Title: Electronic Structure, Bonding and Reactivity in f-Element Chemistry

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ACCOMPLISHMENTS

1. What are the major goals of the project?

The proposed research aims to further develop and apply advanced inorganic spectroscopic methods to f-element systems, including well-defined compounds, in-situ generated complexes (including potentially complex mixtures) and transient species. Our long term goal is to develop and apply advanced inorganic spectroscopic methods in f-element chemistry in order to advance our understanding of electronic structure, bonding and reactivity in f-element systems up to the level currently available for d-block systems. A further goal of our program is the training and development of graduate students in the application of advanced inorganic spectroscopic methods for the study of f-element systems, which is critically underdeveloped at US academic institutions. Towards these goals, we will pursue the following three specific aims in the research proposed herein:

Specific Aim 1: Development and Application of C-term Magnetic Circular Dichroism Spectroscopy in f-Element Systems. We will develop and apply *C*-term MCD spectroscopy to 5f-element systems to further our understanding of electronic structure and spin-orbits effects in f-element systems. Studies will include elucidation of *C*-term MCD features in f-element systems, determination of the polarizations of electronic transitions in non-crystalline materials and development of theoretical methods for the analysis of *C*-term MCD spectra of f-element systems, which is of specific importance for low symmetry systems. Initial studies will focus on high-symmetry uranium complexes as a function of ligand type (e.g. hard vs. soft, σ-donor vs σ/π-donor, etc.), uranium amide and imido complexes, and low-valent lanthanide, uranium and thorium complexes with $C_5H_4SiMe_3$ ligation.

Specific Aim 2: Development and Application of Freeze-Trapped Spectroscopic Methods in f-Element Chemistry. We will utilize our expertise and unique freeze-trap capabilities developed for in-situ speciation, characterization of transientt complexes and insight into reaction mechanisms in d-block systems to study transient and unstable f-block complexes. These studies will enable advanced spectroscopic characterization to progress beyond traditional studies of well-defined species in order to obtain insight into unstable and transiently generated f-element complexes, including intermediates in redox reactions. Representative studies to be used to develop and apply this approach will include in-situ formed neutral and “ate” homoleptic complexes of U with methyl and phenyl ligands in order to demonstrate the utility and impact of freeze-trapped spectroscopic methods. Additional applications include U(V) intermediates in redox reactions, unstable and transient uranium carbenes and intermediates in chemical reactions of U including intermediates in the formation of novel U-N bonded species.

Specific Aim 3: Development and Application of ^{237}Np Mössbauer Spectroscopy. In collaboration with LANL, we will utilize our established expertise in Mössbauer spectroscopy to develop ^{237}Np Mössbauer spectroscopy capabilities in the US for advanced studies of f-element systems. At present there are no ^{237}Np Mössbauer capabilities in the US for detailed studies of air sensitive molecular Np complexes, nor capabilities for studies with high magnetic fields or frozen solution samples. This method will, in turn, be developed and applied to obtaining insight into covalency and electronic structure in Np compounds, including analysis of potentially complex mixtures of Np species in both solid state and frozen solution samples. This spectroscopic capability is expected to have a broad and wide-ranging impact on Np research in the US.

2. What was accomplished under these goals?

A. Development and Application of *C*-term Magnetic Circular Dichroism Spectroscopy in f-Element Systems

Over the duration of this grant, we have worked on the development of *C*-term MCD spectroscopy for studies of electronic structure and bonding in f-element chemistry. These studies can be classified into two general areas: (1) Foundational studies focused on the development of an experimental and theoretical framework for the use of *C*-term MCD for studies of both charge-transfer and f-f transitions in f-element systems (focusing on uranium complexes) and (2) application of C-term MCD spectroscopy to evaluate electronic structure and bonding in studies of lanthanide and actinide complexes. Research accomplished across these two areas during the grant are highlighted below. Combined, this work has now enabled the broader use of *C*-term MCD spectroscopy combined with other spectroscopic methods (EPR, rRaman, etc.) to advance our understanding of electronic structure, bonding and reactivity in f-element chemistry.

