Gallium(III) and Scandium(III) Complexes with Redox-Active Ligands as Mimics of Superoxide Dismutase (32)

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The degradation of superoxide (O₂⁻) to hydrogen peroxide (H₂O₂) and dioxygen (O₂) is catalyzed by a class of enzymes known as superoxide dismutases (SODs). Excessive production of reactive oxygen species (ROS) results in oxidative stress, which is a frequently observed symptom of a wide array of cardiovascular, neurological, and inflammatory diseases. Due to the correlation between ROS and these disorders, there is significant interest in developing a strategy to control their in vivo concentrations. One therapeutic strategy would be to administer a pharmaceutical that would convert the ROS to a more innocuous molecule, such as O₂ or H₂O.

Our lab has prepared and characterized coordination complexes with polydentate ligands that contain redox-active ligands. Mn(II) complexes were originally explored as H₂O₂-responsive MRI contrast agents but were also found to catalyze the decomposition of O₂⁻. We also found that Zn(II) complexes with these ligands display significant antioxidant reactivity.

The notable ability of Zn(II) compounds to catalytically degrade O₂⁻ promoted our interest in exploring additional innocuous metals and their reactivity with our previously synthesized quinol containing ligands. Here we report new gallium and scandium complexes along with their preliminary antioxidant activities.

Key Words: SOD mimics; bioinorganic catalysts; Redox catalysts
**Determination of the electrochemical stability potential windows of anionic metallocages and their use as hosts for redox probes**

*Ryan Bujol, Louisiana State University*

Greener fuel production is vital in the modern day, and electrocatalysis is an important pathway for unlocking more efficient, cleaner uses of generated electricity. Many electrocatalysts in solution are very active, but suffer from bimolecular degradation reactions, which render them inactive. Therefore, preventing these deleterious interactions is a method of increasing the catalysts’ efficiency. Introducing these molecules into the cavities of porous materials is a novel way of doing this, without altering the chemical structure of the catalyst. We have employed supramolecular metallocages as porous hosts for studying the effects of encapsulation on the electron transfer properties of redox active molecules. A series of coordination cages were synthesized, and their window of electrochemical stability determined. Several metallocages exhibit electrochemical stability potential windows that are wide, which is necessary for their use as hosts to electrocatalysts. Several electroactive probes were successfully encapsulated within the cage’s pores, and changes to their electrochemical properties were determined after encapsulation. This work lays the foundation to develop further ways of preventing deactivation of molecular electrocatalysts.

**Key Words:** supramolecular, electrocatalysis, metallocages, host-guest, electrochemistry

**Electrocatalytic Reduction of Nitrite with a Cu(II)-Me6Tren Complex**

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Nitrite in water is toxic to aquatic life and can cause harmful algae blooms and dead zones. Nitrite in water can be difficult to reduce but electrocatalysis is a potential solution. Few reports reduce nitrite to gaseous compounds, most convert to ammonia/ammonium. Of the few that do convert to gaseous compounds, copper or iron catalysts are used. Little work has demonstrated the use of these complexes in water, rather organic solvents are generally used. Therefore, the goal of this project is to reduce nitrite in water to gaseous products such as nitric oxide, nitrous oxide, or nitrogen gas using a copper electrocatalyst for the denitrification of water. The chosen complex is modeled after copper containing nitrite reductases found in nature that easily perform the reduction. Characterization, electrochemical measurements, and product determinations are the main focus of this project. Results indicate electrocatalytic reduction of nitrite in water is possible using these copper complexes. Effective nitrite reduction to gaseous products is observed in water in acidic conditions, which demonstrate the potential of this approach toward denitrification of contaminated water.

**Key Words:** Nitrite reduction, denitrification, electrocatalysis, electrochemistry
Binuclear catalytic enhancement through water splitting (58)

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Binuclear catalysts provide the possibility of enhanced catalytic activity, selectivity and increased stability compared to their mononuclear analogues. Water splitting (conversion of water into its basic components; dioxygen (water oxidation) and dihydrogen (water reduction)) is vital because hydrogen gas (H₂) which is regarded as one of the cleanest sources of renewable energy, can be obtained from water. In recent times, there has been a need for robust and efficient catalysts to be developed for water reduction and water oxidation due to the high energetic cost of water splitting. We hypothesize that; (i) bimetallic complexes of some first-row transition metals act as catalysts capable of oxidizing water, releasing electrons for the transformation of solar energy to chemical energy. (ii) Binuclear species that display cooperativity (two metal centers working concurrently) among metals will lead to efficient conversion of protons to H₂. This research focuses on the development of binuclear cobalt, nickel, manganese, and iron catalysts with a 2,6-bis[bis(2-pyridylmethyl) amino] methyl]-4-methylphenol ligand (HL₁), for water reduction and water oxidation. The nickel and cobalt catalysts have been studied for the presence and mechanisms of cooperation for water reduction whereas the manganese and iron catalysts have been preliminarily assessed for its ability to act as catalysts for water oxidation. From our findings, we have theoretically and experimentally proven that the bimetallic nickel catalyst exhibits no cooperativity while the bimetallic cobalt catalyst shows cooperativity.

Key Words: Cooperativity, binuclear, mononuclear

Aqueous electrocatalytic reduction of Cr(VI): Influence of buffer properties and small electron mediators (91)

Callie Stern, Chemistry, Louisiana State University

Hexavalent chromium, Cr(VI), and trivalent chromium, Cr(III), are stable oxidation states of chromium which exist in aqueous systems. While Cr(III) is generally non-toxic, Cr(VI) is hazardous for human consumption at very low concentrations and ingestion of Cr(VI) contaminated drinking water can lead to serious health complications. Due to the risks associated with Cr(VI) toxicity, it would be advantageous to develop an efficient method for the reduction of Cr(VI) to Cr(III) in aqueous systems. The goal is to electrochemically reduce Cr(VI) to Cr(III), which removes the need for sacrificial reductants and thus reduces waste by-products. This reduction is kinetically challenging and in order to diminish the associated high kinetic barriers caused by the large number of protons and electrons required, strategies are tested to influence the underlying PCET processes. This talk will focus on the impact of the properties of the buffers used to provide protons and control pH, as well as the presence of small electron mediators.
mediators to aid in Cr(VI) reduction. This work opens the way to energy efficient and environmentally conscious water purification methods for the reduction of Cr(VI).

**Key Words:** Cr(VI), electrochemistry, PCET

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**Organo-functionalized Metal Oxide Clusters: Synthesis, Characterization and Structural Analysis (116)**

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Polyoxomealates (POMs) are versatile class of metal oxide clusters. POMs are commonly formed by early transition metals like vanadium, molybdenum, niobium and tungsten in their highest oxidation number. They possess noble physical and chemical attributes such as: solvent and thermal stability, solubility, redox potential and magnetic properties. These structural diversities make possible the tremendous applications which these materials are used for today. POMs have ability to accept electrons in a chemically reversible manner because it comprises, among others, doubly-bonded non-bridging oxygen atom connected to a metal atom (M=Ot) through which electronic interaction occurs leading to $d\pi-p\pi$ electron transfer; metal may get reduced thus forming a mixed valent POM anions. Also, oxygen-metal interaction is commonly indicated by near-UV bands in POM which lend support to redox potential among others that form the basis of their applications. POMs have shown tremendous applications in catalysis, chemical sensing, biotechnology, nanotechnology, electrochemistry, medicine, molecular magnetism etc.

**Key Words:** Polyoxometalate, functionalization, Catalysis, Chemical Sensing, Solid electrolytes