COVER PAGE

Project Title: Tailoring Redox Active Ligands for Probing the Reactivity of Actinides	
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ACCOMPLISHMENTS

1. What are the major goals of the project? With this project, we aim to further enhance our understanding of fundamental f-element chemistry, including electronic structure and bonding behaviors. Given that the remediation of nuclear fuel wastes is made more difficult based on gaps that remain in our fundamental understanding of f-element chemistry, the focus of this project will be bridging areas of chemistry to gather insight into the unique properties of 5f metal ions through the preparation of coordination complexes and the characterization of some of their unusual spectroscopic and structural properties. The fundamental chemistry discovered here can be formative in the development of new materials for waste remediation or extraction agents. Thus, it is important to be able to characterize a range of metal complexes in solutions, in the solid-state, and at interfaces. Key project goals include the characterization of actinide complexes bearing new redox-active ligands, including those of lower-oxidation state uranium, and examining how structural changes to the ligand and coordination sphere affect structure and bonding. The research in its initial stages will focus on the design and synthesis of new ligands, and then ultimately coordination complexes with uranium, thorium, and finally other metals of interest for comparison.

Task 1: Preparation of New Ligands/Actinide Metal Complexes - Soft-Donor Ligands: New ligand systems will be prepared as a series for key comparisons for investigating soft donor interactions. Deliverables include new organic compounds and metal complexes with uranium, thorium, and the lanthanides for characterization. Of particular interest is the redox active metal cerium. Key experiments will be performed to look at the effects on changes in solvent and/or pH on the formation of metal complexes.

Task 2: Metal Complex Characterization: Single Crystal X-ray Diffraction: Characterization in the solid-state by single crystal X-ray diffraction will be the primary goal, but analysis of the metal complex methods and characterization of the stability of the complexes will also be investigated. Deliverables will primarily be new data on novel metal complexes. Electronic properties will be investigated using ultraviolet-visible spectroscopy, fluorescence, and luminescence spectroscopy. Metal complex formation will be followed using UV-Vis-NIR spectroscopy and metal complexation character will be confirmed with a combination of characterization techniques.

Task 3: Electrochemistry/ Reduction chemistry: Metal complexes will be prepared and characterized by standard electrochemical methods using cyclic voltammetry and differential pulse voltammetry to look at the potential for stabilization of less common oxidation states. Also, experiments with the addition of strong reducing agents will be used to determine if lower oxidation states can be prepared in this way – even if only in situ.

Task 4: Modified ligands featuring electron withdrawing groups/thiols/nitriles, etc: Analysis of selectivity for actinides and characterization of the stability of the complexes will also be investigated through model extraction studies and metal complex formation with new ligands prepared from modifications to the phenolic framework of the ligand

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

Graduate students Ethan Hiti, Clay Black, Julie Niklas, Matt Hollingsworth, John Ducilon, and Dylan Gardner that have been supported in part by this project have had opportunities for career development. All of these students have had one on one training interactions with the PI, Prof. Anne Gorden, in proposal and grant preparation, journal article preparation and submission, maintaining an online research presence, as well as in making conference posters and presentations. All of the students have had training in safe handling and radiation safety with actinides. Julie Niklas and Dylan Gardner have been able to train with Prof. John Gorden and Dr. Daniel Unruh on methods of X-ray diffraction for single crystal structure determination. This is particularly challenging for systems of this complex type. These activities will support our future research efforts as well as contribute to their technical skill sets.

Graduate students Ethan Hiti, Julie Niklas, John Ducilon, and Dylan Gardner have been working with mentoring undergraduate students. Ethan Hiti has been a mentor for J. P. Grundhoefer and Grant Wilkenson. Julie Niklas has mentored Katherine Hunter, Madeleine Forbes, Jacob Mayhugh, and Florian Resnik. Dylan Garder has been a mentor for Tessa Hoang and Justin Williamson. John Duclion has been a mentor for Madeleine Forbes and Avery Stilley. The PI has been mentoring the mentors in ways of mentoring while also helping the undergraduate students to learn synthetic techniques and analytical techniques including UV-Vis spectroscopy, nuclear magnetic resonance, inert atmosphere techniques, dry box maintenance, and mass spectrometry.

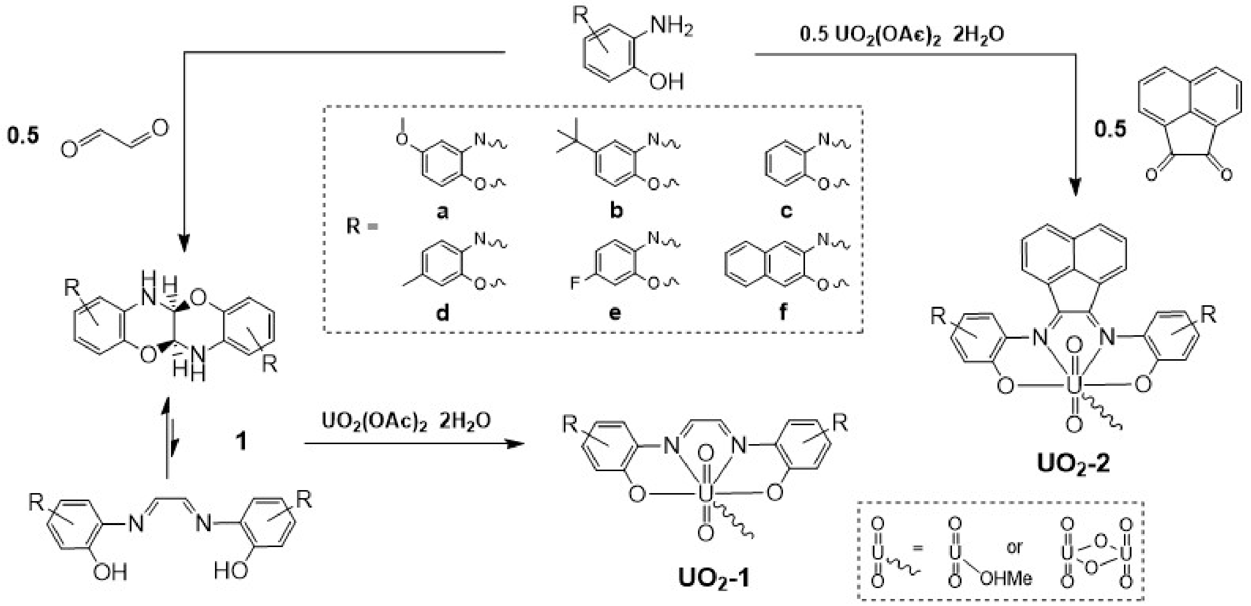
Graduate students Isuru Ariyarathna, Benjamin Jackson, Holden Paz, and undergraduate students Zhongyuan Lu and Jared Stinson were all exposed for the first time to electronic structure calculations of f-block elements. They learned how to tackle the complexities and technical issues that very often accompany these calculations. The graduate students had the chance to supervise undergraduate students.

4. How have the results been disseminated to communities of interest? The PI, Prof. Anne Gorden, has made several presentations about this and related work during this reporting period (9/2020 - 9/2022) including invited talks at the Southeast Regional American Chemical Society meeting and the New Horizons in Molecular f-Element Chemistry hosted online. The PI also organized a symposium on lanthanide and actinide coordination at the Southeast Regional meeting of the American Chemical Society in Birmingham Alabama in November 2021. Conference presentations from SERMACS are listed in the products of this award. Four publications directly related to this work have been published and are listed in the publications detail (items 17-20 below). Two additional publications are in preparation. Since 2008, the PI has been very active with the American Chemical Society and the Auburn Local Section ACS. Prof. Gorden is currently a member of the American Chemical Society National Women Chemists' Committee.

SCIENTIFIC REPORT

Summary: Over the full course of this project, we 1) characterized U(VI) complexes of the aryl-substituted α-diimine glyoxal bis(2-hydroxyanil ligands [GBHA] for comparison to the previously described U(VI)-phen-BIAN complexes 2) characterized derivatives of 2-(1H-imidazo[4,5-b]phenazin-2-yl)phenol (Salmidizine) comparing Cu(II) and U(VI) complexes 3) characterized a cyano-substituted naphthyl salophen with U(VI and lanthanides and tested them in 2 photon up-conversion 4) prepared pyrasal ligands as U(VI)- complexes which resulted in new oxo coordinating species as potential models for peroxide formation 5) prepared new pyrrophen U(VI)-complexes for separations or detection of uranyl 6) prepared crown ethers incorporating conjugated aza species for comparing uranyl and copper ion coordination based on emission and 7) studied computationally the electronic structure thorium-ammonia complexes which were shown to accommodate multiple diffuse electrons.

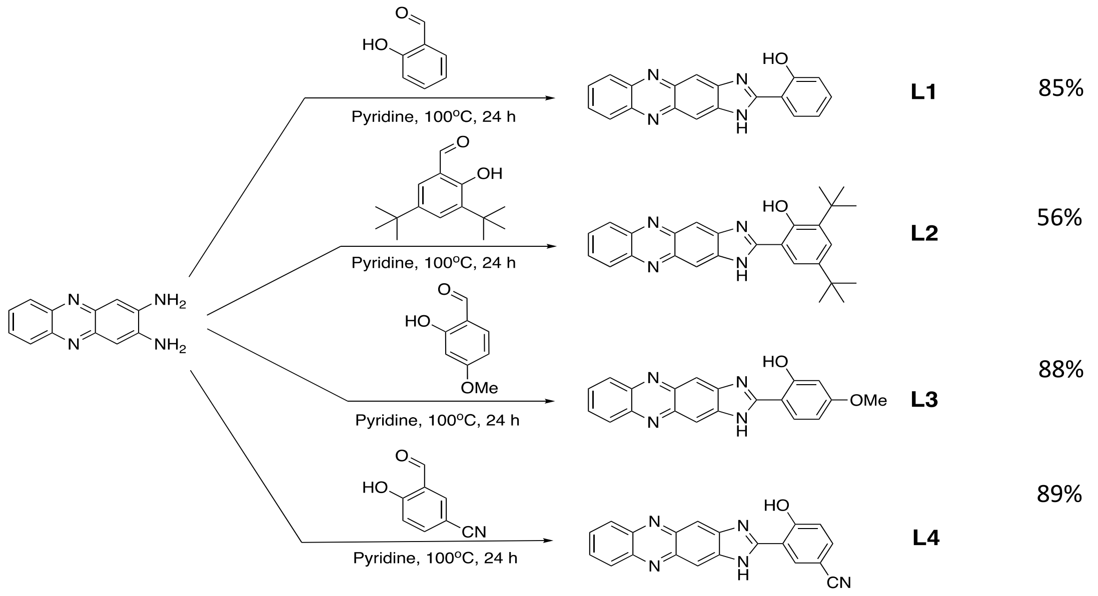
1) **Uranyl α-diimine complexes.** As the inception of this project, we previously described the synthesis and characterization of a new ligand system combining the redox-active backbone of Ar-BIANs (N,N'-bis[(aryl)imino]acenaphthenes) and mixed-donor O-N-N-O binding pocket found in salen-type ligand are reported. In this work, complexes of Co(II), Ni(II), and U(VI) (as UO_2^{2+}) were prepared and characterized through single crystal X-ray diffraction and electrochemical studies using cyclic voltammetry and differential pulse voltammetry. Structural characterization of these complexes revealed the transition metal complexes exist as monomers bearing two O-N-N coordinated ligands, while the uranyl complexes formed as aryloxide bridged dimers with each U(VI) center coordinating phen-BIAN as a tetradentate ligand. Additionally, electrochemical studies with these demonstrated a wealth of redox-activity and allowed the characterization of multiple accessible oxidation states through the formation of U(VI)/U(V) and U(V)/U(IV) mixed-valence complexes in solution. This work was described in “Structural Characterization and Redox Activity of a Uranyl Dimer and Transition Metal Complexes of a Tetradentate BIAN Ligand,” *Organometallics* **2017**, 4626–4634. (DOI: 10.1021/acs.organomet.7b00454).



