Oral Session 1, 8:30 - 8:45

Organophosphorus Bifunctional Lithium Borate Salts

Case Western Reserve University

Presenter: Emalyn Delgado Rosario (Graduate Student)

Coauthors: John Protasiewicz*

Abstract:

Flame Retardant Ions (FRIONs) are bifunctional lithium borate and phosphate salts which have integrated organophosphorus groups to promote char formation upon combustion. These salts, in turn offer promise as potential safety enhancing additives for electrolyte solutions in lithium-ion batteries. Our group has previously generated and structurally characterized three class of FRIONs, with different variations in structure. These past examples of FRIONs suffered from limited solubility. This presentation will report on recent efforts towards synthesis, spectroscopic and structural characterization of new FRIONs that builds on previously reported salts. Specifically, systematic variations of the P(=O)(OR)2 units on these materials are examined for their impact on the overall structure and solubility of these novel functional materials.

Oral Session 1, 8:45 - 9:00

Synthesis and Reactivity of Xanthene based Heterobimetallic Systems for CO Oxidation

Wayne State University

Presenter: Umesh Kaluarachchige Don (Graduate Student)

Coauthors: Stanislav Groysman*

Abstract:

Molybdenum-copper carbon monoxide dehydrogenase (Mo-Cu CODH) is an aerobic bacterial enzyme that catalyze the oxidation of CO to CO2. The active site of the enzyme contains sulfido-bridged Mo(VI) and Cu(I), low-coordinate Cu(I), and highly nucleophilic [Mo(VI)O2S] fragment. It was suggested that Cu(I) serves as an anchor for CO, while nearby highly nucleophilic Mo-oxo readily attacks it. Structural models with one or two sulfido bridges between Mo(VI) and Cu(I) have been designed before and none was capable of operating as a functional model, particularly coordinating CO. In this study we have designed a new heterodinucleating xanthene-bridged ligand (LH2) featuring two different chelating sites, dipyridylamine for Cu(I) and catecholate for Mo(VI). The reaction of LH2 with [Cu(NCMe)4]+ led to the complex of [Cu(LH2)]+. Cu(I) complexes were characterized by multinuclear NMR spectroscopy, high-resolution mass spectrometry, X-ray crystallography, and DFT calculations. Coordination ability of the Cu(I) site of the complex was confirmed by reacting with different monodentate ligands X (PPh3, Cl−, SCN−, CN−, CNR). In addition, transient reactivity with CO was observed. The reaction of LH2 with molybdate [MoO4]2− led to incorporation of [Mo(VI)O3] at the catecholate position. The reaction of [Cu(LH2)]+ with [MoO4]2− formed the heterodinuclear complex. Both complexes were characterized by multinuclear NMR, UV−vis, and HRMS. Additionally, a unique complex featuring oxo-bridged Mo(VI) and Mo(0) was synthesized using the same ligand platform. This complex constitutes a first example of (1) a stable dinuclear Mo(0)/Mo(VI) complex, and (2) a stable metal-carbonyl nearby highly oxidizing Mo(VI) trioxo fragment.

Oral Session 1, 9:00 - 9:15

A bidentate ligand featuring bifurcated Lewis acids in the second-sphere for substrate capture and activation

Univeristy of Michigan

Presenter: Daniel Beagan (Postdoc)

Coauthors: Nathaniel Szymczak*

Abstract:

The structure and function of many metalloenzymes are dictated by the secondary coordination sphere, but the precise role(s) of the second sphere to facilitate substrate capture, activation, and stabilization of reactive intermediates remain unknown. Non-covalent interactions of the nitrogenase enzyme are required for biological N2 fixation; however, the lack of synthetic models containing tunable secondary sphere environments for systematic structure/function studies creates an inherent gap in our understanding of the second sphere in biological systems. To address this problem, we develop discrete metal-ligand platforms with modular secondary spheres to delineate the role(s) of the second sphere on biologically relevant chemical transformations. To this end, we have synthesized a ligand scaffold amenable to the installation of bifurcated Lewis acidic groups in the second sphere. We experimentally and computationally validated an additive Lewis acidity effect for two second sphere boranes compared to known monoborylated analogues. We will detail the coordination to divalent metal precursors, followed by substrate capture and reactivity. We will address the role(s) of the secondary-sphere groups toward small molecule activation, with a focus on redox transformations of nitrogenous substrates (NxHy). Isolation of secondary sphere stabilized intermediates for nitrogenase-relevant transformations will be described.

Oral Session 1, 9:15 - 9:30

Additive-Free Dehydrogenation of Formic Acid Using an Iron Catalyst

University of Cincinnati

Presenter: Bedraj Pandey Pandey (Graduate Student)

Coauthors: Jeanette A. Krause and Hairong Guan*

Abstract:

Bis(2-diisopropylphosphinophenyl)phosphine (or iPrPPHP) ligated iron complexes, trans-(iPrPPHP)Fe(CO)Cl2, (iPrPPHP)FeH(CO)Cl and cis,anti-(iPrPPHP)Fe(CO)H2 have been synthesized. Among these complexes, cis,anti-(iPrPPHP)Fe(CO)H2 catalyzes additive-free formic acid dehydrogenation to yield dihydrogen and carbon dioxide. Mechanistic study suggests that the cis,anti dihydride complex undergoes protonation with formic acid to form the anti-(iPrPPHP)FeH(CO)(OCHO)•HCO2H complex as an intermediate which spontaneously releases carbon dioxide at ambient temperature to complete the catalytic cycle by reforming the cis,anti dihydride complex.

Oral Session 1, 9:30 - 9:45

Synthesis and Characterization of Intermediate Spin Fe(II)-Carbene Complexes Supported by Pyridine-Dipyrrolidine Ligands

West Virginia University

Presenter: Jose Rodriguez (Graduate Student)

Coauthors: Carsten Milsmann*

Abstract:

Transition-metal carbene complexes are important reactive intermediates in fundamental organometallic chemistry and catalytic applications, including olefin metathesis, cyclopropanation, and C-H functionalization. However, one obstacle for the more wide-spread use of currently available transition-metal carbene complexes is the use of precious metals that cause concerns of increasing synthetic cost and hazardous waste generation. Therefore, there has been a growing interest in utilizing Earth-abundant transition metals such as iron in catalytic transformations with carbene intermediates. Several iron-catalysts using several different ligand systems have been developed but come with their own drawbacks. First, most of the reported isolable iron-carbene species exhibit fully saturated coordination environments or exclusively allow trans-coordination of potential substrates. This is unfavorable for synthetic transformations that require cis-coordination of reagents such as olefin metathesis. A second key issue is the limited structural information about catalytically relevant iron-carbene intermediates that would help give better mechanistic insight into catalytic pathways. In the Milsmann Lab, we have developed and isolated pyridine-dipyrrolidine iron(II) carbene complexes, which have shown catalytic and stoichiometric carbene-group transfer potential. Furthermore, studies by NMR spectroscopy, applied-field 57Fe Mössbauer spectroscopy, X-ray diffraction, and SQUID magnetometry revealed that these isolated iron-carbene complexes exhibit exceptional physical properties, such as uniaxial magnetic anisotropy, due to their unique electronic structure. In this presentation, we will discuss how these unprecedented intermediate-spin iron(II)-carbene complexes can help us understand the importance of the connection between physical characteristics and carbene reactivity.

Oral Session 1, 9:45 - 10:00

Deposition of Magnesium Metal Films using Bis(1,4-di-tert-butyl-1,3-diazadienyl)magnesium Precursor

Wayne State University

Presenter: Nilanka Sirikkathuge (Graduate Student)

Coauthors: Charles Winter*

Abstract:

Deposition of Magnesium Metal Films using Bis(1,4-di-tert-butyl-1,3-diazadienyl)magnesium Precursor Nilanka W. Sirikkathuge, Charles H. Winter* Department of Chemistry, Wayne State University, Detroit, MI 48202 United States Magnesium (Mg) is an abundant, alkaline-earth metal that has potential applications in medicine, aerospace, and the semiconductor industries. Pure Mg metal and its Al, Zn, Cu, Ni, and Zn/Si alloys have gained the attention of the research community due to their low density, high specific strength, and eco-friendliness. High quality films of many metals can be obtained by thermal atomic layer deposition (ALD) through sequential, self-limiting surface reactions. However, there have been no reports of ALD and/or chemical vapor deposition (CVD) processes for Mg metal film deposition. This is attributed to the negative electrochemical potential of Mg (Mg2+ + 2e- ↔ Mg, Eo = -2.372 V) that requires the use of powerful reducing agents as co-reactants during the thermal ALD process. Exploration of novel methods to deposit high quality CVD and/or ALD Mg metal films is crucial for the expansion of the semiconductor industry. Therefore, our work demonstrates a new ALD process to deposit Mg metal films using bis(1,4-di-tert-butyl-1,3-diazadienyl)magnesium (Mg(tBu2DAD)2). The film depositions were based on the decomposition of Mg(tBu2DAD)2 to afford Mg metal.

Oral Session 2, 10:30 - 10:45

Exploring secondary coordination sphere effects in flavodiiron nitric oxide reductase model complexes

University of Michigan

Presenter: Abigail Bracken (Undergraduate Student)

Coauthors: Hai T. Dong, Yu Zong, Michael O. Lengel, Nicolai Lehnert*

Abstract:

Nitric oxide (NO) is a versatile molecule with a wide variety of functions in the human body, with involvement in vasodilation, cell signal transduction, and immune defense. However, some bacteria have developed an enzyme, flavodiiron NO reductase (FNOR), to counteract NO toxicity by reducing nitric oxide to nitrous oxide (N2O). As a result, microbes equipped with FNORs show resistance to the human immune defense. Studying model complexes of the active site can provide insight into the structure and reactivity of the enzyme itself. This work focuses on second sphere coordination (SCS) effects in the FNOR active site, their implementation in synthetic model complexes, and the impact of SCS effects on NO binding and reduction. The ligand 2,6-bis[(bis(2-pyridylmethyl)amino)methyl]-4-methylphenol (BPMP) was appended with tert-butyl amide groups to investigate the role of hydrogen bonding. The resulting ligand was metallated using two equivalents of iron (II) triflate in the presence of different equivalents of acetate as a bridging ligand, to make the corresponding diferrous complexes. The resulting ligand was metallated to form diiron complexes then nitrosylated to form hs-{FeNO}7 diiron complexes, which were characterized by various spectroscopic techniques. X-ray crystallography plays a major role in structural characterization of these complexes prior to and after nitrosylation. This work shows that SCS effects from the ligand can play a pivotal role in NO coordination and N-N coupling for N2O formation. Future research includes the investigation of other diferrous BPMP derivatives to better understand how electronic and steric SCS effects impact the reactivities of these complexes.

Oral Session 2, 10:45 - 11:00

Application of the secondary coordination sphere to enhance the reactivity of bimetallic copper complexes.

The Ohio State University

Presenter: Samantha Carter (Graduate Student)

Coauthors: Dr. Wenjie Tao, Dr. Shiyu Zhang*

Abstract:

Many life-sustaining chemical transformations are catalyzed by enzymes with bimetallic active sites. Synthetic models have been developed to understand how Nature performs these essential reactions. For example, particulate methane monooxygenase (pMMO) is a metalloenzyme found in bacteria that is capable of methane oxidation. There are ongoing debates on the structure of pMMO, however, the only synthetic catalyst that has been shown to reliably perform methane oxidation is based on a copper-exchanged (Cu-ZSM-5), which is a dicopper(II,II) oxo intermediate. Other attempts to synthetically replicate the reactivity observed in these small-molecule models have been unsuccessful. This can be attributed to the inability of most model complexes to replicate the unsymmetric environment commonly found in most bimetallic enzymes. We have synthesized several unsymmetric analogs of the symmetric dicopper μ-oxo, μ-nitrosyl complex [LCu2(μ-O)(μ-NO)]2+, where L = 1,2-bis(di(pyridin-2-yl)methoxy)benzene (Py4DMB). The unsymmetric analogs featured 4-substituted catechol linkers with the substituents R = NO2, tBu, Br, OPh, F, NHMe, NH2, N(CH3)2, N(CH2)4. Each dicopper μ-oxo, μ-nitrosyl complex contains unique environments, which can be estimated by the substituent's Hammett parameters (σmeta or σpara). Electron Paramagnetic Resonance (EPR) of the LCu2(μ-O)(μ-NO)]2+ species reveal a strong correlation between the CuII coupling constant and the HAA rate. The EPR indicates that the species with the fastest HAA rate (R = F), also contains more delocalization between the two Cu sites resulting in a faster HAA rate. The overall enhanced reactivity demonstrates a link between the unsymmetric environment, and the high enzymatic reactivity observed in Nature.

Oral Session 2, 11:00 - 11:15

Probing O2 activation and in vivo metalation of a Mn/Fe oxidase

The Ohio State University

Presenter: Josephine Gan (Graduate Student)

Coauthors: Effie C. Kisgeropoulos, Joseph M. Hazel, Jonathan D. McHenry, Hannah S. Shafaat*

Abstract:

Heterobimetallic Mn/Fe proteins represent a relatively new class of proteins whose reactivity is underexplored. The R2-like ligand binding oxidase (R2lox) is of particular interest because it was found to be upregulated in virulent strains of M. tuberculosis. R2lox catalyzes intramolecular cross-link formation that represents a two-electron oxidation process. As it is the first Mn/Fe protein demonstrated to perform multielectron chemistry, its metal binding preferences and chemistry are of great interest to the bioinorganic community. We investigated the R2lox assembly process across two conditions that model distinct in vivo circumstances. Metalation under aerobic/oxidizing environment gives two dominant Mn/Fe spin-coupled intermediates. A strongly coupled species (I3) formed first, followed by a weakly coupled intermediate (I4) that is primed for substrate addition. Pulsed EPR techniques were able to show isotope effects on the exchange coupling between two metals in I4, which can be reproduced by modulating exchange parameters in spin Hamiltonian simulations. On the other hand, when metalation was performed under anaerobic/reducing environment, followed by exposure to O2, a new species was observed, with distinct spin Hamiltonian parameters. The dependence of accumulated intermediates on experimental environment suggests that the relative abundance of metals and O2 is critical in the activation process and suggests a dynamic role for assembly in vivo. Preliminary data suggests that when expressed in E. coli, R2lox also assembles a Mn/Fe cofactor. The combination of spectroscopic studies with in vivo experiments will lead this project towards a better understanding of the physiological role of R2lox.

Oral Session 2, 11:15 - 11:30

The Effect of Flue Gas Contaminants on Electrochemical Reduction of CO2 to Methyl Formate in a Dual Methanol/Water Electrolysis System

University of Louisville

Presenter: Manu Gautam (Postdoc)

Coauthors: Dillon T. Hofsommer Craig A. Grapperhaus and Joshua M. Spurgeon*

Abstract:

Using renewable energy to drive electrochemical CO2 reduction to value-added products has generated tremendous research interest as a scalable technique that could contribute towards mitigation of the greenhouse effect. Upstream processes for capturing and purifying CO2 require energy and raise the overall cost of the electrolysis process. The direct reduction of post-combustion flue gas into multicarbon products is thus an attractive approach to minimize costs, but typically the sensitivity of the cathode catalyst activity to flue gas contaminants and increased hydrogen evolution rates with diluted CO2 in aqueous electrolyte have been major challenges. Herein, the influence of flue gas feedstock on the electrochemical reduction of CO2 in a novel methyl formate synthesis route has been investigated on a Pb-catalyzed electrode in an acidic methanol catholyte in conjunction with an aqueous anolyte for the promotion of a sustainable water oxidation half-reaction. The presence of flue gas contaminant concentrations of 50 ppm SO2 and 50 ppm NO each had a minimal effect on the total faradaic efficiency of CO2 reduction products, while the inclusion of 4% O2 led to a notable improvement in the partial current density for methyl formate that was attributed to the improved durability of the catalyst surface oxide. Measurements with decreased CO2 concentrations showed a corresponding decline in current density and CO2 reduction faradaic efficiency, which was attributed to CO2 mass transfer limitations to the cathode as a result of the decreased partial pressure. XPS analysis indicated the relative stability of the Pb catalyst surface before and after electrochemical operation during exposure to flue gas components, which further highlighted the promising tolerance of this system for direct flue gas conversion to methyl formate.

Oral Session 2, 11:30 - 11:45

Electrosynthesis of amino acids from biomass-derived α-hydroxyl acids

University of Cincinnati

Presenter: Kaili Yan (Graduate Student)

Coauthors: Morgan L. Huddleston, Brett A. Gerdes and Yujie Sun*

Abstract:

Electrochemical conversion of biomass-derived intermediate compounds to high-value products has emerged as a promising approach in the field of biorefinery. Biomass upgrading allows for the production of chemicals from non-fossil-based carbon sources and capitalization on electricity as a green energy input. Amino acids, as products of biomass upgrading, have received relatively little attention. Pharmaceutical and food industries will benefit from an alternative strategy for the production of amino acids that does not rely on inefficient fermentation processes. The use of renewable biomass resources as starting materials makes this proposed strategy more desirable. Herein, we report an electrochemical approach for the selective oxidation of biomass-derived α-hydroxyl acids to α-keto acids, followed by electrochemical reductive amination to yield amino acids as the final products. Such a strategy takes advantage of both reactions at the anode and cathode and produces amino acids under ambient con- ditions with high energy efficiency. A flow electrolyzer was also successfully employed for the conversion of α-hydroxyl acids to amino acids, highlighting its great potential for large-scale application.

