

Supporting Information

A Synthetic Model for the Putative $\text{Fe}^{\text{IV}}_2\text{O}_2$ Diamond Core of Methane Monooxygenase Intermediate Q

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Preparation of [Fe(BPMCN)(OTf)₂], (**1**) and [Fe(5-Me₂-BPMCN)(OTf)₂].

[Fe(BPMCN)(OTf)₂] (**1**). The preparation of **1** was carried out in an anaerobic box. The ligand BPMCN (*N,N'*-bis-(2-pyridylmethyl)-*N,N'*-dimethyl-*trans*-1,2-diaminocyclohexane, 220 mg, 0.68 mmol) was dissolved in THF (8 mL). The solution was then vigorously stirred while Fe(OTf)₂·2MeCN (296 mg, 0.68 mmol) dissolved in THF (10 mL) was added. After stirring for 1 h, the solution was filtered to obtain a white solid. Recrystallization from CH₂Cl₂/hexane afforded the product as colorless fine needles (124 mg, 27%). Anal. Calcd. for C₂₃H₃₂F₆FeN₄O₆S₂·H₂O: C, 37.94; H, 4.34; N, 8.04. Found: C, 37.89; H, 4.18; N, 7.99.

The preparation of [Fe(5-Me₂-BPMCN)(OTf)₂] was carried out in an analogous manner with 5-Me₂-BPMCN in place of BPMCN. Anal. Calcd. for C₂₅H₃₆F₆FeN₄O₆S₂: C, 40.80; H, 4.57; N, 7.93. Found: C, 40.91; H, 4.52; N, 7.93. The ¹H NMR spectra shown in **Figure S1** and their strong similarity indicate that **1** has the *cis*-β ligand topology found crystallographically for [Fe(5-Me₂-BPMCN)(OTf)₂].

Preparation and characterization of [Fe₂(μ-O)₂(BPMCN)₂](CF₃SO₃)₄, (**3**)

A typical preparation of **3** is as follows: To a solution of **1** (13 mg, 2 μmol) in 3 mL CH₂Cl₂ cooled to -83 °C was added 4 μL of a 5M solution of TBHP in nonane (20 μmol) diluted in 1 mL of CH₂Cl₂ also precooled to -83 °C; this mixture was maintained at this temperature for 24 h. 10 mL precooled pentane was then added to the reaction mixture, which was allowed to stand at this temperature until a dark blue solid was deposited. After decantation of the supernatant, the solid was washed three times with cold pentane and dried at low temperature under vacuum. Mössbauer analysis of ⁵⁷Fe enriched samples demonstrated the product to be generally >95% pure. The product was found to be stable for weeks at -83 °C, but slowly decomposed at -70 °C. The isolated solid was used for subsequent spectroscopic characterization or reactivity studies.

