Copper Dioxygen Chemistry
Utilizing Sulfur Containing Ligand Systems
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Certain copper enzymes possess a sulfur atom ligand donor or cofactor at their active sites. The sulfur coordination is presumably playing an important role for their chemistry, such as C-H bond activation of substrates, electron transfer reactions, etc. The aim of this research is to gain insight in understanding how sulfur atom interacts with copper metal performing various chemistry utilizing molecular dioxygen.

First, as a synthetic model study of PHM (peptidylglycine a-hydroxylating monooxygenase) and DβH (Dopamine β-hydroxylase), we have prepared CuI and CuII complexes with new tridentate N2S type ligands (LN2S) containing a thioether donor to study methionine-copper (R2S-Cu) coordination chemistry and reactivity towards O2 or H2O2. Oxygenation of the thioether-CuI complexes leads to ligand sulfoxidation and CuII complexes give sulfonation upon reaction with H2O2. Second, to develop biomimetic models of TyrCys/HisCys crosslinks, thiol or phenol-containing ligands (LSH and LN3O) and their copper complexes have also been synthesized. Thiol-Cu complexes react with added phenolate to give a phenol-sulfur coupled product (LSPhOH). Oxygenation of the thiol-CuI complex leads to a CuII bound sulfonate (LSO3H) complex. The copper complexes and reaction products were characterized by mass spectrometry, X-ray crystallography and various spectroscopic techniques including UV-Vis, NMR, and EPR.