Oral Session 2, 11:45 - 12:00

Translating Catalyst-Polymer Composites to CO2RR Gas Diffusion Electrode (GDE): Identifying and Bridging the Knowledge Gaps

University of Michigan

Presenter: Libo Yao (Postdoc)

Coauthors: Nirala Singh, Charles McCrory*

Abstract:

Electrochemical CO2 reduction reaction (CO2RR) on gas diffusion electrode (GDE) in gas-fed flow reactors with industrial-relevant current densities provides a promising approach for carbon recycling. Developing effective catalyst systems on GDE is critical in achieving such goal. Catalyst-polymer composites was proved to be an effective strategy for catalyst modification. Particularly for molecular catalyst, a coordinating polymer could immobilize metal complexes, mitigate aggregation, modify adsorption energies of reacting species and modulate catalytic microenvironment, which collectively enhances the parent molecule's CO2RR activity. However, the study on catalyst-polymer composites has been primarily confined to liquid-phase, batch platforms. Little effort was put to translate established achievements to a flow system that holds great industrial potential. Therefore, in this study, we demonstrate a case study to probe the knowledge gaps and difficulties in translating catalyst-polymer composites on GDE. We used a poly(4-vinylpyridine)-encapsulated cobalt phthalocyanine (CoPc-P4VP) catalyst-polymer composite, a well-established and active system in batch CO2RR. Opposite to the excellent CO2RR performance it demonstrated in batch system, CoPc-P4VP performed poorly on GDE-based flow cell. We identified that hydrophobicity, an often neglected factor in batch reaction, was critical on GDE. We further identified key knowledge gaps between batch and flow CO2RR reaction systems and provided general considerations for better translation of catalyst-polymer composite on to CO2RR GDE.

Oral Session 3, 2:00 - 2:15

Comparison of physicochemical properties and photodegradation activities among different divalent transition metal tungstate nanoparticles at different calcinated temperatures.

Ball State University

Presenter: Mezbah Hossain (Graduate Student)

Coauthors: Levi Dumpert, Zhihai Li*

Abstract:

Due to various interesting properties (highest melting temperature, high surface area, low sintering temperature etc.), controllable particle size and narrow band gap; divalent metal tungstate nanoparticles (NPs) have been studied in different applications like sensor, microelectronics, solar cell, batteries, drug delivery, catalysis, etc. In this project, four different metal (M = Ni, Co, Cu and Zn) tungstate nanoparticles were synthesized from metal chloride and sodium tungstate salts using coprecipitation technique. These nanoparticles were then calcinated at different temperatures and the resulting materials will be characterized by diffusion reflectance-UV (to measure band gap), transmission electron spectroscopy (TEM, to know particle size), X-ray diffraction (for purity and structural pattern), BET (to get surface area), IR (for functional group), TGA (to get the water loss) analysis. To observe the photocatalytic efficiency, these nanoparticles will also be studied in photodegradation under controlled lighting source with an organic dye molecule, methylene blue. All the experimental data from different samples (four NPs at four temperatures) will be analyzed to discover the annealing effect on particle size, crystallization, and catalytic properties.

Oral Session 3, 2:15 - 2:30

Soft Template Synthesis of Titania using Non-Hydrolytic Sol-Gel Method

University of Toledo

Presenter: Livina Iheme (Graduate Student)

Coauthors: Michal Marszewski*

Abstract:

Soft Template Synthesis of Titania using Non-Hydrolytic Sol-Gel Method Mesoporous metal oxides have attracted more attention in recent years due to their large surface areas, uniform pore size distribution, and unblocked pore structure. Mesoporous materials are widely used in various applications, for example, as semiconductors, catalysts, adsorbents, superconductors, and ceramics. The hydrolytic sol-gel method is a low-temperature technique used for the preparation of mesoporous metal oxides and multicomponent metal oxides. A limitation of hydrolytic sol-gel method arises for mixed metal oxides where individual components show very different hydrolysis rates. In many cases, the issue of different reactivity of different precursors for most transition metal oxides result in loss of morphological control over the final oxide material, leading to the formation of amorphous products. The non-hydrolytic sol-gel process presents an alternative to hydrolytic sol-gel synthesis since it uses organic oxygen-donors like ethers instead of water. The non-hydrolytic sol-gel method offers an excellent route for the preparation of mesoporous metal oxides. In this work, we explored soft-templating strategies for the preparation of mesoporous titania using non-hydrolytic sol-gel method.

Oral Session 3, 2:30 - 2:45

Expanding the Library of Goniopolar Materials

The Ohio State University

Presenter: Andrew Ochs (Graduate Student)

Coauthors: Joshua Goldberger*

Abstract:

Most electronic materials exhibit a single dominant charge carrier type, either holes (p-type) or electrons (n-type), along all crystallographic directions. However, there are a small number of compounds that exhibit simultaneous p-type and n-type conduction behavior along different crystallographic directions. We demonstrate the experimental discovery of three different families of materials with this axis-dependent conduction polarity, or goniopolarity, by identifying a large anisotropy of either the electron and hole effective masses (m*), or both, providing the electron and hole masses dominate along different crystallographic directions. Here, we observe goniopolar behavior in the layered semiconductor system NaSnAs1-xPx and the metallic delafossite PdCrO2 via in-plane and cross-plane thermopower measurements. NaSnAs1-xPx (x = 0.1, 0.2, 0.3) exhibits p-type thermopowers cross-plane and n-type thermopowers in-plane, confirming the first mid-gapped semiconductor system with goniopolar transport. Goniopolar behavior was also observed in PdCrO2 via directional thermopowers. The largest thermopower in PdCrO2 exceeded -80 μV/K, which is very large for a single band metal. PdCrO2 also is the first goniopolar magnetic material, with a antiferromagnetic transition observed at 37.5 K. Overall, this work establishes methods for discovering new goniopolar materials, and offers new systems for studying the interplay of phenomena such as magnetism with goniopolartiy.

Oral Session 3, 2:45 - 3:00

Investigating the Stability of Thermoelectric Composite Interfaces via In Situ Microscopy

University of Kentucky

Presenter: Rose Pham (Graduate Student)

Coauthors: Beth S. Guiton*

Abstract:

The ability to convert between thermal energy and electric energy is what gives thermoelectric materials its great appeal. There have been numerous uses throughout the years that have depended on this thermoelectric phenomenon to either convert heat energy into electric or vice versa. One example of this is of radioisotope thermoelectric generators (RTGs) used for space-bound unmanned missions where solar power is not a viable option for a consistent energy source. With the continued advancements for more efficient thermoelectric materials, it’s imperative to investigate their stability, both in an environment that mimics deep space and possible degradation mechanisms within the RTGs. High-resolution and in situ heating transmission electron microscopy (TEM) were utilized to determine the crystalline and thermal stability of thermoelectric composite interfaces that are used as potential thermoelectric materials in RTGs for next-generation deep space missions. The TEM is used to simulate the environment of deep space as it generates a high-vacuum environment, as well as to characterize and facilitate the real time observations of reactions and/or structural changes through an applied force such as heat or an external change such as oxidation. Understanding the stability and degradation mechanisms of these potential materials will help improve the synthesis and design of materials that will prove to be most effective within these models.

Oral Session 3, 3:00 - 3:15

Connecting Cation Exchange and Metal Deposition Outcomes Via Hume-Rothery Like Design Rules Using Copper Selenide Nanoparticles

University of Pittsburgh

Presenter: Riti Sen (Graduate Student)

Coauthors: Xing Yee Gan, Jill Millstone*

Abstract:

Controlling the solid phases and interfaces in a heterostructure has far reaching implications in both the bulk and at the nanoscale. From bandgap engineering in shelled semiconductor nanocrystals to supported heterogeneous catalysts, nanoscale inorganic interfaces often determine the emergent properties of the resulting structures. However, nanoscale interface engineering via direct synthesis methods is currently a patchwork of methodologies, with limited theoretical framework. Yet, such a framework, like all synthetic efforts, is ultimately necessary for efficient discovery, production, and tuning of nano-heterostructures. In a recent report, our group showed that upon secondary metal addition to colloidal Cu2-xSe nanoparticles, the transformation of the cubic Cu2-xSe lattice will occur via cation exchange reaction when the change in symmetry to the resulting metal selenide phase(s) preserves mutually orthogonal lattice. However, if the new lattice symmetry would be disrupted further, metal deposition is the likely outcome of secondary metal cation addition, forming metal–semiconductor heterostructures. These results suggest a synthesis design rule that relies on an intrinsic property of the material, not the reaction pathway, and indicates that more such factors may be found in other particle and synthetic systems – a potential principle in a broader framework of synthetic design for these structures. To challenge our findings, we use the principles identified in the bimetallic system to create ternary metal chalcogenide particles. Ultimately, our goal is to begin to define the limits to which synthetic design rules, such as those identified for lattice symmetry, can be developed for nanostructure syntheses in general.

Oral Session 3, 3:15 - 3:30

Tri-Cure Hybrid Organo-Silicon Coatings

Bowling Green State University

Presenter: Cory Sims (Graduate Student)

Coauthors: Joseph, C. Furgal*

Abstract:

A tri-cure coating system was developed for the protection of monuments and other building materials. This system utilizes three distinct curing methodologies to undergo a rapid, photo-initiated cure upon exposure to UV light which is quickly followed by a secondary amine-epoxy surface adhesion and sol-gel alkoxysilane crosslinking. The design of the system allows it to be stored as a one-pot system for over one year with repeated usage.

Poster 1

Developing H2 production catalysts by strategic installation of a synthetic cobalt core in protein scaffolds

The Ohio State University

Presenter: Abhishek Saini (Graduate Student)

Coauthors: Hannah S. Shafaat*

Abstract:

Catalytic H2 evolution reaction (HER) from water is considered a vital step in the pursuit of H2-mediated renewable energy infrastructure. The intrinsic instability of metalloenzymes under harsh practical conditions has led to the development of an array of synthetic H2 production catalysts, which rarely match the exceptional enzymatic performance. The omission of the critical protein scaffold enveloping the central metal active site is reckoned as the prime reason for this shortcoming. This surrounding protein motif, known as the outer coordination sphere (OCS), remotely regulates the active site with synchronized electron and proton movement along with structural dynamics. Such an OCS feature has been replicated on the periphery of synthetic metal cores with multifunctional organic molecules that has significantly improved their native catalytic H2 production. This strategy was particularly successful with cobaloxime-based Co-N4 cores that offers O2-tolerant catalytic HER leading to the all-weather-ready catalytic assembly. However, the full potential of artificially designed OCS-decorated cobaloximes has not been realized due to the absence of an authentic protein scaffold. Herein, we have deployed a series of rationally designed Azurin (Az) protein scaffolds to explore their effect on promoting cobalt core-driven HER. Such an Az motif has been regularly utilized in several protein engineering studies and has a well-defined auxiliary coordination sphere. The successful construction of the cobaloxime-Az dyad resulted in a significantly enhanced electrocatalytic HER in aerated water, highlighting the prospects of this bio-inspired catalyst design approach.

Poster 2

A Computational Investigation into Bioinorganic Inverted Ligand Fields

The Ohio State University

Presenter: Adam Jenkins (Postdoc)

Coauthors: Anastasia C. Manesis, Alina Yerbulekova, Effie C. Kisgeropoulos, and Hannah S. Shafaat*

Abstract:

For a sustainable future, pursuing alternate avenues for the generation of the carbon-based products we rely on is of critical import. Nature already provides one solution in the form of metalloenzymes which efficiently activate and upconvert C1 substrates into biomolecules with relevance to energy conservation and biosynthesis. The activity of these metalloenzymes is derived from transition metal cofactors in carefully structured proteins. For example, the Wood-Ljungdahl (WL) pathway evolved as the first primordial metabolism, which utilizes the nickel-based metalloenzymes carbon monoxide dehydrogenase (CODH) and acetyl coenzyme A synthase (ACS) to selectively convert carbon dioxide into carbon monoxide and then couple the resultant carbon monoxide with a methyl group to acetylate coenzyme A (CoA). The development of a molecular level understanding of the catalytic cycle of CODH and ACS has the potential to provide alternate and more sustainable methods for chemical synthesis and energy conservation methods. While we have much to learn from metalloenzymes concerning the undertaking of challenging and important chemistry, they are often difficult to study given the complexity and stability of some of these proteins. An alternative method for developing a fundamental understanding of these catalytic processes is by designing robust models that utilize a bioinorganic scaffold to mimic the active sites of the native metalloenzymes. The Shafaat Lab has developed nickel substituted azurin (NiAz) as a functional model of ACS. Interestingly, the EPR-active, methyl-bound intermediate (S = ½ Ni-CH3 Az) was suggested to have a non-classical electronic structure on the basis of pulsed EPR experiments, where the formal NiIII species was found to be better described as a d9, NiI center bound to a cationic methyl ligand. This highly covalent configuration has been called an “inverted ligand field” (ILF). While observed previously in synthetic complexes, the characterization of the S = ½ Ni-CH3 Az species represented the first example of an ILF in a biochemical system. It was hypothesized that a similar electronic structure may be present in the native ACS enzyme, where it could prevent against degradation of the active species. To probe the electronic structure requirements for ILFs to occur in biological systems, the coordinating cysteine sulfur atom will be replaced with both oxygen and selenocysteine (C112S and C112U). These mutations are expected to perturb the electronic structure of Ni-CH3 Az by modulating the covalency of the Ni-E bond (E = O, S, Se). Density functional theory (DFT) calculations on the series suggested there would be an increase in covalency from C112S to C112 to C112U. The increased covalency for C112U is expected to reinforce the ILF character in S = ½ Ni-CH3 C112U Az. To complement the single-reference DFT calculations and gain higher resolution into the electronic structure of S = ½ Ni-CH3 Az, we have pursued multi-reference methods, including Complete Active Space Self-Consistent Field/N-Electron Valence State Perturbation Theory (CASSCF/NEVPT2) calculations. The mechanistic implications of biologically relevant ILFs will be discussed.

Poster 3

Oxidation of Nonactivated C-H Bonds Using Bioinspired Copper Catalysts

University of Kentucky

Presenter: Alexander Olivelli (Graduate Student)

Coauthors: Levi Wolff, Megan Hwang, Aron Huckaba*

Abstract:

Investigation into the dehydrogenation and oxygenation of nonactivated C-H bonds is of great interest to permit the access of untapped chemical feedstocks. To this end, we look to emulate enzymes found in nature that are known to catalyze the desaturation and hydroxylation of various substrates. Specifically, copper- and iron-centered enzymes are known to exhibit high degrees of selectivity in the oxidation of relatively inert C-H bonds. Here we report the synthesis and characterization of bioinspired copper complexes for the olefination and oxidation of cyclohexane. The novel ligand is based on a tripodal and azole-based cyclohexane scaffold that synthesized in one step, in good yield, and subsequently chelated to a Cu(I) center. Preliminary reactions have revealed the formation of the corresponding alkene, alcohol, and ketone.

Poster 4

Investigating hydrogen bonding interactions between NH-containing systems and bis(NHCs).

Case Western Reserve University

Presenter: Alexander Stone (Graduate Student)

Coauthors: John Protasiewicz*

Abstract:

In previous investigations, our group has observed the versatile bonding of N-Heterocyclic carbene (NHC) compounds like 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene (IPr) when reacting with amine-containing fluorophores such as carbazole/bicarbazole. It was first observed that IPr preferentially forms a hydrogen bond with a carbazole unit. This interaction caused a significant and observable quench in fluorescence. Furthermore, upon dilution of the mixture, fluorescence was observed; hinting that the products dissociate in a more dilute environment and hydrogen bonding is no longer observed. This work, in collaboration with the Streubel group at the University of Bonn, shows our use of their Janus bis(NHC)s. This interesting molecule displays a rigid structure of two NHC molecules bridged together by two heteroatoms, in this case, phosphorus. The addition of the heteroatoms is to establish better chemical diversity and functionality to the overall NHC molecule. The bis(NHC) was studied, and similar reactions were explored utilizing similar diamine-containing fluorophores. Thus, we have observed similar bonding and fluorescence patterns as that of our group's previous investigation.

Poster 5

Rational Design of Ru(II) Polypyridyl Complexes with Extended π-System Ligands to Achieve Long-Lived Triplet Excited States

The Ohio State University

Presenter: Alexia Marques Silva (Graduate Student)

Coauthors: Austin P. Lanquist, Claudia Turro*

Abstract:

The achievement of long-lived excited states in ruthenium(II) polypyridyl complexes is of interest for photoactivated applications, such as photodynamic therapy (PDT) and photochemotherapy (PCT). One strategy to extend the excited state lifetime relies on the development of complexes with a ligand-centered 3ππ* state below the traditional metal-to-ligand charge transfer (3MLCT) excited state. The 1,10-phenanthroline (phen) ligand was synthetically modified to contain aromatic groups in position 2, was then coordinated to a Ru(II) metal center. The series of cis-[Ru(bpy)2(2-R-phen)]2+ where R = H (1), phenyl (2), 2-naphthyl (3), 1-pyrenyl (4) and 3-perylenyl(5)) were synthesized successfully and their photophysical properties characterized. Modification of synthetic methodology resulted in easier purification steps. TD-DFT calculations of complexes 2-4 are consistent with a metal centered highest occupied molecular orbital (HOMO) and a bpy-centered lowest unoccupied molecular orbital (LUMO) in 2-3 and phen-centered LUMO in 4 in the singlet ground state. The emission spectra of 2 and 4 in acetonitrile at 77K result in the energies of the lowest 3MLCT states, exhibit E00¬(1) = 17360 cm-1 and E¬00(2,3) = 16950 cm-1 and E¬00(4) = 16670 cm-1 for 3MLCT. Preliminary DNA intercalation assays shows the appended group as a facilitator for the DNA-Complex interaction by increasing the DNA melting temperature.

Poster 6

Appended Lewis acid-assisted reactivity of small molecules on a group 6 metal TACN complex

University of Michigan

Presenter: Alice Atkins (Graduate Student)

Coauthors: Nathaniel K. Szymczak*

Abstract:

Energy transformations that promote small molecule activation are central to the production of valuable chemical commodities. Specifically, the Fischer-Tropsch process facilitates C-C and C-H bond activations that lead to the generation of valuable hydrocarbon products. Lewis acid additives have been shown to participate in these reactions through enhancing the stability and/or reactivity of a complex. By taking advantage of the reactivity characteristics of Lewis acidic groups, the overall behavior of a small molecule substrate towards various nucleophiles may be modified. This project seeks to understand the potential role(s) that an intramolecular secondary sphere Lewis acidic borane can play regarding the reactivity of a molybdenum or tungsten carbonyl complex bearing a sterically hindered 1,4,7-triazacyclononane ligand. Furthermore, we aim to investigate methods to regulate this reactivity towards small molecule activation with borane Lewis acids of varying Lewis acidity.