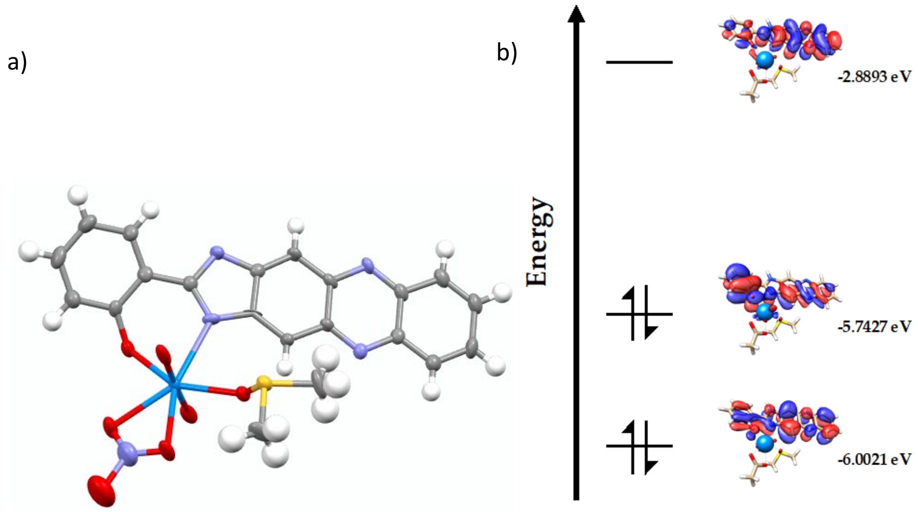
Scheme 1. General synthesis of gbha ligands (**1**) and phen-BIAN ligands (**2**), and uranyl complexes UO_2**-1** and UO_2**-2**.

Continuing this effort, U(VI)- complexes of the aryl-substituted α-diimine ligands GBHA and phenBIAN (gbha (1) = glyoxal bis(2-hydroxyanil); phen-BIAN R = OMe, t-bu, H, Me, F, and naphthyl) were prepared and characterized by X-ray diffraction, FT-IR, NMR, UV-Vis spectroscopy, and electrochemical methods. These ligand frameworks contain an O-N-N-O binding pocket similar to salen-type ligands but are redox-non-innocent. (See Scheme 1 for an illustration of the prepared complexes in this investigation. Impacts of the accessible π-systems of the backbone and effects of ligand substitution on the axial uranium-oxo interactions were evaluated spectroscopically *via* the intraligand charge-transfer (ILCT) processes. These were found to dominate the absorption spectra of these complexes and through changes to the asymmetric (v3) O=U=O stretching frequency. This and analysis of the electrochemical data revealed the effects of the inclusion of the highly conjugated acenaphthene backbone and the importance of π-backbonding ligand electronic structure on the bonding interactions of the uranyl metal ion. We reported three solid-state structures of uranyl complexes and found ligand-radical-type character for in the ligands with larger substituents. This appears to afford a degree of back bonding between the U(VI)- and pi orbital system. This work was published in *Inorganic Chemistry* **2019, 58, 22, 15088-15100. (**https://doi.org/10.1021/acs.inorgchem.9b01695**)** It was initially hoped that this would allow for the direction of future studies of the phen-BIAN system towards isolating and characterizing lower-valent uranium complexes, but this has not proved fruitful. **Further work would continue in this area with attempting the synthesis of further substituted phen-BIAN ligands and low valent uranium complexes, or mixed metal complexes. This is also perhaps the beginning of a new project incorporating the redox active ligands into aza-crown ether ligands.**

2) **SALMIDIZINE** Imidazole and benzimidazole ligands are naturally present in biomolecules and have been exploited in biological and medical applications demonstrating some anti-inflammatory and anti-tumor properties. Complexes with ligands like this have been found to display π-π interactions and derivatives have been used in polymer enhanced catalysis or as fluorescent probes. While examples of this N-C-C-C-O binding motif have been seen with uranyl, little exploration into the effects of extended conjugation or altering the electronics of the binding pockets had been done. This inspired new work to prepare ligands for selective sensing as 2-(1H-imidazo[4,5-b]phenazine-2-yl)phenol or "salimidizine" and its derivatives (See **Scheme 2** below). Four derivatives of 2-(1H-imidazo[4,5-b]phenazin-2-yl)phenol, salimidizine, di t-butylsalimidizine, cyanosalimidizine, and methoxysalimidizine were synthesized. We have reported solid state characterization in the form of X-ray diffraction single crystal structures and solution characterization of UV-Vis emission and fluorescence spectroscopy for each of these and metal with uranyl (UO_2^{2+}) and Cu^{2+}. Cu^{2+} was selected for comparison because of the similar charge to ionic radius ratios and competitive binding with uranyl.



Scheme 2. Synthetic scheme for salimidizine type ligands **L1**, **L2**, **L3**, **L4**



Scheme 3. *a) Salimidizine-UO2 Crystal structure. b) HOMO/LUMO energy diagram*

Experiments to follow coordination in solution using batch titrations were used to allow for monitoring of metal complexation by both UV-Vis spectra and fluorescence. Analysis of the solid-state structural characterization from X-ray diffraction yielded some interesting finding found that, although there was little change in the UV-Vis spectra suggestive of complexation uranyl by salphenazine, crystal structures of all of these complexes were obtained. It was observed that upon coordination of uranyl, fluorescence intensity increased, but it was found to decrease dramatically with copper coordination. To better understand the different ligand-metal interactions with uranyl and Cu (II), quantum chemical calculations were performed to describe the ground and excited electronic states of their complexes salimidizine as a model.

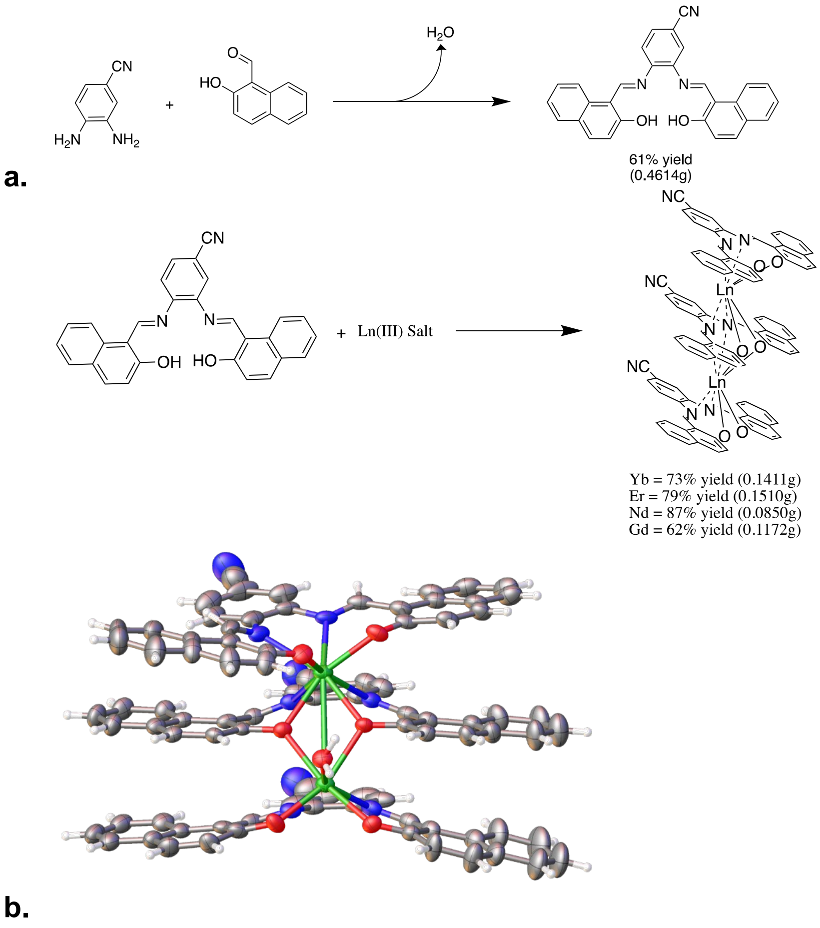
To explain the differences in the activity of the uranyl (UO_2^{2+}) and Cu^{2+}centers upon metal complexation, we compared the metal complexes by studying calculations run on the free ligands and the Cu(II) complexes to compare to U(VI) analogs to characterize electronic effects of the d and f orbitals. We first optimized the structure of the two complexes with the simple unsubstituted salphenzine (L1) at their singlet (uranyl) and doublet (copper) ground states. Above in **Scheme 3** is a) crystal of the salimidizine-UO_2 complex, b) HOMO/LUMO energy levels. The copper and uranyl structures used for the calculations were derived from the crystal structure of $UO_2[L1](OAc)\bullet DMSO$. To complete the first coordination sphere of the metals we added an acetate (AcO) and/or a water ligand, constructing four distinct complexes: $L_1UO_2^{2+}(AcO)$, $L_1UO_2^{2+}(AcO)(W)$, $L_1Cu^{2+}(AcO)$, and $L_1Cu^{2+}(AcO)(W)$. Both metals were coordinated by the ligand and an (OAc) counter ion to achieve a neutral species. Using this geometry, we employed TD-DFT to identify the state with the highest oscillator strength in the region of the absorption frequency used for the experiments (439 nm).This enabled us to see the possible effect of the coordination of different solvent molecules.

