

Oxygen Activation at Mononuclear Nonheme Iron Centers: A Superoxo Perspective.

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Table S1. Summary of Crystallographic Data for **1**·3CH₂Cl₂ and **2**·C₅H₁₂

	1 ·3CH ₂ Cl ₂	2 ·C ₅ H ₁₂
Empirical Formula	C ₃₄ H ₅₉ B Cl ₆ Fe N ₆ O ₄	C ₇₅ H ₁₁₄ B ₂ Fe ₂ N ₁₂ O ₆
fw	895.23	1413.10
<i>T</i> (K)	173(2)	173(2)
Mo Kα λ, Å	0.71073	0.71073
space group	P-1	P2/c
<i>a</i> (Å)	12.549(3)	11.3474(10)
<i>b</i> (Å)	13.537(3)	13.0436(11)
<i>c</i> (Å)	13.733(3)	26.760(2)
α (deg)	88.421(3)	90°
β (deg)	89.132(3)	97.690(1)°
γ (deg)	80.386(3)	90°
<i>V</i> (Å ³)	2299.2(10) Å ³	3925.1(6)
<i>Z</i>	2	2
R1 ^a	0.0473	0.0416
wR2 ^b	0.1358	0.1100

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|; \quad ^b wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$$

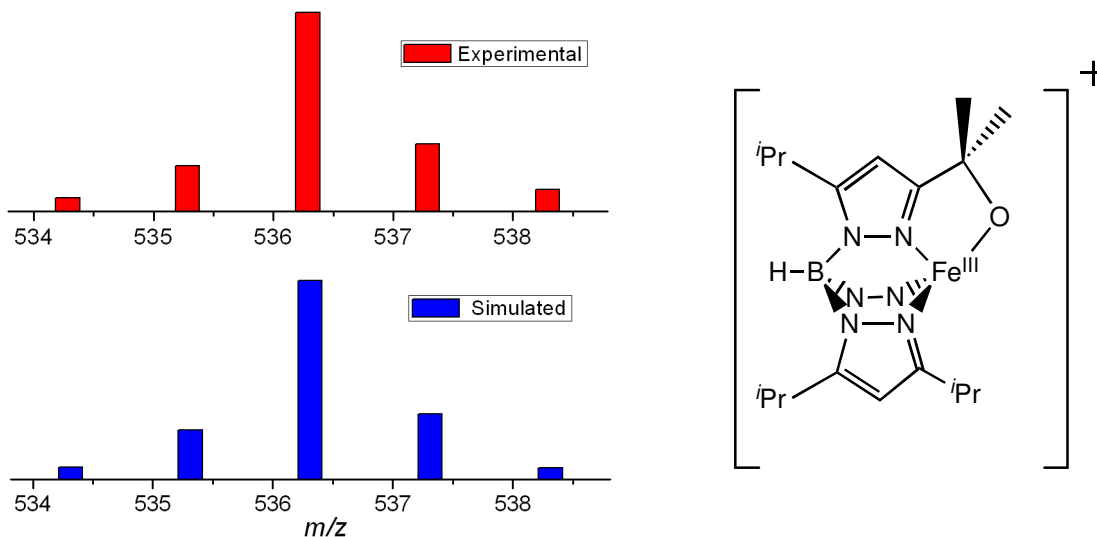


Figure S1 : ESI-MS spectrum when MeCN solution of **1** or **2** (1 mM) is exposed to oxygen at room temperature. The peak at $m/z = 536$, matches with the formula $[\text{Fe}(\text{Tp}^{\text{iPr}_2*})]^+$ as schematically described at right.

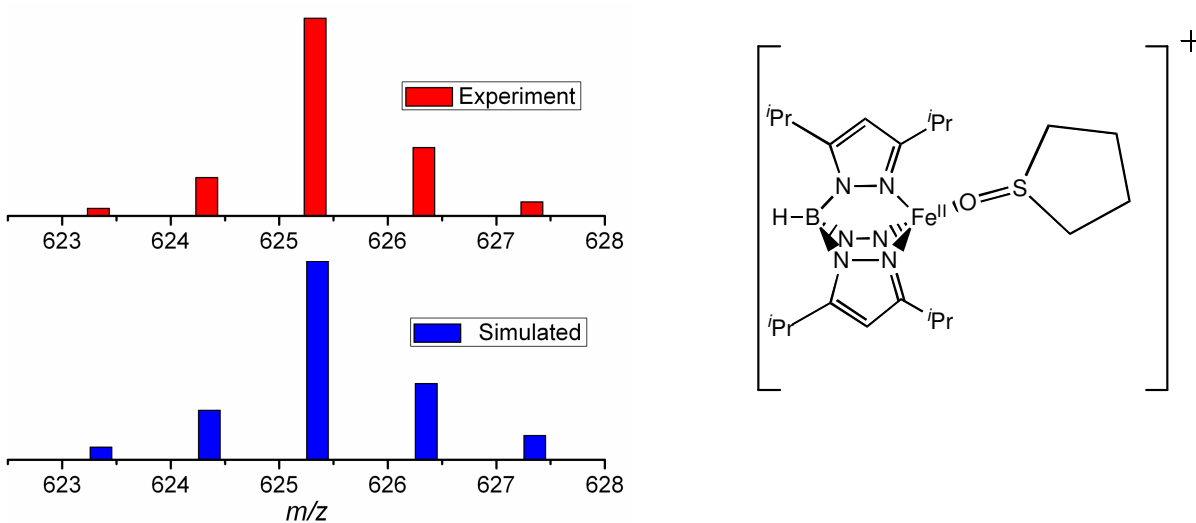


Figure S2 : ESI-MS spectrum, when MeCN solution of **1** or **2** (1 mM) is exposed to oxygen at room temperature in the presence of tetrahydrothiophene (100 mM). The peak at $m/z = 625$, matches with the formula $[\text{Fe}(\text{Tp}^{\text{iPr}_2})(\text{OS}(\text{CH}_2)_4)]^+$ as schematically described at right.