Poster 7

Europium(II/III)-containing complexes encapsulated in a per-fluorocarbon nanoemulsion for imaging oxygen using 19F-magnetic resonance imaging.

Wayne State University

Presenter: Andrea Batchev (Graduate Student)

Coauthors: Jacob C. Lutter, Caitlyn J. Ortiz, Alexander G. Sertage, Jonathan Romero, S. A. Amali S. Subasinghe, Steen E. Pedersen, Md. Abul Hassan Samee, Robia G. Paulter, and Matthew J. Allen*

Abstract:

Given the importance of identifying hypoxic vs normoxic conditions in medical diagnosis, there is a need for facile agents that can identify such conditions. So far, there has been significant progress using redox active magnetic resonance imaging (MRI) probes. Agents containing EuII/III have shown promise, but those agents need to be directly injected to sites of interest due to rapid oxidation of EuII to EuIII. To slow the oxidation of EuII, interfaces formed by the perfluorocarbon n-perfluorooctylbromide were employed to protect EuII from oxidation. A perfluorocarbon-soluble ligand was designed and synthesized to enable EuII and EuIII to enter perfluorocarbon solutions. The europium-containing perfluorocarbon solutions were converted into aqueous emulsions with an average particle size of 199 ± 31 nm. MRI experiments on phantoms of mixtures of the emulsions showed that there is an observable difference in the reduced and oxidized form, as well as an apparent buffer to oxidation with respect to the signal difference. Injection into mice revealed that 19F-MRI signal changes between EuII and EuIII emulsions occur over a period of >30 min compared to <5 min for signal loss with a complex injected without emulsion. These results represent a critical step toward the ability to deliver EuII-containing complexes in vivo for the direct study of hypoxia.

Poster 8

Secondary Sphere Hydrogen Bonds Enable Dioxygen Activation at Iron and Allow Observation of Hydroxyl Radical Transfer

University of Michigan

Presenter: Andrew LaDuca (Graduate Student)

Coauthors: Dr. Jessi Wilson, Dr. Nathaniel Szymczak*

Abstract:

Activation of dioxygen (O2) in biological systems is necessary for the incorporation of O-atoms into organic species. Many non-heme iron enzymes capable of O2 reduction rely on secondary sphere hydrogen bond donors to help capture O2 and position substrates for subsequent oxidation, however the roles of the hydrogen bonds donors on O2 binding, activation, and substrate oxidation is not well understood. Our lab has synthesized a 6-substituted TPA (tris-(2-pyridylmethyl)amine)-based Fe complex with secondary sphere aniline groups ([TPANPhFeIIMeCN2]2+) that is capable of activating O2 in DCM to generate an Fe(III)OH. An authentically prepared TPANPhFe(III)OH species made by chemical oxidation of an Fe(II)OH is capable of transferring OH* to Ph3C* through radical recombination to make Ph3COH in 62% yield. This presentation will discuss recent efforts to determine the effect of hydrogen bonds on O2 activation and radical rebound rates.

Poster 9

CoP2N2 complexes for selective dimerization of terminal alkynes

The Ohio State University

Presenter: Andrew Kollar (Graduate Student)

Coauthors: Joshua Prybil, Casey R. Wade*

Abstract:

A series of novel tetradentate P2N2 ligands have been synthesized and used to prepare Co(II) complexes. The new complexes have been characterized by single crystal X-ray diffraction, NMR spectroscopy, and cyclic voltammetry. The new ligand platforms incorporate donor hemilability that can facilitate reactivity in catalytic reactions. Preliminary catalytic studies show that the P2N2-Co complexes catalyze alkyne dimerization with good activity and selectivity.

Poster 10

Pd(II)-Catalyzed gamma-Alkynylation of Allylamines

University of Toledo

Presenter: Ankita Mishra (Graduate Student)

Coauthors: Michael Young*

Abstract:

The rapid diversification of unprotected amines using organometallic approaches remains an outstanding desirable approach to allow access to new drug-like molecules. Using the inherent directing ability of the amine portion of an allylamine, we have discovered that it is possible to install alkynyl groups at the gamma-position of allylamines under Pd catalytic conditions. Topics will include how we optimized the reaction, as well as initial exploration of the substrate scope for the transformation.

Poster 11

Exploration of the magnetic and electronic properties of the novel van der Waals compounds, Mn2Ga2S5 and Mn2In2Se5

The Ohio State University

Presenter: Archibald Williams (Graduate Student)

Coauthors: Joshua Goldberger*

Abstract:

The development of new families of exfoliatable layered van der Waals (vdW) magnetic compounds has attracted considerable interest in recent years. Exploring van der Waals materials of greater complexity in their atomic structures allows for a better understanding of how to design materials to better understand the complex magnetic ordering behavior seen with multiple structural motifs. Here, we explore the magnetic, electronic and exfoliation properties of two novel vdW systems, Mn2Ga2S5 and Mn2In2Se5, built from a double layer of MnCh6 edge sharing octahedra and capped to the vdW gap by TrCh4 tetrahedra. We have synthesized and isolated pure material of both Mn2Ga2S5 and Mn2In2Se5 and have grown single crystals of each phase from Chemical Vapor Transport and flux growth, respectively. Both materials have both been shown have shown to be indirect semiconductors with optical gaps of 1.58 eV for Mn2Ga2S5 and 1.33 eV for Mn2In2Se5. Both materials show signatures of significant frustration and undergo spin freezing transitions to spin glasses at 10K and 8 K for Mn2Ga2S5 and Mn2In2Se5, respectively. Finally, we have shown that these materials can easily be exfoliated to the few layer form.

Poster 12

Increasing the Stability of Monomeric Methylene Diphenyl Diisocyanate (4,4’-MDI) Using N-Heterocyclic Carbene (NHC) Systems

Wayne State University

Presenter: Asanka Dissanayake (Graduate Student)

Coauthors: Thilini S. Hollingsworth, Elizabeth Madarang, Stanislav Groysman*

Abstract:

4,4’-Methylene diphenyl diisocyanate (4,4’-MDI, or monomeric MDI) is an aromatic diisocyanate extensively used in the chemical industry. It commonly serves as a precursor/monomer for the synthesis of polyurethanes. The dimerization of 4,4’-MDI at various temperatures is being considered a major challenge in its industrial use. Therefore, the polyurethane industry attentively seeks solutions that could suppress dimerization of 4,4’-MDI and to extend its shelf-life. In our study, in order to improve the stability of pure 4,4’-MDI, N-heterocyclic carbenes (NHCs) were used. Preliminary results revealed that the reaction of 4,4’-MDI with mononucleating N-substituted NHCs produced respective zwitterionic bis(amidates) in nearly quantitative yields. The resulted adducts were characterized using NMR and IR spectroscopy, mass spectrometry, and X-ray crystallography. We further studied the stability of these zwitterionic bis(amidates) and the release of 4,4’-MDI from the adduct “on-demand”. Adducts are highly stable under air-free conditions in both solid and solution states. These adducts were treated with Cu(I) to form the respective bimetallic complex, and the effect of temperature on the decomposition rate of the complex was examined. The steric/electronic nature of N-substituents and the insertion of sulfur into these metal complexes have a substantial effect on 4,4’-MDI release.

Poster 13

Looking Past the Secondary Sphere: Relating Dynamics to Catalytic Activity in Nickel-Substituted Rubredoxin, a Model Hydrogenase

The Ohio State University

Presenter: Ashlee Wertz (Graduate Student)

Coauthors: Riley E. Stein, Peter J. Moore, Hannah S. Shafaat*

Abstract:

Nature provides inspiration for carbon-neutral approaches to hydrogen gas production. [NiFe] hydrogenases reversibly reduce protons and electrons to hydrogen gas using a tetrathiolate-coordinated, redox-active Ni center. Despite their efficiency, biotechnology applications of [NiFe] hydrogenases are limited, as the protein suffers from oxygen sensitivity and difficulties associated with large-scale heterologous expression. A [NiFe] hydrogenase mimic, Ni-substituted rubredoxin (NiRd), has been developed as a structural and functional protein-based model of the [NiFe] hydrogenase. Prior studies have suggested that protein dynamics play a critical role in modulating catalytic activity, with increased active site and protein backbone flexibility correlated with higher turnover rates. The present work uses genome mining to identify and characterize novel Rd variants to determine whether activity can be correlated to the optimal growth temperature of the parent organism. Through electrochemical and solution-phase studies, each NiRd variant was shown to catalyze hydrogen production, with distinct properties across the variants. Probing the relationship between activity and protein dynamics provides an indication of which elements in the secondary sphere and beyond are a dominant influence on activity.

Poster 14

Efforts to Improve Ruthenium-Catalyzed Guerbet Chemistry

University of Michigan

Presenter: Benjamin Farris (Graduate Student)

Coauthors: Benjamin M. Farris, Alex M. Davies, Corey R. J. Stephenson, Nathaniel K. Szymczak*

Abstract:

Ruthenium (II) bis(pyridylimino)isoindolato complexes catalyze an ethanol upgrading reaction to more valuable n-butanol and heavier alcohols. This overall sequence, called the Guerbet reaction, proceeds through a series of hydrogen borrowing steps, in which ethanol is first dehydrogenated to acetaldehyde, which then undergoes aldol condensation and finally hydrogenation to give n-butanol. This presentation will outline our current efforts to optimize catalyst stability. In situ IR spectroscopy of the Guerbet reaction, coupled with ex situ ESI-MS and NMR, gives insight into catalyst degradation pathways. Combined with DFT calculations, these results are used to understand and predict new improvements to the bpi ligand that ultimately provide longer lived catalysts.

Poster 15

Determining the pka and BDFE of bound substrates on Zr/Co tris(phosphinoamide) heterobimetallc complexes

The Ohio State University

Presenter: Brett Barden (Graduate Student)

Coauthors: Hongtu Zhang, Christine M. Thomas*

Abstract:

The incorporation of two disparate Earth-abundant metals into a single complex has seen a surge in study over the past 15 years. The metal-metal interactions in these complexes help overcome the tendency of first-row metals to perform one-electron processes, enhancing their reactivity without the use of noble metals. A previously reported (THF)ZrIV(MesNPiPr2)3Co-I-CNtBu complex has been shown to react readily to form Zr-bound oxo-, peroxo-, and hydroxo- species through Co-mediated redox processes. These complexes were studied electrochemically to show multiple redox features corresponding to ZrIV/Co-I, ZrIV/Co0, ZrIV/CoI, and ZrIV/CoII states. pka determination of hydroxo-bound Zr/Co0 and Zr/CoI complexes in conjunction with cyclic voltammetry will further fundamental knowledge about the effect of overall charge and pendent metals on the BDFE of bound substrates and, more generally, cooperative proton-coupled-electron-transfer processes in bimetallic complexes.

Poster 16

Enantio- and chemoselective copper-catalyzed reduction of ketones using a disilane as the reductant

Indiana State University

Presenter: Callie Gernand (Undergraduate Student)

Coauthors: Drew Culley, Ryan Van Hoveln*

Abstract:

Reduction reactions remain under-developed compared to their oxidation counterparts. Reduction reactions are hindered by a lack of functional group tolerance when using traditional reducing agents like boron and aluminum hydrides and hydrogen. Unfortunately, most reductions rely on these reducing agents. Hypothetically, catalytic hydrogenations could be rendered selective, but few catalysts have been developed that achieve good selectivity. More recently, hydrosilylations have been developed which adds silanes to a relatively short list of terminal reductants, however, these cannot selectively reduce aldehydes in the presence of similar carbonyl functional groups. Adding enantioselectivity to this problem only exacerbates the challenge. Herein, we report the synthesis and implementation of chiral ligands for the copper-catalyzed selective reduction of ketones in the presence of other readily reducible functional groups. We use a disilane as a terminal reductant, which is an under-utilized terminal reductant. The substrate scope and enantio- and chemoselectivity will be discussed.

Poster 17

Effects of Trace Metal Contamination from the Li-Ion Battery Recycling Process on the Structure and Composition of LiNi0.6Mn0.2Co0.2 (NMC622)

University of Michigan

Presenter: Christopher Woodley (Graduate Student)

Coauthors: Bart Bartlett*

Abstract:

LiNi0.6Mn0.2Co0.2 (NMC622) is currently used as the cathode in many commercial lithium-ion batteries because it delivers high capacity at high potential. In order to recycle batteries when they reach their end of life, the electrochemical effects of contamination from the metals used in cell manufacturing must be understood and minimized. Copper, zinc, magnesium, and aluminum have been doped as their common ions Cu2+, Zn2+, Mg2+, and Al3+ into NMC622 separately by a co-precipitation synthesis method starting from metal sulfate salts. X-ray diffraction (XRD) and X-ray fluorescence (XRF) are applied to characterize the changes in structure and composition. Upon adding Cu2+, Zn2+, or Al3+, the fraction of Ni2+ in NMC622 is reduced, while Zn2+ also reduces the fraction of Co2+. When Mg2+ is added, the fraction of Mn2+ decreases. Furthermore, scanning electron microscopy (SEM) is coupled with the X-ray techniques to show that no new phases emerge, hinting that dopant ions substitute for the original NMC in the octahedral sites of the host R–3m structure.

Poster 18

The Synthesis of PdSe2 Nanomaterials for Goniopolar Photocatalysis

The Ohio State University

Presenter: Cullen Irvine (Graduate Student)

Coauthors: Joshua Goldberger*

Abstract:

Goniopolar materials, single-crystalline materials that exhibit electron conduction along one direction of the crystal and hole conduction along a perpendicular direction, are intriguing candidates for photocatalysis, as the propensity for electrons and holes to move away from each other in these materials will likely improve charge carrier separation and allow for reduction and oxidation reactions to be isolated to separate crystal facets. We have identified orthorhombic PdSe2 (O-PdSe2) as an ideal semiconductor material to explore the connection between goiniopolarity and photocatalysis. DFT calculations and experimental thermopowers have confirmed that hole conduction occurs along the cross-plane direction and electron conduction occurs along the in-plane directions. Here, we establish a general solution-phase synthesis method that can be used to form either the orthorhombic or monoclinic polymorph of PdSe2, as well as control particle shape and size. We also show the influence of different parameters on these properties. Finally, photodeposition reactions show that silver particles can be selectively deposited on the edge facets of O-PdSe2, offering evidence that electrons and holes can be spatially separated to different facets in this material.

Poster 19

A bidentate ligand featuring bifurcated Lewis acids in the second-sphere for substrate capture and activation

University of Michigan

Presenter: Daniel Beagan (Postdoc)

Coauthors: John J. Kiernicki, Matthias Zeller, Nathaniel K. Szymczak*

Abstract:

The structure and function of many metalloenzymes are dictated by the secondary coordination sphere, but the precise role(s) of the second sphere to facilitate substrate capture, activation, and stabilization of reactive intermediates remain unknown. Non-covalent interactions of the nitrogenase enzyme are required for biological N2 fixation; however, the lack of synthetic models containing tunable secondary sphere environments for systematic structure/function studies creates an inherent gap in our understanding of the second sphere in biological systems. To address this problem, we develop discrete metal-ligand platforms with modular secondary spheres to delineate the role(s) of the second sphere on biologically relevant chemical transformations. To this end, we have synthesized a ligand scaffold amenable to the installation of bifurcated Lewis acidic groups in the second sphere. We experimentally and computationally validated an additive Lewis acidity effect for two second sphere boranes compared to known monoborylated analogues. We will detail the coordination to divalent metal precursors, followed by substrate capture and reactivity. We will address the role(s) of the secondary-sphere groups toward small molecule activation, with a focus on redox transformations of nitrogenous substrates (NxHy). Isolation of secondary sphere stabilized intermediates for nitrogenase-relevant transformations will be described.

Poster 20

Design and synthesis of Naphthoquinone-based Redox-active N-Heterocyclic Carbenes (NHCs) for gold (Au) complexation studies.

Wright State University

Presenter: Dilsha Wickramasinghe (Graduate Student)

Coauthors: Kuppuswamy Arumugam*

Abstract:

Recently, our group developed dual-targeting gold(I) complexes containing naphthoquinone moieties for therapeutic applications. As a part of structure activity relationship (SAR) studies we functionalized naphthoquinone and used them for the preparation of N-heterocyclic carbenes. The newly designed NHCs were ligated to iridium to probe their electrochemical properties. Synthesis followed by characterization is achieved by using NMR, mass spectrometry, X-ray diffraction, cyclic voltammetry, and FT-IR spectroscopy.

Poster 21

Enantio- and chemoselective copper-catalyzed reduction of ketones using a disilane as the reductant

Indiana State University

Presenter: Drew Culley (Undergraduate Student)

Coauthors: Callie Gernand, Ryan Van Hoveln*

Abstract:

Reduction reactions remain under-developed compared to their oxidation counterparts. Reduction reactions are hindered by a lack of functional group tolerance when using traditional reducing agents like boron and aluminum hydrides and hydrogen. Unfortunately, most reductions rely on these reducing agents. Hypothetically, catalytic hydrogenations could be rendered selective, but few catalysts have been developed that achieve good selectivity. More recently, hydrosilylations have been developed which adds silanes to a relatively short list of terminal reductants, however, these cannot selectively reduce aldehydes in the presence of similar carbonyl functional groups. Adding enantioselectivity to this problem only exacerbates the challenge. Herein, we report the synthesis and implementation of chiral ligands for the copper-catalyzed selective reduction of ketones in the presence of other readily reducible functional groups. We use a disilane as a terminal reductant, which is an under-utilized terminal reductant. The substrate scope and enantio- and chemoselectivity will be discussed.

