X-ray Absorption Spectroscopy of Mononuclear and Binuclear $[\text{LCu}_n\text{O}_2]^{2n-}$ Complexes: Understanding $\text{O}_2$ 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. Solomon¹

¹Department of Chemistry, Stanford University, ²Department of Chemistry, University of Tsukuba, ³Department of Chemistry, Johns Hopkins University, ⁴Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, ⁵Stanford 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 $\text{O}_2$ activation in the coupled binuclear proteins, however, the electronic and geometric structure and its relation to $\text{O}_2$ 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$_2$O$_2$ (peroxide and bis-$\mu$-oxide), Cu$_2$S$_2$ (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 ($Z_{\text{eff}}$) on Cu, consistent with change in electronic structure. The mononuclear Cu centers have been characterized as Cu$^{\text{III}}$O$_2^{2-}$ and Cu$^{\text{II}}$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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