

University of Michigan
DEPARTMENT OF CHEMISTRY

INORGANIC CHEMISTRY

Graduate Program



Inorganic Chemistry at the University of Michigan flourishes in the three modern areas of metals in biology (Bioinorganic Chemistry), catalysis for transformation of organic molecules (Organometallic Chemistry), and design of solids with defined properties (Inorganic Materials). These research areas also find applications in Medicinal Chemistry. The remarkable breadth of Inorganic research at Michigan reflects the highly interdisciplinary character of modern Inorganic Chemistry.



Dinitrogen bound intermediate of the active site of nitrogenase from DFT calculations (Coucouveris).

Bioinorganic Chemistry

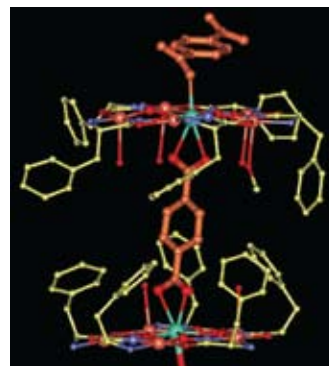
Bioinorganic Chemistry explores the role of metal ions in biology, including electron transfer, small molecule activation, metalloenzyme catalysis, and bioorganometallic chemistry. Metalloproteins and biomimetic model systems are studied.

Iron-sulfur clusters in electron transfer and catalysis are a major research focus in the Department. Synthetic heterometallic iron-sulfur clusters are investigated as models for the active site of the enzyme nitrogenase. This remarkable enzyme is able to catalyze the reduction of the 'inert' molecule dinitrogen to ammonia at room temperature. The ability of iron-sulfur clusters to serve as electron reservoirs for catalysis is also explored using architectures where clusters are linked to cata-

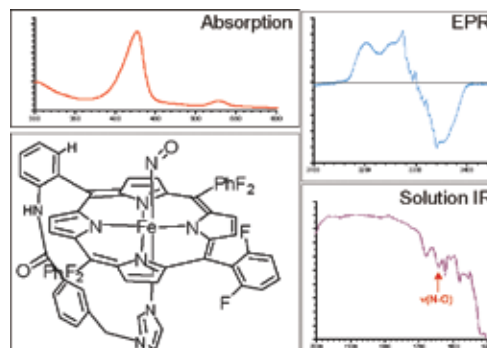
lytically active metal complexes.

Investigating the catalytically active CaMn_4 center for water oxidation in photosystem II is important both for fundamentally understanding photosynthesis and developing new catalysts for alternative energy production. Research focuses on both the metallobiochemistry of photosystem II, and the synthesis of active-site models. Alternative biomimetic oxidation systems are vanadium complexes modeling haloperoxidases, which are being evaluated as pharmaceutically relevant chiral sulfoxidation catalysts. Metallacrowns, the first metallamacrocycles, explore host-guest chemistry and are being tested as magnetic materials and catalysts.

Another key interest in the Department is the biological role of nitric oxide (NO) as a signaling and regulating molecule. Most enzymes involved in NO biochemistry contain heme (porphyrin) cofactors. Correspondingly, functionalized iron-porphyrin nitrosyl complexes are synthesized as structural and functional models for these enzymes. These complexes are then investigated using a variety of physical methods including electronic absorption and resonance Raman spectroscopy, electron paramagnetic resonance (EPR), and magnetic circular dichroism (MCD). These compounds are further devel-



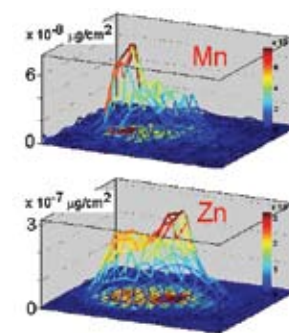
Metallacrown host-guest complex in which the organic guest terephthalate is captured in a compartment formed by two Ga^{III} (15-MC-5) complexes (Pecoraro).



First Fe(II)-porphyrin NO complex that is six-coordinate in solution without excess base added (Lehnert).

oped toward medicinal applications.

The distribution and catalytic function of zinc in biological systems is another focus of bioinorganic chemistry in Michigan. To fully understand the function of zinc, it is necessary to know both the localization and speciation of the metal ion in tissue. Current interests involve the application of x-ray spectroscopy for the imaging of zinc and other metal ions in the hippocampus. Other projects concern the development of new methods of x-ray spectroscopy.