Poster 22

Synthesis of Model Systems for Reactive Intermediates in Cytochrome P450nor

University of Michigan

Presenter: Elizabeth Manickas (Graduate Student)

Coauthors: Nicolai Lehnert*

Abstract:

Nitric oxide (NO) is a biologically relevant molecule in mammals and microorganisms. It further plays a vital role in the denitrification pathway of the biogeochemical nitrogen cycle. Bacteria and fungi that use this pathway utilize enzymes to reduce NO to nitrous oxide (N2O). One enzyme in this class is a Cytochrome P450, which are a superfamily of enzymes that can perform versatile reactions, especially oxidative transformations. The specific enzyme of interest, Fungal Cytochrome P450 nitric oxide reductase (Cyt P450nor), is present in soil-dwelling fungi, such as Fusarium oxysporum, and several strains of yeast, such as Trichosporon cutaneum. Cyt P450nor performs NO reduction efficiently with a turnover number of 1200 s-1, making the mechanistic details difficult to study in the enzyme. Synthetic model complexes can be synthesized and studied to elucidate the mechanism of the enzyme and investigate analogs of key intermediates. For these unstable intermediates, a sterically hindered porphyrin, such as the 3,5-methyl-bisaryloxyfence porphyrin, (3,5-Me-BAFP2-), system can be used to stabilize these species for spectroscopic characterization and reactivity studies.

Poster 23

Exploring Oxide Perovskite Derivatives as Potential Hosts for Exotic Spins States

The Ohio State University

Presenter: Emma Pollock (Graduate Student)

Coauthors: Patrick Woodward*

Abstract:

Quantum spin liquids have been a topic of significant scientific interest due to their potential applications in data storage, memory, and quantum computing. The origin of QSL behavior can be derived from geometric and magnetic frustration within the crystal structure. Perovskite-type materials are interesting platforms for studying fundamental structure and magnetic property relationships. Relatively new to the field, vacancy-ordered quadrupole perovskites (VOQP) oxides contain suitable structural intricacies over the traditional perovskite and double perovskite structures. VOQP oxides of the form A4MM’2O12, where M is a magnetic cation and M’ is a nonmagnetic cation, adopt a cubic close-packed stacking of M’ and M centered ordered octahedral perovskite layers that are corner-sharing and contain octahedral vacancies between adjacent M’ centered octahedral layers. This structural layout forms 2D triangular networks of magnetic cations, leading to magnetic frustration. So far, VOQP oxides have only been reported in limited compositions including A4CoRe7+2O12 (A2+ = Sr, Ba), A2La2MM’6+2O12 (A=Sr, Ba; M=Co2+, Ni2+, Mn2+; M’=W6+, Te6+), and Ba3LaCoRe7+W6+O12. Compositions containing Co2+ and Ni2+ exhibit ferromagnetic (FM) ordering, while those containing Mn2+ exhibit antiferromagnetic (AFM) ordering. Despite low frustration factors in these materials, evidence for some competing exchange interactions is found in the low ordering temperatures, which suggest weak overall exchange interactions. This work presents the synthesis, structure, and magnetic properties of three unreported VOQP oxides: Sr2La2NiW2¬O12, Sr3LaCoReWO12, and Sr3LaNiReWO12. By expanding this class of VOQP oxide materials, we can further explore the tuning capabilities of the triangular magnetic network as we search for materials with QSL behavior.

Poster 24

Synthesis, Characterization, and Hydrogen Evolution Activity of Cobalt[Pyridinethiolate N-Oxide]2

University of Michigan

Presenter: Esmee DenOtter (Undergraduate Student)

Coauthors: Virginia Larson, Nicolai Lehnert*

Abstract:

My project focuses on synthesizing a Cobalt(pyridinethiolate N-oxide)2 catalyst and analyzing its efficiency and durability for electrocatalytic hydrogen production. The hydrogen evolution reaction (HER) can produce Hydrogen (H2), a suitable and clean carrier of energy. Specifically, this method of producing hydrogen has applications for directly converting solar energy into chemical fuel. Upon synthesis of this cobalt complex, it has been characterized using nuclear magnetic resonance (NMR), infrared spectroscopy (IR), elemental analysis, electron paramagnetic resonance (EPR), and mass spectrometry techniques. The catalyst is tested for hydrogen production using acid titration and cyclic voltammetry. Catalytic activity is analyzed when the catalyst is physisorbed onto graphitic electrode surfaces, such as cheap graphite and highly ordered pyrolytic graphite, and embedded into thin films of reduced graphene oxide. However, no reliable HER activity was observed. In solution, small HER active particles can be reductively deposited onto a glassy carbon electrode surface. The morphology of these particles is analyzed using a scanning electron microscope (SEM), and the composition by x-ray photoelectron spectroscopy (XPS). From cyclic voltammetry scans, we can learn the deposited material's onset potential for HER and catalytic current as a function of deposition scans.

Poster 25

Coordination Studies of Nickel(II) Recovery by Ion Flotation

Wayne State University

Presenter: Eva Mwakazi (Graduate Student)

Coauthors: Abigail Cousino, Claudio Verani*

Abstract:

Coordination Studies of Nickel(II) Recovery by Ion Flotation Eva Mwakazi and Cláudio N. Verani Department of Chemistry, Wayne State University, Detroit, MI 48202 Ion flotation is a method that has been used in metal recovery. This involves the removal of metal ions from a solution by using surfactants that have an opposite charge to that of the metal ion. The goal of this project is to understand ion flotation through fundamental inorganic principles of coordination chemistry. NickelII d8 low spin prefers forming a square low spin complex with its ligands because the ligand stabilization energy of is low as compared to a high spin d8 octahedral complex. Because of this we can have selective removal of nickel by using ligands that promote this geometry. In this research ligands: triethylenetetraamine, ethylenediamine, cyclen, 1,2-Bis(3-aminopropylamino)ethane(323), N,N′-Bis(3-aminopropyl)-1,3-propanediamine(333) will be used in nickel recovery. The parameters to be studied include molar ratio of coordination complexes of ligand to metal, optimum concentrations of surfactant and the pH. They will be studied using coordination chemistry experiments with subsequent analysis using UV-visible, mass spectrometry and ICP-MS. Preliminary data obtained shows highest amount of nickel removal occurs at basic pH with ethylenediamine and triethylenetetramine showing 98% nickel recovery. Coordination chemistry studies and a preliminary crystal structure shows nickel coordinates in 2:3, 1:3 with triethylenetetramine, ethylenediamine ligands respectively suggesting an octahedral structure of the complexes. The ligands cyclen, 3,2,3 and 3,3,3 seem to favor a 1:1 binding ratio suggesting a square planar geometry.

Poster 26

In-Situ synthesis of silver nanoparticles on vanadium coordinated hydrogels for antimicrobial applications

Bowling Green State University

Presenter: Fathima Shabna Mohamed Nazim (Graduate Student)

Coauthors: Alexis D. Ostrowski*

Abstract:

In-Situ synthesis of silver nanoparticles on vanadium coordinated hydrogels for antimicrobial applications Fathima Shabna Mohamed Nazim, Alexis D.Ostrowski *Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio, USA Abstract Hydrogels have been extensively used in antimicrobial applications such as wound dressings due to their biocompatibility, air permeability and ability to provide the ideal moist environment for cell growth and proliferation. Formulation of hybrid hydrogels incorporated with silver nanoparticles holds immense potential in wound dressing applications due to the high antimicrobial capacity of silver nanoparticles. Previous studies show that photoresponsive hydrogels with transition metal crosslinks of vanadium(V) can be used as an in situ photoreductant. This study presents the in situ generation of silver nanoparticles (Ag(0)) in Vanadium(V)-incorporated QHE-cellulose/agarose hydrogel by light Irradiation. The hydrogel is soaked in an aqueous solution of AgNO3 and irradiated with LED light (405 nm) for one hour. Silver nanoparticles are formed due to photoreduction of Ag+ to Ag (0) and it is observed as a dark colored layer inside the hydrogel. The results obtained from SEM analysis provides evidence for the formation of silver nanoparticles in these gels. As suggested in previous studies, the change of pore size in the hydrogel structure due to light irradiation is also observed. Further studies on the antimicrobial properties and its changes with light irradiation could lead to the development of a photo responsive hybrid hydrogel for antimicrobial applications. KEYWORDS: Hybrid hydrogel, Silver nanoparticles, Photoreduction, Antimicrobial applications

Poster 27

Studies On Molecular Rectification Through Iodo-Substituted Bisphenolate Iron(III) Surfactants

Wayne State University

Presenter: Gibson Kirui (Graduate Student)

Coauthors: W. K. D. Kaushalya, Claudio Verani*

Abstract:

The use of molecules is presently considered a promising research area to build efficient electronic devices for information storage. The microelectronic industry faces a challenge of heat dissipation and high cost of miniaturization process that aims at reducing the size of solid-state electronic components while enhancing their efficiency. The new field of research seeks to use molecules as a replacement for these solid-state components in various electronic devices. Our research group focuses on the development of transition metal-based complexes that ensure the unidirectional flow of electrical currents that are used to transform the alternating currents into direct currents. This research project involves the synthesis, spectroscopic/spectrometric, and surface property characterization of phenolate-based Iron(III) surfactants with electron withdrawing substituents with an aim of modulating the frontier molecular orbital energies responsible for unidirectional electron/current flow. The main objective of this project is to investigate the phenolate substituent effect on electronic, redox, film formation, and current rectification behavior of the fabricated electronic devices. The Iodo-substituted metallosurfactant has shown the formation of ordered films at a good average surface pressure of 30 mN/m. The most recent findings from the related metallosurfactant with extended hydrophilic ligand framework have shown a significant improvement of film formation property by about 20 mN/m which doubles the current rectification behavior. Our new project aims at developing imino-catecholate-based ligand with rich electrochemical and spectroscopic responses to examine the effects of incorporating the electron rich donor frameworks on modulation of electronic, redox, and current rectification behavior of the fabricated devices.

Poster 28

Two-photon-absorbing ruthenium complexes enable near infrared light-driven photocatalysis

University of Cincinnati

Presenter: Guanqun Han (Postdoc)

Coauthors: Guodong Li, Jie Huang, Chuang Han, Claudia Turro & Yujie Sun*

Abstract:

One-photon-absorbing photosensitizers are commonly used in homogeneous photocatalysis which require the absorption of ultraviolet (UV) /visible light to populate the desired excited states with adequate energy and lifetime. Nevertheless, the limited penetration depth and competing absorption by organic substrates of UV/visible light calls upon exploring the utilization of longer-wavelength irradiation, such as near-infrared light ($\lambda irr > 700$ nm). Despite being found applications in photodynamic therapy and bioimaging, two-photon absorption (TPA), the simultaneous absorption of two photons by one molecule, has been rarely explored in homogeneous photocatalysis. Herein, we report a group of ruthenium polypyridyl complexes possessing TPA capability that can drive a variety of organic transformations upon irradiation with 740 nm light. We demonstrate that these TPA ruthenium complexes can operate in an analogous manner as one-photon-absorbing photosensitizers for both energy-transfer and photoredox reactions, as well as function in concert with a transition metal co-catalyst for metallaphotoredox C–C coupling reactions.

Poster 29

Synthesis and Characterization of a New Benzodioxaphosphole-Tungsten Pentacarbonyl Complex

Case Western Reserve University

Presenter: Hannah Hassoun (Undergraduate Student)

Coauthors: Emalyn Delgado Rosario, Matthias Zeller, John D. Protasiewicz*

Abstract:

Our group has prepared an unusual benzodioxaphosphole molecule (BDOP) containing a phosphorus-phosphorus bond from ortho-phosphino-phenol. The molecule contains two benzoxaphosphole planes, which are joined at an angle along the central P-P bond. In order to illuminate the ligating properties of this molecule and unearth differences in geometry that arise when the molecule coordinates in a complex, reactions with [W(CO)5(NCMe)] were examined to form mono- and di-tungsten complexes of BDOP. We have recently succeeded in determining the solid state structure of the ditungsten complex [W(CO)5]2•BDOP by single crystal X-ray diffraction studies. The resulting structure reveals changes in the ligand’s angle at the P-P bond, twisting of the benzoxaphosphole planes, and shifting of the tungsten pentacarbonyl groups upon complexation on the ligand.

Poster 30

Photo-responsive Cr(III)-Supramolecular Siloxane Polymers with Self-healing potential

Bowling Green State University

Presenter: Herenia Espitia (Graduate Student)

Coauthors: Nai-hsuan Hu and Joseph C. Furgal*

Abstract:

Over the years there has been a surge of interest in developing supramolecular polymers because of the reversibility and tunability of incorporable metal-organic ligand interactions within them. These systems have been used to develop materials with intrinsic healing, which can be induced by internal or external stimuli such as heat, pH, and light. The polymers healing ability is attributed to changes in viscoelastic properties resulting from the temporary demetallation of the metal-ligand complex. Cr3+ supramolecular polymers have shown characteristics desirable for self-healing materials using light stimulus, with favorable excited state de-coordination when irradiated. Siloxanes used in high performance coating and biomedical applications can take advantage of this self-healablity. We have exploited this unique photochemical and photophysical property of Cr3+ ligation in the development of polymeric siloxane systems to imbue stimuli-responsive self-healing capabilities. This investigation entailed the synthesis of siloxane polymers containing photodynamic metal coordination sites (Cr3+-imidazole) and characterizing their photoresponsive behavior for applications in light induced healability.

Poster 31

Rhodium catalyzed intermolecular aziridination using carbohydrate-derived sulfamates

University of Toledo

Presenter: Indunil Alahakoon (Graduate Student)

Coauthors: Kendra K. Shrestha, Satheesh Vanaparthi, Prakash Thapa Jianglong Zhu, Michael C. Young*

Abstract:

ABSTRACT: A facile method for intermolecular olefin aziridination is reported wherein sulfamate esters are used as the nitrogen source1. Our general approach consists of first introducing a sulfamate group to a free alcohol of per-O-protected sugar derivatives2. This forms carbohydrate cores along with one hydroxyl group derivatized as a sulfamate (sugar-OSO2NH2) which are known to be potential drug candidates3, 4. Secondly, these carbohydrate-based sulfamate esters are reacted with a structurally and electronically diverse range of olefins in the presence of various rhodium sources and oxidants. This represents one of the first methodologies that permits conjugating a carbohydrate molecule with a non-carbohydrate molecule under rhodium-catalysis in an intermolecular fashion. REFERENCE: 1. Bois*, K. G. a. J. D., A Unique and Highly Efficient Method for Catalytic Olefin Aziridination. J. Am. Chem. Soc. 2002, 124, 13672-13673. 2. Lopez, M.; Trajkovic, J.; Bornaghi, L. F.; Innocenti, A.; Vullo, D.; Supuran, C. T.; Poulsen, S. A., Design, synthesis, and biological evaluation of novel carbohydrate-based sulfamates as carbonic anhydrase inhibitors. J Med Chem 2011, 54 (5), 1481-9. 3. Lopez, M.; Paul, B.; Hofmann, A.; Morizzi, J.; Wu, Q. K.; Charman, S. A.; Innocenti, A.; Vullo, D.; Supuran, C. T.; Poulsen, S. A., S-glycosyl primary sulfonamides--a new structural class for selective inhibition of cancer-associated carbonic anhydrases. J Med Chem 2009, 52 (20), 6421-32. 4. Awakawa, T.; Barra, L.; Abe, I., Biosynthesis of sulfonamide and sulfamate antibiotics in actinomycete. J Ind Microbiol Biotechnol 2021, 48 (3-4).

Poster 32

Correlating Photo response to mechanical property changes in Metallosupramolecular polymers.

Bowling Green State University

Presenter: Irene Baraza (Graduate Student)

Coauthors: Ankit Dara, Alexis D. Ostrowski*

Abstract:

Modification of polymer chains with specific binding groups enables the coordination of different metals, improved temperature stability of the materials and in some cases tunable mechanical properties. In this study we have used curcumin to synthesize polymers of differing molecular weights and coordinated them to different first row transition metals. Preliminary results show that photoresponsive curcumin polymer has greater affinity to Cu2+ compared to Fe2+. The metal coordination with the curcumin polymer results in quenching the fluorescence as evidenced in the metal-polymer titration spectra results. Dynamic mechanical analysis of the material composites of curcumin metallopolymer with polyurethane shows the effects of metal coordination to the elasticity of the materials

Poster 33

Copper(II) Thiolate Mediated Catalytic sp3 C-H Thioetherification

Michigan State University

Presenter: Isuri Jayasooriya (Graduate Student)

Coauthors: Tolani Kuam Salvador, Timothy Warren*

Abstract:

Copper(II) Thiolate Mediated Catalytic sp3 C-H Thioetherification Isuri U. Jayasooriya, Tolani K. Salvador and Timothy H. Warren The ability of sulfur-based functionalities to impart unique structural and functional properties into organic molecules spurs the development of methods for C-S bond formation. We describe catalytic sp3 C-H thioetherification that creates thioethers R-SR' from sp3 C-H substrates R-H and acyl- or silyl-protected thiols Ac-SR' or TMS-SR' employing tBuOOtBu as oxidant and a copper b-diketiminate catalyst. A variety of substrates that possess benzylic and unactivated sp3 C-H bonds react with protected alkyl and aryl thiols at 90 °C or at RT under blue light to form thioether products. Triisopropylsilyl (TIPS) thioetherification products TIPS-SR from the reagent TIPS-S-TIPS provide access to thiols H-SR upon facile deptrotection. Mechanistic studies reveal a radical relay catalytic cycle, supported by the isolation of copper(II) thiolates [CuII]-SR' that react with sp3 organic radicals R• to form thioether products R-SR'.

Poster 34

Insight into composition of manganese oxide electrocatalysts to study OER selectivity

University of Michigan

Presenter: Jake O'Hara (Graduate Student)

Coauthors: Bart Bartlett*

Abstract:

Developing selective and efficient electrocatalysts for energy-relevant reactions such as water splitting ($2H_2O \rightarrow 2H_2 + O_2$) is at the forefront of research in the energy industry today. Chemical potential energy is stored within these bonds, making it an incredibly useful and sustainable method for energy storage. Many electrocatalysts for water splitting materials have been proposed and explored, but one that has ignited renewed interest is birnessite-phase MnO_2. Recent studies have indicated that birnessite, distorted along the c-axis and with a varying number of oxygen defects, exhibits selective catalytic activity for the oxygen-evolution reaction (OER) in the presence of chloride, an abundant ion in seawater that is typically oxidized faster than water. This selective OER activity occurs on electrochemically deposited birnessite films that are annealed at high temperatures (> 300 ºC). During annealing, the films are reduced as oxygen vacancies form ($MnO_2 \rightarrow MnO_{2-x} + x/2\ O_2$) with an accompanying loss of crystallographic periodicity along the c-axis. This work focuses on synthetically tuning birnessite MnO_2 to develop structure-catalytic activity relationships to study OER and chloride oxidation kinetics and selectivity.

