

Supporting Information

Heme-Cu Binucleating Ligand Supports Heme/O₂ and Fe^{II}-Cu^I/O₂ Reactivity Providing High- and Low-Spin Fe^{III}-Peroxo-Cu^{II} Complexes

Hyun Kim,[†] Savita K. Sharma,[†] Andrew W. Schaefer,[‡] Edward I. Solomon,^{*,‡} and Kenneth D. Karlin^{*,†}

[†]Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, USA

[‡]Department of Chemistry, Stanford University, Stanford, California 94305, USA

To whom correspondence should be addressed. E-mail: karlin@jhu.edu, edward.solomon@stanford.edu

Table of Contents

Figure S1. Reversible dioxygen binding to (P^{ImH})Fe^{II} (**1**) yielding (P^{ImH})Fe^{III}-(O₂^{·-}) (**2**) in THF.

Figure S2. Diagrams of heme-Fe^{III}-superoxide complexes.

Figure S3. Figures of high-spin heme-peroxo-copper complexes.

Figure S4. Diagrams of complexes with low-spin μ -1,2-peroxo configuration.

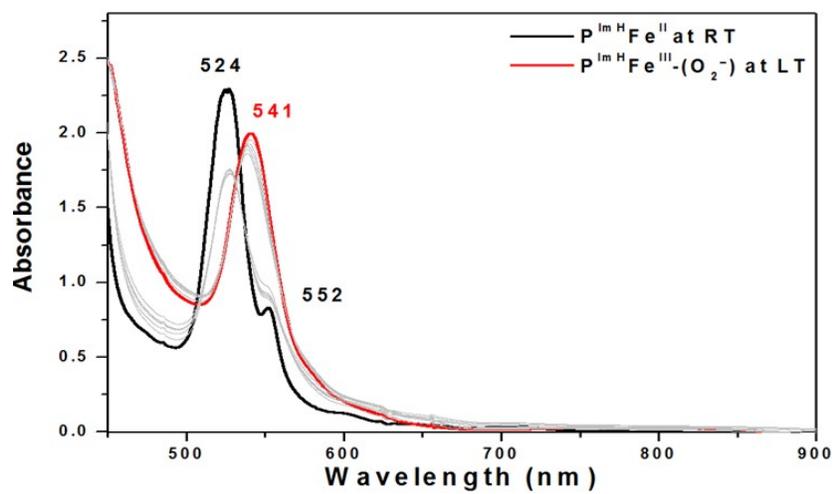


Figure S1. Reversible dioxygen binding to $(P^{ImH})Fe^{II}$ (**1**) (black) yielding $(P^{ImH})Fe^{III}-(O_2^{\cdot -})$ (**2**) (red) in THF. Spectra shown in grey are generated during the transformation. It was repeated five times.

