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-Cl)PhCOO}(MeOH)](ClO\(_4\))\(_3\) (1) was prepared using originally-designed dinucleating ligand, \(\text{N,N-bis-(6-pivalamido-2-pyridylmethyl)-N'-(2-hydroxyethyl)-N'(2-pyridylmethyl)-1,3-diaminopropan-2-ol (HBPHDO)}\). 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 \(\text{H}_2\text{O}_2\) afforded a reddish purple solution with an LMCT (‘OOH to Fe\[^{III}\]) band at 557 nm (\(\varepsilon = 1200 \text{ M}^{-1}\text{cm}^{-1}\)). The resonance Raman spectra of the hydroperoxo adduct exhibited a \(\nu(^{16}\text{O}-^{16}\text{O})\) frequency band at 870.2 cm\(^{-1}\) which shifted to 867.6 and 820.3 cm\(^{-1}\) when \(\text{D}_2\text{O}\) and \(\text{H}_2\text{O}_{\text{18}}\) 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\(_2\text{bppa})(\text{OOH})]\(^{2+}\) which was generated by reaction between the mononuclear iron complex [Fe(H\(_2\text{bppa})(\text{HCOO})](\text{ClO}_4)\(_2\) and \(\text{H}_2\text{O}_2\).