Poster 35

Si-H Bond Activation by a Tetradentate Bis(amido)bis(phosphine) Iron(II) Complex

The Ohio State University

Presenter: Jeremiah Stevens (Graduate Student)

Coauthors: Gillian P. Hatzis, Christine M. Thomas*

Abstract:

In recent decades, interest in replacing noble metals with more sustainable first-row metals has been growing steadily. The primary disadvantage of first row metals in catalysis, however, is their decreased ability to undergo metal-centered two-electron processes—facile reactions for their heavier congeners. To combat this decreased reactivity, a non-innocent ligand can be employed to alleviate the redox burden via metal-ligand (M–L) cooperativity. In such a process, bonds in substrate molecules are heterolytically cleaved across the M–L bond without a concomitant change in oxidation state of the metal. This ligand-enabled pathway allows for novel reactivity at first-row metals that warrant continuing investigation. In this work, we explore the activation of Si–H bonds and formation of Si–Si bonds across Fe–amide bonds in a tetradentate bis(amido)bis(phosphine) iron(II) complex, PNNPFe.

Poster 36

Synthesis of Main Group Metal Complexes Supported by a Tetradentate Bis(amide)bis(phosphine) Ligand

The Ohio State University

Presenter: Jess Fletcher (Graduate Student)

Coauthors: Dr. TJ Yokley, Dr. Christine Thomas*

Abstract:

Homogeneous catalysts have been studied for their application in enzymatic and molecular reactions. “Noble" metals of the late 2nd and 3rd row transition metal series are the most studied for these types of catalytic reactions. These metals are among the least abundant elements and are cost prohibitive. Researchers have explored using more cost-effective metals to mimic the reactivity of precious metals. The Thomas lab studies fundamental catalyst design involving metal centers and non-innocent ligands, and the effect that such metal-ligand cooperativity can have on the chemistry of these more abundant metals. A series of Group 13 metalloligand complexes were synthesized using a planar tetradentate bis(amide)bis(phosphine) ligand (PNNP). The complexes were characterized using Nuclear Magnetic Resonance spectroscopy and single crystal X-ray diffraction. Recently, (PNNP)MCl (M= Al, Ga) have been studied for their potential to coordinate late transition metals to generate transition metal / main group metal bimetallic compounds.

Poster 37

Examination of the effect of monodentate leaving ligands on Ru (II) polypyridyl complexes

The Ohio State University

Presenter: Jessica Vandevord (Graduate Student)

Coauthors: Claudia Turro*

Abstract:

A group of ruthenium (II) complexes with bidentate ligands of varying electron-donating ability were synthesized with monodentate ligands acetonitrile (ACN), pyridine (py), and 1-methy-1,2,4-ltriazole (mtz) to determine the effect of electronic character on the photophysical properties. Complexes all follow the same formula with a ruthenium (II) center and terpyridine ligand, and then vary with bidentate and monodentate ligands. Electronic absorption spectra confirmed that complexes containing more electron-donating bidentate ligands have a red-shifted ground state absorption in comparison with complexes containing bidentate ligands of lesser electron-donating ability. Electrochemical data confirmed the impact of the bidentate ligand on the ruthenium center with the changes seen in the RuIII/II couple. Preliminary data identified mtz-containing complexes were photolabile with blue light, whereas py-containing complexes were not photolabile with blue light. Understanding the depth of these electronic effects will aid in development of ruthenium (II) photosensitizers for numerous applications.

Poster 38

Investigating the substrate binding pocket in the heterobimetalllic Mn/Fe R2lox protein

The Ohio State University

Presenter: Jonathan McHenry (Undergraduate Student)

Coauthors: Hannah S. Shafaat*

Abstract:

R2lox (R2-like ligand-binding oxidase) is a metalloenzyme consisting of a heterobimetallic Mn/Fe cofactor at its active site. R2lox has been discovered in several pathogens and extremophiles and is one of the most upregulated proteins in Mycobacterium tuberculosis. Interestingly, a long-chain fatty acid is directly coordinated to the heterobimetallic active site, suggesting that R2lox may be involved in lipid metabolism. Wild type R2lox contains an alanine at residue 171 which is located very close to the long chain fatty acid. In this work, an A171L R2lox mutant is studied to see the effect of a larger residue (leucine) on the coordination of the fatty acid and the structure and formation of the active site. In order to investigate the A171L mutant, several biochemical and spectroscopic techniques are employed. I express the A171L mutant in E. coli and lyse the cells using sonication and high-speed centrifugation to collect cell lysate. The plasmid containing the sequence for R2lox encodes a His-tag so that R2lox can be isolated from the lysate using a Ni-NTA affinity column. I then reconstitute R2lox using a solution of manganese (II) and iron (II) in either an anaerobic or aerobic environment. The binding of manganese and iron to the active site of R2lox during reconstitution is examined using UV-Vis spectroscopy. The oxidized protein solution is desalted to remove excess Mn or Fe that did not bind to the protein. The desalted protein is analyzed using EPR spectroscopy to study the unpaired electron of the coupled Fe-Mn cofactor.

Poster 39

Postsynthetic modification of metal-organic frameworks for heterogeneous catalysis

The Ohio State University

Presenter: Jordon Hilliard (Graduate Student)

Coauthors: Aidan Greene, Casey R. Wade*

Abstract:

The structural and chemical tunability of metal-organic frameworks (MOFs) makes them promising platforms for single-site heterogeneous catalysis. Our group has been investigating MOF assembly from metallolinkers based on catalytically-active transition metal diphosphine pincer complexes. Additionally, our group has been exploring postsynthetic modification reactions to append transition metal phosphine and 2,2’-bipyridine catalysts in amine functionalized MOFs.

Poster 40

Bimetallic Complexes in the Interconversion of N2 and NH3

Michigan State University

Presenter: Josalyne Beringer (Graduate Student)

Coauthors: Timothy Warren*

Abstract:

An attractive source of renewable green energy, the catalytic interconversion of ammonia (NH3) and nitrogen (N2) represents a critical transformation for carbon-free fuels. The structure and reactivity of dinitrogen (N2), diazene (N2H2), and hydrazine (N2H4) intermediates at dinuclear metal sites may provide important mechanistic clues to developing efficient, low barrier N-H and N-N bond forming and cleaving processes in the interconversion of NH3 and N2. We describe new families of dinuclear □-diketiminato complexes motivated by our lab's recent success employing □-diketiminato copper catalysts for ammonia oxidation that bimolecularly form N-N bonds via [CuII]-NH2 intermediates. Using linkers that control the relative geometry of two □-diketiminato metal centers [M] that may come in close proximity (2.5 – 3.3 Å), we describe the synthesis and reactivity of new copper(I) complexes and their interaction with N2, N2H2, and N2H4. We also describe exploratory studies that extend these concepts to more reducing metals such as Co, Ni, and Fe to understand the role of the metal's d-electron count in the structure and reactivity with nitrogenous ligands relevant to the interconversion of NH3 and N2.

Poster 41

Synthesis and Characterization of Square Planar (PNNP)Co(II) Complexes

The Ohio State University

Presenter: Justin Miller (Graduate Student)

Coauthors: Subha Himel, Christine Thomas*

Abstract:

Transition metal catalysis is typically performed using late 2nd and 3rd row transition metals due to their ability to undergo two electron processes. Performing catalysis using 1st row transition metals is an attractive target because of the lower cost, greater abundance, and lesser environmental impact. The primary disadvantage to 1st row transition metals is their greater tendency to undergo one electron processes. Leveraging metal-ligand cooperativity to activate substrates across a metal-amide bond alleviates the need for metal-centered two-electron processes. A square planar Co(II) complex based on a tetradentate bis(phosphine) bis(amido) ligand, [PNNP]2-, was synthesized. The cobalt(I) analog has been synthesized using PhLi or KC8, resulting in an outer sphere Li+ or K+ cation. Preliminary results suggest these complexes are catalytically active towards hydrosilylation and hydroboration of styrene.

Poster 42

Development of Tetrathiafulvalene (TTF) fused Imidazolium salts for Redox Flow Battery (RFB) Applications

Wright State University

Presenter: Kalpana Sampath (Graduate Student)

Coauthors: Kuppuswamy Arumugam*

Abstract:

Redox flow battery (RFB) can be utilized as electrochemical storage of intermittent renewable energy for large-scale purposes. The energy density of RFB still needs to be increased to achieve better efficiencies. Recently, organic-based materials are started showing promising results in various fields. Tetrathiafulvalene (TTF) is one such stable sulfur-containing heterocyclic organic compound capable of undergoing multiple one electron reversible redox transformations. TTF is having its unique structural and electrochemical properties and it can be subjected to various structural modifications. In this work, we aim to synthesize TTF-based imidazolium salts and it is expected to behave as an excellent electrolyte, having the properties of both a redox active mediator and an ionic liquid. TTF plays a major role in batteries to overcome limitations such as reaction kinetics and energy density, which eventually help to achieve better efficiencies in RFB.

Poster 43

Materials with Axis-Dependent Conduction Polarity make Transverse Thermoelectric Generators a reality

The Ohio State University

Presenter: Karl Koster (Graduate Student)

Coauthors: Michael R. Scudder, Joseph P. Heremans, Joshua E. Goldberger*

Abstract:

Thermoelectric generators have the unique ability to convert waste heat into useable electrical power. However, traditional longitudinal thermoelectric generators (TEGs) that incorporate both p-type (hole-conducting) and n-type (electron-conducting) materials into a single module face major engineering problems. Transverse thermoelectric generators (TTEGs) use materials with axis-dependent conduction polarity to circumvent these challenges. In these materials, p-type and n-type functionalities are integrated along orthogonal directions within a single crystal, decoupling the directions of heat and charge flow in the device and eliminating the insertion losses that stem from electrical series contacts in TEGs. Re4Si7 is an excellent candidate for use in a TTEG because of its axis-dependent conduction polarity and its outstanding thermoelectric properties. In this work, large single crystals of Re4Si7 were used to fabricate transverse thermoelectric generators with two different geometries. The power output and efficiencies of both devices were fully characterized and demonstrate the advantages that TTEGs have over TEGs. While Re4Si7 demonstrates outstanding thermoelectric properties, Re is a rare and costly element. As a result, related phases WSi2 as well as Mo- and W-alloyed Re4Si7 were synthesized, characterized, and evaluated for similar applications.

Poster 44

Probing Electronic Properties of Emergent Quantum Phenomena of Layered Materials with Scanning Probes

University of Kentucky

Presenter: Kathryn Pitton (Graduate Student)

Coauthors: Douglas R. Strachan, Beth S. Guiton*

Abstract:

Ultrathin van der Waals materials and their heterostructures provide a powerful platform for studying emergent phenomena and surface structures in a two-dimensional area. As devices and ultrathin materials shrink in size, characterization methods allowing for localized probing of mechanical and topographical characteristics at a nanoscale level have increased in popularity. In addition to smaller devices, layered materials have shown many unique properties still in the beginning stages of research that can be examined through scanning probe microscopy. Scanning probe microscopy (SPM) offers the opportunity to explore topographical and morphological characteristics at a nanoscale level, while providng a nondestructive approach to probing electronic properties of nanoscale materials. This work will review our methods for making van der Waals heterostructures and our utilization of several SPM modes to quantify the electrostatic properties of various 2D materials.

Poster 45

Synthesis and Characterization of Zn Complex of an 8-Hydroxyquinoline Derivative as a Zinc Transport-Facilitating Agent to kill Multidrug-resistant Staphylococcus aureus

Kent State University

Presenter: Khalil Mudarmah (Graduate Student)

Coauthors: Nalin Abeydeera, Min-Ho Kim and Songping Huang*

Abstract:

The increased incidence of Staphylococcus aureus resistance to multiple antibiotics requires the development of novel antimicrobials alternatives to or in combination with conventional antibiotics. Zinc is essential for all life forms because it is an important structural component of zinc-finger motifs in many proteins, such as transcription factors and intracellular signaling enzymes. However, excess zinc inside the bacteria can disturb their metabolism by altering the balance of the zinc homeostasis in bacteria. Hence, there is a remarkable balancing act of maintaining zinc homeostasis on display by both mammalian and bacterial cells for their survival. Recently, small lipophilic molecules such as 8-hydroxyquinoline and its derivatives exhibit remarkably ability to bind to zinc and transport it across lipid membranes. This motivated us to synthesize, characterize and investigate the capacity of the Zn[(5,7-dichloro-2-methyl-8-hydroxyquinoline)]2 complex (1) as a stealth zinc carrier. This complex can bypass the regulation of zinc trafficking in the bacterial cell, which should constitute a novel strategy for killing pathogenic bacteria by disturbing zinc homeostasis in bacterial cells. As the result, we have evaluated the antimicrobial potential of 1 as an antimicrobial agent in the in vitro models of both multidrug-sensitive Staphylococcus aureus (MSSA) and multidrug-resistant Staphylococcus aureus (MDRSA) bacteria.

Poster 46

Paramagnetic Resonance of High-Spin Co(II) in Biologically-Relevant Environments

Miami University

Presenter: Kumari Walpita (Graduate Student)

Coauthors: Christopher D. James, Tyler Rutledge, and David L. Tierney*

Abstract:

Electron paramagnetic resonance (EPR) spectra of Co(II) complexes are complicated due to the complex electronic structure of high spin Co(II). We present an investigation of a set of 10 well-characterized complexes, including five containing only chelating ligands (forming two bonds each to the Co) and a subset containing two chelating ligands and two monodentate ligands. The study aims to better understand the difference between solid and solution state EPR of Co(II), and why parallel-mode EPR signals are observed for certain complexes, not others. Results of this study will be discussed in terms of spin sub-level mixing.

Poster 47

Synthesis of Zn(I) Dimers for use as Potential Precursors in Metal ALD Processes

Wayne State University

Presenter: Kura Gamage Chamod Dharmadasa (Graduate Student)

Coauthors: Charles H. Winter*

Abstract:

Atomic layer deposition (ALD) is a film deposition technique used in the microelectronics industry for the fabrication of chips that contain atomic scale features. Chemical compounds used in ALD processes are called ALD precursors. To be used as an ALD precursor, a compound needs to be volatile, thermally stable, and highly reactive toward surface reactive sites and co-reactants. Several Zn(I) dimers have been previously reported in the literature, and they are used as mild reducing agents in some synthesis reactions, instead of strong reducing metals such as potassium. As such, Zn(I) dimers are potential candidates for use as mild reducing agents in electropositive metal ALD and precursors for ALD Zn metal film growth. However, all reported Zn(I) dimers contain high molecular weight, bulky aryl groups (such as Mes, Dip, and Dep) in their structures, resulting in limited volatility and reactivity. Therefore, we seek to prepare volatile, thermally stable, and reactive Zn(I) dimers that contain small alkyl groups.

Poster 48

Cyclopropanation Catalyzed by Iron(II) Complexes in Bulky Alkoxide Ligand Environments

Wayne State University

Presenter: Lakshani Wathsala Kulathungage (Graduate Student)

Coauthors: Sudheer Kurup, Stanislav Groysman*

Abstract:

Cyclopropanes are three-membered cycloalkanes undergoing facile ring opening due to the high ring strain. Therefore, they constitute efficient precursors and/or key intermediates in total synthesis of various organic compounds including pharmaceutical drugs. A common synthetic route towards cyclopropanes involves transition metal-mediated carbene group transfer to olefins. Most of the currently used cyclopropanation catalysts employ the combination of expensive noble metals (such as Rh) with diazoalkane precursors. Our research focuses on the development of efficient and sustainable nitrene- and carbene-transfer catalysts employing the combination of inexpensive 3d metals (Mn, Fe, Co) with easily synthesizable alkoxide ligands. In the previous studies, we have demonstrated that the reaction of an iron(II) bis(alkoxide) complex Fe(OCtBu2Ph)2(THF)2 with diazoalkanes (diazoesters) leads to their reductive coupling through the terminal nitrogens instead of the carbene formation. As an alternative approach, we replaced the diazoalkane (carbene) precursors with a hypervalent iodine carbene precursor, bis(methoxycarbonyl)(phenyliodinio)methanide. We have observed that an iron(II) bis(alkoxide) complex Fe[OO]Ph(THF)2; (H2[OO]Ph = [1,1′:4′,1″-terphenyl]-2,2″-diylbis(diphenylmethanol)) catalyzes the conversion of styrene to the corresponding cyclopropane efficiently at low catalyst loadings at room temperature. We are currently investigating the reactivity of the additional substrates and carbene precursors, and are also investigating the reaction mechanism.

Poster 49

Synthesis of a pincer-ligated manganese carbonyl complex featuring an N-heterocyclic phosphenium moiety and its reactivity toward N=N double bonds

The Ohio State University

Presenter: Leah Oliemuller (Graduate Student)

Coauthors: Christine M. Thomas*

Abstract:

While N-heterocyclic carbenes (NHCs) have been well-studied ligands for transition metal complexes, their group 15 analogues, which instead incorporate a phosphorus atom in the heterocycle, remain relatively unexplored in comparison. In contrast to NHCs, N-heterocyclic phosphenium cations (NHP+s) are weak σ-donors and strong π-acceptors, leading to different reactivity, properties, and potential applications. Similar to nitrosyl ligands, NHPs are thought to interconvert between a phosphenium (NHP+) and a phosphido (NHP-) through a two-electron process, which could yield unique properties and coordination in comparison to NHCs. Incorporation of an NHP unit into the center of a rigid chelating pincer ligand and its coordination to a manganese center has yielded a (PPClP)Mn(CO)2Br complex, which can further be treated with two equivalents of a reducing agent to afford a coordinatively unsaturated manganese complex (PPP)Mn(CO)2. Structural characterization of this compound reveals a fluxional geometric process about the manganese center that varies in the solution and solid state. In the solution phase, (PPP)Mn(CO)2 adopts a more trigonal bipyramidal geometry and is analogous to pincer-ligated manganese dicarbonyl complexes used for hydrogenation and dehydrogenative coupling catalysis in the literature. Progress toward reactivity of (PPP)Mn(CO)2 with N=N double bonds in azenes and azides as well as the nature of the metal-phosphorus bonding will be discussed.

