Missouri Inorganic Day

University of Missouri – St. Louis
Department of Chemistry and Biochemistry
May 5th, 2012
Meeting Location: Research Building R120, University of Missouri-St. Louis, North Campus

The Research Building is located between Stadler and Benton Halls. The meeting room and attached atrium is located on the first floor (R120). Parking is available in front of the Science Complex (Benton, Stadler, and Research). For more information see also: http://www.umsl.edu/maps.html

Map
Schedule

8:00 - 8:30  Breakfast, Research 120 Atrium and Patio

Morning Session I (8:40 - 10:00 AM):  Stephen M. Holmes, presiding

8:35 - 8:40  Opening Remarks

8:40 - 9:10  Amitava Choudhury, Missouri University of Science and Technology
“Search for New Cathode Materials for Li-ion Batteries Through Exploratory Solid-state Chemistry”

9:10 - 9:35  Patrick Desrochers, University of Central Arkansas
“Effect of a New Heteroscorpionate on the Catalytic Polymerization of Phenylacetylene.”

9:35 -10:00  Marcus Bond, Southeast Missouri State University
“Unusual Copper(II) Halide Structures Templated by Supramolecular Vicinal Trimethylpyridinium Diactions”

10:00 - 10:20 AM  Refreshments, Outside Research 120 Atrium and Patio

Morning Session II (10:20 - 11:40 AM):  Paul R. Sharp, presiding

10:20 - 10:40  Scott Graham, Saint Louis University
“Development of Ferracarborane Complexes for Bioanodes and Sensors”

10:40 - 11:00  Fengrui Qu, Washington University in St. Louis
“Stable Mononuclear iPrN4Pd(III) and Pd(IV) Complexes: Characterization and Reactivity Study”

11:00 - 11:20  James Carroll, University of Missouri-St Louis
“Study of Siloles and Optical Properties Related to Coordination with Metal Ions”

11:20 - 11:40  Wipark Anutrasakda, Washington University in St. Louis
“Synthesis and Reactivity of Azapentadienyl-Cobalt Complexes”

11:40 - 1:30  Lunch and Poster Session, Research 120 Atrium
Afternoon Session I (1:30 - 3:00 PM): Janet Braddock Wilking, presiding

1:30 - 2:00  Manashi Nath, Missouri University of Science and Technology
“Innovative Synthesis of Functional Nanomaterials: From Superparamagnets to Superconducting Nanostructures”

2:00 - 2:20  Yuanyuan Wang, Washington University in St. Louis
“Isolation of the Magic-Size CdSe Nanoclusters [(CdSe)₁₃(n-octylamine)₁₃] and [(CdSe)₁₃(oleylamine)₁₃]”

2:20 - 2:40  J. Andrew Surface, Washington University in St. Louis
“In Situ High Pressure and Temperature NMR Analysis of Spatial pH Variation During Metal Carbonate Formation from CO₂ with Implications for Carbon Capture, Conversion, and Sequestration”

2:40 – 3:00  Pushkar Shejwalkar, University of Missouri-St. Louis

3:00 - 3:20  Refreshments, Research 120 Atrium

Afternoon Session II (3:20 - 4:35 PM): Liviu M. Mirica, presiding

3:20 - 3:55  Lei Yang, University of Central Arkansas
“Type 1 Copper Site Synthetic Model Complexes with Increased Redox Potentials”

3:55 - 4:15  Daniel Pruitt, Saint Louis University
“Synthesis and Functionalization of Rhenacarboranes as Drug-Delivery Vehicles”

4:15 - 4:35  Anuj K. Sharma, Washington University in St. Louis
“Bifunctional Compounds for Controlling Metal-mediated Aggregation of Aβ42 Peptide”

4:35  Closing Remarks
Oral Presentations

1. **Search for New Cathode Materials for Li-ion Batteries Through Exploratory Solid-state Chemistry.** Amitava Choudhury, Department of Chemistry, Missouri University of Science and Technology

Rechargeable Li-ion batteries are already being considered to be used in the hybrid electric vehicle, plug-in hybrid electric vehicle and battery electric vehicle by the automobile companies. However, for these purposes the batteries are going to be quite large in size and hence needs to be safe enough for successful commercialization. Among the various cathode materials for Li ion batteries, LiFePO₄ is being touted as the safest cathode material because the phosphate (PO₄³⁻) moiety holds the oxygen atoms in the framework tightly through strong covalent bonds and imparts a structural stability. Hence, other phosphates or polyanions-based transition metal compounds are currently being explored to discover a cathode material that can outperform LiFePO₄. In our group we are exploring new compositions and structure types with various polyanions (XOₙⁿ⁻ = PO₄³⁻, SO₄²⁻, SiO₄⁴⁻, BO₃⁻ etc.) and transition metals (M = Ti, V, Mn, and Fe). Exploratory synthetic routes like hydrothermal and molten salt techniques are being employed to investigate these systems by systematically examining the phase diagrams. Towards this goal we have synthesized a series of new metal borophosphate materials, LiM(H₂O)₂B(PO₄)₃-H₂O (M = Fe, Mn, Co, and Ni). In this presentation preliminary data related to the synthesis, structure, magnetic property and Mössbauer spectroscopy of some of these compounds will be discussed.