Experimental Studies and Theoretical Method Development for the Simulation of f-Element C-term MCD spectra in the Charge-Transfer Region. In collaboration with the Autschbach group (U. at Buffalo), we reported a combined *ab initio* theoretical and experimental study of the magnetic circular dichroism (MCD) spectrum of the octahedral UCl_6^- complex ion in the UV-Vis spectral region (Fig. 1). The ground state is an orbitally non-degenerate doublet $E_{5/2u}$ and the MCD is a *C*-term spectrum caused by spin–orbit coupling. Calculations of the electronic spectrum at various levels of theory indicated that differential dynamic electron correlation has a strong influence on the energies of the dipole-allowed transitions and the envelope of the MCD spectrum. The experimentally observed bands were assigned to dipole-allowed ligand-to-metal charge transfer into the 5f shell, and 5f to 6d transitions. Charge transfer excitations into the U 6d shell appeared at much higher energies. The MCD-allowed transitions could be assigned *via* their signs of the *C*-terms: Under O_h double group symmetry, $E_{5/2u} \rightarrow E_{5/2g}$ transitions had negative *C*-terms whereas $E_{5/2u} \rightarrow F_{3/2g}$ transitions had positive *C*-terms if the ground state *g*-factor is negative, as it is the case for UCl_6^-.

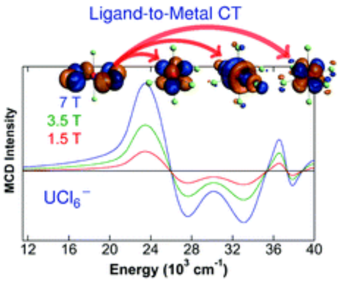

Fig. 1. C-term MCD spectroscopy of UCl_6^- in the charge-transfer region.

Experimental Studies and Theoretical Method Development for the Simulation of f-Element C-term MCD spectra in the f-f Transition Region. We have further extended our work on *C*-term MCD spectroscopy in actinide chemistry to demonstrate the significant fine structure resolution of the f-f transitions of U(V) complexes possible with this technique (Fig 2), including for the low energy $\Gamma_7 \rightarrow \Gamma_8$ transitions in $[UF_6]^-$. The experimental NIR MCD studies were further extended to $[U(OC_6F_5)_6]^-$, $[U(CH_2SiMe_3)_6]^-$, and $[U(NC(^tBu)(Ph))_6]^-$ to evaluate the effects of ligand-type on the f—f MCD fine features. In collaboration with the Autschbach group (U. at Buffalo), theoretical calculations were conducted to calculate the Laporte forbidden f—f transitions and their MCD intensity experimentally observed in the NIR spectra of the U(V) hexahalide complexes, via the inclusion of vibronic coupling, to better understand the underlying spectral fine

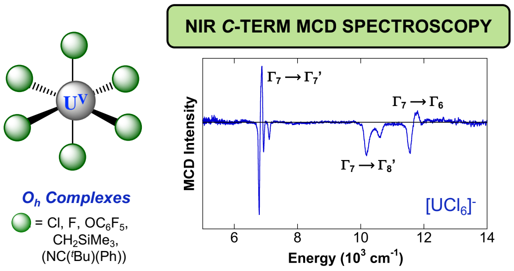

Fig. 2. NIR C-term MCD spectroscopy to evaluate the f-f region of octahedral U(V) complexes.

structure features for these complexes. These spectra and simulations provide an important platform for the application of MCD spectroscopy to this widely studied class of U(V) complexes and identify areas for continued theoretical development.

