

Chemistry Oral Session Titles and Abstracts
Oral Session 1 9:15 – 10:45 am Saturday November 7th, 2009
Oral Session 3 11:00 – 12:30 pm Saturday November 7th, 2009

Oral Session 1

O1-1

Presenter: Yuyang Fan, Grinnell College

Title: Investigation of Succinate Dianion Structure, Dipolar and Scalar Couplings in Liquid-Crystal Solution by Nuclear Magnetic Resonance (NMR)

Advisor: John D. Roberts, Division of Chemistry and Chemical Engineering, California Institute of Technology

Coauthors: Andrew Mahon, Mrinmoy Nag

Succinate dianion is a simple four-carbon compound with a -C—C- bond that is free to rotate. Its dihedral angle for gauche conformation is generally thought to have the classical value of 60°. However, quantum mechanical calculations predict a dihedral angle of 46° in tetrahydrofuran (THF). In nematic phase, liquid crystals are expected to have observable dipolar couplings, which it is hoped would elucidate the intramolecular nuclear magnetic interactions. All the information should be determined by nuclear magnetic resonance spectroscopy—a powerful method for probing the structure and conformation of molecules from their electromagnetic properties. Poor substrate solubility of the dianion in liquid crystal is the limiting factor for getting good signals and impurities can also bring complications to the spectra and cause problems.

O1-2

Presenter: Erin Zimmerman, Carthage College

Title: Identifying the Intermolecular Interactions Responsible for Chiral Recognition in Drug: Micelle Mixtures

Advisor: Kevin Morris, Department of Chemistry, Carthage College

NMR Spectroscopy was used to study the binding of two chiral β -blocker drugs to a chiral surfactant. β -blocker drugs hinder the effects of adrenaline and reduce the force with which the heart contracts. The surfactant investigated is sold by Waters, Inc. as EnantioSelect and is used as a chiral selector in electrokinetic chromatography. Our study was undertaken to identify structural and thermodynamic factors that lead to chiral resolution in chromatography experiments. All four diastereometric drug:surfactant complexes (S:S, S:R, R:R, and R:S) were studied. NMR diffusion experiments with atenolol showed that the binding constants were largest for the S:S and R:R drug:surfactant diastereomers. In contrast, binding constants for the propranolol:surfactant diastereomers were all very large and did not differ significantly. Two-dimensional ROESY NMR experiments were used to establish spatial relationships between drug and surfactant atoms in the bound state. This structural data was then used in molecular modeling calculations to generate molecular structures and energies for the drug:surfactant complexes. In the atenolol studies, the molecular modeling energies were consistent with the association constant measurements.

O1-3

Presenter: Elissa Butler, Macalester College

Title: Dynamic Light Scattering: Analysis of Polydisperse Samples

Advisor: Thomas Varberg, Department of Chemistry, Macalester College

Dynamic Light Scattering (DLS) can be a useful analytical tool to measure the size of nanoparticles, including gold nanospheres and protein aggregates. Because DLS measures the particle size using basic

principles, there is no calibration. However, parameter settings vary with type of particles and solutions. I tested the validity of DLS polydisperse measurements. By mixing different concentrations of 20nm, 100nm, and 1000nm microspheres, I determined the accuracy in both the relative intensities of the peaks and the reported average value of each peak. I also looked at two different distribution bases: volume and scattering light intensity. Overall, in mixtures of the smaller particles, the relative intensities were much more accurate than mixtures of larger particles, as expected by the breakdown of Rayleigh scattering theory as the size of the particle approaches the wavelength of the incident light. Also, the reported average values of each peak for polydisperse samples were inaccurate up to 200%, especially with similar numbers of each particle size. This shows us that DLS can be a useful tool in comparing polydisperse samples qualitatively, but cannot be used to quantitatively measure the particle sizes.

O1-4

Presenter: William Hart-Cooper, Grinnell College

Title: Synthesis and Characterization of Mo(VI) Imido Complexes with *N*-Salicylidene-2-aminothiophenol

Advisor: Martin Minelli, Department of Chemistry, Grinnell College

Coauthor: Guzei, Ilia

One new di-imido complex and four new mono-imido complexes have been synthesized and characterized. By reacting the di-imido complex $\text{Mo}(\text{NAr})_2\text{Cl}_2(\text{dme})$ ($\text{Ar} = 2,6\text{-diisopropylphenyl}$, $\text{dme} = \text{dimethoxyethane}$) with *N*-salicylidene-2-aminothiophenol (sma), $\text{Mo}(\text{NAr})_2(\text{sma})$ (1) was synthesized. Complex 1 was then reacted with several bidentate aromatic ligands that replaced one imido ligand to yield the six-coordinate complexes 2-5 (2-aminophenol, 2; 3,4-dimercaptotoluene, 3; catechol, 4; 3-amino-2-naphthol, 5). All five compounds were characterized by ^1H NMR spectroscopy and four through cyclic voltammetry. Complexes 3, 4 and 5 show one reversible and one irreversible reduction, while 1 exhibits only an irreversible reduction. The structures of complexes 3 and 4 were determined by X-ray crystallography.