Comparison of the two potential energy profiles makes clear the reason for the observed fluorescence quenching in the copper case. For uranyl, the initial excitation to the non-zero oscillator strength excited state is followed by relaxation to its minimum via a series of conical intersections. Radiative decay to ground state generated the recorded fluorescence signal and the system returns to the global minimum of the ground state in a non-radiative manner (lower grey arrow). The same process can in principle occur for copper, but the minimum of the pertinent excited state is shallow. The molecule after a small energy barrier goes to a lower minimum of the same potential energy surface, which has nearly zero oscillator strength and the decay to the ground state happens in a non-radiative manner.

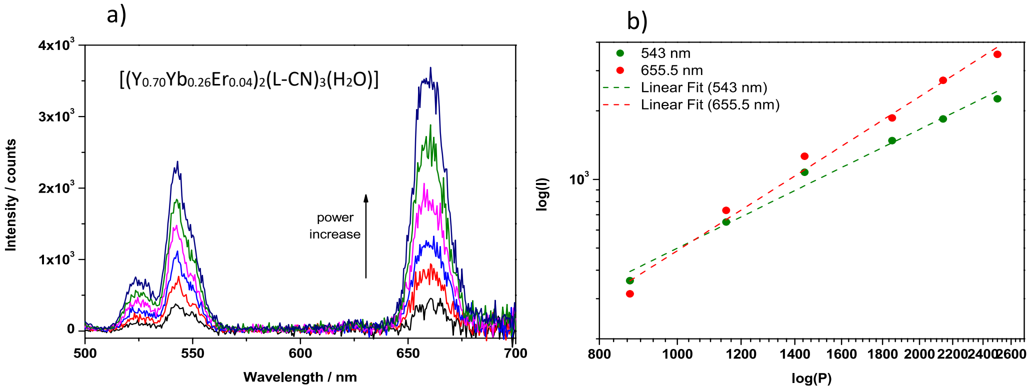
An increase in absorption, in the case of UO_2^{2+} and two new modes of absorbance were observed in the case of Cu. In the presence of greater than a 1 to 1 ratio of UO_2:1 the emission more than doubled; in contrast, in the presence of any ratio of Cu:1 emission was quenched by at least half. Based on the calculated potential energy profiles we were able to explain these observations. The minimum of the pertinent excited electronic state for copper is shallow and decays readily to a different minimum with zero oscillator strength, and thus the decay to the ground state follows a non-radiative pathway. Thus, this initially indicated some selectivity for uranyl, as most other examples of these systems selectively quench in the presence of transition metals. Difficulty in modulating the synthesis of these ligands and their low solubility precluded additional studies. This work was reported in "Comparing Coordination Uranyl (VI) Complexes with 2-(1H-imidazo[4,5-b]phenazin-2-yl)phenol and Derivatives," *Dalton Transactions*, **2021**, 50, 11113-11122. (https://doi.org/10.1039/D1DT02359D)

3) **NAPTHYLSALOPHEN** Previously, we had introduced a new ligand naphtylsalophen, and characterized it in the solid state by X-ray diffraction as metal complexes with Ce(IV) and Th(IV) and noted the first thorium complex to feature fluorescence both in the solid state and in solution. (See *Chemical Communications* **2017** 53, 11984-11987. (DOI: 10.1039/C7CC06868A). We also reported the structural characterization and solution chemistry of uranyl complexes with naphthylsalophen noting their unique hydrogen bonding in the formation of a uranyl tetramer and their electrochemical behavior.(See *Chemical Communications* **2018**, 54, 11693 -11696 (DOI:10.1039/C8CC05242E) We further hypothesized substitution on the back of the ligand would allow for more tunable properties of the coordination core.

A new cyano-substituted naphthylsalophen ligand (H_2L-CN) was prepared along with the U(VI) complex and corresponding 3:2 ligand-to-metal sandwich-type Ln(III) complexes (LnIII = Gd(III), Nd(III), Er(III), and Yb(III). We attempted to characterize the cyanonaphthylsalophen-UO_2 complex and a cyanonaphthylsalophen-Th (IV) complexes, but these did not produce crystals suitable for X-ray diffraction. With the Ln complexes, we found substitutions on the ligand backbone can alter the Förster distance between the two metals affecting their interaction. This Ln-Ln distance then alters the ability of the complexes to do 2 photon up-conversion. The metal-metal distance goes from 3.830Å in the bare ligand complex to 3.816Å in the CN substituted ligand complex which confirms ligand modification can tune these distances. We collaborated with Prof. DeBettencourt-Dias at the Univ. of Nevada to conduct two photon up-conversion experiments. A mixture of the metals Y(III), Yb(III), and Er(III) in the 3 ligands to 2 metal stoichiometry was most efficient at two photon up conversion using 980 nm light as the incident light. These experiments showed a quadratic dependence of emission intensity on laser power as illustrated in **scheme 5b**. These could be of interest in biological imaging as a non-damaging way of introducing an infrared active dye for visualizing cells or metals coordinated in cells. The proof of concept of this exciting result was reported in *Chemical Communications* **2021**, 57, 2551-2554. (https://doi.org/10.1039/D0CC08128K) and from this work a new project was submitted to the National Science Foundation and funded there. Further work in this project will be further alterint the ligand to make it water soluble for applications, to allow for a more stable supramolecular structure and to further tune the emissions for improved utility.

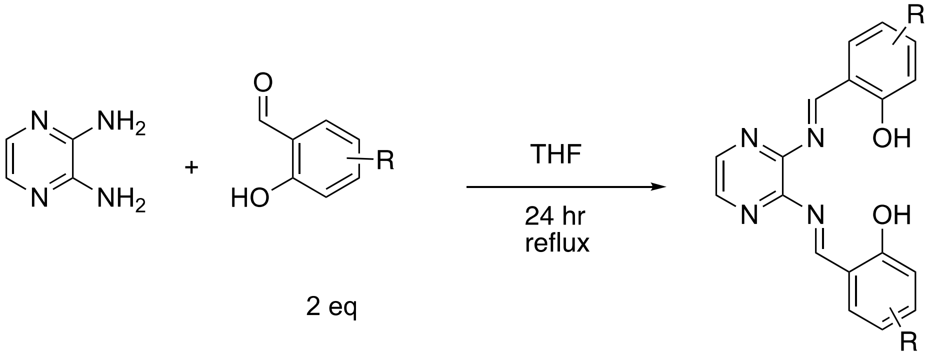


***Scheme** 4.a. Cyano-Naphthylsalophen Metal Complex Synthesis and **b.** Er(III)CN-Naphthylsalophen metal Coordination complex*



***Scheme 5**. a) mixed metal complex laser power dependence; b) quadratic dependence of the emission intensity (I) on the laser power (P)*

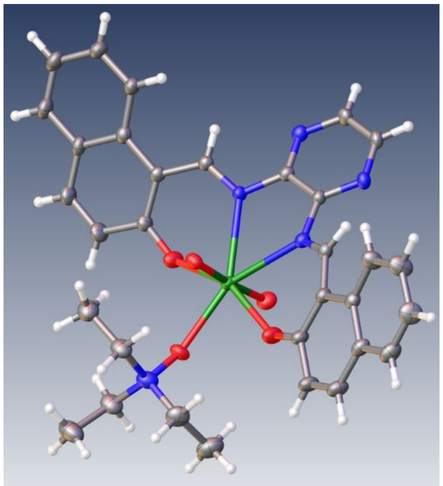
4) **NAPHTHYLPYRASAL** A new ligand naphthylpyrasal was developed- similar to naphthylsalophen except incorporating a heterocyclic diamine backbone. A series of pyrasal salophen ligands was synthesized from the condensation reaction of 2,3-diaminopyrazine with salicylaldehyde, 2-hydroxynaphthaldehyde, and 4-diethylaminosalicylaldehyde. (**See Scheme 6 below**.). This ligand was believed to be of interest as the pyrasal ligands are more electron withdrawing due to the pyrazine ring in the backbone, consequently reducing the nitrogen atom electron density available for bonding with a metal center. Direct comparisons can be made between the naphthylsalophen (1,1-((1E,1E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(na-phthalen-2-ol) and naphthylpyrasal (1,1'-((1E,1'E)-(pyrazine-2,3-diylbis(azaneylylidene))bis(methaneylylidene))bis(naphthalen-2-ol)) ligand to examine the efficacy of this ligand to better stabilize a metal complex, modify the outer coordination sphere, and characterize ligand effects on the coordination sphere. This was done with complexes prepared of uranyl (UO$_2^{2+}$) pyrasal as well as the Th(IV) and Ce(IV) complexes.