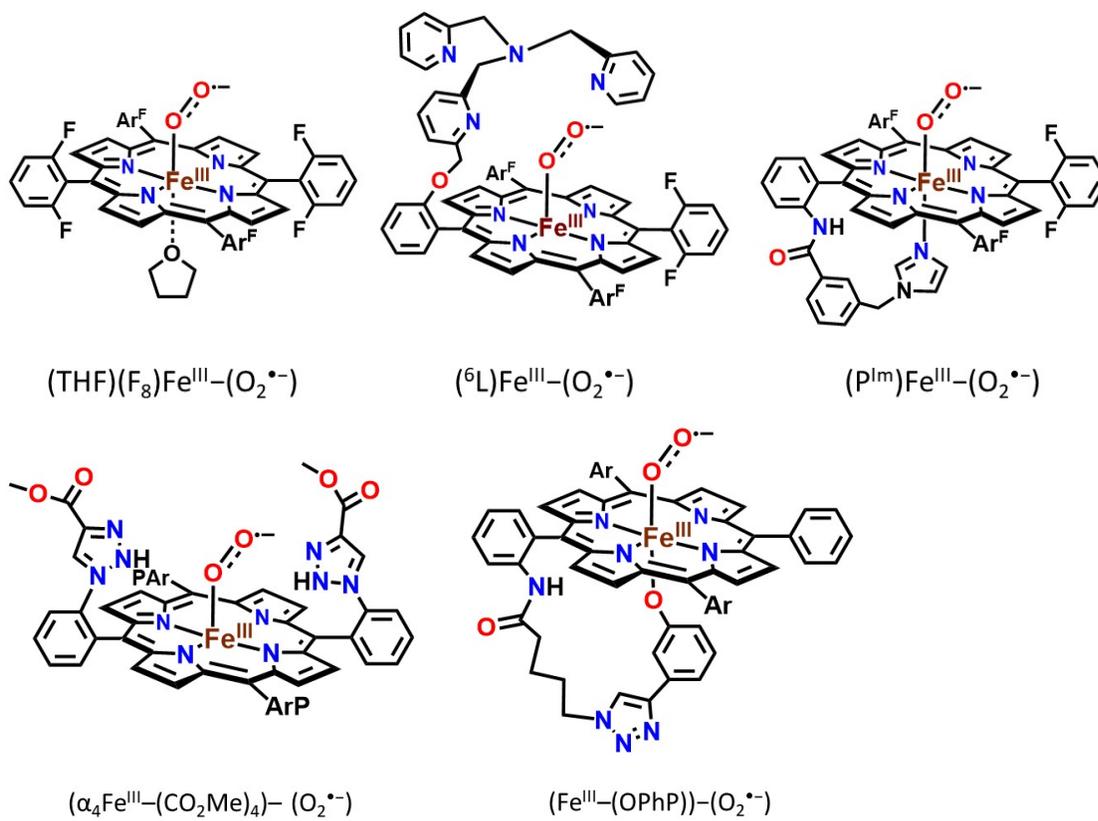


Figure S2. Diagrams of heme-Fe^{III}-superoxide complexes.¹⁻⁵

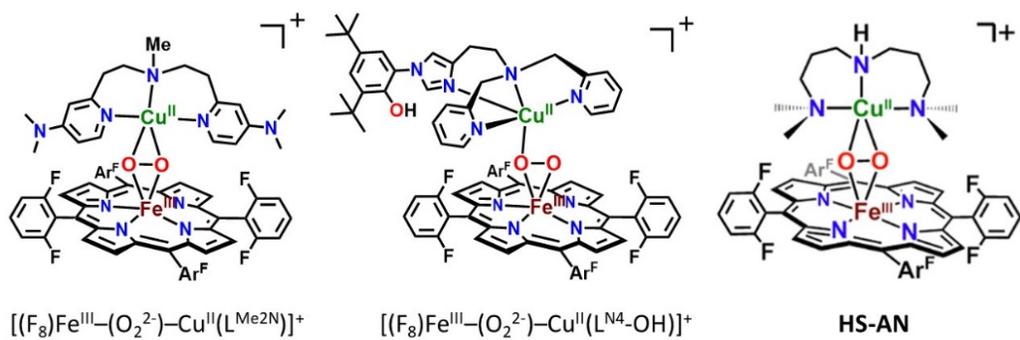


Figure S3. Figures of high-spin heme-peroxo-copper complexes.^{1,6,7}

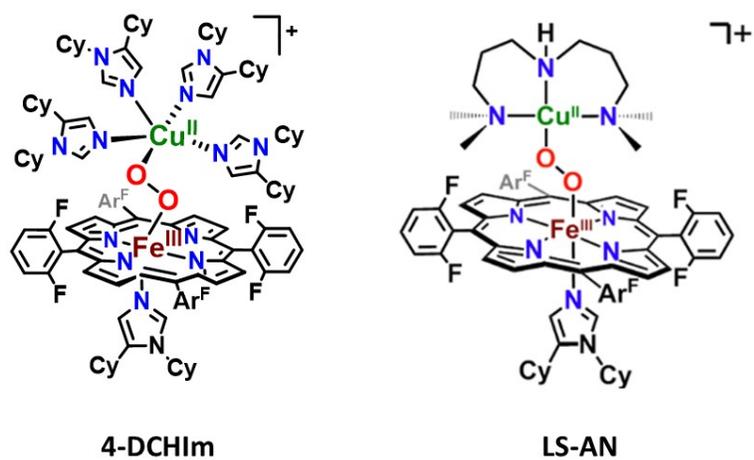


Figure S4. Diagrams of complexes with low-spin μ -1,2-peroxo configuration.⁸⁻¹⁰

References

- (1) Kim, E.; Helton, M. E.; Wasser, I. M.; Karlin, K. D.; Lu, S.; Huang, H.; Moënne-Loccoz, P.; Incarvito, C. D.; Rheingold, A. L.; Honecker, M.; Kaderli, S.; Zuberbühler, A. D. Superoxo, μ -Peroxo, and μ -Oxo Complexes from Heme/O₂ and Heme-Cu/O₂ Reactivity: Copper Ligand Influences in Cytochrome *c* Oxidase Models. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 3623–3628.
- (2) Wasser, I. M.; Huang, H. W.; Moënne-Loccoz, P.; Karlin, K. D. Heme/Non-Heme Diiron(II) Complexes and O₂, CO, and NO Adducts as Reduced and Substrate-Bound Models for the Active Site of Bacterial Nitric Oxide Reductase. *J. Am. Chem. Soc.* **2005**, *127*, 3310–3320.
- (3) Sharma, S. K.; Schaefer, A. W.; Lim, H.; Matsumura, H.; Moënne-Loccoz, P.; Hedman, B.; Hodgson, K. O.; Solomon, E. I.; Karlin, K. D. A Six-Coordinate Peroxynitrite Low-Spin Iron(III) Porphyrinate Complex - The Product of the Reaction of Nitrogen Monoxide ($\cdot\text{NO}_{(g)}$) with a Ferric-Superoxide Species. *J. Am. Chem. Soc.* **2017**, *139*, 17421–17430.
- (4) Mitra, K.; Chatterjee, S.; Samanta, S.; Sengupta, K.; Bhattacharjee, H.; Dey, A. A Hydrogen Bond Scaffold Supported Synthetic Heme Fe^{III}-O₂-Adduct. *Chem. Commun.* **2012**, *48*, 10535–10537.
