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RERC29

Rare Earth Research Conference

June 26-June 30, 2022
Philadelphia, PA

Hosted by the University of Pennsylvania
Science History Institute Conference Center
315 Chestnut St, Philadelphia, PA 19106

Table of Contents

Fanny Rysam Mulford Hitchcock
1851 - 1936

Fanny Rysam Mulford Hitchcock, born on November 7, 1851, was one of only 13 women to receive their doctorates in chemistry in the 1800s. She was the first woman to receive a Ph.D. in Chemistry from the University of Pennsylvania. Her thesis was titled, "The Tungstates and Molybdates of the Rare Earths", conducted under the doctoral supervision of Edgar Fahs Smith. Hitchcock completed post-graduate work in chemistry at the University of Berlin before being elected by the Penn trustees to the Board of Managers of the Graduate Department for Women in October 1897. The following year Hitchcock became Penn's first Director of Women Students.

In her independent career, she began experimenting more with metals. She bought a mountain to have access to Uranium, known as "Taylor Hill" in Bellvale. Aside from her academic studies, she maintained a laboratory in both her home in Philadelphia and her country residence in Warwick, New York. In 1921, she retired from her life as a chemist and donated her equipment to Penn in the case of a women's fund or women's college getting formed. She was known to support the financial needs of students who could not afford to attend the University, and even rented a gym for the women to use while she was Director at Pennsylvania. She died on September 25, 1936 in her Warwick country residence.

The organizers gratefully acknowledge Mr. Roy T. Eddleman for his support of RERC29.

29th Rare Earth Research Conference (RERC29)

Philadelphia, PA
June 26-June 30, 2022

The RERC encompasses topics at the forefront of research with the rare earth and actinide elements, including:

Biological and Bioinorganic Chemistry
f-Element Materials for Quantum Information
Lanthanide and Actinide Coordination Chemistry
Lanthanide and Actinide Organometallic Chemistry and Catalysis
Luminescence and Luminescent Materials
Molecular Magnetism
Separations and Critical Materials
Solid State Chemistry and Physics
Theory Computation and Spectroscopy

Dear Rare Earthers:

Welcome to Philadelphia and the 29th Rare Earths Research Conference! We are so excited to welcome you in person to RERC29 following the postponement of the conference during the past 2 years due to the COVID-19 pandemic! With 1.6 M residents in 2020, Philadelphia, the 'City of Brotherly Love,' is the sixth-most-populous city in the USA and the second-most populous city on the East Coast. Philadelphia was founded in 1682 by William Penn (whose statue sits at the top of city hall) and is one of the oldest and most historically significant cities in North America.

Philadelphia was a key location during the American Revolution and bore witness to the First Continental Congress in 1774, signing of the Declaration of Independence in 1776 at the Second Continental Congress, and adoption of the US Constitution at the Convention of 1787. Independence Hall and the Liberty Bell, located two blocks from the conference center, are important cultural touchstones from that time. Philadelphia was the first capital of the USA and was the capital during the American Revolution. Again from 1790 to 1800, it served as the capital during the construction of Washington, D.C. During the Age of Enlightenment, US 'Founding Father' (and founder of the University of Pennsylvania) Benjamin Franklin visited Europe repeatedly to contribute to the scientific and political debates, bringing the newest European ideas back to Philadelphia.

Today, Philadelphia is a vibrant city of museums, educational institutions, museums, art, and culture. And our conference site, the Science History Institute, is proximate to many wonderful offerings in the old city neighborhood. In addition to our awesome conference program, we hope that you take some time to explore a bit of the many things Philadelphia has to offer!

We are grateful to the Program Committee, headed by Richard Wilson, and the Spedding Award Committee: Gerd Meyer, Vitalij Pecharsky, and Anja Mudring. We are also grateful to Carol Hartranft and especially Marta Guron for their hard work in organizing the meeting. We would also like to extend sincere thanks and appreciation to our sponsors.

Thank you all for coming and participating in the 29th RERC in Philadelphia, Pennsylvania.

Eric J. Schelter
University of Pennsylvania

Plenary Speakers

Aurora Clark
Washington State University
“The ‘Soul Memory of a Million Dead Stars’ – Revealing the Topology of Rare Earth Chemistry”

Aurora Clark is a Professor of Chemistry at Washington State University and joint appointee and Laboratory Fellow at Pacific Northwest National Laboratory. Her research employs both quantum and statistical mechanics to study chemical processes within complex chemical environments, focusing upon solution chemistry and liquid interfaces. This includes concentrated electrolytes, liquid/liquid interfaces related to separations science, structured fluids, and phase phenomena. To reveal the hierarchical organization and dynamic behavior in such systems, her laboratory has expanded the tools of graph theory, algebraic and geometric topology, to analyze data from modeling and simulation. Of particular interest is bridging the separate communities of applied mathematics with Chemistry and Materials Science by creating algorithms that are well-suited to simulation data and that provide new physical insight. Dr. Clark is a Fellow of the American Chemical Society and the American Association for the Advancement of Science.

Jenifer Shafer
Colorado School of Mines
“From Soft Donors to Soft Matter: Understanding Factors Governing Actinide Separations”

Jenifer Shafer is a Professor in the Chemistry Department and Nuclear Science & Engineering Program at the Colorado School of Mines and directs the Fundamental & Applied f-Element Research Group. She came to Mines following a Staff Scientist appointment at Pacific Northwest National Lab. She received her Ph.D. from Washington State University in 2010, and a B.S. from Colorado State University in 2005. Jenifer is interested in developing next-generation f-element separations to support advanced nuclear fuel cycles, national security, and renewable technologies. Current areas of particular interest include the use of new materials, supramolecular assembly, unique oxidation states, and controlling electronic structure.

She is the co-author of numerous book chapters, nearly 70 technical manuscripts, and has led or collaborated on projects receiving over $35M in funding from the DOE, DOD, DHS and NSF, with ~$5M directly supporting the efforts of the Fundamental and Applied F-Element Research Group. She currently serves as a Program Director at the DOE’s Advanced Research Projects Agency-Energy (ARPA-E) managing research portfolios relevant to advanced nuclear energy.

Matthew Allen
Wayne State University
“Tuning Divalent Europium for Magnetic Resonance Imaging”

Matthew Allen is a Professor of Chemistry and Chair of the Chemistry Department at Wayne State University. Matt completed a B.S. in chemistry at Purdue University and did research with Jillian Buriak. He earned his Ph.D. in chemistry from Caltech under the mentorship of Thomas Meade in the area of cellular delivery of gadolinium complexes. Matt was an NIH postdoctoral fellow in the laboratories of Laura Kiessling and Ronald Raines at the University of Wisconsin–Madison studying chemical biology before joining Wayne State University as an Assistant Professor. Matt’s laboratory studies the aqueous chemistry of the lanthanides and related areas.

Plenary Speakers

Rute Ferreira
University of Aveiro, Portugal
“Lanthanide-Based Multifunctional Materials for Green Photonics and Internet of Things-IoT”

Rute A.S Ferreira, PhD from the University of Aveiro (2002) is Associate Professor with Aggregation at the Physics Department of the University of Aveiro, Portugal. She has been vice-director of the CICECO – Aveiro Institute of Materials, since 2021. She is a member of the General Council of the University of Aveiro and of the Scientific Council of the Portuguese Foundation for Science and Technology. She is the Course Director of the Doctoral Program in Physical Engineering at University of Aveiro, Portugal. She has published more than 390 scientific articles in international journals, which have been cited more than 12,500 times. Her current interests focus on materials design towards solid-state lighting, integrated optics and photovoltaics (smart electrochromic windows and luminescent solar concentrators). She has also been working on luminescence magnetic materials (single ion/molecule magnets) and luminescence thermometry focused on primary thermometers and to the application of luminescent materials for the internet of Things (IoT) featuring optical smart tags for traceability and sensing.

Joseph Cotruvo
Pennsylvania State University
“Lessons Learned from Lanmodulin in Selective Recognition and Separation of f-elements”

Joseph Cotruvo, Jr. is currently an Assistant Professor of Chemistry and the Louis Martarano Career Development Professor at Penn State University; he was recently promoted to Associate Professor with tenure, effective July 1, 2022. He graduated with an A.B. from Princeton University, and he received his Ph.D. with JoAnne Stubbe at MIT, where he was an NDSEG Fellow. After postdoctoral work with Chris Chang at UC Berkeley as a Jane Coffin Childs Fellow, he began his independent career in 2016. His laboratory has a particular interest in elucidating mechanisms of selective metal ion recognition in biological systems and applying them to solve important problems in separation science and chemical biology. This work has been recognized by DOE Early Career, NSF CAREER, and NIH MIRA awards, as well as a Sloan Research Fellowship, the Stiefel Young Investigator Award, and a Charles E. Kaufman Foundation New Investigator Award.

Nicholas Chilton
University of Manchester, UK
“Spin-Vibration Coupling in Magnetic Molecules”

Prof. Chilton obtained his undergraduate degree from Monash University (Melbourne, Australia) in 2011, and his PhD from The University of Manchester in 2015 under the supervision of Prof. Richard Winpenny and Prof. Eric McInnes. He was a Ramsay Memorial Research Fellow from 2016-2018, a UoM Presidential Fellow from 2018-2019 and is currently a Royal Society University Research Fellow (from 2019). In 2015 he won the Dalton Young Researchers Award and in 2021 he won a Harrison-Meldola Memorial Prize, both from the Royal Society of Chemistry, and in 2019 he won the 7th Olivier Kahn International Award from the European Institute for Molecular Magnetism.

Venue Information

RERC29 will be taking place at the **Science History Institute Conference Center**. The Institute houses an archive and a library for historians and researchers; a fellowship program for visiting scholars from around the globe; a community of researchers who examine historical and contemporary issues; award-winning digital content that includes videos, articles, and a podcast; an acclaimed museum that is free and open to the public; and a state-of-the-art conference center.

Science History Institute
315 Chestnut Street
Philadelphia, PA 19106-2702
Tel: 215.925.2222
www.sciencehistory.org

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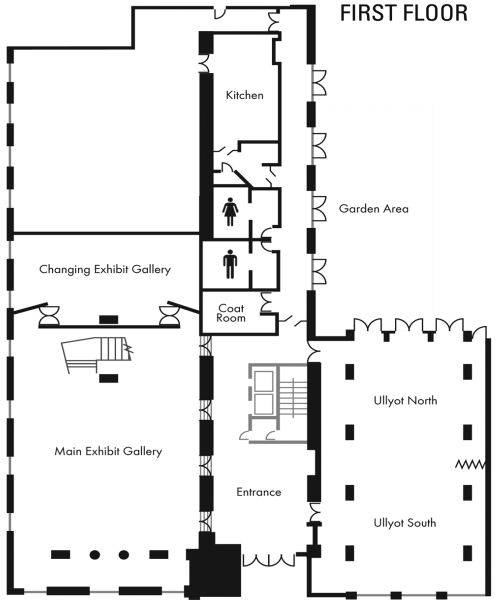

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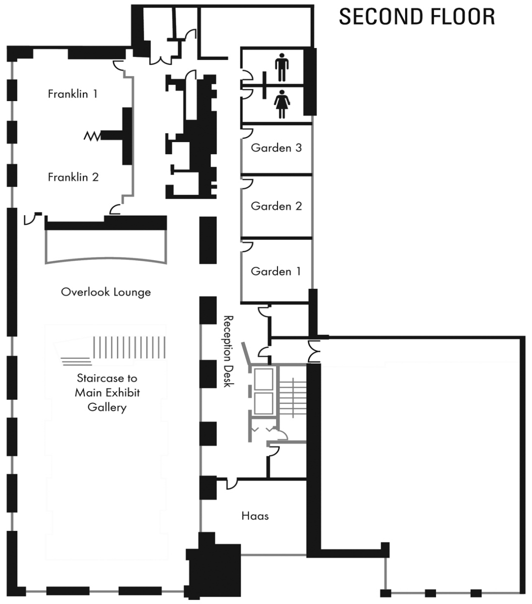

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Conference Agenda Day 1
Sunday, June 26, 2022

5:15 PM	Conference Registration – Science History Institute (SHI)
5:30 PM	Reception – Science History Institute
7:30 PM	Spedding Award Lecture – Science History Institute, Ullyot Room

The History of the Spedding Award

The Frank H. Spedding Award for Outstanding Contributions to Science and Technology of the Rare Earths has been awarded previously fourteen times. The previous awardees include: W. E. Wallace, Georg Busch, S. Legvold and W. Koehler, A. Mackintosch and H. Bjerrum Moeller, B. R. Judd, Karl Gschneidner, Jr., LeRoy Eyring, Gregory R. Choppin, Brian Maple, Lynn Boatner, John Corbett, William J. Evans, Gerd Meyer, and most recently, Joe D. Thompson from Los Alamos National Laboratory.

Spedding received his Ph. D. from Berkeley in 1929 and was quickly recognized for his work in spectroscopy and rare-earth chemistry, being awarded the Langmuir Award from the American Chemical Society, and a Guggenheim Fellowship to Europe for the 1934-5 academic year. In 1935, he received a two-year Baker Fellowship at Cornell, working with Hans Bethe, and joined the faculty at Iowa State College (University) in 1937. As the Rare Earth community well appreciates, the “Fraternal Fifteen” elements - so named by Karl Gschneidner in 1966 - comprise a host of interesting properties that make them noteworthy – Spedding noted in his “Spedding Papers” (ISU Archives, 1951) that pronounced magnetic properties arise from the filling of the 4fshell, leading to magnetic properties of great technological importance. And yet, these fraternal fifteen were considered “contaminants” by many.

The demands of the war years required the development of purification techniques on a grand scale, and the rare earth elements that naturally associated with uranium ores were considered contaminants that needed to be separated. Moreover, rare earth elements are found among the fission products of nuclear reactions, and separation is needed to purify unspent fuels and plutonium. Spedding’s young Institute for Atomic Research was at the heart of some of the most critical separation and purification processes for the Manhattan Project effort, and it would be the separations developed therein that would kindle the processes that would later benefit all of rare earth chemistry and physics.

And so, the Rare Earth Research community recognizes the accomplishments of one of our own by celebrating under the watchful eyes of Frank Spedding, a pioneer among many who recognized the scientific and technological implications of the “Fraternal Fifteen”.

Peter W. Roesky, 2017 Spedding Awardee

Peter W. Roesky obtained his diploma in 1992 from the University of Würzburg and his doctoral degree from the Technical University of Munich (with Prof. W. A. Herrmann) in 1994. He was as a postdoc with Prof. T. J. Marks at Northwestern University (1995–1996). In 1999, he completed his habilitation at the University of Karlsruhe. As a full professor he joined the faculty of chemistry and biochemistry at the Freie Universität Berlin in 2001. Since 2008, he has held the chair for inorganic functional materials at the University of Karlsruhe Institute of Technology (KIT). From 2013-15 he served as dean of the faculty of chemistry and biosciences at KIT. In 1999, Prof. Roesky received a Heisenberg scholarship of the German Science Foundation, and in 2000 a Karl-Winnacker scholarship. Since 2014, he is a fellow of the Royal Society of Chemistry and since 2020 a fellow of the European Academy of Science (EurAsc). In 2019/20, he received a JSPS Invitational Fellowships for Research in Japan and in 2020 a Reinhart Koselleck Project of the German Science Foundation.

Conference Agenda Day 2
Monday, June 27, 2022

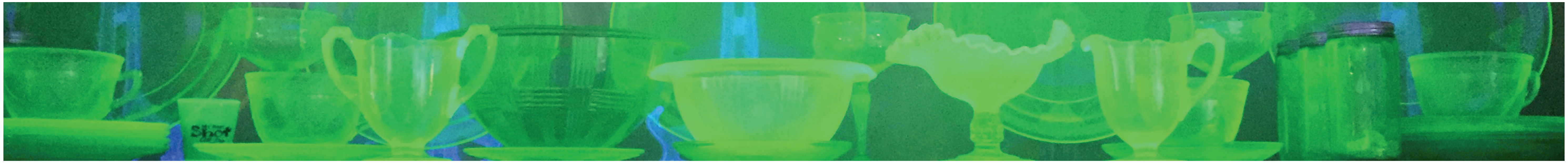
7:30 AM	**Registration Opens – Science History Institute Foyer**	**Breakfast (Ullyot)**	
8:10 AM	**Opening Remarks – SHI, Ullyot Room**		
	Plenary Lecture 1 **Joseph Cotruvo** ***Lessons Learned from Lanmodulin in the Selective Recognition and Separation of f-Elements***		
9:30 AM	**BREAK**		
Concurrent Sessions	**Lanthanide and Actinide Coordination Chemistry (Ullyot)** **Session chair: Suzanne Bart**	**Separations and Critical Materials (Franklin)** **Session chair: Mark Jensen**	**Condensed Matter Physics and Chemistry (Haas)** **Session chair: Eric Bauer**
9:45 AM - 10:15 AM	**James Blakemore** *Redox Tuning of Tripodal Cerium Complexes with Secondary Metal Cations*	**Zhe Lei** *Magnetic Separations of Rare Earth Ions*	**Jeffrey Thompson** *Rare Earth Ions*
10:15 AM - 10:45 AM	**David Mills** *Recent Adventures in Lanthanide and Actinide Silicon Chemistry*	**Michael Servis** *Using the Theory of Critical Phenomena to Understand Structure and Phase Transitions in Separations of Rare Earths.*	**Zhentao Wang** *Tomonaga-Luttinger Liquid Behavior and Spinon Confinement in* $YbAlO_3$
10:45 AM - 11:00 AM	**BREAK**		
11:00 AM - 11:30 AM	**Henry La Pierre** *Bonding, Reactivity, and Magnetism of Tetravalent Lanthanide Ions in Molecules and Extended Solids*	**Erin Bertelsen** *Carbon Treated Diatomaceous Earth for Rare Earth Element Separations*	**Nirmal Ghimire** *Magnetism and Anomalous Hall Efect in the Kagome-Net Magnets* RMn_6Sn_6 $(R = Y, Yb)$
11:30 AM - 12:00 PM	**Scott Daly** *Quantified and Correlated Covalent Metal-Ligand Bonding and Reactivity differences in Isostructural Lanthanide and Uranium Phosphinodiboranates*	**Cecilia Martinez-Gomez** *Lanthanide-Dependent Metabolism by Methylotrophic Bacteria Opens Novel Avenues to Improve Technologies for Recovery of Energy-Critical Metals*	**Benjamin Ueland** *Magnetism, Symmetry, and Topology of* EuM_2Pn_2 *Compounds*
12:00 PM	**LUNCH**		
1:30 PM	**Plenary Lecture 2** **Rute Ferriera** *Lanthanides for Smart Mobile Optical Sensing and the Internet of Things*		
	BREAK		
	Lanthanide and Actinide Chemistry (Ullyot) **Session chair: Karah Knope**	**Molecular Magnetism (Franklin)** **Session chair: Selvan Demir**	**Biological Separations and Rare Earth Spectroscopy (Haas)** **Session chair: Andrew Ferguson**
2:45 PM	**Jerome Robinson** *RE-Designing Catalysts to Overcome Challenges in Polymer Synthesis*	**Stephen Hill** *Rare Earth Molecular Clock Qubits*	**Abigail Knight** *Bioinspired Polymers for Ion Separations*
3:15 PM	**Megan Fieser** *Rare Earth Metal Catalysts for the One-Pot Block Copolymerization of Olefins and Cyclic Esters*	**Annie Powell** *Toroidal Moments in Molecular Magnets*	**Valerie Pierre** *Inorganic Receptors for Phosphate for Medical and Environmental Applications*
3:45 PM	**BREAK**		
4:00 PM	**Christopher Cahill** *Assembly of* $[AnO_2X_4]^{2-}$ *Anions with Assorted Organic Cations: Routes to 'yl' Engagement, Non-covalent Interactions and Photoreactivity*	**Lucie Norel** *Assembling Dysprosium Single-Molecule Magnets with Photochromic Dithienylethene Ligands : an Efficient Strategy for Magnetic Hysteresis Photomodulation?*	**Louise Natrajan** *A Coordination Chemistry Approach to Optical Imaging of Uranium Biotransformations in Model Conditions*
4:30 PM	**Suzanne Bart** *Multi-Electron Redox Chemistry with Thorium(IV) Iminoquinone Complexes*	**Joseph Zadrozny** *Rare-Earth Magnetic Control of Organic Reactions*	**Jean-Claude Bunzli** *Exciting Developments in Lanthanide Photonics*
5:00 PM - 6:30 PM	**Poster Session 1 (see page 16)**	Location: Dow Public Square & Jacobs Reading Room (3rd floor)	

Conference Agenda Day 3
Tuesday, June 28, 2022

7:45 AM	**Building Opens**	**Breakfast (Ullyot)**	
8:30 AM - 9:30 AM	**Plenary Lecture 3, Ullyot Room**		
	Matthew Allen ***Tuning Divalent Europium for Magnetic Resonance Imaging***		
9:30 AM	**BREAK**		
Concurrent Sessions	**Lanthanide and Actinide Coordination Chemistry (Ullyot)** **Session chair: Henry LaPierre**	**Biological Applications of Rare Earths (Franklin)** **Session chair: Ana de Bettencourt-Dias**	**Condensed Matter Physics and Chemistry (Haas)** **Session chair: Zachary Tener**
9:45 AM - 10:15 AM	**Cory Windorff** *Pursuing Biorelevant Uranyl Complexes*	**Jonathan Sessler** *Lanthanide Texaphyrins: An Update on Drug Development Efforts*	**Cristian Batista** *A Microscopic Kondo Lattice Model for the Heavy Fermion Antiferromagnet* $CeIn_3$
10:15 AM - 10:45 AM	**Gregory Nocton** *Unusual Oxidation States and Reactivity in Heterometallic Compounds Combining Lanthanide and Transition Metal Ions*	**David Tatum** *Macrocyclic 1,2-HOPO Bifunctional Chelators for Time-Resolved Europium(III) Luminescence and Radiopharmaceutical Applications*	**Sergey Bud'ko** *Evolution of Magnetic Ground State in Yb-based Heavy Fermion Compounds: Effects of Magnetic Field and Pressure*
10:45 AM - 11:00 AM	**BREAK**		
11:00 AM - 11:30 AM	**Steve Liddle** *Recent Advances in Actinide-Ligand Multiple Bonding*	**Bruce Cohen** *Upconversion and Avalanching in Lanthanide-based Nanocrystals for Imaging*	**Martin Mourigal** *Novel Forms of Quantum Magnetism using Kramers/non-Kramers Rare-Earth Pairs*
11:30 AM - 12:00 PM	**Karah Knope** *Tetravalent Metal Ion Cluster Chemistry*	**Gael Ung** *Circularly Polarized Luminescence Across the f-Block*	**Wei Wei Xie** *Observation of* Yb^{3+} *with Spin-1/2 in* Yb_xPt_5P
12:00 PM	**LUNCH**		
1:30 PM	**Plenary Lecture 4** **Jenifer Shafer** ***Soft Donor versus Soft Matter: Controlling Transplutonium Chemistry***		
	BREAK		
	Lanthanide and Actinide Chemistry (Ullyot) **Session chair: Matthew Polinski**	**Molecular Magnetism (Franklin)** **Session chair: Jeffrey Rinehart**	**Solid State Chemistry (Haas)** **Session chair: Pia Lange**
2:45 PM	**Conrad Goodwin** *Transuranium Metallocene Complexes*	**Michael Nippe** *Generating Magnetic Anistropy Through Exchange and Ligand Field*	**Susan Latturner** *Metal Flux Growth of Stuffed Rare Earth Borocarbides*
3:15 PM	**Julie Niklas** *High-Valent Uranium and Neptunium Imidophosphorane Complexes*	**Kevin Bernot** *Lanthanide Coordination Chemistry: A Key to Design Supramolecular Magnetic Edifices*	**Thomas Schleid** *On Rare-Earth Metal Halide Oxido-Arsenates and -Antimonates*
3:45 PM	**BREAK**		
4:00 PM	**Stefan Minasian** *Pinpointing Chemical Bonding in CeF62- with Spectroscopy, Magnetism, and Electronic Structure Theory*	**Helene Bolvin** *The Versatility of the Magnetic Properties of the Actinyl Cations*	**Daniel Shoemaker** *Materials Growth and Discovery for Europium-based Quantum Information Storage*
4:30 PM	**Nolwenn Mahieu** *Synthesis of Multi-Metallic f-Element Complexes with the Cyclononatetraenyl Ligand*	**Valerie Vallet** *Exploring Excited State Potential Energy Profile and Luminescence Properties of Uranyl-Based Complexes by TRLFS and Ab Initio Method*	**Ingo Hartenbach** *The Flowers Along the Way: Anticipated and Unprecedented Results on the Path to Rare-Earth Metal Molybdates and Tungstates with Luminescent Properties*
5:00 PM - 6:30 PM	**Poster Session 2 (see page 18)**	Location: Dow Public Square & Jacobs Reading Room (3rd floor)	

Conference Agenda Day 4
Wednesday June 29, 2022

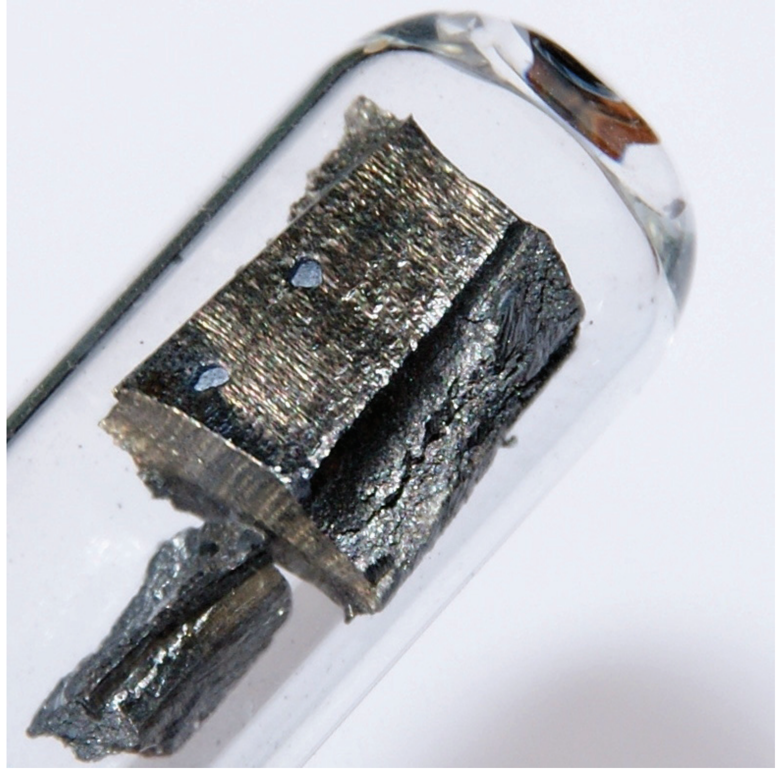
7:45 AM	**Building Opens**	**Breakfast (Ullyot)**	
8:30 AM - 9:30 AM	**Plenary Lecture 5, Ullyot Room**		
	Nicholas Chilton ***Spin-Vibration Coupling in Magnetic Molecules***		
9:30 AM	**BREAK**		
Concurrent Sessions	**Rare Earth Luminescence and Spectroscopy (Ullyot)** **Session chair: Jean-Claude Bunzli**	**Theoretical and Computational Chemistry (Franklin)** **Session chair: David Cantu**	**Condensed Matter Physics and Chemistry (Haas)** **Session chair: Weiwei Xi**
9:45 AM - 10:15 AM	**Mohsen Mirzakhani** *A Bottom Up Approach toward Programmable Luminescent Lanthanidopolymers*	**Nikolas Kaltsoyannis** *Computational Adventures in Molecular f element Chemistry – Two Short Stories*	**Mitchell Bordelon** *MagneticFrustration in Jeff = ½ Yb- and Ce-based Triangular Lattice Antiferromagnets*
10:15 AM - 10:45 AM	**Yuichi Harai** *Bright Triboluminescence of An Inefficient Photoluminescent Eu(III) Complex*	**Lan Cheng** *Spinor-Based Relativistic Coupled-Cluster Study of Lanthanide Thermochemistry and Spectroscopy*	**Ajeesh Omanakuttan** *Narrow-gap Kondo Insulating Ground State of* $Ce_3Bi_4Pd_3$ *Revealed by Applied Pressure*
10:45 AM - 11:00 AM	**BREAK**		
11:00 AM - 11:30 AM	**Ines Taarit** *Molecular Light-Upconversion: When Excited State Absorption (ESA) Overcomes Energy Transfer Upconversion (ETU) In Cr(III)/Er(III) Complexes*	**Remi Maurice** *Chemistry, Spectroscopy and Speciation of Protactinium*	**Ryan Baumbach** *Enhanced thermoelectric properties in* YbT_2Zn_{20} *(T = Co, Rh, Ir)*
11:30 AM - 12:00 PM	**Melissa Gish** *Illuminating the Photophysics of Oxygen Atom Transfer in Rare Earth Metal-Organic Complexes*	**Pere Miro** *Speciation and Nucleation of An(IV) Species in Aqueous Media*	**Daniel Phelan** *Rare-Earth Mediated Cross-Over in Dimensionality of a Spin Density Wave in a Ruddlesden-Popper Nickelate*
12:00 PM	**Lunch on your own.**	Refer to your brochure in the registration packet to find local attractions and dining.	Those signed up for a guided tour of SHI should report to the foyer at noon.

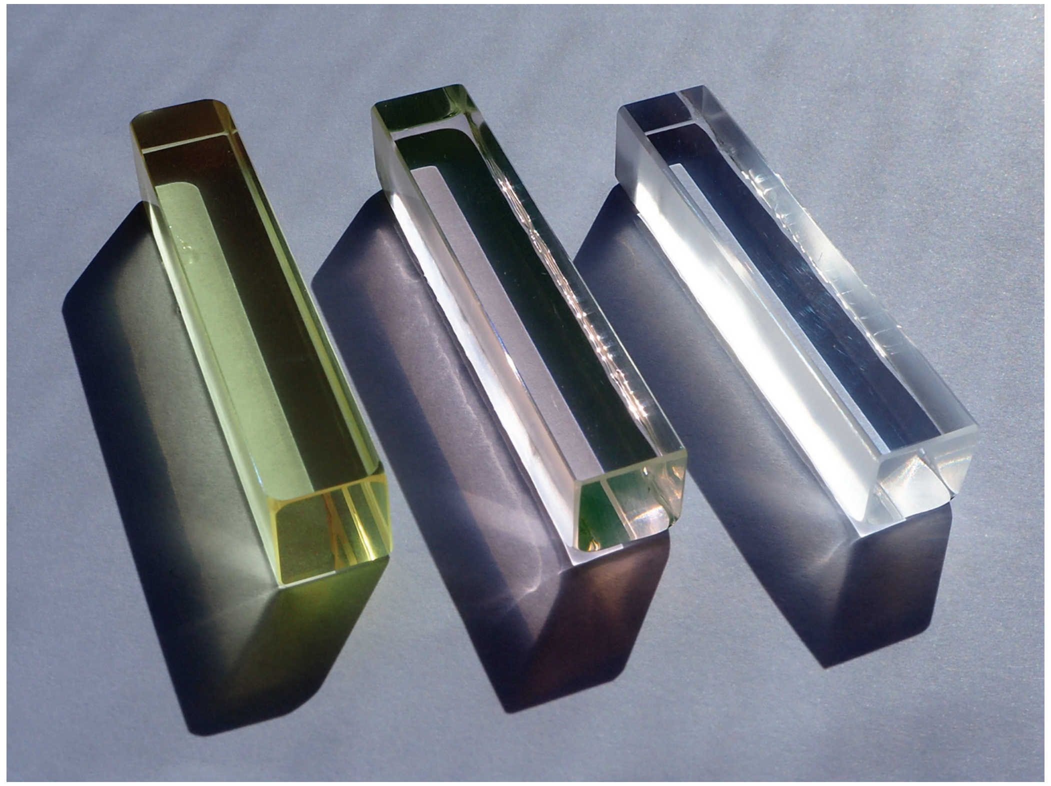


6:00 PM Cocktail Hour 7:00 - 9:00 PM Banquet	**Conference Banquet** **Dress: Smart Casual** The banquet venue may be reached via a 15 minute walk from SHI along the waterfront.	**Moshulu** Penn's Landing 401 S. Columbus Blvd Philadelphia, PA 19106 Tel: 215.923.2500 Fax: 215.829.1604 Email: info@moshulu.com	

Conference Agenda Day 5
Thursday June 30, 2022

7:45 AM	**Building Opens**	**Breakfast (Ullyot)**	
8:30 AM - 9:30 AM	**Plenary Lecture 6, Ullyot Room**		
	Aurora Clark ***The "Soul Memory of a Million Dead Stars" – Revealing the Topology of Rare Earth Chemistry***		
9:30 AM	**BREAK**		
Concurrent Sessions	**Molecular Magnetism & Rare Earth Chemistry (Ullyot)** **Session chair: Michael Nippe**	**Theoretical and Computational Chemistry (Franklin)** **Session chair: Remi Maurice**	**No session in Haas today**
9:45 AM - 10:15 AM	**Selvan Demir** *Multifunctional Lanthanide Metallocenes: From High-Performance Single-Molecule Magnets to Small Molecule Activation*	**Kirk Peterson** *Accurate relativistic quantum chemistry for lanthanide and actinide thermochemistry*	
10:15 AM - 10:45 AM	**Jeffrey Rinehart** *Fine-Tuning the Electron Spin Wavefunction with Magnetic Dipoles in a Series of Er(III)-based Molecular Complexes*	**Bess Vlaisavljevich** *Electronic Structure of Uranium–Arenide Complexes*	
10:45 AM - 11:00 AM	**BREAK**		
11:00 AM - 11:30 AM	**Gerd Meyer** *Pitfalls and Blessings in Reduced Rare-Earth Metal Halide Chemistry*	**David Cantu** *Predicting the Coordination Structures and Thermodynamic Properties of Lanthanides in Solution*	
11:30 AM - 12:00 PM	**Soroush Naseri** *Preorganization of β-Diketonate Lanthanide Adducts with Rigid N-Donor Ligands: Thermodynamics and Photophysics*	**Tyler Del Rose** *Accelerated Discovery of New Rare-earth Compounds by Machine Learning*	
12:00 PM	**Closing Remarks**		





Poster Session 1

Monday, June 27, 2022

5:00 PM - 6:30 PM

	Lanthanide and Actinide Coordination and Organo-Metallic Chemistry
Adrian Hauser	From a Nanoparticular Solid-State Material to Molecular Organo-f-element-Polyarsenides
Cedric Uhlmann	The Archetypal Homoleptic Lanthanide Quadruple-Decker – Synthesis, Mechanistic Studies, and Quantum Chemical Investigations
Fang-Che Hsueh	Reactivity of Multimetallic Thorium Nitrides Generated by Reduction of Thorium Azides
Jack Baldwin	Low-Coordinate Lanthanide Complexes with Bulky Silylphosphide Ligands
Matthew Polinski	f-Element Squarates, Squarate-Oxalates, and the Determination of the Nine-Coordinate Ionic Radius of Cf(III)
Pragati Pandey	Synthesis and Characterization of Organocerium Based Molecular Materials with Fullerene for Charge Transfer Properties
Sergely Bokouende	Solid-State and Solution-Phase Characterization of SmII-Aza[2.2.2]cryptate and its Methylated Analogue
Nicole Byrne	An Experimental and Theoretical Investigation of Actinide-Ligand Bonding and Second-Sphere Interaction Strengths in Families of [AnO2Cl4]^{2}- (An = U, Np, Pu) Materials
Tajrian Chowdhury	Rediscovering the Unsubstituted Trispyrazolylborate Ligand on Lanthanides: Synthetic Versatility, Redox Chemistry, and Small Molecule Activation
Korey Carter	Expanding Uranyl Peroxide Cluster Chemistry via New Synthetic Routes and the Introduction of Free Radicals
Himanshu Gupta	Towards Strongly Correlated Lanthanide-TTF Molecular Materials
Riddhi Golwankar	Electrochemical Activation of the Uranyl Ion
R. Gian Surbella	Crystalline Americium Frameworks: Platforms for Exploring Bonding and Photoluminescence
Qiaomu Yang	Photocatalytic C-H Activation Driven by Cerium Catalysts

	Separations and Critical Materials
Andrew Ferguson	Development of Photochemically Active Ligand Coordination Spheres for Light-driven Separation of Critical Rare Earths
Katherine Johnson	Use of a Selective Aqueous Holdback Reagent for Improved Adjacent Lanthanide Separation in Liquid-Liquid Extraction
Kilian Ortman	Magnetically-Assisted Solvent Extraction (MaSX) of Rare-Earth Ions by Single Ligand-Laden Organic Droplet in Aqueous Bulk
Mark Jensen	Ligand Control of Kinetics in Rare Earth Solvent Extraction Separations

Posters for this session should be brought to SHI on Monday morning. Please follow instructions on site for daytime storage. Please be sure your poster is clearly labeled on the outside. Posters should be taken down and removed from SHI at the conclusion of the poster session.

	Solid State Chemistry and Condensed Matter Physics
Pia Lange	$Cs_3La[AsS_4]_2$: A Cesium-Containing Lanthanum Thioarsenate(V)
Eric Bauer	Quantum Criticality of the Quasi-One-Dimensional Heavy Fermion Material $YbFe_5P_3$
Michael Tarlton	Hybrid Double Perovskites of the f-elements
Gerd Meyer	The Prolific Ternary System Pt/Sn/Nd: Insertion of Pt into Sn/Nd Intermetallics in the Sn_2Nd to Sn_5Nd_2 Region Yields Structural Complexity and Wealth
Durga Paudyal	Enhancing Stability and Magnetism of $ThMn_{12}$-type Cerium-Iron Intermetallics by Site Substitution
Mike Ozerov	Magnetic field tuning of crystal field levels and vibronic states in the spin ice compound $Ho_2Ti_2O_7$ obesrved with Far-IR spectroscopy

Poster Session 2

Tuesday, June 28, 2022

5:00 PM - 6:30 PM

	Biological Chemistry and Bio-Inorganic Chemistry of Rare Earths
Alison Knasin	Structural and Reactivity Studies of Synthetic Model Complexes of a Rare-Earth Dependent Methanol Dehydrogenase
Randall Wilharm	Periodic Trend in Affinity of Lanthanide Receptors for Phosphate
Brett Vincenzini	Synthesis and Electronic Structure Analysis of a Ce^{IV}- Allenyl
S. Olivia Gunther	Ligand K-edge X-ray Absorption Spectroscopy of Organometallic Rare-earth Complexes for Quantum Information Sciences

	Lanthanide and Actinide Coordination and Organo-Metallic Chemistry
Appie Peterson	Amidate Supported Single-Molecule Precursors for Actinide Oxide Materials
Christian Uruburo	Accessing Kinetically Driven Reactions for Rare Earth Separations
Eric Villa	Periodic Trends of Templated Lanthanide Thiosulfate Compounds: Facile Control of Dimensionality
Lauren Anderson-Sanchez	Stabilizing a Series of new Ln(II) Complexes with 2,6-Di-adamantyl aryloxide Ligands
Ziad Shafi	Lanthanide Complexes Containing a Terminal Ln=O Oxo Bond: Revealing Higher Stability of Tetravalent Praseodymium Versus Terbium
Christopher Hossack	Synthesis and Characterization of Nitro-functionalized Lanthanide Trispyrazolylborates
Churna Bhandari	Enhanced Magnetic Anisotropy in Lanthanum M-type Hexaferrites by Quantum-Confined Charge Transfer
Henry Wilson	Metal-Ligand Multibonds of Lanthanides: Electronic Structure Studies in the Hunt for Emergent Quantum Phenomena

	Separations and Critical Materials
Amit Kumar	Harnessing Magnetic Field for Rare-Earth Separations
Iskander Douair	Computational Insight into Critical Lanthanide Separation through Ligand-Based Photophysical Energy Exchange
Kevin Ruoff	Towards Reactive, Element-Specific Separations of Dysprosium through Photochemistry
Maxwell Furigay	Selective Reduction of Niobium(V) Species to Promote Molecular Niobium/ Tantalum Separation
Mark Jensen	Novel Ligands for Rare Earth Solvent Extraction Separations
Brittany Bonnett	Using the Theory of Critical Phenomena to Understand Structure and Phase Transitions in Separations of Rare Earths

Posters for this session should be brought to SHI on Tuesday morning. Please follow instructions on site for daytime storage. Please be sure your poster is clearly labeled on the outside. Posters should be taken down and removed from SHI at the conclusion of the poster session.

	Solid State Chemistry and Condensed Matter Physics
Patrik Djendjur	Unexpected Sodium-Containing Nitride Selenides of the Lanthanoids: NaLn9N4Se8 (Ln = Gd Dy)
Yaroslav Mudryk	Crystallography and magnetism of (Er1-xYbx)2In compounds
Arun Ramanathan	Chemistry and Topology of Spin-Orbit Coupling and Competing Interactions in Ternary, Tetravalent Lanthanide Chalcogenides
Zachery Tener	Optimization of Rare-Earth Content in Bonded Nd2Fe14B-based Magnets Utilizing Applied Magnetic Field Modifications to HDDR Treatment.
Teuta Neziraj	High-Pressure Synthesis of Intermetallic Framework Compounds RESi3

	Rare Earth Computational and Theoretical Chemistry
Stephanie Gamble	Defining Qubit Properties in the Early Actinides

Multi-Electron Redox Chemistry with Thorium(IV) Iminoquinone Complexes

D. M. Ramitha Y. P. Rupasinghe, Makayla Baxter, Matthias Zeller, Suzanne C. Bart

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Thorium complexes primarily exist in the thermodynamically stable (IV) oxidation state, with limited examples of low-valent thorium(III) complexes known. As a result, redox chemistry with thorium is challenging without carefully designed ligand environments. This redox-restricted nature of thorium(IV) makes redox-active ligands an attractive option to facilitate multi-electron redox chemistry. In this work, a series of thorium(IV) complexes featuring the redox-active iminoquinone ligand and its derivatives, including the iminosemiquinone and amidophenolate species, were synthesized and isolated. Oxidation chemistry resulted in formation of a terminal oxo species, which is rare for thorium species. Spectroscopic and structural characterization of each derivative established the +4 oxidation state for thorium with redox chemistry occurring on the ligand. Magnetic and EPR studies confirmed the formation of new thorium species featuring multiple ligand radicals as well.

A microscopic Kondo lattice model for the heavy fermion antiferromagnet $CeIn_3$

Cristian Batista

[1]The University of Tennessee, Knoxville

Electrons at the border of localization generate exotic states of matter across all classes of strongly correlated electron materials. Heavy electron metals are a model example, in which magnetic interactions arise from the opposing limits of localized and itinerant electrons. This remarkable duality is intimately related to the emergence of a plethora of novel quantum matter states, such as unconventional superconductivity, electronic-nematic, hidden order and most recently topological states, including skyrmion crystals, topological Kondo insulators and putative chiral superconductors. The outstanding challenge is that the archetypal Kondo lattice model that captures the underlying electronic dichotomy is notoriously difficult to solve for real materials. Using the prototypical strongly correlated antiferromagnet $CeIn_3$, we will show that a multi-orbital periodic Anderson model embedded with input from ab initio band structure calculations can be reduced to a simple Kondo-Heisenberg model, which captures the magnetic interactions quantitatively. This tractable Hamiltonian is validated via high-resolution neutron spectroscopy that reproduces accurately the full magnon dispersion of $CeIn_3$.

Enhanced thermoelectric properties in YbT_2Zn_{20} (T = Co, Rh, Ir)

Ryan E. Baumbach[1,2,*], Jorge Galeano Cabral[1,3], Benny Schundelmeier[1,2], and Kaya Wei[1]

[1*]National High Magnetic Field Laboratory, Florida State University, baumbach@magnet.fsu.edu
[2]Department of Physics, Florida State University
[3]FAMU-FSU College of Engineering, Florida State University

INTRODUCTION

Thermoelectricity allows for direct conversion between heat and electricity, providing alternatives for green energy technologies. Despite these advantages, for most materials the energy conversion efficiency is limited by the tendency for the electrical and thermal conductivity to be proportional to each other and for the Seebeck coefficient to be small. Here we will discuss promising behavior that is seen for many strongly correlated f-electron systems, where we will focus on the family YbT_2Zn_{20} (T = Co, Rh, Ir) [1].

EXPERIMENTAL METHODS

Single-crystal specimens were synthesized by the molten metal flux technique using the growth protocols described by Torikachvili et al. [2]. Temperature-dependent Seebeck coefficient (S) measurements (gradient sweep method), four-probe resistivity (ρ) measurements, and steady state thermal conductivity (κ) measurements were performed for single crystals of YbT_2Zn_{20} to characterize both the power factor PF and the figure of merit ZT. The single crystals were carefully aligned before mounting so that both the thermal gradient and the electrical current were along the [100] crystallographic direction.

RESULTS AND DISCUSSION

The materials YbT_2Zn_{20} (T = Co, Rh, Ir) feature (i) a strongly hybridized electronic state that originates from hybridization between the Yb f-electrons and conduction electrons and (ii) novel structural features [1,2]. This combination produces a large power factor (PF = 74 μW/cm-K2; T = Ir) and a high figure of merit (ZT = 0.07; T = Ir) at 35 K, as shown in Fig. 1. Motivated by this, we have investigated chemical substitution on the transition metal where the hybridization strength and thermoelectric properties are readily tuned. These results will be discussed in this talk, in order to expose strategies to optimize these systems as potential platforms for applications.

ACKNOWLEDGMENTS

This work was performed at the National High Magnetic Field Laboratory, which is supported by NSF Cooperative Agreement No. DMR-1644779 and the State of Florida. The synthesis of single crystals was supported by the Center for Actinide Science and Technology (CAST), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under award no. DESC0016568. K.W. acknowledges the support of the Jack E. Crow Postdoctoral Fellowship.

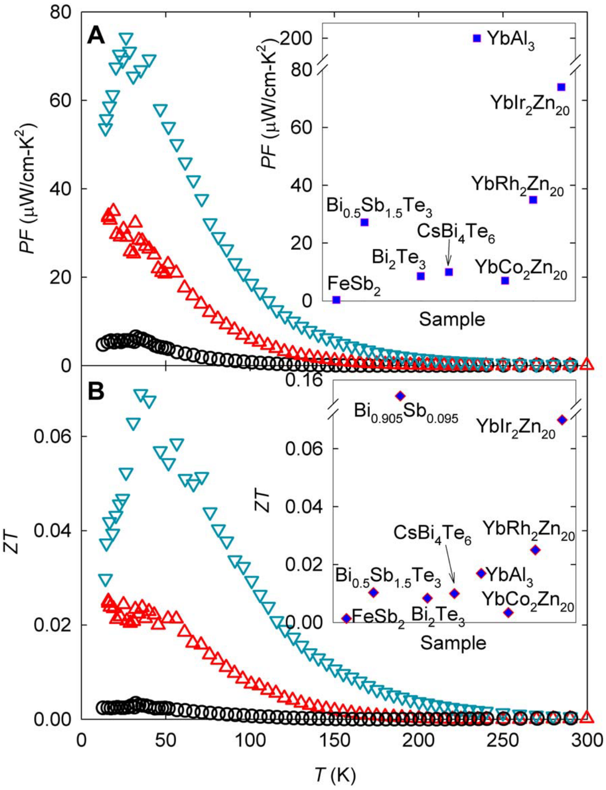

Figure 1. Temperature-dependent power factor PF (panel A) and thermoelectric figure of merit ZT (panel B) for $YbCo_2Zn_{20}$ (circle), $YbRh_2Zn_{20}$ (up-triangle), and $YbIr_2Zn_{20}$ (down-triangle). The insets in (A) and (B) are the PF and ZT values of several well-known thermoelectric materials at 35 K plotted together with parent compounds.

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Lanthanide coordination chemistry : a key to design supramolecular magnetic edifices

Felix Houard[1], Quentin Evrard[1], Frederic Gendron[1], Boris Le Guennic[1], Vincent Dorcet[1], Thierry Guizouarn[1], Guillaume Calvez[1], Yan Suffren[1], Carole Daiguebonne[1], Olivier Guillou[1], Matteo Mannini[2], Kevin Bernot[1,3]*

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INTRODUCTION

In this presentation, we will show how lanthanide coordination chemistry[1] is a very efficient tool to design magnetic and luminescent molecules but also how it allow turning them into materials and then devices.

RESULTS AND DISCUSSION

We will review several years of work of our team and collaborators on lanthanide-based single-molecule magnets (SMM)[2,3] and single-chain magnets (SCM),[4] molecules that are able to behave as magnets at the molecular scale.

First, we will detail how a pure fundamental study on lanthanide dimers allowed the investigation of a full continuum of results from the characterization of the SMM behavior of a molecule to the design of a molecule-based magnetic material and the consecutive creation of tunable luminescent devices.