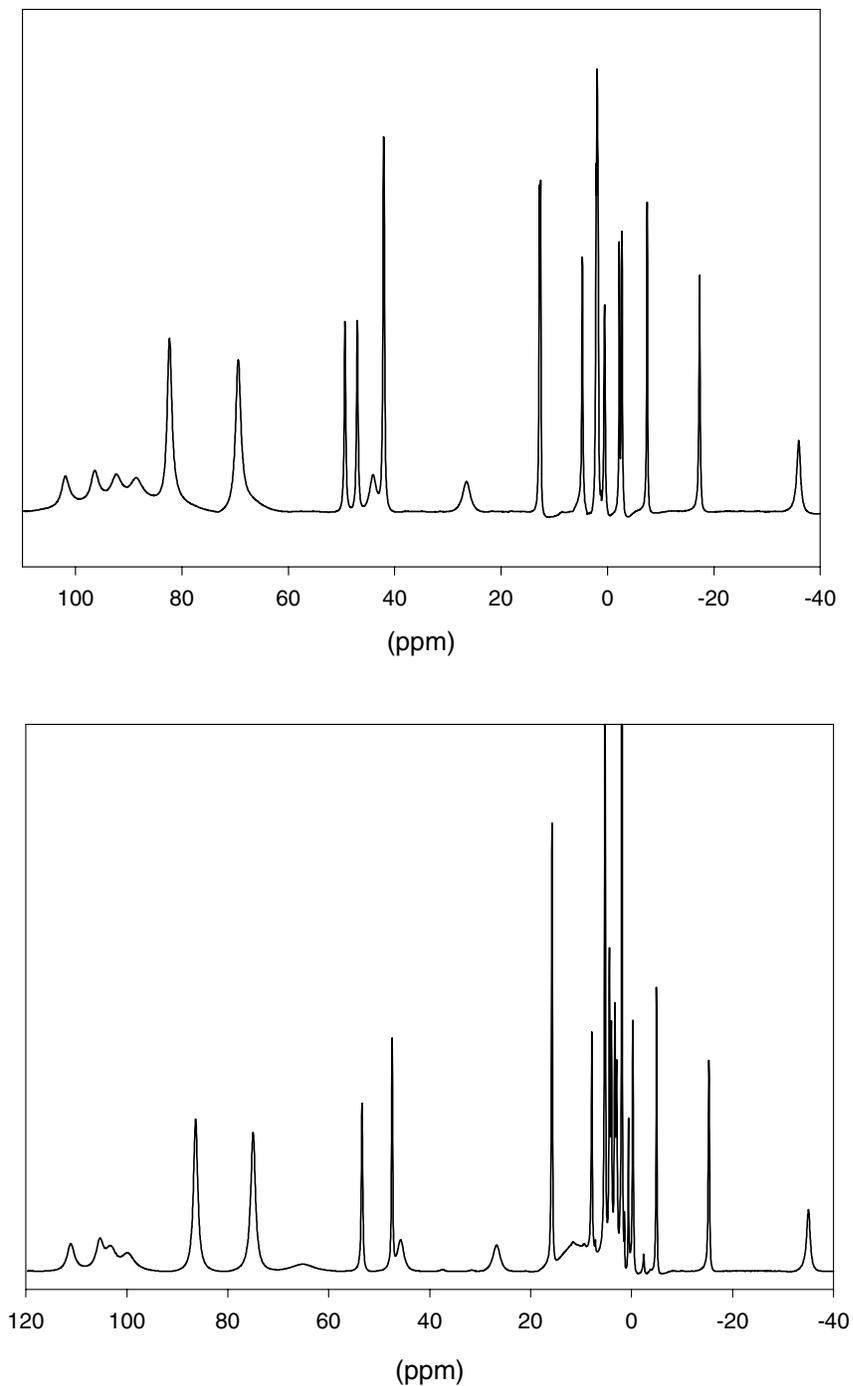
A sample of **3** was dried in vacuo at room temperature for several hours. The yellow powder that remained was subjected to elemental analysis (C, H, N, S, F) by Atlantic Microbab Inc. A portion of this powder was dissolved in 0.1 M HCl and analyzed for Fe content by ICP-AES. Calcd. for C₄₄H₅₆F₁₂Fe₂N₈O₁₄S₄ (found) %C, 38.05 (37.17); %H, 4.06 (4.70); %F, 16.41 (14.57); %Fe, 8.04 (7.18); %N, 8.07 (7.10); %S, 9.23 (8.02). Values for %Fe, %F, %N and %S are 12(1)% lower than expected for the given formulation. However the Fe:N:F:S atom ratio of 1:3.93:5.95:1.94 is almost precisely that predicted for an empirical formula of [Fe(BPMCN)](OTf)₂ for **3**, consistent with the Mössbauer data showing that the iron centers of **3** are >95% in one form. Inclusion of solvent molecules into the formulation may account for the experimental deviation; eg. Calcd. for C₄₄H₅₆F₁₂Fe₂N₈O₁₄S₄·0.5C₅H₁₂·1.5CH₂Cl₂ (found) %C, 37.14 (37.17); %H, 4.22 (4.70); %F, 14.69 (14.57); %Fe, 7.19 (7.18); %N, 7.22 (7.10); %S, 8.26 (8.02).

Reaction of **3** with adamantane

Solid **3** obtained from the reaction of **1** with TBHP was dissolved in 2 mL acetone at -78 °C in an Schlenk flask. To this solution was added 3 mL of a -78 °C adamantane solution in

acetone:CH₂Cl₂ 2:1 v/v (50 equivalents relative to the amount of **1** used to generate **3**). The mixture was purged three times through a vacuum-Ar cycle and left under argon. The reaction mixture was then warmed in a -40 °C bath for two hours, after which time all the blue color of **3** had completely disappeared. Products were analyzed by GC and GC-MS after addition of an internal standard (naphthalene). Yields were reported relative to the amount of **3**, assumed to be formed quantitatively from **1**.

