

David Jenkins

409 Buehler Hall
Assistant Professor of Chemistry
jenkins@ion.chem.utk.edu
(865) 974-8591

Research Overview

Research in my group is broadly based on inorganic synthesis with an emphasis on magnetic materials and organometallic chemistry. We focus on two particular areas: multi-functional spin-crossover materials and group transfer reactions on transition metals supported by macrocyclic carbenes.

I. Spin-Crossover Coordination Polymers for Molecular Sensing and Data Storage Supported by 1,2,4-Triazoles

Spin-crossover materials have been identified as good candidates for many nanoscale applications, including data storage, display devices, molecular electronics, and molecular sensing. Spin-crossover—which occurs when small variations in energy cause the electrons at a metal center to change their spin multiplicity—can induce changes in a material's physical properties that are of critical import to nanoscale applications, such as magnetic moment, metal-ligand bond distances, and electronic transition energies. Also critical are frameworks that exhibit a hysteretic spin-crossover at room temperature. By controlling both spin-crossover temperature and the physical characteristic of spin-crossover materials, new and practical multi-functional materials may be developed. Through rational ligand design, it is possible not only to control this transition temperature, but also to enable multi-functionality by imparting additional properties unto the ligands. For example, by synthesizing ligands that photoisomerize, the conformation of the framework can potentially be altered. We are synthesizing both microporous spin-crossover frameworks for molecular recognition (Figure 1) and ligand-isomerizing spin-crossover coordination polymers for data storage devices (Figure 2). Long term research will include the development of chiral microporous materials that can distinguish among enantiomers and the investigation, in thin films, of materials that can undergo light-induced spin-crossover in the solid-state.

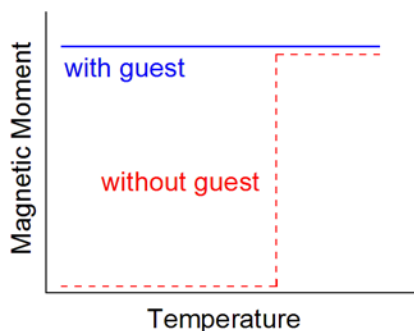


Figure 1. Effect of a guest on the magnetic moment of a spin-crossover complex.

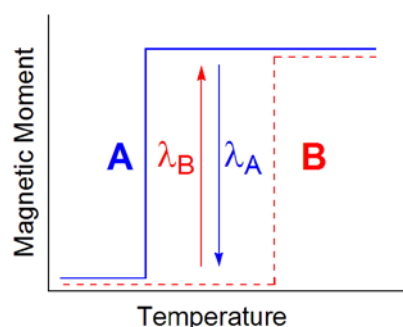


Figure 2. Schematic drawing of one possibility for ligand-driven light-induced spin-crossover. **A** and **B** represent the same complex formed with different isomers. λ_A and λ_B are the irradiating wavelengths used for **A** \rightarrow **B** and **B** \rightarrow **A** conversions, respectively.

II. Group Transfer Reactions with Macrocyclic Tetracarbenes

Macrocyclic ligands play a crucial role across the spectrum of synthetic inorganic chemistry, from stabilizing metal-ligand multiple bonds to aiding catalytic transformations. Despite the advances in carbene ligand synthesis over the last decade, no free macrocyclic carbene ligand has ever been prepared. We are developing new strong donor macrocycles, tetradentate N-heterocyclic carbenes (Figure 3), that will allow for the development of new group transfer reactions from important substrates, such as organic azides and dioxygen, and the stabilization of low valent metal-ligand multiple bonds. These tetracarbene ligands are well-suited for these projects, since carbenes are strong neutral donors and are stable to oxygen.

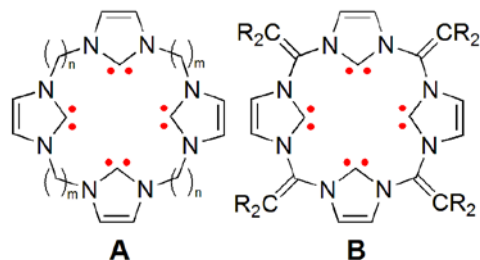


Figure 3. Tetracarbene ligands.

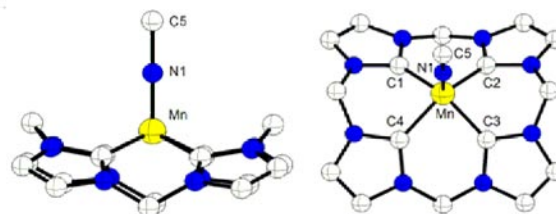


Figure 4. Calculated structure of the complex $[(\text{tetramethylenecarbene})\text{Mn}\equiv\text{NMe}]^+$, shown in side on (left) and top down (right) views.

One of the main objectives of this project is to synthesize metal-ligand multiple bonds with first-row transition metals for use in group transfer reactions. The strong σ -donating ability of tetracarbenes makes synthesizing low valent complexes featuring metal-ligand multiple bonds, such as a Mn^{III} imide, feasible. DFT calculations suggest that the proposed $[(\text{tetramethylenecarbene})\text{Mn}\equiv\text{NMe}]^+$, a Mn^{III} complex, is a stable species structurally similar to the previously synthesized molecule (5,10,15-tris(pentafluoro-phenyl)corrole) $\text{Mn}\equiv\text{N}(2,4,6\text{-trimethylphenyl})$, a Mn^{V} complex (Figure 4). These electron-rich imides are promising for nitrogen-carbon bond-forming reactions, such as aziridination reactions employing organic azides. Such reactions typically use hypervalent iodine reagents such as $\text{PhI}=\text{NTs}$ (Ts = tosylate), bromamine-T, or tosylazide as the nitrene transfer reagent. A $\text{Mn}^{\text{I}}/\text{Mn}^{\text{III}}$ cycle, on the other hand, may allow the inclusion of a variety of organic azides as reagents for catalytic aziridination reactions. Since the azide functionality is easy to install on organic substrates, particularly arylamines, the ability to utilize any organic azide, not just ones with electron withdrawing substituents, would broaden the scope of aziridination reactions in organic synthesis.