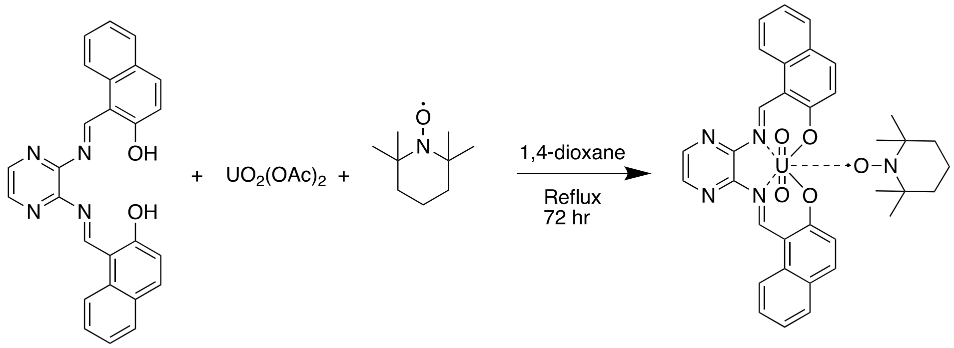
***Scheme 6** Naphthylpyrasal synthesis*

The uranyl (UO$_2^{2+}$) naphthylpyrasal complex can be prepared with the reaction of pyrazine diamine and the desired salicylaldehyde or naphthaldehyde and then templating the complex with uranyl acetate or uranyl nitrate. The ligands can also be prepared as the free ligand refluxing the pyrazine diamine and salicylaldehyde for roughly 24 hours in THF. Crystals suitable for x-ray diffraction were grown from two different solvent systems, 1,4-dioxane with slow diffusion of pentane as well as DCM with slow diffusion of hexanes. The crystals grown from the 1,4-dioxane with slow diffusion of pentane yielded deep red crystals; a structure derived from this can be seen in Scheme 7. The resulting uranyl metal complex was characterized by UV-Vis, IR, NMR, and X-ray single crystal diffraction. On further examination of the structure, it was observed that the ligand is extremely distorted from planarity. This appears to be due to the electron withdrawing nature of the pyrazine backbone and not to accommodate the uranyl metal center or from effects of the crystal packing. We also observed the formation of a coordinated N-oxide substituent. The U-ON-oxide Bond length is 2.328 Å.

The majority of papers concerning N-Oxide donors deals primarily with transition metals such as Mn (II), Zn (II), Cu (I & II), V (V), Pd (II), Rh (II), and Os (III). A survey of the literature yielded only two comparable featuring actinides and N-Oxide donors. (Pool et. al. *J. Am. Chem. Soc.* **2005**, *127* (5), 1338) and a paper by Yahia and Maron (*Organometallics* **2009**, *28* (3), 672–679. https://doi.org/10.1021/om800943a) that computationally examines the reactivity of Th (IV) and U (IV) complexes . As seen in **Scheme 7** below, the U(VI) complex forms pentagonal bipyramidal binding geometry for the uranyl metal center - a triethylamine-n-oxide unit occupies the fifth site. This would be one of 2 reported n-oxide coordination to uranyl; it i unique due to the fact it is an alkyl n-oxide and not a pyridine n-oxide. The O-M bond is 2.337Å is slightly shorter than the previously reported N-oxide bond length of 2.361Å. This may be an opportunity to compare the steric and electronic effects of N-oxide UO_2 complexes which should be interesting electrochemically. We have observed N-oxide actinide complex though selection of crystallization conditions, and this may also be due to the natural formation of peroxides from air during the crystallization of the metal complex. This could present new means to study low valent uranium complexes. This could be an interesting means to study single molecule formation or stabilization of uranium peroxo complexes and should be investigated further. Further experimentation will need to be conducted under inert atmosphere to further corroborate these finding. Also, a more suitable solvent will need to be used to further refine the electrochemical characterization that does not further hinder solubility.

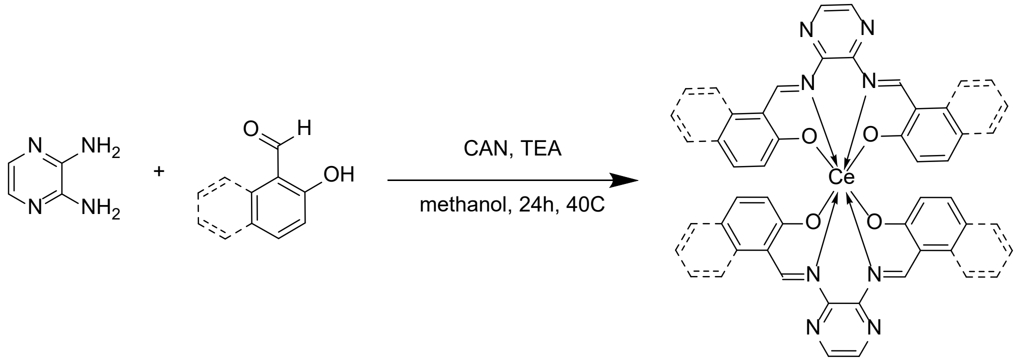


Scheme 7. *X-ray diffraction data of Naphthylpyrasal-UO2 N-oxide structure*



Scheme 8. *Naphthylpyrasal-UO_2-TEMPO Reaction*

Previously, naphthylsalophen complexes with Ce(IV) and Th(IV) were reported demonstrating the expected 8-coordinate sandwich M1L2 complex with square anti-prism coordination geometry (*Chemical Communications* **2017** 53, 11984-11987. (DOI: 10.1039/C7CC06868A). This was not unexpected considering previous work by our group and others. For comparison, upon metalation with cerium (IV), the resultant pyrasal complexes were found to feature sandwich type structures and feature two oxygen and two nitrogen coordination environments to form eight-coordinate square antiprism, bicapped trigonal prismatic, and unusual ten-coordinate bicapped square antiprismatic geometries.

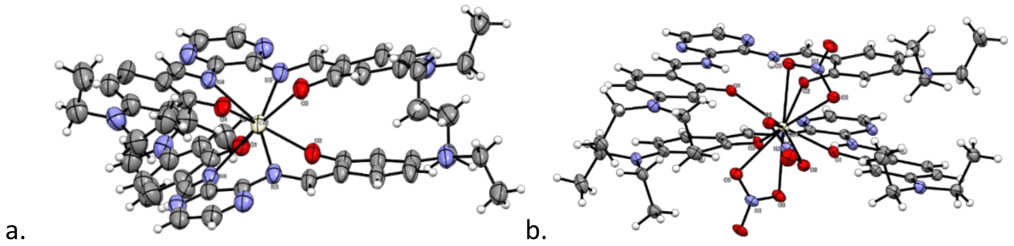


$Ce(L1)_2$ and $Ce(L2)_2$

Scheme 9. Synthesis of Pyrasal Complex 1 (salicylaldehyde, **$Ce(L1)_2$**) and Complex 2 (2-hydroxynaphthaldehyde, **$Ce(L2)_2$**).

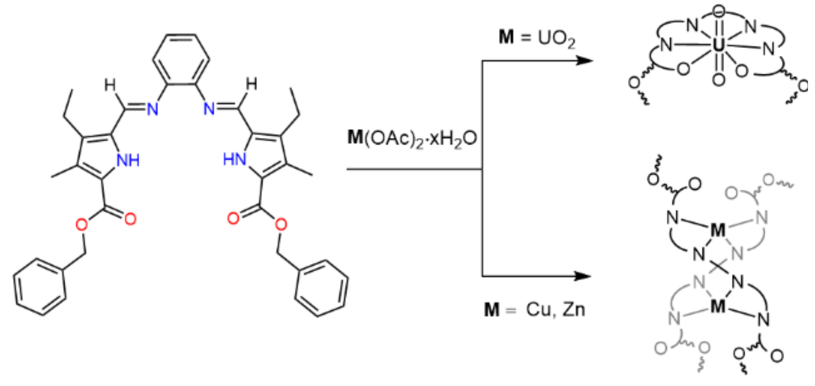
The formation of the resulting geometries was shown to be dependent upon reaction pH, temperature, and availability of appropriate counterions. In this work, we have further extended the ONNO tetradentate coordination geometry via the incorporation of 2,3-diaminopyrazine into the aromatic backbone resulting in a series of differently substituted “pyrasal” Schiff base type ligands upon condensation with substituted salicylaldehydes. Judicious choice of cerium (III) salts, specifically the counter ion, directly affected the coordination geometry of the complexes formed with salophen ligands, but 8-coordinate complexes were still obtained. Through the comparison of the reactivity of CAN with cerium (III) nitrate hexahydrate in the formation of complexes under acidic, neutral, and basic conditions one can elucidate the different reactivity of the species. We sought to understand the species present under different reaction conditions in the solid and in solution through characterization by UV-Vis, NMR, and X-ray crystallography.

When the ligand complexes with cerium as Ce(IV) a red shift can be seen in the UV-Vis that is consistent with other observations of cerium reactions that is a single electron charge transfer. It can also be seen in the UV-Vis that the addition of cerium (III) in air and oxygen free conditions shows a different reactivity under neutral conditions than cerium (IV), but after base is added, cerium (III) can be observed to be autoxidizing to cerium (IV). Under acidic conditions, the reaction is entirely quenched, and no complex at all is formed. The introduction of Th(IV) results in the comparable sandwich structure with little change in the UV-Vis. Further work will look at if this can be used to distinguish or quantify individual lanthanides in solution. The Ce(IV) complex description has been submitted to *Inorganic Chemistry,* and a paper detailing the Th(IV) complexes is in preparation.



Scheme 10. Single Crystal XRD structures of a) Ce(IV)(diaminopyrasal), and b) an unusual 10-coordinate Ce(IV)-(diaminopyrasal)$_2$(NO$_3$)$_2$. Thermal ellipsoids are drawn at the 50% level.

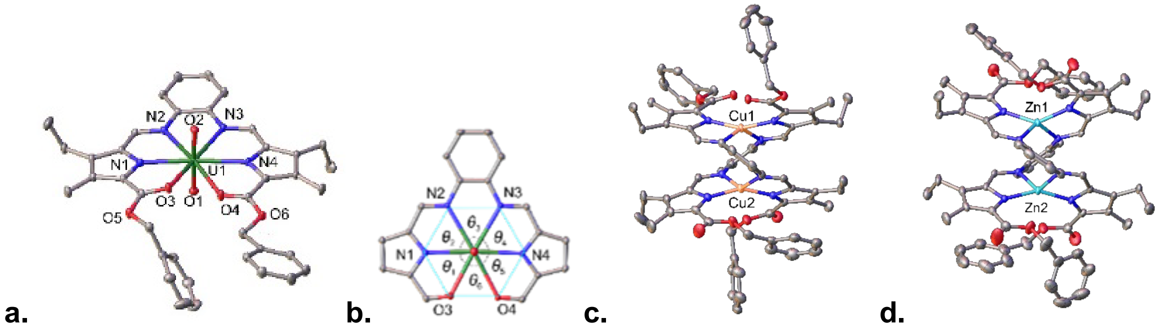
5) PYRROPHEN



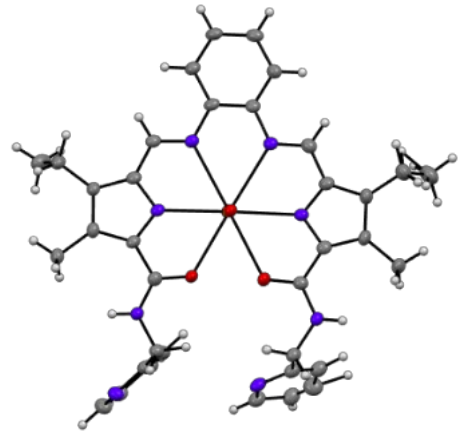
Scheme 11. Coordination modes of pyrrophen.

