

**G066** SPECTROSCOPIC AND KINETIC CHARACTERIZATION OF THE MN SITE IN THE LACTOBACILLUS PLANTARUM MN CATALASE. J.E. Penner-Hahn, R.D. Fronko, G.S. Waldo, C. Toth, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, USA

Catalase activity in *L. plantarum* is mediated by a novel Mn containing enzyme. We report the results of kinetic and spectroscopic studies of this enzyme and compare its active site with that for the Mn cluster in the photosynthetic oxygen evolving complex (OEC). Kinetic studies show that azide, cyanate, thiocyanate, and fluoride are all inhibitors of the catalase. Azide shows pH dependent competitive inhibition. EPR spectroscopy shows that the Mn are contained in a coupled dinuclear site which is mixed valence Mn(III/IV). EPR and proton relaxation enhancement both confirm that azide interacts directly at the Mn site. EXAFS studies show no sign of the 2.7 Å Mn-Mn interaction found in the OEC, thus pointing to a longer Mn-Mn distance.

**G067** MODELING THE OXYGEN EVOLVING COMPLEX OF PHOTOSYSTEM II. REDOX CHEMISTRY AND LIGAND BINDING OF BIOLOGICALLY RELEVANT MANGANESE TETRAMERS. H. Holden Thorp, R.J. Kulawiec, G.W. Brudvig, R.H. Crabtree, Yale University, New Haven, CT 06511, USA.

The physical chemistry of a recently reported  $Mn_4O_2$  butterfly complex [1] has been investigated. This complex is unique in that it exhibits all-oxygen ligation and contains four coordinatively unsaturated manganese centers, two of which have labile sites that are readily substituted. Magnetic susceptibility, EXAFS and EPR measurements have been interpreted in terms of the electronic and spin characteristics of the complex. Electrochemical data show the molecule to be remarkably resistant to reduction, despite the presence of two  $Mn^{III}$  ions. The binding of amine ligands to the complex has been detected by EPR and cyclic voltammetry.

[1] Kulawiec, R.J.; Crabtree, R.H.; Brudvig, G.W.; Schulte, G.K. *Inorg. Chem.* **1988**, 27, 1309.

**G068** PROPOSAL FOR A PLANAR TETRAMANGANESE CENTER IN THE OXYGEN EVOLVING COMPLEX OF PHOTOSYSTEM II. James G. Bentsen, Wolfgang Micklitz, Simon Bott, Stephen J. Lippard, Massachusetts Institute of Technology, Cambridge MA 02139, USA

One of the most important processes in nature is the light induced four-electron oxidation of water to dioxygen. At some stage in this remarkable reaction, two oxygen atoms must approach one another to provide a stereoelectronic pathway for O-O bond formation. While no details are available about this coupling process, it has become increasingly clear that four manganese ions function to accumulate the oxidizing equivalents produced during S state advancement and to bind water and catalyze its oxidation. We present a model for the tetramanganese center in photosystem II that directly addresses the issue of how two bridging hydroxide ligands can be held in juxtaposition by a planar rectangular metal framework to form first a  $\mu_4$ -peroxide, as an intermediate or transition state, and then dioxygen in two  $2e^-$  steps.