2. **Effect of a New Heteroscorpionate on the Catalytic Polymerization of Phenylacetylene.** Patrick Desrochers, Department of Chemistry, University of Central Arkansas

Rhodium(I) scorpionates have demonstrated activity in the polymerization of phenylacetylene, a bright orange conjugated polymer with useful electrical and optical properties. Recently we reported the preparation of scorpionates (Tp’) anchored to polystyrene synthesis beads (bead-Tp’ in *Inorg. Chem.* 2011, p. 1931). These supported chelates offer the versatility of scorpionates to rapid-throughput combinatorial methods. This motivation led to the preparation of Tp’Rh(cod), where Tp’ represents the new tridentate chelate, hydrobis(3,5-dimethylpyrazolyl)(benzotriazolyl)borate. The catalytic activity of Tp’Rh(cod) toward phenylacetylene polymerization was compared to the established analogue Tp*Rh(cod) (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate). Marked differences in catalytic activity of these two complexes are ascribed to the variable hapticity (kappa2 vs kappa3) preferences of the two scorpionates. Completely different rates of activity were also noted when a more electron-rich monomer (p-H₃C-PhC≡CH) replaced phenylacetylene. The present results for homogeneous samples of Tp’Rh(cod) will help describe subsequent activity studies in heterogeneous supported systems, bead-Tp’Rh(cod). Here, the brightly colored polymer-product will allow rapid optical screening of favorable supported-catalyst candidates.
3. Unusual Copper(II) Halide Structures Templated by Supramolecular Vicinal Trimethylpyridinium Diactions. Marcus Bond, Southeast Missouri State University

Copper(II) halide compounds containing trimethylpyridinium (TMPy) cations with vicinal methyl groups (1,2,3- or 1,2,6-substituted) show unusual structures and behaviors, including thermochromism in $\text{A}_2\text{CuX}_4$ salts and a rare aquated complex in $(1,2,3$-TMPy)$_2\text{CuCl}_3(\text{H}_2\text{O})$. Two recently studied compounds from this family provide unprecedented structure types that appear to be templated by a strongly expressed supramolecular organic dication. $(1,2,3$-TMPy)$_2\text{Cu}_5\text{Br}_{12}$ forms layers of cross-hatched $\text{Cu}_5\text{Br}_{12}^{2-}$ quasi-planar oligomers between which are voids into which supramolecular dications nest. Within previously studied $\text{Cu}_n\text{X}_2^{2-}$ structures, quasi-planar oligomers stack in ways that can be rationalized in terms of the parent CuX$_2$ layer structure. But this structure defies such rationalization. $(1,2,6$-TMPy)$_2\text{Cu}_2\text{Br}_6$ contains isolated, non-planar $\text{Cu}_2\text{Br}_6^{2-}$ complexes formed around supramolecular dications. Since previous structures of $\text{Cu}_2\text{X}_6^{2-}$ dimers with planar organic cations show quasi-planar dimers stacked together, rather than isolated dimers, this structure provides, perhaps, the best example of templating by the supramolecular dications. Straining of the $\text{Cu}_2\text{Br}_6^{2-}$ dimer in order to accommodate the dications is evident from intermolecular Br...Br contacts significantly less than the sum of the van der Waals radii and Cu-Br-Cu bridge angles less than 90°.

4. Development of Ferracarborane Complexes for Bioanodes and Sensors. Scott Graham and Paul Jelliss, Department of Chemistry, Saint Louis University

We present the synthesis and application of various ferracarborane derivatives. The primary focus of this work revolves around exploitation of the reversible $\text{Fe}^{III/II}$ redox chemistry in ferracarborane sandwich complexes. Previous work has shown the ability of ferracarboranes to function as electron transfer mediators in a polymer-coated thin film glucose oxidase bioanode. Initially the mediator had been physically adsorbed onto the surface of the polymer. The present work has improved the stability of the electrode assembly by eliminating mediator leaching via covalent attachment to multiwalled carbon nanotubes. Efforts have been taken to improve the efficiency of the mediator by altering the reduction potential of the ferracarborane though bromination to more closely match the reduction potential of FAD, the redox cofactor of glucose oxidase. The bromoferracarboranes have been characterized, but need further functionalization before a more robust bioanode can be made. The second focus of this work investigates ferracarboranes as a fluorescence quenching agents for trisbipyridal ruthenium. Studies utilizing different solvents and different temperatures have been conducted to determine the quenching mechanism.

5. Stable Mononuclear iPrN4Pd(III) and Pd(IV) Complexes: Characterization and Reactivity Study. Fengrui Qu and Liviu Mirica, Department of Chemistry, Washington University in St. Louis

A new tetradentate ligand N,N´-di-iso-propyl-2,11-diaza[3,3](2,6)pyridinophane (iPrN4) was synthesized by a modified procedure reported for its t-butyl analog, tBuN4. A series of its mononuclear Pd complexes, (iPrN4)PdXY (X, Y = Me, Cl) were synthesized. Oxidation studies indicate that the tetradentate ligand iPrN4 was able to stabilize multiple oxidation states (PdII, PdIII, and PdIV) at the Pd center, which offered an unprecedented opportunity to probe the chemistry of these compounds in an identical coordination environment. The thermolysis and photolysis reactivity of these complexes were studied by NMR, EPR, and UV-vis spectroscopy. The unique aerobic reactivity of the iPrN4PdIIIme2 was also investigated extensively.
6. **Study of Siloles and Optical Properties Related to Coordination with Metal Ions.** James Carroll and Janet Wilking, Department of Chemistry and Biochemistry and the Center for Nanoscience, University of Missouri-Saint Louis

Siloles (silacyclopenta-2,4-dienes) are an important class of compounds, with unique optical properties due to a small HOMO-LUMO gap and conjugation with aromatic substituents. Such features make this compound class attractive to many applications, including chemical sensing, organic light-emitting diodes (LEDs), and photovoltaic devices (i.e., for use in solar cells). Most chemical sensing applications developed with siloles have centered on detecting volatile organic compounds. However, studies for detection of environmentally harmful metals, such as nickel, chromium, and mercury, have been slight. This presentation will focus on the interaction of siloles containing moieties that can coordinate with metal ions (e.g., amino functionalities). Several siloles have been synthesized and characterized by multinuclear NMR, UV-visible and fluorescence spectroscopies. The optical spectra of these compounds are compared for both the free siloles and their interaction with various metal ion solutions to test for selectivity and fluorescence enhancement or quenching.