The synthetic accessibility and potential for modularity of salen-type Schiff base ligands have made them attractive targets for use in separations applications; however, their affinity for many different cations often precludes them from use when selectivity is required. Recently, we have employed a new class of ligands utilizing an imine condensation synthetic methodology but replaces the salicylaldehyde with a pyrrol-2-yl analogue. We prepared two benzyl ester derivatives of a previously reported ethyl ester bis(pyrrole)phenylenediamine ligand which we have nicknamed “pyrrophen.” As this system is macroacyclic, it presents a unique opportunity to explore the bridging of the salen-type and extended porphyrin-type systems as it effectively coordinates the uranyl cation while utilizing a softer donor to allow for increased discrimination between metal ions.

This pyrrophen ligand and its derivatives have been used to prepare uranyl and transition metal complexes. We have reported these and described the features that make this framework particularly suitable for uranyl coordination. Complexation with UO_2^{2+} was found to produce planar hexagonal bipyramidal uranyl complexes, while the Cu^{2+} and Zn^{2+} complexes were found to self-assemble as dinuclear helicate complexes (M_2L_2) under identical conditions. The favorable binding of UO_2^{2+} over Zn^{2+} provides was demonstrated and improved coordination kinetics were found with the addition of an electron donating group to the back of the ligand. Structural features of these complexes were examined paying special attention to features of the UO_2^{2+} coordination environment. The metal complex was found to form a planar hexadentate coordination with the uranyl with near exact 60 degrees for each of the bite angles (See Scheme 12). The ability to tune the ligand by altering the substitution presents opportunities for improved coordination kinetics over macrocyclic species. Remarkably, uranyl displaces the only other metal which gives the most similarly colored complex, meaning that the combination of binding preference and colorimetric



Scheme 12. Structure of **UO$_2$-pyrrophen** (**a**) and (**b**) view down the O=U=O units (**c**) Structure of **Cu$_2$(L^1)$_2$** and (**d) Zn$_2$(L^1)$_2$** viewed along planes of phenyl spacers. Thermal ellipsoids are drawn at the 50% level. Hydrogen atoms removed for clarity.



Scheme 12: Structure of ***UO_2*-Pyrropyridine** complex. Thermal ellipsoids are drawn at the 50% level.

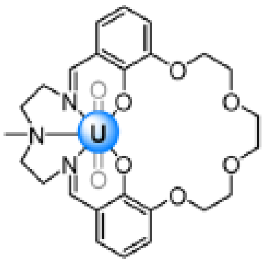
or spectroscopic response allows for identification of uranyl in solution. This ligand and its complexes provide insight into the potential of these soft donor macroacyclic systems as suitable candidates for selective uranyl recognition or extraction by taking advantage of the more covalent f-orbitals of uranyl .The characterization, X-ray structure, selectivity, and solution behavior of the uranyl complexes were reported in *Inorganic Chemistry.* (Mayhugh, J. T.; Niklas, J.E.; Forbes, M. G.; Gorden, J.D. ; Gorden, Anne E.V. "Pyrrophens: Pyrrole-Based Hexadentate Ligands Tailor-Made for Uranyl Coordination and Molecular Recognition," *Inorganic Chemistry* **2020**, 59, 14, 9560–9568. (https://doi.org/10.1021/acs.inorgchem.0c00439) The further characterization of Zn complexes and a para-pyrrophen Zn structure were reported in *Inorganica Chemica Acta* (Niklas, J.E.; Hiti, E. A.; Wilkinson, G. R.; Mayhugh, J. Y.; Gorden, J. D.; Gorden, A. E. V. "Steric control of mesocate and helicate formation: Bulky pyrrol-2-yl Schiff base complexes of Zn2+," *Inorganica Chemica Acta*, **2022**, 529. https://doi.org/10.1016/j.ica.2021.120653)

The ability to tune the ligand by altering the substitution presents opportunities for further improved coordination kinetics over those of macrocyclic species, and for improved binding with uranyl versus other metals. In continuing this project, we have looked at the preparation of thorium complexes with the ortho, meta and para-pyrrophen ligands. While the solution interactions demonstrate notable changes in the UV-Vis that are indicative of metal binding. No Th(IV) complexes have been isolated with crystals suitable for characterization by single crystal X-ray diffraction.

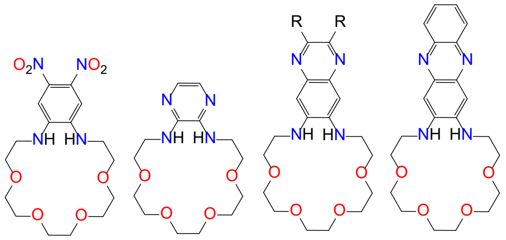
In our ongoing work, we have investigated how changes to the benzene portion of the ligand affect coordination of the UO_2^{2+} metal ion and the UO_2^{2+} binding pocket. It was found that adding electron donating groups increased the rate of metal complex formation while the addition of electron withdrawing groups altered the symmetry of the pocket and made it somewhat more selective. This work is in preparation for publication. Also in new work, it is proposed to further expand the binding pocket accessible to UO_2^{2+} and increase selectivity through the exchange of the benzyl ester arm with an α-picolyl ester arm. (**See Scheme 12**.) The α-picolyl ester arm offers potential extension of the binding pocket or an additional outer coordination mode. This pyridine has been shown by others in the literature to selectively bind to uranyl in solution and demonstrate distinct emission properties in the UV-Vis. A one-armed version of this ligand and its uranyl complex have also been prepared. The expansion of the binding pocket still enables reactivity towards transition metals like zinc. Exploring the synthetic methods, subsequent x-ray characterization, and emission properties of these metal complexes will provide us with greater fundamental knowledge on how changing the electronic nature of the ligand affects its bonding to the metal, ultimately providing us with more in-depth knowledge on ligand design and further increase coordination to the metal and spectrochemical responses.

6) Redox Active Heterocycle functionalize crownether ligands

In parallel to our existing pyrrrophen redox active ligand project, within this same theme of exploring selectivity and increased detection through redox active ligands is our aza crown project. Simple crown ethers have been explored for potential use in extractions, because they can be made more selective using specific cavities for ion size exclusion for specific metal ions. This has limits as size exclusion is not highly selective in most cases. The incorporation of aza subsituents has been shown as one means to enhance binding capabilities of receptors, by altering the mode of coordination and hard/soft donor interest, and this in turn provide selective binding to uranyl through its smaller aza substituted cavity while lanthanides have shown greater preference for the ether cavities. Recently, Blakemoore and co-workers have reported heteroditopic marcocycles incorporating smaller schiff base-aza cavities to larger ether crown sites. These frameworks enable electronic tuning by holding UO_2^{2+} in close proximity to redox inactive metals. . They oberserved uranyls preferential binding to the Schiff base (O-N-N-O) cavity while the Lewis acidic metal is encorporated into the crown cavity. (A. Kumar, D. Lionetti, V. W. Day, J. D. Blakemore. Journal of the American Chemical Society. 2020, 142, (6) 3032–3041.)



Scheme 13. Ditopic UO_2^{2+} crown ether type complex as prepared by Blakemore and Co-workers.

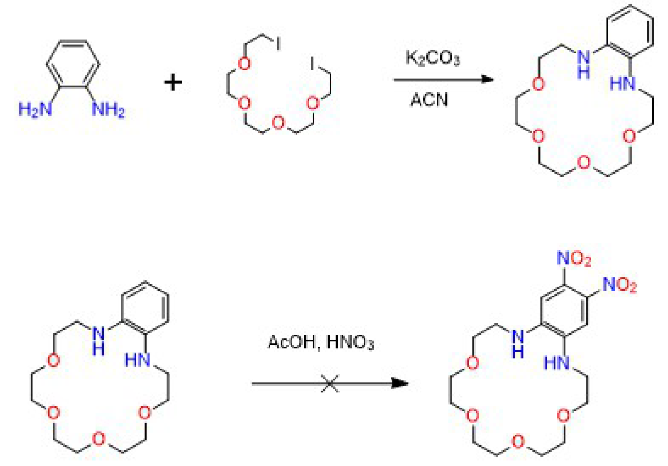


Scheme 14: dinitrobenzene, pyrazine, quinoxaline, and phenazine functionalized crown ethers

For this new effort, it was thought that the incorporation aromatic heterocyclic substituents into the crown ether ring may further enhance the selectivity of coordination and increase the emission or fluorescence capabilities of ligands. Such a difference in the ligand could make it easier to differentiate between uranyl and other +2 transition metal ions in solution This could take advantage in the flexible nature of ether chains for coordinatoin and but provided a distinction in coordination due to the softer donor aza substituent groups. The extiniction coefficeints and stronger emission or fluoresent properties should result from the integrated aromatic groups. Examples of proposed ligands are shown in Scheme 14. This raises the question, if electron rich aromatic functionalized systems are in direct contact with uranium atoms via aza substiteunts, will it provide selective binding to uranyl ions, and will it allow for a distinct observation and characterization via UV-Vis spectroscopy?

Originally, it was attempted to synthesize the aza-crown by following a previously reported benzo-aza crown synthetic method with some adjustments, condensing pentaethylene glychol diodide with ortho phenylenediamine using potassium carbonate in acetonitrile.(A. I. Vedernikov; Yu. A. Strelenko; L. G. Kuz'mina; J. A. K. Howard; N. A. Kurchavov ;S. N. Dmitrieva; S. P. Gromov. Russian Chemical Bulletin. 2009, 58 (5), 978-1001.) Attempts in preparation of the crown with the ditosylated glychol led to a partially condensed side product which was very dificult to purify.The second issue we encountered was the nitration of the phenyl group. Unfortunately, the amines tended to react again and cyclize into an imidazole functionalized crown after the first nitration.