O1-5

Presenter: Michael Lipschutz, Washington University in St. Louis

Title: Novel Oxapentadienyl Cobalt Complexes

Advisor: John Bleeke, Department of Chemistry, Washington University in St. Louis

The synthesis, structure and reactivity of novel Cobalt complexes with the oxapentadienyl ligand have been investigated. The oxapentadienyl ligand is known to exhibit many different bonding modes taking up varying numbers of coordination sites on the metal center, which makes it a promising ligand for the creation of a catalytic system. Our research aims to characterize these systems, laying the groundwork for a future catalytic cycle. Compounds and ligands are synthesized under inert atmosphere conditions with dry solvents and are purified via crystallization. Characterization is performed by ^1H , ^{13}C and ^{31}P NMR as well as x-ray crystallography. We have characterized several novel oxapentadienyl cobalt phosphine complexes and examined their reactivity with carbon monoxide. We have begun expanding our investigations of reactivity into reactions with electrophilic reagents such as methyltriflate.

Oral Session 3

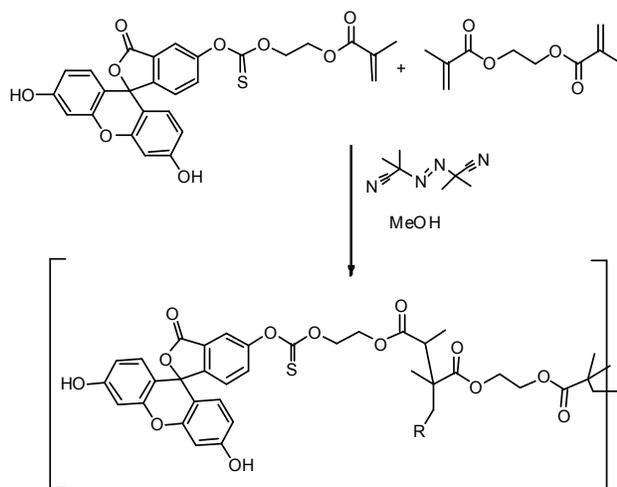
O3-1

Presenter: Christina Konecki, Carthage College

Title: The development of a facile approach for monitoring flash chromatography via fluorescence

Advisor: CJ Stephenson, Department of Chemistry, Carthage College

Flash chromatography is difficult to monitor since the identity of a compound can only be determined once it is removed from the column. The ability to monitor the column during the separation process would further increase the utility of flash chromatography. A fluorescein containing polymer that changes from non-fluorescent to fluorescent under specific environmental conditions was added to the stationary phase of the chromatography column. The addition of an environmentally sensitive fluorescent polymer will provide a novel method for monitoring a compound as it moves down the column. Fluorescein is a xanthenone dye that can switch from a non-fluorescent lactone (off) to a fluorescent carboxylic acid form (on). The on form primarily exists under basic conditions. This property allows for fluorescein to be manipulated as a fluorimetric sensor when in the presence of basic analytes. Fluorescein isothiocyanate (FITC) was coupled with a polymerizable substituent to create an off/on colorimetric monomer. This monomer was used to form a polymer with an off/on colorimetric switch. The fluorescein polymer was dried and sized and added to the stationary phase of a silica gel column. A moderate color change was observed when basic compounds were run down a column containing the silica doped with the fluorescein polymer. We are currently exploring methods of enhancing the signal change. We are also investigating how the polymer affects the fidelity of the silica gel column.



O3-2

Presenter: Zach Wickens, Macalester College

Title: Conformational Analysis of N,N-Dimethylethylenediamine N-Oxide

Advisor: John D. Roberts, Department of Chemistry, California Institute of Technology

Molecular conformations influence reactivity, structure and ultimately function of organic molecules. Chemists rely on fundamental principles to formulate qualitative guidelines and predict conformational preferences. Unfortunately, these guidelines consider molecules as they were in the gas phase and most chemistry occurs in condensed phases. The following is an investigation of hydrogen bonds in disubstituted ethane systems to elucidate nitrogen-oxygen intramolecular hydrogen bonding in a variety of solvents. The *gauche* preferences have been determined to better understand the overall influence of the intramolecular hydrogen bond. Curves will be shown depicting ^{13}C shift as a function of pH. These curves were used to determine pK_1 , pK_2 and the K_1/K_2 ratio of N,N-dimethylethylenediamine N-oxide in D₂O. The conformational preferences of each protonation state of N,N-dimethylethylenediamine N-oxide have been calculated using the Karplus equation as modified by Altona et al. Acceptably high-resolution spectra are simulated via gNMR 4.1 to extract accurate vicinal coupling constants. These coupling constants are ultimately used to determine to conformational preferences of N,N-dimethylethylenediamine N-oxide in D₂O and DMSO.