7. **Synthesis and Reactivity of Azapentadienyl-Cobalt Complexes.** Wipark Anutrasakda and John R. Bleeke, Department of Chemistry, Washington University in St. Louis

We report the synthesis, structure, spectroscopy, and reactivity of the first examples of azapentadienyl-cobalt complexes. Treatment of (Cl)Co(PMe₃)₃ with potassium tert-butylazapentadienide leads to the production of ((1,2,3-η)-5-tert-butyl-5-azapentadienyl)Co(PMe₃)₃ (1). Compound 1 reacts with 1 equiv of P(OMe)₃ or CO to produce the ligand-substituted analogs, ((1,2,3-η)-5-tert-butyl-5-azapentadienyl)Co(PMe₃)₂[P(OMe)₃] (2) or ((1,2,3-η)-5-tert-butyl-5-azapentadienyl)Co(PMe₃)₂(CO) (3), respectively. Treatment of 1 with 1 equivalent of triflic acid (HO₂SCF₃) leads to protonation at the nitrogen center and production of (η⁴-4-tert-butylamino-butadiene)Co(PMe₃)₃'O₂(SCF₃)⁻ (4). Similarly, monoprotonation of 2 or 3 with triflic acid occurs at nitrogen, producing and (η⁴-4-tert-butylamino-butadiene)Co(PMe₃)₃[P(OMe)₃]'O₂(SCF₃)⁻ (5) or (η⁴-4-tert-butylamino-butadiene)Co(PMe₃)₃(CO)'O₂(SCF₃)⁻ (6), resp. Attempts to synthesize 5 or 6 from 4 (by treatment of 4 with excess P(OMe)₃ or CO) lead instead to displacement of tert-butylammoniobutadiene and prodn. of Co(PMe₃)₃[P(OMe)₃]'O₂(SCF₃)⁻ (7) or Co(PMe₃)₃(CO)₂'O₂(SCF₃)⁻ (8), respectively. Treatment of 2 with two equiv. of triflic acid results in double protonation at nitrogen, generating (η⁴-4-tert-butylammonium)Co(PMe₃)₃[P(OMe)₃]'O₂(SCF₃)⁻ (9). Compounds 1-4 and 6-9 have been characterized by single-crystal X-ray diffraction.
8. Innovative Synthesis of Functional Nanomaterials: From Superparamagnets to Superconducting Nanostructures. Manashi Nath, Department of Chemistry, Missouri University of Science and Technology

As the technology for designing miniaturized devices advances rapidly, nanomaterials are getting all the more attention as the appropriate functional components for the nano-devices with their applications ranging from electronics to pharmaceuticals. Of all the properties that are affected in the nano-scale, superconductivity and magnetism are the ones that are expected to show the most exotic alteration as function of reduced size. Among the superconductors, iron selenide and iron pnictides have created the most furors recently owing to the unexpected discovery of superconductivity in these families. We have directed our research towards synthesizing nanostructures of these superconductors and study the effect of size on the superconducting parameters like TC (critical temperature), JC (critical current density) and HC (critical field), all of which collectively define the usability of a superconductor. In this presentation I will show some results on FeSe superconducting nanocables and the effect of nano-structuring on the TC. Similar efforts towards creating iron pnictide based superconductors led us to the superparamagnetic FeAs@C core-shell nanoparticles which show an exceptionally high TB. This talk will focus on the synthetic strategies, detailed characterization and property studies of these novel nanostructures, and provide some insights into their applicability in practical devices.

9. Isolation of the Magic-Size CdSe Nanoclusters [(CdSe)$_{13}$(n-octylamine)$_{13}$] and [(CdSe)$_{13}$-(oleylamine)$_{13}$]. Yuanyuan Wang and W. E. Buhro, Department of Chemistry, Washington University in St. Louis

The preparation, isolation, stoichiometric characterization, and dissolution of purified (CdSe)$_{13}$ are described. We and others recently reported that (CdSe)$_{13}$ nanoclusters were intermediates in the synthesis of CdSe quantum belts (nanoribbons). We now demonstrate that a lamellar intermediate phase collected from the quantum-belt synthesis is [(CdSe)$_{13}$(n-octylamine)$_{13}$], the smallest, discrete, magic-size nanocluster of CdSe that has been observed. Kinetic data show that free, soluble [(CdSe)$_{13}$(oleylamine)$_{13}$] nanoclusters are released from the insoluble [(CdSe)$_{13}$(n-octylamine)$_{13}$] upon ligand exchange.

10. In Situ High Pressure and Temperature NMR Analysis of Spatial pH Variation During Metal Carbonate Formation from CO$_2$ with Implications for Carbon Capture, Conversion, and Sequestration. J. Andrew Surface, Sophia E. Hayes, and Mark S. Conradi, Departments of Chemistry and Physics, Washington University in St. Louis

Carbon dioxide geological sequestration is currently being explored and used as a long-term CO$_2$ storage alternative as part of the growing international carbon capture, conversion, and sequestration (CCCS) initiative. The success of this method relies on the formation of magnesium and calcium carbonates from reaction with CO$_2$ and water at the high pressures and temperatures that exist deep underground. There are many factors that affect the kinetics and success of these reactions including pressure, temperature, pH, and reactant availability due to physical transport limitations. Herein we describe a new state-of-the-art solid state NMR method which allows in situ spatial pH measurement of these reactions in near-geological reaction conditions. We will also discuss the implications of these spatial pH variations on the kinetics and formation of products as well as ex situ analysis of solid carbonate products.
11. Synthesis and Characterization of Iron(II) complexes of α-Imino Pyridine and Their Catalytic Application in Oxidation of Activated Methylene Group and Secondary Alcohols. Pushkar Shejwalkar and Dr. Eike B. Bauer, Department of Chemistry and Biochemistry, University of Missouri-St. Louis

