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Diiron(IV)oxo Crystal Structure Modeling Intermediate Q of Methane Monooxygenase

G. Rohde¹, G. Xue¹, L. Que, Jr.¹

¹University of Minnesota, Department of Chemistry, Minneapolis, USA

Nonheme iron enzymes catalyze a wide variety of reactions by O₂ activation, including the biosynthesis of the antibiotic chloramphenicol, the radical initiator in the production of deoxyribonucleotides from ribonucleotides by ribonucleotide reductase intermediate X (RNRX) in all eukaryotic life-forms and the selective oxidation of methane to methanol by the soluble form of methane monooxygenase intermediate Q (sMMOQ).[1] High-valent diiron active intermediates have been identified for both sMMOQ and RNRX and are formulated as a diiron(IV)-bis- μ -oxo and a mixed valent Fe(III)Fe(IV)-bis- μ -oxo respectively.[1] Previously, the crystal structure of a mixed-valent Fe(III)Fe(IV)-bis- μ -oxo model complex was reported.[2] A high-yielding synthesis of the reported diiron(IV)-bis- μ -oxo has allowed for the successful structural solution of a high-valent diiron(IV) model complex for sMMOQ.[3] This sMMOQ model complex, along with four other diiron-bis- μ -oxo model complexes in different oxidation and protonation states are compared to sMMOQ and RNRX and related to the mechanism of O₂ activation by nonheme enzymes.

[1] B. Wallar, J. Lipscomb, *Chemical Reviews*, 1996, 2625-2658, [2] H. Hsu, Y. Dong, V. Young, Jr., L. Que, J., *Journal of the American Chemical Society*, 1999, 5230-5237, [3] G. Xue, D. Wang, R. De Hont, et al. *Proceedings of the National Academy of Sciences of the United State of America*, 2007, 20713-20718

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