Figure S1. ¹H-NMR of **1** (top) and [Fe(**5-Me₂-BPMC**N)(OTf)₂] (bottom) in CD₃CN.



Analysis of the Mössbauer Spectra of **3**

The Mössbauer spectra of **3** were analyzed with a spin Hamiltonian appropriate for an exchange coupled system involving two $S_1 = S_2 = 1$ Fe^{IV} sites.

$$H = JS_1 \cdot S_2 + \sum_{i=1}^2 \{D_i(S_{iz}^2 - \frac{2}{3}) + E_i(S_{ix}^2 - S_{iy}^2) - g_n \beta_n \mathbf{B} \cdot \mathbf{I}_i + \frac{eQ_i V_{iz'z'}}{12} [3I_{iz'}^2 - \frac{15}{4} + \eta_i(I_{ix'}^2 - I_{iy'}^2)]\}$$

In this eq the index i sums over the two Fe sites, J is the exchange coupling constant, \mathbf{D}_i is the zero-field splitting (ZFS) tensor of site i (principal components D_i and E_i), \mathbf{g}_i and \mathbf{A}_i are the g - and A -tensors of the sites, and $H_Q(i)$ describes the quadrupole interaction of site i (ΔE_{Q_i} and η_i). In order to obtain satisfactory fits we had to allow that the A -tensors and the EFG-tensors are rotated by Euler angles $(\alpha_A, \beta_A, \gamma_A)$ and $(\alpha_{\text{EFG}}, \beta_{\text{EFG}}, \gamma_{\text{EFG}})$ relative to the ZFS tensor. We have no evidence for inequivalent Fe sites, and therefore we used the same fine structure and hyperfine structure parameters for both sites.

For $J < 0$ a ground state with total spin $S = 2$ results. The magnetic features of the high field Mössbauer spectra result from mixing the $M_S = \pm 1$ sublevels of the quintet with the $M_S = 0$ ground state. However, the large local zero-field splittings of the Fe^{IV} sites also mix the $S = 1$ and $S = 0$ multiplets with the $S = 2$ manifold, somewhat modifying the expectation values of the electronic spin. For antiferromagnetic coupling, $J > 0$, the mixing is more elaborate. Thus, the zero-field mixing terms mix the substates of the $S = 2$ manifold into the diamagnetic ground state. Because the energies of the levels of the $S = 2$ multiplet depend on the applied magnetic field, the energy denominators of the second-order mixing terms depend on the applied field, and thus the expectation values of the electronic site spins become field dependent, producing field dependent magnetic hyperfine splittings in the Mössbauer spectra.

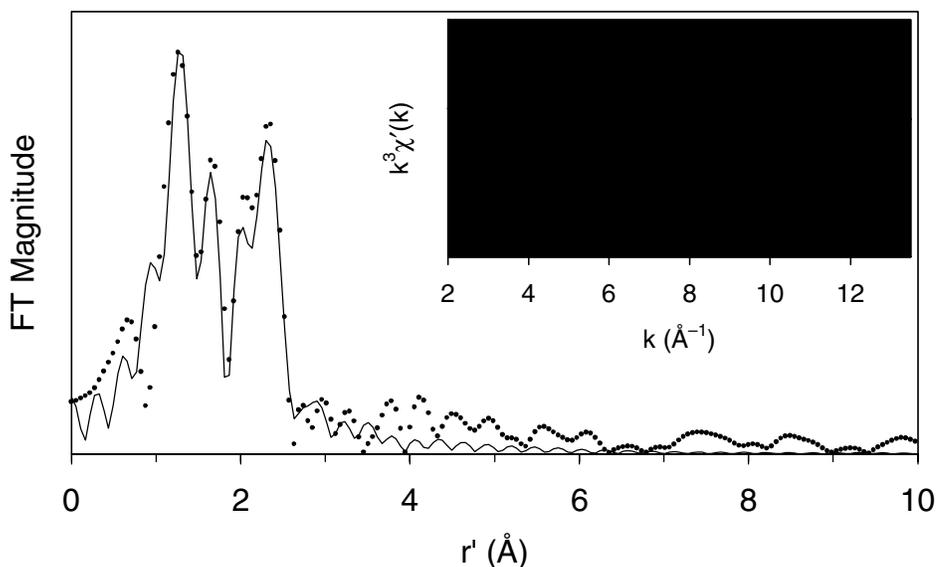
Good fits were obtained as long as $|J| < 5 \text{ cm}^{-1}$. For antiferromagnetic coupling and $J > 5 \text{ cm}^{-1}$, the ground state did not produce the required size of the hyperfine field. For the ferromagnetic case and $D < -5 \text{ cm}^{-1}$ the 4.2 K data could be fit, but when these fits were checked against spectra taken at higher temperature, the theory produced hyperfine fields that were too large. [If only a single multiplet is considered, the internal magnetic field, at 4.2 K and saturation, is proportional to S whereas at high temperature the field follows the Curie law and is thus proportional to $S(S+1)$. If $J < -5 \text{ cm}^{-1}$ the $S = 2$ multiplet has too much weight at higher temperature.]