O3-3

Presenter: Joshua Borycz, Hope College

Title: The Forensic Relevance of Mineral Identification with Cathodoluminescence Spectrometry

Advisor: Graham Peaslee, Department of Chemistry, Hope College

Coauthors: Brokus, Sarah, Silletti, Danielle, Lunderberg, Justin

In modern forensic analysis, trace evidence such as soil is often important. The current methods used to determine the origins of trace geological evidence are limited in their provenance determination and are time consuming. To address this problem, cathodoluminescence (CL) spectroscopy has the potential to rapidly identify minerals provenance and basic makeup. By studying various CL spectra of minerals with known origins, the reasons behind the spectral characteristics and consistencies could be determined.

To demonstrate the potential power of this method, several classes of minerals were studied from samples collected from different, well-known locations around the US. Reflected light and CL images of single mineral grains were digitally photographed, and spectral analysis performed on replicate grains from each location. Color analysis of the CL photographs was done with different grain sizes, and spectra for each sample were analyzed using commercial peak-fitting software. Results were compiled into spreadsheets and trends in mineralogy noted. Local sand-dune samples were examined similarly to check for consistency and distinctive CL signatures. Preliminary results indicate that minerals from the same region have similar spectral features and that they remain distinct compared to samples from other regions. Mineralogical and statistical analysis of sand and soil samples provide two types of discriminatory tools that would be very useful in the development of a reliable forensic geology method for provenance determination.

O3-4

Presenter: Meareg Amare, Lawrence University

Title: Synthesis of novel cobalt-alkyne drugs and evaluation of their anti-cancer activity

Advisor: Professor Stefan Debbert, Chemistry Department, Lawrence University

Most commonly used drugs are small organic compounds; however, the organometallic drug Cisplatin has successfully been used to treat breast and ovarian cancer. We developed organometallic drugs of Aspirin analogues containing a $\text{Co}_2(\text{CO})_6$ -alkyne complex. These compounds have been shown to be even better at killing cancer cells than Cisplatin. However, the mechanism by which this is achieved is not well understood.

One possible mechanism for this increased toxicity is that the cobalt complex stabilizes formation of a propargyl cation, which makes an alkylating agent that targets DNA. This can be used in chemotherapy to kill cancer cells. We used different analogues of salicylic acid such as those with electron-withdrawing or electron-donating groups, to help us determine the relationship between cation formation and cytotoxicity. Alkyne groups attached to the analogues were also varied to test for the same effect. We tested some of these compounds for efficacy in killing cancer cells and we found that one compound, 2-acetoxy-4-bromodicobalt alkyne complex has twice the cytotoxicity of Cisplatin in killing cancer cells. More tests are going to be carried out to test the efficacy of other synthesized compounds.

O3-5

Presenter: Danielle Silletti, Hope College

Title: Forensic Identification of Neutron Irradiation Signatures

Advisor: Graham Peaslee, Chemistry, Hope College

Coauthors: Borycz, Joshua

Nuclear proliferation and the potential threat to national security from unsecured special nuclear materials around the world have renewed our national interest in nuclear forensics. One important aspect to the forensic identification of nuclear materials is to identify new methods to detect not only the presence of special nuclear materials, but also the detection of materials pathways into this country. The only current method to identify where special nuclear materials have been stored involves measuring induced radiation in adjacent materials, which is typically short-lived. We have identified a permanent change to the luminescent properties of certain common mineral that is due to neutron irradiation that could potentially be developed into a nuclear forensics tool.

Feldspars, quartzes and carbonates are ubiquitous minerals that are known to luminesce under electron bombardment. We have measured the UV-Vis light spectra of hundreds of feldspars and carbonates with cathodoluminescence (CL) spectroscopy. CL spectroscopy uses an electron beam to induce fluorescence in certain minerals due to their chemical composition and defects in their crystal lattice structure. By comparing these measurements of natural minerals to a selection of minerals that have been exposed to neutron irradiation, we can determine whether neutron bombardment permanently alters the CL spectra in a predictable or quantifiable manner. Preliminary results from a source study and a reactor study will be presented.

O3-6

Title: Superhydrophobic Polystyrene Nanotube Sheets

Presenter: Jamie Eversage, Beloit College

Advisor: George Lisensky, Chemistry Department, Beloit College

Polystyrene nanotubes are prepared by dissolving packing peanuts in xylene and coating the pores of an alumina membrane. The filter is removed by etching with NaOH to produce sheets of superhydrophobic tubes with a diameter of 200 nm. Water drops bead up on the open side and spread out on the closed side of the sheet, demonstrating the importance of size and shape in determining properties. The procedure was adapted from M. Jin, X. Feng, L. Feng, T. Sun, J. Zhai, T. Li, and L. Jiang, *Adv. Mater.*, 17, 1977-1981 (2005).