Oxidation of relatively inert C-H bonds catalyzed by iron complexes has been a ‘hot topic’ of research in catalysis for a while. Current research is directed towards improvement in selectivity, relative ease and milder reaction conditions. Mimicking motifs found in nature have already shown to be catalytically active in the title reaction. Our group is particularly interested in nitrogen-based ligands that are easy to synthesize, tunable (sterically and electronically), and give better conversion towards the oxidation of C-H bonds. Here we report the use of ‘imine based’ bi-dentate ligand systems that are relatively unexplored, simple, rigid, and show increased resistance towards oxidation conditions compared to the corresponding amine. The electronic and steric properties of these ligands can be easily tuned. We synthesized a set of sterically and electronically tuned Fe(II) complexes of α-iminopyridines (L) of the general formula [Fe(OTf)₂L₂]. The new complexes were subsequently employed as catalysts in oxidations reactions utilizing tert-butylhydroperoxide (TBHP) at room temperature in 4 hr. The yields are moderate to good. The new complexes specifically oxidize benzylic CH₂ groups as well as secondary alcohols to the corresponding ketone. Primary alcohols and methyl groups are not oxidized under these conditions. Preliminary mechanistic investigations revealed the radical pathway and that the oxidation of benzylic CH₂ groups goes through a different pathway than the oxidation of secondary alcohols. We also present UV-Vis spectroscopic evidence for the formation of an [Fe-O-O-tBu] intermediate.

12. Type 1 Copper Site Synthetic Model Complexes with Increased Redox Potentials. Lei Yang and William B. Tolman, Department of Chemistry, University of Central Arkansas

Reactions of NaSCPh₃ with (R₃taen)Cu(OTf)₂ (R = Me, iPr; OTf = CF₃SO₃⁻) yield blue complexes identified as ((R₃taen)CuSCPh₃)(OTf) on the basis of UV-vis, resonance Raman, and EPR spectroscopy and ESI mass spectrometry. These complexes exhibit spectroscopic properties typical of type 1 copper sites in proteins, including diagnostic Sp → Cu(dx²-y²) LMCT transitions at ~610 - 630 nm and small A|| values in EPR spectra < 100 x 10⁻⁴ cm⁻¹. Cyclic voltammetry experiments revealed redox potentials for the complexes similar to several low potential type 1 copper proteins (e.g., azurin, stellacyanin) and ~0.5 V higher than previously reported model compounds. Thus, the new complexes mimic key aspects of both the structure and function of type 1 copper sites.

Rhenacarboranes and their derivatives provide an attractive area of research due to their ability to cross over the blood-brain barrier (BBB). As potential drug-delivery vehicle candidates, an array of these rhenacarboranes can be synthesized and functionalized via coupling to various amino acids and polypeptides. Our foremost objective is to synthesize a rhenacarborane complex functionalized with a pendant polyether side-chain containing a terminal target functional group (-OH/NH2) that will be able to bind with the desired polypeptide Met-enkephalin. Met-enkephalin is commonly known as opioid growth factor (OGF) and is present in biological systems in the central nervous system (CNS). OGF can then bind to opioid growth factor receptors (OGFr) which can lead to suppression. When connected to the rhenacarborane, OGF could be transported past the BBB and then biologically cleaved off the vehicle, allowing for distribution into the CNS. Recently, rhenacarborane derivatives with pendant amino or hydroxyl groups have been successfully synthesized with the capability to be coupled to the carboxylate functionality of several peptides. Various coupling methods are being examined to idealize both the success of coupling and the maximization of pharmacophore potency in vitro. During synthesis, all complexes and intermediate species were characterized by IR and NMR spectroscopy.


Abnormal interactions of Cu and Zn ions with the amyloid-β (Aβ) peptide are proposed to play an important role in the pathogenesis of Alzheimer’s disease (AD). Disruption of these metal–peptide interactions using chemical agents holds considerable promise as a therapeutic strategy to combat this incurable disease. Recent efforts in studying the Aβ-metal interactions have focused on small molecules, bifunctional chelators (BFCs), which can interact with the Aβ peptide and also bind the metal ions from the Aβ-metal species. Such bifunctional compounds should potentially lead to more effective therapeutic agents, as well as provide an increased understanding of the metal–Aβ associated neuropathology. We have been able to generate a that were designed following the linkage approach and contain metal-binding N-(2-pyridylmethyl)amine groups and amyloid-interacting 2-phenylbenzothiazole and o-vanillin molecular fragments. Our BFCs L1 and L2 exhibit high stability constants for Cu2+ and Zn2+ and thus are good chelators for these metal ions. In addition, they show strong affinity toward Aβ species. Both compounds are efficient inhibitors of the metal–mediated aggregation of the Aβ42 peptide and promote disaggregation of amyloid fibrils, as observed by ThT fluorescence, native gel electrophoresis/Western blotting, and transmission electron microscopy (TEM). Interestingly, the formation of soluble Aβ42 oligomers in presence of metal ions and BFCs leads to an increased cellular toxicity. These results suggest that for the Aβ42 peptide – in contrast to the Aβ40 peptide, the previously employed strategy of inhibiting Aβ aggregation and promoting amyloid fibril disaggregation may not be optimal for the development of potential AD therapeutics, due to formation of neurotoxic soluble Aβ42 oligomers.
Poster Presentations

1. Degradation Mechanisms of Prussian Blue Pigments in Paint Layers. Fernande Grandjean and Gary J. Long, Department of Chemistry, Missouri University of Science and Technology

