Diiron Complex with An Asymmetric Metal Center Directed toward Oxyhemerythrin

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Hemerythrin (Hr) is one of non-heme iron proteins that can reversibly bind dioxygen. The active site of deoxyHr contains dinuclear iron center with an asymmetric coordination environment; one iron site is six-coordinated and another one is five-coordinated. A dioxygen binds to the coordinatively unsaturated iron atom in an end-on fashion to form peroxide accompanied by a rapid two electrons transfer from the two iron(II) ions, and then the hydroxo hydrogen is transferred to the generated peroxide and interacts with the bridging oxo ion by a hydrogen bond. In order to construct the diiron(III) complex with hydroperoxide in the end-on mode as Hr model, a new diiron(III) complex $[Fe^{III}_2(BPHDO)\{(p\text{-}Cl)PhCOO\}(MeOH)](ClO_4)_3$ (**1**) was prepared using originally-designed dinucleating ligand, *N,N*-bis-(6-pivalamido-2-pyridylmethyl)-*N'*-(2-hydroxyethyl)-*N'*-(2-pyridylmethyl)-1,3-diaminopropan-2-ol(HBPHDO). X-ray analysis revealed that the two iron ions have asymmetric environments with six- and seven-coordinate diferric centers, in which the six-coordination iron site is coordinated by MeOH molecule replaceable with a hydroperoxide ion ($^-$OOH). Interestingly, the reaction of complex **1** with H_2O_2 afforded a reddish purple solution with an LMCT ($^-$OOH to Fe^{III}) band at 557 nm (ε = 1200 $M^{-1}cm^{-1}$). The resonance Raman spectra of the hydroperoxo adduct exhibited a $\nu(^{16}O\text{-}^{16}O)$ frequency band at 870.2 cm^{-1} which shifted to 867.6 and 820.3 cm^{-1} when D_2O_2 and $H_2{}^{18}O_2$ were used, respectively, indicating that the diiron(III) complex with a hydroperoxide ion was generated. It is supported from the previously reported data of a mononuclear iron hydroperoxo complex $[Fe(H_2bppa)(OOH)]^{2+}$ which was generated by reaction between the mononuclear iron complex $[Fe(H_2bppa)(HCOO)](ClO_4)_2$ and H_2O_2.