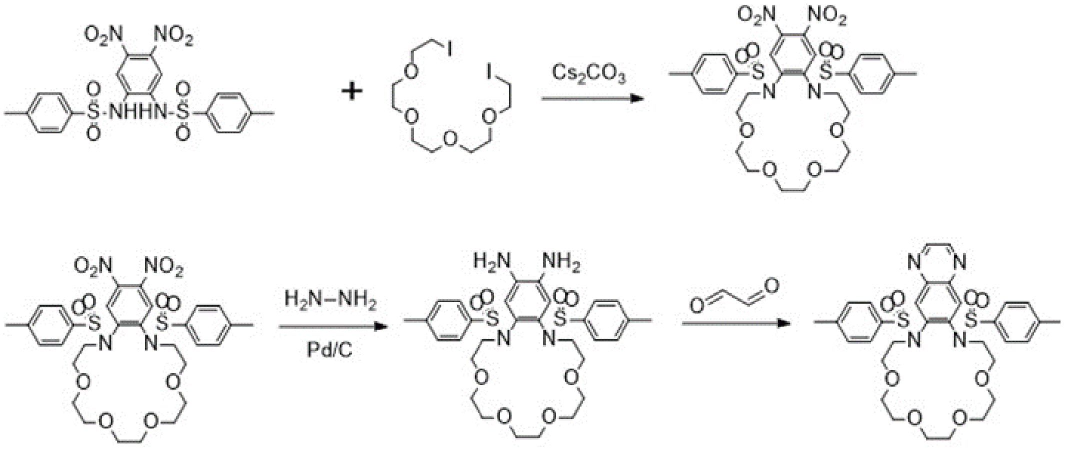
In order to prevent this second cyclization from occurring, it was determined that the best method of prevention was to protect the amine using para-toluenesulfonyl groups. (See Scheme 16 below.) Although the sulfonyl groups solved the issue of intermolecular cyclization, purity of product was again a problem. Therefore, at the exchange of a greater yield for improved stability



Scheme 15 Original synthesis of the dinitro aza 18-Crown-6

and ease of purity, it was decided to use the nitrated form of N,N'-ditosyl-1,2-benzenediamine followed by a condensation with cesium carbonate in acetonitrile. This was then followed by the reduction of the nitro groups to the amines and subsequent condensation of the amines with glyoxal to form the second ring. The final synthetic step to conclude synthesis of the aza-crown to make the quinoxaline crown is to deprotect the crown ether from the tosylates. Now, with this method developed, we can modify this reaction to make additional new ligands and investigate if changing the heterocycle in the backbone changes emission or fluorescence properties.

With this initial crown in hand, the next goals for this project will be to prepare metal complexes and obtain crystal structures of the crown after chelation to the UO_2^{2+} and for comparasion, Cu^{2+} . Crystal structures of the protected and deprotected versions of the crown will be collected to compare the coordination of the uranyl in the solid state coordination environment to the computational models. Spectrofluorometric studies will be conducted to examine distinctive fluorescent responses for uranyl and copper, this will enable us to examine the influence or electronic effect of the heterocyclic quinoxaline on the metal. Altering the ligand backbone may be affected by solubility, but this will allow us to see if increasing the conjugation or modifying the heterocycle can be used to increase the signal to noise observed in emission on coordination with metals. Finally, we will conduct UV-Vis titrations in the presence of inorganic ions to examine the binding capabilities of the crown and determine the metal complex formation constants.

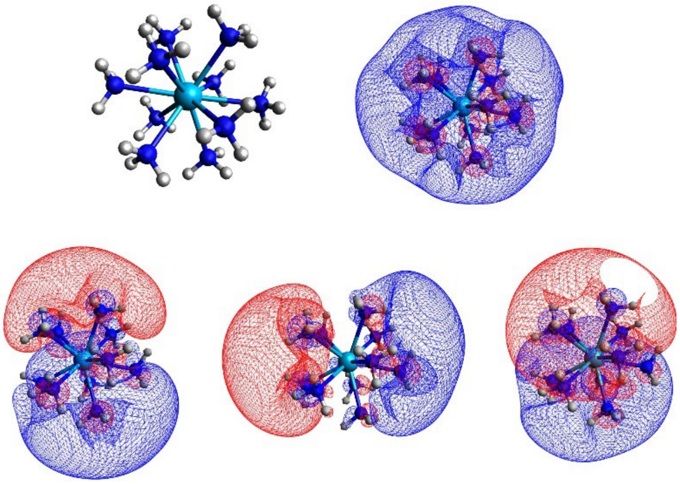


Scheme 16 New synthetic method towards quinoxaline backboned 18-Crown-6

7) **Electrides vs. expanded metals made of molecular thorium complexes**

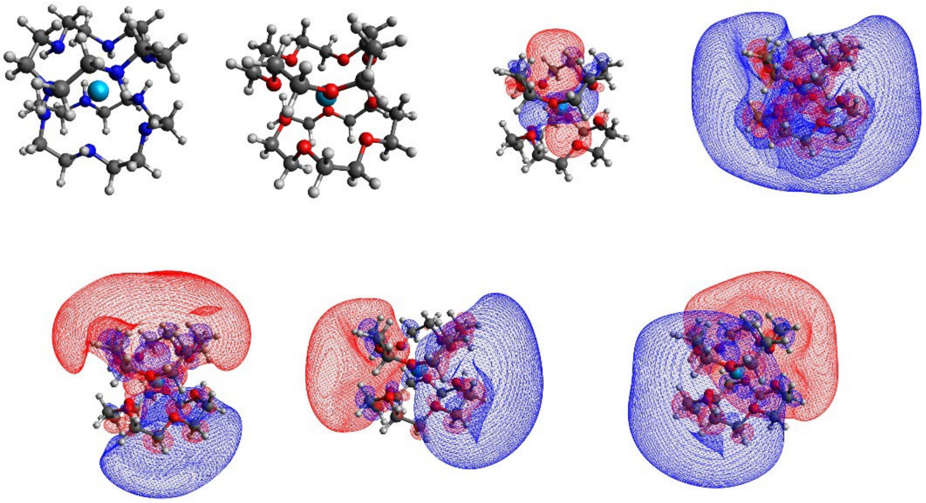
Electrides are solids that contain trapped electrons in their cavities or pores. Numerous systems have been identified in the literature and classified as organic or inorganic (I. R. Ariyarathna and E. Miliordos, Physical Chemistry Chemical Physics 2021, 23, 20298-20306). Organic electrides are commonly composed of an alkali metal coordinated by crown ethers or cryptands (10. M. Y. Redko, J. E. Jackson, R. H. Huang and J. L. Dye, J. Am. Chem. Soc. 2005, 127, 12416–12422). The valence electron of the metal is displaced to the periphery of a complex. A cluster of such species create a grid of metal complexes and free electrons occupying the space among the complexes.

Expanded metals are similar systems but the metals are coordinated by ammonia ligands. These complexes are called solvated electron precursors. Ammonia is known to solvated electrons. Our group has studied numerous such systems considering alkali, alkaline-earth and transition metals (see 11. B. Jackson and E. Miliordos, Journal of Chemical Physics 2022, 156, 194302 and references therein). We showed that more than one electron per complex can be delocalized in the latter two cases. This will affect the electronic properties of the corresponding expanded metal materials. Within this proposal, we studied the first f-block SEP, and specifically Th. We showed that Th can coordinate ten ammonia ligands and displace all four valence electrons. This is the largest number of delocalized/diffuse electrons. These electrons occupy hydrogenic orbitals with a configuration s^{2}p^2 (see Scheme 17).



Scheme 17 *Contours of the orbitals occupied by the diffuse outer electrons of* $Th(NH_3)_{10}$ *complex.*

In addition, we decided to explore metal-cyclam (MCy) and metal-crown-ether (MCE) complexes. Cyclams are crown ether rings, but oxygen is substituted by ammonia. Such complexes can bridge the two types of materials (electrides and expanded metals). We considered MCy/MCE with four and five N atoms. We show that MCy/MCE



Scheme 18 *Contours of the orbitals occupied by the diffuse outer electrons of* $Th(15C5)_2$ *crown-ether and cyclam complexes.*

can indeed displace Th electrons in the periphery, but only two out of the four. The first two occupy a Th-dz^2-type orbital residing in the interstitial space at the center of the crowns and in-between the crowns. Overall, we have a Th^{2+} center and two electrons in one of the same outer orbitals as in $Th(NH_3)_{10}$ (see Scheme 18).

This observation renders the electronic structures of metal ammonia and MCy/MCE complexes very distinct. This will affect the band structure of the corresponding materials (electrides vs. expanded metals). We are currently finalizing the calculations on the geometric features of the ground states and are exploring low-lying excited electronic states of these species. Periodic DFT calculations for a “polymeric” $Th(NH_3)_{10}$ and Th-MCy/MCE material are under way.

PUBLICATIONS DETAIL

1. **Thesis/Dissertation**: Redox-Active α-Diimines and Novel Schiff Base Ligands for Uranium Coordination Chemistry
   Author(s): Julie Elizabeth Niklas
   Institution: Auburn University
   Completion Date: 05/08/2020
   Acknowledgement of DOE Support: Yes

2. **Thesis/Dissertation**: Copper(II) 2- Quinoxalinol Salen Type Ligands as Catalysts for C-H oxidation
   Author(s): Clayton C. Black
   Institution: Auburn University
   Completion Date: 05/08/2020
   Acknowledgement of DOE Support: No

3. **Thesis/Dissertation**: The effects of extended conjugation and ligand electronics on Schiff base uranyl complexes
   Author(s): Katherine Hunter
   Institution: Auburn University
   Completion Date: 05/08/2020
   Acknowledgement of DOE Support: No

4. **Thesis/Dissertation**: Emission properties of Coordination Complexes: The Impact of Mixed Donors on f-Block Elements
   Author(s): Ethan A. Hiti
   Institution: Auburn University
   Completion Date: 05/08/2021
   Acknowledgement of DOE Support: Yes

5. **Conference Paper/Presentation**: Properties of Naphthylsalophen Triple-Decker Dimetallic Lanthanide (III) Sandwich Complexes
   Conference Name: American Chemical Society Virtual Meeting and Expo
   Conference Location: online due to covid
   Publication Status: presentation
   Conference Date: 08/19/2020
   Author(s): Anne E. V. Gorden
   Acknowledgement of DOE Support: Yes

6. **Conference Paper/Presentation**: Heterocycles and U: Actinide Coordination with Imines
   Conference Name: Welch summer scholars program
   Conference Location: online due to covid
   Publication Status: presentation
   Conference Date: 07/28/2021
   Author(s): Anne E. V. Gorden