Metal distributions in a yeast cell (Penner-Hahn & Fierke)

Interest in bioinorganic chemistry at Michigan also covers the role of metal ions in human neurological diseases such as Alzheimer's disease (AD). Accumulation of toxic amyloid- β ($\text{A}\beta$) aggregates, distinct feature of AD, is accelerated by divalent ions such as Cu^{II} and Zn^{II} . Metal-induced $\text{A}\beta$ aggregation can be alleviated by metal chelators. Therefore, current research is focused on the development of a new generation of non-toxic, small molecule-based metal chelators for Cu^{II} and Zn^{II} as effective therapeutics for AD.

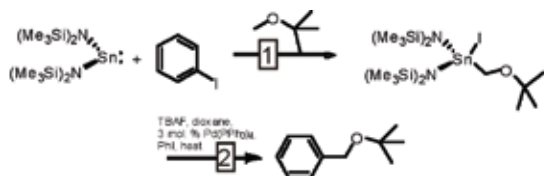


Amyloid- β ($\text{A}\beta$) aggregates (top) and Alzheimer's brain (bottom) Image courtesy Alzheimer's Assoc. (Lim).

Organometallic Chemistry

Organometallic (OM) Chemistry is centered around properties of the metal-carbon bond, and the utilization of metal complexes for organic synthesis and catalysis.

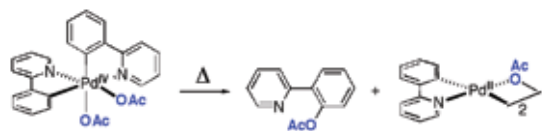
Research projects in main group organometallic chemistry are focused on the properties of germylenes and stannylenes as ligands for transition metals, and their application for C-H activation. They can also be utilized for the functionalization of phenones.



Application of stannylenes as reagents for C-H activation (Banaszak Holl).

In addition, new heteroaromatics with unusual heteroatoms (B, P, As, etc.) are synthesized. These heterocycles can then be used for the preparation of new catalysts for olefin polymerization.

Another field of extraordinary importance in OM chemistry is C-H activation and functionalization. Research in the Department is focused on oxidative C-H activation using Pd and Pt catalysts. Regioselectivity in these reactions is achieved by the attachment of directing groups to substrates that are able to coordinate to the transition metal catalyst. Application of developed methodology to the synthesis of important pharmaceuticals is explored. In addition, synthetic studies are underway to access novel high oxidation state complexes of Ni, Pd, and Rh. The reactivity of these species is being explored as a model of key intermediates in catalysis.

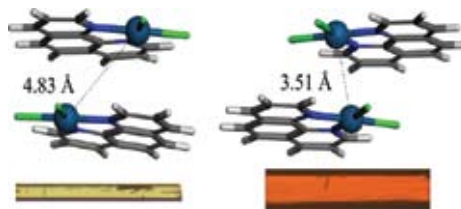


Isolation of unusually high oxidation state Pd(IV) species and studies of their reactivity (Sanford).

Materials Chemistry

Materials chemistry at UM seeks to discover new materials for advanced applications such as energy production and storage, catalysis, and sensing. The focus is on designing novel compounds having specific properties, rationally synthesizing these new materials, and understanding the relationship between the structure and physical properties of these materials. Research projects in renewable energy include porous solids for hydrogen storage, transition metal oxides as water splitting photocatalysts, studies of heterogeneous charge transfer at nanostructured III-V semiconductor/solution junctions, and hybrid organic-inorganic layered

materials as high-capacity battery electrodes and new superconducting materials. In addition, inorganic groups at Michigan are involved in the catalytic production of conjugated polymers, chemical sensing, and selective discovery/production of crystalline polymorphs that have improved functionality.



Polymer-induced heteronucleation, a technique for discovering new crystalline forms of compounds, was used to create polymorphs of Pt(phen)Cl₂ with different Pt...Pt distances in the solid state (Matzger).

Further Information

For more information about specific research interests, go to: www.umich.edu/~michchem. Please feel free to contact faculty directly:

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How to Apply

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Inorganic Chemistry