Insight into the Electronic Structure of Formal Lanthanide(II) Complexes using Magnetic Circular Dichroism Spectroscopy. In collaboration with the Evans group (UC-Irvine), we have utilized *C*-term MCD spectroscopy to evaluate the electronic structure of tri(cyclopentadienyl) rare-earth complexes, [K(2.2.2-cryptand)][LnCp'$_3$] (Ln = Y, La, Pr, Eu, Gd; Cp' = $C_5H_4SiMe_3$), which contain ions in the formal +2 oxidation state (Fig. 3). These complexes were chosen to evaluate the $4f^n5d^1$ electron configuration assignments of the recently discovered La(II), Pr(II), and Gd(II) ions versus the traditional $4f^{n+1}$ configuration of the long-known Eu(II) ion. The $4d^1$ Y(II) complex provided another benchmark complex in the MCD study. Transitions with f-orbital character were observed in the NIR MCD spectra of the $4f^25d^1$ complex [PrCp'$_3$]$^-$. This study provided the first direct observation of f-f transitions in such Ln(II) species. The broadening of these transition for Pr(II) provided further confirmation of the $4f^n5d^1$ versus $4f^{n+1}$ electronic configurations previously proposed and supported by restricted active-space RAS calculations. For further insight into the electronic structure of these [LnCp'$_3$]$^-$ complexes, experimental UV-vis MCD spectroscopy were coupled to spectral calculations (in collaboration with the Autschbach group, U. at Buffalo) which allowed for the assignment of transitions in the high energy region. The sensitivity of UV-Vis MCD to spin-orbit coupling (SOC) and the increased spectral resolution compared to electronic absorption spectroscopy enabled identification of low energy nd to (n+1)p transitions in this class of complexes. Combined, these studies provided further insight the electronic transitions and overall electronic structure of low-valent lanthanide (II) organometallic complexes.

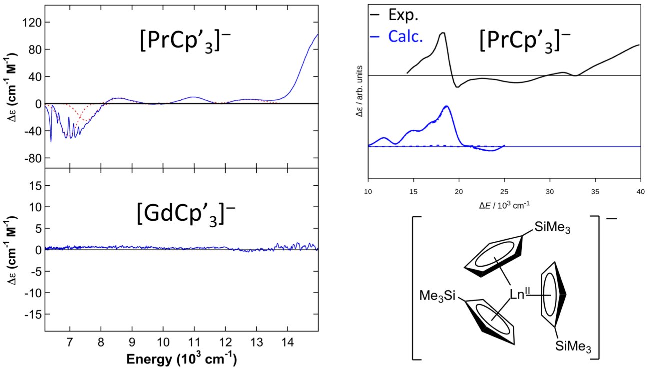

Fig. 3. Experimental and calculated C-term MCD spectra of tri(cyclopentadienyl) lanthanide(II) complexes.

Ligand Effects on Electronic Structure and Bonding in U(III) Coordination Complexes. The trivalent oxidation state of uranium has been shown to undergo unique reactivity, from its ability to activate a variety of small molecules to its role in the catalytic reduction of ethene to ethane amongst others. Central to this unique reactivity and ability to rationally design ligands for isotope separation is the underlying uranium electronic structure. While electronic structure studies of U(IV), U(V), and U(VI) have been extensive, by comparison, analogous studies of more reduced oxidation states such as U(III) remain underdeveloped. To address this challenge, we utilized MCD and EPR spectroscopic studies combined with density functional theory and multireference wavefunction calculations to elucidate the effects of ligand perturbation in three uranium(III) Tp* complexes (in collaboration with the Autschbach group, U. at Buffalo, and the Bart group, Purdue U.) (Fig. 4). Overall, the experimental and computational insight suggested that the change in ligand environment across this series of U(III)

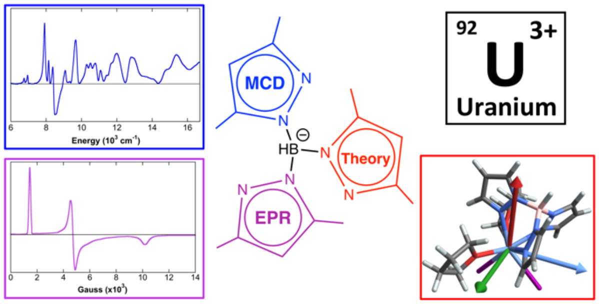

Fig. 4. MCD, EPR and computational studies to define electronic structure in U(III) Tp* complexes.

complexes resulted in only minor perturbations in the uranium electronic structure. This combined approach was also used to redefine the electronic ground state of a U(III) complex with a redox non-innocent Bipy$^-$ ligand. Overall, these studies demonstrated the efficacy of the combined experimental and theoretical approach towards evaluating electronic structure and bonding in U(III) complexes and provided important insight into the challenges in altering ligand environments to modify bonding and reactivity in uranium coordination chemistry.