Second, we will illustrate how a SCM behavior can be observed on lanthanide–radical chains with original topologies such as chiral molecular nanotubes[6] and in various packing organization.[7,8]

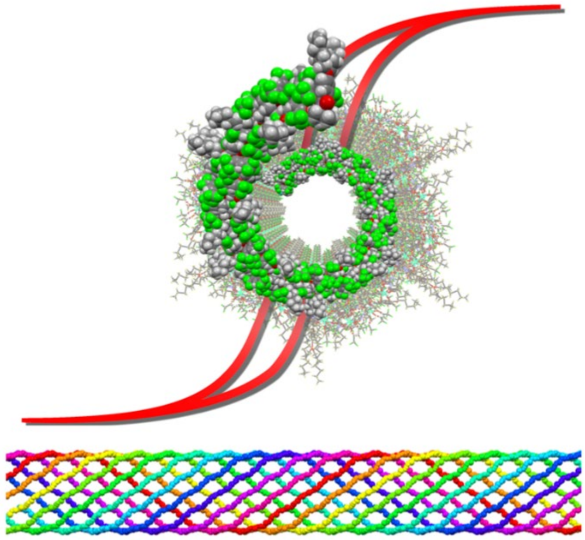

Figure 1: Supramolecular Nanotubes of Single-Chain Magnets[6]

CONCLUSIONS

We will show in this presentation how coordination chemistry is one of the best tools for building molecular edifices from lanthanide ions because it allows careful control of the ion environment and of the dimensionality of the final compound. This is particularly important for optimizing the magnetic properties of lanthanide-based molecules.

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ACKNOWLEDGMENTS

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Carbon Treated Diatomaceous Earth for Rare Earth Element Separations

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INTRODUCTION

Diatomaceous earth (DE), also known as kieselguhr or diatomites, is a porous siliceous rock deposit[1] and has been utilized as a support for the development of several extraction chromatographic materials.[2] Their low cost, small particle size, porosity, and relative abundance makes them an attractive support candidate. Carbon-based materials are interesting separation supports in that they provide higher chemical and thermal stability than their silica-based counterparts. Here, DE was coated with carbon using chemical vapor deposition prior to functionalizing the hybrid material with a lanthanide selective extractrant.

EXPERIMENTAL METHODS

Chemical vapor deposition

DE earth was placed in a tube furnace and purged with argon under vacuum three times. The inert atmosphere was maintained with argon while the pressure was returned to atmospheric conditions. The furnace was then ramped to 900 °C and vaporized *n*-hexane-loaded argon was injected. After depletion of *n*-hexane, the gas flow was returned to argon and the temperature was held for one hour before cooling.

HDEHP physisorption

Functionalization was achieved by suspending approx. 300 mg of carbon-treated DE (CDE) in methanol in a 7.5 mL vial. A solution containing 209.8 g bis-(2-ethylhexyl)phosphoric acid (HDEHP) in methanol was added to the vial and shaken for 24 h at room temperature. After shaking, the material was quantitatively transferred to a crucible using methanol. The methanol was evaporated in a fume hood under a heat lamp yielding 39.94(2) wt% HDEHP-CDE.

Batch distribution analyses

Aqueous solutions were prepared with with an ionic strength of 1 M using $NaNO_3$ and the appropriate HNO_3 concentration. The uptake of Eu^{3+} was measured by contacting 0.5 mL of solution (0.490 mL of 1 M $H/NaNO_3$, 5 µL of 20 ppm $Eu(NO_3)_3$ in 0.001 M HNO_3, and 5 µL of the radiotracer $^{152}Eu(NO_3)_3$ in 0.001 M HNO_3) with approximately 5.0 mg of material. The phases were contacted at 1200 rpm for 30 min at 25 °C. Each sample, done in triplicate, was fitered using a 0.45 µm syringe filter and 450 µL aliquots were taken for gross gamma counting.

RESULTS AND DISCUSSION

The 39.94(2) wt% HDEHP-CDE exhibits Eu^{3+} sorption typical to chromatographic materials[3,4] containing HDEHP, such that Eu^{3+} uptake is low at higher HNO_3 concentrations and increases with decreasing acid concentration. Unfunctionalized CDE did not uptake Eu^{3+} at any HNO_3 tested.

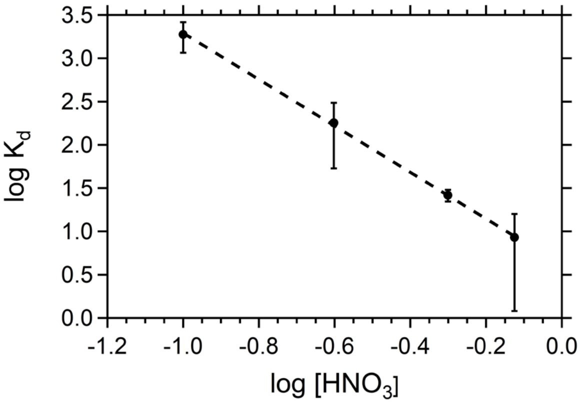

Figure 1. Uptake of Eu^{3+} with increasing HNO_3 using 39.94(2) wt% HDEHP-CDE. Error bars represent ±3σ.

CONCLUSIONS

HDEHP-CDE provides Eu^{3+} uptake comparable to similar extraction chromatographic materials using HDEHP. Further studies using this material are currently underway. Through chemical vapor deposition, it may be possible to coat more advanced silica-based materials.

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ACKNOWLEDGMENTS

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Luminescent Lanthanide Complexes for Imaging, Sensing, and as Photosensitizers for Therapy

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Judicious choice of the ligands used in the antenna effect for sensitization of lanthanide emission leads to complexes with additional functionalities. The luminescence, which makes the resulting complexes interesting for imaging applications, can be modulated through the temperature and viscosity of the medium. Thus, these compounds are potentially interesting as nanoscale temperature or viscosity probes. Some of these complexes can generate singlet oxygen, a cytotoxic species, which makes the compounds useful as photosensitizers for photodynamic therapy.

Redox Tuning of Tripodal Cerium Complexes with Secondary Metal Cations

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ABSTRACT

Development of new strategies for rationally tuning the thermodynamics and kinetics of electron transfer in the cerium(IV/III) redox manifold could unlock new applications for this versatile element, as well as provide a testbed for approaches to tuning the properties of other rare earths as well as actinides. In this presentation, the synthesis of a family of heterobimetallic cerium complexes will be described; the framework used to support the complexes is heteroditopic and tripodal in nature, featuring a heptadentate binding site for cerium as well as a hexadentate site capable of selectively binding mono- and divalent cations. Spectroscopic, structural, and electrochemical studies of the heterobimetallic complexes reveal significant effects driven by the secondary cations, an intriguing result considering the minimal expected metal-ligand covalency in this system. In particular, we have found that incorporation of the secondary cations engenders a positive shift in the Ce(IV/III) reduction potential of ca. 160 mV/pKa unit; to the best of our knowledge, this value represents the greatest tuning sensitivity (as judged by the average potential shift, reported in mV per pK_a unit) among all the known heterobimetallic complexes of the general type explored here. Our most recent work will be discussed, including efforts aimed at understanding the noted shifts in terms of the charges and/or ionic radii of the secondary metal ions, as well as the charge density effects resulting from their incorporation.

ACKNOWLEDGMENTS

The authors thank Victor Day (University of Kansas) & Allen Oliver (University of Notre Dame) for assistance with X-ray crystallography, Justin Douglas & Sarah Neuenswander (University of Kansas) for assistance with NMR spectroscopy, and Thaige Gompa & Henry La Pierre (Georgia Institute of Technology) for assistance with X-ray absorption spectroscopy. This work was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences through the Early Career Research Program (DE-SC0019169).

The versatility of the magnetic properties of the actinyl cations

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INTRODUCTION

In the $[AnO_2]^{n+}$ cations, the unpaired electrons lie in the nonbonding f_δ and f_φ orbitals. Their electronic structure depends strongly on the nature of the equatorial ligands, and as a consequence, their magnetic properties[1].

EXPERIMENTAL METHODS

The magnetic properties probed by paramagnetic NMR (pNMR) spectroscopy and SQUID magnetometry are modelled based on quantum chemistry calculations, including spin-orbit coupling (SO-CASPT2).

RESULTS AND DISCUSSION

pNMR measures the NMR chemical shift of paramagnetic complexes compared to their diamagnetic counterpart, the so-called Actinide Induced Shifts (AIS). This shift may be split into a *dipolar* term, arising from the magnetic dipolar interaction between the metal center and the NMR active nucleus, and a *contact* term, due to the spin delocalization leaking from the paramagnetic center towards the ligand[2]. On one hand, when the dipolar term is dominant, the AIS gives access to the magnetic susceptibility tensor. Further, the temperature dependence allows to determine the energy levels and magnetic parameters as exemplified by the $[AnO_2(DPA)_2]^{2-}$ complexes (cf Figure 1)[3]. We will show that in some cases, the AIS provides structural information, as it is the case in biological molecules[4].

On the other hand, when the contact term is dominant, the AIS allows an experimental determination of the spin densities of the ligands, and the hyperfine contact constants of the NMR active nuclei. This allows to access to the degree of covalency in the actinide – ligand bonding.

In lanthanide complexes, pNMR chemical shifts are efficiently modeled using crystal-field theory, but due to the larger covalent effects in actinide complexes, those models do not apply to actinide complexes. We will show how ab initio CAS based and DFT methods are complementary tools to the experimental data in order to unravel the dipolar and contact contributions.

The magnetic susceptibility tensor of the actinyl complexes is strongly anisotropic. When they are combined to an other magnetic center, the complexes may show a Single Magnet Molecule (SMM) behavior. In this case, the anisotropy of the monomeric species leads to an anisotropic exchange magnetic coupling. The case of a trimeric $[Mn^{II}\text{-}U^{V}\text{-}Mn^{II}]$ will be analyzed in details (cf Figure 2).

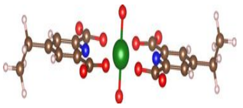

Fig. 1

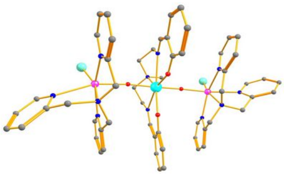

Fig. 2

CONCLUSIONS

The actinyl cations show a large variety of anisotropic magnetic properties, depending on the nature of the equatorial ligands. Probed by temperature dependent pNMR, one can access to the electronic structure of the metallic center and/or the spin delocalisation of the ligands. Associated to other magnetic centers, the local anisotropy of the actinyl cation imparts SMM behavior to the polymetallic structure.

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Magnetic frustration in J_{eff} = 1/2 Yb- and Ce-based triangular lattice antiferromagnets

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ABSTRACT:

Magnetic frustration is a generous source of phases of matter with unusual physical properties where magnetic order is dictated by the interdependence of local electronic states and their real-space interactions. These local states can compete to drive differing magnetic phases that range from typical collinear (anti)ferromagnets to more exotic highly-entangled ground states with emergent phenomena. Typically, these entangled phases are sought after in materials comprised of small spin 1/2 moments decorating lattice geometries inciting multiple equivalent interactions. These small moments can form from crystalline electric field interactions splitting a total angular momentum manifold of a Kramers' magnetic ion producing an effectively small J_{eff} = 1/2 moment at low temperature.

In this work, magnetic frustration and J_{eff} = 1/2 moments are studied in select members of the $ALnX_2$ family of materials (A = alkai; Ln = lanthanide; X = chalcogenide) with bulk magnetic measurements and neutron scattering. Triangular lattice antiferomagnet $NaYbO_2$ shows no signs of conventional magnetic order to 50 mK and a continuum of magnetic excitations consistent with a Dirac spin liquid [1]. Its magnetic ground state evolves under an external field into an equal moment up-up-down structure originating from the triangular lattice XXZ Hamiltonian [1-2]. On the other hand, triangular lattice $KCeO_2$ shows signatures of magnetic ordering below 300 mK, yet contains an unexplained additional crystalline electric field mode [3]. This extra mode reappears in the series of $RbCeX_2$ compounds, evolving with the change in crystalline electric field from X = O to X = Te. This anomalous mode is resolution limited, resides above the phonon background cutoff in $KCeO_2$ and $RbCeO_2$. One extra cryalline electric field mode is anomalous, and so far it has not been explainable via conventional phonon coupling, chemical disorder, or multiple Ce environments. Further investigations of this anomalous mode has begun in other trivalent Ce lattices of $CeLi_3Pn_2$ (Pn = Sb, Bi). Overall, our investigations establish triangular lattice antiferromagnets based on trivalent lanthanides host unconventional magnetic phenomena and are promising materials for researching exciting physics.

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Evolution of magnetic ground state in Yb-based heavy fermion compounds: effects of magnetic field and pressure

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A brief overview of our recent work on search for magnetic field– and pressure– induced quantum critical point / quantum phase transition will be given. After brief general introduction three different cases will be discussed: possible ferromagnetism and avoided quantum criticality in $\text{YbFe}_2\text{Zn}_{20}$ under pressure [1]; magnetic field - induced quantum critical point in antiferromagnetic YbPtBi as seen in bulk measurements and neutron scattering [2-4]; and complex amplitude-modulated magnetic ordering in the H – T phase diagram of frustrated YbAgGe [5].

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Exciting Developments in Lanthanide Photonics

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A wealth of practical applications rely on lanthanide photonics, with a peculiar characteristic, namely the fact that only minute amounts of lanthanides are required to lighten up a luminescent material. For instance, the screen of a smart phone contains 7 lanthanides, representing a total weight of 100-200 mg; an optical quartz fibre doped with less than 0.1% of erbium is an efficient amplifier for optical telecommunications; highly sensitive immunoassays use much less than 1 µg of luminescent lanthanide.[1] Yet the design of these materials has to include careful thoughts about efficient excitation in order to attain a workable brightness. The luminescence of trivalent lanthanide ions, Ln^{III}, features several key properties that make it ideally suited for lighting, displays, lasers, forensic and bio-applications: (i) narrow emission bands spanning a broad UV-to-NIR spectral range, which enables facile multi-plexing, (ii) large ligand-induced Stokes' shifts favorable to wavelength discrimination, (iii) long excited state lifetimes facilitating time-resolved measurements and leading to detection limits in the fM range, and (iv) sizeable photostability. The design of lanthanide-based luminescent materials has to include careful thoughts about efficient excitation and minimization of quenching processes in order to attain a workable brightness.[1]

This presentation first briefly review well-established applications of lanthanide luminescence, based on either inorganic phosphors or on chelates, that ruled the field in the 20th century. It then discusses present trends, including work by the author, with bias towards biosciences.

Lanthanide-based time-resolved immuno-assays were commercialized in the 1980s and are presently ubiquitous in bioanalysis. Time-resolved bioimaging started ten years later but had a slower development mainly because of the lack of adapted commercial microscopes. Both chelates and inorganic phosphors are used in these analyses, the latter often under the form of nanoparticles.

Since then, lanthanide photonics has progressively, but with increasing pace, moved towards more sophisticated materials. Indeed, the turn of the century has seen a revolution in the field by the introduction of nanophotonics[2,3] mostly based on up-converting and long persistent luminescent nanoparticles. In particular, the impact of nanomaterials has been a welcome rejuvenating factor opening vast perspectives[3] not only in biosciences but, also, in more conventional applications. For instance, the development of nanospectroscopy and single-particle detection are bringing optical imaging and photostimulated therapies closer to reality,[4,5] especially in view of the development of NIR-II optical probes.[6]

In addition, theoretical interpretation of spectroscopic data has also progressed significantly, and much hope is put in machine learning algorithms to unravel structure-properties relationship,[7] while more subtil ways of tuning lanthanide luminescence are being explored; for instance taking advantage of Zeeman splitting opens the way to magnetic tuning.[9]

Although already an old companion of scientists and engineers, lanthanide photonics is keeping surprising the community by its innovation ability. New aspects and applications continue to unfold and we can trust to see unexpected achievements in the future.

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Assembly of $[AnO_2X_4]^{2-}$ Anions with Assorted Organic Cations: Routes to ‘yl’ Engagement, Non-covalent Interactions and Photoreactivity

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INTRODUCTION

The synthesis and characterization of hybrid materials bearing actinyl ions is of considerable interest as a platform for probing assembly criteria, structural systematics and electronic structure. Insight herein may inform efforts in (for example) nuclear waste stewardship,[1] nuclear forensic analysis, and catalysis[3] as we continue to develop our understanding of structure-property relationships, particularly those involving second-sphere, non-covalent interactions (NCIs).

To this end, we have been successful in pairing $[AnO_2X_4]^{2-}$ anions (An = U, Np, Pu; X = Cl, Br) with a variety of organic cations including methylated pyridiniums and substituted viologens. Beyond charge balance, these species offer opportunities for second-sphere (NCIs) with the actinyl ions which may influence assembly, and in some cases, affect electronic structure. For the former, we have delineated criteria for selectively engaging the nominally terminal ‘yl’ oxo groups based largely on sterics and cation basicity. For the latter, interrogation of electronic structure may be realized through kinetic luminescence experiments where uranyl-viologen compounds exhibit luminescence quenching upon exposure to UV radiation.

EXPERIMENTAL METHODS

Two families of compounds have been prepared from room-temperature slow-evaporation of aqueous solutions of $[AnO_2X_4]^{2-}$ anions and organic cations. Crystalline products were characterized with single-crystal X-ray diffraction, solid-state UV-Vis, Raman and luminescence spectroscopy. Computational methods, specifically density functional theory-based natural bonding orbital (NBO) and quantum theory of atoms in molecules (QTAIM), were employed to probe the influence of assembly on the nature of An=O and An-X bonds. **Family 1:** Over 30 novel compounds featuring $[AnO_2X_4]^{2-}$ anions (An = U, Np, Pu; X = Cl, Br) paired with methyl substituted pyridinium cations; **Family 2:** Three novel compounds containing $[UO_2Cl_4]^{2-}$ units paired with methyl (MV), ethyl (EV), and propyl (PV) viologen dications.

RESULTS AND DISCUSSION

Family 1 may be subdivided into four categories based on H-bonding structural motifs: linear, bifurcated, oxo or none, and Raman spectra correlate as anticipated-stronger NCIs tend to stabilize An=O bonds. A detailed NBO treatment (including second-order perturbation theory (SOPT) and natural localized molecular orbital analysis is forthcoming.

Compounds in **Family 2** exhibit no substantive NCIs and instead may be distinguished by their distinct quenching of photoluminescence upon UV irradiation; kinetic analysis indicates a second order rate law. An atypical reaction mechanism is proposed to involve electron transfer *from* uranyl centers to the viologen cations to form stable radicals.

CONCLUSIONS

The structural diversity in **Family 1** may be rationalized via sterics and basicity of the organic cation, and influences on An=O bonding have been probed with Raman spectroscopy. Quantitative treatment of relevant bonding via computational methods is forthcoming. **Family 2** provides evidence for an atypical electron transfer mechanism in compounds without NCIs.

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Predicting the Coordination Structures and Thermodynamic Properties of Lanthanides in Solution

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INTRODUCTION

Lanthanide (Ln) separation techniques such as solvent extraction, froth flotation, or ion exchange, involve Ln^{3+} ions in solution. Solution structures are challenging to identify due to their disorderd nature. To predict coordination structures in solution, and thermodynamic properties of Ln-ligand complexes, it is necessary to consider the electronic structure due to reactions and dynamics to sample molecular conformations.[1]

METHODS

To predict Ln solution structures, ab initio molecular dynamics (AIMD) simulations were performed with density functional theory (DFT) in CP2K, which uses a mixed Gaussian and plane wave approach.[2] The PBE functional was used with D3 dispersion corrections using GTH-type pseudopotentials and polarizable double-zeta basis sets with additional plane wave basis set. All AIMD simulations included explicit solvent molecules, in periodic conditions, to simulate the solution phase. Analysis of simulation structures were done >10 ps of stable dynamics. To verify with experiment, FEFF[3] was used to predict EXAFS spectra from simulation and compare it with measured EXAFS.

For thermodynamic properties (acidity constants and binding energies), electronic structure calculations were perfomed with ORCA[4] using a relativistic Douglas–Kroll–Hess (DKH2) Hamiltonian, the M06 functional, segmented all-electron relativistically contracted (SARC) basis set for the Ln elements, and minimally augmented ma-def2-TZVPP basis set for other atoms.

RESULTS AND DISCUSSION

To benchmark the AIMD protocol with well known structures across the Ln series, the coordination structures of Ln^{3+} aqua ions were predicted with Ln-O bonds within 0.05 Å from experiment. EXAFS measurements were done to compare with predicted spectra and verify that the simulated Ln coordination structure matches experiment.

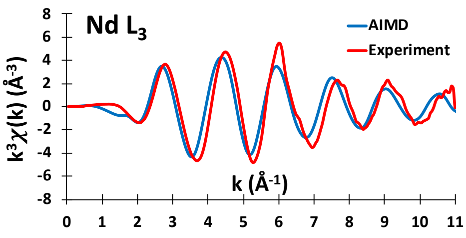

Figure 1. Predicted (blue) and measured (red) EXAFS of the Nd^{3+} aqua ion.

The same computational protocol was used to predict the structure of Ln complexes with EDTA, and verify if the computational approach can predict Ln-complex structure, including coordination number and number of coordinated water molecules.

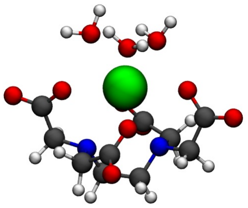

Figure 2. Predicted structure of Eu-EDTA

With the predicted structures, relative binding energies of Ln-ligand complexes were calculated and found to match experimental stability constants.[5]

Table 1. Relative binding energies

Ln-ligand	Relative free energies of binding (EXPERIMENT)	Relative binding energies (COMPUTATION)
La – HEDTA	0.14	0.12
La – EDTA	1 (reference)	1 (reference)
Eu – EDTA	1.12	1.22
Gd – EDTA	1.12	1.25
Lu – EDTA	1.28	1.40

CONCLUSIONS

The computational approach described here can predict the Ln coordination sphere for Ln^{3+} aqua ions[6] and Ln-ligand complexes[7]. Based on solution structures from simulation, electronic structure calculations can predict the acidity constants of Ln^{3+} aqua ions[8] and relative binding energes of Ln-ligand complexes[9] to replicate experimental trends. Contraction decreases the temperature-induced disorder of the Ln coordination sphere, for Ln-ligand, and Ln-solvent, complexes.[9,10]

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Spinor-Based Relativistic Coupled-Cluster Study of Lanthanide Thermochemistry and Spectroscopy

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INTRODUCTION

Relativistic and electron-correlation effects in the f-electrons of rare earth elements pose significant challenges for relativistic quantum mechanical calculations of rare earth atoms and molecules. In this study, we explore wave function-based electronic-structure methods with spin-orbit coupling included in orbitals, i.e., in the spinor representation, aiming at accurate calculations of thermochemistry and spectroscopy for rare earth atoms and molecules.

COMPUTATIONAL METHODS

Based on the exact two-component (X2C) theory,[1,2] we have developed an atomic mean field approach to enable efficient and accurate treatment of two-electron spin-orbit interactions, the X2CAMF scheme,[3] together with an implementation of spinor-based coupled-cluster (CC) methods with improved efficiency and enhanced capability to calculate molecular properties and explore potential energy surfaces.[4]

Here we present X2CAMF-CC calculations for ionization energies, electron affinities, and bond energies for lanthanide atoms and lanthanide-containing small molecules and compare the computational results with experimental measurements. Further, we report representative calculations for spectroscopy of lanthanide-containing small molecules including NdO$^-$,[5] YbF,[6] and YbOH in collaboration with experimental collaborators.

RESULTS AND DISCUSSION

Spinor-based relativistic CC calculations are demonstrated to provide promising results for a wide range of lanthanide-containing molecules, including many open-shell species. For example, as shown in Table 1, CC calculations have obtained accurate electron affinity for the NdO molecule containing three unpaired 4f electrons. We mention that the size extensivity of CC methods play an indispensable role in accurate calculations of thermochemistry parameters and spectroscopic constants.

The computational study of YbF and YbOH has provided results for the energy-level positions of low-lying excited states involving excitation of a Yb 4f electron into the Yb 6s orbital as well as the vibrational branching ratios from the $A^2\Pi_{1/2}$ state to these states. The computational predictions are being used to guide measurements for these electronic excited states in order to identify pathways for laser cooling of these molecules to enhance the sensitivity for the search of new physics Beyond Standard Model using precision spectroscopy on these molecules.

	MRCI+Q	CCSD(T)	Experiment
R_e(Å)	1.782	1.800	1.799
ω_e (cm^{-1})	878	835	834
EA (cm^{-1})	4239	8093	8139

Table 1. Molecular parameters of NdO including the electron affinity (EA) obtained from multireference configuration interaction (MRCI) and CC calculations.

CONCLUSIONS AND OUTLOOK

We demonstrate the usefulness of spinor-based relativistic coupled-cluster calculations for studying thermochemistry and spectroscopy of lanthanide-containing molecules. Interestingly, the transition to the spinor representation often reduces the size of active spaces required in calculations, e.g., the inclusion of spin-orbit coupling in orbitals and the use of complex-valued wave functions enable accurate calculations of the ground-state and low-lying excited states of many open-shell species using single-reference coupled-cluster methods. Perspective of extending these methodologies to large molecules is discussed.

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The study of YbF and YbOH pertinent to laser cooling and search for new physics has been supported by the National Science Foundation AMO physics program (Grant no: PHY-2011794).

Upconversion and Avalanching in Lanthanide-based Nanocrystals for Imaging

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Multiphoton imaging techniques that convert low energy excitation to higher energy emission are widely used to improve signal over background, reduce scatter in subsurface imaging, and limit sample photodamage. Multiphoton imaging relies on luminescent probes able to efficiently sum the energies of 2 or more incident photons, as well as lasers powerful enough for anti-Stokes excitation. Lanthanide-based upconverting nanoparticles (UCNPs) are phosphors that absorb multiple photons in the NIR and emit at higher energies in the NIR or visible, at efficiencies far greater than the best 2-photon fluorophores. We have shown that Yb/Er-doped $NaYF_4$ UCNPs offer complete resistance to photobleaching even under extended single-particle imaging,[1] they have no measurable NIR-excited emission overlap with fluorophores or cellular autofluorescence, and are excited at NIR wavelengths that are significantly less phototoxic to cells than visible wavelengths.[2] Using core/shell designs, we have developed antibody-sized, Yb/Er alloyed UCNPs (*aUCNPs*) that can be imaged at the single particle level at laser intensities less than 300 W/cm^2, ca. a billion-fold lower than required imaging of single organic fluorophores, and lower than many standard 1-photon fast-scanning confocal techniques.[3]

We have also recently reported the first nanoscale realization of photon avalanching in nanoscale materials with Tm^{3+}-doped UCNPs.[4] Avalanches are steeply nonlinear events in which outsized responses arise from a series of minute inputs and for optics, photon avalanching (PA) enables technologies such as optical phase-conjugate imaging, IR quantum counting, and efficient upconverted lasing. Previously, PA had been observed only in bulk materials and aggregates, often at cryogenic temperatures, preventing its application to imaging. Avalanching nanoparticles (ANPs) can be pumped by either continuous-wave or pulsed lasers and exhibit all of the defining features of PA, including a dominant excited-state absorption that is >10,000 times larger than ground-state absorption and a non-linear order of $s \geq 15$, where emission increases as the s power of pump intensity. Beyond the avalanching threshold, Tm^{3+}-doped ANP emission scales with up to the 31st power of pump intensity, an extreme nonlinearity caused by the induced positive optical feedback within each nanocrystal. $NaYF_4$ ANPs with 8-20% Tm^{3+}content can be excited at either 1064 or 1450 nm, with avalanching emission at 800 nm. We find that b-phase core/shell $NaYF_4$ UCNPs with core 8-10% Tm^{3+} content offer the steepest non-linearity, while >5-nm undoped $NaYF_4$ shells show the lowest thresholds. ANPs enable the experimental realization of sub-70 nm spatial resolution using only simple scanning confocal microscopy and before any computational data analysis. Single ANP characterization and modeling shows the shortest point of shell thickness controls avalanching threshold, while nonlinearity is determined largely by Tm^{3+}content.[5] Paired with superresolution techniques and computational methods, ANPs allow for imaging with higher localization accuracy and at ~100-fold lower excitation intensities than possible with other probes. The low PA thresholds, extreme non-linearities, and exceptional photostability of ANPs open up possibilities in diverse applications, including sub-wavelength imaging, high density data storage, and optical sensing.

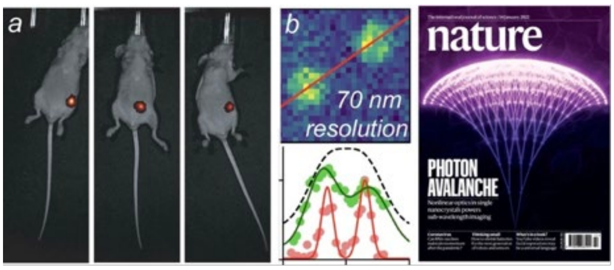

Fig 1a) Low-intensity, deep-tissue NIR imaging with Yb/Er aUCNPs.[3] b) Lowering the diffraction limit with Tm-doped photon avalanching nanoparticles.[4]

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Quantified and Correlated Covalent Metal-Ligand Bonding and Reactivity Differences in Isostructural Lanthanide and Uranium Phosphinodiboranates

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INTRODUCTION

One of the most critically debated questions in f-element science centers on how differences in covalent metal-ligand bonding with trivalent lanthanides and actinides manifest with respect to measurable differences in reactivity. As first proposed by Seaborg and coworkers,[1] suspected differences in covalent metal-bonding with 4f and 5f metals are often invoked when differences in extractant selectivity are observed in trivalent actinide/lanthanide separations. However, quantifying and correlating changes in both covalency and reactivity in trivalent lanthanide and actinide complexes remains a challenge, especially in ways that rule out competing variables that could also account for the observed differences.

Here we report the mechanochemical synthesis and structures of borohydride complexes called phosphinodiboranates with the formula $M_2(H_3BP^tBu_2BH_3)_6$ (M = U, La, Ce, Pr, Nd, and Sm). These complexes exist as dimers in the solid state, but deoligomerize to different extents when dissolved in organic solvents like benzene (Fig. 1). This allowed us to quantify how the identity of the metal ion influences the energy of deoligomerization in solution. The experimental results, which are corroborated by supporting DFT calculations, quantify how small, but significant differences in covalent metal-ligand bonding with U^{3+} correlate to measurable differences in solution deoligomerization reactivity.

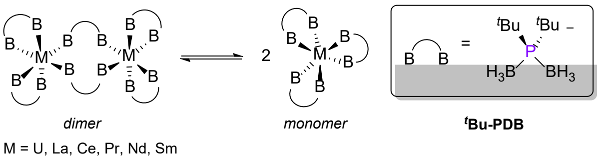

Fig. 1. Structures and deologinomerization reactivity of $M_2(H_3BP^tBu_2BH_3)_6$ when dissolved in benzene.

RESULTS AND DISCUSSION

$M_2(H_3BP^tBu_2BH_3)_6$ complexes were prepared by grinding LnI_3 or $UI_3(THF)_4$ with three equiv. of $K(H_3BP^tBu_2BH_3)$, as described previously.[2] Single-crystal XRD studies and comparison of the bridging M-B bond distances that hold the dimeric complexes together revealed that the U-B distances were ca. 0.04 Å shorter than expected when compared to the Ln-B distances with similar-sized lanthanides (Fig. 2). Consistent with this structural hallmark of increased metal-ligand covalency with uranium, variable-temperature NMR studies and van't Hoff analysis of the $M_2(H_3BP^tBu_2BH_3)_6$ complexes in benzene revealed a small, but measurable increase in the ΔH° of deoligomerization (1.0 kcal/mol) that correlates to the increased metal-ligand covalency when M = U. These experimental data are supported by DFT calculations that also reveal a unique increase in the enthalpy of deoligomerization for the actinide (M = U^{3+}) compared to lanthanides.

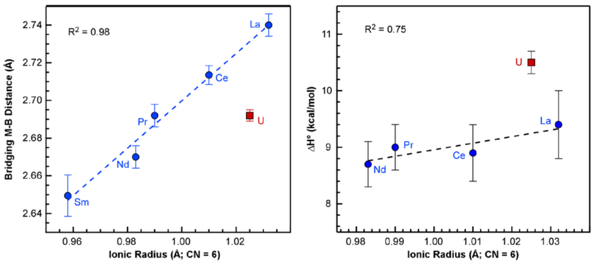

Fig. 2. *Left* - Plot of average bridging M-B distances from single-crystal XRD data for $M_2(H_3BP^tBu_2BH_3)_6$ vs. metal ionic radii. *Right* - Experimental ΔH° values for the deoligomerization of $M_2(H_3BP^tBu_2BH_3)_6$ complexes plotted vs. metal ionic radii.

CONCLUSIONS

The results strongly suggest that differences in solution deoligomerization reactivity for $M_2(H_3BP^tBu_2BH_3)_6$ can be ascribed to differences in metal-ligand covalency when M = U vs. M = lanthanide. This experimental evidence supports a longstanding, but difficult-to-test hypothesis about the measured effect of variation in metal-ligand covalency on the reactivity of isostructural trivalent actinide and lanthanide complexes.

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Accelerated Discovery of New Rare-earth Compounds by Machine Learning

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Materials discovery can take place through multiple pathways, e.g. experimental synthesis, density-functional theory (DFT) methods, and machine learning (ML) prediction. Each approach has its advantages and disadvantages: experimental research is time and resource consuming but gives definitive results, DFT requires existing structural details but is faster than experiments, and ML requires large datasets and can be unreliable at times but it enables the assessment of a large material space in a short amount of time. In light of this, recent works have incorporated two, or even all, of these methods into an "assembly line" (ML » DFT » experimental verification) utilizing their strengths and minimizing their weaknesses. However, most systematic studies neglect rare-earth compounds due to added complexity in treating 4f electrons [1].

In this work, we employ all three aforementioned methods to accelerate the discovery of new rare-earth based compounds. We utilize an in-house Ames Laboratory database with miscellaneous R-X compositions (R = rare earth, X = non-rare-earth) such as R_2X, RX, RX_2, RX_3, RX_5, and R_5X_3 to train and test ML models, gauge their outcomes against DFT results, and experimentally verify selected compounds. Furthermore, we developed a method to filter the structure of non-stoichiometric compounds such as disordered $Ce(Fe, Cu)_2$, which has $MgCu_2$-type $CeCu_2$ and KHg_2-type $CeFe_2$ parents [2]. Positive and negative results are reincorporated back into the database, creating a feedback loop and improving ML interpolation.

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Multifunctional Lanthanide Metallocenes: From High-Performance Single-Molecule Magnets to Small Molecule Activation

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Molecules that possess an energy barrier to spin inversion have intriguing potential applications in areas such as magnetic refrigeration, molecular spintronics and high-density information storage. For these applications, however, key performance characteristics such as large spin-relaxation barriers (U_{eff}) and high magnetic blocking temperatures (T_{B}) are required. Lanthanides have been proven to be particularly well-suited for the design of single-molecule magnets owing to their large magnetic moments and magnetic anisotropy that stem from strong spin-orbit coupling of the 4f orbitals. By using lanthanide ions such as Tb^{3+}, Dy^{3+}, and Er^{3+} which possess intrinsically large orbital angular momentum, significantly higher U_{eff} and T_{B} can be achieved. A general methodology to improve T_{B} in multinuclear single-molecule magnets is to generate strong magnetic exchange between lanthanide centers through the employment of radical bridging ligands with diffuse spin orbitals. Another successful approach to strong coupling targets the use of heavy p-block elements since their diffuse valence orbitals facilitate better penetration of the core electron density of the lanthanide ions relative to diamagnetic ligands comprising lighter p-block elements. Here, we will present the synthesis of multiple lanthanide single-molecule magnets that contain radical ligands and bismuth clusters, respectively. The latter class of compounds were synthesized through a solution organometallic approach and represent the first single-molecule magnets containing bismuth donors which lead to new prospects in synthetic chemistry and physics, Figure 1[1].

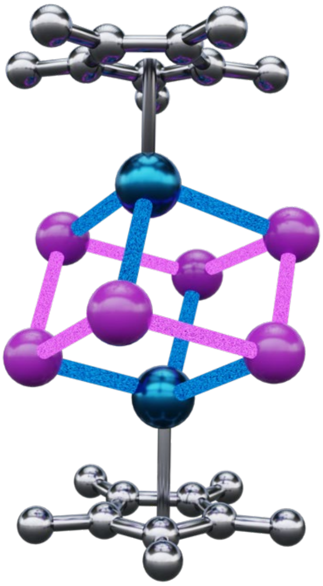

Figure 1. Structure of the $[\mathrm{Cp}^*{}_2\mathrm{Ln}_2\mathrm{Bi}_6]^{2-}$ dianion in a crystal of $[\mathrm{K(THF)}_4]_2[\mathrm{Cp}^*{}_2\mathrm{Ln}_2\mathrm{Bi}_6]$.
Blue, purple, and gray spheres represent Ln, Bi, and C atoms, respectively.

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Recent Advances in the Synthesis of Complexes of the Rare-Earth Metals in the +2 Oxidation State

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The reductive chemistry of the rare-earth metals was transformed by the discovery that the +2 oxidation state was available in crystallographically-characterizable molecular complexes not only for Eu, Yb, Sm, Tm, Dy, and Nd, but for *all* the rare-earth metals (except radioactive Pm).[1,2] The new +2 ions were discovered in the tris(silyl-cyclopentadienyl) complexes, $(Cp'_3Ln)^{1-}$ and $(Cp''_3Ln)^{1-}$, where Cp' = $C_5H_4SiMe_3$ and Cp" = $C_5H_3(SiMe_3)_2$. In these trigonal ligand fields, reduction of $4f^n$ Cp'_3Ln and Cp''_3Ln Ln(III) precursors of La, Ce, Pr, Gd, Tb, Ho, Er, and Lu form $4f^n5d^1$ Ln(II) products rather than the traditional $4f^{n+1}$ Ln(II) ions previously found for Eu, Yb, Sm, Tm, Dy, and Nd. The $(Cp'_3Nd)^{1-}$ and $(Cp'_3Dy)^{1-}$ complexes were found to contain $4f^35d^1$ and $4f^95d^1$ ions, respectively, and these Ln(II) ions were called configurational crossover ions because they have different ground state electron configurations depending on the ligand environment. Since the synthesis of these $4f^n5d^1$ tris(silylcyclopentadienyl) complexes, several new ligand environments have been found to support the new $4f^n5f^1$ ions. As more complexes are obtained, patterns are starting to emerge regarding the factors that contribute to the synthesis and isolation of the new +2 ions as well as their reactivity. The latest results on the chemistry of this class of complexes will be presented along with a discussion of collaborative EPR studies that suggest applications of the new ions as qubits.

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Rare Earth Metal Catalysts for the One-Pot Block Copolymerization of Olefins and Cyclic Esters

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INTRODUCTION

Well-defined block copolymers of olefins and polar monomers, such as acrylates, have led to materials with advanced physical properties[1]. Cationic alkyl rare earth metal catalysts, activated by organoborates, are promising for the polymerization of isoprene or styrene and ε-caprolactone, suggesting that cyclic ester derived polyesters could be a more degradable replacement for polyacrylates[2-4]. These polyolefin/polyester block copolymers could exhibit adhesive and dye adsorption properties similar to polyacrylate, while also providing a practical route to partial degradation or recycling. We have identified rare earth metal bis(alkyl) complexes supported by simple β-diketiminate or pincer ligand systems, that can seamlessly catalyze the block copolymerization of six or more pairs of olefins and cyclic esters (five of which are new block copolymers) with excellent molecular weight control.

EXPERIMENTAL METHODS (if relevant)

Polymerization Methods. In a glovebox, catalyst (10 μmol, 200 μL of a 0.5 M stock solution) was placed in a stir bar charged 20 mL vial and diluted in toluene (7 mL). Trityl (tetrakis(pentafluorophenyl)borate [Ph$_3$C][B(C$_6$F$_5$)$_4$] (10 μmol, 1 mL of a 0.01 M stock solution) was add to the vial and reaction was stirred for 10 min. Olefin (300-800 equiv.) was added by micro syringe in one portion, and the polymerization was carried out for the designated time with constant stirring during which the reaction turned from orange to gold. Then cyclic ester (300-800 equiv.) was added by micro syringe to the above system and polymerization was continued for the designated time. The gel like reaction mixture was poured into a large quantity of ethanol (100 mL) to give colorless copolymer that was dried in a vacuum oven at 40 ºC for 12 h to a constant weight.

RESULTS AND DISCUSSION

Subtle changes to the ligand structures were found to have a large impact on polymerization rate and control for one or both monomers. In particular, addition of a stronger donor to the ancillary ligand led to faster polymerization of ε-caprolactone, but slower polymerization of isoprene. Alternatively, a weak field donor led to the opposite impact, having faster polymerization for isoprene, but slower polymerization of ε-caprolactone. These results indicate that a catalyst needs to be suitably matched to both monomers, not just one.

Additionally, activation conditions to convert the dialkyl metal complex to a cationic monoalkyl complex could be manipulated to adjust the molecular weight of the copolymers. This allowed for a catalyst efficiency to be optimized to 96 %.

In addition, selective degradation of the ester block in poly(isoprene-*b*-caprolactone) enabled recovery of the polyisoprene block with identical spectroscopic and thermal properties (**Figure 1**). Significantly, recopolymerization of the recovered polyolefin with fresh ε-caprolactone reproduced the desired diblocks with nearly identical thermal and physical properties to those of virgin copolymer, illustrating a plausible recycling scheme for these materials.

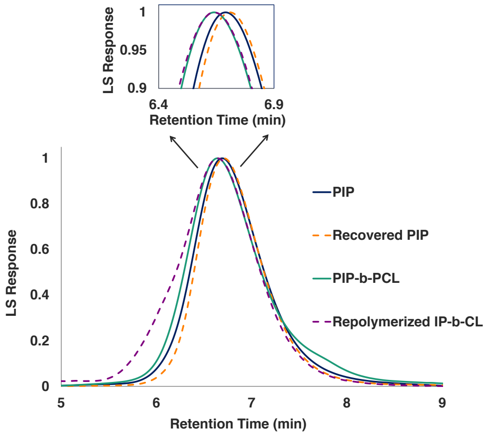

Figure 1. GPC traces of PIP (M$_n$=42 kDa, Đ=1.15), recovered PIP (M$_n$=43 kDa, Đ=1.15) and PIP-*b*-PCL (M$_n$=55 kDa, Đ=1.09). repolymerized PIP-*b*-PCL (M$_n$= 56 kDa, Đ=1.16

CONCLUSIONS

Rare earth metal complexes have been varied to identify proper design principles to optimize the block copolymerization of olefins and cyclic esters with fast rates, high polymerization control, and high catalyst efficiency. The resulting polyester block can be selectively degrded and repolymerized to identify a reasonable recycling path.

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Magnetism and anomalous Hall effect in the kagome-net magnets RMn_6Sn_6 (R = Y, Tb)

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An increasingly popular class of materials to investigate the interplay of topological magnetic and electronic properties are the kagome-net magnets[1]. In a purely two dimensional (2D) construct a kagome geometry in the tight-binding model is well known to lend itself to the formation of Dirac cones and flat bands in the electronic structure. The inclusion of spin-orbit coupling (SOC) and time reversal breaking in such a system has the effect of spin-splitting the spin-degenerate Dirac bands leading to gapped phases that can manifest exotic properties such as quantized anomalous Hall effect. More recently, such an effect has been found relevant even in 3D systems. However, the applicability of the purely 2D model scaled to a 3D system, is less understood and a thorough study is still lacking.

RMn_6Sn_6 compounds (R = a rare earth element) are the latest addition to 3D systems with the kagome-net of magnetic elements[2], where the Mn atoms form the kagome net in the basal plane of the hexagonal lattice. More interestingly, these compounds form a wide variety of magnetic structures due to various competing energy scales including the inter-layer nearest and next-nearest exchange interactions that can be tuned with external perturbations such as magnetic field, and doping. Additionally, these compounds exhibit large anomalous Hall conductivity (AHC) in the ferro (or ferri) magnetic phase.

In this talk I will discuss on the magnetic structure of two compounds YMn_6Sn_6 and $TbMn_6Sn_6$. The former forms a series of competing magnetic phases[2,3,4] including a distorted spiral, a transverse conical spiral, and a fan-like phase before polarizing to a forced ferromagnetic state for the in-plane magnetic field. The latter one orders fermimagnetically formed by ferromagnetic Mn spins arranged antiferromagnetically with the Tb spins at about 423 K. With the decrease in temperature an interesting spin-reorientaiton transition occurs at 310 K whereby both the Tb and Mn moments move together towards c-axis mantianing their ferrimagnetic ordering. I will then present the anomalous Hall (AHE) in the ferro(ferri)magnetic state of these compounds and show that the AHE in these compounds comes from multiples points in the Brilliouin zone rather than the kagome-derived Dirac points[5,6]. Our results show that while these materials have interesting magnetic and electronic structures, and unusual magnetotransport behavior, the AHE primarily comes from the 3D bands rather than the 2D kagome-derived bands.

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Illuminating the Photophysics of Oxygen Atom Transfer in Rare Earth Metal-Organic Complexes

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INTRODUCTION

Industrial separations of rare earth metals are reliant on selectivity based on ionic radii, which are time, energy, and resource consuming.[1] The unique and discontinuous manifold of energy states associated with the *f*-electron configurations of the rare earth ions[2] offer an opportunity to overcome some of these limitations by incorporating light into the separation process. Here, we use transient absorption spectroscopy to understand the differences in mechanism of light-initiated oxygen atom transfer (OAT) in yttrium (Y) and dysprosium (Dy) rare earth complexes. These metal-organic complexes are functionalized with hexfluoroacetylacetonate (hfac) and 4-methylmorpholine-*N*-oxide (NMMO). After light absorption in the presence of triphenyl phosphine (TPP), the NMMO in the Y-NMMO complex is replaced by the TPPO OAT reaction product. Because the Dy *f*-electron manifold is accessible to the ligand excited states, while there are no accessible states associated with *f*-electrons for Y, there are significant differences in reactivity.

EXPERIMENTAL METHODS

Transient absorption spectroscopy (TAS) was used to monitor changes after 340 nm photoexcitation of Dy/Y-NMMO or the product complex Dy/Y-TPPO. TAS is a pump-probe technique where a white light probe pulse is delayed relative to a visible pump pulse, which photoexcites a sample. Differences between the ground and excited states are monitored over time. With TAS, we access time scales from 100 fs-400 µs to determine the photophysics of the complexes of interest.

RESULTS AND DISCUSSION

Photoexcitation of Y-NMMO (**Fig. 1A**) creates a broad photoinduced absorption (PIA) that evolves into a sharp positive feature over 4.2 ps centered at 450 nm. A secondary feature centered at 550 nm grows in with a 200 ps time constant and remains through the 5 ns time window of our experiment. Control experiments for Y-TPPO reveal that the feature at 450 nm is due to internal dynamics of the hfac ligand, while the 550 nm shoulder is due to the presence of the NMMO. Comparing kinetics at 550 nm for Y-NMMO and Dy-NMMO (**Fig. 1B**) shows that while Y exhibits a distinct growth in the NMMO feature, the Dy decays almost completely within 5 ns. Control experiments with Dy-TPPO prove that the ligand excited states centered on the hfac ligand are deactivated via energy transfer to the Dy manifold within 200 ps. This deactivation leads to significant differences in OAT reactivity between Y and Dy.

CONCLUSIONS

TAS reveals the origin for the observed reactivity differences in OAT between Y and Dy complexes, showing the promise for incorporation of light into industrial separation processes based on kinetic control.

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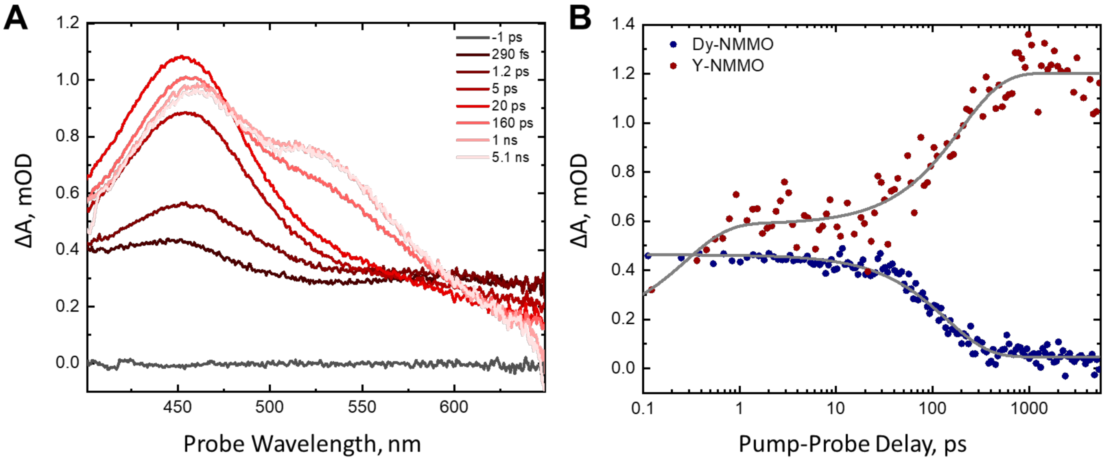

Figure 1. A. TAS of Y-NMMO at 340 nm (100 nJ) photoexcitation. **B**. Kinetics of Y-NMMO (red) and Dy-NMMO (blue) at 550 nm.

Transuranium Metallocene Complexes

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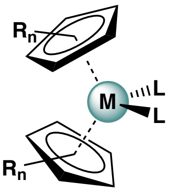
Cyclopentadienide (C_5H_5, Cp) complexes are known for almost every metal in the periodic table. The linear *bis*-Cp sandwich structure exemplified by ferrocene, $[Fe(Cp)_2]$, dominates for the lighter main group and transition metals, while the *tris*-Cp $[M(Cp)_3]$ motif is ubiquitous for the lanthanide (Ln) and actinide (An) elements due to their large ionic radii. As such, bulky kinetically stabilizing Cp derivatives, Cp^R, are often used instead.