Prussian blue is a modern synthetic pigment discovered in Berlin at the beginning of the eighteenth century. Prussian blue is a hydrated iron(III) hexacyanoferrate(II) mixed-valence complex whose color results from an intervalence charge transfer between the iron(II) and iron(III) ions when light is absorbed at ca. 700 nm. Because of both its highly intense color and its low cost, Prussian blue enjoyed immediate popularity among artists and was widely used as a pigment in paintings until the 1970s. However, the permanence of Prussian blue had already been questioned by the mid-eighteenth century, because it exhibits a tendency to fade in light and to turn green. The preparative methods were rapidly recognized as a contributory factor in the fading of the pigment. The main objective of this work is the identification of degradation mechanisms of Prussian blue pigments in paint layers. Prussian blue has thus been synthesized according to both ancient and modern preparation methods. A thorough analysis of the pigments revealed a dependency upon the type of synthesis, the crystallite size, and vacancy content, all properties that influence the local electronic and structural configurations of the iron ions in Prussian blue. The presence of nanocrystalline ferrihydrite as an undesirable iron ion containing reaction product was identified by iron-57 Mössbauer spectroscopy, pair distribution function analysis, and extended x-ray absorption fine structure studies of the Prussian blue pigments prepared according to eighteenth-century procedures. The presence of these nanocrystalline ferrihydrite impurity leads to color change from blue towards a yellow or green color. The discoloration upon light exposure in Prussian blue paint layers was induced by accelerated ageing. Pure Prussian blue painted in a dark shade is extremely light fast but fades when either painted in a lighter shade or mixed with white pigments. The fading of Prussian blue was attributed to a reduction of the iron(III) ions at the surface of the paint layer. A partial oxidation of Prussian blue in the entire paint layer was also observed. This presentation is centered on the results obtained by iron-57 Mössbauer spectroscopy on unaged and aged samples of Prussian blue pigments prepared by different methods and painted in different shades.

2. Magnetic Anisotropy Trends in \{Fe^{III}Cu^{II}\}_n Complexes and One Dimensional Chains. Philip Janini and Stephen M. Holmes, Department of Chemistry and Biochemistry and the Center for Nanoscience, University of Missouri-St. Louis

Molecule-based magnetism gives the ability to control optical and magnetic behavior of materials with atom economical efficiency. In doing so, materials can be prepared with the goal of improved or novel applications on the interface between chemistry and physics. A common synthetic strategy involves the controlled aggregation of molecular precursors where the formation of bridging cyanides can be controlled by reaction stoichiometry and capping ligands to engineer a number of Fe^{III}(\mu-CN)Cu^{II} units with predetermined spatial arrangements. The present work describes the preparation and characterization of dinuclear (1) and octanuclear (2) \{Fe^{III}Cu^{II}\}_n (n = 1, 1; 4, 2) clusters and a one-dimensional \{Fe^{III}_2Cu^{II}\}_n (3) chain constructed from Fe^{III}(\mu-CN)Cu^{II} units. Magnetic measurements indicate that the \(S = \frac{1}{2}\) spin centers (Cu^{II} and low-spin Fe^{III}) are ferromagnetically coupled leading to \(S_T = 1, 4\), and \(\frac{3}{2}\) spin ground states for 1-3, respectively. Compound 3 is unusual in that it exhibits complicated magnetic behavior where long-range magnetic order is seen at ca. 6 K, while at lower temperatures, slow magnetic relaxation consistent with single-chain magnetism is observed. A qualitative model that can be used to predict magnetic relaxation behavior in discrete clusters and one-dimensional chains derived from tricyanometalate building blocks is also described.
3. Non-bridging Ligand Supported $d^8$-$d^8$ Bond in Pd(II) and Pt(II) Complexes. Jia Luo and Liviu M. Mirica, Department of Chemistry, Washington University in St. Louis

Numerous natural and synthetic metal-containing systems employ binuclear and multinuclear metal clusters for catalyzing difficult reactions such as small molecule activation and multielectron reactions. In such multinuclear complexes, the presence of metal-metal interactions plays an important role in their reactivity. While several Rh(I), Ir(I) and Pt(II) dinuclear complexes that exhibit weak $d^8$-$d^8$ interactions have been characterized, only a few Pd(II) dinuclear species with metal-metal interactions have been reported up to date and all are supported by either dinucleating or bridging ligands. Reported herein are the rare examples of dinuclear Pd and Pt complexes that display $d^8$-$d^8$ interactions supported by a mononucleating tetradentate ligand, 2,11-dithia[3.3](2,6)pyridinophane (N$_2$S$_2$). The variable-temperature $^1$H NMR and UV-vis spectroscopy studies in different solvents imply that these dinuclear complexes may convert to mononuclear analogs in solution. Density Function Theory (DFT) analysis supports the presence of $d^8$-$d^8$ interactions in these Pd and Pt complexes, which could play an important role in the reactivity of these complexes based on our preliminary reactivity studies on Pd(II)-monomethyl dimer.

4. Pt(II) and Pt(IV) hydroxo complex synthesis and Pt(IV) photochemistry. Lasantha Wickramasinghe and Paul R. Sharp, Department of Chemistry, University of Missouri

Storing solar energy in chemical bonds is an important goal of transition metal photochemistry. Toward this goal we have studied the Pt(IV) complexes Pt$^{IV}$(OH)$_2$(OHR(PEt$_3$)$_2$ (1), PtCl(OH)$_2$(OHR(PEt$_3$)$_2$ (2) and Pt(OH)$_3$(OHR(PEt$_3$)$_2$(3). The synthesis of 1 was done with H$_2$O$_2$ extracted and concentrated in ether. Crystal structure of compound 1 was obtained. Pt$^{II}$(OH)$_2$(OHR(PEt$_3$)$_2$, 1 and PtCl$_3$(OHR(PEt$_3$)$_2$ have been used in synthesis of 2 and 3. Photolysis of mono-hydroxo Pt$^{IV}$ (1) gives Pt$^{II}$CIR(PEt$_3$)$_2$. The other potential photochemical product(s) of 1, 2 and 3 are HOCl, H$_2$O$_2$, Cl$_2$, O$_2$ and have yet to be identified.

