V-I Bioinorganic Studies on Structures and Functions of Non-Heme Metalloenzymes Using Model Complexes

Metal-containing enzymes have been widely distributed in both plants and animals and have been related to metabolic processes such as hydroxylation, oxygen transport, oxidative catalysis, electron transfer, and so on. In this project the structures and functions for the metal complexes are studied as a model of several metallo-enzymes by some physico-chemical methods.

V-I-1 A Novel Diiron Complex as a Functional Model for Hemerythrin

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Diiron(II) complexes with a novel dinucleating polypyridine ligand, *N*,*N*,*N*',*N*'-tetrakis(6-pivalamido-2-pyridylmethyl)-1,3-diaminopropan-2-ol (HTPPDO), were synthesized as functional models of hemerythrin. Structural characterization of the complexes, $[Fe^{II}_2(Htppdo)(PhCOO)](ClO_4)_3$ (**1**), $[Fe^{II}_2(Htppdo)(p\text{-}Cl\text{-}PhCOO)](ClO_4)_3$ (**2**), $[Fe^{II}_2(Htppdo)(p\text{-}Cl\text{-}PhCOO)](BF_4)_3$ (**2'**) and $[Fe^{II}_2(tppdo)(p\text{-}Cl\text{-}PhCOO)](ClO_4)_2$ (**3**), were accomplished by electronic absorption and IR spectroscopic, electrochemical, and X-ray diffraction methods. The crystal structures of **1** and **2'** revealed that the two iron atoms are asymmetrically coordinated with HTPPDO and bridging benzoate. One of the iron centers (Fe(1)) has a seven-coordinate capped octahedral geometry comprised of an N_3O_4 donor set which includes the propanol oxygen of HTPPDO. The other iron center (Fe(2)) forms an octahedron with an N_3O_3 donor set and one vacant site. The two iron atoms are bridged by benzoate (**1**) or *p*-chlorobenzoate (**2**). On the other hand, both Fe atoms of complex **3** are both symmetrically coordinated with N_3O_4 donors and two bridging ligands, benzoate and the propanolate of TPPDO. Reactions of these complexes with dioxygen were followed by electronic absorption, resonance Raman and ESR spectroscopies. Reversible dioxygen-binding was demonstrated by observation of an intense LMCT band for O_2^{2-} to Fe(III) at 610 (**1**) and 606 nm (**2**) upon exposure of dioxygen to acetone solutions of **1** and **2** prepared under an anaerobic conditions at –50 °C. The resonance Raman spectra of the dioxygen adduct of **1** exhibited two peaks assignable to the ν(O–O) stretching mode at 873 and 887 cm^{-1}, which shifted to 825 and 839 cm^{-1} upon binding of $^{18}O_2$. ESR spectra of all dioxygen adducts were silent. These findings suggest that dioxygen coordinates to the diiron atoms as a peroxo anion in a μ-1,2 mode. Complex **3** exhibited irreversible dioxygen binding. These results indicate that the reversible binding of dioxygen is governed by the hydrophobicity of the dioxygen-binding environment rather than the iron redox potentials.

V-I-2 Reactivity of Hydroperoxide Bound to a Mononuclear Non-Heme Iron Site

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The first isolation and spectroscopic characterization of the high-spin mononuclear iron(III) complex with hydroperoxide in an end-on mode, $[Fe(bppa)(OOH)]^{2+}$, and the stoichiometric oxidation of substrates by the mononuclear iron-oxo intermediate produced by its decomposition have been described. The purple species (**2**) obtained from reaction of $[Fe(bppa)(HCOO)](ClO_4)_2$ with H_2O_2 in acetone solution at -50 °C gave characteristic UV-vis (λ_{max} = 568 nm, ε = 1200 $M^{-1}cm^{-1}$), ESR (g = 7.54, 5.78 and 4.25, S = 5/2), and ESI mass spectra (m/z = 288.5 corresponding to the ion, $[Fe(bppa)(OOH)]^{2+}$). The resonance Raman spectrum of **2** in d_6-acetone revealed two intense bands at 621 and 830 cm^{-1}, in which the former band shifted to 599 cm^{-1} when reacted with ^{18}O-labeled H_2O_2 and the latter band showed a small isotope shift to 813 and 826 cm^{-1} upon reaction with of $H_2{}^{18}O_2$ and D_2O_2, respectively. Reactions of the isolated $(bppa)Fe^{III}$-OOH (**2**) with various substrates (single turnover oxidations) revealed that the iron-oxo intermediate generated by decomposion of complex **2** is a nucleophilic intermediate formulated as $[(bppa)Fe^{III}–O^{\bullet}]$.