The kinetic inertness, electronic stabilizing effects, and high crystallinity of Cp^R ligands has allowed the synthesis of *tris*-Cp $[An^{III}(Cp^R)_3]$ complexes (**I-An**, An = U, Np, Pu), which were readily reduced to formal An^{II} complexes;[1] and also to isolate and structurally characterize the first M–C bonding with highly radioactive isotopes ^{243}Am and ^{249}Cf in $[Am(C_5Me_4H)_3]$ and $[Cf(C_5Me_4H)_2Cl_2K(OEt_2)]_n$ (**II**) – both representing the first structurally authenticated examples of organometallic complexes with these elements.[2,3]



M^{3+} = Ln, An

Figure 1. General molecular representation of f-element bent metallocenes.

Whilst the shielding provided by three Cp^R ligands is often desireable, as in **I-An** above, it produces usually gives coordinatively-saturated complexes with few opportunities for reactivity/bonding studies beyond those of the M–Cp interaction itself, or axial coordination of small molecules. The wedge-shaped $\{M(Cp^R)_2\}^{n+}$ moiety of *bis*-Cp^R complexes (Figure 1), like **II**, is a robust backbone for supporting diverse metal–element (e.g., =N(R), =P(R), =O, ≡N) interactions.[4] Despite its ubiquity with Th and U, only a handful of bent metallocenes have been structurally authenticated for transuranium elements including **I**, and more recently $[An(C_5Me_5)_2(I)(THF)]$ (An = Np, Pu).[5]

Here we describe the synthesis of trivalent bent metallocene complexes for some of the transuranium elements and show that, much like seminal advances in Th/U chemistry and electronic structure afforded by this motif,[6] the binding of co-ligands to transuranium bent metallocenes has revealed unexpected insights in f-block periodicity and bonding patterns.[7] Characterization efforts include X-ray diffraction, UV-vis-NIR spectroscopy, and multi-nuclear NMR spectroscopy. Advancements in the synthesis of anhydrous halide precursors across the transuranium series was required, and together these results will expand the chemists' toolkit into an area of the periodic table where advancement in organometallic chemistry has been slow.

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The flowers along the way: Anticipated and unprecedented results on the path to rare-earth metal molybdates and tungstates with luminescent properties.

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Introduction

Rare-earth metal molybdates and tungstates have proven to be suitable candidates for luminescence applications due to the usability of their ligand-to-metal charge transfer as "inorganic antenna" for harvesting UV or blue light and its subsequent transfer to an active center. Different to most studies, which focus on "pure" rare-earth metal molybdates and tungstates, this work highlights a multi-anionic approach comprising complex refractory metalates and monoatomic halides.

Fluoride derivatives

Fluoride derivatives of rare-earth metal molybdates with the composition $Ln\mathrm{F[MoO_4]}$ are achieved either by solvochemical synthesis (for Ln = Ce − Nd)[1] or via flux assisted solid-state methods (for Ln = Y, Sm − Tm)[2] with $\mathrm{MoO_3}$ functioning as both, reactant and fluxing agent. With the latter method it is also possible to obtain condensed molybdate entities as seen in compounds of the formula $Ln\mathrm{FMo_2O_7}$ (Ln = Y, Eu − Yb)[3]. Extending the molybdate group is accompanied by a shift within the O→Mo CT from $\mathrm{YF[MoO_4]{:}Eu^{3+}}$ (288 nm) towards a maximum of the CT band at lower energies in $\mathrm{YFMo_2O_7{:}Eu^{3+}}$ (331 nm). Unfortunately, these facile synthesis techniques do not work with the analogous tungstates. Especially the solid-state synthesis proves challenging, due to the high melting points of the reactants. While experimenting with a variety of fluxing agents, several attempts were performed with AgF. Although, the desired representatives of $Ln\mathrm{F[WO_4]}$ were not obtained, several silver derivatives with the composition $\mathrm{Ag}Ln\mathrm{W_2O_8}$ (Ln = Gd, Ho, Er, Yb) were yielded (see Fig. 1), which crystallize in space group $C2/m$ and comprise $\mathrm{[W_4O_{16}]^{8-}}$ polytungstate units besides twofold coordinated $\mathrm{Ag^+}$ cations and square $[Ln\mathrm{O_8}]^{13-}$ antiprisms.

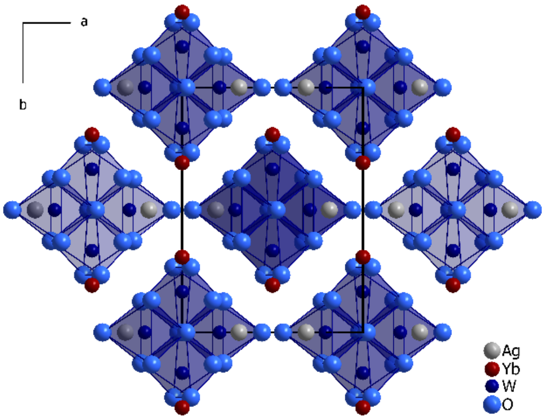

Fig. 1: View at the crystal structure of $\mathrm{AgYbW_2O_8}$ along [001].

Chloride derivatives

While the harder fluoride anion as part of the host lattice for a luminescent material is usually preferred to the softer chloride anion, there are some impressive successes to be reported comprising the latter halide. Representatives of the composition $Ln_3\mathrm{Cl_3[WO_6]}$ not only contain trigonal prismatic $\mathrm{[WO_6]^{6-}}$ entities but also decacoordinated Ln^{3+} cations. Remarkably their realm of existence comprises the range from Ln = La −Nd and Sm − Tb, if emerging from reactions under ambient conditions and Ln = Dy, Er from high pressure syntheses (among other by-products).[4] Attempts to synthesize derivatives with the smaller Ln^{3+} cations Y and Dy − Lu utilizing LiCl as flux, resulted in black crystalline materials of the composition $\mathrm{Li}_{1-x}Ln_{5+x}\mathrm{W_8O_{32}}$. Substituting tungsten for molybdenum resulted in the $Ln_3\mathrm{Cl_3[MoO_6]}$ mini-series, which is isotypical to the aforementioned tungstates, however exhibit O→Mo CT transfer bands in the visible region of the electromagnetic spectrum, so that luminescence of activator-doped materials can be excited by a blue LED (see Fig. 2).[5]

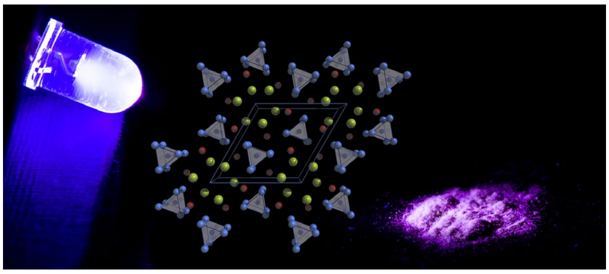

Fig. 2: Luminescence of $\mathrm{La_3Cl_3[MoO_6]{:}Eu^{3+}}$ (crystal structure seen in the middle) upon excitation with a blue LED.

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Rare Earth Molecular Clock Qubits

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The fundamental building-block of a quantum device is the physical quantum bit, or qubit, which can be any two-state quantum system. Many promising qubit candidates are currently under intense investigation, including superconducting circuits, trapped ions, photons, topological states in condensed matter, as well as electron and nuclear spins in solids or on surfaces. However, continued scale-up remains challenging. For this reason, research focusing on next-generation quantum technologies is highly active.

The spin degree of freedom associated with unpaired electrons represents one of the simplest quantum systems that can be manipulated relatively easily using decades-old and well understood magnetic resonance techniques. Nature provides a rich, albeit finite variety of spin states in atoms and ions. By comparison, coordination chemistry affords almost limitless tunability of the quantum states associated with unpaired electron spins in molecules, whilst also offering routes to large scale assembly via supramolecular approaches[1]. However, this flexibility comes at a cost in terms of coherence due to the inherent coupling to magnetic and vibrational noise associated with the environment[1,2].

This presentation will focus on recent synthetic efforts aimed at protecting rare earth molecular spins from various environmental decoherence sources, with emphasis on the so-called clock transitions – avoided level crossings associated with the Zeeman splitting of qubit states[3]. Named after the principle that gives atomic clocks their exceptional temporal stability, spin clock transitions provide an optimal operating point at which the resonance frequency, f, becomes insensitive to the local magnetic field, B_0, i.e., $df/dB_0 = 0$. In this way, a molecular clock qubit is immune to magnetic noise[4]. There are several synthetic strategies for generating molecular clock transitions. All that is needed is an interaction term in the spin Hamiltonian that does not commute with the Zeeman interaction. For molecules containing rare earth ions with integer total spin (even number of unpaired electrons), the crystal field interaction can do the job. Crucially, such clock transitions can be tuned through manipulation of the coordination environment around the metal center. In the first molecular example, a crystal-field clock transition was demonstrated for a $\mathrm{Ho^{III}}$ ion ($[\mathrm{Xe}]4f^{10}$ electronic configuration) encapsulated within a polyoxometalate moiety, resulting in a significant enhancement in spin coherence for a crystal rich in fluctuating electron and nuclear spins[5].

An alternative strategy that works for rare earth ions possessing half-integer spin states (odd number of unpaired electrons) involves the electron-nuclear hyperfine interaction, a strategy that is employed widely in trapped-ion quantum devices. Crucially, in the molecular case, the hyperfine interaction can again be controlled using coordination chemistry to maximize unpaired electron spin density at the relevant nuclear site. A recent example involving a $\mathrm{Lu^{II}}$ ($[\mathrm{Xe}]4f^{14}5d^{1}$) organometallic compound has demonstrated that this is possible by varying the degree of s-orbital mixing into the spin-bearing d-orbital[6]. This approach has the added advantage of increasing the s-orbital character, which also reduces spin-orbit coupling that, in turn, suppresses spin-lattice relaxation – one of the other stubborn decoherence mechanisms in molecular spin qubits.

The presentation will begin with an introduction to spin qubits, decoherence and electron spin resonance, along with the principles via which clock transitions protect rare earth molecular qubits against magnetic noise. This will be followed by a survey of the synthetic strategies that have been employed up to now for developing molecular rare earth clock qubits, together with the spectroscopic studies that demonstrate their enhanced coherence properties. The talk will conclude with an outline of potential implementations of molecular clock qubits in future quantum technologies.

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Bright Triboluminescence of An Inefficient Photoluminescent Eu(III) Complex

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INTRODUCTION

Triboluminescence (TL) refers to the fracture-induced luminescence without any light source, which is observed only at the moment of applying force. Despite its long history and versatility, TL has not been elucidated in terms of the general molecular designs and the underlying photophysical processes.

Strong TL has been reported for various lanthanide(III) complexes with dibenzoylmethide, thenoyl-trifluoroacetylacetonate, hexafluoroacetylacetonate and so on which also show strong photoluminescence (PL).[1] Since the absorption coefficients of lanthanide(III) ions are intrinsically small, organic chromophores are necessary to achieve visibly strong PL.[2] Thus, the photosensitization process (antenna effect) has been accepted as a general explanation for the bright lanthanide(III) TL.[3] On the other hand, we reported that the lanthanide(III) TL does not always follow the principles of PL by demonstrating the clear TL/PL color differences in Tb(III)/Eu(III)-mixed coordination polymers.[4] Therefore, exploring the TL/PL difference would lead to the theoretical breakthrough and to the development of a new class of mechanophores.

In this study, we attempted to design a TL-active but PL-inert lanthanide(III) complex. Based on the previously proposed "f-f priority rule",[4] we focused on three conditions: 1) inefficient antenna effect, 2) low coordination symmetry and 3) high mechanical sensitivity. In order to eliminate the antenna effect (condition 1), a combination of Eu(III) ions and 2,2,6,6-tetramethylheptane-3,5-dione (tmh) ligands was selected. The ligand-to-metal charge transfer states of Eu(III)-tmh systems quench the Eu(III)-centered emission through state transition, resulting in low PL quantum yields (~ 1%); while, low-symmetrical seven-coordinated structures induced by bulky tmh ligands can elevate f-f transition probability (condition 2).[5,6] As Clegg *et al.* reported the TL of Ln(tmh)$_3$(DMAP) (Ln = Tb or Sm, DMAP: 4-dimethylaminopyridine),[7] lanthanide(III)-tmh systems also have potential to gain the mechanical sensitivity (condition 3).

RESULTS AND DISCUSSION

Single crystal X-ray analysis of the target lanthanide(III) complex revealed a dinuclear structure composed of two lanthanide(III) ions (lanthanide(III) = Tb(III) and/or Eu(III)), six tmh ligands and a fluorene-based bridging ligand. Bright TL was obaserved for both complexes despite their significant difference in PL quantum yields (> 50 times, Figure 1), and a heterodinuclear Tb(III)/Eu(III) complex showed TL/PL color difference. Mechanical flexibility of the crystals was also indicated by nanomechanical tests, which is ideal to accumulate the large deformation energy.

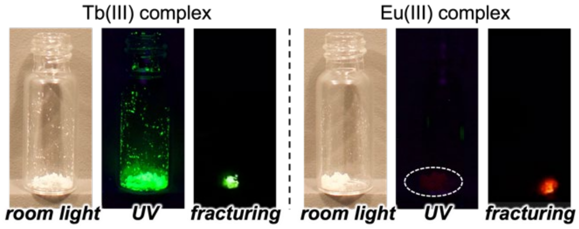

Figure 1. Pictures of Tb(III) and Eu(III) complexes left) under room light, center) UV and right) fracturing.

CONCLUSIONS

We prepared dinuclear lanthanide(III) complexes with bulky β-diketonate and rigid bridging ligands and demonstrated that bright TL can be generated even when the PL quantum yield is negligibly small. It directly suggested the existence of distinct excitation mechanisms of TL and PL. Nanomechanical tests also indicated that the characteristic deformation property of the crystals provided the mechanical sensitivity. The presented strategy for lanthanide(III) mechanophores would trigger the new generation of mechanically-sensitive luminescent materials

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Computational Adventures in Molecular F element Chemistry – Two Short Stories

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At RERC in 2017 I discussed the coordination of He atoms to Ac^{3+}, and unveiled $AcHe_{17}^{3+}$, at the time the compound with the highest known coordination number.[1] In the first part of my RERC29 presentation I shall discuss our further work in this area,[2] using density functional and wavefunction theory methods, and ab initio molecular dynamics calculations. I will show that the highest coordination number is actually 18: in $AcHe_{18}^{3+}$, all of the He atoms are accommodated in the primary coordination shell, and this record coordination number also holds for Th^{4+} and Th^{3+}. For Pa and U in their group valences, the largest number of coordinated He atoms is 17. For $AnHe_{17}^{q+}$ (An = Ac, $q = 3$; An = Th, $q = 4$; An = Pa, $q = 5$; An = U, $q = 6$), the average An-He binding energy increases significantly across the series, and correlates linearly with the extent of He to An^{q+} charge transfer. Quantum Theory of Atoms-in-Molecules (QTAIM) metrics indicate that covalency increases from $AcHe_{17}^{3+}$ to UHe_{17}^{6+}. The most stable complexes of Ac^{3+} with the heavier noble gases (Ng) Ar–Xe are 12 coordinate, best described as Ng_{12} cages encapsulating an Ac^{3+} ion. There is enhanced Ng to Ac^{3+} charge transfer as the Ng gets heavier, and Ac-Ng covalency increases.

Bursten's "FEUDAL" (Fs Essentially Unaffected Ds Accommodate Ligands) model for the bonding in early actinide compounds implies that the f orbitals have little role in directing geometric structure. In the second part of my presentation I shall discuss an unusual situation in which this is not the case, and describe our study of Ce(IV), Th(IV) and U(IV) carbene, imido and oxo complexes supported by a model for the $BIPM^{TMS}$ ligand.[3] Electrostatic potential surfaces, Natural Localised Molecular Orbitals and QTAIM metrics are all analysed to understand the electronic and geometric structures. In all 9 target systems, the electrostatic potential around the metal ion is *cis*-directing, but for the Ce and U oxo complexes, "anti-FEUDAL" f orbital involvement in the metal-oxo sigma bonding orbital overcomes the electrostatic potential, resulting in *trans* geometries.

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Bioinspired Polymers for Ion Separations

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The selective binding profiles of proteins are currently unparalleled by synthetic macromolecules, yet synthetic materials offer a number of advantages including comparatively unrestrained chemical diversity and scalability. While methods for diversifying the toolbox of synthetic materials have expanded in the last couple of decades, rational design of these materials for target applications remains challenging with limited established structure-function relationships.

Despite the traditional “lock and key” paradigm of protein binding that implies a crystalline structure is required for selectivity and affinity, research in both protein and polymer chemistry has illustrated that less rigid macromolecules can have tailored properties as well. For example, the protein landmodulin has evolved to bind rare earth ions with over 100 million-fold selectivity over calcium, but undergoes a conformational change upon binding.[1–3] Both rational design[4–7] and molecular imprinting[8] – polymer synthesis in the presence of a template – have illustrated the potential for macromolecules with limited intramolecular interactions and crystallinity to bind target molecules.

Motivated by these findings, we hypothesize that polymeric materials are uniquely positioned to tackle the challenge of rare-earth metal separations. However, these materials can be readily synthesized with a wide range of functional groups and architectures yielding innumerable possibilities for polymer design. To rapidly target the identification of structure-function relationships and guide the rational design of separations materials, we have designed a workflow to strategically screen for rare earth ion affinity across a broad design space of polymer composition and architecture. Variables for the design space are guided by principles of protein-binding, including 1) the selection of carboxylic acids, the predominant coordinating moiety in lanmodulin, and other amino acid mimetic functional groups as pendent moieties and 2) the incorporation of entropic constraints to decrease the energetic cost of binding.

Using a design of experiments workflow, modular polymer scaffolds, and analysis with isothermal titration calorimetry and inductively coupled plasma mass spectrometry, we aim to identify polymer properties that lead to the selective coordination of rare earth ions for implementation in separations.

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Tetravalent metal ion cluster chemistry

Karah E. Knope, Jennifer N. Wacker, Anamar Blanes Diaz

Structural chemistry has played an important role in our understanding of the chemical and physical behavior of the actinides. Yet our understanding of the chemistry, bonding, and reactivity of actinide complexes and clusters still lags behind that of the rest of the Periodic Table. This lack of structural and chemical information has led to large discrepancies in thermodynamic data, significant challenges in process chemistry, and the unexpected mobility of heavy elements in the environment. With an eye towards filling this knowledge gap, over the past several years our group has harnessed both ligand complexation and noncovalent interactions towards the isolation of novel An(IV) and Ce(IV) structural units from aqueous solution. In particular, we have focused on the hydrolysis and condensation behavior of the tetravalent metal ions (i.e. formation of metal-oxo clusters) as this chemistry is known to thwart current efforts to predict and control actinide behavior. We have examined the effects of metal ion- and ligand-identity as well solution conditions on cluster formation and reactivity. More recently; however, we have turned away from aqueous solutions and towards ligand scaffolds that afford a greater degree of control over metal ion hydrolysis. In this presentation both our past efforts to explore metal-oxo chemistry and our more recent efforts to control metal-oxo cluster formation will be discussed.

Bonding, Reactivity, and Magnetism of Tetravalent Lanthanide Ions in Molecules and Extended Solids

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The increased crystal field splitting and metal-ligand covalency in tetravalent lanthanide ions in comparison to their isoelectronic, trivalent cogners leads to divergent and, potentially, exciting magnetic behavior and chemical reactivity. However, redox chemistry to access and stabilize reactive tetravalent lanthanide (Ln^{4+}) complexes and materials is a critical impediment to the fundamental physical understanding of these ions and the development of their applied chemistry. In this talk, I will present my group's synthetic studies to isolate and characterize both molecular complexes and extended solids of tetravalent lanthanide ions. Through the discussion of the spectroscopic, structural, and thermomagnetic properties of these systems, I will develop a cohesive model of their electronic structure across both classes of materials and identify critical open questions.

Cerium had long been the only lanthanide readily accessible as a molecular complex in its tetravalent oxidation state.[1,2] However, the conditions and coordination environment can have a dramatic effect on the $\mathrm{Ce}^{3+/4+}$ redox couple and the stability of each oxidation state. These observations help to motivate efforts to expand the lanthanide ions accessible in solution in their tetravalent oxidation state by several groups.[3] The synthesis and electrochemical behavior of the series of trivalent lanthanide imidophosphorane complexes, K[Ln^{3+}(NP(1,2-*bis*-^{t}Bu-diamidoethane)(NEt_2))$_4$] (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, and Ho) and related homoleptic imidophosphorane complexes,[1,4,5] will be presented in this talk along with the structural and in situ spectroscopic (CW X-band EPR and electronic absorption spectroscopy) characterization of the accessible tetravalent products, [Ln^4(1,2-*bis*-^{t}Bu-diamidoethane)(NEt_2))$_4$], where Ln = Ce, Pr, and Tb). These studies are complemented by theoretical modeling of the redox chemistry and the UV-vis spectra. The bulk molecular tetravalent lanthanides are further interrogated by high-frequency and -field EPR to probe of metal-ligand covalency as function of oxidation state.[6] Additionally L_3-edge XANES and HERFD-XANES spectra of these and related complexes will be presented to consider the role of ground- and excited-state multiconfigurational behavior.[1,4,5]

In order to bring a wider suite of spectroscopic and thermomagnetic tools to bear, ternary, tetravalent chalcogenides were examined. These systems allow the control of local symmetry (Ln^{4+}; O_h to D_{2d}), the intermetallic distance, and lattice symmetry. In studies of a Kitaev material candidate ($\mathrm{Na_2PrO_3}$) with a $J_{\mathrm{eff}}=1/2$ ground state by thermomagnetic measuremnts coupled with inelastic neutron scattering, the largest first crystal electric field in lanthanide ion was identified at ~230 meV. This result, combined with the observation substantial antiferromagnetic exchange, led to detailed studies of a series of Pr^{4+} systems showing evidence of increased metal-ligand covalency compared to the traditional trivalent lanthanides. A combination of X-ray (L_3-edge XANES, $M_{4,5}$-edge XANES/XMCD, O *K*-edge XANES/XMCD), optical (FIRMS), and neutron (INS) spectroscopies, are utilized to understand the single-ion properties, exchange interactions, and bulk behavior driven by covalency and increased CEF in Pr^{4+}. Lastly, a model of ground state donor covalent bonding is developed in several series of ternary Ln^{4+} chlacogenides to explain both the L_3-edge XANES, HERFD-XANES, and RIXS spectra and the observed thermomagnetic properties of the systems.

Opportunities for expanding the known molecular tetravalent lanthanides will be discussed in the context of these results. Additionally, our early studies on building functional magnetic systems with Ln^{4+} ions based on increased exchange coupling and intermediate coupling will be presented with sufficient time.

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Metal Flux Growth of Stuffed Rare Earth Borocarbides

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INTRODUCTION

Rare earth borocarbide intermetallics $R_xB_yC_z$ exhibit structural complexity, featuring a wide variety of borocarbide units surrounded by rare earth cations.[1] Borocarbide chains, sheets, and networks are stabilized by strong covalent B-C bonding. The positioning of rare earth cations determines the magnetic properties of the materials, which can include long range magnetic ordering, heavy fermion effects, and superconductivity.[2] These compounds are often synthesized using high temperature methods such as arc melting. We have found that they can be grown as large crystals from reactions in rare-earth rich eutectic melts such as La/Ni (67 at% La; mp 517°C) or Ce/Cu (72 at% Ce; mp 424°C).[3,4] This technique favors the formation of rare-earth rich products, featuring shorter borocarbide chains instead of extended sheets or networks. The structures also have interstitial sites surrounded by rare earth cations, which can incorporate small atoms such as hydrogen and fluorine. By using reactants such as anthracene and decafluorobiphenyl, we have isolated several "stuffed" rare earth borocarbide phases such as $Ce_4B_2C_2H_{2.4}$ and R_3BC_2X (R = La – Pr; X = H, F, Cl).[4]

EXPERIMENTAL METHODS

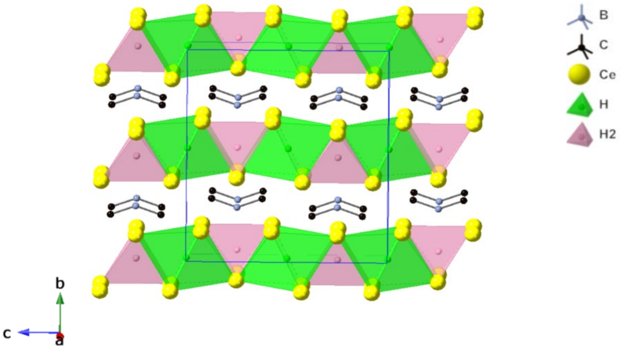
$R_xB_yC_zX_n$ compounds were grown from metal flux reactions. The fluxes were made by arc-melting the appropriate molar amounts of R and T = Ni or Cu. Pieces of flux were placed in an alumina crucible, with other reactants (boron powder, carbon powder, $C_{14}H_{10}$, $C_{12}F_{10}$, LaF_3, $LaCl_3$). The crucibles were sealed in silica tubes under vacuum and heated using a variety of heating profiles, ending with centrifugation at 600°C to remove the excess molten flux.

Crystalline products were handled under argon or nitrogen to prevent oxidation. Characterization methods included single crystal X-ray diffraction, neutron diffraction (TOPAZ, ORNL), elemental analysis using SEM-EDS, and magnetic susceptibility measurements.

RESULTS AND DISCUSSION

$Ce_4B_2C_2H_{2.42}$ is grown from reactions of boron and anthracene in Ce/Cu flux and is a stuffed variant of the monoclinic Nd_2BC structure type.[5] Single crystal neutron diffraction confirms that hydride ions occupy the tetrahedral and octahedral interstitial sites within the layers of cerium cations. If anthracene is replaced by $C_{12}F_{10}$ in the reaction, an isostructural product is formed with fluorine occupying the octahedral interstitial sites.

A series of $R_3BC_2X_{2-n}$ compounds with the orthorhombic $Ca_3C_3Cl_2$ structure type[6] have been grown from reactions of boron with $C_{14}H_{10}$ or $C_{12}F_{10}$ in rare earth rich fluxes. Rare earth cations occupy the calcium sites of the parent structure; a BC_2 chain replaces the allenylide C_3^{4-} unit, and interstitial anions (X = H, F) occupy the chloride sites (see Figure). Attempts to incorporate chlorine into $R_3BC_2X_{2-n}$ interstitial sites leads to a change in structure type.



CONCLUSIONS

Rare earth rich borocarbide compounds can incorporate small interstitial species produced by decomposition of C_nX_m compounds during metal flux reactions. Addition of interstitials may enable tuning of electronic properties. Given the ubiquity of hydrogen sources such as surface hydroxyls, intermetallics that are rich in rare earth elements may have hydride interstitials.

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Magnetic Separation of Rare-Earth Ions

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The rare-earth(RE) elements are a raw material class of superior priority for the high-tech/ conventional industries. The state-of-art RE beneficiation relies on their marginal chemical property differences in separating them individually from mixed ore. This is accompanied by a missing gap on an economically advantages recycling technology for end-of-life RE products. The industrial solvent extraction is realized with hundreds of stages of hyperlinked mixer-settlers involving large amount of non-recyclable chemicals and consequently lead to critical environmental issues. In recent years, by us and peers in different groups, a fascinating phenomenon in the formation of enriched RE ions has been repeatedly observed close to the magnetic source. This potentially unlocks a green RE separation technology with effective hydrodynamic scales in the μm-particle range in microfluid cells or elevated valorization flux in high-gradient magnetic separators all the way down to the level of ions

Nevertheless, the phenomenon was physically surprising since a change in the ion concentration, $c \propto c0[1 - \exp(-\mu 0HMV/kT\ )]$, cannot be expected for Boltzmann-distributed ions as their thermal energy kT is much higher than the magnetic term. Taking Dy(III) as model material, this puzzle has been solved [1] by actively controlling the evaporation at solution interface. Consequently, the loss of water molecules give rise to Dy(III) enrichment at the vicinity of magnetic source. Then, the hyper-diffusive growth of the concentration boundary layer observed was elucidated by quantifying the intriguing role of the Kelvin-force-driven microconvection, i.e. solutomagnetic convection. Thus, it leads to a transient toroidal vortex inside the enrichment zone. The resulting mass transport and momentum transfer interactively reshapes the initial planer enrichment flux into an oval distribution dictated by the magnetic source used [2]. Beyond a certain RE concentration enrichment, the RE content in the boundary layer can no longer be trapped near magnet. A hydrodynamic instability in form of a Rayleigh-Taylor instability sets in. To predict the limit of magnetic separation, a stability criterion was quantified by a 1D stability diagram based on Rayleigh number; and further extended to 3D via an analysis of the generalized density of a potential energy, which combines Kelvin force and gravity[3]. Furthermore, a material property database is provided for the solutal expansion coefficient and the magnetic susceptibility of 11 out of 17 trivalent RE. Besides, a novel protocol is developed to enhance and resolve the magnetic term of the Kelvin force [4].

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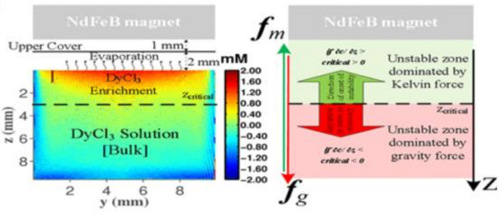

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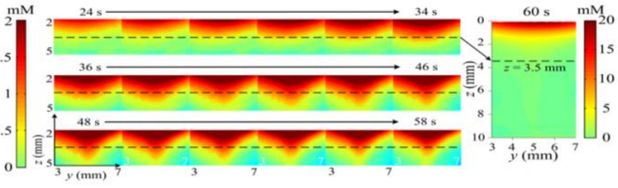

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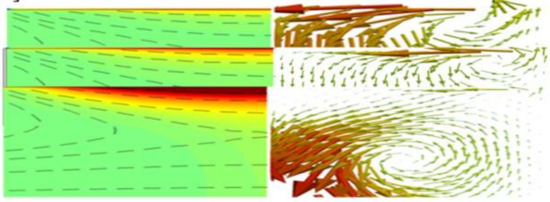

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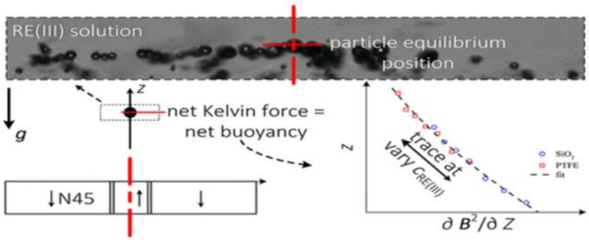

Recent Advances in Actinide-Ligand Multiple Bonding

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A central aim of f-block chemistry is to quantify the extent and nature of covalency in the bonding of these ions. When considering ways to achieve this aim, studying early actinide-ligand multiple bonding is an attractive place to start because such linkages tend to, by definition, exhibit appreciable amounts of covalency and thus they are amenable to being probed using a wide range of structural, spectroscopic, magnetic, and quantum chemical calculation techniques. Additionally, whilst of interest in their own right, early actinide-ligand multiple bonds can provide a baseline for comparisons to transuranium and lanthanide analogues; this will in turn provide a rounded picture and understanding of these ions overall, enabling contextualization of their bonding with respect to the d-transition metals as well.

For some time now we have been studying the synthesis, reactivity, spectroscopy, magnetism, and computational characterization of lanthanide and early actinide-ligand multiple bonding interactions, including the occasional foray into actinide-actinide bonding[1]. This has revealed a range of metal-ligand linkages that have contributed to foundational work in terms of addressing the aim of quantifying the extent and nature of covalency in the bonding of f-block ions.

Here, we will provide an update on our work to date, including the evolution of our work to include transuranium complexes[2,3]. These complexes are enabling comparisons with respect to actinide-actinide *and* lanthanide-actinide bonding relationships. Certain comparisons had proved elusive for studies centered around thorium and uranium alone, so this work demonstrates the value of studying transuranium chemistry, sometimes delivering novel actinide-ligand linkages before thorium and uranium analogues, despite the significant challenges associated with working with transuranium radioistotopes.

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Synthesis of Multi-metallic f-element Complexes with the Cyclononatetraenyl Ligand

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INTRODUCTION

The field of single-molecule magnets (SMMs) has been greatly advanced thanks to the development of organolanthanide chemistry. Indeed, if the first lanthanide-based complexes to show slow magnetization relaxation typical of an SMM were coordination complexes,[1] the best performing compounds usually display cyclopentadienyl (Cp) derivative ligands.[2–4] Other aromatic ligands have shown interesting behaviors with regards to the lanthanide ions, and the cyclooctatetraenyl (Cot) ligand is particularly suited to accommodate the prolate electronic density of erbium and thulium centers.[5–7]

Another interesting ligand in this series is the cyclononatetraene (Cnt) ligand. Indeed, its large size confers a similar electronic density than that of the Cot to the metallic center but also provides great flexibility to the structures. This has been shown to give rise to unexpected sandwich complexes such as in Er(Cot)(Cnt), in which the structure displays an η^6 coordinated Cnt in addition to being an SMM.[8,9] Then, similarly to a typical Cp ligand, the Cnt ligand is monoanionic but its reaction with several different lanthanide starting materials indicates a rich redox-active behavior, making it an interesting brick for the construction of multi-metallic complexes with lanthanides whether in their trivalent or divalent state.

RESULTS AND DISCUSSION

After the development of the lanthanidocene series for the classical divalent lanthanide (Sm, Eu, Yb and to a certain extent Tm),[10] we decided to tackle the behavior of the less classical lanthanide which are still found as divalent precursors, namely dysprosium and neodymium.

By reacting those precursors with the Cnt ligand we synthesized a series of multi-metallic complexes such as shown in figure 1.

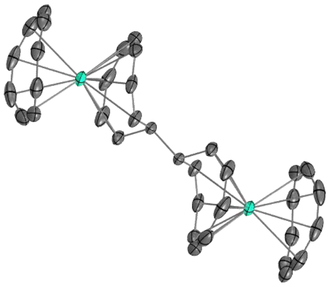

Figure 1. *X-ray structure of Dy_2Cnt_4, carbon atoms are in grey, dysprosium in green, hydrogens are removed for clarity.*

Those species were investigated through several techniques including SC-XRD, magnetic studies and CASSCF calculations.

CONCLUSIONS

The use of a new ligand with structural flexibility and rich redox behavior has allowed for the synthesis of new multi-metallic species with interesting properties.

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Lanthanide-dependent metabolism by methylotrophic bacteria opens novel avenues to improve technologies for recovery of energy-critical metals

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INTRODUCTION

The recent discovery that metals known as rare earth elements (REE), specifically lanthanides, have an active role in metabolism, particularly in methylotrophy, has opened avenues to resolving long-standing metabolic mysteries across diverse biological systems. Until recently, it was believed that methanol oxidation was catalyzed in the periplasm solely by the extensively studied Ca- and pyrroloquinoline quinone (PQQ)-dependent methanol dehydrogenase (MeDH) encoded by the *mxaFI* genes (MxaFI). It is now recognized that methanol oxidation can be driven by the periplasmic MeDH XoxF, that utilizes lanthanide cofactors in place of Ca. XoxF is highly divergent but widespread in environmental strains including all methylotrophs and numerous non-methylotrophs. My research program is leading efforts in defining the role of lanthanides in biology, focusing on the methylotrophic organism *Methylobacterium extorquens* AM1. We have recently demonstrated far-reaching impacts of lanthanide biochemistry beyond methylotrophy: from the identification of new enzymes and pathways dependent on rare earth-chemistry to identifying the effects of lanthanide-dependent metabolism on the local environment and developing biological platforms for efficient recovery.

RESULTS AND DISCUSSION

Genetic studies confirmed that lanthanide metals are scavenged by using a parallel system to the well-studied, TonB-ABC-transport dependent Fe scavenging pathway. The localization of the lanthanide during trafficking in the cell was possible by combining genetic and phenotypic studies with transmission electron microscopy (Fig. 1). Two intriguing findings resulted from the integration of these studies: lanthanides are not readily bioavailable in the periplasm, and lanthanides are stored in the cytoplasm in mineral form. Secretion of a chelator for lanthanides (a.k.a. a lanthanophore) was identified when using poorly soluble forms of lanthanides. Transcriptomic analysis comparing growth of strain AM1 with soluble vs poorly soluble lanthanide sources enabled the identification of the lanthanophore biosynthetic pathway. We are currently characterizing these lanthanide scavenging molecules, and additional peptides involved in REE trafficking. We have shown that engineered variants of *M. extorquens* cannot only use light lanthanides but also heavy lanthanides, enabling a microbial platform that can use numerous lanthanide sources including mining ores, electronic waste, and contaminated water streams.

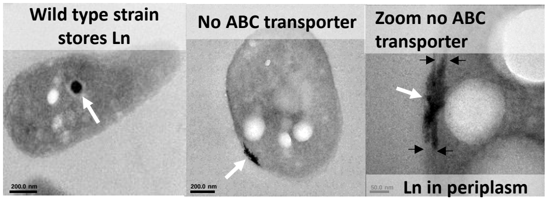

Fig 1. TEM tracking lanthanide localization

CONCLUSIONS

The identification of the lanthanide-transport and lanthanide-chelation system is leading us to develop *M. extorquens* as a system for many potential applications, including an efficient and safe platform for recovery of lanthanides from electronic waste and to improve medical imaging techniques.

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Chemistry, spectroscopy and speciation of protactinium

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INTRODUCTION

It is of fundamental interest to understand and predict the chemistry of rare radioelements. In this work, we focus on protactinium ($Z = 91$), an element that is sandwiched in between thorium and uranium in the periodic table. Protactinium may naturally occur in environment (protactinium-231 results from the decay of naturally occurring uranium-235) and also appear in thorium-based nuclear fuel cycles. From a chemical point of view, protactinium is a crossing point in the actinide series[1] and its chemistry is hard to predict[2,3]. We hypothesize that relativistic quantum chemistry should allow us to understand the enigmatic chemistry of protactinium and even predict it.

EXPERIMENTAL METHODS

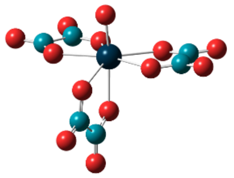
For our first study, we have chosen to focus on the coordination sphere of protactinium and on the computation of equilibrium constants for experimentally known systems[3–5]. The occurrence of 1:1, 1:2 and 1:3 complexes of protactinium(V) with sulfate and oxalate ligands is thus studied by means of quantum mechanical calculations, in particular based on density functional theory. The solvent effects, inherent to solution chemistry, are introduced by means of a polarisable continuum model[6] and the explicit treatment of water molecules (microsolvation).

RESULTS AND DISCUSSION

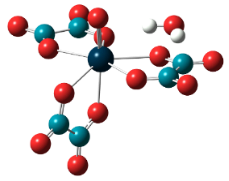
The coordination sphere of protactinium has been obtained by geometry optimizations performed both in the gas phase and in solution. It involves an oxygen atom from the Pa=O mono-oxo bond and also oxygen atoms from the bidentate sulfate or oxalate ligands, and in some cases from additional water molecules.

Coordination	1:1	1:2	1:3
Sulfate	8	8	7
Oxalate	8	8	7

The computation of equilibrium constants and comparison with experimental data is more subtle. First, only apparent constants were experimentally determined. Since the occurrence of a mono-oxo bond was confirmed[5] even in the case of the 1:3 complex with oxalate ligands (corresponding to the stronger complexation), we hypothesize that this bond is also present in all the studied complexes. Second, number of explicitly treated water molecules should not be randomly chosen, it should ideally (i) lead to saturation of the coordination sphere of protactinium and (ii) be sufficient to stabilize the anionic ligands. We find that adding n+1 water molecules (*n* being the number of water molecules in the first coordination sphere of protactinium) is enough to satisfy both conditions in all the six studied complexes.



n = 0 water molecule



n+1 = 1 water molecule

By doing so and computing ligand-exchange equilibrium constants, we reproduce well the experimental trends for the exchange of 2 and 3 ligands, while the exchange of only one ligand (1:1 complexes) is still hard to reproduce from computations.

CONCLUSIONS

We report recent progress concerning the basic chemistry of protactinium. We have shown that its coordination sphere may include up to 8 oxygen atoms (from the original mono-oxo bond and from ligand and solvent molecule complexation) and find an approximate way of determining trends in equilibrium constants, opening the way for future predictions.

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Pitfalls and Blessings in Reduced Rare-Earth Metal Halide Chemistry

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Rare-earth metal trihalides, RX_3 (R = Sc, Y, La-Lu), are known comprehensively with one exception, EuI_3. One of the prolific ways to produce trichlorides and tribromides is the ammonium halide route [1]. Following this process, oxygen can easily enter or is preserved as oxide-halide, ROCl, in the raw product. In subsequent reduction processes, either via conproportionation or metallothermic routines, the oxide may be retained, e.g., as in $\{OSm_4\}Cl_6$. Other light elements may also be incorporated in cluster-like halides, an important historic pitfall, as the examples of $\{H_xGd\}Cl$, $\{NGd_2\}Cl_3$, or $\{C_4OR_9\}I_9$ (R = Y, Ho, Er, Lu), may show. To turn these pitfalls into a blessing, a large number of the elements of the periodic table have been tested as endohedral atoms Z *aka* interstitials in rare-earth metal "clusters", of non-metallic and metallic elements alike. These "clusters", $\{Z_zR_r\}$, with r between 3 and 8 for the individual unit, are not really clusters in Cotton's sense, as there is hardly any bonding interaction between the cluster atoms R. Rather, bonding between the endohedral atom (or atom group) Z and the surrounding R atoms is mandatory.

Transition metal atoms, $Z = T$, especially of the 5d row, have turned out to be excellent endohedrals owing to their voluminous 5d orbitals that interact with the 5d electron of the R atoms [2, 3]. One of the most prolific compound type is $[\{ZR_6\}X_{12}]R$ with the number of examples decreasing in the sequence X = I, Br, Cl. There are thermodynamic reasons for this observation as the ionicity and therefore the lattice energy increases within this sequence and, thus, the stability of the trihalides, RX_3, increases. This is also the reason why fluorides with clusters are hardly known.

What seemed like another pitfall was the observation that transition/rare-earth metal, T/R, intermetallics like $Ru_{11}Lu_{20}$ were observed, here as a by-product during the attempt to synthesize $[\{RuLu_6\}Cl_{12}]Lu$. Meanwhile, there are examples of T/R intermetallics with all rare-earth elements known—preferably on the low T/R ratio side—with the exception of those R's = Nd, Sm, Eu, Dy, Tm, Yb that are known to form stable divalent states. So far, T:R ratios of 1:3 to 1:6 were employed in conproportionation reactions, for example targeting $\{AuTb_3\}Cl_3$ but yielding $AuTb_2 + TbCl_3$. Quite obviously there is a thermodynamic competition between the formation of a cluster complex halide and an intermetallic compound. Here, $TbCl_3$ acts as an "innocent" (molten salt) solvent rather than a reactant. Other innocent solvents may be halides like NaCl. Metallic melts, such as of tin, take part in the formation of intermetallics as we have recently shown in a case study for the Pt/Sn/Nd system. In a rather narrow region, eight ternary intermetallics have been discovered, PtSnNd, $Pt_{0.21}Sn_2Nd$, $PtSn_2Nd$, $Pt_{1.33}Sn_2Nd$, $Pt_{1.73}Sn_{2.27}$, Pt_3Sn_2Nd, $Pt_{1.5}Sn_{5.16}Nd_2$, and $Pt_3Sn_5Nd_{1.84}$, a true blessing!

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Recent Adventures in Lanthanide and Actinide Silicon Chemistry

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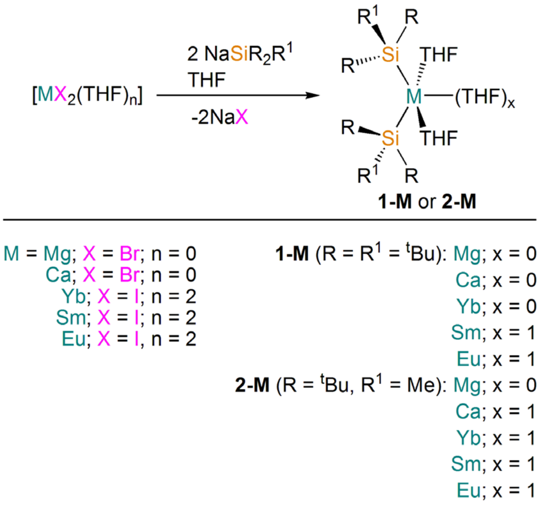
INTRODUCTION

Molecular f-block silicon chemistry is immature, and is predominated by the hypersilanide ligand, $\{Si(SiMe_3)_3\}$, and its derivatives.[1] Attention is now turning to probing the nature of the metal-silicon linkage in order to better understand the physicochemical properties of these polarised covalent bonds. One method that has been extensively used to experimentally probe the nature of metal-ligand linkages is Nuclear Magnetic Resonance (NMR) spectroscopy, which provides chemical shift data; this can be a direct probe of the electronic environment, and when combined with Density Functional Theory (DFT) it becomes a powerful reporter of the amount of covalency.[2] Here we present some of our recent results in lanthanide (Ln) and actinide (An) silicon chemistry.

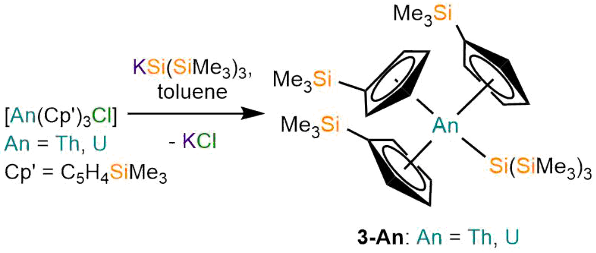
RESULTS AND DISCUSSION

The M(II) complexes $[M(Si^tBu_3)_2(THF)_2(THF)_x]$ (**1-M**: M = Mg, Ca, Yb, x = 0; M = Sm, Eu, x = 1) and $[M(Si^tBu_2Me)_2(THF)_2(THF)_x]$ (**2-M**: M = Mg, x = 0; M = Ca, Sm, Eu, Yb, x = 1) have been synthesized and characterized (Scheme 1). DFT calculations and ^{29}Si NMR spectroscopic analysis of **1-M** and **2-M** (M = Mg, Ca, Yb, and No, the latter *in silico* due to experimental unavailability) together with $\{Si(SiMe_3)_3\}$, $\{Si(SiMe_2H)_3\}$, and $\{SiPh_3\}$-substituted known analogs provides twenty representative examples spanning five silanide ligands and four divalent metals. When the metal is kept constant, direct, linear correlations are found between δ_{Si} (of the metal-bound silicon) and computed delocalisation indices, DI(M,Si), and interatomic exchange-correlation energies, V_{XC}(M,Si), measures of bond covalency. Calculations indicate that the covalency of these M(II)–Si linkages is ordered as No(II) > Yb(II) > Ca(II) ~ Mg(II), challenging the traditional view of late An chemical bonding being equivalent to the late Ln.[3]

The An(IV) complexes $[An(Cp')\{Si(SiMe_3)_3\}]$ (**3-An**, An = Th, U; Cp′ = $C_5H_4SiMe_3$) were synthesized by salt metathesis protocols (Scheme 2),[4] allowing us to directly compare Th–Si and U–Si chemical bonds. ^{29}Si NMR spectroscopy was used to detect the metal-bound silicon resonances, with the signal for the U(IV) complex (δ_{Si}: –137.09 ppm) paramagnetically shifted from that of the Th(IV) example (δ_{Si}: –108.92 ppm). DFT calculations showed that the An%:Si% 7s-, 6d- and 5f-orbital contributions are similar in **3-Th** and **3-U**, with the latter showing marginally greater covalency.



Scheme 1. Synthesis of **1-M** and **2-M**.



Scheme 2. Synthesis of **3-An**.

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Pinpointing Chemical Bonding in CeF_6^{2-} with Spectroscopy, Magnetism, and Electronic Structure Theory

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INTRODUCTION

Measuring X-ray absorption spectra (XAS) at the K-edges for light atoms directly bound to actinide centers (collectively referred to as "Ligand K-edge XAS") is an effective approach for evaluating f-electron behavior.[1] Previous work on small molecules and extended solids has provided new experimental evidence of covalent 4f-orbital mixing in cerium bonds, and helped unravel the complex behavior of covalent (band-like) vs ionic (atomic-like) 4f-electrons.[2] This presentation describes an in-depth examination of the electronic structure of the CeF_6^{2-} molecule. By using numerous experimental and theoretical techniques, we are able to evaluate chemical bonding in CeF_6^{2-} with a high degree of confidence.