5. Synthesis of Transition Metal p-Toluenesulfonates Optimized for Secondary and Postsecondary Education. Hung Nguyen and Stephen M. Holmes, Department of Chemistry and Biochemistry and the Center for Nanoscience, University of Missouri-St. Louis.

While the uses of trifluoromethanesulfonate ("triflates") salts have been extensively described over the past two decades much less is known for the related p-toluenesulfonates ("tosylates") salts. While many of these binary salts are prepared using standard inert atmosphere techniques in the present contribution we describe the syntheses of three transition metal p-toluenesulfonates of [M$^{II}$(H$_2$O)$_6$][OT$_3$]$_2$ (M$^{II}$ = Fe, Co, Ni) stoichiometry. Their synthetic procedures were modified to allow for educational institutions with limited equipment, time, and starting materials to prepare these inexpensive salts. Dehydration of the aquated complexes and recrystallization from dimethylformamide/diethyl ether mixtures afford various solvated complexes whose preparation, structures, and infrared spectra are presented.
6. SAPT Calculations: Comparison with Experiment. Bradley Welch and Charles Kirkpatrick, Department of Chemistry, Saint Louis University

Symmetry Adapted Perturbation Theory (SAPT) calculations have been carried out on a variety of systems. In particular we have looked at noble gas ion (Rg-X X=F,Cl) and neutral-neutral noble gas systems (Rg-Rg). Infinite basis set extrapolation was done on the energy and energy components. The basis sets used in the extrapolation were augmented 5z&6z Dunning basis sets. Some comparisons were made with infinite basis set DFT-SAPT calculations to see the accuracy of that method. For the rare gas systems the polarization term was compared with experimental polarization parameters. We fitted a $-a/2x^4$ function over a range of points (12-20 angstroms), where $a$ is the polarization in Å$^3$. When looking at the % between the experimental polarization and calculated polarization we found that the difference was only a few percent.

7. The Preparation of a Pseudo-Tridentate Pyridinophane Ligand and its Corresponding Organometallic Palladium Complexes. Jason Schultz and Liviu M. Mirica, Department of Chemistry, Washington University in St. Louis

Recently, our lab has successfully isolated and characterized various mononuclear palladium(III) complexes using the tetradentate ligand, N,N’-di-tert-butyl-2,11-diaza[3.3](2,6)pyridinophane. As a result, several variations of the pyridinophane ligands have been synthesized and their effect on the stability and reactivity of the corresponding Pd complexes was studied. To better understand the importance of the tetradentate nature of these pyridinophane ligands, a modification was made to make the pyridinophane macrocycle act as a pseudo-tridentate ligand. By studying the effect of ligand denticity on the organometallic reactivity of these complexes, we aim to develop novel oxidative C-C and C-heteroatom bond formation reactions.

8. Steric and electronic effects of mononuclear Pd$^{III}$ complexes. Fengzhi Tang and Liviu M. Mirica, Department of Chemistry, Washington University in St. Louis

Several Pd(III) complexes supported by the tetradentate ligand N,N’-di-tert-butyl-2,11-diaza[3,3](2,6)pyridinophane (tBuN4) were reported with unique structural and electronic properties for a d$^7$ Pd(III) center. The tBuN4 ligand was found to play a crucial role in stabilizing the Pd(III) oxidation state. In order to further explore the Pd chemistry with this type of ligand, N,N’-dimethyl-2,11-diaza[3,3](2,6)pyridinophane (MeN4) and N, N’-dimethyl-2,11-diaza[3,3](2,6)4-methoxylpyridinophane(MeO-MeN4) were used to study the steric and electronic effects on similar Pd(III) complexes. Interestingly, the presence of a smaller N-methyl group allows a stronger interaction between the Pd center and the axial nitrogen donors. This steric difference leads to notable characteristic changes in structures, cyclic voltammetry, UV-Vis, and EPR spectra of the corresponding Pd complexes, while the electron-rich p-methoxy-pyridine groups have a dramatically reduced effect. Moreover, the MeN4 ligand was found to stabilize a series of complexes in both Pd(III) and Pd(IV) oxidation states by substantially lowering the Pd$^{III/IV}$ oxidation potentials.
9. **Electron-nuclear interactions in GaAs.** Dustin Wheeler and Sophia E. Hayes, Department of Chemistry, Washington University in Saint Louis

Semiconductors play an extremely important (and dominant) role in the electronics used in day-to-day life. In our research, we strive to understand how atomic structure and defects in a material affect electrons. One technique that offers insight into the electronic structure of a material is optically pumped nuclear magnetic resonance (OPNMR). By optically exciting electrons, we create situations where the NMR signal reflects changes in the electronic populations. Our recent work has involved varying the energy of the excitation light and observing the effects on the nuclear polarization in a sample of bulk GaAs. Simulations of experimental results involve incorporation of the simulated energy-dependent electron orientation and laser penetration depth into the sample to predict the nuclear spin polarization within the material. Good agreement is shown between simulated and experimental OPNMR profiles. Important investigations on quantum wells of AlGaAs/GaAs (materials present in many CD players, bar code scanners, etc.) have been made through OPNMR. Our current measurements involve the evolution of OPNMR signal intensity as a function of photon energy. Experimental investigations of these quantum wells show unique behavior when compared to non-quantum-confined samples.

