Unusual Spin States and Spin-Dependent Reaction Trajectories in Biorelevant Dicopper/O_2 and Diiron/NO Chemistry

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For achieving the activation and transformation of small molecules, many enzymes take advantage of the cooperative action of two (or more) proximate metal ions hosted within the protein active site. Understanding the functional principles of nature's sophisticated systems provides great inspiration for the development of novel bioinspired catalysts, especially for catalysts mediating small molecule transformations relevant to the global energy challenge. Metal ion spin states as well as spin state changes are important factors for determining the catalysts' reactivity and selectivity.

This presentation will discuss spin state effects and spin dependent reaction trajectories in model systems of prominent classes of metalloenzymes with coupled dinuclear active sites. It will address:

(i) O_2 binding at biological type 3 dicopper sites, unusual interactions of Cu_2/O_2 intermediates with Lewis acids, as well as proton- and redox-mediated interconversions between, and equilibria of, different Cu_2/O_2 species.[1]

(ii) structure-activity correlations for reductive coupling of NO to give N_2O in complexes with two adjacent $\{FeNO\}^7$ units akin to flavodiiron nitric oxide reductases (FNORs),[2] and comparison with recently reported phenolate-based FNOR model systems.[3]

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