RESULTS AND DISCUSSION

Octahedral CeF_6^{2-} was targeted because we hypothesized that it would contain significant Ce 4f- and F 2p-orbital mixing due to enhanced overlap with the compact F 2p orbitals. CeF_6^{2-} could also be characterized using both fluorine K-edge and cerium L_3-edge XAS spectroscopies, thus providing an opportunity to evaluate bonding from both the ligand and metal perspectives. CeF_6^{2-} was advantageous for computational studies because it is a small molecule with a highly symmetric O_h point group, containing an inversion center that prohibits complications due to 5f-6d hybridization. In addition, it could be modeled without requiring periodic boundary conditions needed for extended solids such as CeO_2. Our efforts initially involved developing new synthetic methods to isolate CeF_6^{2-} without H-bonding interactions from co-crystallized water molecules by using non-coordinating Ph_4P^{1+} countercations. Our experimental measurements of F K-edge XAS have been facilitated by access to the scanning transmission X-ray microscope (STXM) on ALS beamline 11.0.2, which can mitigate the self-absorption and saturation effects that may thwart measurements on non-conducting systems. Figure 1 shows the results of the spectroscopic work, including experimental F K-edge and Ce L_3-edge XAS compared with computed spectra. Ab-initio calculations of the F K-edge and Ce L_3-edge spectra with MC-WFT methods, including SO coupling show spectacular agreement with the experimental spectra, and provide confidence in the transition assignments. The results show significant mixing between the Ce 4f- and F 2p-orbitals that occurs primarily in the orbitals of t_{1u} symmetry. Corroboration for this effect is obtained by also observed in the magnetic data, which show a large amount of temperature-independent paramagnetism, suggesting electron delocalization from the F ligands.

CONCLUSIONS

This work shows that CeF_6^{2-} can be used as a benchmark in future quantitative F K-edge studies of actinide fluorides. In addition, efforts to advance computational methodology for f-elements benefit greatly from these spectroscopic studies, because the technique provides high energy resolution, feature-rich spectra while also probing interactions with both the f- and d-orbitals.

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ACKNOWLEDGMENTS

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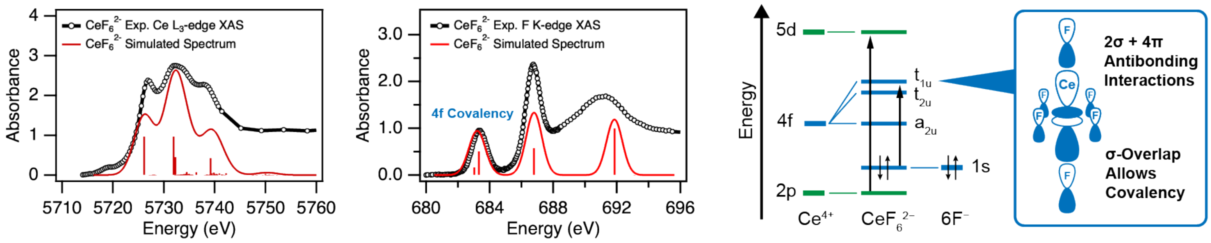

Figure 1. Comparison of the experimental spectra for CeF_6^{2-}, measured at the L_3-edge (left) and F K-edge (middle), with spectra calculated with Molcas, MC-WFT with PT2 dynamic correlation corrections for the state energies. A schematic depicting assignment of the spectral transitions (right) shows that the majority of the F 2p mixing is with the Ce 4f-orbitals of t_{1u} symmetry.

Speciation and Nucleation of An(IV) Species in Aqueous Media

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Actinide polyoxometalates are a family of nanoclusters composed of a variable number of actinide centers connected through a network of bridging and terminal oxygen ligands. These species have many potential applications in nuclear waste reprocessing and environmental remediation. However, our knowledge on the speciation of An(IV) ions and the formation mechanism of actinide polyoxometalates is very limited compared to their transition metal counterparts. Here, we present a computational study on the speciation and nucleation of thorium, uranium, neptunium, and plutonium ions in aqueous media in the presence of various ligands such as zwitterionic carboxylic ligands, chloride, or nitrate. We explored the key role of zwitterionic carboxylic ligands to quench the nucleation of actinide dimers via olation and oxolation reactions and the influence of the chloride-aquo ligand ratio on the formation of dimeric structures with oxo and hydroxo bridging moieties (Figure 1).

Figure 1. $[An(H_2O)_8]^{4+}$ (left) and examples of olation (right-top) and oxolation (right-bottom) dimeric products.

A Bottom Up Approach toward Programmable Luminescent Lanthanidopolymers

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INTRODUCTION

Complexation of multisite polymeric receptors with open-shell d-block or f-block elements produces metallopolymers. This class of hybrid materials combines the electronic and optical properties of transition metals with the versatility of organic polymers. Metallopolymers have found a wealth of applications in light-emitting diodes, in solid cells for photovoltaics, in magnetically active and light-emissive layers, in telecommunication devices, and in temperature sensors.[1] Despite the favourable properties, the lack of rational control on metal loadings in multisite polymers limits their design to empirical and poorly reproducible materials. In order to produce predictable and consistent metallopolymers, it is critical to determine the thermodynamic parameters that control polyvalent ligand-metal complexation. Accordingly, the site-binding model (Figure 1), describs complexation of a linear multi-site polymer with labile lanthanides in terms of two independent and quantifiable parameters. The first parameter is the free energy for connection of a lanthanide (Ln) ion to a binding site $\Delta G^{\mathrm{Ln},\mathbf{P}^N} = -RT\ln(f^{\mathrm{Ln},\mathbf{P}^N})$ and the second parameter is the free energy of interaction occurring when two adjacent sites are occupied $(\Delta E_{i,j}^{\mathrm{Ln,Ln}})$.[2]

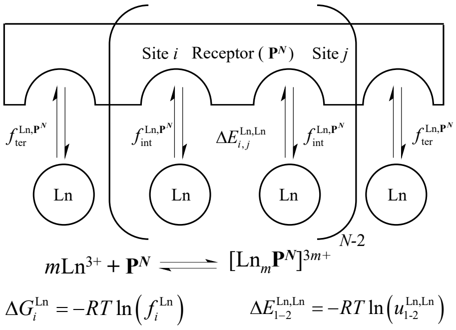

Figure 1. The site binding model.

RESULTS AND DISCUSSION

The intrinsic metal-receptor affinity for the coordination units within the polymer traditionally derived from that measured for the analogous monomeric ligand. However, this oversimplified approach is misleading and causes a significant discrepancy between the intrinsic affinity for the same binding unit taken either separately or within the polymeric backbone.[3] Taking this into consideration, we exploit NMR titrations to study the complexation of a series of oligomers (**L1**-**L5**) with [Ln(hfac)$_3$]. The exact origin of the unusual changes in thermodynamic affinities can be then safely rationalized. The extracted microscopic parameters are then used to predict the binding isotherms for any oligomers ($\mathbf{P}^N$) with *N* binding units. For each constructed binding isotherm, the single average affinity is calculated, and the trends are shown in Figure 2b.

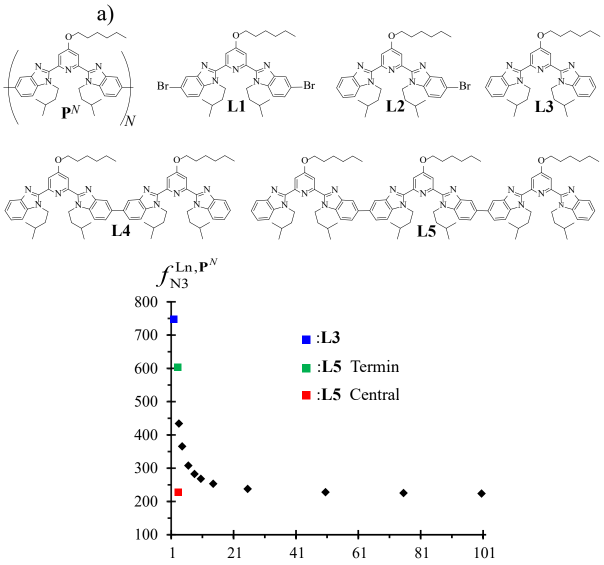

Figure 2. a) Chemical structures of the polymer and Ligands, b) Calculated intrinsic affinities $(f_{\mathrm{N3}}^{\mathrm{Ln},\mathbf{P}^N})$ for a linear polymer $\mathbf{P}^N$ (black diamonds).

CONCLUSIONS

While increasing the number of binding sites in the polymer, the affinity of the tridentate sites for the [Ln(hfa)$_3$] guests stepwise decreases (negative power dependence). The origin of this trend can be attributed to the connection of two unfavorable electron-attractive substituents at the 5 position of the benzimidazole side arms within the polymeric core. The situation changes for the two terminal sites where only one 5-position is occupied.

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Novel Forms of Quantum Magnetism using Kramers/non-Kramers rare-earth pairs

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ABSTRACT

Insulating magnets combining the effects of geometrical frustration with strong spin-orbit coupling offer a prime route to realize correlated quantum states with exotic ground-states and excitations. Spin-space anisotropy and bond-directional magnetic exchange interactions are naturally present in rare-earth oxides. One of the most celebrated consequence is the existence of classical and quantum "spin-ice" physics in rare-earth pyrochlores, materials in which magnetic ions occupy a three-dimensional network of corner-sharing tetrahedra. In this talk, I will present the discovery of distinct flavors of exotic magnetic matter in families of rare-earth oxides with perfect two-dimensional triangular [1,2] and kagome [3,4] geometries. This experimental work relies on recent advances in materials synthesis and combines thermodynamic characterization with state-of-the-art neutron scattering experiments to unravel the classical or quantum nature of these newly discovered two-dimensional spin-liquid candidates highlight the crucial role played by hyperfine interactions in frustrated quantum magnets, and motivate further investigations of correlated nuclear spins.

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ACKNOWLEDGMENTS

The triangular lattice work was supported by the NSF under award NSF-DMR-1750186. The kagome lattice work was supported by the DOE under award DE-SC-0018660

Preorganization of β-Diketonate Lanthanide Adducts with Rigid N-Donor Ligands: Thermodynamics and Photophysics

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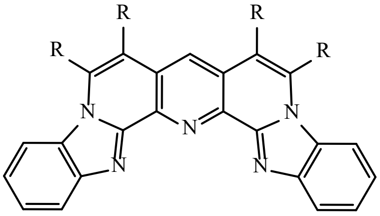
INTRODUCTION

Lanthanide-containing (bio)organic polymers have attracted great attention because of their vast applications as materials for energy storage and energy conversion,[1] drug delivery,[2] modern light-emitting diodes (OLEDs),[3] and as fluorescent (bio)probes.[4] However, various (supra)molecular interactions (H-bond, solvation effects, dative bonds, halogen bonds, etc.) are the main source of difficulties in understanding the formation of such assemblies. In order to rationalize these intermolecular forces and bring them within the frame of chemical control we need to understand the thermodynamic principle of these host-guest assemblies. The free-energy changes ($\Delta G_{m,n}^{\mathrm{H,G}}$) corresponding to the formation of such compounds can be splitted into two major parameters:[5] (i) the entropy changes accompanying the complexation process,[6] and (ii) the chemical intercomponent interactions such as host-guest (H-G), guest-guest (G-G) and host-host (H-H).[7] Adopting these two parameters rationalizes the metal loading in linear lanthanidopolymers, which leads to two highly wished, but opposite strategies. Firstly, the formation of metallic clusters by occupying neighboring sites finds applications, e.g., in sensing.[8] Secondly, the alternate arrangement of occupied and empty sites is highly desired for light-upconversion.[9] A rational control of the latter parameters requires improved preorganization and rigidity in the binding sites dispersed along the polymeric backbone. In this regard, we have designed and prepared new neutral and highly preorganized ligands (**L1**-**L5**) (Figure 1) based on the well-known bis(benzimidazole)-pyridine edifice. Besides their synthesis via C–H activation and alkyne condensation, the effect of the ligand preorganization on the thermodynamic stability and photophysical properties of 1:1 adducts with different trivalent lanthanide containers [Ln(hfac)$_3$(diglyme)] will be discussed.



L1: R= phenyl(Ph)
L2: R= 3,5-dimethylPh
L3: R= propyl
L4: R= ethyl
L5: R= methyl

Figure 1. Chemical structure of **L1**-**L5**.

RESULTS AND DISCUSSION

The rigidified ligands **L*k*** are synthesized via C-H activation by using Rh(III) as catalyst.[10] Their reaction with neutral complexes [Ln(hfac)$_3$dig] (Ln = La, Eu, Y, Yb) provided mononuclear 1:1 complexes [Ln(hfac)$_3$**L*k***] (***k*** = 1, 2). ^{1}H NMR titration of **L*k*** (***k*** = 1, 2; 1 mM) with [Ln(hfac)$_3$] as lanthanide carriers (CD$_2$Cl$_2$ + 0.14 M dig) exhibit the stepwise formation of [Ln(hfac)$_3$**L*k***], from which the binding isotherm diagram can be plotted. The formation constants $\beta_{1,1,\mathrm{cond}}^{\mathrm{Ln},\mathbf{L}k}$ and intrinsic affinities $f_{\mathrm{N3,cond}}^{\mathrm{Ln},\mathbf{L}k}$ are eventually provided by nonlinear least-squares fits of the binding isotherms with respect to the experimental occupancy factors. Final results indicate an increase of about three orders of magnitude for $f_{\mathrm{N3,cond}}^{\mathrm{Ln},\mathbf{L}k}$ upon rigidification. The photophysical measurements carried out at room temperature in CH$_2$Cl$_2$ for the free ligands exhibit a global red-shift in their absorption and emission spectra due to the extension of π-system. Photophysical investigation of their corresponding Eu(III) complexes revealed that at room temperature, the ligands' low-lying triplet excited states promote back-energy transfer, resulting in a significant drop in quantum yields.

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A coordination chemistry approach to optical imaging of uranium biotransformations in model conditions

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The assessment of long term nuclear waste repositories requires an absolute knowledge of radionuclide mobility reactivity and bioavailability. Of particular threat are the actinides, as these constitute the greatest long-term radiological hazard of high-level waste. In order to address these issues, we have been involved in a programme of work to establish a comprehensive understanding of the electronic properties and physical and chemical properties of the radioactive actinide metals using state of the art emission spectroscopic techniques.

Our approach to this is to firstly use coordination chemistry to synthesise uranium compounds with ligands that model environmentally complexed species and use optical spectroscopy to understand and map both the chemical and physical behaviour of these species. We have recently established that uranyl(V) and U(IV) complexes are emissive and will demonstrate that uranium in the +IV and +VI oxidation states can be detected simultaneously at relatively low concentrations. Furthermore, the form of the emission spectra of uranyl compounds are sensitive to the nature of the ligand bound in the equatorial plane and the complex nuclearity (extent of aggregation), potentially giving a sensitive method of assessing the solution forms of uranium in environmental conditions. We will next discuss how the optical properties of these model compounds can be extended to the *trans*-uranics and applied to disproportionation reactions and redox events in solution and finally how this knowledge can be applied to the bacterial reduction of uranium using optical imaging techniques.

High-Valent Uranium and Neptunium Imidophosphorane Complexes

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Two-electron oxidative atom transfer reactions are typically restricted to the $3^+/5^+$ couple in molecular uranium chemistry,[1] and reactions of tetravalent, homoleptic uranium complexes to form hexavalent, metal-ligand multiply bonded (MLMB) complexes are rare.[2,3] Because the mid-actinides become less oxidizable as the series is traversed, the redox chemistry and small-molecule transformations established in uranium complexes are not directly transferable to neptunium and plutonium complexes, and the development of more reducing ligand frameworks that can support the $4^+/6^+$ couple is crucial to expanding this chemistry. The strategic design of ligand systems that both shift redox couples to more negative potentials and sterically and electronically stabilize high-valent actinide ions are necessary to isolate complexes of rare oxidation states and unique metal-ligand bonds.

The tetrahomoleptic imidophosphorane ligand field has shown excellent utility for stabilizing high-valent *f*-element species. These ligands are anionic 1σ, 2π donors with tunable steric and electronic properties.[3] We have recently reported the synthesis of hexavalent uranium mono-oxo and mono-imido complexes via two-electron atom transfer reactions.[3] Structural characterization of these species was complicated by whole-molecule and ligand disorder,[3] necessitating modification of the ligand framework prior to the extension of this chemistry to Np. Disruption of the ligand pseudo-threefold symmetry has allowed for high-quality structural data to be obtained for several formal oxidation states of U and Np. Presented here are the complexes ($[An(NP(R_3)_4]^q$, where An = U and Np and q can be -1, 0, or +1) and the reactivity of these complexes with two-electron oxygen atom transfer reagents to form high-valent mono-oxo complexes (($[An(O)(NP(R_3)_4]^q$, Scheme 1).[3-5] The utility of several oxygen-atom transfer reagents is evaluated, including nitrous oxide, trimethylamine N-oxide, dioxygen, and DBABH-NNO (9,10-dihydro-11-nitroso-anthracen-9, 10-imine), Ligand design processes to afford high-quality, single crystals of the mono-oxo complexes in good yield and on small-scale (10-40 mg of isotope) and the one electron oxidation and reduction chemistry of the mono-oxo complexes will be described.[4-6] Detailed spectroscopic and solution and solid-state structural analyses will address changes in the inverse trans-influence across mid-actinides with MLMBs– a phenomenon which is uniquely addressable by this series of complexes.[3-6] Additional topics to be covered may include electrochemistry, magnetism, and EPR spectroscopy of selected complexes.

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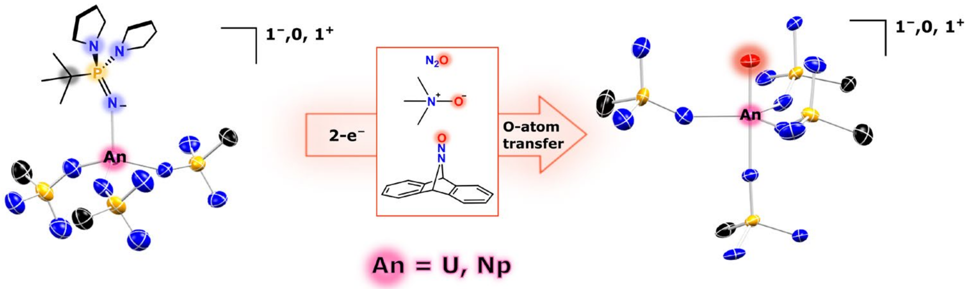
ACKNOWLEDGMENTS

These studies are made possible by the Georgia Tech Transuranic Synthetic Facility which, after three years of construction and a year of COVID shutdown, fully opened in 2020 and the support of the DOE Heavy Element Chemistry Program (DE-SC0019385).



Scheme 1. Reaction scheme for the oxidation of tetravalent uranium and neptunium homoleptic complexes with two-electron, oxygen atom transfer reagents to form mono-oxide products. The complexes are shown as molecular structures as determined by SC-XRD and thermal ellipsoids are plotted at 50%. The ligands are truncated to core N and C atoms to reveal connectivity at the metal. A single ligand on the homoleptic complex (left) is drawn to depict the full ligand connectivity.

Generating Magnetic Anistropy Through Exchange and Ligand Field

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This presentation will discuss two different approaches that share the common goal of generating magnetic anisotropy in *4f*-based complexes. The first part will discuss our group's recent results concerning the utilization of new heterocycles as ligands for lanthanide ions to generate high-performance single-molecule magnets (SMMs). The second part of the talk will focus on how fairly strong magnetic coupling between lanthanides can be achieved in the absence of open-shell bridging ligands, yielding exciting new SMM platforms.

Unusual oxidation states and reactivity in heterometallic compounds combining lanthanide and transition metal ions

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Complexes containing redox non-innocent ligands have been well developed in the last decade with transition metal ions and have led to very important chemical transformations at the lowest environmental and economic costs.[1] Nonetheless, examples with f-element are rare. This is unfortunate since divalent lanthanides are excellent sources of a single electron and would provide good control of the ligand reduction of strong electron correlation in these systems.[2] As an original expansion of lanthanide complexes containing redox-active ligand, we have started to work on the synthesis of original complexes containing lanthanides, redox non-innocent ligands, and transitions metals will be presented. The first provides reversible electron(s) source(s) (*remote control*), the second acts as electron(s) reservoir and controls the electron correlation strength ("*dimmer switch*"), and the last is the site of the selective reaction. Since the original synthesis and the first spectroscopic characterization of several of these new organometallics will be presented along with the unusual stabilization of a tris-alkyl Pd(IV) species[3] as well as easy formation of Ni(0) complexes from simple $NiMe_2$ fragments.[4] In these examples, the electronic structure was investigated and showed that the modification of the bridged redox non-innocent ligand tends to drastically modify the electronic outcome, which in turn, leads to tunable reactivity. We wish to present our latest results in the field with the stabilization of tetra-alkyl palladium fragments with potential reactivity in alkyl cross-coupling (Figure 1) and alkene isomerization featuring selectivity towards mono-isomerization with Ni complexes (Figure 1).

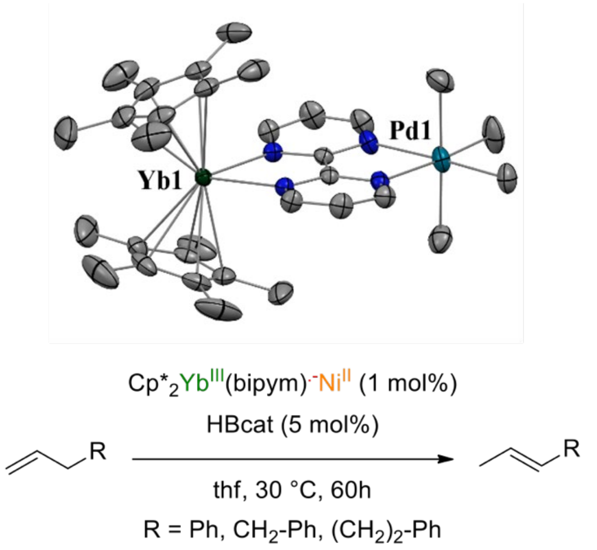

Figure 1. Example of a tetra-alkyl palladium fragment (top) and alkene isomerization with a heterobimetallic Ni complex (bottom).

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Assembling Dysprosium Single-Molecule Magnets with Photochromic Dithienylethene Ligands : an Efficient Strategy for Magnetic Hysteresis Photomodulation ?

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INTRODUCTION

Molecules that exhibit slow magnetic relaxation resulting from a bistable ground state, called Single-Molecule Magnets (SMM) are attractive candidates for next generation information storage schemes.[1] Efficient control of their magnetization via an external stimulus[2] such as electric potential,[3] temperature[4] or light[5] could considerably increase the scope of application of these magnetic molecules. We are particularly interested in using light to manipulate the magnetic characteristics in order to obtain fast and contactless control. More specifically, we target mononuclear lanthanide complexes with strong anisotropy in order to maintain magnetic bistability at rather high temperatures.[6] Since these complexes are not intrinsically photoresponsive, our strategy rely on the introduction of photochromic ligands in order to modify the lanthanide coordination environment upon the ligand photoisomerization.

RESULTS AND DISCUSSION

We found a supramolecular strategy to assemble lanthanide based building units into photoswitchable chains and cages. Air stable and highly anisotropic dysprosium complexes [Dy(Tp^{py})F(pyridine)$_2$]PF$_6$ (Tp^{py} = tris(3-(2-pyridyl)pyrazolyl)hydroborate) featuring a short Dy-(η^1-F) bond and previously shown to exhibit slow magnetic relaxation were reacted with a ditopic bispyridyl dithienylethene (DTE) ligand. This yielded infinite chains exhibiting slow magnetic relaxation and magnetic hysteresis below 4K. Importantly, the compound, initially featuring the DTE as its closed isomer can undergo single-crystal-to-single-crystal transformation under visible light irradiation with full conversion of the organic moieties to their open isomer. The change was monitored by photocrystallography and revealed that the chain structure was maintained. At high temperature, both compounds exhibited slow relaxation with very similar behavior and ab initio calculations revealed that the energy splitting of the ground state is indeed very similar in the two compounds since the coordination sphere of dysprosium is only slightly modified upon isomerization. Below 4 K, differences in the shape of the magnetic hysteresis were clearly observed and were related to different quantum tunneling rates in the two isomers. Ab initio calculations could also evaluate how the change in the dysprosium-dysprosium distances within the crystal could modify the dipolar coupling and affect the overall behavior.

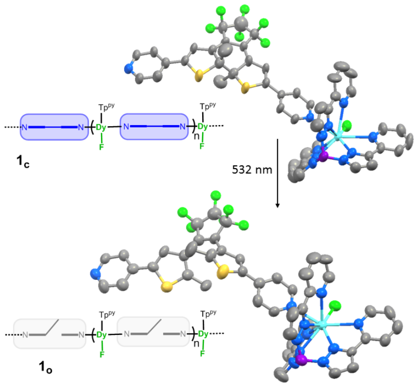

Figure 1: Asymmetric unit (single-crystal X-ray diffraction) of the starting compound 1c at 300 K and of the photo-generated compound 1o (293 K).

CONCLUSIONS

Most of the results describing this hysteresis photomodulation via single-crystal-to-single-crystal isomerization of a photochromic chain of dysprosium SMM are published.[7] More recent results obtained on a supramolecular cage following a similar strategy will also be discussed during this presentation.

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Narrow-gap Kondo insulating ground state of $Ce_3Bi_4Pd_3$ revealed by applied pressure

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INTRODUCTION

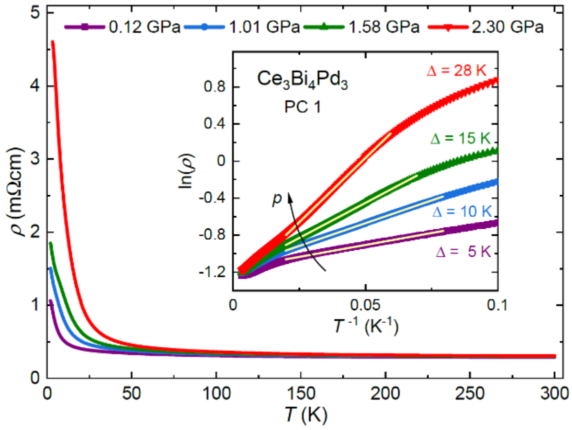
Recent theoretical predictions of non-trivial topological states in Kondo insulators have boosted investigations on candidate materials. For instance, $Ce_3Bi_4Pd_3$, a non-centrosymmetric compound crystallizing in the same structure of the prototypical Kondo insulator $Ce_3Bi_4Pt_3$, has been predicted to be a Weyl Kondo semimetal driven by spin-orbit coupling[1], stimulating experimental investigations of its ground state properties. Two conflicting scenarios have emerged from independent studies: either $Ce_3Bi_4Pd_3$ is a spin-orbit coupling driven topological semimetal or a Kondo insulator with smaller Kondo energy scale than its Pt counterpart[2-4]. In order to determine the ground state of $Ce_3Bi_4Pd_3$, here we employ electrical-resistivity measurements under hydrostatic pressure, which is a clean symmetry-preserving tuning parameter that increases hybridization but virtually preserves spin-orbit coupling.

EXPERIMENTAL METHODS

Electrical-transport measurements are carried out on single crystal samples of $Ce_3Bi_4Pd_3$ grown using Bi/Bi-Pb flux technique. Hall resistivity is measured on a microstructure device (600×50×50 μm^3) of $Ce_3Bi_4Pd_3$ fabricated using focused ion beam (FIB), ensuring excellent sample geometry and alignment of electrical contacts. A piston-cylinder-type pressure cell with Daphne 7373 oil as pressure transmitting medium is used for electrical-transport measurements under external pressures up to 2.3 GPa.

RESULTS AND DISCUSSION

Electrical-resistivity measurements at ambient pressure on well-polished samples of $Ce_3Bi_4Pd_3$ reveal an insulating behavior at low temperatures with a narrow energy gap. The compound becomes progressively more insulating under the application of pressures up to 2.3 GPa, which is a signature of Ce-based Kondo insulating materials in the considered pressure range. Its hybridization gap estimated from Arrhenius fit of the activated behavior in $\rho(T)$, increases quadratically with pressure. This is similar to the behavior observed in the substitution series $Ce_3Bi_4(Pt_{1-x}Pd_x)_3$, which indicates that Pt substitution and applied pressure have a similar effect. The carrier density at low temperatures, obtained from Hall resistivity measurements on a microstructure device of $Ce_3Bi_4Pd_3$, decreases with increasing pressure in a manner consistent with the increase in the energy gap under pressure.



Electrical resistivity of $Ce_3Bi_4Pd_3$ as a function of temperature at different applied pressures. Inset shows the corresponding Arrhenius plot, ln(ρ) vs 1/*T*, along with linear fits.

Our results suggest that the Kondo coupling prevails as the primary tuning parameter in these materials and $Ce_3Bi_4Pd_3$ is a narrow-gap version of the prototypical Kondo insulator $Ce_3Bi_4Pt_3$[5].

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Magnetically-assisted solvent extraction (MaSX) of rare-earth ions by single ligand-laden organic droplet in aqueous bulk

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Rare-earth (RE) elements are important for a variety of high-tech products such as batteries, LEDs, displays, high powered magnets etc.[1]. However, their separation relies on marginal chemical differences, realized in solvent extraction (SX), that include large amounts of non-recyclable chemicals. The resulting environmental issue is further exacerbated by a lack of recycling. For this reason, increasing the separation efficiency of Rare Earths is paramount to increase the yield and reduce the environmental impact of mining. Over the past years, the fascinating phenomenon of RE(III) enrichment at the vicinity of magnet, together with its working principles are reported [2]. This opens up a new separation possibility of a magnetically-assisted solvent extraction concept. The addition of Kelvin-force gives rise to a coupled solutomagnetic convection at a concentration stratification and a magnetophoresis of organic dispersed in rare-earth solution. It is our aim to monitor the transport processes of rare-earth cation exchange towards an increased separation factor.

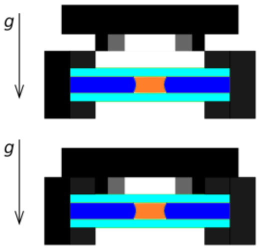

Fig. 1 Hele-Shaw Cell with aqueous and organic phase and Ring magnet (27x16x5mm) 42kJ/m^3

The current phase of investigation is illustrated in Fig.1, it consists of a liquid-liquid solvent extraction. A paraffin droplet containing 0.75 M Pc88a is dispersed into a 0.75 M $DyCl_3$ aqueous phase with pH 1 tuned by HCl. The system is confined in a Hele-Shaw cell with 1 mm gap oriented perpendicular to gravity. The droplet is connected to the top and bottom surfaces of the cell, so that the sidewalls of the droplet are the only reactive interface, as proven by an experiment with an ink dyed aqueous phase.
The extraction reaction of Pc88A-HCl system reads according to [3,4]

$$RE^3 + 3\overline{H_2A_2} = \overline{RE(HA_2)_3} + 3H^+$$

with RE as the rare earth and H_2A_2 as the dimeric form of the organic acid.
Additionally, a magnetic field provided by a ring magnet is introduced to the SX process.
The RE(III) concentration stratification for both cases, i.e. with/ without magnetic field, are monitored by a laser-based Interferometer, preliminary results are illustrated in Fig. 2.

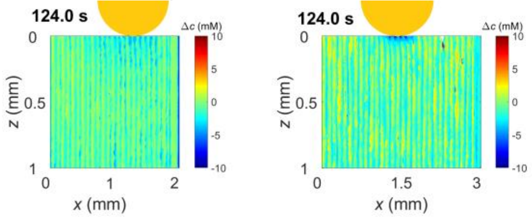

Fig. 2 Concentration gradient below a droplet (yellow half-sphere) after 160s without (left) and with a magnetic field (right)

The snapshot concentration field at 160 s after extraction takes place clearly shows a more pronounced depletion of RE(III) at the vicinity of the organic droplet with a magnetic field present. The concentration field is more stratified in this case as well. The change in concentration around the droplet, after 160 seconds is significantly larger for the magnetic field experiment, reaching 8-9 mM, while it stayed below 5 mM in the other case. This difference continues until the experiment was stopped at 200 seconds. Currently, we are doing systematic studies on this system with parametric variations, to establish scaling laws for MaSX.

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Accurate relativistic quantum chemistry for lanthanide and actinide thermochemistry

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While limited to molecules of relatively small size, accurate quantum chemistry approaches based primarily on coupled cluster theory can yield themochemistry quantities such as bond dissociation enthalpies to within chemical accuracy, i.e., 1-3 kcal/mol. These accuracies typically require the use of composite methodologies whereby several contributions are combined to obtain the final result, e.g., valence electron correlation effects, outer-core correlation, and spin-orbit coupling contributions. The present work utilizes the relativistic Feller-Peterson-Dixon (FPD) approach,[1-2] which has been successfully applied to numerous lanthanide and actinide atomic and molecular systems (as well as other heavy elements throughout the periodic table).

The present talk will focus on three applications, (1) the bond dissociation enthalpies of various thorium- and uranium-containing small molecules, (2) the bond dissociation enthalpy and ionization potential of SmO and (3) predicting the selectivity of model phosphinic acid ligands in Eu(III)/Am(III) separation.

In each case the CCSD(T) method with the scalar relativistic DKH3 Hamiltonian is primarily used with sequences of large correlation consistent basis sets that allow for extrapolation to the complete basis set (CBS) limit. Important spin-orbit coupling contributions are obtained using full 4-component relativistic treatments.

The synergy between theory and experiment will be demonstrated by previous results for the bond dissociation enthalpies of molecules such as ThO^+, $ThCO^+$, and UN^+.[3-5] In nearly all cases the relativistic FPD approach yields results within the experimental uncertainty. In addition, the magnitudes of the individual contributions included in FPD provides insight into what is required for chemical accuracy in these systems.

Experimentally the accuracy of the SmO bond enthalpy has slowly improved over the last many years, with the most recent determination having an accuracy well below 1 kcal/mol.[6] Like many lanthanide oxides, this molecule is also challenging for theory, but as shown in this work, a careful application of the relativistic FPD approach is able to achieve excellent agreement with the most recent experiments.[7]

In order to assess the ability of density functional theory (DFT) to predict the selectivity of Eu(III)/Am(III) separation in soft-donor dichalcogen-phosphinic acid ligands, the exchange reaction $Am(H_2PO_2)_3+Eu(H_2PX_2)_3 \rightarrow Am(H_2PX_2)_3 + Eu(H_2PO_2)_3$ where X=S, Se, or Te, was benchmarked by a CCSD(T)-based FPD approach.[8] It was found that selectivity trends nearly opposite to those of FPD were obtained by DFT unless a signficant amount of exact exchange was included in the chosen functional.

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Rare-Earth Mediated Cross-Over in Dimensionality of a Spin Density Wave in a Ruddlesden-Popper Nickelate

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INTRODUCTION

Charge and spin density waves (CDWs and SDWs) are quantum states that are now recognized to be of fundamental importance in modern condensed matter physics. Nickelates are a platform for investigating the coupling between various forms of charge and magnetic order including SDWs and CDWs and their relation to insulator-metal transitions as well as superconductivity [1]. An intriguing metal-metal transition occurs at temperature T_{MMT} in $R_4Ni_3O_{10}$ (R=trivalent rare earth). Recently, the metal-metal transition was argued to arise from the simultaneous formation of a strongly coupled quasi-2D SDW and 3D CDW based on analysis of incommensurate superlattice peaks observed in single-crystal neutron and X-ray diffraction of $La_4Ni_3O_{10}$ below $T_{MMT} \approx 148$ K [2]. In this work, we investigated the effect of replacing La^{3+} cations, which are non-magnetic having an empty 4f shell, with Pr^{3+} ($4f^2$). In contrast to the vast majority of density waves which don't change dimensionality with temperature, the SDW in $Pr_4Ni_3O_{10}$ morphs from quasi-2D to 3D upon cooling due to an induced SDW on the Pr sites.

EXPERIMENTAL METHODS

Neutron diffraction was collected on MACS and SPINS (NIST Center for Neutron Research) and Corelli (Spallation Neutron Source). Resonant X-ray diffraction was performed at Sector 6-ID-B at the Advanced Photon Source.

RESULTS AND DISCUSSION

Comparison of single crystal neutron diffraction from $Pr_4Ni_3O_{10}$ and $La_4Ni_3O_{10}$ demonstrated both materials developed quasi-2D SDWs at the metal-metal transition as evidenced by broad peaks along the stacking ($\boldsymbol{c^*}$) axis. However, below $T_f \approx 27$ K, significant changes were observed in the $Pr_4Ni_3O_{10}$ data that were not observed in $La_4Ni_3O_{10}$. Specifically, significant enhancement in the total intensity was observed, and the broad scattering along $\boldsymbol{c^*}$ was redistributed into narrow peaks, indicative of cross-over into 3-D order with a doubling of the magnetic unit cell along $\boldsymbol{c}$. The temperature dependence of these changes was consistent with an induced moment on the Pr^{3+} cations. Resonant polarized X-ray scattering confirmed ordering of magnetic moments on Pr^{3+} sites. If the sample was warmed up from the ground-state such that $T_f<T<T_{MMT}$, a metastable state was observed in which the stacking of the SDWs was modified from the original cooled state due to an imprinting effect of the low temperature state. This imprint could only be erased by melting the CDW and SDW states (heating above T_{MMT}). We developed models of stacked SDW layers for the intermediate-temperature (Ni moment only) state on warming and cooling as well as the ground-state which contained SDWs on both the Ni and Pr^{3+} sites. The modelling determined that there was a reorientation of the spin direction in the ground-state as well as the phase shifts between layers that occurred due to exchange interactions along $\boldsymbol{c}$. A Hamiltonian including the exchange interactions and single ion anisotropy was developed which explains the metastable imprinting.

CONCLUSIONS

We observed a cross-over from a quasi-2D SDW involving only Ni moments into a 3D SDW which results from the interactions between induced moments on the Pr cations with the Ni moments. The CDW on the Ni sites is unaltered by this magnetic cross-over. After the Pr order melts, a metastable imprint is left upon the Ni SDW. The results demonstrate the viability of controlling density wave states via *d-f* interactions.

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Inorganic Receptors for Phosphate for Medical and Environmental Applications

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INTRODUCTION

Accumulation of phosphate in many inland and coastal waters primarily due to wastewater discharge and agricultural runoff can lead to eutrophication, causing substantial detrimental environmental impact including harmful algal blooms, fish-kills, and the formation of hypoxic dead zones. Accumulation of phosphate in blood, a condition called hyperphosphatemia, affects most patients with advanced chronic and acute kidney disease and kidney failure. Maintenance hemodialysis does not remove phosphate from blood effectively; thus, almost all patients on maintenance hemodialysis have hyperphosphatemia. The inability to manage this disorder contributes significantly to the increase in morbidity and mortality of advanced kidney disease. Both of these problems could be resolved with immobilized phosphate receptors that have high affinity for phosphate in water and that are highly selective over competing anions, notably bicarbonate and chloride. Through the development of these receptors, we determined how minor differences in the ligand lead to substantial changes in recognition of anions by the metal complex. The nature of the coordinating group, that of the metal ion, the geometry of the metal complex, its charge, and the presence of a hydrogen-bonding network all affect anion recognition, binding, and selectivity. Lastly, in order to be translatable and economically viable, any blood- or water-filtering technology must also be regenerable. This property requires receptors that are both reversible and controllable. The ability of our inorganic receptors complexes to catch phosphate and release it at will upon addition of an external trigger makes them promising candidates for the development of a new class of recyclable selective filtration technology.

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Soft Donor vs Soft Matter: Controlling Transplutonium Chemistry

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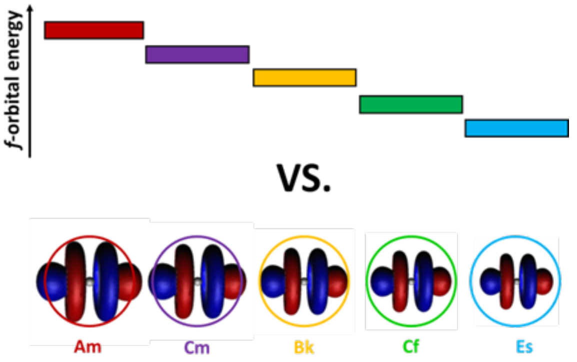
INTRODUCTION

The elements at the basement (er…foundation) of the periodic table represent where chemistry is both the least understood and most desperately needs to be controlled to address 21st century energy and security needs. Recent discoveries in the chemistry of the actinides heavier than plutonium have suggested our current understanding of chemical bonding is insufficient to fully predict actinide chemistry across the series.[1-3] This has ramifications for our ability to develop more efficient and proliferation resistant advanced nuclear fuel cycles, secure the actinides for long-term geological disposal and advance nuclear forensics technologies. This presentation will focus on highlighting the unique, fun chemistry of the heaviest actinides. Heavy actinide chemistry discussions will consider how covalency manifests for the heavier actinides and provide some preliminary thoughts regarding what questions still exist in controlling actinide-ligand interactions relevant to practical systems. The material presented will both highlight how experimental chemical information can be discerned from nanogram amounts of a given element and interpreted in more detail using computational methodologies. We will seriously consider the chemistry of dipicolinic acid, and derivatives thereof, as well as thio-based extractants in this discussion.



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Lessons Learned from Lanmodulin in the Selective Recognition and Separation of f-Elements

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ABSTRACT

Lanthanides have been shown recently to be essential enzyme cofactors in certain bacteria.[1] Understanding the coordination chemistry underlying biological recognition of lanthanides promises to yield new strategies for the selective detection, extraction, and separation of rare earths, with applications ranging from mining to medicine.

I will describe my laboratory's work providing the first biochemical insights into how lanthanides are selectively recognized and acquired in biological systems, including the discovery and characterization of lanmodulin, the first selective, natural macrochelator for lanthanides.[2-4] In addition to presenting fundamental aspects of biochemical rare earth recognition emerging from our biophysical and mechanistic characterization of this remarkable protein, I will also discuss case studies illustrating how our team has leveraged lanmodulin itself, as well as the principles learned from it, for the development of robust and efficient biotechnologies for detection,[4-5] extraction,[6] and separations[7] of rare earths and actinides[8-9]. These studies highlight the unexpected yet unique potential of proteins to address long-standing challenges in f-element chelation and separation.

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Lanthanides for smart mobile optical sensing and the Internet of Things

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Abstract

Sensors play a key role on the Internet of Things (IoT) providing monitoring inside and outside the communication networks in a multitude of parameters[1]. The coupling of optical sensors to smartphones appears as an exciting strategy for the new generation of mobile optical (mOptical) sensing. Photoluminescence stands out as a non-invasive spectroscopic method based on the dependence of the phosphor emission on the measurand (*e.g.*, temperature) which is often translated into color variation easily accessed by the smartphone camera. The intrinsic characteristics of the intra-4f transitions of lanthanide ions (Ln^{3+}) provide color purity and tuneability required for image-based sensing. Nowadays, the IoT has an astonishingly societal impact in which healthcare services stand out. Amplified by the COVID-19 pandemic scenario, challenges include the development of authenticatable smart IoT devices with the ability to simultaneously track people and sense in real-time human body temperature aiming to infer a health condition in a contactless and remote way through user-friendly equipment such as a smartphone[2]. Luminescence thermometry and physically unclonable functions (PUFs) will be simultaneously combined allowing non-contact temperature detection, identification, and connection with the IoT environment through a smartphone.

Keywords. Lanthanides, Internet of Things, optical sensor, mobile sensing; smartphone

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Tuning Divalent Europium for Magnetic Resonance Imaging

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Hypoxia has implications in the study of many diseases,[1] making it a critical target for imaging. One potential method to image hypoxia is using oxygen-responsive contrast agents for magnetic resonance imaging. Divalent europium, which is isoelectronic with Gd^{III} that is used clinically for imaging, was studied as a means to perform such imaging around the turn of the last century.[2] Those pioneering studies revealed a need to tune the electrochemistry of the $Eu^{II/III}$ couple to enable in vivo imaging studies. We hypothesized that this need could be met by modifying ligands to favor divalent Eu over trivalent Eu. Testing this hypothesis let to a series of studies that unearthed new europium chemistry as well as in vivo imaging of hypoxia. I will present our studies that explore the tuning of the $Eu^{II/III}$ electrochemical potential; the properties of Eu^{II}-containing complexes as contrast agents for magnetic resonance imaging; in vivo studies of Eu^{II}-containing complexes as oxygen-responsive contrast agents for magnetic resonance imaging; and ways to detect Eu^{III} upon oxidation of Eu^{II}-based contrast agents. These studies are advancing our ability to image hypoxia

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The “Soul Memory of a Million Dead Stars” – Revealing the Topology of Rare Earth Chemistry

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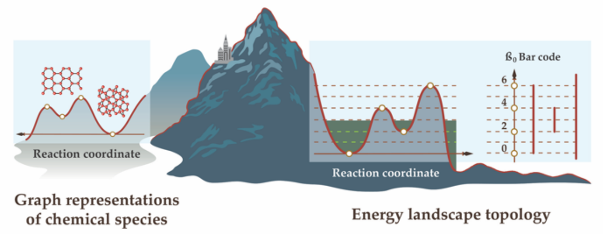
Rare earth chemistry is imbued with notions of shape: the distributions of electrons influenced by relativity, the design of ligands preorganized for selectivity, the phase boundary traversed during separations. Characterizing and predicting shape is the domain of topology and geometry. Integrating the state-of-the-art tools of applied math with rare earth chemistry provides new avenues for fundamental science and improved applications. Such tools further maintain interpretability when employed in machine learning. This work provides background and examples to create an appreciation for the role of topology within rare earth chemistry, inspire new chemical models and the adoption within modelling and experiment.

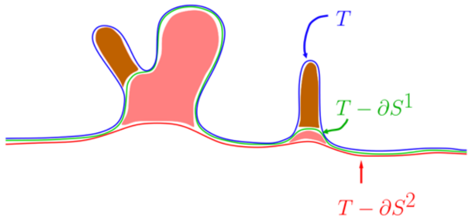
INTRODUCTION

Rare earth chemistry, whether in isolated molecules, hard materials, or disordered soft matter is often highly nuanced, influenced by small variations in distributions of relevant variables. Consider how sublte changes to hydration, primary coordination geometry and charge distributions are leveraged for design strategies in selective complexation and separations across the lanthanides.[1,2] Although much empirical knowledge exists regarding the essential “shape of data” associated with rare earths, few attempts provide mathematical descriptions for the topological and geometric foundations of electronic and geometric structure underpinning variations in chemical behavior. Yet mathematical descriptions provide the basis for new chemical and predictive models that leverage experimental and simulation data.

Within the last decade, concepts from algebraic topology have been combined with computation to characterize the global shape of data. Advanced network analysis tools based upon graphs of chemical data (e.g., networks of intermolecular interactions) fall within this realm and have been used to identify speciation of rare earths in complex multicomponent solutions, and to characterize complexation and transport mechanisms at oil/water phase boundaries.[3] As a means to encompass higher dimensionality, topological data analysis (TDA) is an approach that has observed massive development over the last decade. For example, persistent homology is a TDA method that produces compact summaries of the global shape and topology of sets of points in the form of barcodes. Given a collection of data sets, persistent homology quantifies and compares global shapes of the data by measuring distances between their barcodes. Statistical analyses on collections of such barcode distances may also be used to distinguish between different distributions. This approach can be used to identify chemical reactions, analyze electron density distributions in dynamic chemical environments, and make connections to underlying energy landscapes.[4]



Complementing graph theory and TDA applications for rare earths is the analysis of geometric structure, specifically through the use of geometric measure theory. In this case, the surfaces associated rare earth hard or soft matter (e.g., the solvent accessible surfaces of metal-laden amphiphile assemblies in the organic phase, or the surface macrostructures that support transport) can be analyzed to reveal differentiating characteristics that would not normally be feasible.[5]



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Toroidal Moments in Molecular Magnets

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The first molecule to be identified as possessing a toroidal moment was a Dy_3 triangle which was synthesized in our group.[1-3] A toroidal arrangement of magnetic spins can be recognized a chiral propeller structure with the sense of rotation being either clockwise or anticlockwise. This leads to exotic behavior in the toroidal regime which above a given critical applied field moves to a more normal magnetic regime, including that characteristic of Single Molecule Magnets (see Figure 1). Progress on investigating toroidal systems will be described in this contribution with a particular emphasis on systems involving the Dy^{III} ion.

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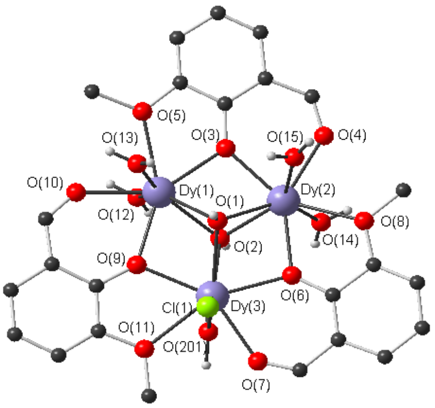

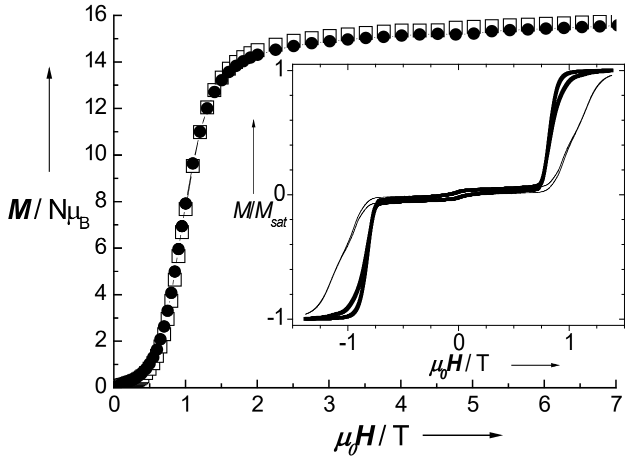

Figure 1. Molecular structure of $[Dy^{III}_3(m_3\text{-}OH)_2(van)_3(OH_2)_2(Cl)]^{3+}$ (left) and magnetization and hysteresis typical for a toroidal system transitioning to single molecule magnet behavior (right).

