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 Cu^{I} and Cu^{II} complexes with new tridentate N_2S type ligands (L^{N2S}) containing a thioether donor to study methionine-copper (R_2S-Cu) coordination chemistry and reactivity towards O_2 or H_2O_2. Oxygenation of the thioether-Cu^{I} complexes leads to ligand sulfoxidation and Cu^{II} complexes give sulfonation upon reaction with H_2O_2. Second, to develop biomimetic models of TyrCys/HisCys crosslinks, thiol or phenol-containing ligands (L^{SH} and L^{N3O}) and their copper complexes have also been synthesized. Thiol-Cu complexes react with added phenolate to give a phenol-sulfur coupled product (L^{SPhOH}). Oxygenation of the thiol-Cu^{I} complex leads to a Cu^{II} bound sulfonate (L^{SO3H}) 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.