X-ray Absorption Spectroscopy of Mononulear and Binuclear $[LCu_n-O_2]^{n-}$ Complexes: Understanding O_2 Activation by Copper Proteins

Ritimukta Sarangi,[1] Kiyoshi Fujisawa,[2] Kenneth D. Karlin,[3] William B. Tolman,[4] Britt Hedman,[5] Keith O. Hodgson,[1,5] and Edward I. Solomon[1]

[1]Department of Chemistry, Stanford University, [2]Department of Chemistry, University of Tsukuba, [3]Department of Chemistry, Johns Hopkins University, [4]Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, [5]Stanford Synchrotron Radiation Laboratory, SLAC, Stanford University

Oxygen activation is performed by many binuclear copper-containing proteins that play pivotal roles in biological and enzymatic pathways. These proteins are categorized as coupled (*e.g.* hemocyanin, tyrosinase and catechol oxidase) or non-coupled (*e.g.* peptidylglycine R-hydroxylating monooxygenase (PHM) and dopamine beta-monooxygenase (DBM)) based on magnetic interactions between the two copper centers. XAS and optical spectroscopies combined with DFT calculations have shed light on the mechanism of O_2 activation in the coupled binuclear proteins, however, the electronic and geometric structure and its relation to O_2 activation of the noncoupled proteins has been unclear.

To understand these sites and their different reactivities, model complexes containing side-on and end-on bound Cu_2O_2(peroxide and bis-μ-oxide), Cu_2S_2(disulfide) moieties and side on bound CuO_2 (peroxide and superoxide) monomers have been characterized using Cu K- and L-edge and S K-edge XAS combined with DFT calculations. The results obtained for the binuclear complexes indicate large differences in covalency in these complexes due to differences in bonding. The results also indicate a variation in the effective nuclear charge (Z_{eff}) on Cu, consistent with change in electronic structure. The mononuclear Cu centers have been characterized as $Cu^{III}O_2^{2-}$ and $Cu^{II}O_2^{-}$ complexes. The difference in bonding and the role of the 'innocent' nitrogenous ligation in tuning the electronic structure of these complexes is explored using broken-symmetry UDFT calculations and VBCI L-edge simulations.

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