Acknowledgement of DOE Support: Yes

7. **Conference Paper/Presentation**: Imidazole and Schiff Based Ligands for Coordination of Uranium (VI) and Copper (II)
   Conference Name: 2021 Southwest Regional American Chemical Society meeting
   Conference Location: Austin, Texas
   Publication Status: invited presentation
   Conference Date: 11/03/2021
   Author(s): Anne E. V. Gorden
   Acknowledgement of DOE Support: Yes

8. **Conference Paper/Presentation**: Metal-Mediated Oxidative Coupling of Ortho-substituted 3,3'-Diaminobenzidine and Applications in the Preparation of new Salophen Ligands for Uranyl (UO22+))
   Conference Name: 2021 Southwest Regional American Chemical Society meeting
   Conference Location: Austin, Texas
   Publication Status: poster presentation
   Conference Date: 11/02/2021
   Author(s): Dylan Gardner, Justin A. Williamson, Anne E. V. Gorden
   Acknowledgement of DOE Support: Yes

9. **Conference Paper/Presentation**: Pyrrophens and Pyrropyridines: Hexadentate Coordination systems for Uranyl UO22+
   Conference Name: 2021 Southeast Regional American Chemical Society meeting
   Conference Location: Birmingham, Alabama
   Publication Status: poster presentation
   Conference Date: 11/11/2021
   Author(s): John Ducilon, Avery Stilley, Anne E. V. Gorden
   Acknowledgement of DOE Support: Yes

10. **Conference Paper/Presentation**: Tailoring Redox Active Ligands for Probing the Reactivity of Actinides
    Conference Name: 2021 Southeast Regional American Chemical Society meeting
    Conference Location: Birmingham, Alabama
    Publication Status: presentation
    Conference Date: 11/12/2021
    Author(s): Anne E. V. Gorden
    Acknowledgement of DOE Support: Yes

11. **Conference Paper/Presentation**: Tailoring Redox Active Ligands for the Actinides
Conference Name: Main Group Chemistry (IOS) Webinar
Conference Location: online
Publication Status: presentation
Conference Date: 11/18/2021
Author(s): Anne E. V. Gorden
Acknowledgement of DOE Support: Yes

12. **Conference Paper/Presentation**: Tailoring Redox Active Ligands for Probing the Reactivity of Actinides
Conference Name: New Horizons in Molecular f-Element Chemistry
Conference Location: online due to covid
Publication Status: presentation
Conference Date: 01/25/2022
Author(s): Anne E. V. Gorden
Acknowledgement of DOE Support: Yes

13. **Conference Paper/Presentation**: Ligands to Probe the Fundamental Properties of the Actinides and Lessons Learned Along the Way
Conference Name: 2022 Spring American Chemical Society Meeting
Conference Location: San Diego, California
Publication Status: presentation
Conference Date: 03/21/2022
Author(s): Anne E. V. Gorden
Acknowledgement of DOE Support: Yes

14. **Conference Paper/Presentation**: Preparation of Cerium and Thorium Pyrasal Salophen Complexes and Single Crystal X-ray Diffraction Structural Analysis
Conference Name: 2022 Inorganic Chemistry Gordon Research Conference
Conference Location: Newport, Rhode Island
Publication Status: poster presentation
Conference Date: June 1, 2022
Author(s): Dylan Gardner, Tessa Hoang, Daniel Unruh, Anne E. V. Gorden
Acknowledgement of DOE Support: Yes

15. **Conference Paper/Presentation**: Pyrrophens: Self-Assembly of Schiff Base Pyrrole Ligand Systems in Uranyl and Transition Metal Complexes
Conference Name: 2022 Inorganic Chemistry Gordon Research Conference
Conference Location: Newport, Rhode Island
Publication Status: poster presentation
Conference Date: June 2, 2022
Author(s): John Ducilon, Avery Stilley, Anne E. V. Gorden
Acknowledgement of DOE Support: Yes

16. **Conference Paper/Presentation**: Pyrrophens: Self-Assembly of Schiff Base Pyrrole Ligand Systems and Steric Tailored Architectures with Uranyl and Transition Metals
Conference Name: 2022 International Symposium of Supramolecular and Macrocyclic Chemistry
Conference Location: Eugene, Oregon
Publication Status: presentation
Conference Date: June 22, 2022
Author(s): John Ducilon, Avery Stilley, Anne E. V. Gorden
Acknowledgement of DOE Support: Yes

17. **Journal Article**: Pyrrophens: Pyrrole-Based Hexadentate Ligands Tailor-Made for Uranyl Coordination and Molecular Recognition
Journal: Inorganic Chemistry
Publication Date: June 26, 2020
Publication Status: published
Volume: 59
First Page Number or eLocation ID: 9560
Issue: 14
Publication Location: Washington, DC
Author(s): Jacob T. Mayhugh, Julie E. Niklas, Madeleine G. Forbes, John D. Gorden, and Anne E. V. Gorden
Publication Identifier Type: link
Publication Identifier: https://doi.org/10.1021/acs.inorgchem.0c00439
Acknowledgement of DOE Support: Yes
Peer Reviewed: Yes

18. **Journal Article**: New up-conversion luminescence in molecular cyano-substituted naphthylsalophen lanthanide(iii) complexes
Journal: Chemical Communications
Publication Date: February 15, 2021
Publication Status: published
Volume: 57
First Page Number or eLocation ID: 2551
Issue: Not Provided
Publication Location: London, England
Author(s): Jorge H. S. K. Monteiro, Ethan A. Hiti, Emily E. Hardy, Grant R. Wilkinson, John D. Gorden, Anne E. V. Gorden, and Ana de Bettencourt-Dias
Publication Identifier Type: link
Publication Identifier: https://doi.org/10.1039/D0CC08128K
Acknowledgement of DOE Support: Yes
Peer Reviewed: Yes

19. **Journal Article**: Comparing Coordination Uranyl (VI) Complexes with 2-(1H-imidazo[4,5-b]phenazin-2-yl)phenol and Derivatives,
Journal: Dalton Transactions
Publication Date: July 23, 2021
Publication Status: published
Volume: 50
First Page Number or Location ID: 11113
Issue: Not Provided
Publication Location: London, England
Author(s): Ethan A. Hiti, Grant R. Wilkinson, Isuru R. Ariyarathna, Charmaine D. Tutson, Emily Hardy, Branson A. Maynard, Evangelos Miliordos, and Anne E. V. Gorden
Publication Identifier Type: link
Publication Identifier: https://doi.org/10.1039/D1DT02359D
Acknowledgement of DOE Support: Yes
Peer Reviewed: Yes

20. **Journal Article**: Steric control of mesocate and helicate formation: Bulky pyrrol-2-yl Schiff base complexes of Zn2
Journal: Inorganica Chemica Acta
Publication Date: January 2022
Publication Status: published
Volume: 529
First Page Number or eLocation ID: 120653
Issue: Not Provided
Publication Location: Amsterdam
Author(s): Julie E. Niklas, Ethan A Hiti, Grant Wilkinson, Jacob. T. Mayhugh, John D.Gorden, and Anne E.V.Gorden
Publication Identifier Type: link
Publication Identifier: https://doi.org/10.1016/j.ica.2021.120653
Acknowledgement of DOE Support: Yes
Peer Reviewed: Yes

PARTICIPANTS DETAIL (2020-2022)

1. **Participant:** Mr. Clayton C Black
   Project Role: Graduate Student (Research Assistant)
   Person Months Worked: 3
   Funding Support (if other than this award): Auburn University and Auburn University Malone-Zallen Award
   Contribution to the Project: Clay Black was a graduate student at Auburn University who started in the program August of 2015. His primary research focus to date has been in ligand synthesis and design. He has been working on modifying the BIAN ligand for improving the synthesis and making modifications to improve solubility and add functionality. He also worked on making a diamine for the synthesis of Schiff bases with various aldehydes starting with a diketone and doing a reductive amination. He developed a new means of formylation for pyrroles. In this period, he also worked on new napthylsalophen ligands, pyrasal ligands, pyrroles, and pyrrophen ligands. He completed his Ph.D. in Spring 2020. He was awarded the 2019 Auburn University Malone-Zallen Award. He is now working for Ecolabs in Houston.
   International Collaboration: No
   International Travel: No

2. **Participant:** Mr. John Ducilon
   Project Role: Graduate Student (Research Assistant)
   Person Months Worked: 12
   Funding Support: Texas Tech University
   Contribution to the Project: : John is a graduate student from University of West Florida who started at Auburn University in 2019. He moved to Texas Tech University in 2020. He was paid by DOE funds summer 2020. He has been the primary researcher on the synthesis and characterization of new pyrrophen ligands as well as crown ligand complexes with phen-BIAN or quinoxaline backbones. He has mentored Madeleine Forbes and Avery Stilley.
   International Collaboration: No
   International Travel: No

3. **Participant:** Madeleine Forbes
   Project Role: Undergraduate Student
   Person Months Worked: 3
   Funding Support: not funded
   Contribution to the Project: : Madeleine Forbes is an undergraduate student majoring in chemistry at Auburn University. She was supported summer 2020 with salary from DOE funds. She started research in the program in January of 2019 and worked with us until the fall of 2020 on the preparation of new ligands and their characterization. She is learning electrochemistry for characterization of solution behavior of metal complexes. She graduated from Auburn University in Spring of 2022. Madeleine is now a graduate student at the University of Florida in nuclear engineering working with Prof. Nathalie Wahl in radiochemistry.
   International Collaboration: No
   International Travel: No

4. **Participant:** Dylan Gardner
   Project Role: Graduate Student (Research Assistant)
   Person Months Worked: 12
   Funding Support: Texas Tech University
   Contribution to the Project: : Dylan is a graduate student who came to start at Texas Tech University in January of 2020 from Tennessee Tech University where she earned her masters degree in analytical chemistry. She has been the primary researcher taking over the project preparaing complexes with lanthanides for comparison. She has served as a mentor for Justin Williamson and Tessa Hoang. She has done all of the X-ray crystallography since the group has moved to TTU.
   International Collaboration: No
   International Travel: No