An Unexpected Plan of Covalency in Ce(III) and Bk(III) Terpyridyl Complexes. In collaboration with the Albrecht-Schmitt group at FSU, we provided spectroscopic insight into a 10-coordinate cerium complex that was part of this comparative study using EPR and MCD spectroscopies. The 5 K solid EPR spectra consisted of three transitions at g = 2.7, 1.1, and 0.6 respectively. Theoretical insight predicts these values to be g = 2.7, 1.2 and 0.8, consistent with what is observed experimentally. The 5 K, 7 T MCD spectrum has several transitions and, with theoretical support, was fit to six transitions in the UV-vis region. Each of these transitions was assigned using TD-DFT. The final predicted transition was not observed by MCD as it is a fully ligand-based transition and will therefore be suppressed using MCD spectroscopy.

Additional applications of C-term MCD Spectroscopy in Uranium Chemistry. In addition to our work on U(V) and U(III) complexes previously described, we have also applied MCD spectroscopy across several additional studies of uranium complexes in order to probe electronic structure and bonding. One example includes our own study on a series of homoleptic U(IV)-aryl complexes that was part of our work on transient iron species (see section B below). In addition, we have utilized this technique in collaboration with Tondreau and co-workers at LANL as part of a study of a pseudotetrahedral U(V) complex. In collaboration with the Baker group at Trinity College Dublin, we have also employed near-IR MCD to evaluate the effects of geometric perturbations on electronic structure and bonding in a series of U(IV) thiocyanate complexes, $[X]_4[U(NCS)_8]$ (X = Cs, Me_4N, Et_4N, and $^nPr_4N$).

B. Development and Application of Freeze-Trapped Spectroscopic Methods in f-Element Chemistry

Over the duration of this grant, we have applied advanced low temperature synthetic method combined with freeze-trapped EPR and MCD spectroscopies to develop into transient uranium complexes in order to further our understanding of electronic structure, bonding and reactivity in actinide chemistry. Our work focused specifically on long-standing challenges in organouranium chemistry and provided access to both novel and long sought after homoleptic alkyl and aryl complexes. This work provides both opportunities to further studies bonding and reduction pathways in such species as well as a fundamental infrasctructure in low temperature and freeze-trapped methods that can be applied to reactive actinide chemistry including the reaction pathways of uraniyl complexes.

Homoleptic Aryl Complexes of Uranium (IV). The synthesis and characterization of sterically unencumbered homoleptic organouranium aryl complexes containing U-C σ-bonds has been of interest to the chemical community for over 70 years. Previous synthetic efforts in uranium-aryl chemistry have focused on bulky aryl ligands, such as the C_6H_3-2,6-$(C_6H_4\text{-}4\text{-}^tBu)_2^-$ (Terph$^-$) ligand which provide thermal stability to the resulting organouranium complex. Previous work in our group isolating thermally unstable homoleptic iron-aryl species utilizing low temperature synthetic techniques motivated us to re-explore this longstanding challenge in uranium chemistry; isolating homoleptic organouranium species with simple aryl substituents. The addition of 6 equiv. of phenyllithium to a slurry of $[UCl_4(1,4\text{-dioxane})]_2$ in THF/Et_2O at -80 °C resulted in an immediate