The J -values compatible with our data are rather small. However, there are no precedents for Fe^{IV}Fe^{IV} systems with local $S_i = 1$ sites. The exchange coupling for MMO-**Q** is antiferromagnetic with $J > 60 \text{ cm}^{-1}$, but the Fe^{IV} sites of compound **Q** are high-spin, $S_1 = S_2 = 2$.

Good fits were also obtained for $J = 0$, again for equivalent sites. This situation would accommodate an Fe^{IV} monomer and also the (somewhat unlikely) case that **3** is a symmetric dimer with an isolated $S = 1$ ground state.

EXAFS analysis of **3**

Fourier transform of the Fe K-edge EXAFS data (r' space) and Fourier-filtered EXAFS spectrum ($k^3\chi'(k)$, inset) of **3** in frozen butyronitrile solution; Fourier-transformed range $k = 2\text{--}13.5 \text{ \AA}^{-1}$ (Back-transformation range $r' = 0.85\text{--}3.15 \text{ \AA}$); experimental data ($\bullet\bullet\bullet$) and best fit (---). Fitting: 1 O at 1.79 \AA ($\Delta\sigma^2, -0.0007 \text{ \AA}^2$), 3 N at 1.99 \AA (0.0038), 1 Fe at 2.81 \AA (0.009), and 7 C at 2.92 \AA (0.010).



The r' space spectrum exhibits prominent features centered at $r' = 1.3, 1.7, 2.0$ and 2.3 \AA , where r' corresponds to the actual metal-scatterer distance r after a phase shift correction of approximately 0.4 \AA ($r \sim r' + 0.4 \text{ \AA}$). The presence of an intense peak in the outer-sphere region is typical for the metal-metal scatterer of rigid $M_2(\mu\text{-O})_2$ cores.^{1,2} In contrast, in complexes where only C scatterers contribute to the outer-sphere EXAFS spectrum, the corresponding peaks have much less intensity, e.g. $[\text{Fe}(5\text{-Me}_3\text{-TPA})(\text{acac})](\text{ClO}_4)_2$.¹

The parameters of the best fit for **3** agree well with those found for the crystallographically characterized $[\text{Fe}_2(\mu\text{-O})_2(5\text{-Et}_3\text{-TPA})_2](\text{ClO}_4)_3$: 1 O at 1.82 \AA ($\Delta\sigma^2, -0.0007 \text{ \AA}^2$), 3 N at 2.00 \AA (0.0032), 1 Fe at 2.61 \AA (0.0065), and 7 C at 2.87 \AA (0.0036).¹ Comparison of this fit with the crystal structure shows that the coordination numbers for the first coordination sphere as determined by EXAFS analysis are underestimated while distances are found to be in good agreement.

(1) H.-F. Hsu, Y. Dong, L. Shu, V. G. Young, Jr., L. Que, Jr., *J. Am. Chem. Soc.* **1999**, *121*, 5230–5237.

(2) L. Que, Jr., W. B. Tolman, *Angew. Chem. Int. Ed.*, *accepted for publication*.