10. **Effect of Parameter Variation of hybrid functionals on the Interaction of Cl(-) with neutral gases.** Pennante Bruce-Vanderpuije and Chuck Kirpatrick, Department of Chemistry, Saint Louis University

We present results from a DFT investigation on the consequence of varying the original parameters ao, ax, ac) of Becke’s hybrid exchange-correlation functional on application to the interaction potential between Cl- and Ar. The aug-cc-pV-6Z basis set was used in our calculations to optimize the parameters by minimizing the difference between the B3LYP density and that of our reference -Wright potentials. The optimized parameters are based on two constraints- we assume approximately similar parameter values for the gradient correction for exchange and correlation (ac=ax). We also assume that the sum of the exact exchange and gradient correction for exchange approximately equals 1: (ao=1-ax), giving an indication of how much of the exact exchange should be included to obtain accurate calculations for a system. The obtained potentials, which are comparable to a wide range of experimentally verified potentials, were tested by calculating the transport coefficients for the mobility of Cl- in Argon. We conclude that there is not a single unique set of parameters that produces a B3LYP density of Wright potential quality for the interaction of Cl- with other neutral gases.

11. **New Iron Amine Complexes and Their Catalytic Activity in Oxidation Reactions.** Matthew Lenze and Eike Bauer, Department of Chemistry and Biochemistry, University of Missouri- St. Louis

Oxidation is a powerful and versatile method to rapidly and strategically functionalize a wide range of substrates. However, the use of oxidation reactions in industry is limited on large scales due to the use of hazardous oxidants and precautions needed to be taken in order to properly handle the oxidants. Non-toxic alternatives to the current methodologies are being investigated. Our goal is to develop an environmentally friendly, iron based, catalyst systems that are capable of efficiently oxidizing unactivated substrates using hydroperoxides as the oxidant. Reported herein is the preparation of a series of sterically and electronically modified bis and trisdentate N-donor ligands. The respective complexes of these “pyridyl-based” ligand systems, have been isolated in 67-93% yields and have displayed efficacy in the oxidation secondary alcohols
and activated methylene groups to the corresponding ketones (37-93% isolated yields) using tertbutylhydroperoxide as the oxidant. The substrate scope of these oxidation reactions will be presented as well as mechanistic and kinetic investigations.

12. Reductive Photoelimination of Molecular Chlorine from Platinum(IV)Chloro Complexes. Tharushi Perera and Paul R. Sharp, Department of Chemistry, University of Missouri

Solar energy storage in chemical bonds is vital in renewable fuel technologies. Halogen photoelimination is a crucial step in possible transition metal catalyzed solar energy storage processes but is uncommon. We have found molecular chlorine photoelimination from the Pt(IV) centers of chloro complexes in the presence of a chlorine trap. Our studies of these reactions will be reported.


Metallic aluminum nanoparticles (Al NPs) have many demonstrated energy-related applications, including dense energy storage, and hydrogen storage and production. One of the primary challenges associated with pyrophoric metal nanoparticle production is kinetic passivation of the nanoparticle surface. We have previously reported on the synthesis of air-stable aluminum nanoparticles capped with alkyl-substituted epoxides. We report here on air-stable aluminum nanoparticles using copolymerization of alkyl-substituted epoxides and methyl methacrylate as capping agents. Since poly(methyl methacrylate) is photodegradable, irradiating these core-shell nanoparticles with UV light may activate the nanoparticles toward reaction with water and/or oxygen. FTIR and 1H NMR spectroscopy indicate the copolymerization of alkyl-substituted and methyl methacrylate has been achieved. Powder X-ray diffraction (PXRD) and differential scanning calorimetry/thermal gravimetric analysis (DSC/TGA) confirm the presence of crystalline aluminum.

14. NMR in Inorganic Systems. Sophia E. Hayes, Department of Chemistry, Washington University in St. Louis

We are conducting a variety of solid-state NMR on inorganic systems including metal clusters, semiconductors, and metal carbonates. I would like to present several approaches that we use for analysis of materials, especially structure-property relationships, experimental conditions for monitoring specific chemical reactions in the solid state (i.e., with light irradiation or at elevated temperature and pressure), and other themes that are focused on inorganic and solid-state materials chemistry.
15. Synthesis of highly water-soluble nanoparticles. Elseddik Abdelkader and Steve Buckner, Department of Chemistry, Saint Louis University

Reverse micelles can function as nanoscale reaction volumes and are used to prepare many types of nanoparticles. They have been used to make binary and ternary semiconductor nanostructures for many systems based on precipitation reactions within the reverse micelles. By using different water to surfactant ratio in the water in oil microemulsion (w/o), size and sometimes shape of nanoparticles can be controlled. The question arises as to the applicability of this method for producing lower thermodynamic stability nanoparticles – those for high solubility salts. In this work, we describe the synthesis of sodium halides. System consists of water/dioctylsodium sulfosuccinate/toluene in which the core of reverse micelle has the water-soluble salt. After evaporation of the volatile compounds under vacuum (water and toluene), the final solid nanoparticles coated with surfactant were redispersed in toluene. Dynamic light scattering was used to determine the sizes of nanoparticles and showed that all salts have sizes less than 4 nm. Nanoparticles were confirmed to be present using transmission electron microscopy (TEM) and selected area electron diffraction (SAED). The effect of changing water to surfactant ratio on the size of nanoparticles was also studied.

16. Molecular and Electronic Structure of Transition Metal and Actinide Complexes with Salicylaldiminate Ligands. Justin Walensky, Department of Chemistry, University of Missouri

Transition metal and actinide complexes with Schiff base ligands are well established, however the subsequent chemistry with this class of ligand is limited. Our work has focused on uranyl, U(IV), and divalent first row transition metal coordination chemistry and we have begun to study the reactivity of these complexes. This will be presented.