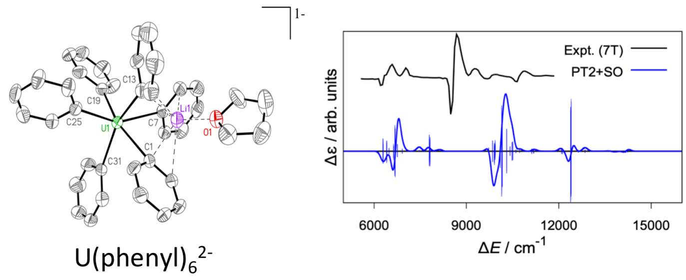

Fig. 5. X-Ray structure and MCD spectra (experimental and calculated) of UPh_6^{2-}.

color change from yellow to red. After filtering through celite and addition of hexane, storage at -80 °C resulted in the formation of red needle crystals identified as $[Li(THF)_4][(THF)LiUPh_6]\cdot 1.5THF$ (Fig. 5). This complex was found to be air and temperature sensitive, decomposing readily above -80 °C. With a successful method identified for isolation of **1**, the substituents of the *p*-position of the aryl group were varied to further explore the electronic contribution of the aryl ring on the nature of the U-C bond. Following similar synthetic procedures but using *p*-tolyllithium and *p*-Cl-phenyllithium, the analogous six coordinate uranium species were isolated, $[(THF)_3LiXLi(THF)_3][(THF)LiU(p\text{-}tolyl)_6]\cdot Et_2O\cdot 0.62THF$ and $[Li(THF)_4]_2[U(p\text{-}ClPh)_6]$. To gain insight into the electronic effects of the perturbation of the ligands, magnetic circular dichroism (MCD) studies were performed. The 7 T, 5 K MCD spectra of the phenyl and *p*-tolyl complexes are nearly identical, consistent with their geometrical similarities suggesting the electronic effect of the *p*-tolyl group is negligible. Significant shifts in energy are observed for the *p*-ClPh complex, likely due the geometrical perturbations due to the *p*-Cl substituent. Overall, this study provides insight into the electronic effects of ligand character on the nature of U-C bonding as well as providing the first examples of sterically unencumbered uranium aryl species.

The Exceptional Diversity of Homoleptic Uranium-Methyl Complexes Historically, the synthesis of homoleptic uranium-alkyl complexes has relied on sterically encumbering alkyl substituents for kinetic stabilization. Notably, there exists only one example, to date, of a homoleptic uranium-methyl complex which utilizes the cation complexant additive *N,N,N',N'*-tetramethylethylenediamine (TMEDA), $[(Li(TMEDA))_2UMe_6]$. In the absence of TMEDA, formation of intractable reaction mixtures limited further characterization of any non-stabilized uranium-methyl species. The precedent for a dramatic shift in d-block organometallic speciation in the presence of cation complexant additives, motivated us to explore uranium-methyl speciation without TMEDA. Utilizing cryogenic synthesis and handling techniques, we were able to circumvent the need for additives and reported the isolation of several homoleptic uranium-methyl complexes, including the first example of a homoleptic uranium-alkyl dimer, $[Li(THF)_4]_2[U_2Me_{10}]$ (Fig. 6). Additionally, the analog to the TMEDA stabilized monomeric complex was successfully synthesized, $[(Li(THF)_4][Li(THF)_2UMe_6$. By changing the reaction medium from THF to Et_2O, two more uranium-methyl monomeric complexes were isolated and characterization by X-ray diffraction. The 7-coordinate U(IV)-methyl complex, $\{Li(OEt_2)Li(OEt_2)_2UMe_7Li\}_n$, was isolated from this reaction mixture. Prior to this discovery, a 6-coordinate uranium(IV) center was hypothesized to be the upper limit in uranium(IV) coordination number. A homoleptic uranium(V)-methyl complex was also isolated from this reaction medium. However, due to difficulties in XRD analysis, the complexant, 18-crown-6, was used which led to the isolation of $[Li(18\text{-}crown\text{-}6)(THF)_2][UMe_6$ Further characterization and electronic structure