Chemistry and Topology of Spin-Orbit Coupling and Competing Interactions in Ternary, Tetravalent Lanthanide Chalcogenides

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Rare-earth-based insulating magnets are of broad interest because of their strong spin-orbit coupling (SOC) and inherent anisotropy. In the traditional picture, the SOC multiplet is split by the crystal electric field (CEF) which acts as a second order perturbation on the Hund's rule ground state multiplet. Overall, metal-ligand bonds are not very covalent in trivalent lanthanides and an ionic picture often prevails. By changing the oxidation state of the lanthanide from +3 to +4, however, the metal-ligand bond becomes much more covalent ($4f$-$2p$ hybridization). This change makes leads to SOC and CEF in tetravalent lanthanides (Ln^{4+}) to be of comparable energy scales and requires an intermediate coupling model. A a result, Ln^{4+} materials could potentially host interesting phenomena usually associated with d-electrons, such as superconductors, spin-liquids, Mott insulators, and metal-insulator transitions.[1] In fact, Na_2PrO_3, a honeycomb oxide with Pr^{4+} has been proposed to host Kitaev interactions. [3]

In this presentation, I will describe our studies towards understanding the topology of competing interactions (SOC vs CEF, hybridization (V_{eff}) vs charge transfer (CT)) in insulating Ln^{4+} oxides. Through a combination of spectroscopic, structural, and thermomagnetic measurements, I will establish a cohesive model to understand the electronic structure of Ln^{4+} materials and apply it towards developing fundamental design principles for quantum information sciences.

In order to understand the ground state electronic structure of Ln^{4+} ions, CEF measurements using INS and FIRMS were carried out on a series of Ln^{4+} oxides with primary focus on Pr^{4+}.[4] Pr^{4+} with $4f^1$ electronic configuration is isoelectronic to Ce^{3+}. Based on our recent investigations on Na_0PrO_3, the first CEF level was identified at 230 meV with a substantially large antiferromagnetic exchange interaction ~ 1.2 meV (typically 0.3-0.5 meV for Ln^{3+}) both of which have been attributed to enhanced $4f$-$2p$ hybridization.[3] The series of Pr^{4+} oxides allows us to tune CEF by changing the local symmetry (CEF ranges from 160 meV to 230 meV based on the local symmetry). A point charge model using Stevens operators in the intermediate coupling limit was developed to extract the ground state wavefunction of Pr^{4+} single-ion. Due to competing CEF and SOC interactions, ground state has contributions from different excited states. Evidence of $4f$-$2p$ hybridization in Pr^{4+} and consequences of increased covalency on single-ion properties, exchange interactions, and collective beghavior in Pr^{4+} oxides were studied using a combination of $M_{4,5}$ edge and O K-edge XAS and XMCD spectroscopies.

I will also present our recent efforts towards understanding ground state donor covalent bonding in a series of Ln^{4+} oxides.[5] A band structure model to describe ground state donor covalent bonding was developed using a combination of O K-edge XMCD, $M_{4,5}$ edge XAS/XMCD, L_3 edge XANES, L_3-edge HERFD-XANES, and thermomagnetic measurements. Donor covalent bonding in the ground state has been attributed to competition between charge transfer and hybridization energies. Comparisons will be made to high-valent transition metal oxides where a similar behavior has been observed resulting in a universal model to describe donor covalent bonding in high-valent insulating oxides. The universal model will be differentiated from multiconfigurational behavior observed in lanthanide/actinide intermetallics using a directional hybridization scheme.

Lastly, a chemical approach to tune oxidation state in a series of layered lanthanide materials using reductive intercalation/ oxidative deintercalation will be discussed. Change in oxidation state has been tracked via L_3-edge XANES, in-situ/ex-situ UV/Vis, thermomagnetic measurements, and structural changes. With these observations, I will lay out our fundamental design principles for developing applications of these properties in functional magnetic materials including qubits.[6]

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Fine-Tuning the Electron Spin Wavefunction with Magnetic Dipoles in a Series of Er(III)-based Molecular Complexes

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Many of the models of lanthanide electronic structure honed within the field of molecular magnetism are optimized for creating maximal anisotropy. Redirecting these models toward more complex challenges in quantum information science and spin-charge interaction offers an exciting possibility to expand the palette of viable materials of interest for synthetic magnetochemists while also contributing to new fields. To do this effectively, however, a focused research effort on developing more intuitive means of controlling the spin wavefunction at small energy scales is needed. At the ~1 cm^{-1} energy scale, the dominant interactions are often difficult-to-predict, transient combinations of competing effects. Thus, a predictable, isolated mechanism dominating the wavefunction interactions could be highly useful.

This talk will focus on use of a highly predictable local anisotropic dipolar coupling as a mechanism to generate state interactions with the potential for a priori knowledge of the resulting density matrix. To facilitate the discussion, we present a series of mono-, di-, and tri-nuclear erbium-based single-molecule magnets with intranuclear coupling at the Ising dipolar limit ($\alpha = 1$, Figure 1). Magnetic data coupled with detailed ab initio computational studies are used to discern the role and effects of dipolar coupling on relaxation behaviors and understand how to gain control over low-lying quantum states through angular orientation of dipole interactions between single-ion cluster subunits.

The predictable nature of coupling in the model built up from magnetic relaxation and ab initio data justifies a simple, a priori design principle for complex, ground-state manifolds based on control of only two crystallographically derived geometric parameters. This immense simplification and tethering of spin space and crystallographic space offers a path toward intuitive paradigms for design of magnetoelectronic structure of materials with higher symmetric complexity and higher dimensionality.

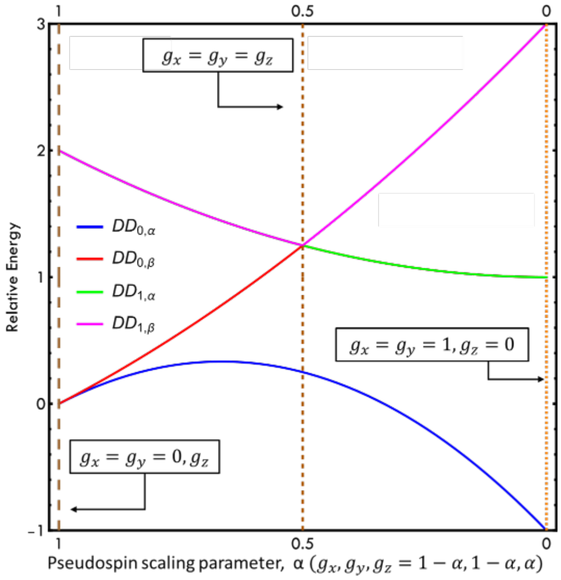

Figure 1. Representative energy diagram for two identical pseudospin ½ states interacting via the magnetic dipole-dipole interaction as a function of the initial state anisotropy. The diagram is represented as eignevalues of the Dipole Doublet (DD) states comprised of linear combinations of pseudospin ½ states with $g_x = g_y = 0$ and $g_z = 1$ (i.e. $\alpha = 1$).

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RE-Designing Catalysts to Overcome Challenges in Polymer Synthesis

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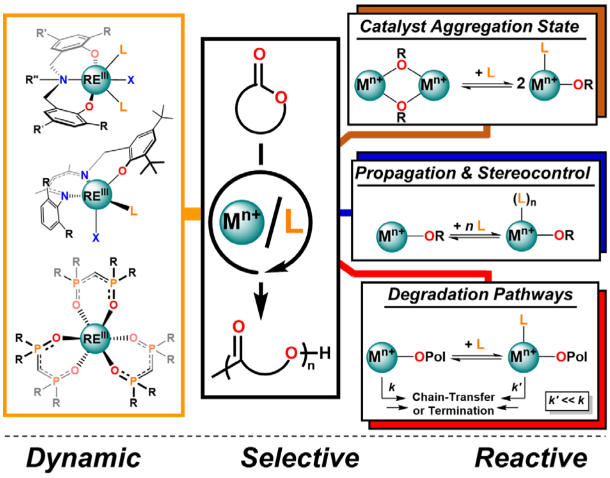
Polymers play a central role in nearly every aspect of our lives, but the remarkable production volumes and slow environmental degradation of traditional polyolefins is contributing to one of the greatest environmental concerns for current and future generations. This continues to drive the search for more sustainable alternatives that not only meet the materials properties needed in current and future applications, but also deliver enhanced degradability and possible chemical recyclability. The ring-opening polymerization (ROP) of cyclic esters can provide access to biodegradable polymers with materials properties that can be tailored through appropriate catalyst design, where rare-earth catalysts are among the most active and selective discovered to date. Conventional catalyst design and reaction optimization have focused on systematic covalent modifications of ancillary ligand frameworks, yet many significant challenges remain unanswered.

In this talk, I will present our group's recent efforts towards the design of highly dynamic, selective, and reactive catalysts to address these challenges in the ring-opening polymerization of cyclic esters.[1-5] This largely takes advantage of labile neutral donor ligands, which can dramatically amplify catalyst performance in a rational, inexpensive, and operationally simple manner. For aminobisphenolate-based catalysts, this can enable new reactivity and selectivity patterns that are inaccessible to tethered (hemi-labile) systems, and generates some of the most active and isoselective catalysts for the ROP of *rac*-β-butyrolactone reported to date. For multifunctional β-diketiminate aryloxide catalysts, control of ligand dynamics can carefully tune reactivity and selectivity in stoichiometric and catalytic processes. Finally, highly-fluxional, homoleptic bis(phosphine-oxide)methanide catalysts display unique, metal-ligand cooperativity which can be leveraged to access ultra-high molecular weight polylactide. Strong connections between catalyst structure, ligand exchange dynamics, and catalyst performance will be made, which set the stage for leveraging these effects more broadly in polymerization, catalysis, and beyond.



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On Rare-Earth Metal Halide Oxido-Arsenates and -Antimonates

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Halide oxidoarsenates(III) containing trivalent rare-earth metals (*RE*) occur with three different compositions so far, when only chloride and bromide derivatives (X = Cl and Br) are considered: $RE_5X_3[AsO_3]_4$, $RE_3OX[AsO_3]_2$ and $RE_3X_2[As_2O_5][AsO_3]$. Their commonalities are ψ^1-tetrahedral $[AsO_3]^{3-}$ anions as triangular pyramids with stereochemically active non-binding electron pairs (lone pairs) at the As^{3+} cations along with mixed coordination polyhedra of oxygen atoms and halide anions around the RE^{3+} cations providing them coordination numbers as high as seven, eight or nine if necessary. The monoclinic examples $RE_5X_3[AsO_3]_4$ crystallize with the space groups $C2/c$ or $P2/c$ [1] displaying $[REO_4X_4]^{9-}$ and $[REO_8]^{13-}$ polyhedra in the shape of square antiprisms. All members of the tetragonal $RE_3OX[AsO_3]_2$ series with the space groups $P4_2/mnm$ or $P4_2nm$ [2] show additional O^{2-} anions not bonded to any As^{3+} cations, which govern the crystal structures by forming chains of *trans*-edge connected $[ORE_4]^{10+}$ tetrahedra. For the triclinic representatives with the structured formula $RE_3X_2[As_2O_5][AsO_3]$ adopting the space group $P\bar{1}$ [3], pyroanionic $[As_2O_5]^{4-}$ anions consisting of two vertex-sharing $[AsO_3]^{3-}$ units recruit the extra ingredient.

Analogous compounds with the heavier congener antimony seem to be restricted to the formula type $RE_5X_3[SbO_3]_4$ (monoclinic, $P2/c$) [4] and only occur after reactions under halide-rich conditions. Otherwise rare-earth metal(III) oxidoantimonate(III) halides with the composition $RESb_2O_4X$ are encountered, which exhibit completely different structural features in their three different crystal structures known so far. All RE^{3+} cations have only contact to oxygen atoms by forming square $[REO_8]^{13-}$ prisms. With lanthanum and the light lanthanoids (*RE* = La – Sm) their tetragonal crystal structure (space group: $P4/nmm$ or $P4/mmm$) contains anionic layers of vertex-sharing square pyramidal $[SbO_4]^{5-}$ units (square ψ^1-pyramids) according to ${}^{2}_{\infty}\{[SbO_{4/2}]^-\}$. The halide anions have little or no contact to the RE^{3+} cations, but settle with far away Sb^{3+} cations at positions, where four of them encircle their stereochemically active non-binding electron pairs (lone pairs) [4]. The $RESb_2O_4X$ representatives with mid-size lanthanoids (*RE* = Eu – Dy) show monoclinic crystal structures with space group $P2_1/c$ and contain meandering chains ${}^{1}_{\infty}\{[SbO_{2/2}O'_{1/1}]^-\}$ of vertex-sharing triangular pyramidal $[SbO_3]^{3-}$ units (ψ^1-tetrahedra) and again square $[LnO_8]^{13-}$ prisms without halide contacts, but halide anions in proximity to Sb^{3+} cations at positions rather close to their electronic lone pairs [4]. Finally the tetragonal examples $RESb_2O_4X$ with *RE* = Y and Gd – Lu, crystallizing with the non-centrosymmetric space group $P42_12$ repeat all the features of the two above-mentioned other structures (edge-sharing square $[REO_8]^{13-}$ prisms without any X^- ligands, halide anions not far from Sb^{3+} lone pairs), but the antimony-oxygen partial structure is now built up from eight-membered $[Sb_4O_8]^{4-}$ rings of corner-sharing $[SbO_3]^{3-}$ ψ^1-tetrahedra [4, 5], all pointing with their lone pairs at the Sb^{3+} cations into the same direction along [001]. So there is a strong diversity of the antimony-oxygen partial structure $(SbO_2)^-$ for the three different $RESb_2O_4X$ examples: the $P4/mmm$ case shows layers of vertex-sharing square $[SbO_4]^{5-}$ ψ^1-pyramids according to ${}^{2}_{\infty}\{[SbO_{4/2}]^-\}$, the $P2_1/c$ case exhibits ${}^{1}_{\infty}\{[SbO_{2/2}O'_{1/1}]^-\}$ chains of vertex-sharing triangular $[SbO_3]^{3-}$ ψ^1-tetrahedra and the $P42_12$ case has the same building blocks, but now offers ${}^{0}_{\infty}\{([SbO_{2/2}O'_{1/1}]^-)_4\}$ rings as tetragonal *cyclo*-alternative to the monoclinic *catena*-example.

In the realm of fluoride derivatives, the formula type $RE_5F_3[AsO_3]_4$ shows up again, but the tetragonal crystal structure of $La_5F_3[SbO_3]_4$ (space group: $P4/ncc$) [6] with *RE* = Y, Ho – Lu [7] avoids to form a layer-like arrangement as found in the monoclinic $RE_5X_3[AsO_3]_4$ representatives (*RE* = La – Sm; X = Cl and Br) [1]. In fact a three-dimensional network occurs, using mixed-anionic $[REO_8F]^{14-}$ and $[REO_6F_2]^{11-}$ polyhedra along with discrete $[AsO_3]^{3-}$ or $[SbO_3]^{3-}$ ψ^1-tetrahedra as most prominent structural features.

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Using the Theory of Critical Phenomena to Understand Structure and Phase Transitions in Separations of Rare Earths

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INTRODUCTION

Understanding the molecular-scale origins of structure and phase transitions in multicomponent, hierarchically structured soft matter phases is a fundamental challenge. One application affected by these phenomena is liquid-liquid extraction, a predominant low-energy separations technique. This technique is a go-to process for materials recycling, including the recovery of rare earth elements [1]. The complex solutions encountered in these applications feature structure at the nanoscale, which is understood to affect the subtle energetic balance used to control the separation process [2]. Further, a fundamental limitation to liquid-liquid extraction are undesirable liquid-liquid phase transitions that occur upon sufficient loading of, e.g., lanthanide ions into extractant-containing organic phases. Here, we discuss ongoing work seeking to understand how solution structure and phase behavior are fundamentally connected in a way that can be understood by applying the theory of critical phenomena.

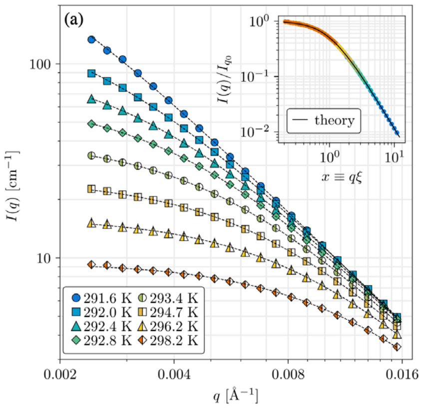

Figure 1: Temperature dependent structure of the organic phase, upon extraction of cerium nitrate by a malonamide extractant, is consistent with critical point theory [1].

RESULTS AND DISCUSSION

Mesostructuring in organic phases upon extraction of different lanthanides using different extractants all follow critical point theory (Fig. 1), showing critical fluctuations consistent with a psudeobinary compositional order parameter [3,4]. By combining small angle X-ray scattering with molecular dynamics simulations, we demonstrate how organic phase structure over a wide range of process-relevant composition space is dominated by critical fluctuations [5,6]. Scaling relations provided by critical point theory create a quantitative connection between aggregation in the organic phase and its phase behavior, deepening our understanding of both.

CONCLUSIONS

The relationship investigated here between structure and phase behavior will inform the design of more efficient separations processes and, more broadly, explore how critical phenomena manifest in complex solutions whose structure and thermodynamics are governed by intermolecular interactions that span length and energy scales.

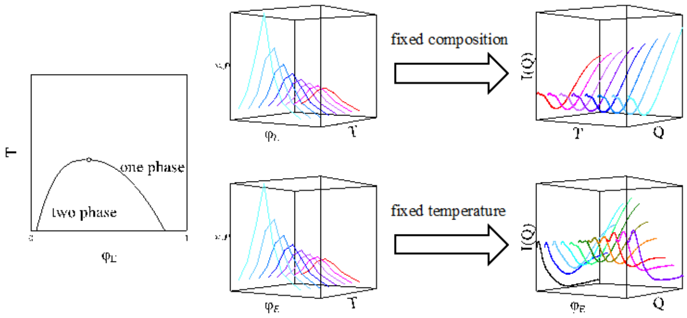

Figure 2: Critical composition fluctuations explain the relationship between structure and phase behavior for changes to system parameters, such as composition and temperature.

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Lanthanide Texaphyrins: An Update on Drug Development Efforts

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INTRODUCTION

Texaphyrins were the subject of two clinical drug development programs under the aegis of Pharmacyclics, Inc. in the 1990s and early 2000s. Neither program culminated in an FDA approval. Starting a decade or so ago our group in collaboration with a number of other researchers began to develop texaphyrins as platform carrier for other active drug species. This presentation will provide an update on these efforts, which are now being spearheaded by OncoTEX, Inc.

RESULTS AND DISCUSSION

This lecture will present the development of expanded porphyrins as potential drug leads. The presentation will begin with a personal story of a 3x cancer survivor and how with the assistance of great coworkers and collaborators an effort has been made to fight back against this disease by studying the chemistry and anti-cancer biology of gadolinium(III) texaphyrins.

Texaphyrins were the first of the so-called expanded porphyrins--larger analogues of heme pigments--to stabilize a 1:1 complex with a metal cation.[1] Subsequently, and continuing as a focus today, an effort has been made in our laboratories and those of many others to create additional expanded porphyrins. Hundreds are now known. Several from our laboratory have proved useful at stabilizing actinide cation complexes.[2] The texaphyrins have received particular focus in the context of drug development. These efforts will be the primary focus of this presentation.

The best developed system is a lead compound termed OxaliTEX-Pt(IV). It is a conjugate between a Pt(IV) analogue of the FDA approved drug oxaliplatin and a modified version of the original gadolinium texaphyrin studied by Pharmacyclics, Inc. (motexafin gadolinium or MGd). This conjugate shows promise in so-called patient derived xenografts in both ovarian and colorectal cancer mouse models.[3] The evolution of this lead and the results of preclinical testing supporting the licensing of this system to OncoTEX will be detailed. Work involving other therapeutic-derived texaphyrin conjugates will also be summarized, as well as potential applications in photoacoustic imaging will be detailed.[4]

As time permits unrelated studies involving the use of other so-called expanded porphyrins as ligands to support the formation of actinide complexes, including those of Np(IV) will be presented.

New work involving a modified version of an FDA approved iron decorporation agent as a chelator for lanthanides and actinides will also be discussed.

CONCLUSIONS

We conclude that texaphyrins have a role to play as unique platforms for drug delivery and that, as a class, expanded porphyrins are well positioned to advance our understanding of rare earth chemistry. The search for new ligands also remains important. Our recent contributions along the latter lines provide a springboard for future efforts.

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Materials Growth and Discovery for Europium-based Quantum Information Storage

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The optical excitations of rare-earth ions provide uniquely long coherence times, and their ability to couple to other optical systems gives them an intrinsic advantage when forming integrated systems for quantum information storage, communication, or computing. Historically, rare-earth ions in transparent crystals have been used as laser gain media, where the rare-earth ions are dopants, present in small concentrations, and randomly substituted with optically-inactive host ions. While much is understood about these systems, serious challenges arise when storing quantum information because the variation in coordination environments of the rare-earth ions leads to spectral broadening that makes the hyperfine splittings unresolvable. In order to access and write distinct states, the coordination environments must be sufficiently uniform, which has been demonstrated to be achievable in a stoichiometric (undoped) crystal $EuCl_3 \cdot 6H_2O$ by Ahlefeldt, *et al.* [1-2] This material possesses the requisite crystallographic perfection to resolve the nuclear hyperfine states, ultimately with 25 MHz inhomogeneous linewidth. Deploying a viable quantum information system should reproduce these metrics without the shortcomings of $EuCl_3 \cdot 6H_2O$: it is hygroscopic and degrades in air, and the electron-phonon coupling necessitates isotopic purification with ^{35}Cl.

We are developing new candidates for Eu^{3+}-based quantum information storage, with a focus here on two framework materials, Eu-formate $Eu(HCOO)_3$ and Eu-formate-formamide $Eu(HCOO)_3 \cdot (HCONH_2)_2$. These materials display the required $^5D_0$-$^7F_0$ transition at 579 nm and have large Eu-Eu spacings of 4.0 and 6.6 Å, respectively. [3] This preliminary work leads to a broader set of questions: (1) what is the maximum density of Eu^{3+} permissible in such a material for the individual ions to be equivalent, (2) how close can Eu^{3+} ions be in a solid to retain "atom-like" optical spectra, and (3) given these constraints, how many undiscovered materials are likely to host the ideal set of properties? We will present results on synthesis and computational modeling that addresses these questions.

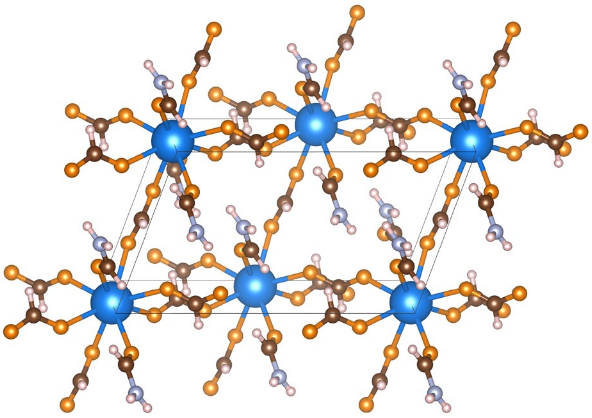

Figure 1. Unit cell of Eu-formate-formamide. The shortest Eu-Eu (blue) distance is 6.6 Å.

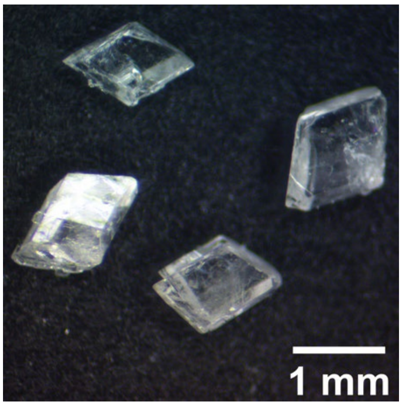

Figure 2. Crystals of Eu-formate-formamide.

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Rings and Cages in Rare Earth Chemistry

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INTRODUCTION

The synthesis and structural characterization of ferrocene [$FeCp_2$] (Cp = C_5H_5) paved the way to modern organometallic chemistry about 70 years ago.[1-3] Ever since, sandwich complexes became widely used in different fields of chemistry ranging from basic research to industrial applications. Therefore, there is still a high demand for new synthetic approaches towards ever new sandwich compounds with striking properties and structural features.

In terms of cages, Zintl anion and Zintl cluster chemistry is a traditional topic in inorganic chemistry.[4] However, recent spectacular new findings did not only result in new structural motifs but also shed some light into the formation of nanomaterials.

RESULTS AND DISCUSSION

Aromatic organic and inorganic ring systems were coordinated to the lanthanides. The synthesis of the first well-defined neutral and homoleptic (same metal, same ligand) all-carbon based quadruple-decker complex along with other unique sandwich complexes is shown. Besides the synthesis of this archetypal compound mechanistic studies for its formation were performed (Figure 1, left).[5]

By using unusual heterocycles, we succeed in the synthesis and characterization of heteroleptic lanthanide complexes bearing a dianionic η^5-plumbole ligand in their coordination sphere (Figure 1, right). In-depth *ab initio* calculations show that the aromaticity of the dianionic plumbole is retained upon coordination. Electron delocalization occurs from the plumbole HOMO to an orbital of mainly d-character at the lanthanide ion. The magnetic properties of the erbium congener were investigated in detail.[6]

For the first time, we also introduced aromatic inorganic rings as ligands in f-metal chemistry. For this purpose, the cyclic units E_4^{2-} (E = P, As) were synthesized by a reduction of P_4 or As_4 with Sm^{II} reagents.[7-8]

Lanthanide polypnictogenide compounds were synthesized as cage compounds. Here we focused mainly on Zintl compounds. By the activation of the solid state material $As^0_{(nano)}$ (nanoscale gray arsenic) with multi electron reducing agents, the Zintl anions As_3^{3-}, As_7^{3-} and As_{14}^{4-} were coordinated to the lighter lanthanides. These Zintl anions were previously not accessible in molecular 4f-element chemistry. Additionally, the corresponding compounds with As_{14}^{4-}-moieties represent the largest organo-lanthanide-polyarsenides known to date.[9]

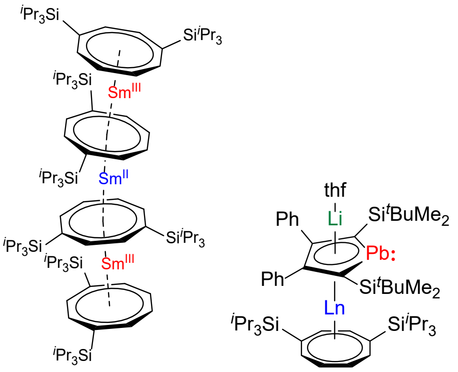

Figure 1. (left) The first well-defined neutral and homoleptic (same metal, same ligand) all-carbon based quadruple-decker complex. (right) The first plumbole complex of the f-elements.

CONCLUSIONS

Our findings highlight that the structural diversity of 4f-element metallocenes and Zintl compounds is still far from being fully explored. New synthetic stratgies and precursor open the door to fundemtal new compounds.

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Molecular Light-Upconversion: When Excited State Absorption (ESA) Overcomes Energy Transfer Upconversion (ETU) In Cr(III)/Er(III) Complexes

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For a long period, metal-based linear light-upconversion, i.e. the conversion of near infrared (NIR) light into emitted visible light by successive linear absorption of NIR photons, was limited to statistical doping of low phonon bulk solids and garnets. The design of closely related upconversion processes operating in nanoparticles allowed to reach the nanoscale.[1] The next miniaturizing step aims at implementing linear light upconversion at the molecular level.

Achieving this goal requires either the piling up of low-energy near-infrared photons onto a single short-lived lanthanide center via excited state absorption (ESA), or the alternative energy transfer upconversion (ETU) mechanism, which combines a short-lived lanthanide activator surrounded with long-lived sensitizers.[2] However, only a very few numbers of sophisticated multi-center devices, which exploit the indirect ETU mechanism, have been evidenced in molecular complexes and the ESA mechanism has been only recently implemented in a few isolated coordination complexes. The judicious wrapping of three polyaromatic ligand strands around trivalent erbium in $[\mathrm{GaErGa}(\mathbf{L1})_3]^{9+}$ or $[\mathrm{CrErCr}(\mathbf{L1})_3]^{9+}$ indeed brought a small revolution with the demonstration that low-power room temperature near-infrared to green light upconversion can be programmed in mononuclear coordination complexes.[3]

In this contribution, the erbium-centered downshifted emission and NIR to visible upconversion and their quantifying in molecular complexes will be discussed as well as their mechanisms. The associated quantum yields measured for ESA and ETU appear to be larger than those predicted with theoretical models. An unexpected boosted ESA process is proposed for reconciling predictions and measurements.[4]

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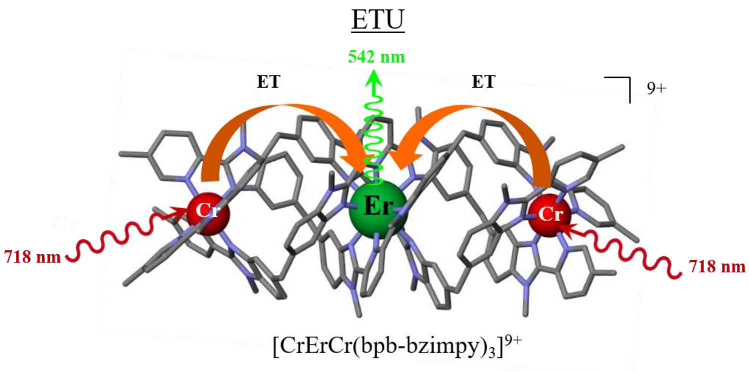

Figure 1. Molecular structure of Erbium-based coordination complexes exhibiting linear upconversion processes and associated kinetic model for the single- ion ESA process.

Macrocyclic 1,2-HOPO Bifunctional Chelators for Time-Resolved Europium(III) Luminescence and Radiopharmaceutical Applications

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The usefulness of a bifunctional chelator (BFC), in both time-resolved europium(III) luminescence and radiopharmaceutical applications, depends largely on the ability of the chelator to retain the metal ion of interest under challenging conditions. Macrocyclic BFCs are therefore preferred, since macrocyclic chelators can form metal complexes with greater stability (both kinetic and thermodynamic) than nonmacrocyclic analogs. With the aid of a new bridging variant of 1-hydroxypyridin-2-one (1,2-HOPO), we have synthesized and characterized a new family of macrocyclic 1,2-HOPO BFCs which form bright and stable europium(III) complexes. The peak absorbance of the europium(III) complexes (~362 nm) is well-suited to take advantage of inexpensive UV LED light sources operating at 365 and 385 nm. The bright europium(III) time-resolved luminescence has been leveraged to investigate the significantly improved kinetic and thermodynamic stability of these macrocyclic europium(III) complexes compared to nonmacrocyclic 1,2-HOPO analogs. Consistent with the photophysical data, crystallographic characterization of the parent europium(III) complex confirms that the inner coordination sphere of the europium(III) cation is fully saturated by the four bidentate 1,2-HOPO binding units (Fig. 1). The new macrocyclic BFCs have also been labelled with lutetium(III), zirconium(IV), and thorium(IV), which occurs quickly at room temperature. The ease of metalation and excellent stability of these additional metal complexes support development of novel radiotheranostic agents using one BFC for Lu-177, Zr-89, and Th-227. The lanthanide-free BFCs can be coupled (with amide linkages) to a variety of targeting moieties using N-hydroxysuccinimide (NHS) coupling chemistry. As a demonstration of utility, we have conjugated an antibody with one of the new macrocyclic 1,2-HOPO BFCs (Lumi804), and the conjugate was quantitatively labelled with europium(III) in 5 min at room temperature. The resulting Eu-Lumi804-antibody conjugate was then used to quantify immunoreactivity in a cell culture assay by time-resolved luminescence. The theranostic potential of Lumi804-antibody conjugates has also been recently reported for Lu-177 therapy and Zr-89 PET imaging in a murine tumor allograft model.[1]

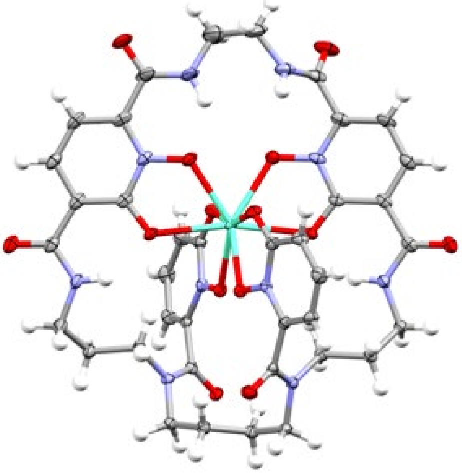

Figure 1. XRD crystal structure of the new [Eu(parent BFC)][NMe4] complex (simplified for clarity).

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Quantum technologies with rare earth ions

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Atomic defects in solid-state crystals are widely explored as single-photon sources and quantum memories for large-scale quantum communications networks based on quantum repeaters. Rare earth ions, in particular Er^{3+}, have attracted recent attention because of the demonstration of extremely large Purcell enhancement in nanophotonic cavities, which overcomes the slow intrinsic photon emission rate. Using this approach, we have demonstrated the first atomic source of single photons in the telecom band, and high-fidelity single-shot readout of the Er^{3+} electron spin using cavity-induced cycling transitions. Furthermore, we have realized optical manipulation and single-shot readout of multiple atoms with spacings far below the diffraction limit of light, using a novel frequency-domain super-resolution technique. I will conclude by discussing some recent work on coherent control of nearby nuclear spins, as well as a systematic investigation of new host materials with the potential to realize longer spin and optical coherence times.

Magnetism, symmetry, and topology of EuM_2Pn_2 compounds

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EuM_2Pn_2 compounds, where M is a metal and Pn is a pnictide, exhibit phenomena including complex helical magnetic order, coexisting local-moment and itinerant magnetism, and magnetic control of topological phases. I will give an overview of our group's recent work on various EuM_2Pn_2 compounds, including the potential magnetic topological semimetal $EuMg_2Bi_2$ [1] and magnetic Weyl semimetal $EuCd_2As_2$ [2]. I will then focus on recent neutron diffraction, density functional theory, and symmetry analysis results for the topological-crystalline-insulator $EuIn_2As_2$ [3] This compound possesses a remarkable broken-helix magnetic order which protects novel topological surface states and axion electrodynamics. We predict that the direction of an applied magnetic field of ~1 T will switch which surfaces offer quantum-anomalous-Hall-type conductivity and which offer dissipationless spin-momentum-locked charge transport. Some recent neutron diffraction data illustrating how the broken-helix order changes under a magnetic field will also be presented.

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Strong Circularly Polarized Luminescence at 1550 nm from Enantiopure Molecular Erbium Complexes

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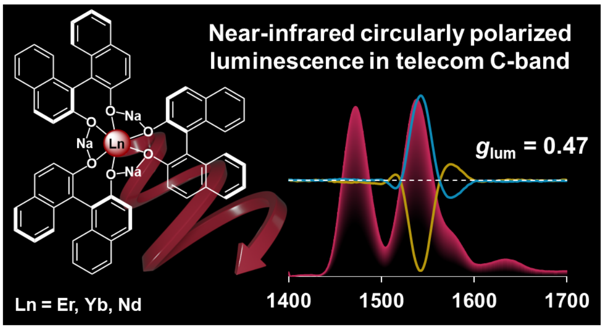

INTRODUCTION

The 1550 nm wavelength is critical for long-distance telecommunication, as the so-called "1550 nm telecom band" presents very low transmission loss in optical fibers.[1] When combined with polarization control, promising applications in quantum network[2] and quantum communication technologies[3] can be expected. Circularly polarized luminescence (CPL) is the preferential emission of light with right- or left-handed circular polarization. Generating CPL in the telecom band would therefore be highly desirable. Erbium possesses a luminescent transition (${}^4I_{13/2} \rightarrow {}^4I_{15/2}$) that is well suited for generating strong CPL,[4] and more importantly emits around 1550 nm, making it an excellent candidate for the aforementioned applications. We recently modified the so-called Shibasaki complexes [(Binol)$_3$LnM$_3$] into the reduced [(H$_8$-Binol)$_3$LnM$_3$] to match the energy levels of lanthanide emitting in the visible region.[5] Since the emissive level of erbium is much lower than the visible lanthanide emitters, we reasoned that the original non-reduced binolate complexes could be well-suited for erbium emission. In addition, we hypothesized that the loss of any C$_{sp3}$-H vibrations and overall rigidity of the system could prevent some quenching. Recently, other air-stable binolate-lanthanide complexes with non-alkali metal cations (notably tetramethylguanidinium) have been reported,[6] however, to minimize additional quenching, we decided to prioritize the use of an alkali-metal and targeted [(Binol)$_3$ErNa$_3$].

RESULTS AND DISCUSSION

Circularly polarized luminescence spectra of [(*R*/*S*-Binol)$_3$ErNa$_3$] were collected in tetrahydrofuran solutions. A tetrasignate pattern was observed with an exceptionally high maximum dissymmetry factor of +0.47 at 1540 nm for [(*S*-Binol)$_3$ErNa$_3$]. The spectrum of the enantiomer [(*R*-Binol)$_3$ErNa$_3$] is a perfect mirror image with a dissymmetry factor of −0.47 at 1540 nm. This is the first reported example of CPL observed beyond 1200 nm, and the dissymmetry factors we obtained are amongst the highest observed for any lanthanides. This result also confirms the prediction made by Zinna and Di Bari, who observed strong circular dichroism from a similar complex.[7] Owing to the strong dissymmetry factors, the calculated CPL brightness of our erbium complexes (B_{CPL} = 57 M^{-1} cm^{-1}) is high, although no comparison can be made with other emitters in this region.

CONCLUSIONS

We have synthesized molecular lanthanide complexes [(Binol)$_3$LnNa$_3$] (Ln = Er, Yb, and Nd) emitting CPL in the NIR. The erbium complexes synthesized here are the first reported examples of CPL observed beyond 1200 nm, and the emission is importantly centered within the 1550 nm telecom band. Additionally, the CPL magnitude observed are exceptionally high (|glum| = 0.47). Strong CPL is also observed for the ytterbium analogues, with an improvement of two orders of magnitude for their CPL brightness. We also observed that the cation significantly impacts CPL magnitude. Preliminary studies on cation effects will also be presented.

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Exploring excited state potential energy profile and luminescence properties of uranyl-based complexes by TRLFS and ab initio method

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INTRODUCTION

Uranyl complexes have been the subject of many research works for fundamental chemistry of actinides, environmental issues, or nuclear fuel cycle processes. The formation of various uranyl complexes, with organic and inorganic ligands in solution must be characterized for a better understanding of U(VI) speciation. As uranyl-ligand interactions and the symmetry of the complexes affect the electronic structure of U(VI) and thus its luminescence properties, time-resolved laser induced fluorescence spectroscopy (TRLFS) is one of the major techniques to characterize U(VI) complexes, with high sensitivity and selectivity. However, most of the relevant systems have complex chemical composition in solution and the identification of each species from spectroscopic data is challenging.

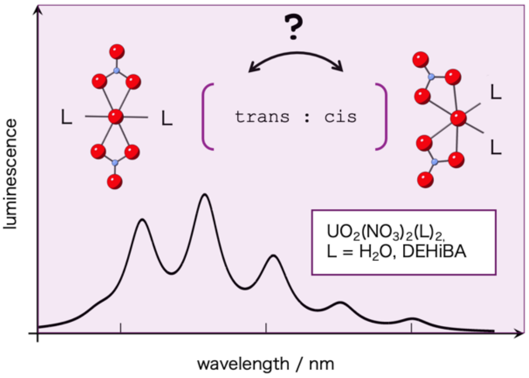
EXPERIMENTAL METHODS

In our study, the synergy between TRLFS and *ab initio*-based interpretation appears as a promising route for complexation data. Luminescence spectra of uranyl complexes in solution show in general a narrow energetical range about 6000 cm^{-1} and we can identify a single electronic transition between the initial and target states with the vibrationally resolved band [1].

The main challenge consists in exploiting a computationally cheap and effective theoretical approach, in a relativistic context, to characterize the main spectral parameters of the ground and luminescent states of symmetrical uranyl compounds (*i.e.* $UO_2Cl_4^{2-}$, $UO_2F_5^{3-}$, $UO_2(CO_3)_3^{4-}$, $UO_2(NO_3)L_2$) with different organic or inorganic counter ions after the photo-excitation. We will illustrate that TD-DFT with the CAM-B3LYP functional is able to provide accurate excitation/emission energies for these systems, together with accurate vibronic progressions allowing the assignment of experimental data.

RESULTS AND DISCUSSION

As a benchmark system serving the purpose of assessing the accuracy of our theoretical protocol, the uranyl tetrachloride $UO_2Cl_4^{2-}$ was selected because of the extensive amount of structural and spectroscopic data available [2]. A good agreement was found between ours and previously obtained theoretical data (structural parameters, orbitals nature, excitation energies) [3]; the final luminescence spectrum is in remarkable agreement with our TRLFS measurements [4]. We will also quantify the effects of organic or inorganic counterions [5, 6], along with that of first-sphere ligands that might perturb the uranyl(VI) moiety.



CONCLUSIONS

This work showcases how one can predict vibrationally resolved spectra to assign the recorded TRLFS data, and shed light on the relationship between the uranyl coordination and its luminescence properties.

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Electronic Structure of Uranium–Arenide Complexes

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In an effort to further understand the oxidation state assignment and bonding in a series of uranium-arenide complexes, a combined density functional theory (DFT) and second-order multireference (CASSCF/CASPT2) study was performed. First, the ion pairing effects on the electronic structure of unsupported uranium–arenide sandwich complexes was studied. Of note, CASSCF calculations on the model complex $\{[U(\eta^6\text{-}C_{14}H_{10})(\eta^4\text{-}C_{14}H_{10})(\mu\text{-OMe})]_2\}^{2-}$ show the highly polarized uranium–arenide interactions are defined by π-type bonds where the metal contributions are primarily comprised by the 6*d*-orbitals (7.3 ± 0.6%) with minor participation from the 5*f*-orbitals (1.5 ± 0.5%). These unique complexes provide new insights into actinide–arenide bonding interactions and show the sensitivity of the electronic structures of the uranium atoms to coordination sphere effects. The second family of complexes studied are mononuclear uranium bis(anthracenide) complexes where a haptotropic ring migration is observed. The bonding and oxidation states are explored and compared to that of the previously characterized dimeric complex. Finally, three homoleptic uranium-arenides are studied where spectroscopic results suggest different oxidation states for each complex.

Tomonaga-Luttinger Liquid Behavior and Spinon Confinement in $YbAlO_3$

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INTRODUCTION

The spin $S=1/2$ antiferromagnetic Heisenberg Hamiltonian is one of the simplest models of condensed matter physics containing fractional quantum number excitaitons. The phase diagram of this model includes both quantum critical and gapped phases. Spinons are topological excitations which may be pictured as domain walls between different Néel ground states of the system. The three-dimensional metallic system Yb_2Pt_2Pb is a recent example, where the neutron scattering revealed the existence of one-dimensional spinon continuum. However, the metallic nature of this material complicates the analysis of its magnetic properties. Here we discuss the insulating analog, namely Yb-based quasi-1D quantum magnet, $YbAlO_3$.

EXPERIMENTAL METHODS

$YbAlO_3$ single crystals were grown by the Czochralski technique. Magnetization and specific heat measurements were carried out. Neutron scattering measurements were performed with the time-of-flight Cold Neutron Chopper Spectrometer, at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory.

RESULTS AND DISCUSSION

$YbAlO_3$ crystallizes in an orthorhombically distorted perovskite structure. The local point-group symmetry of the Yb^{3+} ions creates a ground doublet state $m_J=\pm 7/2$ well separated from the first excited levels. The low temperature and low field magnetic properties can be described by a pseudospin-1/2 model. Importantly, the magnetization measurements reveals significant uniaxial (Ising-like) anisotropy, with effective g-factors $g^{xx}=g^{yy}=0.46$, and $g^{zz}=7.6$.

Single crystal inelastic neutron scattering measurements at zero field are shown in Fig. 1 (left column). Gapless spinon excitations along the chain direction (00L) are observed at 1.0 K ($T>T_N$), with a broad two-spinon continuum. In contrast, a significant gap is observed below the ordering temperature, with a massive triplet mode and multi-spinon continuum. The neutron scattering spectrum, combined with other thermodynamic measurements, shows that $YbAlO_3$ can be described by the effective spin-1/2, nearly isotropic Heisenberg chain with a staggered field B_{st}, which arises from coupling to the ordered moments in the neighboring chains (B_{st} becomes finite below T_N). Our DMRG calculation of the longitudinal spin excitation spectrum (Fig. 1, right column) shows excellent agreement with the neutron scattering resuls.

With a magnetic field applied along the *a*-axis, the static AFM order is suppressed at the critical field $B_c=0.35T$ in favor of incommensurate magnetic ordering, and finally the moments become saturated at $B_s=1.13T$. This $B=B_s$, $T=0$ QCP is a Gaussian fixed point because the effective dimension of the low-energy effective theory is $D=3+1$. For temperatures higher than the exchange anisotropy and the interchain coupling, we expect a crossover into a regime controlled by a free fermion fixed point ($\nu=1/2$) in dimension $D=1+2$. The scaling analysis of the magnetization and specific heat data indeed agrees with this picture, and narrows down the range of the exchange anisotropy to $0.88 \lesssim \Delta \lesssim 1$.

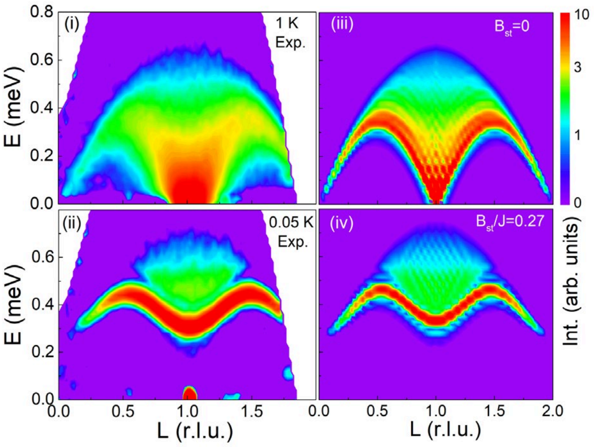

Figure 1 Inelastic neutron scattering spectra (left) and DMRG calculation (right) for $YbAlO_3$.

CONCLUSIONS

$YbAlO_3$ is found to provide a natural realization of the spin-1/2 XXZ chain, which shows quantum fractional spinon continuum above T_N and the transition into a confined (magnetically ordered) low-temperature state characterized by massive excitations. Both the gapless spinon spectrum and the critical behavior around the saturation field at $T>T_N$ unambiguously demonstrate that the intrachain exchange is Heisenberg-like to a very good approximation.

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Pursuing Biorelevant Uranyl Complexes

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The recent discovery of bacteria capable of reducing soluble hexavalent uranium to insoluble tetravalent uranium has lead researchers to probe the mechanism of reduction. In general this takes the form of the uranyl ion, UO_2^{2+}, being reduced to UO_2.[1] The full details of reduction are not yet known, but a few statements can be made including: the presence of a reduced uranyl intermediate, UO_2^{1+}, that undergoes disproportionation, and the use of iron as the functional reductant and.[2]

One of the bacteria known to affect uranyl reduction is *Geobacter Sulfurreducens*, which typically reduces sulfate, SO_4^{2-} to sulfide, SH^{1-}.[1] With the high likelihood of sulfur being present during uranyl reduction we saught ligands featuring sulfur amenable to reducing environments. The diaminodisulfide ligand, "$(N_2S_2)^{2-}$" features a cyclic diamine backbone and two linear thiol "arms," **Fig 1**.[4] $(N_2S_2)^{2-}$ ligands have been used to mimic [NiNi] and [FeNi] hydrogenase bacteria, reducing $2H^+$ to H_2.[4b] In particular the $M(N_2S_2)$ (M = Ni, Co, Fe) complexes redily coordinate iron and other metals through the sulfur atoms to form a bimetallic complexes of the general form $M(\mu\text{-}N_2S_2)M'L_x$ (M′ = Fe, Ni, Cu, etc).[4a] Furthermore, the N_2S_2 ligand can be derivatized to change the size and solubility of the ligand.[4c]

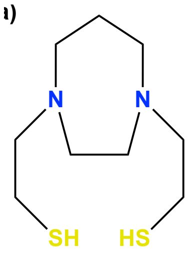
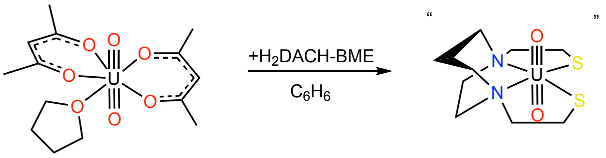


Fig 1. Example of $H_2N_2S_2$ ligand.

To date, the chemistry of N_2S_2 ligands have not been explored with the uranyl ion. Only a limited amount of research has been performed on vanadyl complexes, $VO(N_2S_2)$,[5] with no reports for more electropositive metals.