- (5) Das, P. K.; Mitra, K.; Dey, A. Spectroscopic Characterization of a Phenolate Bound Fe^{II}-O₂ Adduct: Gauging the Relative “Push” Effect of a Phenolate Axial Ligand. *Chem. Commun.* **2014**, *50*, 5218–5220.
- (6) Kim, E.; Kamaraj, K.; Galliker, B.; Rubie, N. D.; Moënne-Loccoz, P.; Kaderli, S.; Zuberbühler, A. D.; Karlin, K. D. Dioxygen Reactivity of Copper and Heme–Copper Complexes Possessing an Imidazole–Phenol Cross-Link. *Inorg. Chem.* **2005**, *44*, 1238–1247.
- (7) Halime, Z.; Kieber-Emmons, M. T.; Qayyum, M. F.; Mondal, B.; Gandhi, T.; Puiu, S. C.; Chufán, E. E.; Sarjeant, A. A. N.; Hodgson, K. O.; Hedman, B.; Solomon, E. I.; Karlin, K. D. Heme-Copper-Dioxygen Complexes: Toward Understanding Ligand-Environmental Effects on the Coordination Geometry, Electronic Structure, and Reactivity. *Inorg. Chem.* **2010**, *49*, 3629–3645.
- (8) Adam, S. M.; Garcia-Bosch, I.; Schaefer, A. W.; Sharma, S. K.; Siegler, M. A.; Solomon, E. I.; Karlin, K. D. Critical Aspects of Heme–Peroxo–Cu Complex Structure and Nature of Proton Source Dictate Metal–O Peroxo Breakage versus Reductive O–O Cleavage Chemistry. *J. Am. Chem. Soc.* **2017**, *139*, 472–481.
- (9) Garcia-Bosch, I.; Adam, S. M.; Schaefer, A. W.; Sharma, S. K.; Peterson, R. L.; Solomon, E. I.; Karlin, K. D. A “Naked” Fe^{III}-(O₂²⁻)-Cu^{II} Species Allows for Structural and Spectroscopic Tuning of Low-Spin Heme-Peroxo-Cu Complexes. *J. Am. Chem. Soc.* **2015**, *137*, 1032–1035.
- (10) Kieber-Emmons, M. T.; Qayyum, M. F.; Li, Y.; Halime, Z.; Hodgson, K. O.; Hedman, B.; Karlin, K. D.; Solomon, E. I. Spectroscopic Elucidation of a New Heme/Copper Dioxygen Structure Type: Implications for O–O Bond Rupture in Cytochrome *c* Oxidase. *Angew., Chem. Int. Ed.* **2012**, *51*, 168–172.