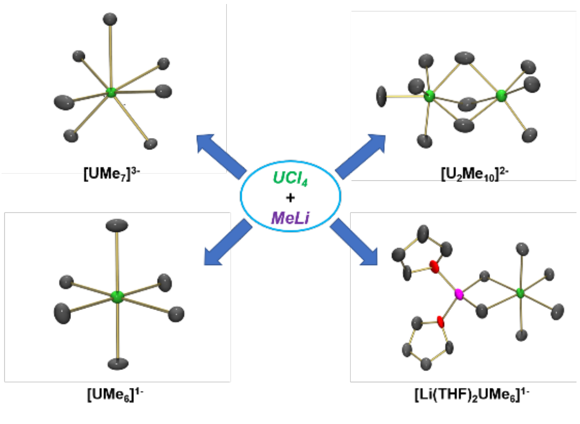

Fig. 6. Crystal structures of several unprecedented uranium-methyl complexes.

descriptions of these complexes using NMR, EPR, and computational analysis provided insight into structure and bonding in organouranium chemistry.

C. Development and Application of ^{237}Np Mössbauer Spectroscopy

To bring a ^{237}Np Mossbauer capability back to the United States actinide research community, we have worked over the past few years to design and develop a ^{237}Np Mössbauer spectrometer, which is currently under construction and will be operating in 2021 following several delays related to both COVID and ^{241}Am approvals (both receiving the material and preparing sources) at FSU that have now been successfully resolved. The instrument is being housed in the laboratory of Thomas Albrecht-Schmitt at Florida State University (FSU) in Tallahassee, Florida. This instrument location was selected for several reasons. First, being located at a university allows for this instrument to be readily available for use by a wide range of academic and national laboratory researchers. Second, the Albrecht-Schmitt lab is equipped to handle synthetic ^{241}Am chemistry, which is essential for ^{241}Am source development work. Lastly, housing the instrument in a laboratory in which Np synthetic chemistry can be performed is ideal for enabling studies of a wide array of Np complexes and materials, including sensitive materials that may be challenging to transport.

The ^{237}Np Mössbauer currently under construction utilizes a vibration insensitive Mössbauer spectrometer (VIMS) configuration in which the ^{241}Am source, sample, and detector are all contained within a single cryostat. This configuration is ideal for ^{237}Np Mössbauer spectroscopy since, in contrast to the more common ^{57}Fe Mössbauer spectroscopy, both the source and sample must be held at liquid He temperatures for ^{237}Np Mössbauer. Furthermore, the VIMS design results in the source and sample being closer together than is achievable in a traditional Mössbauer spectrometer design, enabling good signal to noise with smaller sample sizes typically employed in traditional Mössbauer spectrometers. In addition to these advantages, the instrument is capable of the high velocity shift ranges ($\geq \pm 200$ mm/s) required for ^{237}Np Mössbauer spectroscopy with an integrated laser interferometer for calibration. Lastly, the requirement of liquid He temperatures for ^{237}Np Mossbauer spectroscopy has been mitigated in the design through the integration of a Cryomech He reliquefier in order to minimize the need for the continued purchase of liquid He.

3. What opportunities for training and professional development has the project provided?

This project has contributed to the training of 4 graduate students throughout the project period. Val Fleischauer is a Ph.D. graduate of the group who worked on Ln(II) MCD. Jeff Sears (6th year PhD student) completed our studies of uranium-methyl complexes and has recent submitted his Ph.D. thesis for defense. Nikki Wolford (5th year PhD student) worked on the uranium-aryl, Ln(II), U(III) Tp* and Ce EPR/MCD. She is currently working on additional EPR studies in collaboration with the Tondreau group at LANL (lanthanide, U and Np samples). Dan Curran (5th year PhD student) has worked on our MCD studies of U(V) and U(IV)-NCS complexes, the development of freeze-trapped EPR spectroscopy for studies of transient uranium species and the development of low temperature rRaman studies of uramium coordination complexes. All three students have gained significant expertise in syntheses of highly air and temperature sensitive complexes, freeze-trapped spectroscopic methods (including freeze-trapped EPR spectroscopy) and computational studies. Nikki and Dan have also been involved in our ^{237}Np Mössbauer spectrometer design and development, providing critical experience in such instrumentation. The students have also presented their work at multiple research conferences during the Ph.D. work, providing opportunities for networking and improvement of their oral presentation skills.

