, P Ercius, A Minor, R Abergel,** Lawrence Berkeley National Laboratory

INVITED

From the nuclear fuel cycles to the therapeutic use of radioisotopes for cancer diagnostics and treatment, the solution chemistry of lanthanides and actinides has become increasingly relevant to a number of applied problems. Understanding the fundamental bonding interactions of selective metal assemblies and the intrinsic differences between f-elements presents a rich set of scientific challenges and is critical to the development of highly efficient separation reagents and new actinide- or lanthanide-based therapeutics.

Our approach to these challenges uses a combination of techniques (EXAFS, liquid-liquid extraction, protein crystallization, UV-vis, fluorescence, DFT...) to characterize f-block aqueous complexes with highly selective and bio-inspired chelators or with more classical aminocarboxylate ligands. With the goal of always minimizing the amount of radioactive material needed and the worker's radiation exposure, we are also investigating the use of TEM spectroscopy to characterize inorganic salts of heavy actinides (BkCl₃, CfCl₃...) while using only a few nanograms of actinides.

Our journey into the chemistry of the f-elements, and especially that of Am, Cm, Bk, and Cf, led us to capture subtle difference within the trivalent actinide series. A broad study on the aminocarboxylate complexes of Am³⁺, Cm³⁺, Bk³⁺, and Cf³⁺ by EXAFS spectroscopy revealed an unexpected change in speciation between the Cf chelates and its Am, Cm, and Bk analogues. Similarly, the study of the chelation of the lanthanide and actinide cations by some bio-inspired chelators (ex: siderophore derivatives), led us to develop versatile and highly efficient liquid-liquid extraction processes for the purification radioisotopes.

3:00pm AC-ThA-3 Improving the Understanding of Actinides Through Spectroscopy, Samantha Cary, J Su, Los Alamos National Laboratory; **S Galley, T Albrecht-Schmitt,** Florida State University; **E Batista, M Ferrier, S Kozimor, V Mocko, B Scott, B Stein,** Los Alamos National Laboratory; **F White,** Florida State University; **P Yang,** Los Alamos National Laboratory

INVITED

Understanding the fundamental aspects of bonding is important in predicting an element's behavior, unfortunately when it comes to the actinides, there is little known. Acquiring a better understanding of these elements will affect a number of different areas including nuclear forensics, national security, and nuclear fuel cycles. Here we will describe the preparation of M(S₂CNET₂)₃(X) (M^{III} = Nd, Sm, Eu, Gd, Am, Cm, and Cf; X = n-heterocyclic aromatic ligands) and compare their structure, X-ray absorption spectroscopy, and electronic structure calculations.

4:00pm AC-ThA-6 Structural Chemistry of M(IV) (M = Ce, Th, and U) Complexes Isolated from Aqueous Solution, Karah Knope, Georgetown University

INVITED

Understanding actinide metal ion speciation and reactivity is of great strategic and scientific importance, and relates to a number of areas ranging from waste management to separations chemistries. Speciation depends on oxidation state, and our knowledge of the structural and energetic properties of tetravalent actinide complexes is relatively limited in comparison to the higher valent oxidation states. This lack of structural and chemical information has resulted in large discrepancies in thermodynamic data, significant challenges in process chemistry, and unanticipated behaviors in environmental systems. As a means of filling this knowledge gap, we have been examining the solid-state structural chemistry of tetravalent Ce, Th, and U complexes obtained from aqueous solutions with an eye towards understanding the directing effects of inner and outer coordination sphere interactions. Moreover, using spectroscopic and X-ray scattering techniques, we have been probing the correlation between the precipitated phases and the solution phase species. Presented

here will be an overview of recent efforts to elucidate the effects of both inner- and outer- coordination sphere interactions on the structural chemistry of tetravalent metal ion (Ce, Th, and U) complexes. How the synthetic conditions, identity of the counter-ions, and nature of complexing ligands affect the speciation and reactivity of the Ce(IV), Th(IV)- and U(IV)-building units will be discussed.

4:40pm AC-ThA-8 Hundess, Coherence and Magnetism in URu₂Si₂- and USb₂-family Materials, L. Andrew Wray, L Miao, H He, New York University; **S Ran,** University of Maryland, College Park; **N Butch,** Nist / Umd; **J Denlinger, Y Chuang,** Advanced Light Source, Lawrence Berkeley National Laboratory

INVITED

The uranium compounds URu₂Si₂ and USb₂ present fascinating low temperature phase diagrams, and are focal points of long-standing debates regarding how the crossover between strong correlations and electronic itinerancy should be conceptualized and evaluated. It has recently been found that uranium O-edge resonant X-ray spectroscopies can help to image this multi-natured wavefunction by providing a fingerprint of the f-electron atomic multiplet states. I will present a systematic O-edge spectroscopic characterization of URu₂Si₂ and USb₂ as a function of doping, and show that these data align well with a "Hund's metal" picture for both compounds. Distinct differences in the degree of "Hundess" (same-atom alignment of electron magnetic moments) as a function of chemical composition are found to underlie important features of the low temperature phase diagrams, such as the transition from a "hidden order" phase to antiferromagnetism, and the loss of a low temperature coherence feature in transport measurements. Based on these results, I will propose that developing a more quantitative experimental characterization of Hundness in many-body wavefunctions is of fundamental importance to the broader goal of understanding the phase diagrams in metallic systems with non-trivial local moment physics.

Author Index

Bold page numbers indicate presenter

— A —

Abergel, R: AC-ThA-1, **1**
Albrecht-Schmitt, T: AC-ThA-3, **1**

— B —

Batista, E: AC-ThA-1, **1**; AC-ThA-3, **1**
Booth, C: AC-ThA-1, **1**
Butch, N: AC-ThA-8, **1**

— C —

Cary, S: AC-ThA-3, **1**
Chuang, Y: AC-ThA-8, **1**

— D —

Deblonde, G: AC-ThA-1, **1**
Denlinger, J: AC-ThA-8, **1**

— E —

Ercius, P: AC-ThA-1, **1**

— F —

Ferrier, M: AC-ThA-3, **1**

— G —

Galley, S: AC-ThA-3, **1**

— H —

He, H: AC-ThA-8, **1**

— K —

Kelley, M: AC-ThA-1, **1**

Knope, K: AC-ThA-6, **1**

Kozimor, S: AC-ThA-3, **1**

— M —

Miao, L: AC-ThA-8, **1**

Minor, A: AC-ThA-1, **1**

Mocko, V: AC-ThA-3, **1**

Müller, A: AC-ThA-1, **1**

— R —

Ran, S: AC-ThA-8, **1**

— S —

Scott, B: AC-ThA-3, **1**

Stein, B: AC-ThA-3, **1**

Su, J: AC-ThA-1, **1**; AC-ThA-3, **1**

— W —

White, F: AC-ThA-3, **1**

Wray, L: AC-ThA-8, **1**

— Y —

Yang, P: AC-ThA-1, **1**; AC-ThA-3, **1**