17. Novel Five-coordinate, Square-planar Ruthenium-Phosphoramidite Complexes and Their Catalytic Activity in Propargylic Amination Reactions. Eike Bauer, Department of Chemistry and Biochemistry, University of Missouri-St. Louis

The first five-coordinate ruthenium complexes of the general formula [RuCl₂(PPh₃)₂L] will be presented, where L is a phosphoramidite ligand. As shown by X-Ray, the complexes take a square-pyramidal coordination geometry and the phosphoramidite ligand L occupies the position trans to the open coordination site. As opposed to the precursor complex [RuCl₂(PPh₃)₃], the new complexes are configurationally stable and exhibit no dynamic behavior in solution. The new complexes were employed as catalysts for the amination reactions of propargylic esters (18 h, room temperature or 45 °C, Cs₂CO₃) to give propargylic amines in isolated yields up to 94%. The complexes are ruthenium-based catalytic system for this reaction, and the reaction presumably proceeds through an allenylidene species Ru=C=C=CR₂.
18. Synthesis and Catalytic Applications of Platinum(II) and Palladium(II)-PTA and DAPTA Complexes. Sitaram Acharya, Janet Braddock-Wilking, and Nigam P. Rath, Department of Chemistry and Biochemistry and the Center for Nanoscience, University of Missouri-St. Louis

Some water soluble platinum(II) and palladium(II) alkyl, halide, and alkynyl complexes bearing the 1,3,5-triaza-7-phosphadamantane (PTA) and DAPTA (DAPTA = 1,3-diacetyl 1,3,5-triaza-7-phosphadamantane) ligands have been synthesized and characterized. Utilization of platinum(II) and palladium(II)-PTA and DAPTA complexes as catalysts for the hydrosilylation reactions has been investigated for the first time. The catalytic activity of cis-Pt(Me)₂(PTA)₂ (1) in hydrosilylation reactions with different unsaturated organic substrates such as alkenes, alkynes, and alkadiynes/diynes has been explored utilizing different tertiary hydrosilanes including siloles and silafluorenes. Compound 1 was found to exhibit a good catalytic activity for these reactions forming predominantly the desired regioselective hydrosilylated products. The β-trans isomers were selectively formed during the hydrosilylation of alkynes and alkadiynes. Some of the palladium(II)-PTA complexes, trans-Pd(Me)Cl(PTA)₂ and cis-PdCl₂(PTA)₂ were applied as pre-catalysts in Suzuki-Miyaura cross-coupling reactions and copper-free Sonogashira cross-coupling reactions, respectively and were found to exhibit a good catalytic activity with minimal side reactions such as homo-coupling and β-hydride elimination. These metal complexes have their potential applications to use in the biphasic catalytic reaction system for efficient recycling of the catalyst which is one of the major concerns in homogeneous catalysis. The synthesis and characterization of the metal complexes and the results from the metal-catalyzed hydrosilylation reactions as well as cross-coupling reactions will be presented.

19. Reversible Thermally- and Photo-Induced Electron Transfer in Cobalt-Iron Cyanometalates. Yuanzhu Zhang, Dongfeng Li, Rodolphe Clérac, Corine Mathonière, and Stephen M. Holmes, Department of Chemistry and Biochemistry and the Center for Nanoscience, University of Missouri-St. Louis

Multi-functional molecule-based materials that exhibit tunable physical properties as a function of external stimuli are a class of materials that may have applications in sensing, information storage and molecular electronics technologies. Over the past six years we have strived to systematically prepare a class of structurally related polynuclear cyanometalates that exhibit dramatic changes in their optical and magnetic properties with changing temperature and light exposure. Structural and electronic tuning of the molecular properties, such as the environment of the metallic ions and the intermolecular interactions (H-bonds, π–π stacking, etc.) have been investigated as possible avenues altering the optical and magnetic bistability in a series of {FeCo}ₙ complexes. Current efforts are aimed towards elucidating structural and electronic factors necessary for encoding information storage at molecular length scales. Several cyanide-based {FeCo}ₙ complexes containing [(Tp²⁻Fe³⁺(CN)₃]⁻ (Tp²⁻ = tris- or tetrapyrazoylborates) anions will be described. We find that several analogues exhibit reversible thermally and photo-induced electron transfer behavior that can be tuned up to room-temperature.
20. Compounds Designed to Bind Conserved Regions of Human Papillomavirus (HPV) DNA Show Broad-Spectrum Activity against High-Risk Genotypes. James K. Bashkin, Terri G. Edwards, Kevin Koeller, Urszula Slomczynska, and Chris Fisher, Nanovir (Kalamazoo, MI) and the Department of Chemistry and Biochemistry and the Center for Nanoscience, University of Missouri-St. Louis

HPV exists as hundreds of genotypes with exquisite tissue tropism for squamous epithelia, perhaps better known as “skin” to inorganic chemists. Approximately 40 types of HPV have been shown to infect ano/genital, oral, and other mucosa. Few, if any, so-called “druggable” targets are found in HPV due to the very limited number of proteins encoded by the small genome (see below). An alternative approach to HPV antivirals is to target viral DNA sequences important for binding the proteins involved in maintaining and replicating viral DNA using DNA-binding drugs. This approach is feasible because the virus has a double-stranded DNA genome. Polyamides (PAs) can physically block access to target DNA sequences by DNA-binding proteins or alter DNA structure to prevent protein binding. Previous studies from other labs have shown that PAs cause local physical changes in DNA structure such as widening of the minor groove, narrowing of the major groove, raising the Tm and stiffening the double helix. We describe effective antiviral compounds identified by their ability to decrease the viral DNA concentration in human cell and tissue culture. Preclinical drug development of these compounds is ongoing.