The strong disproportionation of UO_2^{1+} has made this ion difficult study. Recent efforts have shown the reduced uranyl ion to be isolable under the right conditions,[3a] including one remarkable example in water.[3b] Most reductions take plce in organic solvent using reductants much stronger than iron. We aim to pursue the stabilization of UO_2^{1+} using the $(N_2S_2)^{2-}$ platform, in particular to understand how the presence of iron affects the accessibility of UO_2^{1+}.

Herein we will describe our efforts to synthesize and characterize $UO_2(N_2S_2)$ complexes using various methods including ^1H NMR, UV-vis, and IR spectroscopies. Initial results show that when pale yellow H_2DACH-BME ($H_2N_2S_2$) is added to a bright yellow suspension of $UO_2(acac)_2(THF)$ in C_6H_6, a dark red precipitate quickly forms, **eq 1**. The red product is formulated as a putative "$UO_2(N_2S_2)$" complex as supported by ^1H NMR and IR spectroscopies, and is soluble in DMF or DMSO. Crystallography will play a critical role in the confirmation of complex formation.[6] Future efforts will focus on full characterization of "$UO_2(N_2S_2)$" by UV-visible spectroscopy and electrochemical methods in addition to single crystal X-ray diffraction. Other ligand derivitives with increased solubility will be sought as well.



The understanding of how the uranyl ion can be reduced by iron may provide novel methods for uranium removal from water.

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Observation of Yb^{3+} with Spin-1/2 in Yb$_x$Pt$_5$P

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INTRODUCTION

Understanding the electronic interactions in intermetallic compounds and designing the functional materials with targeted physical properties accordingly have been long-standing challenges in materials science. On one side, the classical chemical concepts, such as charge balance arguments and electron-counting rules, do not work for intermetallic compounds with strong electron correlation, partially for the valence orbital manifold, and occasionally for relativistic effects. On the other side, quantum-chemical techniques including machine learning are hindered by the limited data of materials with specific properties, such as superconductivity. The interplay between superconductivity and magnetism, which can happen under very restricted conditions, has the potential to lead to exotic, new condensed matter physics and quantum devices. The coexistence of superconductivity and magnetism in a single material system is very rare. Materials physicists have worked to realize this state by fabricating hybrid nanostructures that combine both superconducting and magnetic layers, and along similar lines, chemists have used solvent methods to build up hybrid materials with superconducting and magnetic fragments, most of which are not fully ordered. It is highly demanding to design and synthesize a new bulk material that displays the coexistence of superconductivity and magnetism in a single substance.

One chemical perspective for discovering new functional materials, especially superconductors is to posit that similar physical properties can be observed in structural families. A well-known example is the HoCoGa$_5$-type structure motif type becoming intriguing after the discovery of heavy Fermion superconductivity in CeCoIn5. The indium analogs CeTIn$_5$ (T-transition metals) show an intricate interplay of superconductivity and magnetism, e.g., unconventional superconducting CeCoIn$_5$ and antiferromagnetic CeRhIn$_5$.

Heavy Fermion superconductors, most of which are 4f1 Ce-based, are one way that the two kinds of electronic systems can interact, and an alternative is for more weakly coupled rare earth-metal systems, such as is seen for rare earth Chevrel phases and the lanthanide borocarbides. Yb^{3+}, with a 4f^{13} electronic configuration, is often considered the hole analog of Ce3+; however, only a single Yb-based heavy-fermion superconductor, YbAlB$_4$ has been reported to date, with Tc = 0.08 K; the large discrepancy must be due to unfavorable Yb-metal hybridization energies in most cases.

The ternary compound LaPt$_5$As, synthesized in rhombohedral symmetry under high pressure, provides a new avenue for research because, although nonmagnetic, it hosts superconductivity with Tc $\approx$ 2.6 K. Consisting of Pt-rich layered networks, superconducting LaPt$_5$As inspired us to incorporate a magnetic rare earth element (Yb^{3+}) into the platinum-pnictide system. The much smaller ionic radius of Yb compared to La led us to replace As^{3-} with smaller P^{3-} to stabilize a hypothetical YbPt$_5$P at ambient pressure. This may yield both superconducting and magnetic properties in a single material.

RESULTS, DISCUSSION AND CONCLUSIONS

Thus, here we report a new material Yb$_x$Pt$_5$P with a thorough crystallographic and physical properties characterization. Yb$_x$Pt$_5$P crystallizes in a tetragonal TlPt$_5$As-type structure with the space group P4/mmm. The structure can be considered as the anti-format of CeCoIn$_5$. According to single-crystal X-ray diffraction, the Yb content (x) in Yb$_x$Pt$_5$P varies significantly from x = 0.23–0.96. We studied the magnetic and electronic properties of two samples with x = 0.23 (1) and 0.96 (1). In both samples, we observed antiferromagnetic transitions of Yb3+ around 0.3 K. Moreover, the zero-resistivity transition was observed around ~0.6 K only in low ratio Yb samples, Yb$_{0.23(1)}$Pt$_{4.87(4)}$P$_{0.90(5)}$ and Yb$_{0.29(1)}$Pt$_5$P, but not in Yb$_{0.96(1)}$Pt$_5$P. Our new quantum material is a new ideal platform to study the interplay between superconductivity and magnetism. Our new quantum material appears to be a distinct platform for studying the interactions between superconductivity and magnetism, in a material where the strong spin-orbit coupling is present.

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Rare-Earth Magnetic Control of Organic Reactions

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INTRODUCTION

The synthetic design of chemical reactions is often made on the basis of steric effects or electronic effects. In contrast, magnetic effects are relatively less explored, in part because magnetic effects are often relatively small energy scales, *ca.* 10^{-2} kcal/mol in magnitude, relative to the multi-kcal activation energies of reactions.

In certain photochemical reactions bearing radical-pair intermediates, magnetic effects can be incredibly important for governing reactivity.[1] Turro and coworkers, as well as Sakaguchi, showed three decades ago that rare-earths can modify the outcomes of chemical reactions that incorporate these radical pairs.[2,3] Yet the exact magnetic parameters responsible for that control e.g. spin ground state, bulk magnetic moment, or spin relaxation time, among others, are still undefined.

We are currently designing ligand shells that will provide that understanding by serving as molecular models of the initial magnetic systems. We are specifically targeting predominantly O- and N-atom donor chelate backbones, with radical-pair forming groups appended to them. Yet, prior to designing the whole ligand shell, it is necessary to show as a proof of concept that the proposed radical-pair forming unit will exhibit reactivity controlled by the magnetism of the rare-earth ions. As an initial proof of concept, we are studying the role that magnetic rare earths play in governing the photolysis of benzyl esters, specifically benzylglycine, which will comprise the radical-pair forming groups we eventually append to the ligand scaffolds (**Fig. 1**).

RESULTS AND DISCUSSION

Photolysis studies of solutions of benzylglycine in water demonstrate photocleavage of the C–O ester bond over the course of hours or minutes (based on the experimental setup) to form benzyl alcohol and glycine. Addition of YCl_3 ($S = 0$) to the reaction mixture results in no change to the photolysis reaction rate. In contrast, addition of $S = {}^{5}/_{2}$, $DyCl_3$ ($S = {}^{5}/_{2}$, $L = 5$, $J = {}^{15}/_{2}$) to the reaction mixture accelerates the reaction rate by up to 40 % (**Fig. 1**). This change in reaction outcome is consistent with the possibility of spin catalysis[4] of the photochemical reaction by the rare-earth species. Additional results exploring this effect, as well as the role of other rare-earth additives, will be discussed.

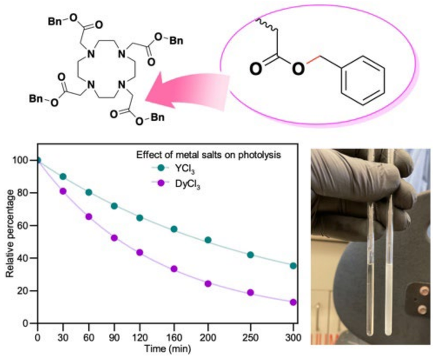

Fig. 1. Overview of target ligand sets and preliminary data suggesting magnetic control over the photoreactivity of the building block. Bottom right: example visible change in reaction system upon photolysis.

CONCLUSIONS

The presented results show that it is possible to see rare-earth control of the photochemical outcome of benzylglycine's photolysis, driven by a magnetic effect. Future work will explore this specific system in greater detail and proceed to building the full ligand shell.

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Stabilizing a Series of new Ln(II) Complexes with 2,6-Di-adamantyl aryloxide Ligands

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ABSTRACT

The sterically bulky aryloxide ligand OAr* (OAr* = OC_6H_2-2,6-Ad_2-4-^{t}Bu; Ad = 1-adamantyl) has been used to generate thermally stable Ln(II) complexes across the lanthanide series, an accomplishment that to date has not been possible with any other ligand system. The Ln(III) precursors, $Ln^{III}(OAr^*)_3$, **1-Ln**, were synthesized by reacting 1.2 equivalents of $Ln(NR_2)_3$ (R = $SiMe_3$) with 3 equivalents of HOAr* for Ln = La, Ce, Nd, Gd, Dy, Yb, and Lu. **1-Ce**, **1-Nd**, **1-Gd**, **1-Dy**, and **1-Lu** were identified by single-crystal X-ray diffraction studies. Reductions of **1-Ln** (Ln = Nd, Gd, Dy, Yb, Lu) with potassium graphite (KC_8) in THF in the presence of 2.2.2-cryptand (crypt) yielded the Ln(II) complexes $[K(crypt)][Ln^{II}(OAr^*)_3]$, **2-Ln**. By using 18-crown-6 (18-c-6) as the potassium chelator rather than crypt, La(II) and Ce(II) complexes $[K(18\text{-}c\text{-}6)][La^{II}(OAr^*)_3]$, **3-La**, and $[K(18\text{-}c\text{-}6)][Ce^{II}(OAr^*)_3]$, **3-Ce**, could be isolated and crystallographically characterized. The thermal stabilities of **2-Ln** and **3-Ln** were evaluated using UV-visible spectroscopy and showed that these Ln(II) complexes decompose at room temperature more slowly than other previously reported $4f^n5d^1$ Ln(II) complexes. The synthesis of complexes with traditional $4f^{n+1}$ Ln(II) ions with OAr* from LnI_2 precursors will also be described.

Low-coordinate lanthanide complexes with bulky silylphosphide ligands

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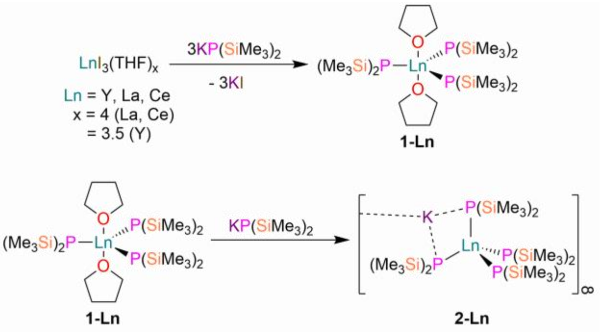
INTRODUCTION

Lanthanide (Ln) ions are hard Lewis acids, and prefer to interact with hard Lewis bases; this is evidenced by the rich coordination chemistry of ligands containing oxygen and nitrogen donor atoms.[1] Conversely, there are fewer Ln complexes which contain heavier p-block donor ligands, such as phosphides.[1] Bis(trimethylsilyl)-amide, $\{N(SiMe_3)_2\}$, has been intrinsic to the development of Ln coordination chemistry for over half a century since the disclosure of the synthesis of the landmark trigonal pyramidal complexes $[Ln\{N(SiMe_3)_2\}_3]$.[2,3] The Ln chemistry of the softer heavy pnictogen analogue bis(trimethylsilyl)phosphide, $\{P(SiMe_3)_2\}$, is immature in comparison. Only a handful of structurally characterised examples of Ln complexes containing this phosphide ligand have been reported previously, namely $[Y\{P(SiMe_3)_2\}_2\{\mu\text{-}P(SiMe_3)_2\}]_2$,[4] $[Ln\{P(SiMe_3)_2\}_3(THF)_2]$ (Ln = Nd, Tm).[5,6] and $[Sm\{P(SiMe_3)_2\}\{\mu\text{-}P(SiMe_3)_2\}_3\text{-}Sm(THF)_3]$.[7]

RESULTS AND DISCUSSION

Here we expand upon the Ln chemistry of $\{P(SiMe_3)_2\}$ through the synthesis of two structurally analogous series of complexes, $[Ln\{P(SiMe_3)_2\}_3(THF)_2]$ (Ln = Y, La, Ce) (**1-Ln**) and $[Ln\{P(SiMe_3)_2\}_4K]$ (Ln = Y, La, Ce) (**2-Ln**), Scheme 1. Whilst both synthetic routes utilise a salt metathesis method, **2-Ln** is synthesised by the addition of one equivalent of $K[P(SiMe_3)_2]$ to the respective **1-Ln** complexes.



Scheme 1. Synthesis of the phosphido-substituted Ln complexes, **1-Ln** and **2-Ln**.

The five-coordinate **1-Ln** series consist of three silylphosphide ligands in the equatorial plane with two tetrahydrofuran (THF) solvent molecules in the axial positions. A distortion from ideal trigonal bipyramidal geometry is illustrated by the deviation of the O-Ln-O angle from 180°; this distortion increases with reduction in size of the Ln^{3+} ion. The presence of coordinated THF in **1-Ln** is a consequence of longer Ln-P bonds than the Ln-N bonds in $[Ln\{N(SiMe_3)_2\}_3]$.[2,3] Chemiluminescence is exhibited by **1-Ce** upon exposure to air.

For the four-coordinate **2-Ln** series, a distorted tetrahedral structure is seen with inclusion of a potassium cation in the coordination sphere. In the solid state intermolecular electrostatic contacts between this cation and a silylphosphide ligand of a separate molecule of **2-Ln** results in a polymeric chain. Coordination of a fourth silylphosphide ligand in **2-Ln** satisfies the Ln^{3+} coordination spheres so as to eclude any coordinated solvent.

CONCLUSIONS

Two series of Ln silylphosphide complexes have been synthesized. These low coordination number complexes expand upon the known examples of Ln complexes of the bis(trimethylsilyl)phosphide ligand. Although still at an early stage, Ln silylphosphide coordination chemistry could potentially expand to provide results that complement and contrast with those achieved previously for silylamide ligands in Ln chemistry.

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Quantum Criticality of the Quasi-One-Dimensional Heavy Fermion Material $YbFe_5P_3$

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Quantum criticality has been an organizing principle to explain the behavior of many families of quantum materials including the high-temperature cuprate and iron-based superconductors and f-electron heavy fermion compounds. A central, unresolved issue is the role of quantum fluctuation dimensionality on the properties of the system. Most work to date has focused on quantum criticality with two-dimensional (2-D) and three-dimensional (3-D) fluctuations. Strong quantum fluctuations are expected in quasi-1-D materials and have recently been explored in 1-D f-electron materials such as $CeRh_6Ge_4$ [1], Yb_2Pt_2Pb [2], and $YbAlO_3$ [3].

$YbFe_5P_3$ crystallizes in the orthorhombic YCo_5P_3 structure type [4] with 1-D Yb chains along the b-axis with an Yb-Yb distance of 3.65 Å, while the inter-chain Yb-Yb spacing is 5.61 Å. Below about 5 K, the electrical resistivity reflects the presence of strong quantum fluctuations. Specific heat measurements show a similar strong enhancement at low temperatures reaching a constant value of C/T=1.5 J/mol K^2 below T = 0.5 K, indicating a heavy Fermi liquid state. No magnetic ordering is observed down to 80 mK. Chemical substation of Co or Ru for Fe drives $YbFe_5P_3$ to a quantum critical point. A magnetically ordered state is found for Co concentrations greater than 20%, beyond the quantum critical point. In this poster, I will describe the physical properties of the quasi-1D heavy fermion material $YbFe_5P_3$ and the nature of quantum criticality in $Yb(Fe_{1-x}M_x)_5P_3$ (M=Co, Ru).

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Enhanced Magnetic Anisotropy in Lanthanum M-type Hexaferrites by Quantum-confined Charge Transfer

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Iron-based hexaferrites are critical-element-free permanent magnet components of magnetic devices. Of particular interest is electron-doped M-type hexaferrite i.e., $LaFe_{12}O_{19}$ (LaM) in which extra electrons introduced by lanthanum substitution of barium/strontium play a key role in uplifting the magnetocrystalline anisotropy. We investigate the electronic structure of lanthanum hexaferrite using a density functional theory with localized charge density which reproduces semiconducting behavior and identifies the origin of the very large magnetocrystalline anisotropy.[1] Localized charge transfer from lanthanum to the iron at the crystal's 2*a* site produces a narrow $3dz^2$ valence band strongly locking the magnetization along the c axis. The calculated uniaxial magnetic anisotropy energies from fully self-consistent calculations are nearly double the single shot values, and agree well with available experiments. The chemical similarity of lanthanum to other rare earths suggests that LaM can host for other rare earths possessing non-trivial 4*f* electronic states for, e.g., microwave-optical quantum transduction.

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Using the Theory of Critical Phenomena to Understand Structure and Phase Transitions in Separations of Rare Earths

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INTRODUCTION

Understanding the molecular-scale origins of structure and phase transitions in multicomponent, hierarchically structured soft matter phases is a fundamental challenge. One application affected by these phenomena is liquid-liquid extraction, a predominant low-energy separations technique. This technique is a go-to process for materials recycling, including the recovery of rare earth elements [1]. The complex solutions encountered in these applications feature structure at the nanoscale, which is understood to affect the subtle energetic balance used to control the separation process [2]. Further, a fundamental limitation to liquid-liquid extraction are undesirable liquid-liquid phase transitions that occur upon sufficient loading of, e.g., lanthanide ions into extractant-containing organic phases. Here, we discuss ongoing work seeking to understand how solution structure and phase behavior are fundamentally connected in a way that can be understood by applying the theory of critical phenomena.

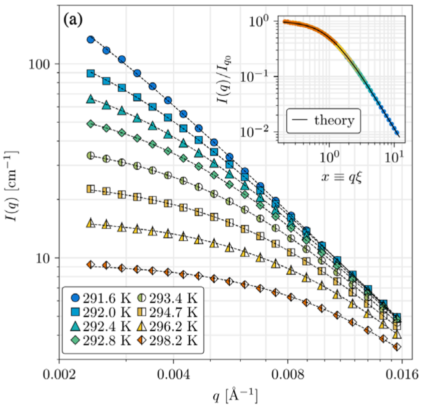

Figure 1: Temperature dependent structure of the organic phase, upon extraction of cerium nitrate by a malonamide extractant, is consistent with critical point theory [1].

RESULTS AND DISCUSSION

Mesostructuring in organic phases upon extraction of different lanthanides using different extractants all follow critical point theory (Fig. 1), showing critical fluctuations consistent with a psudeobinary compositional order parameter [3,4]. By combining small angle X-ray scattering with molecular dynamics simulations, we demonstrate how organic phase structure over a wide range of process-relevant composition space is dominated by critical fluctuations [5,6]. Scaling relations provided by critical point theory create a quantitative connection between aggregation in the organic phase and its phase behavior, deepening our understanding of both.

CONCLUSIONS

The relationship investigated here between structure and phase behavior will inform the design of more efficient separations processes and, more broadly, explore how critical phenomena manifest in complex solutions whose structure and thermodynamics are governed by intermolecular interactions that span length and energy scales.

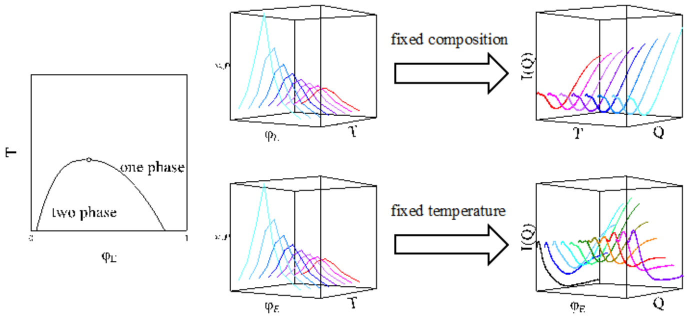

Figure 2: Critical composition fluctuations explain the relationship between structure and phase behavior for changes to system parameters, such as composition and temperature.

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Solid-State and Solution-Phase Characterization of Sm^{II}-Aza[2.2.2]cryptate and its Methylated Analogue

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Abstract

Complexes of divalent lanthanide ions (Ln^{II}) have applications in small molecules activation, imaging, luminescent materials, catalysis, organic synthesis, and magnetism due to their electrochemical, luminescence, and magnetic properties. The electrochemical, luminescence, and magnetic properties of Ln^{II}-complexes can be modulated through changes in electronic and steric properties of donor atoms. Ln^{II}-crypates are an example of Ln^{II}-complexes that have received much attention because small changes in electronic and steric properties of donor atoms in the cryptand lead to drastic changes in electrochemical and luminescence properties. Most studies on the structural, spectroscopic, and electrochemical properties of Ln^{II}-cryptates to date have however focused only on ethereal cryptates. Thus, it is important to study the impact of other donors on the aforementioned properties of Ln^{II}-cryptates. Reported secondary and tertiary amines containing Ln^{II}-cryptates (Ln^{II}-azacrypates) have shown promising luminescence and electrochemical properties that are relevant in applications such as light-emitting diodes, catalysis, and organic synthesis. However, studies of Ln^{II}-azacryptates to date have focused only on Eu^{II}- and Yb^{II}-azacryptates. To establish trends in bonding, spectroscopic, and electrochemical properties of Ln^{II}-azacryptates across the Ln^{II} series, the study of Sm^{II}-azacryptates is the next critical step. To this end, we have investigated the solid- and solution-state coordination environment and the spectroscopic and electrochemical properties of two Sm^{II}-azacryptates. The tertiary amine containing Sm^{II}-cryptate is eight coordinate in the solid and solution-states, and has a more negative electrochemical potential than the secondary amine containing Sm^{II}-cryptate which is most likely nine-coordinate in solution. Our results represent a step forward toward a broader understanding of the impact of strong Lewis base on the properties of Ln^{II}-crypates across the Ln^{II} series.

An Experimental and Theoretical Investigation of Actinide-Ligand Bonding and Second-Sphere Interaction Strengths in Families of $[AnO_2Cl_4]^{2-}$ (An = U, Np, Pu) Materials

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INTRODUCTION

Hybrid materials have provided an attractive forum for investigating structure-property relationships, and in particular, probing the influence of second-sphere interactions on bonding and spectroscopic signatures. As such, we used this approach to serve as a platform for studying actinyl (AnO_2^{2+}) bearing materials. Our interest surrounds the $[AnO_2Cl_4]^{2-}$ (An = U, Np, Pu) building unit, pairing it with a suite of systematically altered organic cations to produce a cohesive family of materials for study. We were successful in preparing a suite of fifteen novel compounds, which can be subdivided by either actinide identity or their second-sphere hydrogen bond assembly motif. In doing so, we are able to assess systematic trends across the actinide series, as well as define criteria necessary for engaging the terminal actinyl oxo directly. Furthering our study with spectroscopy and density functional theory based calculations, we are able to comment on the composition and character of actinide-ligand bonding and strengths of second sphere interactions within these compounds, with a latter goal of commenting on actinyl covalency across the series.[1]

EXPERIMENTAL METHODS

All compounds were prepared via room-temperature slow-evaporations out of aqueous solutions of low pH and high anion concentration, to promote $[AnO_2Cl_4]^{2-}$ speciation. This effort afforded 15 compounds, which feature the $[AnO_2Cl_4]^{2-}$ dianion paired with variously substituted methylpyridinium cations. Single crystals of product were characterized by X-ray diffraction, Raman spectroscopy. Computational analyses were performed using density functional theory (DFT) methods in Gaussian16, using the B3LYP functional and ECP60MWB basis set and pseudopotential. Natural bonding orbital (NBO) analysis was employed, in addition to Bader's quantum theory of atoms in molecules (QTAIM), to probe the character and composition of actinide-ligand bonds, and the influence of second sphere interactions.

RESULTS AND DISCUSSION

An initial set of compounds featuring the $[UO_2Cl_4]^{2-}$ dianion paired with variously substituted methylpyridinium cations were crystallized, in order to delineate assembly motifs and probe structure-property relationships. Extending this effort, we moved to $[NpO_2Cl_4]^{2-}$ and $[PuO_2Cl_4]^{2-}$ phases, to identify similarities and/or differences in assembly, in addition to systematic trends in bonding. As expected, most phases were isomorphous across the actinide series. Resultantly, we observe crystallographic bond lengths contracting across the series, in both actinide-ligand bonds and second-sphere interaction distances. A detailed DFT/QTAIM based study followed, which allowed us to probe bond composition, hybridization, and order, with further aims of commenting on covalency.

CONCLUSIONS

Structural diversity present in individual families of $[AnO_2Cl_4]^{2-}$ compounds with the same anion can be rationalized as the influence of the organic cation's sterics and basicity as methyl substitution changed. These trends in assembly, apart from individual outliers, hold across the series, forming isomorphous structures, including those showing direct '-yl' engagement. Computational analyses allow us to then interrogate the nature in bonding across the isomorphous series. In doing so, we observe that across the series, decreases in crystallographic bond distances trend with increased Wiberg bond indices, bond composition, and QTAIM metrics, which support An=O and An-Cl bond strength increasing across the series.

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ACKNOWLEDGMENTS

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Expanding Uranyl Peroxide Cluster Chemistry via New Synthetic Routes and the Introduction of Free Radicals

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INTRODUCTION

Uranyl peroxide clusters (UPCs) are a subclass of polyoxometalates (POMs) that have grown substantially since the first structure was reported in 2005.[1] These complexes are known to self-assemble in aqueous solution and have potential for applications in the nuclear fuel cycle as well as nuclear medicine; however, synthetic routes to produce these materials have thus far been limited.[2] Understanding and expanding the synthetic toolbox for producing these unique metal assemblies presents a rich set of scientific challenges and herein we will highlight initial results from our experimental approach, which uses a combination of inorganic and in situ methods to access and characterize new peroxide cluster species, including kinetic intermediates.

EXPERIMENTAL METHODS

Materials have been prepared via either hydrothermal or photochemical syntheses and characterized via single crystal X-ray diffraction and Raman and Infrared (IR spectroscopies. For complexes containing free radicals, insight into radical identity and behavior have been ascertained from room temperature continuous wave electron paramagnetic resonance (EPR) spectroscopy measurements.

RESULTS AND DISCUSSION

Initial results have yielded three distinct new complexes or families of complexes from hydrothermal or photochemical synthesis routes. These include the largest UPC (U_{96}) containing only uranyl ions and peroxide and hydroxide ligands that is built from topological nonagons (Figure 1a), new analogues of the well-known U_{24} cluster[1] that have been made photochemically with topologies that vary based on the identity of the charge balancing alkali metal cation (Figure 1b), and a kinetic intermediate ($U_{60}Ox_{30}$*) of the previously synthesized oxalate cage cluster, $U_{60}Ox_{30}$,[3] which contains carbon and oxygen based free radical species (Figure 1c).

Alkane and dioxygen radicals are known as important radiolysis products, and identification of these species in UPCs is significant for improving the chemical understanding actinide interactions with free radicals in systems relevant to nuclear waste separations and reprocessing. Vibrational and EPR spectroscopies confirmed the presence and stabilization of carbon-centered and hydroperoxyl radicals in $U_{60}Ox_{30}$* and initial reacvtivity studies for both species will be detailed.

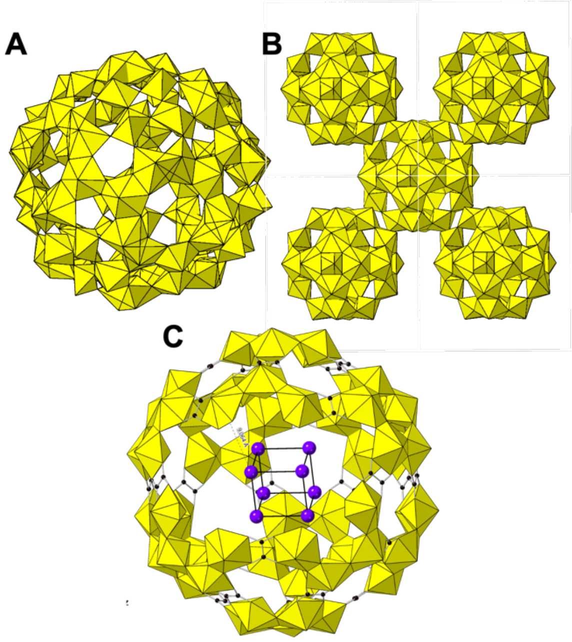

Figure 1 Polyhedral representation of new UPCs including **A)** U_{96}, **B)** photochemically synthesized U_{24}, and **C)** $U_{60}Ox_{30}$*.

CONCLUSIONS

Our findings indicate that there is significant untapped potential in UPC chemistry that can be unlocked through a systematic exploration of alternative synthetic methods and via the controlled introduction of carbon and oxygen free radicals. Kinetic products are also often overlooked in f-element systems and the methodological developments for isolation and characterization of these complexes, developed as part of this work, are anticipated to be valuable for continuing the expansion of UPC chemistry.

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Rediscovering the unsubstituted trispyrazolylborate ligand on lanthanides: synthetic versatility, redox chemistry, and small molecule activation

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INTRODUCTION

The unique chemical properties of lanthanide (Ln) complexes are utilised in catalysis, redox chemistry, and small molecule activation.[1-3] Ln complexes also display remarkable physical properties, both optical and magnetic.[4-6] Synthesis of reactive Ln complexes requires judicial choice of ancillary ligands, and the substituted cyclopentadienyl (Cp) ligands are widely used.[7] The hydrotris(1-pyrazolyl)borate (Tp) ligands present an alternative.[8-10] Ln coordination chemistry is dominated by substituted analogues of Tp, *e.g.* $[\mathrm{Ln(Tp^{Me2})_2}]^+$ or very bulky Tp ligands.[11,12] The Ln chemistry of the unsubstituted Tp ligand in the *bis*-Tp $[\mathrm{Ln(Tp)_2}]^+$ ancillary ligand environment has remained largely unexplored.

RESULTS AND DISCUSSION

Here we report the synthesis of the heteroleptic precursors $[\mathrm{Ln(Tp)_2(OTf)}]$ **1-Ln** (OTf = $\mathrm{CF_3SO_3}$, **Figure 1a**).[13] Metathesis chemistry of **1-Ln** was explored to synthesise the 8-coordinate complexes $[\mathrm{Ln(Tp)_2(hfac)}]$ **2-Ln** (hfac = hexafluoroacetylacetonate) and subsequently extended to 7-coordinate complexes $[\mathrm{Ln(Tp)_2(X)}]$ **3-Ln** (X = N″ or $\mathrm{N(SiMe_3)_2}$). The $[\mathrm{Ln(Tp)_2}]^+$ scaffold has also been shown to support very small bridging X ligands $[\{\mathrm{Ln(Tp)_2}(\mu\text{-X})\}_2]$ **4-Ln** (X = $\mathrm{NH_2}$) by metathesis of **1-Ln** (**Figure 1a**) and **5-Ln** (X = OH) by protonolysis of **3-Ln** (**Figure 1b**). Accommodating very bulky X ligands in the $[\mathrm{Ln(Tp)_2}]^+$ scaffold was also successful, by protonolysis of **3-Ln** to $[\mathrm{Ln(Tp)_2(OAr)}]$ **6-Ln** (OAr = 2,6-$^t\mathrm{Bu_2}$-4-Me-phenoxide) (**Figure 1b**). Preliminary reactivity studies of **3-Ln** with $\mathrm{CO_2}$, resulted in the isolation of $[\mathrm{Ln(Tp)_2(OSiMe_3)}]$ **7-Ln** (**Figure 1b**).

Complexes **1-Ln** (Ln = Eu and Yb) yield adduct-free homoleptic Ln(II) complexes $[\mathrm{Ln(Tp)_2}]$ **8-Ln**, upon reduction with $\mathrm{KC_8}$ or Al(I) in toluene (**Figure 1c**).[14] Complexes **8-Ln** are stable towards Lewis base coordination enabling synthesis of $[\mathrm{Ln(Tp)_2(OPPh_3)_2}]$ **9-Ln** (**Figure 1d**). This has enabled the comparison of the structural and electronic properties of Ln(II) ions in the presence and absence of Lewis bases. Complexes **8-Ln** also reduce the redox-active 1,10-phenanthroline-5,6-dione (pd) ligand to the semi-quinone radical anion,[15] to yield $[\mathrm{Ln(Tp)_2}(O,O'\text{-pd}^{\bullet-})]$ **10-Ln** complexes (**Figure 1d**), which are important in the synthesis of multimetallic $\mathrm{Ln_4}$ and Ln-Ln′ complexes.[16]

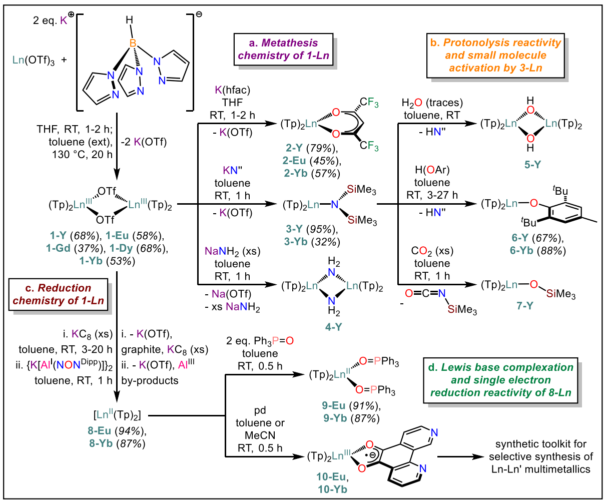

Figure 1. Synthesis of novel trispyrazolylborate lanthanide complexes showcasing the versatility of the $[\mathrm{Ln(Tp)_2}]^+$ ancillary ligand environment.

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Unexpected Sodium-Containing Nitride Selenides of the Lanthanoids: $\mathrm{Na}Ln_9\mathrm{N}_4\mathrm{Se}_8$ (Ln = Gd – Dy)

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INTRODUCTION

Nitride chalcogenides as well as nitride halogenides of the lanthanoids feature interesting compositions and connections of the structurally involved $[\mathrm{N}Ln_4]^{9+}$ tetrahedra, and have been excessively described throughout the last thirtyfive years [1].
Although the quaternary derivatives containing both chalcogenide and halogenide anions are characterized sufficiently as well, quaternary compounds containing additional alkali-metal components fall short in these descriptions. The only findings are lithium- and sodium-containing nitride iodides [2] besides some caesium-containing nitride tellurides [3].
All these compounds feature single-strands of interconnected $[\mathrm{N}Ln_4]^{9+}$ tetrahedra. In the case of the nitride iodides, the remaining alkali-metal cations form isolated units of $[\mathrm{LiI}_5]^{4-}$ and $[\mathrm{NaI}_6]^{5-}$ polyhedra, respectively.
The tellurides in contrast, embed their chains of $[\mathrm{N}Ln_4]^{9+}$ tetrahedra in two-dimensional networks of face-sharing bicapped trigonal $[\mathrm{Cs}_2\mathrm{Te}_{12}]^{22-}$ prisms, which are further connected to form corrugated layers.

The compounds $\mathrm{Na}Ln_9\mathrm{N}_4\mathrm{Se}_8$ (Ln = Gd – Dy) at hand show another structure, not only because they exhibit a mixed occupation Na^+/Ln^{3+} site in their crystal structures, adapting sodium and the respective lanthanoid on the same crystallographic position, but also because of their more condensed double-strands of *cis*-edge connected $[\mathrm{N}Ln_4]^{9+}$ tetrahedra (Figure 1). The mixed cation site (M) is located in *trans*-edge connected $[M\mathrm{Se}_6]^{10-}$ octahedra to form one-dimensionally infinite $^1_\infty\{[M\mathrm{Se}_{2/1}\mathrm{Se}_{4/2}]^{6-}\}$ chains (Figure 2).

EXPERIMENTAL METHODS

The three quaternary nitride selenides $\mathrm{Na}Ln_9\mathrm{N}_4\mathrm{Se}_8$ with sodium and lanthanoid metal (Ln = Gd – Dy) were obtained first as a side-product by the reaction of the respective metal (Ln: ChemPur, 99.9%) with sodium azide (NaN_3: Roth, 99%), selenium (Se: Aldrich, 99.999%) as well as the respective lanthanoid trichloride ($Ln\mathrm{Cl}_3$: ChemPur, 99.9%) and sodium chloride (NaCl: ChemPur, 99.96%) as fluxes in a solid-state reaction, originally aiming for the $Ln_4\mathrm{N}_2\mathrm{Se}_3$ representatives to form. But according to

$$8\,Ln + 8\,\mathrm{Se} + 4\,\mathrm{NaN}_3 + Ln\mathrm{Cl}_3 \rightarrow \mathrm{Na}Ln_9\mathrm{N}_4\mathrm{Se}_8 + 3\,\mathrm{NaCl} + 4\,\mathrm{N}_2$$

the unexpected side-products $\mathrm{Na}Ln_9\mathrm{N}_4\mathrm{Se}_8$ occurred instead. All reactands were handled under argon atmosphere in a glove box (GS MEGA *E*-Line, Malsch, Germany) and their mixtures were heated to 900°C for 8 days in evacuated and fused silica tubes. The described compounds crystallize as transparent orange-colored bars. Attempts to synthesize the calcium-containing derivatives $\mathrm{Ca}Ln_8\mathrm{N}_4\mathrm{Se}_8$ with no mixed metal site remained unsuccessful so far.

RESULTS AND DISCUSSION

The new compounds $\mathrm{Na}Ln_9\mathrm{N}_4\mathrm{Se}_8$ (Ln = Gd – Dy) cystallize in the monoclinic crystal system with the space group $C2/m$ (a = 1358 – 1341 pm, b = 399 – 394 pm, c = 1016 – 10026 pm and β = 109.1 – 109.3°) with one formula unit per unit cell. Their crystal structure contains two crystallographically different Se^{2-} anions, one unique N^{3-} anion, two crystallographically independent Ln^{3+} cations, all at 4*i* *Wyckoff* positions, and as already mentioned, one mixed occupation site at the *Wyckoff* position 2*a* with sodium (Na^+) and the respective lanthanoid trication (Ln^{3+}), sharing it in a 1:1 molar ratio.

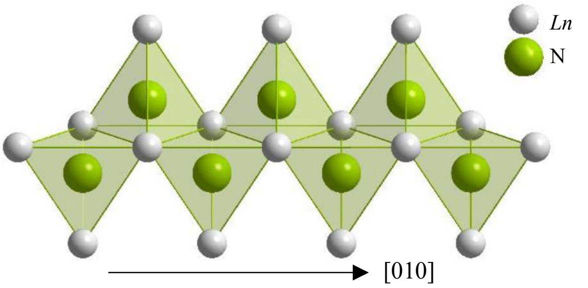

Figure 1. View at a $^1_\infty\{[\mathrm{N}Ln_{1/1}Ln_{3/3}]^{3+}\}$ strand of *cis*-edge connnected $[\mathrm{N}Ln_4]^{9+}$ tetrahedra propagating along [010].

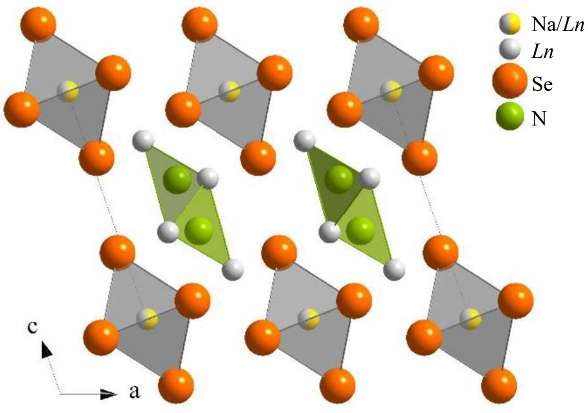

Figure 2. View at the (010) plane showing $^1_\infty\{[M\mathrm{Se}_{2/1}\mathrm{Se}_{4/2}]^{6-}\}$ chains (M = Na and Ln, 1:1 molar ratio) and $^1_\infty\{[\mathrm{N}Ln_{1/1}Ln_{3/3}]^{3+}\}$ strands arranged as rod packings.

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Computational Insight into Critical Lanthanide Separation through Ligand-Based Photophysical Energy Exchange

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INTRODUCTION

As essential parts of today's advanced materials, the demand for lanthanides is high, making them critical materials. However, the separation of lanthanides is still a very challenging task due to the similarities among different elements in their physical and chemical properties[1]. The current way to separate them at an industrial scale is based on liquid-liquid extraction with solvents and wastes resulting in a considerable negative environmental impact[2]. Therefore, we aim to develop a novel approach to separate them by exploiting the unique and discontinuous electronic structures of the lanthanides' 4*f* orbitals, via *element specific photo-induced modifications* of the chemical environment surrounding the metal ions[3-4]. Two complexes have been chosen to be the initial targets to accomplish this task: (**Thrust 1**) Yttrium (Y) or Dysprosium (Dy) tris-hexafluoroacetyl-acetonate (hfac) complexes appended with reactive *N*-oxide ligands to explore how the Dy excited *f*-states may alter photochemical reactivity, enabling kinetic separation; (**Thrust 2**) Different organo-phosphorus ligands effects on Europium (Eu) and Terbium (Tb) complexes altering the solubility by photo-excitation to enable dynamic separation.

This project is conducted in a close collaboration between a computational and an experimental team at NREL, the Schelter Research Group at the University of Pennsylvania (**Thrust 1**) and the Jensen and Sellinger groups at Colorado School of Mines (**Thrust 2**). We will present results of computational investigations in both thrusts. All calculation were carried out at the DFT level of theory using the Gaussian 16 suite of programs.

RESULTS AND DISCUSSION

Thrust 1: Experimental results showed a clear kinetic difference in the Dy vs Y complexes for the photo-induced oxygen-atom transfer in the ligand exchange reaction of *N*-Methylmorpholine *N*-oxide (NMMO) to Triphenylphosphine oxide (TPPO). Spectroscopic studies of excited state dynamics suggests excited states are shared between ligands (hfac and NMMO).

For hfac/NMMO complexes with Y, the computed UV/VIS spectra show a large absorption band from 250 nm to 350 nm similar to the known absorption of the hfac ligands. A Natural Transition Orbitals (NTO) analysis was performed on each absorption in this band and a common trend is observed: a shared excitation from the O atoms of both the hfac and NMMO into the π*system of the hfac, with accompanying weakening of the NMMO binding to the Y in the excited state. Further analysis and construction of reaction pathways in various excited states will be used to to investigate in detail the underlying mechanisms.

Thrust 2: Three organo-phosphorus ligands chosen for initial studies, have shown experimentally a difference in dipole moment[5], which may modulate solubility and reactivity with lanthanides. The computed dipole moment for the 3 ligands on Eu and Tb atoms are in agreement with the experimental values but we have found no significant difference between dipole moments when bound to Eu versus Tb. However, the calculated molecular orbital (MO) diagram suggests a difference in the LUMO between the Eu and Tb complexes. In the case of the Eu the LUMO is mainly located on the metal ion but for the Tb it is located on a ligand. Those computational results imply that the ligands are unlikely to affect the ground-state *solubility* for Eu and Tb, but the predicted impact on the character of the LUMO suggests that the complexes may display distinct excited state UV/Vis photochemistry.

CONCLUSIONS

In this project, 4 different lanthanides (Y, Eu, Tb and Dy) have been studied computationally in order to understand prospects to separate them by photo-induced reaction. Both thrusts show promising experimental and theoretical results. In thrust 1, once the underlying mechanism of the kinetic difference between Y and Dy is better understood, we will seek to to improve and export it to other lanthanides. In thrust 2, the computational difference in the LUMO between Eu and Tb points at a possible excited state feature that can lead to rational design of ligands for optical separation.

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Development of Photochemically Active Ligand Coordination Spheres for Light-driven Separation of Critical Rare Earths

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INTRODUCTION

To overcome limitations of cation-size based separations of critical rare earth elements[1], or rare earths (REs), we are developing a novel approach that exploits the *unique and discontinuous electronic structures* of well-shielded 4*f* orbitals of the individual rare earth ions[2-3], via *dynamic and element specific photo-induced modifications of the chemical environment* surrounding the metal ions. This concept is built on synthesis of ligands with the desired chemical and physical motifs[4-7] that will ultimately enable demonstration of efficient solution-phase separations *via* control of (i) large, dynamic excited-state perturbations of the photophysical properties of the complexes or (ii) sensitization of ligand-centered photo-chemical reactions[8-9]. This will expand our understanding and manipulation of excited-state energy flow in rare earth complexes, to enable control of solubility and separation, by:

- Developing chemical descriptors of ground-state electronic structure & excited-state dynamics
- Probing energy transfer between rare earth ions and surrounding coordination ligands
- Inducing rare earth-selective photophysical or photochemical changes in the coordination sphere
- Evaluating changes in the strain and solubility within the coordination complexes

APPROACH

Our effort focuses on development of two systems: Rare earth complexes of (**1**) Asymmetric organo-phosphorus ligands appended with light harvesting (and ultimately photoswitchable) chromophores (Fig.1); and (**2**) a mixed ligand systems of light-harvesting tris-hexafluoro-acetyl-acetonate (hfac) and reactive *N*-oxide ligands (Fig. 2). This work is a close collaboration between the Jensen and Sellinger Groups at Colorado School of Mines (**1**), the Schelter Group at the University of Pennsylvania (**2**), and a combined experimental spectroscopy and computational chemistry team at NREL.

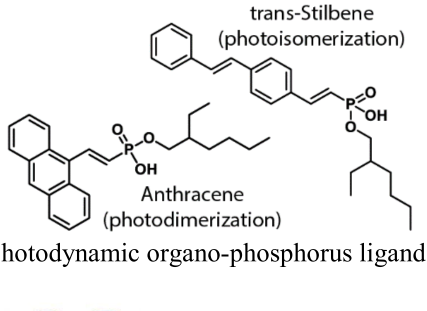

Fig. 1. Photodynamic organo-phosphorus ligands.

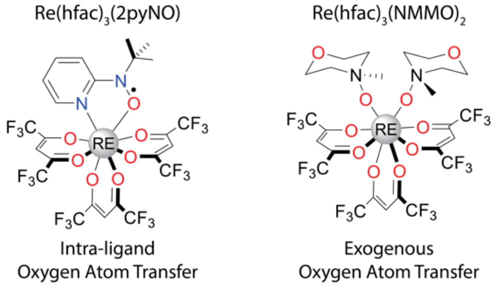

Fig. 2. Photodynamic organo-phosphorus ligands.

RESULTS AND DISCUSSION

We will illustrate recent progress made in the design, synthesis, and characterization of light harvesting organo-phosphorus ligands (Fig. 1), such as derivatives containing photodimerizable anthracene or trans-to-cis photoisomerizable stilbene chromophores. We will also highlight recent efforts to develop complexes that enable control over energy transfer to ligands containing known oxygen atom transfer moieties (Fig. 2). Finally, we will show preliminary data related to the photophysics in these systems, and discuss the implications related to the use of photochemical transformations for separations of critical rare earth elements.

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Selective Reduction of Niobium(V) Species to Promote Molecular Niobium/Tantalum Separation

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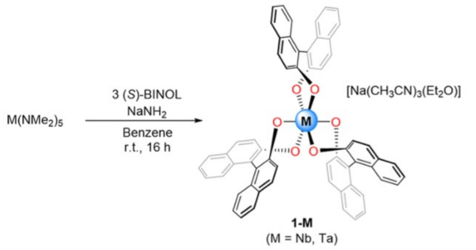
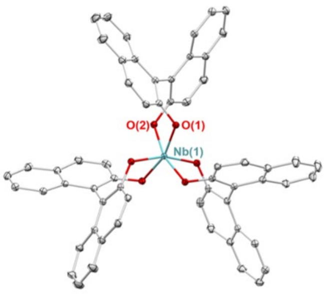
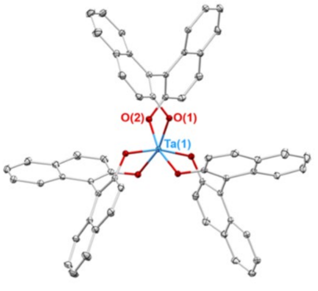
The demands for tantalum, used in capacitors, and niobium, widely used in steel alloys, have recently exploded, with global production doubling for Ta and quadrupling for Nb since 2000.[1] Nb and Ta are sourced from the minerals columbite and tantalite, and are invariably found together in their mineral matrices.[2] As such, a separation step is required to purify the two elements from one another. However, Nb and Ta exhibit similar chemical properties, with essentially identical ionic radii,[3] reactivity, and hardness, making their separation challenging.[4] The current industrial separation process requires fluorination of the mixed-metal oxides using hydrofluoric acid, with associated toxicity, and safety concerns.[5] Given the interest in sustainable Nb/Ta separations, we report the synthesis of isostructural complexes $[Na(CH_3CN)_3(Et_2O)][M((S)\text{-}BINOLate)_3]$ [M = Nb (**1-Nb**), Ta (**1-Ta**)] and describe a method for separating these compounds.

