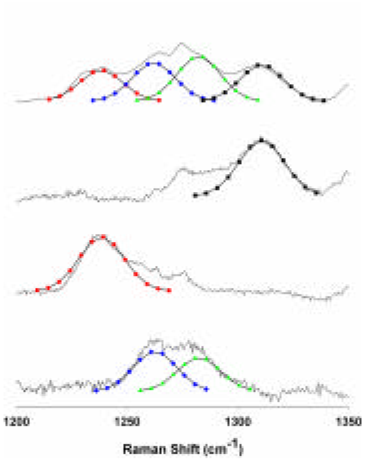
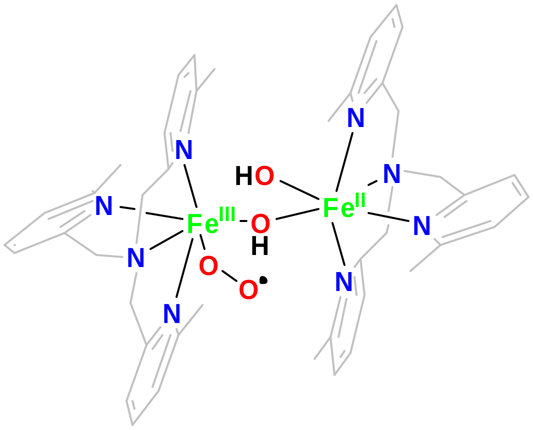
The First Example of a Nonheme Diiron(II,III) Superoxo Species

Xiaopeng Shan and Lawrence Que, Jr.

Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota,
Minneapolis, Minnesota 55455 (e-mail: xiaopeng@chem.umn.edu)

Diiron(II,III) superoxo species have been proposed as initial intermediates in the oxygenation of nonheme diiron proteins, such as the oxygen carrier hemerythrin and the hydroxylating enzyme methane monooxygenase. To date only indirect evidence has been obtained in kinetic studies of methane monooxygenase. Herein we report the first evidence of a diiron(II,III) superoxo species that is formed in the reaction of $[Fe_2(\mu\text{-}OH)_2(6\text{-}Me_3\text{-}TPA)_2]^{2+}$ ($6\text{-}Me_3$-TPA = tris(6-methyl-2-pyridylmethyl)amine) with O_2 in CH_2Cl_2 at –80 °C prior to the formation of previously characterized $[Fe_2(\mu\text{-}O)(\mu\text{-}1,2\text{-}O_2)(6\text{-}Me_3\text{-}TPA)_2]^{2+}$. This superoxo species has been characterized by resonance Raman spectroscopy to have its ν(O-O) at 1310 cm^{-1} with a –71 cm^{-1} ^{18}O isotope shift. A doublet peak pattern for the $^{16}O^{18}O$ isotopomer of this species in mixed-isotope Raman experiments strongly suggests that the superoxide ligand is bound end-on. Further studies revealed that this superoxo species, unlike the subsequent peroxide, is capable to oxidize 2,4-di-*tert*-butylphenol through a proton coupled electron transfer mechanism.





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