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

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

\[ 2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2 \] (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-ZOHSalpn (X=H, Cl, NO$_2$, OCH$_3$) 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$_2$O$_2$ disproportionation. In contrast, the lower valent, symmetric complexes as Mn(II,II) and Mn(III,III), disproportionate H$_2$O$_2$. The rates of disproportionation of H$_2$O$_2$ by these lower valent complexes will be compared to [Mn(IV)(Salpn)(O)]$_2$ 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. Mn$_2$(5-NO$_2$-2-OHSalpn)$_2$

FIGURE 2. Mn$_2$(5-Cl-2-OHSalpn)$_2$(CH$_3$OH)