Standard synthetic chemical and computational methods were used. For details, see citation.[6]

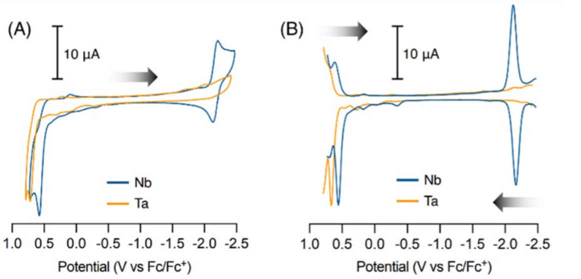
The synthesis of **1-M** and associated crystal structures are presented below.



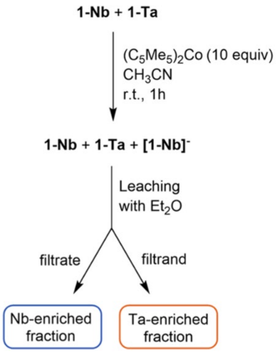




Cyclic voltammetry (A) and differential-pulse voltammetry (B) of **1-M** revealed a reduction feature present in the electrochemical window of **1-Nb** but not for **1-Ta** which are rationalized through computational studies in the context of ligand−metal π interactions.



Using this observed difference, **1-Nb** was selectively reduced and leached away.



Differences in the redox properties of **1**-**M**, allow for the selective reduction of **1-Nb**. After reduction, the niobium product ($[(C_5Me_5)_2Co]$[**1-Nb**]) was leached from unreacted **1-Ta** (separation factor = 6 ± 2). DFT calculations closely reproduced experimental spectra and electrochemical redox features for **1-M**, indicating that the *ca.* 0.75 V cathodic shift in the $M^{V/IV}$ redox couple of **1-Ta**, compared to **1-Nb**, is amplified by a greater degree of metal-ligand π bonding in **1-Ta**. These results demonstrate a novel molecular Nb/Ta separation process and provide a framework for alternative methods of the separation of these critical metals.

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Defining Qubit Properties in the Early Actinides

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Abstract

The realization of a quantum computer would change our world by boosting computation times and cracking currently highly safe encryption algorithms, and *f*-element systems have shown exceptional promise in quantum information processing (QIP). Specifically, relativistic effects cause the energetics of the 5*f* and 6*d* orbitals to change as the actinide series is traversed left to right, imparting a rich and complex chemistry wherein control of quantum bit (qubit) could be possible. This talk will explore high-valent $5f^1$ actinide complexes as qubits by evaluating how its unique atomic properties, including spin-orbit coupling (SOC), crystal electric field (CEF), and nuclear spin, can be exploited through coordination chemistry to observe long-lived coherence times. Specifically, we will discuss purification of legacy actinide material, synthesis of potential actinide qubits, and development of first-principle derivation of SOC and CEF parameters for $5f^1$ complexes. The research will leverage both experimental and theoretical findings to generate a set of features to enhance quantum coherences in actinide molecules.

Electrochemical Activation of the Uranyl Ion

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ABSTRACT

The redox chemistry of uranium is dominated by the uranyl ion [UO_2^{2+}], a species which features a high-valent uranium center in the +VI oxidation state and two terminal oxo ligands with a mutual *trans* geometry. The U–O bonds of the uranyl ion are very strong, a finding attributable to involvement of both 6*d* and 5*f* orbitals in covalent bonding between the oxo ligands and the uranium center; the U−O bond dissociation energy has been estimated at ca. 133 kcal mol^{-1} from gas phase measurements,[1] testifying to a high nominal bond order of three, as predicted computationally. Under aerobic and aqueous conditions, uranium undergoes speciation to form the water-soluble uranyl ion quite readily, with the result that this species can be a persistent pollutant. Reduction processes, however, have been shown to take place in anaerobic environments and under the influence of certain microorganisms; these are relevant to conditions found in nuclear material storage facilities. The reduction processes are desirable, as reduction of the uranyl ion to form, for example, uranium(IV) dioxide, results in diminished aqueous solubility and lowered environmental mobility.

In light of these considerations, a fundamental challenge in uranium chemistry lies in designing pathways for activation of the U–O bonds in uranyl, since such pathways could be used to strategically control the speciation of uranium and selectively engender new chemistry. Foundational work in this area showed that the uranyl(V) monocation, [UO_2^{+}], a species formed by one-electron reduction of [UO_2^{2+}], is more reactive and thus a target for study of U–O bond activation.[2] However, uranium(V) species are typically prone to disproportionation and other uncontrolled reactivity, making study of U–O functionalization at this oxidation state challenging. Important work carried out under anaerobic conditions has shown that the basicity of the oxo groups increases upon reduction, favoring interaction of the oxo ligands with electrophilic reagents.[3] With chemical reductants and suitable electrophiles, functionalization of one or both uranyl oxo groups to yield new, lower-valent products can be achieved. Reductive silylation, borylation,[4] and metalation[5] have all been demonstrated to date, suggesting that U–O functionalization reactions can be controlled under chemical conditions and enabling new exploration of actinide-oxo chemistry. In this realm, however, rather harsh chemical reductants and strongly electrophilic reagents appear required to access the oxo activation pathways explored to date, suggesting that high energy barriers may be involved in these chemistries. In particular, oxo-functionalization via borylation (U–O–B formation) has been carried out primarily with tris(pentafluorophenyl)borane ($B(C_6F_5)_3$; i.e., BCF), a strong electrophile that is commonly used in organometallic catalyst activation, although other boron-containing reagents have been utilized in related contexts.[6] To the best of our knowledge, however, neither use of electrochemical reduction nor use of milder triaryl boranes have been explored, suggesting an opportunity lies in probing uranyl activation under electrochemical conditions where the applied potential can be controlled to avoid unnecessary energetic losses and unselective reaction channels.

Here, we report a new oxo-functionalization scheme that can be achieved with electrochemical or chemical reduction through use of triphenylborane (BPh_3) as the electrophile. Following generation of a metastable U^V species by one-electron reduction of UO_2^{2+}, we find that the uranyl ion can be readily functionalized to form either mono- or bis-borylated derivatives that have been characterized in the solid state. Comprehensive electrochemical, spectrochemical, and spectro-electrochemical studies have been used to reveal a stepwise, highly selective reaction sequence involved in accessing these borylated complexes, a sequence which begins in all cases with reduction, as BPh_3 does not react with the parent UO_2^{2+} complex. Our latest results from this project will be discussed, including mechanistic insights and analysis of structural data for the key compounds involved in the oxo activation.

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Ligand K-edge X-ray Absorption Spectroscopy of Organometallic Rare-earth Complexes for Quantum Information Science

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ABSTRACT

Quantum information science (QIS) shows great promise for applications in sensing, communication, and computing. if one can generate controllable quantum objects, or “qubits.” Developing qubits based on molecular species gives one the opportunity to isolate ions within a tunable ligand environment. Linear metallocenes, especially those based on cyclopentadienyl ligands, have been shown to effectively stabilize discrete electronic states for anisotropic rare-earth ions.[1-4] Neutral metallocenes offer the added benefit of being sublimable, allowing for a well-defined array of qubits to be deposited on a surface.

The ability to tune the properties of a molecular-based qubit through chemical synthesis allows us to quickly screen and identify different qubit targets whose properties can be tuned by a change in the ligand. We use ligand K-edge X-Ray Absorption Spectroscopy (XAS) to interrogate the ligand field and interpret our findings with an MO model. The electronic structures of a series of organometallic rare-earth metallocenes with a variety of ligand modifications were studied with carbon K-edge XAS and the electronic configuration data was assessed against computed multi-reference spin-orbit coupled electronic states. This work aims to direct the evolution of novel molecular qubit targets.

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Towards Strongly Correlated Lanthanide-TTF Molecular Materials

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Strongly correlated materials have been of interest in solid-state chemistry for a variety of applications including spintronic devices, superconductors and fundamental quantum effects.[1,2] CeCoIn5 is one such material where superconductivity at lower temperatures is observed due to participation of *f*-electrons into the conduction band.[3] This electron delocalisation in intermetallic compounds is referred to as Kondo interaction. Such interactions have never been observed before in any molecular materials. However, Andersen and coworkers found cerrocene molecules to show similar interactions at a molecular level.[4] Cerrocene shows multiconfigurational ground state, i.e. Ce(III) and Ce(IV), both of which contribute to the ground state because of strong correlation of *f*-electron with the conduction band.

The goal of this project is to extend such local Kondo interactions to molecular materials. Our hypothesis is that these molecular materials will then mimic the intermetallic compounds. Discovering such strong electron correlation in molecular systems would give birth to a new field of fundamental chemistry. To achieve this, judicious ligand environments around *f*-elements would give us a good control that is missing in the intermetallic compounds. We have undertaken a donor-acceptor approach towards this goal. Redox-active lanthanide complexes when paired with an appropriate organic donor/acceptor can lead to the formation of molecule based strongly correlated materials.

Among well studied classes of organic donors, tetrathiafulvalene (TTF) stands out as a well studied organic donor that have shown emergent properties including high conductivity, magnetic ordering, superconductivity.[5] Herein, we report the synthesis and solid-state structures of TTF-based lanthanide molecular materials of the form $(TTF)_3[LnCl_6]$. These materials are isolated by recombination of $LnCl_3$ with photoinduced *in-situ* generated TTF^+Cl^-. All compounds are characterized by single crystal X-ray diffraction and Raman spectroscopy. Oxidized radical cation form of TTF is confirmed by central C-C bond length elongation and significant Raman shifts. These compounds also show size dependency across the lanthanide series and have been utilized to separate La/Dy and La/Nd pairs. Magnetic and conductivity property measurements are underway to understand the electronic structure and *f*-electron delocalisation in these materials.

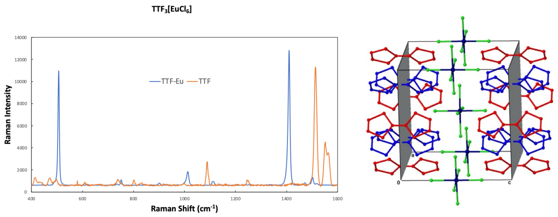

Figure: (a) Raman shift in $(TTF)_3[LnCl_6]$ due to the radical cation form of TTF. (b) X-ray structure of the series $(TTF)_3[LnCl_6]$.

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From a nanoparticular solid-state material to molecular organo-f-element-polyarsenides

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INTRODUCTION

For group 15 Zintl ions, the research on molecular coordination compounds is heavily focused on phosphorus and transition metals or main group elements, which can be ascribed to the availability of the molecular and soluble phosphorus allotrope P_4.[1] The heavier congener As_4 is inconvenient to synthesize and highly prone to decompose into gray arsenic. With the synthesis of As^0_{nano}, we have presented an approach to this issue that allows the stoichiometric usage of an elemental As source. The activation of As^0_{nano} by the application of different reducing agents from f-element and main group chemistry was recently reported.[2] In this study, we report a new pathway towards organo-f-element arsenic Zintl ions by combining the solid-state material As^0_{nano} with the high redox potentials of molecular non-classical divalent lanthanide compounds.[3]

RESULTS AND DISCUSSION

The non-classical divalent lanthanide three electron reducing agents **A** and four electron reducing agents **B** (Fig. 1) were employed for the activation of As^0_{nano}.

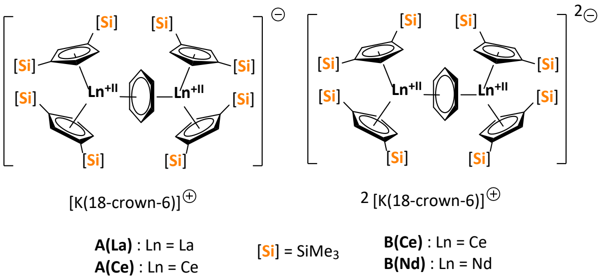

Fig 1. Three- (**A(La)**, **A(Ce)**) and four- (**B(Ce)**, **B(Nd)**) electron reducing agents, featuring non-classical divalent lanthanides ([Si] = $SiMe_3$).[4]

On the one hand, the clean formation of an As_7^{3-} Zintl anion with a nortricyclic structure in **1** (Fig. 2) is observed by using the 3-electron reducing agents **A(La)** and **A(Ce)**. On the other hand, the formation the As_{14}^{4-} Zintl species **2** as sole isolable product is seen by applying the 4-electron reducing agent **B(Nd)** at elevated temperature. Compound **2** represents the largest known organo-lanthanide-polyarsenides to date. In between these boundaries, mixtures of various compounds with a polyarsenide as central motif were obtained (Compounds **3** and **4** with **B(Nd)**). These results show that the formation of sophisticated structures directly out of nanoscale gray arsenic, which is a kind of polymer, is a complex process with various intermediates. Only careful tuning of the reaction conditions and the use of an optimized reducing agent leads to isolable and unprecedented products.

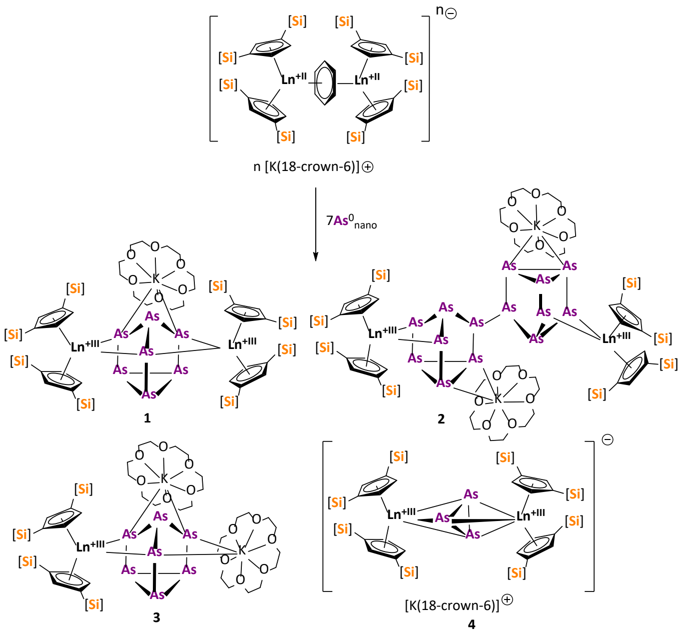

Fig 2. Overview of the variety of synthesized polyarsenides ([Si] = $SiMe_3$).

In summary, we have demonstrated that the solid state material As^0_{nano} can be activated via 3- and 4-electron reducing agents of the early non-classical divalent lanthanides to obtain a variety of new molecular organo-lanthanide-polyarsenides. This significantly extends the bridge from solid-state gray arsenic to molecular f-element polyarsenides, contributing to a better understanding of the formation and properties of such polyarsenide materials.

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Synthesis and Characterization of Nitro-functionalized Lanthanide Trispyrazolylborates

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INTRODUCTION

Lanthanide (Ln) pyrazolylborates are a diverse class of materials that have found applications as light-emitting and magnetic devices, owing to properties such as sensitized Ln^{3+} emission and slow magnetic relaxation.[1, 2] Currently, there has been very little work done on lanthanide pyrazolylborates functionalized to have strongly electron-donating or withdrawing groups and their introduction presents the opportunity to tune the properties of the resultant lanthanide pyrazolylborate *via* judicious choice of ring substituent.[3] The inclusion of a nitro (NO_2)-group could have a structure-directing effect, as a fourth binding site is available in the form of the oxygen atoms (Figure *1*). Moreover, the electron-withdrawing nature of this group will lower the energy of the π* orbitals of the pyrazolylborate ligand, affecting the material's photophysical and possibly magnetic properties. Herein, we present the syntheses, crystal structures, photophysical and magnetic properties of two families of lanthanide complexes with asymmetrically functionalized *n*-nitrotrispyrazolylborates, $n\text{-}NO_2Tp^-$ (n = 3 or 4).

EXPERIMENTAL METHODS

The reported lanthanide *n*-nitrotrispyrazolylborates were characterized by single crystal X-ray diffraction (SCXRD) and their optical properties by luminescence spectroscopy, lifetime measurements, quantum yields and time-dependent density functional theory (TD-DFT) calculations. SQUID magnetometry was also employed to analyse their magnetic properties.

RESULTS AND DISCUSSION

Lanthanide complexes with $n\text{-}NO_2Tp^-$ (n = 3 or 4) display remarkable structural diversity and tunable nuclearity with monomeric, dimeric and tetrameric complexes across six different structural types owing to new a Ln—ONO coordination mode (Figure 1). Optical measurements, supported by TD-DFT calculations reveal that $3\text{-}NO_2Tp^-$ is a good sensitizer of Ln^{3+} emission while $4\text{-}NO_2Tp^-$ is not and both $n\text{-}NO_2Tp^-$ ligands utilize a triplet intra-ligand charge transfer (^{3}ICLT) pathway sensitize to Ln^{3+} luminescence. The Nd^{3+} complex with $4\text{-}NO_2Tp^-$, $Nd(4\text{-}NO_2Tp)_3$ exhibits single-molecule magnet properties under an applied field, analogous to the non-functionalized $NdTp_3$.

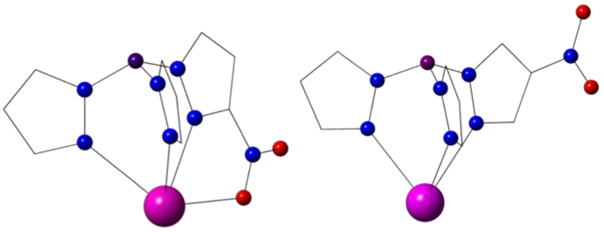

Figure 1: Diagrams of the coordination modes of the asymmetric *n*-nitrotrispyrazolylborate ligands, $3\text{-}NO_2Tp^-$ (left) and $3\text{-}NO_2Tp^-$ (right). Eu (pink), N (blue), O (red), C (black lines), B (purple) and H atoms are omitted for clarity.

CONCLUSIONS

The diversity in properties afforded by the reported compounds allow us to study how substituent effects influence both the luminescence and magnetic properties of Ln-materials and may be a useful platform to probe magneto-luminescent properties. By establishing trends in these materials, this work will inform the rational design of Ln-based luminescent single-molecule magnets.

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Reactivity of Multimetallic Thorium Nitrides Generated by Reduction of Thorium Azides

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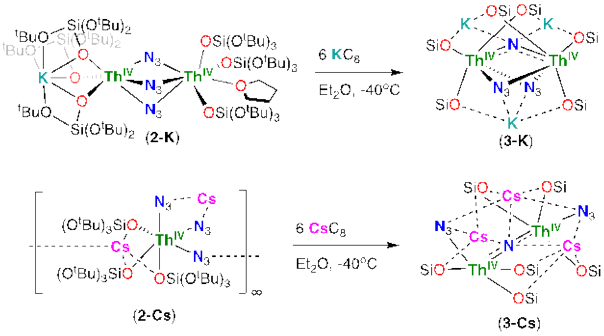
INTRODUCTION

Thorium nitrides are likely intermediates in the reported cleavage and functionalization of dinitrogen by molecular thorium complexes and are attractive compounds for the study of multiple bond formation in f-element chemistry, but only one example of thorium nitride[1] isolable from solution was reported. Here, we show that stable multimetallic azide/nitride thorium complexes $[K_3\{(Th(OSi(O^tBu)_3)_3)_2(\mu\text{-}N)(\mu\text{-}N_3)_2\}]$[2], **3-K**, and $[Cs_3\{(Th(OSi(O^tBu)_3)_3)_2(\mu\text{-}N)(N_3)_2\}]$[2], **3-Cs** can be generated by reduction of thorium azide precursors, a route that has failed so far to produce Th nitrides. The nature of the cation plays an important role in generating a nitride product and results in large structural differences with a bent Th=N=Th moiety found in the K-bound nitride as a result of a strong K-nitride interaction and a linear arrangement in the Cs-bound nitride. Reactivity studies demonstrated the ability of Th nitrides to cleave CO in ambient condition yielding CN^-.

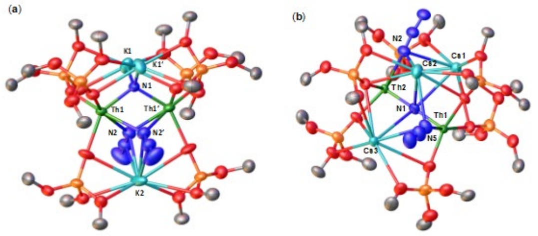
RESULTS AND DISCUSSION

To promote nitride formation, we investigated the reduction of complexes **2-K**[2] and **2-Cs**[2] with excess KC_8 and CsC_8, in Et_2O at -40°C, allowing the isolation of bis-azide, mononitride, **3-K** and **3-Cs** in 48% and 71% yield.



Scheme 1: Synthesis of **3-K** and **3-Cs**.

Both **3-K** and **3-Cs** complexes were characterized by X-ray crystallography, NMR spectroscopy and density functional theory calculations. In the solid-states structure, they both display a dinuclear Th(IV) complex, featuring a bridging nitride and two azide ligands, but the presence of two different counterions gives rise to paramount structural differences in the two complexes. In **3-K**, Th(IV) ion is bound by a bent bridging nitride (Th=N=Th = 114.4(3)°), and the two bridging azide ligands. In contrast, **3-Cs** has a linear bridging nitride (Th=N=Th = 178.1(15)°), and two terminal azide ligands.



Scheme 2: Solid-state molecular structure of **3-K** (a) and **3-Cs** (b) (50 % probability ellipsoids).

We also investigated the reactivity of **3-K** and **3-Cs** toward CO. Both **3-K** and **3-Cs** reacted with excess ^{13}CO, yielding $^{13}CN^-$ in 30% (**3-K**) and 22% (**3-Cs**) after hydrolysis with D_2O (pD = 13). We hypothesized that removal of the alkali ions might favor the loss of the azide ligands, affecting the reactivity of complex. Addition of 2.0 equiv of 2.2.2-cryptand to a solution of **3-K** in toluene at −40 °C resulted in the formation of putative nitride "$[\{KTh_2(OSi(O^tBu)_3)_6)(\mu\text{-}N)\}]$", **X**. Addition of excess ^{13}CO to complex **X**, yielding $^{13}CN^-$ in 70% after hydrolysis. The increased reactivity is likely to be the result of a less crowded Th center allowing for easier CO binding.

CONCLUSIONS

In conclusion, we have synthesized the first multimetallic Th_2K_3 and Th_2Cs_3 azido/nitrido complexes, which are the second examples of isolable molecular thorium nitrides and studied the reactivity toward CO. We anticipate that the synthetic route presented here, which takes advantage of alkali azides to stabilize both the reactions intermediates and the final nitride, will lead to the development of thorium nitride chemistry.

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Poster abstract for 29th Rare Earth Research Conference June 26-30, 2022, Philadelphia

Ligand Control of Kinetics in Rare Earth Solvent Extraction Separations

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Industrial-scale separations of rare earth elements are based on repeated liquid-liquid separations over many stages to isolate pure rare earths from their mixtures, and the rates of rare earth transport across the liquid-liquid interface place intrinsic limitations on the throughput of these separation systems. To understand how aqueous ligands affect the rate limiting phase transfer processes of rare earth cations, we have studied the effects of aqueous ligands on the extraction of neodymium(III) by 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEHEHP) using both microfluidic determinations of the rate of partitioning and a novel real time spectroscopic approach in systems where the extraction reaction is controlled by the chemical kinetics rather than simple diffusion. Depending on the aqueous ligands present and the acidity, a variety of equilibrium binary and ternary complexes could be identified in both the bulk aqueous and organic phases. The phase transfer mechanisms of the Nd were similarly complex. The extractant HEHEHP was involved in the rate limiting step of both the Nd extraction and the stripping reactions regardless of the aqueous ligands present, except for the Nd-EDTA-citrate/ HEHEHP system. In all other cases, the rate limiting step of the partitioning mechanism is influenced by formation of Nd-HEHEHP complexes (extraction direction) or dissociation of Nd-HEHEHP complexes (stripping direction). The influence of aqueous ligands on the rate of partitioning is more complicated. Regardless of the ligands present, we find the mechanism for extraction of Nd in these systems also involves the dissociation of aqueous complexes, but the rates of Nd stripping vary greatly with the nature of the aqueous ligands present and suggest complex reaction mechanisms and competing pathways for the Nd partitioning reactions.

Poster abstract for 29th Rare Earth Research Conference June 26-30, 2022, Philadelphia

Novel Ligands for Rare Earth Solvent Extraction Separations

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Acidic organophosphorus ligands have been the principle reagents for separations of individual lanthanide cations for the past 50 years. While the fundamental rare earth coordination chemistry of the core phosphinic, phosphonic, or phosphoric acid moieties of these ligands is similar, there remains an opportunity to introduce new functionalities into these ligand frameworks by varying the ligand's organic substituents. Such variations of the substituents can alter the intra-lanthanide selectivity of the ligands as well as the solubility of the ligands and lanthanide complexes in organic solvents. However, incorporation of new substituents also can affect the dipole moment, acidity, and hydrogen bond strength of the acidic group, which in turn affect the extraction strength of the ligand. We describe here the extraction behavior of monoacidic 2-ethylhexyl esters of phosphonic acid where the substituents directly attached to the phosphorus center are varied by the incorporation of a versatile aromatic vinylene linking group. Substantial variation in the extraction of europium is observed across the series of ligands, although the general metal coordination environment changes little. These variations can be attributed to changes in the complexation strength of the ligands brought about by the electronic effects of the new substituents, and they provide an avenue for increasing extraction strength when ligand functionalization limits the ligand's the partition coefficient or solubility.

Use of a selective aqueous holdback reagent for improved adjacent lanthanide separation in liquid-liquid extraction

Katherine R. Johnson, Darren M. Driscoll, Joshua Damron, Alex S. Ivanov, Santa Jansone-Popova

Rare earth elements, which include the lanthanide series, are ubiquitous and indispensable materials used in a wide range of technologies such as smartphones, wind turbines, and electric vehicles. Due to the growth of these applications and challenges of the supply chain, new strategies for recycling and mining of lanthanides are an important and emerging goal, as stated by both the U.S. Department of Energy and the E.U. Commission. The difficulty in delivering pure lanthanides lies not only in the separation of lanthanides from ores, mining waste, or end-of-life products, but also in the separation of lanthanides from one another and is largely due to their similar physical and chemical properties.

One preferred separation method is liquid-liquid extraction because of its simplicity, speed, and broad applicability. Traditionally, the successful separation of targeted lanthanides relied on a highly selective ligand in the organic phase to extract lanthanides from an aqueous solution. In this study, we investigate how an aqueous holdback agent can be leveraged for its affinity for light lanthanides, while diglycolamide-based ligands extract heavy lanthanides to the organic phase.

Structural and Reactivity Studies of Synthetic Model Complexes of a Rare-Earth Dependent Methanol Dehydrogenase

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INTRODUCTION

The active sites of XoxF-type methanol dehydrogenase (MDH) enzymes contain a redox-inactive rare-earth (RE) cation coordinated to a redox-active pyrroloquinoline quinone (PQQ) cofactor. These enzymes are similar to MxaF-type MDHs, whose active site features a redox-inactive calcium cation. The discovery of XoxF-type MDHs showed the relevance of RE ions in biology.

RESULTS AND DISCUSSION

Our group has previously reported the first RE-containing synthetic functional model for this RE-dependent MDH.[1] The ligand L_{QQ} can coordinate to lanthanum (La) to form $[La(L_{QQ})(NO_3)_3]$, which catalytically dehydrogenates alcohols to their corresponding aldehydes. More recently, we have explored the structure and reactivity of other analogous structures containing calcium and other RE ions (RE = neodymium, europium). The differences in reactivity depending on the identity of which redox-inactive metal is coordinated to the ligand could potentially indicate a switch in the active mechanism of oxidation or shut off reactivity. For instance, minimal conversation is observed when Eu is coordinated to L_{QQ}, whereas La shows catalytic activity when bonded to L_{QQ}. Further synthetic and computational studies will be conducted to provide details in the redox cycling of L_{QQ} and the mechanism of the multielectron oxidation of alcohols.

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Harnessing Magnetic Field for Rare-Earth Separations

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ABSTRACT

Industrially, rare-earth (RE) elements are separated using technologies such as solvent extraction, ionic exchange, and selective precipitation, all of which use the difference in sizes of the RE elements. However, these processes require a large amount of material and energy, which further increases the price and generates waste causing severe environmental stress. Therefore, new approaches to separating RE mixtures by harnessing the magnetic properties of these critical metals are needed. The central theme of our work is to design complexes of RE elements with strongly donating axial ligands that can increase their magnetic anisotropy. To achieve the syntheses of the metal complexes, molecular design principles and studies of structure-property relationships are crucial. Once the complexes are isolated, the anisotropic nature of the RE ions (oblate – equatorially elongated vs. prolate – axially elongated;)[1] will primarily be responsible for the separations of the REs, and the separation factors for fractional crystallization will be improved in the presence of an applied magnetic field (~0.1-0.2 T) coupled with a temperature gradient.[2] The idea is that the spin distribution (shape) of RE ions for a given open-shell $4f^n$ configuration will be manipulated when the magnetic field interacts with these ions. Furthermore, the axial ligand field should favor separation of REs with oblate free ion shape (Ce–Nd, and Tb–Ho), and an equatorial ligand field should prefer RE ions with prolate shape (Sm and Er–Yb).

Here, we synthesized analogues of literature Dy single-ion magnets using axially bound tricyclohexylphosphine oxide (Cy_3PO) due to its higher ligand field strength.[3,4] We chose these molecules since they show large magnetic anisotropy and have relatively simple structures. The syntheses of a series of isostructural compounds, formulated as $REX_3(O{=}PCy_3)(thf)$, RE = Dy, Y; X = $Cl^–$, $Br^–$, $I^–$ will be discussed. We expect to see an increase in the $SF_{RE1/RE2}$ with the increased barrier height (ground-excited state energy gap) from $Cl^– < Br^– < I^–$. This is due to the increase in the magnetic anisotropy, which can be directly related to the decrease in the equatorial ligand field strength from $Cl^– > Br^– > I^–$. Detailed solid-state X-ray diffraction augmented with spectroscopic characterization revealed the atom connectivity and isostructural nature of these compounds. Initial data on the separation factors $SF_{RE1/RE2}$ will also be presented. The positive correlation between barrier height and separation factors will be useful in further designing effective molecular systems for achieving greater low energy separations.

We will also discuss the synthesis of molecules that are air and moisture stable and that exhibit high magnetic anisotropy. We are seeking systems from the literature on which magnetic data is available and for practical purposes, are deemed to be air and moisture stable. Assembly of ligands around rare-earth metals with groups that provide a strong axial field creating high energy barriers between ground and first crystal excited state is also necessary in our design principles. To accomplish this goal, we synthesized and characterized RE-DOTA complexes that are soluble in water. The magnetism data from the literature indicated that these complexes display varying magnetic anisotropy when different RE ions are bound to the DOTA ligand which can be exploited further to separate these RE ions from each other under the influence of a magnetic field and temperature gradient.[5] Selective separations of REs from the mixtures of these complexes using magnetic crystallization have been attempted and show a two-fold increase in the $SF_{Dy/La}$ compared to the separations performed without a magnet. The use of a 3D printed setup made of cheap polymers such as polylactic acid for magnetic crystallization has been discussed. This setup ensures the least disturbance of the vial and the magnet resulting in effective crystallization.

Another approach to separating RE mixtures is exploiting different polymorphic properties at the molecular level. We will discuss various polymorphic forms of one of the most polymorphic organic molecules, ROY.[6] Unprecedented results on its metalation using *d*- and *f*-block elements have also been discussed.

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$Cs_3La[AsS_4]_2$: A Cesium-Containing Lanthanum Thioarsenate(V)

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INTRODUCTION

The structural diversity of alkali-metal thiophosphates with transition or even rare-earth metal participation has been studied intensively in the past years. However, only few investigations on thioarsenates(V) were conducted although they might as well exhibit a large variety of different structures and stoichiometric arrangements.

EXPERIMENTAL METHODS

The target compound was synthesized from metallic lanthanum (La), cesium polysulfide (Cs_2S_x, $x \approx 3$), arsenic sesquisulfide (As_2S_3) and elemental sulfur in a stoichiometric ratio of 1:1:1:6. Cesium polysulfide was prepared from the elements (two equivalents of cesium with three equivalents of sulfur) via ammonothermal synthesis in an autoclave for two days until the complete conversion of the elemental cesium. The starting materials were filled into a fused glassy silica ampoule in an argon-filled glove box and sealed under dynamic vacuum. The ampoule was placed inside a muffle furnace and heated to 600 °C with 30 K/h, held for 4 days and then cooled back to room temperature with 3 K/h. Afterwards, the bulk product was inspected for suitable single crystals as the powder X-ray diffraction pattern revealed more than one phase.

RESULTS AND DISCUSSION

Here we present a cesium-containing lanthanum thioarsenate(V) with the composition $Cs_3La[AsS_4]_2$ (CSD number: 2156995). This stoichiometric formula seems familiar as $K_3\mathit{RE}[AsS_4]_2$ compounds with *RE* = Nd, Sm, Gd and Dy have previously been published by Bensch et al. [1,2]. The novel cesium compound $Cs_3La[AsS_4]_2$ does not share the same structure type ($K_3Gd[AsS_4]_2$: a = 1034.84(7) pm, b = 1880.39(14) pm, c = 882.38(6) pm, β = 117.063(7)°, Z = 4; monoclinic, $C2/c$) [2], however. $Cs_3La[AsS_4]_2$ crystallizes monoclinically as well, but with the non-centrosymmetric space group $P2_1$ and the lattice parameters a = 1014.71(6) pm, b = 702.68(4) pm, c = 1192.35(7) pm, β = 90.232(3)° for Z = 2. There is only one unique La^{3+}-cation position within the asymmetric unit surrounded by eight S^{2-} anions ($d(La^{3+}–S^{2-})$ = 295.5 – 299.9 + 325.4 + 327.3 pm) building a bicapped trigonal prism. Connected via corners, these $[LaS_{6+2}]^{13-}$ prisms form one-dimensional infinite chains propagating along the *b*-axis, which are separated from each other by three crystallographically independent Cs^+ cations in 9- to 11-fold sulfur coordination. Moreover, all sulfur atoms participate in the arsenic(V) coordination forming isolated $[AsS_4]^{3-}$ tetrahedra ($d(As^{5+}–S^{2-})$ = 212.2 – 218.9 pm, $\sphericalangle$(S–As–S) = 97.3 – 123.2°).

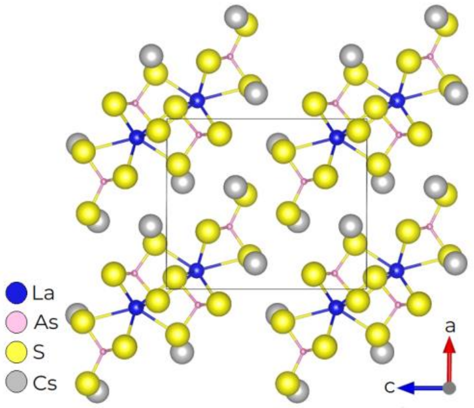

Figure 1. Extended unit cell of $Cs_3La[AsS_4]_2$ as viewed along the *b*-axis.

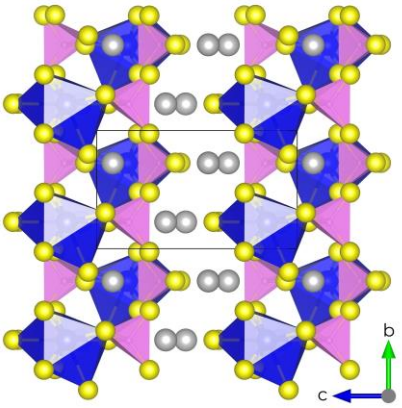

Figure 2. (001) projection of the crystal structure of $Cs_3La[AsS_4]_2$ with highlighted $[LaS_8]^{13-}$ and $[AsS_4]^{3-}$ polyhedra to emphasize the chains along [010].

CONCLUSIONS

The title compound $Cs_3La[AsS_4]_2$ was successfully synthesized from lanthanum, cesium polysulfide, arsenic sesquisulfide and sulfur in a molar ratio of 1:1:1:6. The structure was solved and refined from single-crystal X-ray diffraction data as inversion twin. $Cs_3La[AsS_4]_2$ crystallizes in its own structure type and not isotypically with the $K_3\mathit{RE}[AsS_4]_2$ compounds [1,2] described previously.

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The Prolific Ternary System Pt/Sn/Nd: Insertion of Pt into Sn/Nd Intermetallics in the Sn_2Nd to Sn_5Nd_2 Region Yields Structural Complexity and Wealth

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The lower melting tin-rich part of the binary system Sn/Nd contains two congruently melting intermetallic compounds, Sn_2Nd (1180°C, 66.7 mol% Sn) and Sn_3Nd (1150°C, 75 mol% Sn) encapsulating not only an eutectic but also two incongruently melting compounds, Sn_7Nd_3 and Sn_5Nd_2. While Sn_3Nd crystallizes with the Cu_3Au type of structure, the other three crystallize with ordered three- (Sn_2Nd), five- (Sn_7Nd_3), and seven-fold (Sn_5Nd_2) super-structures of that type. The addition of platinum to 2:1 mixtures of tin and neodymium produces, without or with the use of NaCl as an innocent flux, at reaction temperatures at and below 1000°C, eight ternary Pt/Sn/Nd compounds, four of which have not been reported before. Except for PtSnNd (**1**), five compounds lie on or close to the Sn_2Nd—Pt section of the Pt/Sn/Nd triangle, $Pt_{0.21(1)}Sn_2Nd$ (**2**), $PtSn_2Nd$ (**3**), $Pt_{1.33}Sn_2Nd$ (**4**), $Pt_{2-x}Sn_{2+x}Nd$ ($x = 0.27(3)$, **5**), and Pt_3Sn_2Nd (**6**), as well as two close to the Sn_5Nd_2—Pt section, $Pt_{1.5}Sn_{5-x}Nd_2$ ($x = 0.16(2)$, **7**) and $Pt_3Sn_5Nd_{2-x}$ ($x = 0.161(8)$, **8**). While in the binaries, as superstructures of the pseudo-face-centered ordered Cu_3Au/Sn_3Nd structure, the coordination numbers (CN) of the metal atoms are 12, stuffing of these structures with Pt atoms affords higher CN for Nd, the largest of the three constituents, between 14 and 17. The persevering coordination environment of Pt are interpenetrating, antiparallel square pyramids, $[PtSn_5]$ and $[PtNd_5]$, forming the cluster $\{PtSn_5Nd_5\}$, exclusively in **2**, **3**, **4**, and **7**, and partially in **5**, **6** and **8**; $[PtSn_n]$ polyhedra with $n = 4$ occur in **1**, **5**, **6** and with $n = 6$ and 7 in **8**.

Crystallography and magnetism of $(Er_{1-x}Yb_x)_2In$ compounds

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RERC'29 Conference Abstract

Rare-earth (R) - indium compounds that form at the R_2In stoichiometry undergo discontinuous magnetoelastic transitions when R = Pr, Nd, Eu [1-3]. The first-order transitions are nearly anhysteretic and the compounds exhibit large magnetocaloric effects, all of which makes them promising for cryogenic magnetocaloric cooling. The emergence of first-order transitions in R_2In that closely resemble itinerant electron metamagnetism (IEM) also presents an interesting science question of why the IEM-like behaviors occur in materials where the indirect RKKY-type exchange is dominant. Further, Pr_2In, Nd_2In and other trivalent R_2In adopt the hexagonal Ni_2In-type crystal structure, while divalent Eu_2In and Yb_2In crystallize in the orthorhombic Co_2Si type. Yet, phenomenologically, the magnetoelastic transitions in Eu_2In and Pr_2In are very similar and they occur at nearly same transformation temperatures, T_C, of 55 and 57 K, respectively [1,2].

In this work we examine the possibility to design a magnetostructural phase transformation between ferromagnetic Co_2Si and paramagnetic Ni_2In type structures, which is known to occur in selected transition-metal alloys, in the $(Er_{1-x}Yb_x)_2In$ pseudobinary system. A series of compounds with x = 0, 0.25, 0.5, 0.75, and 1 were synthesized in sealed Ta crucibles and analyzed using room temperature X-ray powder diffraction and physical property measurements. Preliminary results indicate that both Co_2Si- and Ni_2In-type phases are present in the x=0.75 sample. The x=0.25 and x=0.5 samples adopt Ni_2In structure indicating the formation of a Ni_2In-based solid solution. The ErYbIn compound is a low-temperature spin-glass with $T_f = 3$ K.

This work was performed at Ames Laboratory and was supported by the Division of Materials Science and Engineering of the Office of Basic Energy Sciences of the U.S. Department of Energy (DOE). Ames Laboratory is operated for the U.S DOE by Iowa State University under Contract No. DE-AC02-07CH11358.

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High-Pressure Synthesis of Intermetallic Framework Compounds *RE*Si$_3$

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INTRODUCTION

Covalent framework compounds are a very attractive class of materials regarding structural diversity and physical properties. Earlier investigations of the reactions between silicon or germanium with rare-earth metals (*RE*) have led to the discovery of a rich variety of binary high-pressure phases[1,2]. These compounds usually exhibit multicenter interactions and atoms tend to enhance their coordination numbers[3]. The early studies focused mainly on compounds of non-magnetic cations, in the present study we report on synthesis and magnetic properties of *RE*Si$_3$ (*RE* = Gd[4], Tb, Dy, Er, Tm) compounds.

EXPERIMENTAL METHODS

The metastable binary rare-earth trisilicides *RE*Si$_3$ were obtained by synthesizing precursor samples by arc melting of rare earth metal and silicon, followed by high-pressure high-temperature synthesis at typically 9.5 GPa and 823-923 K before quenching to ambient conditions.

RESULTS AND DISCUSSION

Metallographic analyses of polished samples indicate that the composition is in good agreement with 1:3 stoichiometry. At ambient pressure, *RE*Si$_3$ compounds decompose exothermally upon heating into Si and *RE*Si$_{2-x}$. Refinements using powder diffraction data (Fig. 1) reveal that the crystal structure of the compounds is isotypic to that of YbSi$_3$[5].

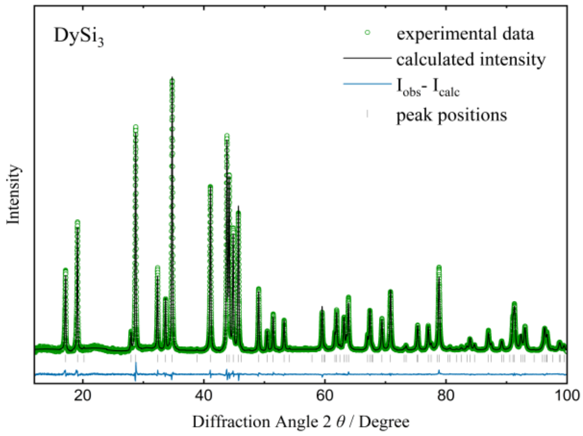

Fig. 1 Synchrotron powder XRD pattern of DySi$_3$ and results of Rietveld refinement.

The values of cell parameters, respectively the cell volume, decrease from Gd to Tm as it is expected due to the lanthanide contraction (Table 1).

Table 1 Lattice parameters refined using LaB$_6$ as an internal standard and effective magnetic moment of *RE*Si$_3$.

Chemical composition	Lattice parameters a/ Å	c/ Å	Magnetic moment μB
GdSi$_3$	7.2372(3)	10.9433(7)	8.13
TbSi$_3$	7.2160(4)	10.8228(8)	9.81
DySi$_3$	7.2069(4)	10.7526(9)	10.63
ErSi$_3$	7.1948(3)	10.6216(5)	9.21
TmSi$_3$	7.1850(3)	10.5573(8)	8.09

Magnetic measurements reveal for DySi$_3$ (Fig. 2) Curie-Weiss paramagnetic behaviour with a calculated effective moment $\mu_{eff} = 10.63\ \mu_B$ which is consistent with the $^6H_{15/2}$ ground state of the $4f^{\,9}$ configuration of dysprosium (Dy^{3+}, $\mu_{eff} = 10.65\ \mu_B$). The value of $\Theta = -4{,}2$ K determined from the linear fit, indicates antiferromagnetic ordering of DySi$_3$. Similar behaviour was observed for other *RE*Si$_3$ compounds (Table 1).

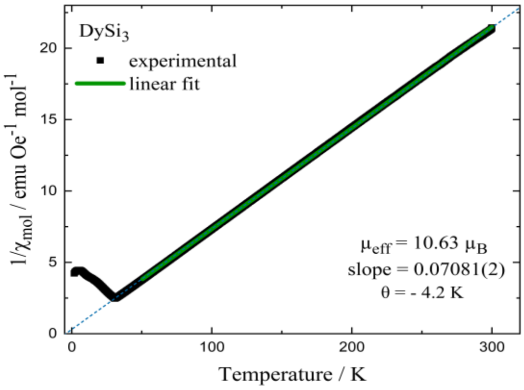

Fig. 2 Inverse magnetic susceptibility $1/\chi$ of DySi$_3$ vs temperature.

CONCLUSIONS

The metastable binary rare-earth trisilicides *RE*Si$_3$ (*RE* = Gd, Tb, Dy, Er, Tm) are synthesized by high-pressure synthesis. They adopt the crystal structure of YbSi$_3$ type[5]. Magnetic measurements on *RE*Si$_3$ compounds reveal Curie-Weiss paramagnetic behaviour and antiferromagnetic ordering at low temperatures.

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Magnetically-assisted solvent extraction (MaSX) of rare-earth ions by single ligand-laden organic droplet in aqueous bulk

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Rare-earth (RE) elements are important for a variety of high-tech products such as batteries, LEDs, displays, high powered magnets etc.[1]. However, their separation relies on marginal chemical differences, realized in solvent extraction (SX), that include large amounts of non-recyclable chemicals. The resulting environmental issue is further exacerbated by a lack of recycling. For this reason, increasing the separation efficiency of Rare Earths is paramount to increase the yield and reduce the environmental impact of mining. Over the past years, the fascinating phenomenon of RE(III) enrichment at the vicinity of magnet, together with its working principles are reported [2]. This opens up a new separation possibility of a magnetically-assisted solvent extraction concept. The addition of Kelvin-force gives rise to a coupled solutomagnetic convection at a concentration stratification and a magnetophoresis of organic dispersed in rare-earth solution. It is our aim to monitor the transport processes of rare-earth cation exchange towards an increased separation factor.

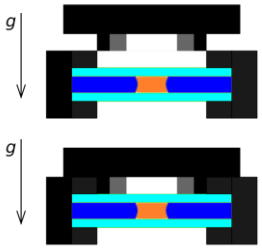

Fig. 1 Hele-Shaw Cell with aqueous and organic phase and Ring magnet (27x16x5mm) 42kJ/m^3

The current phase of investigation is illustrated in Fig.1, it consists of a liquid-liquid solvent extraction. A paraffin droplet containing 0.75 M Pc88a is dispersed into a 0.75 M $DyCl_3$ aqueous phase with pH 1 tuned by HCl. The system is confined in a Hele-Shaw cell with 1 mm gap oriented perpendicular to gravity. The droplet is connected to the top and bottom surfaces of the cell, so that the sidewalls of the droplet are the only reactive interface, as proven by an experiment with an ink dyed aqueous phase.
The extraction reaction of Pc88A-HCl system reads according to [3,4]

$$RE^3 + 3\overline{H_2A_2} = \overline{RE(HA_2)_3} + 3H^+$$

with RE as the rare earth and H_2A_2 as the dimeric form of the organic acid.
Additionally, a magnetic field provided by a ring magnet is introduced to the SX process.
The RE(III) concentration stratification for both cases, i.e. with/ without magnetic field, are monitored by a laser-based Interferometer, preliminary results are illustrated in Fig. 2.

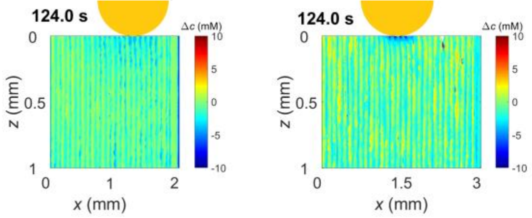

Fig. 2 Concentration gradient below a droplet (yellow half-sphere) after 160s without (left) and with a magnetic field (right)

The snapshot concentration field at 160 s after extraction takes place clearly shows a more pronounced depletion of RE(III) at the vicinity of the organic droplet with a magnetic field present. The concentration field is more stratified in this case as well. The change in concentration around the droplet, after 160 seconds is significantly larger for the magnetic field experiment, reaching 8-9 mM, while it stayed below 5 mM in the other case. This difference continues until the experiment was stopped at 200 seconds. Currently, we are doing systematic studies on this system with parametric variations, to establish scaling laws for MaSX.

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Magnetic field tuning of crystal field levels and vibronic states in the spin ice compound $Ho_2Ti_2O_7$ obesrved with Far-IR spectroscopy

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INTRODUCTION

Low-temperature optical spectroscopy in applied magnetic fields provides clear evidence of magnetoelastic coupling in the spin ice material $Ho_2Ti_2O_7$. In far-infrared reflectometry measurements, we observe field-dependent features around 30, 61, 72, and 78 meV, energies corresponding to crystal electronic field (CEF) doublets. The calculations of the crystal field Hamiltonian model confirm that the observed features in IR spectra are consistent with magnetic-dipole-allowed excitations from the ground state to higher $^5I_8$ CEF levels. We present the CEF parameters that best describe our field-dependent IR reflectivity measurements.

