A Comparison of Carboxylate and Phosphinate Bridge Effects on Nonheme Diiron(II)/O_2 Reactivity

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Nonheme diiron enzymes activate oxygen for use in reactions with a variety of substrates. An overview of the ligands in these systems reveals that minor differences may alter the method used for and the efficiency of O_2 activation. A diphenylphosphinate bridged complex of the dinucleating ligand N-Et HPTB (N,N,N',N'-tetrakis (1-ethyl-2-benzimidazolylmethyl)-2-hydroxy-1,3-diaminopropane) has been synthesized, characterized and reacted with O_2 in various solvents in an attempt to gain a better understanding of the role of the phosphinate bridge in modulating the oxygenation of the diiron complex and the subsequent decay. Earlier research indicated that a CH_2Cl_2 solution of the benzoate bridged complex irreversibly binds O_2 and decays following first-order kinetics.[1] It has also been shown that in CH_3CN the decay is accelerated by the presence of electron-donating groups on the benzoate bridge.[2] Our current research shows no difference between the first-order decay kinetics of oxygenated DMF solutions of the benzoate and phosphinate bridged complexes. However, when exposed to O_2, a CH_2Cl_2 solution of the phosphinate complex behaves quite differently from the analogous benzoate complex solution. A multi-step decay occurs, revealing the presence of two intermediates not observed during reaction of the benzoate complex under the same conditions.

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