

Stable Porphyrinoid Mn(V)-Oxo Species Capable of Oxygen Atom Transfer and Hydrogen Atom Abstraction

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The balance between the stability and reactivity of high-valent metal-oxo porphyrinoid species is of central importance to the functioning of heme proteins (e.g. cytochrome P450, peroxidases, catalases). We are synthesizing transition metal porphyrinoid complexes using a relatively new ring-contracted porphyrinoid ligand called corrolazine. The corrolazine ligand has been used to synthesize a high-valent, Mn(V)-oxo complex that is stable enough for isolation at room temperature. With this complex in hand, we are able to address questions regarding the reactivity and mechanism of high-valent metal-oxo species in a direct manner. This complex is capable of both oxygen atom transfer and hydrogen atom abstraction reactions in the presence of certain substrates, despite its inherent stability. The mechanism of oxygen atom transfer is revealed through substrate/product and isotopic labeling studies, including an unexpected mechanistic finding under catalytic conditions. The mechanism of oxidation of a series of phenol substrates in reaction with the Mn(V)-oxo complex is probed by product analysis studies and kinetic measurements (e.g. Hammett analysis, kinetic isotope effect). These data provide a consistent picture of hydrogen atom abstraction as the dominant mechanism for oxidation of phenols. Further kinetic evidence also suggest the Mn(V)-oxo complex is capable of hydrogen atom abstraction of weak C-H bonds (e.g. cyclohexadiene, dihydroanthracene).

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