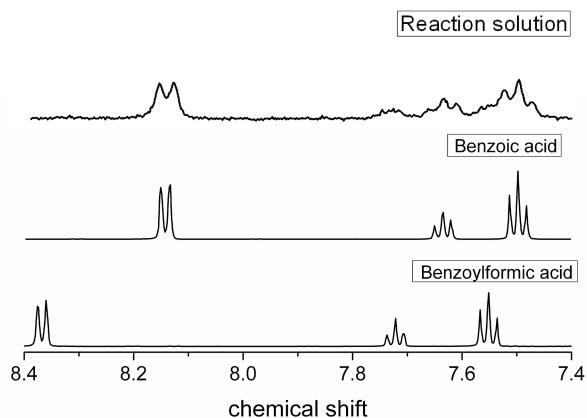


Figure S3 : ^1H -NMR spectrum (300MHz, CDCl_3 at 25°C) of the organic product after reaction of **2** with O_2 .

Mössbauer Spectroscopy

We have analyzed the Mössbauer spectra of the green diiron(III) peroxo intermediate using the spin Hamiltonian ($S_1 = S_2 = 5/2$)

$$\hat{\mathcal{H}} = J\hat{S}_1 \cdot \hat{S}_2 + \sum_{i=1,2} \left\{ 2\beta\hat{S}_i \cdot \hat{\mathbf{B}} + A_o\hat{S}_i \cdot \hat{\mathbf{I}}_i - g_n\beta_n\hat{\mathbf{B}} \cdot \hat{\mathbf{I}}_i + \hat{\mathcal{H}}_{Q,i} \right\}$$

$$\hat{\mathcal{H}}_{Q,i} = \frac{1}{12} eQV_{i,zz} \left[3\hat{I}_{i,z}^2 - I(I+1) + \eta_i (\hat{I}_{i,x}^2 - \hat{I}_{i,y}^2) \right]$$

where all symbols have their conventional meanings. For the analysis of the antiferromagnetically coupled peroxo dimer the zero-field splitting terms of the Fe^{III} site do not matter and have been dropped. The simulations were performed by assuming the fast relaxation regime for the spin of the coupled system and by assuming two identical Fe^{III} sites. The simulations of Figure 6 were obtained with the following parameters: $A_o/g_n\beta_n = -21$ T, $\Delta E_Q = +1.32$ mm/s, $\eta = 1$, $\delta = 0.65$ mm/s and $J = 70$ cm^{-1} .

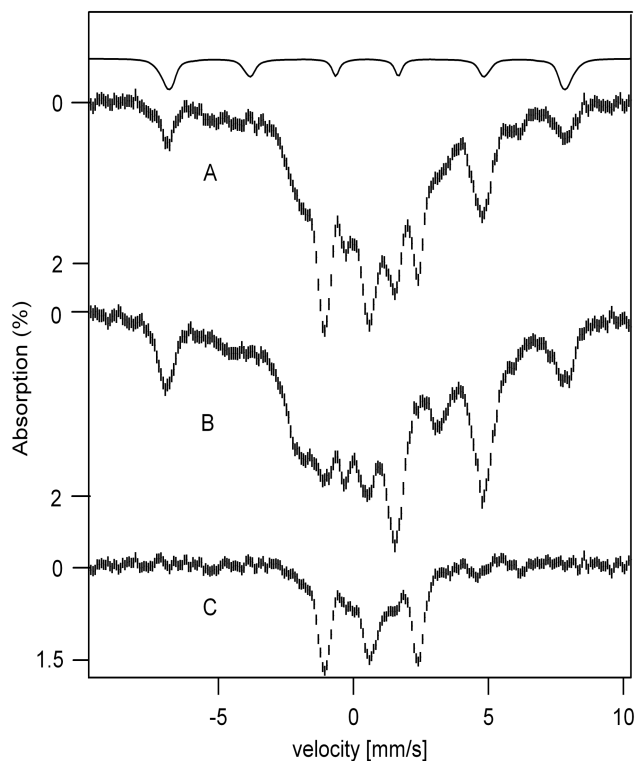


Figure S4. (A) 8.0 T/4.2 K Mössbauer spectrum of a sample containing the green intermediate (sample of Figure 6). The solid line drawn above the experimental spectrum is a simulation for a monomeric high-spin Fe^{III} contaminant (10% of Fe). (B) 8.0 T spectrum obtained after the sample of (A) was kept for 30 min at $-30\text{ }^{\circ}\text{C}$ and then refrozen; this procedure led to ca. 90 % decay of the green intermediate. Roughly 50 % of the iron of the green intermediate decayed to a state essentially identical to the ferrous starting material, the remainder (10%) into high-spin Fe^{III} and into two not yet identified, poorly resolved species. We have prepared 8.0 T spectra of the green intermediate by subtracting a fraction of the spectrum of (B) from that of (A), cancelling essentially the contribution of the Fe^{II} and monomeric Fe^{III} species. This procedure led to spectrum (C), which is the same spectrum as that shown in Figure 6B (the shoulder at -2 mm/s reflects contributions from unidentified decay products).