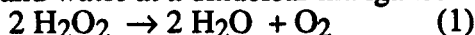


## D056 LOW VALENT, DINUCLEAR MANGANESE COMPLEXES AS FUNCTIONAL MODELS FOR MANGANESE CATALASES

**Andrew Gelasco and Vincent L. Pecoraro\***,

*Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055.*

The manganese catalases are enzymes that disproportionate hydrogen peroxide to oxygen and water at a dinuclear manganese site (Eq. 1).



Presently, the best model for this system proposes that the enzyme cycles between Mn(II,II) and Mn(III,III) levels. A third oxidized form of the enzyme, containing an Mn(III,IV) center has been characterized by EPR, and is inactive.

We have used the pentadentate ligand X-2-OHSalpn (X=H, Cl, NO<sub>2</sub>, OCH<sub>3</sub>) to prepare dinuclear manganese complexes having the various oxidation levels proposed for the enzyme. Structural analysis of these materials demonstrates that the dimers fall into two classes: symmetric (with short Mn-Mn distances, Figure 1) and asymmetric (with long Mn-Mn distances, Figure 2). Earlier work with Mn complexes of this ligand gave only asymmetric compounds[1] that are inactive toward H<sub>2</sub>O<sub>2</sub> disproportionation. In contrast, the lower valent, symmetric complexes as Mn(II,II) and Mn(III,III), disproportionate H<sub>2</sub>O<sub>2</sub>. The rates of disproportionation of H<sub>2</sub>O<sub>2</sub> by these lower valent complexes will be compared to [Mn(IV)(Salpn)(O)]<sub>2</sub> which exhibits a catalase reaction using high valent manganese.[2] The reactivity of the X-2-OHSalpn complexes with t-butyl hydroperoxide and other oxidants will also be presented.

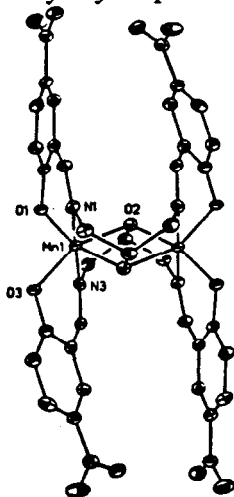


FIGURE 1.  $\text{Mn}_2(5\text{-NO}_2\text{-2-OHSalpn})_2$

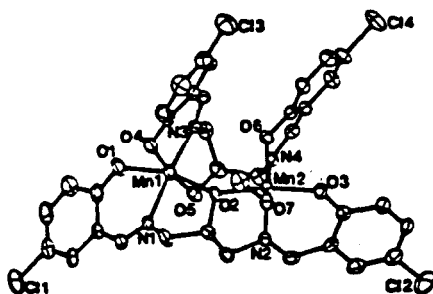


FIGURE 2.  $\text{Mn}_2(5\text{-Cl-2-OHSalpn})_2(\text{CH}_3\text{OH})$

1. J. A. Bonadies, M. L. Kirk, M.S. Lah, D. P. Kessissoglou, W. E. Hatfield, V. L. Pecoraro, *Inorg. Chem.*, **28**, 2037 (1989).
2. E. J. Larson, V. L. Pecoraro, *J. Am. Chem. Soc.*, **113**, 7809 (1991).