

The Development of Copper-Sulfur Chemistry Relevant to Modeling the Active Site of Nitrous Oxide Reductase

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The structure of the enzyme, nitrous oxide reductase (N₂OR), has recently been determined by crystallographic methods and contains two copper sites, the dinuclear Cu_A site and the tetranuclear Cu_Z site. The Cu_Z site, which is the active site of the enzyme, catalyzes the two-electron reduction of nitrous oxide to dinitrogen and water. The structure of the Cu_Z site consists of a distorted tetrahedral sulfide bound to four copper ions, whose Cu₄S core is unique in Nature. Since N₂OR is the only reported example of copper/N₂O chemistry, understanding the mechanism of reduction and discerning the oxidation states required for catalysis are extremely important. Synthetic modeling studies should contribute greatly to a better understanding of the Cu_Z site and the reaction it catalyzes. Our goal is to develop new copper-sulfur and copper cluster chemistry and then apply that chemistry to make novel model compounds, which mimic the structural arrangement, spectroscopic properties and reactivity of the Cu_Z site. Our results on developing new copper-disulfide complexes from mononuclear copper complexes and different sulfide reagents will be presented. Furthermore, the first example of a nitrogen-ligated Cu complex where the S-S bond has been cleaved will be discussed, along with a description of its electronic structure and reactivity with different substrates.