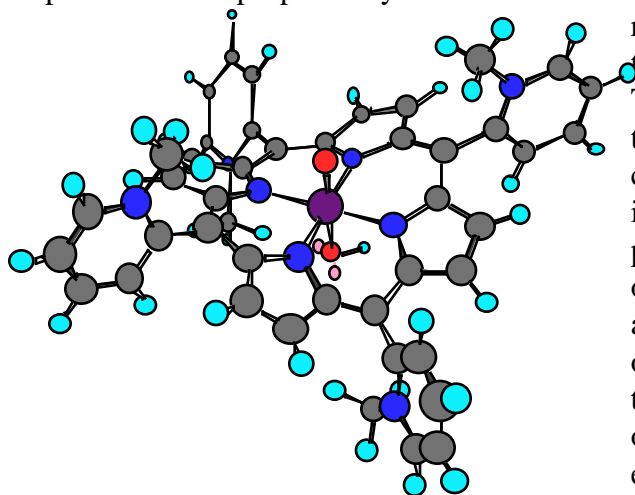


Reactive Metal-Oxo Complexes in Biology. Understanding Cytochrome P450, AlkB, Methane Monooxygenase and Myoglobin

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Reactive oxoiron and oxomanganese species are involved in a wide-range of biological and catalytic processes involving oxygen activation and transfer. Such species are proposed to participate in the hydroxylation of hydrocarbons by heme proteins such as cytochrome P450 and non-heme enzymes such as AlkB and methane monooxygenase and in the photosynthetic production of oxygen. Synthetic iron and manganese porphyrins and related Schiff base complexes have also been shown to be versatile catalysts for the oxidation of a wide variety of organic substrates. The correlation of electronic structure to the reactivity of such species and a deeper understanding of those reactions has remained an elusive goal. We have shown that oxomanganese(V) complexes can be prepared by the direct oxidation of a Mn(III) precursor. These species are shown to be



reactive oxidants in oxygen atom transfer and electron transfer reactions. Oxomanganese(V) complexes are rare. Two previously characterized species involve the use of tetraanionic ligands to stabilize the high-valent manganese center. Both compounds are diamagnetic, as are the isoelectronic nitridomanganese(V) and oxo-chromium(IV) porphyrin complexes. The spin state of the oxomanganese(V) porphyrin complex was unambiguously assigned by observing the proton NMR spectrum of this oxoMn(V) complex. Moving the site of positive charge toward the oxoMn(V) center in an isomeric set of oxomanganese(V) porphyrin complexes results in an extraordinary kinetic stability as measured by the rates of electron transfer, hydrogen atom abstraction and oxygen

transfer reactions. This kinetic stability is shown to be related to the low spin, d^2 electronic state of the oxidant. The mechanisms of oxygen transfer reactions including C-H bond insertion and the reaction of oxymyoglobin with nitric oxide will be discussed.

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