5. **Participant:** Prof. Anne E. V. Gorden
   Project Role: Co-Investigator
   Person Months Worked: 2
   Funding Support: Texas Tech University
   Contribution to the Project: This report covers work from 2020-2022. The Co-Investigator has been responsible for organizing and identifying the participants, obtaining and setting up equipment, training the students participating in synthetic methods, and coordinating this multifaceted effort. Along the way, guidance is provided in mentoring and in presentation preparation and scientific communications.
   International Collaboration: No
   International Travel: No

6. **Participant:** John P Grundhoefer
   Project Role: Undergraduate Student
   Person Months Worked: 6
   Funding Support: Auburn University - Undergraduate Research Fellowship 2019- 2020
   Contribution to the Project: John "J.P." Grundhoefer was an undergraduate student at Auburn University. He was not supported with salary from DOE. He began working with this research group in the summer of 2017 until he graduated in the spring of 2020 with a major in biochemistry. He has been participating in the project working on the design of new ligand systems. He is now a graduate student in environmental and inorganic chemistry at Louisiana State University with Prof. Matt Chambers.
   International Collaboration: No
   International Travel: No

7. **Participant:** Mr. Ethan Hiti
   Project Role: Graduate Student (Research Assistant)
   Person Months Worked: 12
   Funding Support:
   Contribution to the Project: Ethan Hiti was a graduate student at Auburn University who started in the program August of 2015. His primary research focus to date has been in the preparation of new ligands and metal complexes with thorium and lanthanides for comparison. He has been learning computational methods to help better explain the effects of ligand electronics on the stability and formation of metal complexes. His primary research efforts have been on the imidazole based ligands. He has served as a mentor to J. P. Grundhoefer and Grant Wilkenson. He has also prepared new ligands and lanthanide complexes for comparison. He is now a postdoctoral research associate working at the University of Alabama with Prof. Robin Rogers on lanthanide/actinide separations and ionic liquids.
   International Collaboration: No
   International Travel: No

8. **Participant:** Tessa Hoang
   Project Role: Undergraduate Student
   Person Months Worked: 6
   Funding Support: Texas Tech University - Center for Transformative Undergraduate Research Experiences Fellowship
   Contribution to the Project: Tessa is an undergraduate chemistry major at Texas Tech University. She has been preparing and characterizing complexes with cerium and thorium and characterizing their solution behavior with pH. She has won awards for the most outstanding student in both inorganic chemistry as well as analytical chemistry in 2022.
   International Collaboration: No
   International Travel: No

9. **Participant:** William Matthew Hollingsworth
   Project Role: Graduate Student (Research Assistant)
   Person Months Worked: 3
   Funding Support: Auburn University
   Contribution to the Project: Matt is a graduate student that started at Auburn University in the fall of 2018. He has been working on this project making new salqu ligands and uranyl complexes. He has been learning synthetic methods and analytical characterization for solutions work.
   International Collaboration: No
   International Travel: No

10. **Participant:** Katherine Hunter
    Project Role: Undergraduate Student
    Person Months Worked: 3
    Funding Support: Auburn University - Undergraduate Research Fellowship 2019- 2020
    Contribution to the Project: Katherine Hunter was an undergraduate student in biochemistry at Auburn University. She began working with this research group in the fall of 2017. She has been

working with the preparation and characterization of all of the gbha uranyl complexes as well as solution thermodynamics and electrochemistry. She won the Dean's medal for Chemistry and Biochemistry for 2020. She is now attending graduate school at the University of Michigan. The title of her honor's thesis was "The effects of extended conjugation and ligand electronics on Schiff base uranyl complexes." Here is a link to the website about Katherine and her award as Dean's Medalist. https://www.auburn.edu/cosam/honors-convocation-2020/katherine-hunter/index.htm

International Collaboration: No

International Travel: No

11. **Participant:** Jacob Mayhugh

    Project Role: Undergraduate Student

    Person Months Worked: 1

    Funding Support: Auburn University - Undergraduate Research Fellowship 2019- 2020, University of Oregon

    Contribution to the Project: Jacob Mayhugh was an undergraduate student in chemistry at Auburn University who graduated in May 2019. He was not supported by DOE in the 2018-2019 academic year. He was supported by this project in the summer of 2019. He assisted with the design and synthesis of new ligands for selective identification of uranyl. He graduated and moved to the chemistry program at the University of Oregon. He has continued to participate in following up with publications to which he contributed. He has been helping with calculations and solution thermodynamics.

    International Collaboration: No

    International Travel: No

12. **Participant:** Julie Elizabeth Niklas

    Project Role: Graduate Student (Research Assistant)

    Person Months Worked: 3

    Funding Support: Auburn University and Auburn University Malone-Zallen Fellowship, Georgia Tech University

    Contribution to the Project: Julie Niklas was a graduate student at Auburn University who started in the program August of 2015. Her primary research focus was inorganic complexes and structural characterization. She has been heavily involved in the program from the origin. She did the initial work on the phen-BIAN complexes on which this program is based. She has designed and helped prepare all of the phen-BIAN and gbha uranyl complexes. She has been working on the preparation of lanthanide complexes for comparison. She has been lead on all of the electrochemical characterizations of the metal complexes. She has been doing all of the X-ray diffraction single crystal characterization for the group. She has acted as a mentor to Katherine Hunter and Madeleine Forbes. She completed her Ph.D. in Spring 2020. She has continued working with the group by working on preparing publications from her work. She has had a postdoctoral position with Prof. Pete LaPierre at Georgia Tech University and is now going to be research faculty in that position. She was awarded the Dean's Research award for Graduate students in 2020.

    International Collaboration: No

International Travel: No

13. **Participant:** Avery Stilley
    Project Role: Undergraduate Student
    Person Months Worked: 2
    Funding Support: Texas Tech University
    Contribution to the Project: Avery is an undergraduate student in chemistry at Texas Tech University. He has been working on the synthesis of new pyrrophen ligands.
    International Collaboration: No
    International Travel: No

14. **Participant:** Grant Wilkenson
    Project Role: Undergraduate Student
    Person Months Worked: 3
    Funding Support: not provided
    Contribution to the Project: Grant Wilkenson was an undergraduate student double majoring in chemistry and physics at Auburn University. He will be supported summer 2020 with salary from DOE funds. He started with research in the program in January of 2019. He has focused on the preparation of new ligands and is learning with vanadyl and lathanide complexes for comparison with uranyl. He has also worked on learning computational methods and analysis. He was awarded a 2021 National Science Foundation Graduate Research Fellowship and was named the 2021 Graduation Marshal for the College of Sciences and Mathematics. He is now a graduate student working with Prof. Henry “Pete” LaPierre in lanthanide and actinide chemistry at Georgia Tech.
    International Collaboration: No
    International Travel: No

15. **Participant:** Justin Williamson
    Project Role: Undergraduate Student
    Person Months Worked: 3
    Funding Support: Texas Tech University
    Contribution to the Project: Justin is an undergraduate student and biochemistry major at Texas Tech University. He has been working on the preparation and characterization of uranyl complexes.
    International Collaboration: No
    International Travel: No

16. **Participant:** Isuru Ariyarathna
    Project Role: Graduate Student (Research Associate)
    Person Months Worked: 12
    Funding Support:
    Contribution to the Project: Isuru performed the calculations (geometry optimizations and excited states) for the thorium ammonia complexes. He was able to demonstrate that all four

valence electrons of thorium can be displaced in the periphery of the complex. He became post-doc at the Massachusetts Institute of Technology and now hired by Intel.
International Collaboration: No
International Travel: No

17. **Participant:** Benjamin Jackson
    Project Role: Graduate Student
    Person Months Worked: 3
    Funding Support: Auburn University
    Contribution to the Project: Ben supervised the calculations made by the undergraduate students (Zhongyuan Lu and Jared Stinson). He is also performing periodic DFT calculations to produce the band structures of solid-state thorium ammonia vs. thorium cyclam systems. He is still in our PhD program, but he is currently at the Pacific Northwest National Laboratory as Science Graduate Student Research (SCGSR) awardee. He will stay there for three months with the objective to perform periodic DFT calculations and study the catalytic performance of metal ammonia expanded metals towards the capture and utilization of CO_2.
    International Collaboration: No
    International Travel: No

18. **Participant:** Zhongyaun Lu
    Project Role: Undergrduate Student
    Person Months Worked: 5
    Funding Support: not provided
    Contribution to the Project: Zhongyuan performed the calculations (geometry optimizations and excited states) for the thorium-crown ether complexes under the supervision of Benjamin Jackson. He is currently looking for a Ph.D. program.
    International Collaboration: No
    International Travel: No

19. **Participant:** Jared Stinson
    Project Role: Undergraduate Student
    Person Months Worked: 5
    Funding Support: not provided
    Contribution to the Project: Jared performed the calculations (geometry optimizations and excited states) for the thorium-cyclam complexes under the supervision of Benjamin Jackson. He is currently looking for a Ph.D. program.
    International Collaboration: No
    International Travel: No

20. **Participant:** Holden Paz
    Project Role: Graduate Student (Research Assistant)
    Person Months Worked: 6
    Funding Support:

Contribution to the Project: Holden performed some calculations on the crown ether complexes of Project 2. The PI is working on the completion of these calculations. Holden graduated with a Master's degree and is looking currently for a Ph.D. program.
International Collaboration: No
International Travel: No

21. **Participant:** Evangelos Miliordos
Project Role: PI
Person Months Worked: 3
Funding Support:
Contribution to the Project: The PI has been responsible for managing the research group, supervising the students, asking guidance from the Co-Investigator (Anne Gorden), writing/editing reports/journal articles and presenting the results to meetings and conferences.
International Collaboration: No
International Travel: No

OTHER COLLABORATORS DETAIL

1. **Description of the Contribution**: Professor Byron Farnum of Auburn University helped with identifying needed electrochemistry set up and electrochemical characterization
2. **Description of the Contribution**: Professor John D. Gorden of Texas Tech University helped with students learning X-ray crystallography and structural determination in particular with challenging or solvent inclusion in the matrix of the crystal cell.
3. **Description of the Contribution**: Dr. Daniel Unruh of Texas Tech University helped student with learning X-ray crystallography and structural determination
4. **Description of the Contribution**: Professor Ana DeBettencourt-Dias of University of Nevada-Reno has aided in characterization of the lanthanide complexes for two photon up conversion.
5. **Description of the Contribution**: Professor Jorge H. S. K. Monteiro of California State University – Humboldt, has aided in characterization of the lanthanide complexes for two photon up conversion.