Poster 50

Development of Novel Carbonic Anhydrase Biomimetic Zn-Complexes for Carbonyl Hydration

University of Kentucky

Presenter: Levi Wolff (Undergraduate Student)

Coauthors: Alexander Olivelli, Aron J. Huckaba*

Abstract:

Catalyzing the hydration of carbonyl groups like carbon dioxide could be a way to address global climate change by instituting carbon capture at the point of pollution. Carbonic anhydrase, a naturally occurring enzyme in many biological systems, is one of the fastest known enzymes and catalyzes CO2 hydration. Inspired by carbonic anhydrase's catalytic activity, the focus of this project to date has been the design, synthesis, and characterization of novel biomimetic Zn-metal complexes and the evaluation of their catalytic activity. This project seeks to mimic the carbonic anhydrase active site by accurately replicating the metal-ligand bond angles with a rigid cyclohexane-based ligand. Here we report the synthesis and characterization of the ligand and metal complexes, as well as preliminary catalytic testing results.

Poster 51

Synthesis and functionalization of potassium bis(ethyleneglycol)organosilicates

Indiana State University

Presenter: Luke Hargrave (Undergraduate Student)

Coauthors: Ryan Van Hoveln*

Abstract:

Formation of carbon-heteroatom bonds remains a significant challenge in modern organic chemistry. One strategy is to oxidize nucleophiles such as boronic acids and esters or silicates, which are employed in reactions such as the Chan-Lam Coupling and the Fleming-Tamao Oxidation. Our efforts have been to synthesize a set of bis(ethyleneglycol)silicates, which have only been proposed as intermediates in a single reaction, and then oxidize them to form several different types of carbon-heteroatom bonds. Notably, we can oxidize aryl silanes under fluoride-free conditions, which has been remarkably challenging up to this point. Herein, we report the fluoride-free oxidation aryl-Si bonds to make aryl-O, aryl-N, and others. Our target products include phenol, phenyl morpholine, and phenyl benzoate. We have also put effort into developing a new, simpler synthesis of bis(ethyleneglycol)organocsilicate salts.

Poster 52

Cytotoxicity and Stability of Liposomal Nanoparticles of Near-Infrared Activable Platinum(IV) Prodrugs

Kent State University

Presenter: Man Kshetri (Graduate Student)

Coauthors: Yaorong Zheng*

Abstract:

The FDA-approved platinum(II) drugs (cisplatin, carboplatin, oxaliplatin) have been widely used in cancer treatments in the US and worldwide. However, drug efflux by membrane transporters, intracellular detoxification, off target nucleophile binding, and DNA damage repair have stymied the efficient cellular entry, drugs stability, and DNA adduct formation, which lead to development of drug resistance, and it has been a long-standing challenge for cancer therapy. In this project, we developed a number of novel Pt(IV) liposomal nanoparticles(NPs) that are able to overcome this issue. Different with their Pt(II) counterparts, the octahedral Pt(IV) complexes are more kinetically inert and the additional two axial ligands can be employed to modify their physical, chemical, and biological properties. Liposomal nanoparticles are formed by interacting Pt(IV) prodrugs of cisplatin, oxaliplatin and carboplatin containing near infrared (NIR) activable axial head ligand and lipophilic tail ligand with 1,2-Dioleoyl-sn-glycero-3-phosphocholine (DOPC) and 1,2-Distearoyl-sn-Glycero-3-Phosphoethanolamine conjugated with methoxyl poly(ethylene glycol) (DSPE-mPEG) to achieve maximum loading capacity and encapsulation efficiency. This formulation allows us to anchor Pt(IV) prodrugs into liposomal bilayer and retard premature reduction. Upon entering cancer cells, these NPs can be photoreduced upon NIR irradiation (830 nm) to Pt(II) species triggering cell death. The utilization of high tissue penetrability of NIR Light for the intracellular activation of liposome encapsulated Pt(IV) nanoparticles (NPs) is a novelty of this research. Furthermore, reduction profiles of the NPs against reducing agents, cytotoxicity profiles, intracellular reactive oxygen species (ROS) generation, apoptosis induction have been evaluated.

Poster 53

Modified Pechini Method: Developing Surface Area and Pore Volume of Catalyst Supports

University of Toledo

Presenter: Manjula Madde Kandage (Graduate Student)

Coauthors: Michal Marszewski*

Abstract:

Modified Pechini Method: Developing Surface Area and Pore Volume of Catalyst Supports Hydrogen could be considered a good alternative to fossil fuels due to its high gravimetric energy density of 142 MJ kg-1. However, storage and transportation of hydrogen are difficult due to its low volumetric energy density of 10.1 MJ L-1. Ammonia is considered a good candidate as a hydrogen carrier due to its high hydrogen weight percentage of 17.6 wt%, and the requirement of mild conditions to liquefy. Onsite generation of hydrogen from ammonia is challenging since currently, ammonia decomposition requires catalysts. Composition and structural properties, including specific surface area and pore volume, are among the main factors that govern the activity of the catalyst support. The present research aims to increase the structural properties of perovskite catalyst supports which will cause better catalytic performance in ammonia decomposition. Yttrium and nickel doped perovskites were synthesized using the Pechini method. To improve the structural properties including specific surface area and pore volume of perovskite supports, a two-step heat treatment process was implemented in the Pechini method. In this modified method, organic-inorganic composite resulting from Pechini synthesis was first carbonized at 650-1000°C to form a hard carbon template and a perovskite framework. The carbonized samples were then calcined at 400-650°C to remove carbon. As a result, the specific surface area increased from 29 m2 g-1 to 104 m2 g-1 and the total pore volume increased from 0.12 cm3 g-1 to 0.18 cm3 g-1 compared to the conventional Pechini method.

Poster 54

C-H Trifluoromethylation with a Formally Cu(III)-CF3 Complex

The Ohio State University

Presenter: Margaret Ball (Graduate Student)

Coauthors: Jamey Bower and Shiyu Zhang*

Abstract:

We describe the synthesis and reactivity of Cu(II) and Cu(III) monotrifluoromethyl complexes supported by pyridinedicarboxamide ligand (L). We have demonstrated that the formal copper(III) monotrifluoromethyl complex LCu(III)CF3 can be accessed under mild conditions via one-electron oxidation of LCu(II)-CF3 precursors with a wide range of oxidants, including O2. While the LCu(II)-CF3 complex is unreactive toward C-H trifluoromethylation, the LCu(III)-CF3 complex undergoes high yielding Csp-CF3, Csp2-CF3, Csp3-CF3 bond formation reaction via the release of CF3 radical (or CMD). These studies support the potential viability of Cu(III)-CF3 intermediates in Cu-catalyzed C-CF3 bond formation reactions.

Poster 55

Functionalization of Pyridinedipyrrolide Supported Zirconium Photosensitizer with Polar Groups

West Virginia University

Presenter: Marisa Tordella (Graduate Student)

Coauthors: Carsten Milsmann*

Abstract:

Making the switch from nonrenewable energy to renewable alternatives is an increasingly important and sought for avenue in today's science. An example of such alternatives is solar energy, an option that utilizes photosensitizers to convert sunlight into energy. Most work in the literature involve photosensitizers that contain precious metals, a less sustainable option on an industrial scale due to the expense of the scarce materials. A solution to this problem is to use earth abundant transition metal photosensitizers, a field that is far less studied. Photosensitizers containing precious metals exhibit metal-to-ligand charge transfer (MLCT) when excited. Less commonly seen in the literature is ligand-to-metal charge transfer (LMCT), which occurs for early transition metals. The Milsmann group explores Zr(IV) complexes, an earth abundant alternative that exhibits LMCT characteristics. This poster presentation will address the functionalization of the pyridinedipyrrolide (PDP) ligand of the zirconium complex, Zr(MesPDPPh)2, to enhance the complex's solubility in water as well as to make it a viable option for semiconductor surface attachment. The 3-phenyl substituent of the pyrrole is targeted over the pyridine position because of its accessibility and its low impact on the complex's photophysical properties. Due to the reactivity of the zirconium starting material necessary for the synthesis of the air and water stable complex, functionalization must occur post Zr(MesPDPPh)2 synthesis. Because of this, various protecting groups have been explored for the synthesis of the PDP ligand. Ultimately, the zirconium complex will be deprotected post-synthesis for the attachment of an anchoring group.

Poster 56

Single-Source Precursors for the Controlled Aqueous Synthesis of Bismuth Oxyhalides

Indiana University - Bloomington

Presenter: Matt Gordon (Graduate Student)

Coauthors: Yanyao Liu, M. Kevin Brown, Sara E. Skrabalak*

Abstract:

Bismuth oxyhalides represent a promising class of photocatalysts for harvesting solar energy. These materials are often synthesized in aqueous media with poor synthetic control resulting from the extremely fast nucleation and growth rates of the particles. These fast rates are caused by the poor solubility of bismuth precursors and their rapid precipitation with free halide ions. We have developed water-soluble precursors combining bismuth with either chlorine or bromine atoms in the same metal-organic complex. With the application of heat, halide ions are released which then precipitate with bismuth ions as BiOX (X = Cl, Br). By controlling the rate of free halide ion formation, the nucleation and growth rates of BiOX nanomaterials can be lessened, providing additional synthetic control. We demonstrate the potential of these precursors by fabricating thin films of BiOX via spray pyrolysis of the aqueous precursor solutions.

Poster 57

Catalytic hydroelementation of terminal alkenes by a (PPP) pincer-ligated cobalt(II) complex

The Ohio State University

Presenter: Matthew Fitzsimmons (Graduate Student)

Coauthors: Matthew Fitzsimmons, Azamat Yessengazin, Gillian Hatzis, Christine Thomas*

Abstract:

A Co(II) complex, (PPHP)CoI2, was synthesized and evaluated as a pre-catalyst for the hydrogenation and hydroboration of various alkenes. Initial results have shown that (PPHP)CoI2, when activated with KBEt3H (4 mol%) is capable of selective reduction of terminal alkenes in nearly quantitative yields under mild conditions. Interestingly, saturated frameworks bearing a terminal olefin were found to produce a mixture of the fully saturated product and internal olefins via a chain-walk mechanism. This chain-walking phenomenon was not observed when pyridine was used as an additive (6 mol%). We hypothesize that a pyridine-cobalt adduct generated in-situ slows the process of catalyst deactivation and may play a part in this observed selectivity. Additionally, this catalyst was shown to effectively hydroborylate terminal alkenes with high selectivity for the anti-markovnikov products with low catalyst loading (1 mol%) in three hours. The sole metal-containing product observed upon completion of catalytic reactions, [(PPP)CoH]2, suggests a monomeric (PPP)CoIIH active species that is deactivated by dimerization when substrates are depleted.

Poster 58

Solution Dynamics of Cobalt-Based Single Ionic Magnets

Miami University

Presenter: Matthew Grindle (Graduate Student)

Coauthors: David L. Tierney*

Abstract:

Single Ionic Magnets (SIMs) are a class of materials defined by their large per-molecule magnetism and their ability to hold a directional magnetic field. Currently, applications of SIMs are limited by the need for cryogenic working temperatures (< -193o C). Most applications involve use of the solid materials. We are working to understand the importance of physical properties that are derived from constraining the molecule in a crystalline form, relative to those that are inherent to the molecules themselves. We are measuring the magnetic properties of dissolved SIMs at near room temperature (-66oC to 74oC), using Nuclear Magnetic Resonance (NMR) spectroscopy. Data will be presented on two similar five-coordinate complexes (TpPh,MeCo(guaiacol) and TpPh,MeCo(thioguaiacol) (TpPh,Me = tris-3-phenyl-5-methyl-1-pyrazolylborate)), that differ only by the substitution of one atom (S for O) coordinated to the central metal. Both complexes show approximate trigonal bipyramid geometry in their crystalline solids. In solution, TpPh,MeCo(thioguaiacol) is stable and five-coordinate under all conditions, while TpPh,MeCo(guaiacol) is much more dynamic, rapidly converting between four-coordinate and five-coordination at elevated temperatures.

Poster 59

Fluorophore Imaging and Cancer Therapy by Reduction-Triggered Platinum(IV) Prodrug-conjugated Fluorescein Monitor

Kent State University

Presenter: May Cheline (Undergraduate Student)

Coauthors: Suha Alqarni, Yaorong Zheng*

Abstract:

In this research, we have developed a new approach in order to control the reduction of Pt(IV) prodrugs within cancer cells. In this context, fluorophores have emerged as useful optical monitors for signaling biological processes; thus, to help to indicate the reduction by light. on the reduction of Pt(IV) prodrugs within cancer cells, we synthesized a platinum-based Pt(IV) prodrug bearing an acetylized fluorescein group. The acetylized fluorophore decreases the measured light-absorption of the prodrug within the 450-550 nm range; however, when the acetate groups are removed the absorption increases. Investigation of an analogue bearing the acetylized fluorophore confirmed that these compounds are reduced by esterase, and subsequently show a proportionally increased absorbance in the 450-550 nm range after 24 hours. The prodrug was synthesized by conjugating the oxidized cisplatin with a succinate ligand, this ligand was coupled with 1-azido-propylamine. The product reacted with the acetylized dye through a click reaction. The acetylized dye was formed by reacting Fluorescein Isothiocyanate (FITC) with dibenzylcyclooctene-amine (DBCO), then refluxing the product with acetic anhydride the acetylized dye was formed. The prodrug was then used to observe the cellular uptake and reduction within the cell. This compound shows the time required for the cell to uptake the drug and the amount of time for the reduction process to complete. This method highlights the use of organometallic chemistry principles to develop indicators for platinum(IV) based cellular reduction methods, which can help design more effective chemotherapeutic options.

Poster 60

Systemic Delivery of Divalent Europium with Implications to Direct Imaging Hypoxia

Wayne State University

Presenter: Md Mamunur Rashid (Graduate Student)

Coauthors: Md Mamunur Rashid, Brooke A. Corbin, Caitlyn J. Ortiz, Md. Abul Hassan Samee, Robia G. Pautler, and Matthew J. Allen*

Abstract:

Hypoxia is linked to a variety of disease states including kidney disease; hepatic and neurological toxicities; and the progression, proliferation, and therapy resistance of many cancers, making hypoxia an important diagnostic and therapeutic target. Contrast-enhanced magnetic resonance imaging (MRI) using EuII-containing complexes that directly react with oxygen has been proposed as a possible technique to image hypoxia. Although EuII has been demonstrated to effectively image low-oxygen regions, the oxygen-sensitivity of the EuII -containing agents confounds the systemic delivery of EuII, limiting the usefulness of such potentially outstanding hypoxia sensors to regions of interest that are accessible with direct injection. Therefore, the search for complexes of EuII that are resistant to oxidation for systemic delivery of Eu-containing probes has been actively pursued. Here we report the identification, synthesis, and study of a new class of phosphonate-containing ligand-types for Eu that show unprecedented oxidative stability in biological conditions.

Poster 61

Investigation of the Kinetic and Electrochemical Features of Eu(II)-Based Macrocyclic Complexes

Wayne State University

Presenter: Md Sydul Islam (Graduate Student)

Coauthors: Matthew J. Allen*

Abstract:

Magnetic resonance imaging using the EuIII/II redox couple is one of the most promising approaches for noninvasively visualizing hypoxia in vivo. In particular, the EuII ion endows positive contrast enhancement when hypoxic conditions persist in tissues. Conversely, the EuIII ion with the appropriate ligand shows contrast under normoxic conditions via chemical exchange saturation transfer magnetic resonance imaging. Moreover, in comparison to GdIII-based contrast agents, EuII-containing complexes have greater relaxivity values at ultra-high field strengths. However, there are two important criteria for EuII-based contrast agents: (1) they should have a relatively positive electrochemical potential to minimize oxidation to EuIII and (2) they should be inert to avoid dissociation of europium from the ligand. We are using coordination chemistry to address these two criteria by testing the hypothesis that increasing the distance between EuII and negative charges on the ligand, the electrochemical potential become more positive, and dissociation will be increased. To test the hypothesis, we are synthesizing a series of europium complexes with different distances between the metal ion and ligand charge, and we are studying their electrochemical potentials and kinetic dissociation rates. Here, we will present our progress toward testing the hypothesis. These studies have implications in the design of ligands for divalent europium-based contrast agents that detect hypoxia.

Poster 62

Synthesis and characterization of non-heme iron hyponitrite complexes

University of Michigan

Presenter: Michael Lengel (Graduate Student)

Coauthors: Michael O. Lengel, Hai T. Dong, Debangsu Sil, Carsten Krebs*, Nicolai Lehnert*

Abstract:

Flavodiiron NO reductases (FNORs) are enzymes involved in microbial pathogenesis. Pathogens equipped with these enzymes have resistance towards nitric oxide (NO), which is a human immune defense agent. These FNOR enzymes utilize a non-heme diiron active site to reduce NO to nitrous oxide (N2O), allowing for microbial proliferation. Despite significant efforts, intermediates that provide insight into how the non-heme diiron active sites of FNORs reduce NO to N2O have not been observed. Computational studies predict that the key species involved in N-N coupling of the two NO units to form N2O are iron-hyponitrite species. However, the exact coordination chemistry of non-heme iron centers with hyponitrite remains largely unknown. In synthetic complexes, hyponitrite binding has been observed primarily at nickel, ruthenium, platinum, and copper metal centers. Only two iron-hyponitrite species have been structurally characterized in the literature thus far, one heme complex and one dinitrosyl iron complex (DNIC). Herein, we describe the structural and electronic characterization of non-heme iron complexes with pre-formed hyponitrite. Utilizing derivatives of the tris(2-pyridylmethyl)amine (TPA) ligand, we were able to study the coordination chemistry of hyponitrite with non-heme iron centers. Our work provides us the opportunity, for the first time, to obtain structures of non-heme iron-hyponitrite complexes and study their reactivity.