Due to their work on this project, both Nikki and Jeff have received Hooker Fellowships from the University of Rochester. Nikki has also received an ACS Division of Inorganic Chemistry travel award for the ACS National Meeting and a G.T. Seaborg Institute Research Fellowship for LANL. Lastly, our f-element work has also led to a postdoctoral position for Stephanie Carpenter, a formed PhD student in the group who worked in d-block chemistry, at LANL working in f-element chemistry with Dr. Aaron Tondreau.

4. How have the results been disseminated to communities of interest?

This project to date has directly contributed to 7 conference papers/presentations (all prior to 2020 due to COVID-19), 2 thesis/dissertations (with 2 more expected later in 2021) and 9 publications (1 of which is submitted). An additional two papers beyond those listed are currently in preparation for submission later in 2021.

PRODUCTS

A. Conference Papers/Presentations

7. Sears, J. D.; Neidig, M. L., “Synthesis and characterization of homoleptic uranium-methyl complexes,” 2019 GRC Organometallics, Newport, RI.
6. Wolford, N. J.; Neidig, M. L., “Synthesis and characterization of homoleptic uranium(IV) aryl species,” 52nd Inorganic Discussion Weekend, Oshawa, ON.
5. Wolford, N. J..; Neidig, M. L., “Synthesis and characterization of homoleptic uranium(IV) aryl species,” 2019 Western New York Inorganic Symposium, Rochester, NY.
4. Sears, J.D.; Sergentu, D.-C.; Baker, T. M.; Brennessel, W. W.; Autschbach, J.; Neidig, M. L., “Synthesis and characterization of homoleptic uranium-methyl complexes,” 2019 Western New York Inorganic Symposium, Rochester, NY.
3. Neidig, M. L., “Homoleptic methyl speciation and reaction pathways,” 2019 GRC Inorganic Reaction Mechanisms, Galveston, TX.
2. Sears, J. D.; Neidig, M. L., “The complexities of homoleptic uranium-methyl speciation,” 51st Inorganic Discussion Weekend, Waterloo, ON.
1. Wolford, N. J.; Neidig, M. L., “Synthesis of unstable homoleptic uranium complexes,” 51st Inorganic Discussion Weekend, Waterloo, ON.

B. Theses/Dissertations

2. Sears, J. D., “Bonding and reactivity in iron-catalyzed carbon-carbon (C-C) cross-coupling and organouranium chemistry,” University of Rochester, submitted March 2021.
1. Fleischauer, V. E., “Applications of physical inorganic spectroscopy to d- and f-block metals: catalysis, electron structure and bonding,” University of Rochester, August 2018.