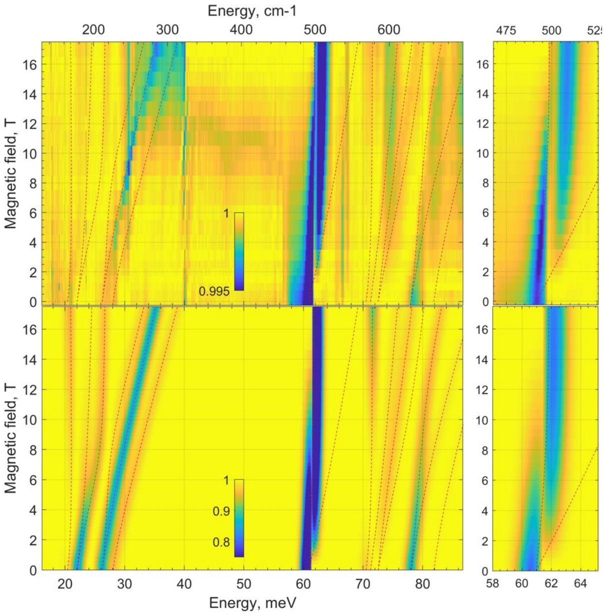
Additionally, we identify a weak field-dependent shoulder near one of the CEF doublets. This indicates that this level is split even in zero field, which we associate with a vibronic bound state. Modeling of the observed splitting shows that the phonon resides at slightly lower energy compared to the CEF level that it couples to, which is in contrast with previously published inelastic neutron measurements. The magnetic field dependence of the vibronic state shows a gradual decoupling of the phonon with the CEF level as it shifts. This approach should work in pyrochlores and other systems that have magnetic dipole transitions in the IR spectroscopic range, which can elucidate the presence and the ability to tune the nature of vibronic states in a wide variety of materials.

EXPERIMENTAL METHODS (if relevant)

The magnetoinfrared spectroscopy was performed at the National High Magnetic Field Laboratory employing a 17 T vertical-bore superconducting magnet coupled with Fourier- transform infrared spectrometer Bruker Vertex 80v. The low-temperature reflection spectra were measured in the spectral range between 50 and 800 cm−1 with an instrumental resolution of 0.3 cm^{-1}. The reflective surface of the sample was oriented parallel to the magnetic field applied along [001] crystallographic direction. The sample temperature was kept at about 5.5K.

RESULTS AND DISCUSSION

Figure 1 shows the normalized far-IR reflection spectrum as a function of the applied magnetic field. The bottom panel shows the simulation of the transition intensity between ground and high-energy CEF levels, while the field dependencies of the transition energy are plotted with red dashed lines. Both experimental and calculated spectra were normalized to the reference spectrum obtained from the statistical approach (averaging spectrum for all magnetic fields). The panels on the right show field evolution of the strongest CEF transition in the vicinity of 61 meV. A very good agreement between modeling and experimental observation is found.



CONCLUSIONS

The main results presented in this work are as follows:
(1) The observation and modeling of magnetic-dipole-allowed transitions between CEF levels and their evolution in applied magnetic fields using far-infrared reflectivity measurements.
(2) Finding and modeling the magnetic field dependence of a spectroscopic feature associated with a CEF-phonon coupled (vibronic) state.

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Synthesis and characterization of organocerium based molecular materials with fullerene for charge transfer properties

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Abstract

Fullerenes are very important class of compound in material chemistry. It possess a very unique structural and electronic properties. Fullerene due to its electron accepting properties can be utilized in the field of metallic conductivity[1], superconductivity[2], magnetic ordering of spin[3] and supramolecular chemistry. Reaction of fullerene with transition metal complexes including metallocene to form charge transfer complexes is well documented in the literature[4]. However charge transfer complexes of fullerenes with lanthanides are very rare. Only few handful of examples are known[5]. For effeicient charge transfer from donor to acceptor one of the prerequisites is the redox potential match between two counter parts. The reported one electron reduction of C_{60} is $E_{1/2} = -0.98$ V (vs Fc/Fc$^+$)[6]. Herein C_{60} is reacted with organocerium complexes $(CpMe_4)_3Ce$ and [Cp*$_2$Ce(*ortho*–oxa)] in different stoichiometry to obtain compond C_{60}.**1** and C_{60}.**2**. We reported for the first time structurally characterized cocrystals of fullerene with organocerium complexes like $(CpMe_4)_3Ce$, [Cp*$_2$Ce(*ortho*–oxa)] (figure 1) and try to investigate the extend of charge transfer in the title compounds *via* exploiting a series of physical measurements including magnetic susceptibility measurements X-ray absorption near edge structure (XAENS) spectroscopy and computation studies.

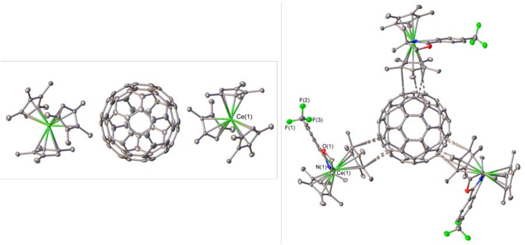

Figure 1. Cocrystal C_{60}.**1** (left) and C_{60}.**2** (right) of organocerium complexes with fullerene.

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Enhancing stability and magnetism of $ThMn_{12}$-type cerium-iron intermetallics by site substitution[1]

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Iron-rich $ThMn_{12}$-type (1:12) rare-earth (R) intermetallics (RFe_{12}) are potential candidate materials for permanent magnets with a large magnetocrystalline anisotropy (MCA) that stems from the interplay between strong spin-orbit coupling (SOC) and crystal field effect in R- 4*f* states, and a large magnetization from the 3*d* transition metal elements. Still, the existing challenge is to predict a high-performance 1:12 permanent magnetic material as par with champion neomagnet, that is cost-effective and stable at operating temperatures. Especially the cerium-based 1:12 materials have been attractive because cerium is naturally abundant that could drastically reduce the cost of permanent magnets. In addition, rare earth and iron 1:12 phases can be stabilized experimentally by the elemental substitutions and or the addition of extra elements in the interstitial sites. For example, $CeTi_xFe_{12-x}$ has been successfully synthesized by substituting iron (Fe) with titanium (Ti). Analogously one could synthesize the isovalent Zr-substituted compositions with improved magnetic anisotropy. The interstitial *p*-block elements such as nitrogens as well as the substituted elements help in tuning the valence state of cerium including the intrinsic magnetic properties such as MCA, magnetization, and Curie temperature of $CeTi_xFe_{12-x}$. More importantly, their phonon-driven stability is yet to be examined.

By performing the first-principles electronic structure calculations, we investigate the lattice stability and the intrinsic magnetic properties of Ti- or Zr-substituted Ce-based 1:12 materials. The formation energies indicate that all the compositions can form in the bulk structure except $CeFe_{12}$. We compute the phonon dispersions for Ti/Zr-substituted rare-earth-based (Ce 1:12) intermetallic compounds. We find no soft-mode frequencies that indicate all compositions are dynamically stable. The mixed valency of Ce is confirmed by examining the electronic structure in different approximations, e.g., with Ce(4*f*) as core- and valence- electrons, including the on-site electron-correlation effect. The computed Ce(4*f*) charges suggest that the valence state fluctuates between Ce^{3+} and Ce^{4+} depending upon the substituted element as well as the nitrogens. Interestingly, the net magnetic moment is predicted larger in Zr substitution than in Ti substitution, which is attributed to a more delocalized nature of Zr(4*d*) orbitals. The interstitial nitrogens improve the net magnetic moment for all consistent with experiments. The on-site electron correlation is crucial for the MCA due to the mixed-valence character of Ce. The predicted values of K_1 show all compositions uniaxial along the crystalline c-direction. Specifically, the value of K_1 is the largest for $CeZrFe_{11}$ caused by the polarization of Ce(4*f*) charge along the c-axis and stronger SOC (Figure 1), which would be interesting to examine experimentally.

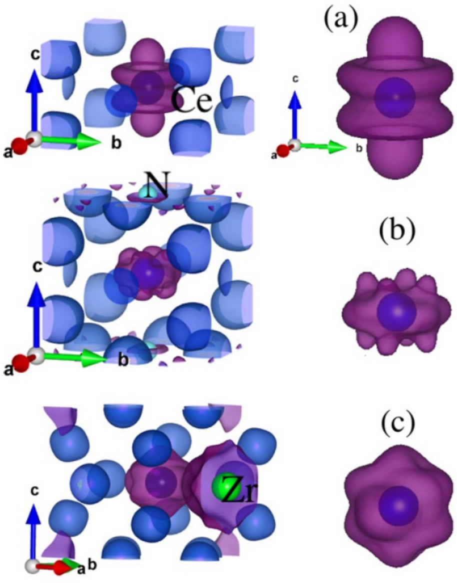

Figure 1. Electron spin density contours of Ce and nearby atoms (left) and enlarged view of Ce-only (right) where contours in blue are spin-↑ and purple are spin-↓ electrons. Spin-↑ corresponds to net electron occupying Ce(4f) states (isosurface 0.006 e/Å3) in (a) $CeFe_{12}$*, (b)* $CeFe_{12}N$*, and (c)* $CeZrFe_{11}$*. Contour (a) corresponds to an admixture of 4f states with strongly quenched orbital moment. The shape of the contour is drastically modified by itinerant electrons of nitrogens in* $CeFe_{12}N$ *(b), which reduces the magnetic anisotropy. On the other hand, Zr enhances the magnetic anisotropy by perturbing the contour (c) in* $CeZrFe_{11}$*.*

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Amidate Supported Single-Molecule Precursors for Actinide Oxide Materials

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Abstract

Information about the behavior of nuclear fuel materials can be garnered from studying the properties of AnO_2 materials (An = actinide),[1] particularly with regard to controlling grain size to mitigate the hazards of self-heating nuclear fuel.[2] While the relationship between synthetic perturbations (i.e., size, morphology) and electronic behavior for many transition-metal nanomaterials is well-understood, the field of rare earth nanomaterials is comparatively young, albeit with great opportunity for synthetic and spectroscopic advancement. Single-molecule uranium and thorium amidate complexes have demonstrated utility as precursors to size-controlled uranium dioxide (UO_2) and thorium dioxide (ThO_2) thin-film nanomaterials, which inspired the extension of analogous techniques to transuranic actinides.[3-5] In this work, we explore the synthesis, spectroscopic characteristics, and decomposition to AnO_2 materials of homoleptic amidate complexes of trivalent cerium and americium, and tetravalent neptunium and plutonium. The volatile amidate ligands allow for direct decomposition from the homoleptic complex to actinide oxides without contamination from organic byproducts, ultimately revealing electronic structure and reactivity of AnO_2 materials through rigorous spectroscopic characterization.

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f-Element Squarates, Squarate-Oxalates, and the Determination of the Nine-Coordinate Ionic Radius of Cf(III)

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INTRODUCTION

Understanding the chemical similarities and differences between the trivalent lanthanides and transneptunic elements is of immense importance. Due to the scarcity and radioactivity of the elements Plutonium through Californium, our understanding of the fundamental properties of these elements is lacking and many of the basic properties of these transplutonium elements have yet to be sufficiently explored.[1,2] This lack of knowledge poses challenges related to nuclear energy and waste, separations, storage, and applied materials applications. Often times, the trivalent lanthanides will be used as surrogates for the trivalent actinides owing to their similar ionic radii. However, reliable ionic radii for the transplutonium elements with larger coordination environments are often lacking. This poses difficulties when attempting to develop periodic trends between these two series. Access to reliable ionic radii and structural data for the later actinides is clearly paramount, as these factors inform separation processes and inorganic syntheses. In this work, five new metal−organic compounds comprising trivalent lanthanides and actinides along with squarates or squarate-oxalates were prepared: $M_2(C_4O_4)_3(H_2O)_4$ (M = Eu, Am, Cf), $M_2(C_4O_4)_2(C_2O_4)(H_2O)_4$ (M = Am, Cf), While the Am and Cf structures in this work are isotypic to previously reported lanthanide analogues[3-7], the two series do not parallel one another when synthesized under identical reaction conditions, providing yet another example of the nonparallel chemistry between the two *f*-element series. The production of an isotypic set of compounds between these two series also provides the opportunity to determine the ionic radius of trivalent californium with a nine-coordinate geometry. Prior to this, the only ionic radius values known for trivalent californium were for a coordination number (CN) of 6 (0.95 Å and 0.932 Å)[8,9].

EXPERIMENTAL METHODS

All of the reported compounds were synthesized *via* the following: $MCl_3 \cdot xH_2O$ (5.00 mg, ~0.015 mmol, M = Eu, Am, Cf), squaric acid (20.00 mg, 0.175 mmol), 0.75 mL of acetone, and 0.25 mL of deionized water were charged into a 10 mL PTFE-lined Parr 4749 autoclave. The autoclave was then sealed and heated to 150 °C for 12 h under autogenous pressure, followed by cooling at a rate of 3 °C/h. The resulting crystalline materials were washed extensively with boiling deionized water to remove any excess reactants or soluble byproducts.

RESULTS AND DISCUSSION

Prior to this work, the nine-coordinate ionic radius for Cf^{3+} was unknown. As **Cf1** belongs to an isotypic set of compounds, crystallographic data allow the determination of the nine-coordinate ionic radius for Cf^{3+}. While there are several methods that can be used to determine the ionic radius of a metal center, the method employed in this work was to prepare a plot of unit cell volume (V) as a function of the cube of the ionic radius (r^3) and fit a linear regression to the data. For this method to be valid, an isotypic series of compounds is needed in which the ionic radii for the majority of ions are well-known and the coordination number and the oxidation state of the ions remain constant. The nine-coordinate ionic radius of Cf^{3+} was determined by linear regression of a plot of V as a function of r^3 for the isotypic series $M_2(C_4O_4)_3(H_2O)_4$ (M = La−Nd, Sm, Eu). From the equation for the line of best fit, the nine-coordinate ionic radius of Cf^{3+} was determined to be 1.127 ± 0.003 Å.[10]

CONCLUSIONS

We have prepared a series of new trivalent *f*-element squarates and squarte-oxalates, with the former being part of a larger isotypic family of compounds. This provided the opportunity for the first determination of the nine-coordinate ionic radius of Cf^{3+} to be calculated (1.127 ± 0.003 Å).

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Chemistry and Topology of Spin-Orbit Coupling and Competing Interactions in Ternary, Tetravalent Lanthanide Chalcogenides

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Rare-earth-based insulating magnets are of broad interest because of their strong spin-orbit coupling (SOC) and inherent anisotropy. In the traditional picture, the SOC multiplet is split by the crystal electric field (CEF) which acts as a second order perturbation on the Hund's rule ground state multiplet. Overall, metal-ligand bonds are not very covalent in trivalent lanthanides and an ionic picture often prevails. By changing the oxidation state of the lanthanide from +3 to +4, however, the metal-ligand bond becomes much more covalent (4*f*-2*p* hybridization). This change makes leads to SOC and CEF in tetravalent lanthanides (Ln^{4+}) to be of comparable energy scales and requires an intermediate coupling model. A a result, Ln^{4+} materials could potentially host interesting phenomena usually associated with *d*-electrons, such as superconductors, spin-liquids, Mott insulators, and metal-insulator transitions.[1] In fact, Na$_2$PrO$_3$, a honeycomb oxide with Pr^{4+} has been proposed to host Kitaev interactions. [3]

In this presentation, I will describe our studies towards understanding the topology of competing interactions (SOC vs CEF, hybridization (V_{eff}) vs charge transfer (CT)) in insulating Ln^{4+} oxides. Through a combination of spectroscopic, structural, and thermomagnetic measurements, I will establish a cohesive model to understand the electronic structure of Ln^{4+} materials and apply it towards developing fundamental design principles for quantum information sciences.

In order to understand the ground state electronic structure of Ln^{4+} ions, CEF measurements using INS and FIRMS were carried out on a series of Ln^{4+} oxides with primary focus on Pr^{4+}.[4] Pr^{4+} with 4f^1 electronic configuration is isoelectronic to Ce^{3+}. Based on our recent investigations on Na$_0$PrO$_3$, the first CEF level was identified at 230 meV with a substantially large antiferromagnetic exchange interaction ~ 1.2 meV (typically 0.3-0.5 meV for Ln^{3+}) both of which have been attributed to enhanced 4*f*-2*p* hybridization.[3] The series of Pr^{4+} oxides allows us to tune CEF by changing the local symmetry (CEF ranges from 160 meV to 230 meV based on the local symmetry). A point charge model using Stevens operators in the intermediate coupling limit was developed to extract the ground state wavefunction of Pr^{4+} single-ion. Due to competing CEF and SOC interactions, ground state has contributions from different excited states. Evidence of 4*f*-2*p* hybridization in Pr^{4+} and consequences of increased covalency on single-ion properties, exchange interactions, and collective beghavior in Pr^{4+} oxides were studied using a combination of $M_{4,5}$ edge and O *K*-edge XAS and XMCD spectroscopies.

I will also present our recent efforts towards understanding ground state donor covalent bonding in a series of Ln^{4+} oxides.[5] A band structure model to describe ground state donor covalent bonding was developed using a combination of O *K*-edge XMCD, $M_{4,5}$ edge XAS/XMCD, L_3 edge XANES, L_3-edge HERFD-XANES, and thermomagnetic measurements. Donor covalent bonding in the ground state has been attributed to competition between charge transfer and hybridization energies. Comparisons will be made to high-valent transition metal oxides where a similar behavior has been observed resulting in a universal model to describe donor covalent bonding in high-valent insulating oxides. The universal model will be differentiated from multiconfigurational behavior observed in lanthanide/actinide intermetallics using a directional hybridization scheme.

Lastly, a chemical approach to tune oxidation state in a series of layered lanthanide materials using reductive intercalation/ oxidative deintercalation will be discussed. Change in oxidation state has been tracked via L_3-edge XANES, in-situ/ex-situ UV/Vis, thermomagnetic measurements, and structural changes. With these observations, I will lay out our fundamental design principles for developing applications of these properties in functional magnetic materials including qubits.[6]

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Towards Reactive, Element-Specific Separations of Dysprosium through Photochemistry

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Optimal separations techniques rely upon significant differences in properties that can be practically exploited to facilitate the selective transfer of one species away from another. Industrial rare-earth element (REE) separations are currently based on differences in ionic radii, which represents a significant limitation to the process. The small size differences between REEs do not promote effective separations of the whole suite of metals, especially metals of similar size such as dysprosium and yttrium. ***A promising direction for rare-earth separations lies in the exploitation of property differences other than ionic radii.*** **An intriguing candidate for a more exploitable property that is more variable amongst REEs is photophysics. The key to a successful light-driven separation is control over a selective photochemical reaction.** ***Using light to induce rare-earth identity-controlled reactions based on excited-state properties has the potential to effect efficient separations.*** **A description of such a kinetic separation based on a photochemical reaction will be provided, as well as future prospects for tying selective photochemistry to reactive separations.**

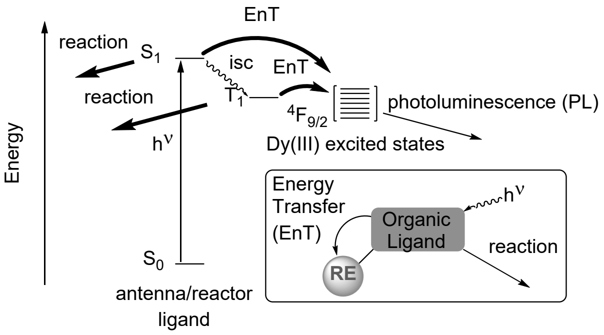

Figure 1: Jablonski diagram depicting a rate competition between (i) energy transfer from an organic chromophore to a rare earth ion and (ii) a photochemical reaction of that same organic chromophore

Lanthanide Complexes Containing a Terminal Ln=O Oxo Bond: Revealing Higher Stability of Tetravalent Praseodymium Versus Terbium

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We report on reactivity of gas-phase lanthanide-oxide nitrate complexes, $[\mathrm{Ln(O)(NO_3)_3}]^-$ (denoted LnO^{2+}), produced via elimination of $\mathrm{NO_2}^{\bullet}$ from trivalent $[\mathrm{Ln^{III}(NO_3)_4}]^-$ (Ln = Ce, Pr, Nd, Sm, Tb, Dy). These complexes feature a $\mathrm{Ln^{III}—O^{\bullet}}$ oxyl, $\mathrm{Ln^{IV}=O}$ oxo, or intermediate $\mathrm{Ln^{III/IV}}$ oxyl/oxo bond, depending on the accessibility of the tetravalent $\mathrm{Ln^{IV}}$ state. Hydrogen atom abstraction reactivity of the LnO^{2+} complexes to form unambiguously trivalent $[\mathrm{Ln^{III}(OH)(NO_3)_3}]^-$ reveals the nature of the oxide bond. The result of slower reactivity of PrO^{2+} versus TbO^{2+} is considered to indicate higher stability of the tetravalent praseodymium-oxo, $\mathrm{Pr^{IV}=O}$, versus $\mathrm{Tb^{IV}=O}$. This is the first report of $\mathrm{Pr^{IV}}$ as more stable than $\mathrm{Tb^{IV}}$, which is discussed with respect to ionization potentials, standard electrode potentials, atomic promotion energies, and oxo bond covalency via 4f- and/or 5d-orbital participation.

Crystalline Americium Frameworks: Platforms for Exploring Bonding and Photoluminescence

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INTRODUCTION

Actinide bearing metal-organic frameworks (MOFs) are an emerging class of materials that are experiencing a period of tremendous growth in terms of scientific interest and study.[1-2] While these permanently porous network solids provide ample opportunities for functional material design, our motivation to study actinide MOFs is much more fundamental. The well-defined crystalline environments common to MOFs render these materials attractive hosts to immobilize the highly radioactive and scare transuranic elements. Their inherent stability and diverse coordination geometries permit targeted investigations into structure-property relationships, chemical reactivity, and electronic structure. A brief overview of this approach will be presented, and examples discussed where crystalline americium ($^{243}Am^{3+}$) containing frameworks were prepared, structurally characterized, and metal-ligand bonding and photoluminescence properties explored.

EXPERIMENTAL METHODS

Am^{3+} containing MOFs are prepared via hydro- or solvothermal methods where the metal:ligand:solvent ratios are optimized for crystal growth. Typical reactions are carried out at 60-150°C for ~12-72 hours within Teflon Savillex or glass vials.

RESULTS AND DISCUSSION

Presented here will be an overview of the synthesis, crystal structure, and spectroscopic properties of three novel ^{243}Am-containing frameworks of increasing complexity. Compound **1**, $(AmCHO_2)_3$, is an Am^{3+}-formate that adopts a non-porous 3D structure, representing perhaps the simplist form of a coordination polymer (CP) from which to establish a baseline for chemical behavior. Compound **2**, $(Am(C_2O_4)(H_2O)_3Cl)$, is a Am^{3+}-oxalate containing 2D CP that features a sheet-like structure and is an active phosphor. Compound **3**, $(Am(C_9H_3O_6)(H_2O))$, is a 3D MOF that exhibits elements common in **1**-**2**, creating a forum to investigate these themes in a more complex system. The crystallographic data is presented along side a complementary computational investigation into the Am^{3+}-O bond nature. The Quantum Theory of Atoms in Molecules was used to quantify the electron density topology within the bond region while the Natural Localized Molecular Orbital approach elucidated the molecular orbital contributions therein. In short, the Am^{3+}-O bonds are overwhelmingly ionic and feature little interaction between the 5f shell and ligand orbitals. This assessment is consistent across **1**-**3** and is supported with experimental diffuse reflectance (DR) data, which is used as a spectroscopic tool to evaluate Am^{3+}-based 5*f*-5*f* transitions energies. Interestingly, the position of the $^7F_0 \rightarrow {}^5L_6$ band in the DR spectrum is known to red shift with increased Am^{3+}/ligand orbital overlap, a possible measure of covalency.[3] The energy of the $^7F_0 \rightarrow {}^5L_6$ transition was similar across **1**-**3**, indicative of ionic bonding. Subsequent photoluminescence measurements were noteworthy. Compound **1** features Am^{3+}-based emission after direct excitation (at 509 nm) where the $^5D_1 \rightarrow {}^7F_1$ transition is unexpectantly predominant compared to the more commonly observed $^5D_1 \rightarrow {}^7F_0$ band. Compound **2** emits bright blue light courtesy of the oxalate ligands and Am^{3+}-based emission is notably quenched, contrary to the anticipated behavior based on surrogate lanthanide systems. Compound **3** features only weak Am^{3+} emission after direct excitation (at 509 nm) and fails to exhibit 5f emission when trying to leverage the antenna effect (i.e. using the ligand as a light harvesting species to poplate the Am^{3+} excited state). This behavior is at odds with the highly luminescent Sm^{3+}, Tb^{3+}, and Eu^{3+} variants of this 3D MOF archetype. Each of these systems provide valuable and informative insight into the photoluminesnece behavior of Am^{3+} in the solid-state, where the rules governing these processes are still being delineated.

CONCLUSIONS

This poster presentation will provide an overview of our efforts to utilize MOFs (and CPs) to probe the fundamental bonding and electronic properties of $^{243}Am^{3+}$ and more broadly, the 5f elements. This work serves as a forum to explore themes of resonance energy transfer, metal-site symmetry, and luminescence quenching. These concepts are presented in context with Am^{+3}/ligand bonding and are used to rationalize the unexpected luminescence behavior noted above.

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Rare Earth and Actinide Hybrid Double Perovskites

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INTRODUCTION

Organic-Inorganic Hybrid Double Perovskites (HDP) comprise a class of extended solids of the form $A_2BB'X_6$ (A = organocation, B and B' = cationic metal centers, X = anion), that have been shown to possess material characteristics of great industrial utility.[1] Most HDPs include oxides or halides as X, and either main group or transition metals for the B and B'-sites, but incorporation of rare earths into such phases can impart an additional, unique set of characteristics including luminescent and multiferroic properties. Each site in the phase can be occupied by a variaety of ions enabling tuning of the functionality, and while most include oxide and halide X-sites, nitrate has recenty been shown to serve as a suitable and robust ligand for the formation of such phases with potential industrial application as multiferroics.[2-4] Our group has endeavored to expand the landscape of rare earth HDPs, and to systemtatically examine their fundamental characteristics via the synthesis and analysis of a periodic series of rare earth nitrato HDPs and their analogous minor actinide phases, of the form $[Me_4N]_2[KM(NO_3)_6]$ (M = La-Nd, Sm-Lu, Y, Am, Cm).

EXPERIMENTAL METHODS

The series was obtained via evaporative crystallization from a mixture of $Ln(NO_3)_3$ or $An(NO_3)_3$, KNO_3, and $[Me_4N][NO_3]$ in a 1:1:2 ratio in either DI H_2O or 4.0 M HNO_3, and characterized via single crystal X-ray diffraction, and IR and Raman spectroscopy.

RESULTS AND DISCUSSION

An isostructutral, cubic series of rare earth and actinide complexes of the form $[Me_4N]_2[KM(NO_3)_6]$ (M = La-Nd, Sm-Lu, Y, Am, Cm). A trivalent rare earth or actinide hexanitrato moiety forms an extended solid with K^+ counterions via coordination by the distal oxygens on the nitrates, resulting in a second six-coordinate octahedral site with the remaining charge balancing Me_4N^+ cations occupying the interstitial voids in the lattice, Figure 1. These compounds represent a rare example of single crystal structures of an Am-nitrato compound, and the first reported for Cm. This series serves as an excellent foundation for exploring the fundamental characteristics of rare earths and actinides, and as a template for the synthesis of functional materials.

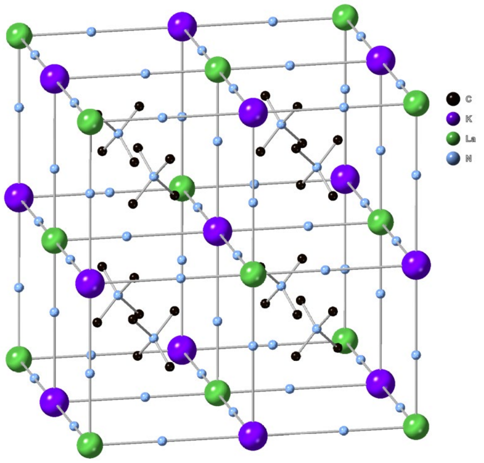

Figure 1. Representative structural model of $[Me_4N]_2[KM(NO_3)_6]$ (M = La-Nd, Sm-Lu, Y, Am, Cm). Oxygen and hydrogen atoms have been omitted for the sake of clarity.

CONCLUSIONS

A periodic and isostructural series of rare earth and actinide organic-inorganic hybrid double perovskite phases of cubic symmetry was synthesized and characterized. Systematic analysis of their solid-state structural and spectral characteristics has provided a useful foundation facilitating experimental design to achieve targeted properties in similar compounds. In addition to further characterization of the fundamental properties of these phases, different counterions and alkali metals will be incorporated into these phases in an attempt to achieve useful material properties.

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Optimization of rare-earth content in bonded $Nd_2Fe_{14}B$-based magnets utilizing applied magnetic field modifications to HDDR treatment.

Zachary P. Tener, Xubo Liu, Ikenna Nlebedim, Matthew J. Kramer, Michael A. McGuire, Michael S. Kesler

In this study, we investigate how a magnetic field applied throughout the established Hydrogenation Disproportionation Desorption Recombination (HDDR) process alters the magnetic properties of the resulting powder. The cutting edge of HDDR processing of $Nd_2Fe_{14}B$ produces finely-sized, anisotropic powders. These powders are an optimal source material for bonded magnets, and provide a framework towards permanent magnets with reduced critical material concentration. We show that the application of an industry-relevant magnetic field magnitude throughout the HD and DR steps improves the energy product of the resulting $Nd_2Fe_{14}B$ powder, and we discuss methodological improvements towards further optimization. Samples were sectioned from a drop cast ingot and placed in a controlled H_2 gas partial pressure in 0 and 2 T applied magnetic fields. Both the H_2 partial pressure and magnetic field variable effects on hydrogen disproportionation (HD) and desorption and recombination (DR) steps were explored. Samples were characterized using X-ray diffraction and magnetometry measurements to gauge improvements to phase fraction, magnetization, and magnetic coercivity caused by thermomagnetic processing.

This work is supported by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office.

The Archetypal Homoleptic Lanthanide Quadruple-Decker – Synthesis, Mechanistic Studies, and Quantum Chemical Investigations

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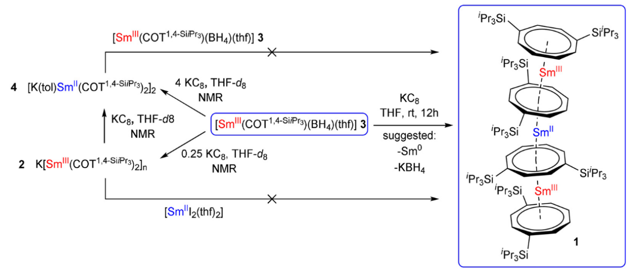
INTRODUCTION

Numerous multiple-decker complexes have been reported all over the periodic table starting with s-block poly-decker assemblies over classical d-metal triple-decker complexes to cationic p-block species triple-decker.[1] However, well-defined neutral and homoleptic all-carbon-based quadruple-decker complexes are to the best of our knowledge unknown. In 4f-element chemistry, sandwich complex and multiple-decker chemistry is considerably underdeveloped and essentially limited to COT (COT=C_8H_8) derivatives as bridging ligand.[2] Despite decades of research in this area homoleptic quadruple-decker complexes of the f-elements are unknown. This missing link of textbook complexes may be theoretically constructed from four COT-ligands and three lanthanide ions. The corresponding neutral compound would necessarily have to be mixed-valent. While examples for mixed-valent d-metal carbon-based sandwich compounds have been known for a longtime,[3] analogue 4f species are hitherto unknown. In this study we showcase the formation of a novel mixed-valent lanthanide quadruple decker.[4]

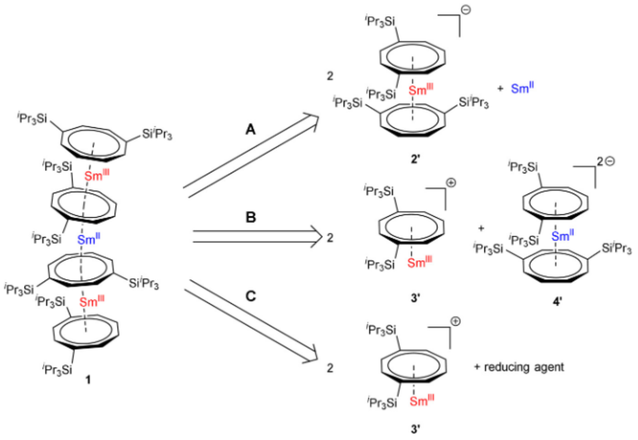
RESULTS AND DISCUSSION

Reduction of $[Sm^{III}(COT^{1,4\text{-}SiiPr3})(BH_4)(thf)]$ ($COT^{1,4\text{-}SiiPr3}$ = 1,4-$(^iPr_3Si)_3C_8H_6$) with KC_8 resulted in $[Sm^{III/II/III}(COT^{1,4\text{-}SiiPr3})_4]$, the first example of a homoleptic lanthanide quadruple-decker.



Scheme 1. Transformation based on the $Sm^{II/III}$-$COT^{1,4\text{-}SiiPr3}$ system, that are accessible by reduction with KC_8.

As indicated by an analysis of the bond metrics in the solid-state, the inner Sm ion is present in the divalent oxidation state, while the outer ones are trivalent.This observation could be confirmed by quantum chemical calculations. Mechanistic studies revealed not only insight into possible formation pathways of $[Sm^{III/II/III}(COT^{1,4\text{-}SiiPr3})_4]$ but also resulted in the transformation to other mixed metal sandwich complexes with unique structural properties. These are the 1D-polymeric chain structured $[KSm^{III}(COT^{1,4\text{-}SiiPr3})]_n$ and the hexametallic species $[(tol)K(COT^{1,4\text{-}SiiPr3})Sm^{II}(COT^{1,4\text{-}SiiPr3})K]_2$ which were initially envisioned as possible building blocks as part of different retrosynthetically guided pathways that we developed. As shown in Scheme 2, three potential retrosynthetic approaches were investigated, of wich only approach C was successful.



Scheme 2. Possible retrosynthetic fragmentation of a Sm(III/II/III) quadruple-decker to its formalbuilding blocks. The synthons **2'**, **3'** and **4'** are depicted structurally simplified.

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Accessing Kinetically Driven Reactions for Rare Earth Separations

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INTRODUCTION

The Rare-Earth (RE) elements are invaluable in society for their vast applicability in modern technology. Their magnetic, optical, and catalytic properties are leveraged in MRI contrast agents, wind turbines, and metal nickel hydride batteries, among others[1]. However, their recycling, isolation, and purification from these materials comprise some of the most challenging chemical separation processes in industry. The most prevalent method of purifying rare-earth containing ores, solvent-solvent extraction, is environmentally unfriendly and energy intensive on an industrial scale. In a recent effort to combat this challenge, we have developed a new separations system that involves a rearrangement of the ligand, H_6Clamp, promoted by Hydrogen Atom Transfer (HAT). The rate of this reaction was found to be mediated by the size of the rare-earth ion. The varied solubilities between starting material and product, and rate differences across the RE series, represent a new example of kinetically controlled separation as an efficient separation method for these elements.

We present a synthesis and characterization for a roster of RE complexes based on the H_6Clamp ligand titled RE(H_3Clamp)THF (RE = La, Nd, Dy, Y, Yb) first reported by Seth Brown[2]. HAT reactivity with pendant N-H bonds with the weak acceptor, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) have shown drastic rate difference when ligated to Fe(II) and Co(II) complexes[3]. Upon reaction with TEMPO, these RE(H_3Clamp)THF complexes undergo an irreseversible HAT rearrangement whose rate is dictated by the identity of the RE^{3+} ion.

Noticeably, we observed a ~5x rate difference in reactivity between Nd and Dy analogues. These two RE elements are commonly found togther in metal nickel hydride batteries found in wind turbines (ref). The difference in solubilities between the starting materials and products within a 1:1 mixture of Nd/Dy analogues allowed for an acetonitrile/hexanes liquid-liquid separation with a separation factor of 201 ± 51 in a single step.

This separation method and other kinetically-controlled RE separations systems[4,5] display a linear dependence across the RE series. In contrast to thermodynamic-controlled RE separations, which rely on phase equilibria or filtration, kinetically-controlled separations do not feature a ‘plateau’(ref) at some point in the RE series. These results indicate the potential utility of kinetic separations for RE ions to maximize efficiency for both mining and recycling applications.

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Periodic Trends of Templated Lanthanide Thiosulfate Compounds: Facile Control of Dimensionality

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INTRODUCTION

The lanthanide elements have been applied to many profitable innovations in medicine and technology.[1,2] Of our particular interest are explorations into the coordination chemistry of hard lanthanide cations with soft ligands, which have the potential to lead to new and innovative discoveries. The soft ligand employed in this study is thiosulfate ($S_2O_3^{2-}$), which is an effective metal complexing agent[3,4] that has industrial and medical applications.[5,6] To increase the complexity and usefulness of the material, we have incorporated an organic templating agent, as thiosulfate-based inorganic-organic frameworks have been shown to be effective photocatalysts.[7] Herein, we discuss the syntheses and structural characterizations of two new series of templated lanthanide thiosulfate compounds synthesized at room temperature.

EXPERIMENTAL METHODS

All the templated lanthanide thiosulfate structure types presented herein were reacted at room temperature and crystallized *via* solvent layering.

RESULTS AND DISCUSSION

Initial studies in our group showed that the lanthanide thiosulfate complexes all formed isostructural crystal structures with the general formula of $K_9[La(S_2O_3)_6] \cdot KCl \cdot 6\ H_2O$.[8] It was generally surprising that paring of hard lanthanide cations with soft thiosulfate anions only formed the one structure, as such disparate ions should have allowed for more flexibility in the structure-type. As such, we decided to incorporate a small, organic templating agent to see if the subtle differences in the size of the lanthanide(III) cations would then be able to dictate the structures observed. Here, we focused on the use of a simple templating agent 1,10-phenanthroline (1,10-phen). This bidentate ligand has a bite angle large enough to accommodate the size of the lanthanide cations and yet small enough (minimal steric bulk) to allow for the subtle differences in the sizes of the lanthanide cations to be able dictate the structure-types observed (**Figure 1**).

Furthermore, by changing the amount of solvent used in the layering, a completely different series of 1,10-phen templated lanthanide thiosulfates can also be formed (*not shown in **Figure 1***).

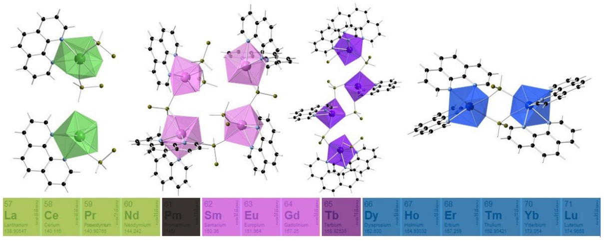

Figure 1: Compounds 1-4 here show the structural transformations that take place as one crosses the lanthanide series (save Pr). The larger, early lanthanide cations form nine-coordinate ion pairs. As the cations become smaller, the coordination number decreases from nine to eight, and interesting changes in the structure are observed. In all structures, the lanthanide cations are coordinated to at least one thiosulfate and one 1,10-phen.

CONCLUSIONS

The coordination complexes and extended structures derived from the reactions of hard lanthanide cations and soft thiosulfate anions is currently underexplored and represents a promising area for applications. By reacting the lanthanide cation with an organic templating agent, we have illuminated two new series of lanthanide thiosulfate complexes. We continue to explore this area of lanthanide chemistry and are excited for the results to follow.

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Synthesis and Electronic Structure Analysis of a Ce^{IV}-Allenyl

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Since the original elaboration of the peculiar spectroscopic and magnetic properties of cerrocene ($Ce(COT)_2$ with COT = Cyclooctatetraene), complexes featuring Ce^{IV}-C chemical bonds have gathered increasing interest among the scientific community. But, to properly understand the origins of this growing interest it is necessary to offer a cursory glance at key historical developments in fundamental lanthanide chemistry. Until recently, metal-ligand bonding interactions involving lanthanides were considered purely ionic. This notion has come under great scrutiny in recent decades and traditional modes of thought about chemical bonding in the lanthanide series are now regarded as inadequate inasmuch as they fail to account for the growing number of lanthanide complexes which, with the aid of modern analytical and computational techniques, have been shown to contain partially covalent metal-ligand bonds. Among the lanthanides, cerium offers a singular challenge to the traditional view of bonding in the lanthanides. It the most abundant lanthanide on the earth's crust, it enjoys access to trivalent and tetravalent states, and it's chemistry has proven to be unique in the series and increasingly finds effective analogy in the chemistry of transition metals. The Ce^{IV} oxidation state is of special interest in relation to the phenomenon of covalency in lanthanides. The energies of the 4f orbitals in Ce^{IV} are significantly reduced as compared to Ce^{III} and there is a concomitant shrinkage of the radial extent of the 4f orbitals. Modern experimental and computational analysis of cerium-carbon bonds in tetravalent complexes have revealed significant covalency which has been attributed to the near degeneracy of the metal and ligand localized orbitals (degeneracy driven covalency) as opposed to covalency resulting from the spatial overlap of atomic orbitals on the bonded nuclei. Examples of partial covalency in Ce^{IV} complexes include Ce^{IV}-metallocenes, -carbenes, -oxides, -halides and more. Perhaps the most salient example comes from cerrocene which is well known for its puzzling but fascinating electronic structure which has long been the subject of much debate. Some clarity was obtained when it was recently shown that the L_3 XANES spectra of cerrocene may be computationally simulated only by supposing the ground electronic state to be multiconfigurational. This property is intimately tied to the partially covalent character of the metal-ligand interactions. The combination of strong degeneracy driven covalency and weak or absent overlap driven covalency appears to be a necessary but perhaps insufficient condition for the existence multiconfigurational states. This unusual form of covalent bonding causes the charge transfer states to be close in energy. Provided that the states satisfy the quantum mechanical desiderata, they become eligible to mix and in so doing, produce a multiconfigurational state. A systematic investigation into the structural and symmetry related criteria for producing multiconfigurational ground electronic states has not been undertaken. The known examples of Ce^{IV} complexes with simple carbanionic ligands feature comparatively pronounced covalency in the metal-carbon bonds indicating that carbon is an auspicious coordinating atom for the design of multiconfigurational complexes. Ce^{IV}-C bonds are rare in the chemical literature and examples have been limited to metallocenes, α-heteroatom stabilized carbenes, and bis(iminophosphorano)methandiides. The dearth of examples can be attributed to the inherent instability of Ce^{IV}-C bonds which have been observed to undergo facile homolytic cleavage yielding Ce^{III} products and organic radicals. Nevertheless, in 2021, a former member of our group, Dr. Panetti, reported the first known example of a Ce^{IV}-aryl complex. The study made significant strides in breaking down barriers to Ce^{IV} complexes and offered valuable synthetic strategies. In view of the foregoing, we set out to expand the library of known Ce^{IV} complexes, utilizing $TriNO_x$ as a supporting ligand which offers necessary redox and kinetic stability to the Ce^{IV} metal center as well as a distinctive C_3-symmetric coordination environment with a vacant apical coordination site. Drawing inspiration from the pioneering work done by the Hayton group at UCSB in the synthesis and electronic structure analysis of actinide-allenyls and -allenylidenes, we developed the first known example of a Ce^{IV}-allenyl featuring a rare sp^2-hybridized Ce^{IV}-C bond. We launched experimental and computational studies to fully characterize this system and understand its properties. To that end, we mobilized spectroscopic, crystallographic, and electrochemical techniques and paired them, where possible, with computational analyses to rigorously interrogate the properties of the cerium-carbon bond and construct a detailed picture of the electronic structure.

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Periodic Trend in Affinity of Lanthanide Receptors for Phosphate

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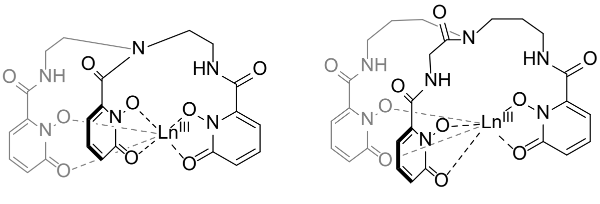
INTRODUCTION

Lanthanide receptors for anions have garnered much attention due to their strong metal-ligand bonds that can overcome hydration of the anion and their spectroscopic and magnetic properties providing applications as responsive imagin probes. While some studies have been done on anion supramolecular chemistry across the series they are limited to a handful of lanthanides (Ln^{III}), not enough to draw general conclusions on the trend. We have previously developed a class of Ln^{III} receptors for phosphate that have high affinity and high selectivity in water,[1] this work investigates the tend across the length of the lanthanide series for phosphate affinity, $Ln^{III}L$ stability, and insights into the mechanism of selectivity for phosphate.

RESULTS AND DISCUSSION


Ln^{III-}**1**: Ln^{III}-2,2-Li-HOPO

Ln^{III-}**2**: Ln^{III}-3,3-Gly-HOPO

Figure 1. Chemical structures of the lanthanide phosphate receptors.

Monitoring of phosphate binding to some lanthanide complexes is easily accomplished by luminescence studies due to replacement of quenching water molecules by phosphate. However, this requires a luminescent lanthanide AND good matching of the antennae ligand, limiting direct comparisons to a handful of Ln^{III} at best. Using a reporting Eu^{III} complex (Eu^{III}**1** or Eu^{III}**2**, Figure 1) which has a known overall association constant (β) for phosphate in water at pH 7.4,[1] in competition for limited phosphate with $Ln^{III}L$ ($Ln^{III} \neq Eu^{III}$) complexes allows for the determination of phosphate association constants relative to $Eu^{III}L$. These relative association constants were then converted to the overall association constants shown in Table 1.[2] An extremely steep dependence of β on the identity of the Ln^{III} was observed, increasing from La^{III} to Lu^{III}, which is attributed to the Lewis acidity of the metal. A similarly steep trend was observed for the thermodynamic stability of Ln^{III}**1** (increasing from La^{III} to Lu^{III}), also attributed to the metal's Lewis acidity.

Table 1. Overall Phosphate Association Constants, $\log\beta = \log([Ln^{III}L \cdot Pi_n]/([Ln^{III}L][Pi]^n))$, of selected Ln^{III}**1** and Ln^{III}**2**, and Stability Constants of Ln^{III}**1**.

	$\log\beta$ (Ln^{III}**1**)	pLn (Ln^{III}**1**)	$\log\beta$ (Ln^{III}**2**)
La^{III}	<9.8	15.0	<14.5
Nd^{III}	9.8	18.3	-
Eu^{III}	10.4	19.6	14.5
Dy^{III}	>14	20.4	15.1
Tm^{III}	>14	21.2	-
Lu^{III}	>14	>22	>17

DFT and CASSCF studies were conducted on a similar tripodal, hexadentate Ln^{III} complex to gain insight into the structure and dynamics of these phosphate receptors.[3] Unlike most other anion hosts which utilize rigid preorganization to achieve selectivity for a target anion, these computations confirmed the highly fluxional and dynamic nature of these tripodal systems. Therefore, selectivity for phosphate is achieved only by direct metal-ligand binding and acid-base interactions[4] rather than any steric or secondary interactions. This fluxionality and selectivity does not negatively affect phosphate affinity as these complexes bind multiple phosphates with very high affinity.

CONCLUSIONS

There is a steep and continuous trend of increasing affinity for phosphate as well as receptor stability down the lanthanide series from La^{III} to Lu^{III}. This trend is directly linked to the Lewis acidity of the metal rather than any steric interaction or periphery group stabilization as supported by computational studies. Future work aims to utilize these ligands for lanthanide separation, employing their large difference in stability across the series, and as to remove excess phosphate for medical treatment of hyperphosphatemia as well as in environmental runoff remediation.

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Metal-Ligand Multibonds of Lanthanides: Electronic Structure Studies in the Hunt for Emergent Quantum Phenomena

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Today's industrial superconductors suffer from requiring extremely low temperatures to operate. Experimental superconductors can reach high temperatures but are poorly tunable or require extreme conditions to function. f-element molecular materials are uniquely positioned as highly tunable materials with the opportunity to express emergent quantum phenomena, such as superconductivity, that depend on the unique properties of f-elements. These unique properties stem in part from the behavior of f-orbitals in bonding interactions. Deepening our understanding of f-orbital behaviors in bonding is required to pursue new materials utilizing these orbitals. Complexes featuring metal-ligand multiple bonds of lanthanides are at the frontier of f-element bonding which is still a juvenile field. In this study we expand on previous work synthesizing complexes with lanthanide-ligand multiple bonds utilizing the tris(hydroxylaminato) ligand framework TriNOx^{3-}, here used to stabilize a linear μ_2-nitrido Ce=N=Ce motif, the first of its kind in the lanthanides. Computations indicated significant f-orbital participation in bonding, and experimental characterization was consistent with cerium in the +4 oxidation state and diamagnetic behaviour according to both NMR and magnetometry.

Spin-Vibration Coupling in Magnetic Molecules

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Our group has been developing methods for calculating spin-phonon coupling in molecules from first principles. I will present our most recent results in determining the T1 and T2 rates in molecules, and in the calculation of vibronic spectra. I will also discuss our recent work examining the bonding and magnetic interactions in the first example of a lanthanide-lanthanide single-electron bond, which leads to compounds showing coercive magnetic fields five-times larger than industry-leading neodymium magnets.