Poster 63

Optimization of NiFe electrocatalysts for water-splitting reactions

Indiana State University

Presenter: Mikal Lange (Undergraduate Student)

Coauthors: Fan Zuo*

Abstract:

As moving into the future, a transitioning away from fuels that produce greenhouse gasses to clean energy is happening. One fuel humanity is looking into is hydrogen gas that is specifically made from water, and returns to H2O after its consumption. It is necessary to use a catalyst to split H2O into H2 and O2. The gold-standard electrocatalysts are precious metals like platinum, but these catalysts are very expensive and low reserves in earth crust. Research in our group is focused on optimizing catalysts that are electrodeposited onto Nickel foam. Herein, extensive efficiency and stability tests were performed on these catalysts synthesized by altering their composition, pH, and temperature at the time of synthesis. It is interesting to find that NiFe catalysts with a higher Fe/Ni ratio are more efficient, catalysts synthesized in more alkaline environments are more stable, and lower synthetic temperature could effectively improve stability and efficiency of catalysts. These findings guide us toward creating a cheap and easy-to-make catalyst that rivals the efficiency and stability of platinum. Coupling this green hydrogen gas production route with the cutting-edge energy conversion techniques in fuel cells will allow us to create 100% clean fuel for vehicles, and remedy the rapid developing climate problems.

Poster 64

Synthesis and Characterization of Phosphinoamide-Supported Group 4/Cobalt Heterobimetallic Compounds

The Ohio State University

Presenter: Nathanael Hunter (Graduate Student)

Coauthors: Christine M. Thomas*

Abstract:

Early-late heterobimetallics have been shown to exhibit a wide range of reactivity, through several different pathways. The presence of an early metal has been effective in the stabilization of a highly-reactive, low-valent late transition metal. The Lewis acidity of the early metal in combination with this has proven useful in binding substrates and directing small molecule activation. In this work, we explore the modification of the coordination environment around a series of M/cobalt (M = group 4 metal) bimetallic center and how it relates to electronic structure, bonding, and reactivity toward small molecules.

Poster 65

Synthesis of Amino Alkoxide Alanes for Atomic Layer Deposition of Aluminum Metal

Wayne State University

Presenter: Nilanka Sirikkathuge (Graduate Student)

Coauthors: Charles H. Winter*

Abstract:

Synthesis of Amino Alkoxide Alanes for Atomic Layer Deposition of Aluminum Metal Nilanka W. Sirikkathuge, Charles H. Winter* Department of Chemistry, Wayne State University, Detroit, MI 48202 United States Growth of atomically precise, conformal aluminum (Al) metal films is desired due to their applications in microelectronics, plasmonics, energetic materials, and hydrogen storage processes. Thermal atomic layer deposition (ALD) can be employed to grow high quality films through sequential and self-limiting surface reactions. Al metal possesses a very negative electrochemical potential (Al3+ + 3e- ↔ Al, Eo = -1.676 V), which necessitates the use of powerful, thermally stable reducing agents as co-reactants during thermal ALD processes. There have been only two literature reports on the thermal ALD of Al metal films, both of which came from our laboratory. Considerable work remains to be carried out to develop strongly reducing co-reactants that can be used for Al metal ALD. In the present work, we will describe the synthesis, characterization of amino alkoxide alanes of the formula [LAlH2]2 where L is a monoanionic, bidentate oxygen or nitrogen ligand. The applicability of these complexes as reducing agents in the thermal ALD of Al and other metal deposition processes will be overviewed.

Poster 66

Ligands on solid support resin for separation of rare earth elements

Wayne State University

Presenter: Nuwangi Kulasekara (Graduate Student)

Coauthors: D. Nuwangi Kulasekara, Arvind B. Kajjam, Timothy M. Dittrich and Matthew J. Allen*

Abstract:

Rare earth elements (REE) which comprise 17 elements are key components in permanent magnets, phosphors, catalysts, batteries, and many other devices that are used in clean energy technologies. However, due to similar physical and chemical properties of REEs, the extraction and separation have been a challenge with the growing demand. The most common oxidation state of lanthanides is +3, however, some elements can be reduced to +2 state under an oxygen-deficient environment. Resultantly, similar coordination chemistry and size between +3 lanthanides can be altered by changing the oxidation state. Therefore, we hypothesized that if 2.2.2-cryptand is covalently linked to a resin as a solid support, lanthanides can be separated by size and charge because 2.2.2-cryptand favorably binds to divalent lanthanides over trivalent lanthanides. To test the hypothesis, we grafted 2.2.2-benzo-isothiocyanate onto an amine-based resin and test for a mixture of EuII and GdIII which have the most and least positive reducing potentials among the lanthanides. We will present our progress towards testing our hypothesis to separate a mixture of EuII and GdIII using a cryptand modified resin.

Poster 67

Selective Mizoroki–Heck Reactions on Allylamines

University of Toledo

Presenter: Olutayo Farinde (Graduate Student)

Coauthors: Michael C. Young*

Abstract:

Over 80% of the top-selling small molecule drugs contain at least one phenyl ring, and in addition 80% of small molecule drugs contain nitrogen. Incidentally, cinnamylamines, which contain at least one phenyl ring and one nitrogen, are of great importance in natural products, as well as in medicinal, agricultural, and even in materials chemistry. Palladium-catalyzed organometallic transformations, though a powerful tool for synthetic chemistry, are difficult to perform on free amine-containing substrates due to the substrates' susceptibility to side reactions such as oxidation via β-hydride elimination, allylic deamination, intramolecular cyclization, and even N-functionalization. However, it is critical to develop methods that are compatible with amines without the need for protection and deprotection of the reactive nitrogen, particularly in pharmaceuticals, where the protecting group can interfere with the physical and chemical properties of the drug targets. As a result, a Pd-catalyzed regioselective functionalization of unprotected allylamines was sought. Previous work has shown that for allylamines it is possible to achieve selective γ-arylation by use of CO2 as a transient protecting group, however, stereoselectivity was poor due to competing pathways between a C–H activation and a nanoparticle-catalyzed Mizoroki-Heck reaction which stereospecifically gave Z and E-products respectively. To improve the use of this chemistry for pharmaceutical production, there is a need to develop a method to obtain selective products. A better understanding of the controlled Pd-catalyzed reactions of allylamines can also be used to access new bond disconnections.

Poster 68

Heteroleptic dirhodium(II,II) paddlewheel complexes for proton reduction

The Ohio State University

Presenter: Piyush Gupta (Graduate Student)

Coauthors: Claudia Turro*

Abstract:

Bimetallic complexes have been shown to exhibit high electrocatalytic and photocatalytic activity, specifically for CO2 activation and proton reduction. Dirhodium compounds having a paddlewheel structure with a Rh-Rh bond have become promising candidates for these reactions with high turnover numbers and catalytic efficiency. Recently, diimmine complexes with short metal-metal bond distance ([Rh2(DToLF)2(bncn)2]2+) have been shown to possess long lived excited state and work as a single molecular photocatalyst for proton reduction under red light with good turnover number. The mechanism behind their activity is still not completely known. To further understand the mechanism and thus increase the efficiency of such compounds, the present work focuses on the preparation of complexes with uncapped axial sites with the aim of reducing the intermetallic distance by varying the bridging ligands. Reducing the Rh-Rh bond distance should result in increasing the energy level of the Rh2(σ*) molecular orbital leading to longer lived excited states. Two different types of heteroleptic compounds of the form cis-[Rh2(DPhF)(OAc)(bncn)2][BF4]2 and cis- [Rh2(DPhF)(OAc)(bncn)(CH3CN)2][BF4]2 (DPhF= N,N′-Diphenylformamidine; OAc= CH3COO-; and bncn= benzo[c]cinnoline) have been synthesized and are being studied. The latter builds a pathway to form tetraheteroleptic paddlewheels. The poster discusses the synthetic routes for preparation of these complexes along with their crystal structures, DFT calculations and spectroscopic properties.

Poster 69

Properties of amine-containing ligands that are necessary for visible-light-promoted catalysis with divalent europium

Wayne State University

Presenter: Ramiro Barraza (Graduate Student)

Coauthors: Ramiro Barraza Jr., Alexander Sertage, Aravind B. Kajjam, Jacob C. Lutter Cassandra L. Ward, H. Bernhard Schlegel, and Matthew J. Allen*

Abstract:

Photoredox catalysis is a growing field in which photoactivated precatalysts initiate reactions. Light-mediated conditions enable access to reactions that would be otherwise available under harsher conditions, and the use of visible light minimizes the occurrence of unwanted side reactions potentially caused by higher energy UV light. Our laboratory recently reported a europium(II)-containing cryptate that absorbs blue light and promotes photoredox activity in the excited state. The bathochromic shift, relative to other Eu(II)-containing complexes, was found to be a result of coordinating amines that are stronger-field donors than the ethers of other cryptates. We hypothesized that the cryptand framework is not necessary for catalysis. To understand how the structure of amine-containing ligands affect the photoredox properties of Eu(II)-containing complexes, we studied the effect of various amine-containing ligands on the photoredox properties of Eu(II). The scope of the ligands studied was aimed at observing the effects of varying degrees of functionality of each amine, the effects of macrocycles, and the effects of varying ligand denticity. Ligands that contain secondary amines bathochromically shift the absorbance of EuCl2 relative to ligands that contain primary or tertiary amines. Similarly, ligands of larger denticity have a larger bathochromic shift of the absorbance than ligands of smaller denticity. We observed that macrocyclic ligands have a larger effect on the absorbance of EuCl2 than nonmacrocyclic ligands. Also, we observed the photoredox reactivity of four new EuII-containing complexes. These observations are potentially influential in understanding ligand properties that promote the use of EuII in visible-light-promoted photoredox catalysis.

Poster 70

Experimental Insights on the Mechanism of Nickel-Substituted Rubredoxin

The Ohio State University

Presenter: Riley Stein (Undergraduate Student)

Coauthors: Ashlee E. Wertz, Hannah S. Shafaat*

Abstract:

Biological systems can perform transformative energy conversion reactions but are typically limited by complexity and stability. Simpler and more robust artificial enzyme mimics can offer insights into these complex biological systems and suggest features of efficient catalysts for future rational design. Nickel-substituted rubredoxin (NiRd) is one such artificial enzyme that is a functional and structural mimic of the [NiFe] hydrogenase. Experimental evidence of the mechanism and catalytic intermediates has remained both challenging and elusive. The mechanism can be experimentally probed by quantitative protein film electrochemistry (qPFE). Buffer systems are an important factor in catalysis as they serve as a proton donor in solution. The role of buffer on catalysis was experimentally explored by varying buffer pKa and charge and its effect on catalysis was investigated with qPFE. Of the buffers surveyed, pKa was found to have a weak effect on catalysis. Additionally, current work for identifying catalytic intermediates is presented. Optical and EPR spectroscopic techniques are being pursued for characterizing reduced states and putative catalytic intermediates. Collectively, these results provide experimental insight on the mechanism of NiRd as well as its intermediates, offering evidence to previous computational modeling.

Poster 71

Axis-dependent conduction polarity in bulk crystals of PdSe2, an air-stable 2D semiconductor

The Ohio State University

Presenter: Ryan Nelson (Graduate Student)

Coauthors: Joshua Goldberger*

Abstract:

Axis-dependent conduction polarity, or goniopolarity, is an electronic property of a small, but growing, group of materials, in which the charge polarity of conduction is different (p-type or n-type) depending on the direction of travel through the crystal. Most materials that exhibit goniopolarity are metals, and very few semiconducting materials with this effect exist. Here, we establish that PdSe2, a 0.5 eV band gap semiconductor that is air- and moisture-stable exhibits goniopolarity. We show that single crystals with >5 mm scale dimensions are readily formed in Se flux. Lightly electron doped PdSe2 exhibits p-type conduction in the cross-plane direction and n-type conduction in the in-plane directions, in agreement with DFT calculations. The cross-plane thermopower peaks at around 600 μV·K-1 near room temperature while the in-plane thermopower is -60 μV·K-1. Lightly p-doped samples lose the goniopolarity, showing p-type thermopower in both the in-plane and cross-plane directions, where the room temperature in-plane and cross-plane thermopowers sit at 600 - 800 μV·K-1. Finally, we show that goniopolarity is sensitive to the ratio of carrier concentrations between holes and electrons and the ratios where goniopolarity can exist depend on the degree of effective mass anisotropy.

Poster 72

Lewis acid-imparted divergent reactivity of nickel imido and related species

University of Michigan

Presenter: Sang gyu Seo (Postdoc)

Coauthors: Baolu Wang, Cuijuan Zhang, Jiaxiang Chu, Nathaniel K. Szymczak*

Abstract:

Late first-row transition metal imido complexes have been actively studied for their reactivities in C-H activation and nitrene group transfer reactions. Our group has been working on incorporating Lewis acid functional groups in the metal's secondary sphere in order to impart a divergent reactivity and selectivity. This poster presentation will describe the synthesis of a series of nickel diphosphine complexes with an appended borane, and the formation of imide species from organoazides. We will show a nickel imide species formed from 1-azidoadamantane exhibits reactivity toward sp2 C-H activation of arenes to form LNi(Ar)(NHAd) as a result of an appended Lewis acid. This presentation will outline experimental and computational efforts in elucidating the nature of the reactive species and illustrate principles of ligand design that can be used to tune reaction selectivity. We will also present our ongoing endeavours in utilizing low valent nickel complexes for other bond activation reactivities.

Poster 73

Strategic transposition: non-selective lanthanide binding followed by sequential release enables efficient recovery of rare-earth elements

Wayne State University

Presenter: sara worku (Graduate Student)

Coauthors: Sara A. Worku, Timothy M. Dittrich, Jennifer L. Stockdill,* and Matthew J. Allen*

Abstract:

Rare-earth elements are ubiquitous in modern society, including uses in catalysis, electric cars, and cell phones. Driven by the importance of rare-earth elements, there is a need for a stable supply of rare earth elements. Recycling and isolation of rare-earth elements is one pathway to address some of the demand for rare-earth elements, but both approaches require selective separation of rare-earth elements from mixtures. Although many methods have been introduced to separate rare-earth elements, the similarity in coordination chemistry among rare-earth elements poses challenges to selectivity. Thus, there is a need for methods that can selectively separate each rare-earth element from other rare-earth elements. We hypothesized that if a mixture of different rare-earth elements is coordinated to diethylenetriaminepentaacetic-acid-functionalized electrodes, then the elements can be sequentially eluted in the order of electrochemical potential due to the differences in dissociation kinetics between trivalent and divalent rare-earth elements. We have successfully modified electrodes with diethylenetriaminepentaacetic acid and reduced europium from the electrode surface. Here, we present our progress toward the elusive goal of selective isolation of rare-earth elements from solution.

Poster 74

A Self-supported Dirhodium(II) Heterogeneous Catalyst: An Efficient Nitrene Transfer

The University of Toledo

Presenter: Satheesh Vanaparthi (Postdoc)

Coauthors: Michael C. Young*

Abstract:

A homogeneous catalyst displays good activity, but non-recycle in catalysis. Whereas a heterogeneous catalyst can be easily reused. Homogeneous metal catalysts are mostly being used in the fine chemical synthesis due to their high activity. However, their applications are prohibited since the challenging recovery in the synthesis of pharmaceutical products, even smallest metal contaminations must be avoided both for medical and legal reasons. On the other hand, recycling the catalyst, metals like Platinum group are to be recycled owing to their most expensiveness. Self-supported catalysts hold fundamental advantages over other immobilized catalyst concerning high density of catalytic sites with uniform distribution. Considering the advantages of heterogeneity of precious metals, we present here, the synthesis and characterization of a self-supported dirhodium polymer-based catalyst, which blends stability with high catalytic activity for the nitrene transfer.