C. Publications

9. Gaiser, A. N.; Celis-Barros, C.; White, F. D.; Beltran-Leiva, M. J.; Sperling, J. M.; Salpage, S. R.; Poe, T. N.; Jian, T.; Wolford, N. J.; Jones, N. J.; Ritz, A. J.; Lazenby, R. A.; Gibson, J. K.; Baumbach, R. E.; Paez-Hernandez, D.; Neidig, M. L.; Albrecht-Schonzart, T. E., "Creation of an unexpected planed of enhanced covalency in cerium(III) and berkelium(III) terpyridyl complexes," *Nature Chem.*, submitted.
8. Curran, D. J.; Ganguly, G.; Heit, Y. N.; Wolford, N. J.; Minaisian, S. G.; Loble, M. W.; Cary, S. K.; Kozimor, S. A.; Autschbach, J.*; Neidig, M. L.*, "Near-infrared C-term MCD spectroscopy of octahedral uranium(V) complexes," *Dalton Trans*. **2021**, accepted.
7. Wolford, N. J.; Radovic, A.; Neidig, M. L.*, "C-term magnetic circular dichroism (MCD) spectroscopy in paramagnetic transition metal and f-element organometallic chemistry," *Dalton Trans.* **2021**, *50*, 416-428.
6. Sears, J. D.; Sergentu, D. -C.; Baker, T. M.; Brennessel, W. W.; Autschbach, J.*; Neidig, M. L.*, "The exceptional diversity of homoleptic uranium-methyl complexes," *Angew. Chem. Int. Ed.* **2020**, *59*, 13586-13590.
5. Wolford, N. J.; Yu, X.; Bart, S. C.; Autschbach, J.*; Neidig, M. L.*, "Ligand effects on electronic structure and bonding in U(III) coordination complexes: A combined MCD, EPR and computational study," *Dalton Trans.* **2020**, *49*, 14401-14410.
4. Wolford, N. J.; Sergentu, D. -C.; Brennessel, W. W.; Autschbach, J.*; Neidig, M. L.*, "Homoleptic aryl complexes of uranium(IV)," *Angew. Chem. Int. Ed.* **2019**, *58*, 10266-10270.
3. Fleischauer, V. E.; Ganguly, G.; Woen, D. H.; Wolford, N. J.; Evans, W. J.*; Autschbach, J.*; Neidig, M. L.*, "Insight into electronic structure of formal lanthanide(II) complexes using magnetic circular dichroism spectroscopy," *Organometallics* **2019**, *38*, 3124-3131.
2. Tondreau, A. M.; Duignan, T. J.; Stein, B. W.; Fleischauer, V. E.; Autschbach, J.; Batista, E. R.; Boncella, J. M.*; Ferrier, M. G.; Kozimor, S. A.; Mocko, V.; Neidig, M. L.; Cary, S. K.; Yang, P., "A pseudotetrahedral uranium(V) complex," *Inorg. Chem.* **2018**, *57*, 8106-8115.
1. Gendron, F.; Fleischauer, V. E.; Duignan, T. J.; Scott, B. L.; Löble, M. W.; Cary, S. K.; Kozimor, S. A.; Bolvin, H.; Neidig, M. L.*; Autschbach, J.*, "Magnetic circular dichroism of UCl_6^- in the ligand-to-metal charge-transfer spectral region," *Phys. Chem. Chem. Phys.* **2017**, *19*, 17300-17313.

IMPACT

1. What is the impact on the development of the principal discipline(s) of the project?

Our studies have had impacts in actinide chemistry in three major areas. First, the development and application of *C*-term MCD spectroscopy has contributed to our broader understanding of electronic structure and bonding in f-element chemistry in uranium complexes across multiple oxidation states. Our developments in this area, including our improving ability to calculate these spectra, will provide an important characterization resource for the broader discipline. Second, our ability to synthesize and characterize electronic structure and bonding in unstable, transient uranium complexes including organouranium species continue to broaden our understanding of fundamental structure and reaction pathways in actinide chemistry, moving the field beyond static, thermally stable complexes. Third, the ^{237}Np Mössbauer spectrometer constructed as part of this grant will enable important new characterization studies of Np compounds for the entire heavy element community in the United States.

2. What is the impact on other disciplines?

Nothing to report.

3. What is the impact on the development of human resources?

This research project continues to train the next generation of PhD chemists to contribute to US science of the heavy elements. Overall, this project has contributed to the training of four PhD students, including the development of skills in synthetic, spectroscopic and theoretical studies of actinide complexes. Our group has also sent a recent Ph.D. graduate to LANL for postdoctral studies on f-element systems with Dr. Aaron Tondreau and another PhD student will start this summer working with Dr. Ben Stein at LANL as a G.T. Seaborg Institute Research Fellow.

4. What is the impact on physical, institutional, and information resources that form infrastructure?

The grant has contributed to the construction of a ^{237}Np Mössbauer spectrometer that will be a long-term resource to the broader f-element community for studies of electronic structure and bonding in f-element chemistry. This grant has also contributed to the extension of our X-band EPR spectrometer to a higher magnetic field range (via a new water chiller and power supply), enabling resolution of high-field (low g-value) EPR transitions in lanthanide and actinide complexes.