Poster 75

Solid-State and Solution-Phase Characterization of SmII-Aza[2.2.2]cryptate and its Methylated Analogue

Wayne State University

Presenter: Sergely Steephen Bokouende (Graduate Student)

Coauthors: Sergely Steephen Bokouende, Tyler Jenks, Cassandra L. Ward, Aravind Kajjam, and Matthew J. Allen*

Abstract:

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

Poster 76

Hydrogen atom transfer from an aquo-adduct of a reduced polyoxovanadate cluster

University of Rochester

Presenter: Shannon Cooney (Graduate Student)

Coauthors: A. A. Fertig, M. R. Buisch, E. M. Matson*

Abstract:

Oxygen atom vacant sites at the surface of reducible metal oxides have been studied given their relevance in energy storage and conversion processes. However, the heterogeneous nature of the material prohibits in situ studies from being performed to elucidate the mechanism of reactivity at these surface defect sites. Previously, our group has reported the uptake of hydrogen atoms on the surface of polyoxovanadates via hydrogen atom transfer (HAT). The proposed mechanism resulted in two subsequent hydrogen atom transfers followed by an intermediate VIII-OH2 before being displaced by an acetonitrile ligand. Interested in studying the effect of substituting a sterically bulky and electron-withdrawing calix arene ligand on a POV with HAT vacancies, the VIII-OH2 intermediate previously proposed was isolated, the aquo stabilized by two hydrogen-bonded tetrahydrofuran molecules. Isolation of [(calix)V6O5(OH2)(OMe)8] allowed for determination of bond dissociation free energy for the O-H bonds of the surface aquo moieties (62.4 kcal/mol), revealing a significant weakening from that of water (108 kcal/mol). Hydrogen atom transfer reactions from the aquo-adduct of the reduced assembly were investigated; mechanistic studies revealed the reaction is first order with respect to cluster and hydrogen atom acceptor and Eyring analysis shows that the cluster undergoes concerted proton coupled electron transfer to regenerate the oxidized cluster, [(calix)V6O6(OMe)8], and the hydrogenated product, giving insight to a novel pathway for HAT at the surface reducible metal oxides

Poster 77

Photoelectrocatalytic and Electrocatalytic Chloride Mediated Selective Ethanol Oxidation in Solvent-free and Aqueous Conditions

University of Michigan

Presenter: Siqi Li (Graduate Student)

Coauthors: Andrew G. Breuhaus-Alvarez, Bart M. Bartlett*

Abstract:

Alcohols are the major derivatives from the conversion of agriculture-based biomass feedstocks with industrialized production. While direct alcohol oxidation is limited by slow reaction kinetics and irreversible substrate adsorption, indirect oxidation carried out by redox mediators can circumvent these problems. Chloride anion has been considered as a promising mediator for this purpose thanks to its fast kinetics as well as the generation of active species that can readily oxidize substrates. With spin-coated HxWO3 semiconductor photoelectrodes, selective chloride oxidation to hypochlorous acid has been achieved, which subsequently oxidizes ethanol to acetaldehyde and acetic acid. Despite the high integrated yield, acetaldehyde is found to be a long-lived intermediate with the acid as the thermodynamic product. Stopping the reaction at the 2-electron aldehyde products remains as a key challenge that requires alternation in mechanism. By shifting into neat ethanol (solvent-free condition) and using an alkylammonium chloride electrolyte on a glassy carbon electrode, 1,1-diethoxyethane (DEE), which could serve as a protective platform for acetaldehyde from overoxidation, was prepared electrochemically with a high and stable current density >15 mA/cm2 and a high faradaic efficiency > 95%. UV-vis spectroscopy reveals the generation of an ethyl hypochlorite intermediate as the only chloride oxidation product, which decomposes unimolecularly to release HCl and acetaldehyde. In the presence of acid, acetaldehyde undergoes nucleophilic attack from the ethanol solvent and forms DEE. Such a scheme provides a novel mediated electrochemical approach with high atom economy for the selective oxidation of other alcohols with a series of abundant and inorganic mediator.

Poster 78

Earth abundant elements as photosensitizers; cyclometallation as a strategy for extending excited state lifetimes

The Ohio State University

Presenter: Spencer Burton (Graduate Student)

Coauthors: Claudia Turro*

Abstract:

In the search for clean energy, the abundance of elements such as iron, cobalt and nickel in the earth's crust make them attractive candidates for large scale industrial applications that are both affordable and sustainable. Due to contracted d orbitals of third row transition metals, low lying metal centered states exist which allows for ultrafast deactivation of excited states. This inhibits charge transfer ability, hindering their usefulness in many energy applications. An approach to overcome this problem is the use of strong field ligands to raise the energy of the metal centered states above that of the charge transfer state, thus removing the states that promote ultrafast relaxation. Cyclometallation is an extension of this strategy and is predicted to suppress the deactivation pathways through metal centered states to provide modest excited state lifetimes. Presented here is an experimental and computational study of a series of transition metal complexes, M(ppy)2L (M = Co(III), and L = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) or 1,12-diazaperylene(DAP)), with 2-phenylpyridine (ppy) functioning as cyclometallating bidentate ligands. The focus of the poster is on preliminary computational data of the cyclometallated cobalt series, as well as initial lifetime, absorption and emission data that has been collected thus far.

Poster 79

Copper Catalyzed sp3 C-H Functionalization for C-C Bond Formation

Michigan State University

Presenter: Ting-An Chen (Graduate Student)

Coauthors: Otome E. Okoromoba, Eun Sil Jang and Timothy H. Warren*

Abstract:

Direct sp3 C-H functionalization to form new C-C bonds represents an attractive strategy to expand access to new synthetic space containing both simple and complex organic molecules. Employing catalysts based on earth abundant copper, we will discuss our approach that involves radical relay catalysis to generate new C-C bonds. Initially focusing on C(sp3)-C(sp3) bond formation, we outline a system utilizing di-tert-butyl peroxide that generates versatile [CuII]-OtBu intermediates. Acid-base reactions with substrates possessing mildly acidic □-C-H bonds such as acetophenone give reactive [CuII](enolate) intermediates. These copper(II) enolates capture radicals R• formed via H-atom abstraction of sp3 C-H substrates R-H by tBuO• to give □-alkylated ketones. The radical nature of this reaction enables the formation of crowded 4° carbon centers difficult to form via electrophile-nucleophile pathways. DFT studies support synthetic studies that reveal that the copper(II) enolate intermediate may dimerize to form 1,4-diketones. Exploratory studies also reveal that related copper(II) organometallic intermediates can be exceptionally reactive towards H-atom abstraction from sp3 C-H bonds, opening up new mechanistic opportunities for C-C bond formation via sp3 C-H functionalization.

Poster 80

Optimization of copper complexes for the study of the use of ammonia as a fuel

Michigan State University

Presenter: Uran Iwata (Undergraduate Student)

Coauthors: Timothy Warren*

Abstract:

Ammonia has been identified as a potential carbon-free fuel due to its high energy density compared to other carbon-free fuels and its high accessibility regardless of the consumers' status and living place. Therefore, it is important to fully understand how ammonia can be used as a fuel. To do so, the most important reaction step when consuming ammonia as a fuel, the nitrogen-nitrogen bond formation, is studied using copper complexes that contain a nitrogen atom. The goal of my research is to optimize a copper complex by changing its substituents to enable the study of the nitrogen-nitrogen formation mechanism. In this project, the effect of the different substituents on the copper complex was investigated in terms of spin density on the nitrogen atom and the change in free energy of the nitrogen-nitrogen bond formation reaction. A computational modeling method called the Density Functional Theory was used to investigate this. In my poster presentation, I will review the previous studies of the optimization of the copper complex and how it led to my current project. I will also present the data collected, analyze it, and share my future research plans to further optimize the complex to achieve the research goal.

Poster 81

Length vs. strength of the three-center M•••B–H bond in the heteroleptic scorpionate complexes [(Tp3R,5R)M(Bp3R',5R')] (R = Me, Ph; R' = H, Me, Ph; M = Mn, Fe, Co, Ni)

Ohio University

Presenter: Vahdat Jahed (Graduate Student)

Coauthors: Ahmed Aboelenen, Tapash Deb and Michael P. Jensen*

Abstract:

Heteroleptic scorpionate complexes of the type [(Tp)M(Bp)] (Tp = hydrotris{pyrazolyl)borate; Bp = dihydrobis{pyrazolyl)borate; M = Mn - Ni) are nominally 5-coordinate, with a pentaza ligand set in a distorted square-pyramidal geometry. Tilting of the Bp ligand with respect to the equatorial plane enables a pseudo-axial bonding interaction of the endohedral B-H bond with the chelated metal ion. The distance of the M-H-B interaction can be controlled by varying the substituents on the 3-position of the Tp and Bp ligands (i.e., 3R = Me, Ph; 3R' = H, Me, Ph) proximal to the metal. The resulting bond distances are quantified in X-ray crystal structures and the relative strength of the interaction is assessed by trends in highly sensitive paramagnetic contact shifts and in B-H stretching energies. The issue of length vs. strength is thus determined in these 3-center bonding interactions. Strikingly, some degree of interaction is suggested by DFT calculations at M-HB separations up to 3.5 Angstrom, and this is reflected in the experimental data.

Poster 82

Elucidating the structure of a reactive Ni(IV)(O)(TAML) species with spectroscopy and density functional theory calculations

University of Michigan

Presenter: Virginia Larson (Graduate Student)

Coauthors: Deepika Karmalkar, Jason Shearer*, Wonwoo Nam*, Nicolai Lehnert*

Abstract:

High valent transition metal-oxygen species are often implicated as key intermediates for bioinorganic oxidation reactions in proteins and renewable energy related reactions. While these intermediates are often invoked, detailed studies of the geometric and electronic structures of these species are rare. High valent cobalt-, nickel-, and copper-oxygen bonds are unstable, reactive, and often have significant oxyl character. This is due to the so-called “oxo-wall”, where populating the π-antibonding molecular orbitals of a low spin MIV-O bond electronically forbids a formal metal-oxo double bond in tetrahedral symmetry for metals of groups 9 and higher. I will present our collaborative studies with the Nam and Shearer groups of a NiIV(O)(TAML) species, especially focusing on how spectroscopic characterization and density functional theory calculations inform our understanding of the geometric and electronic structure of this unstable intermediate. This species, formed from NiII(O)(TAML) with an oxo-atom donor molecule, iodosylbenzene, and acid, is reactive for C-H activation and oxo-atom transfer. It is characterized by UV-Visible spectroscopy, electron paramagnetic resonance, X-ray absorption spectroscopy, extended X-ray absorption fine structure, and magnetic circular dichroism variable temperature variable field spectroscopy. Density functional theory (DFT) on suspected structures and comparing calculated properties with this wealth of data, informs our understanding of the species. We have elucidated that this reactive species is a Ni(O)(OH)(TAML) species, agreeing well with the experimental spectroscopic data. Spectroscopic data interpretation, DFT calculations, and discussion of the electronic properties of this NiIV-oxo complex will be presented.

Poster 83

Synthesize and Photocatalytic Study of Colloidal Zinc Cobalt Nanocrystal Prepared from A Solvothermal Method

University of Michigan

Presenter: Wanrui Xie (Graduate Student)

Coauthors: Siqi Li, Bart Bartlett*

Abstract:

Nanoparticles with unique morphologies and chemical patterns are essential for various photoelectronic and photocatalytic applications. It is crucial to understand how to control the structure of particles to tune and utilize their light-absorbing ability for renewable energy purposes. A previous study demonstrated that colloidal zinc ferrite nanocrystals could be synthesized by treating a heterobimetallic triangular complex, as a single source precursor, under the solvothermal reaction condition.1 On the other hand, Cobalt has a similar size and charge to iron but is equipped with phenomenal properties for catalysis. Thus, we seek to develop the synthesis of colloidal Zinc Cobalt nanocrystals under adapted conditions as we did for Zinc Iron Nanocrystals. Adjustments to synthesis protocol result in different sizes of nanocrystals, which are required by various applications as their properties change with size. In this case, the size control of the Zinc Cobalt nanocrystals is achieved by adjusting the oleic acid and oleylamine ligands and reaction temperature for the solvothermal step. TEM, EDS, UV-Vis, and PXRD have been used to characterize the synthesized particles. Photocatalytic activity of the as-synthesized nanocrystals has also been tested under simulated solar irradiation for dye degradation reaction.

Poster 84

Near Infrared-Activatable Platinum-Based Anticancer Agents

Kent State University

Presenter: Wjdan Jogadi (Graduate Student)

Coauthors: Wjdan Jogadi, Parmeet Multani, Yaorong Zheng*

Abstract:

In this study, we present a new design of near infrared (NIR)-activatable Pt(IV)-based anticancer agents. The photoactivatable Pt(IV) prodrug approach is a promising strategy for engineering novel metallodrugs with high efficacy and low systematic toxicity. The octahedral low spin d6 Pt(IV) complex is more inert to ligand substitution than the Pt(II) counterpart, therefore being “inactive”. Light irradiation converts the photoactivatable Pt(IV) species to the more labile, cytotoxic Pt(II) product in a spatio-temporal manner, therefore enhancing efficacy and minimizing systematic toxicity. The major drawback of reported photoactivatable Pt(IV) prodrugs is that they require high-energy UV-vis light for activation, and such irradiation has very limited tissue penetration capability and is not suitable for phototherapy. NIR activation is highly sought-after for phototherapy, due to deep tissue penetration. In this project, we utilized a copper-free click reaction approach to develop a novel NIR-activatable Pt (IV) prodrug. The prodrug was synthesized by conjugating doxorubicin to the Pt (IV) linker and Cy7 dye via click reactions. This Pt (IV) prodrug can be photoactivated by NIR irradiation triggering photoreduction to release the cytotoxic Pt (II) and doxorubicin. Moreover, The Pt (IV) complexes exhibited stability under physiological conditions in the dark and can release the payloads upon irradiation (730 nm). In addition, upon NIR-irradiation, the complex readily induced cytotoxicity and triggered cell death in cancer cells, as evidence by live-cell imaging. Overall, we demonstrated the novel design of controllably activated Pt (IV) prodrugs that shows a sustained drug release upon irradiation, exhibiting cytotoxicity in cancer cells.

Poster 85

Elucidating Structures of Mn/Fe Metallocofactors in Point-Mutated Active Sites of the R2lox Protein

The Ohio State University

Presenter: Yuri Lee (Postdoc)

Coauthors: Joseph M. Hazel, Yunqiao J. Gan, Jonathan D. McHenry, and Hannah S. Shafaat*

Abstract:

Oxidative processes using molecular oxygen generally occur within diiron-containing active sites in the ferritin-like proteins. However, recent discoveries suggest heterobimetallic Mn/Fe active sites also perform oxygen-dependent reactions, for example, hydrocarbon oxidation. The Mn/Fe site in the R2-like ligand-binding oxidase (R2lox) catalyzes the selective two-electron oxidation of the tertiary C–H bond of valine to generate a tyrosine-valine cross-link. Similar oxidative reactivity by a Mn/Fe cofactor has not been observed in other proteins. As an example, the heterobimetallic Mn/Fe cofactor found in the R2 subunit of class Ic (R2c) ribonucleotide reductases (RNRs), which shows a very similar active site structure with that of R2lox, performs a long-range radical transfer. This discrepancy in reactivity implicates a yet-unresolved geometric and electronic structure for the cross-link formation reaction in the R2lox protein. To elucidate the molecular level elements contributing to this reaction pathway, we characterized geometric parameters of point-mutated active sites of R2lox in solution phase using Mn K-edge X-ray absorption spectroscopy. Critical amino acid sites in the R2lox active site, Y175 and Y162, were selected to perturb (i) the hydrogen bonding network in the secondary sphere and (ii) the tyrosine-valine cross-link formation, respectively. The experimental data show variances among the point-mutated active sites, suggesting selective structure-reactivity relationships to carry out the two-electron oxidation at the heterobimetallic Mn/Fe active site of R2lox. This information on selective structure-reactivity relationships can be applied to design sustainable catalysts for multi-electron redox processes that use earth-abundant transition metals and “green” oxidants like O2.

Poster 86

Electrocatalytic Ammonia Oxidation by a Low Coordinate Copper Complex

Michigan State University

Presenter: Md Estak Ahmed (Postdoc)

Coauthors: Pokhraj Ghosh, Mahdi Raghibi Boroujeni, Christine Greene, and Timothy H. Warren*

Abstract:

Ever increasing greenhouse gas emissions and global energy demands motivate the development of carbon free, sustainable energy sources. While hydrogen has attracted much attention, practical limitations connected to distribution challenges call for alternative approaches. Owing to its high energy density and established global production and distribution networks, ammonia (NH3) is an especially appealing energy carrier. Thus, there is growing need for catalysts that electrocatalytically oxidize ammonia for fuel cells or on-demand hydrogen production that produce only nitrogen (N2) as a byproduct. We describe the electrocatalytic oxidation of ammonia using molecular complexes based on Earth-abundant copper. Electrochemical studies of a□□-diketiminato copper(I) ammonia complex [CuI]-NH3 reveal its robustness as an electrocatalyst for ammonia oxidation in 1.3 M NH3 solution in MeCN at moderate overpotential (700 mV) with high turnover frequency (ca. 940 h-1). Detailed mechanistic studies supported by synthesis and computation reveal that oxidation of [CuI]-NH3 to {[CuII]-NH3}+ enables the deprotonation of the cationic copper(II) amine complex in the presence of excess NH3 to form the reactive copper(II) amide [CuII]-NH2 that undergoes swift N□N coupling to the dicopper(I) hydrazine complex [CuI]-NH2NH2-[CuI]. Controlled potential electrolysis experiments demonstrate long-lived catalytic activity while mechanistic studies point towards strategies to lower the overpotential and increase the electrocatalytic rate.

Poster 87

Copper (II) Mediated Reduction of Nitrate to Nitric Oxide by Thiols and H2S as Biologically Relevant Reductants

Michigan State University

Presenter: Pokhraj Ghosh (Postdoc)

Coauthors: Molly Stauffer, Md Estak Ahmed, Jeffery A. Bertke, Timothy H. Warren*

Abstract:

Nitrate fertilizer runoff poses chemical challenge for their remedial as relatively inert nitrate-oxoanions require stringent conditions for reduction. Molybdenum sites at nitrate reductase enzymes are known to reduce nitrate to nitrite. While various Cu or Fe based enzymes reduce nitrite to nitric oxide in denitrification or directly to ammonium, nitrate reduction is particularly challenging due to the weak coordinating ability of this polyoxoanion to transition metals. Particularly attractive would be nitrate reduction pathways that take advantage of the large biological pool of thiols (RSH) and hydrogen sulfide as reductants, perhaps revealing unexpected roles for nitrate in NO signaling. We report a □-diketiminato copper(II) nitrate complex [CuII](κ2-O2¬NO) that undergoes reduction to NO upon reaction with 4 equiv. thiols RSH. Reduction of nitrate (Nox = +5) to NO (Nox = +2) along with copper(II) to copper(I) occurs in an overall 4-electron process that produces 2 equiv. RS-SR. Detailed mechanistic studies reveal that [CuII](κ2-O2¬NO) undergoes 2-electron reduction to [CuII](κ2-O2¬N) with RSH to generate the corresponding sulfenic acid RSOH that rapidly reacts with excess thiol RSH to form RS-SR and H2O. Subsequent reaction of the [CuII](κ2-O2¬N) with RSH results in transnitrosation producing S-nitrosothiol (RSNO) and [CuII]-OH, that rapidly reacts with RSH to give [CuII]-SR that reacts with RSNO to give RS-SR, NO, and [CuI]. Computational studies underscore the favorability of O-atom transfer to thiols RSH due to the thermodynamic favorability of the RSOH sulfenic acid tautomer. Importantly, H2S also generates NO from [CuII](κ2-O2¬NO), revealing a new role for nitrate in H2S/NO crosstalk.