Supporting Information

for

Structural and Spectroscopic Characterization of (μ-Hydroxo or μ-oxo)(μ-peroxo)diiron(III) Complexes: Models for Peroxo Intermediates of Non-Heme Diiron Proteins

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Synthesis of Ligand. *N*,*N*-bis(6-methyl-2-pyridylmethyl)-3-amino-propionic acid (6Me₂-BPPH·0.5H₂O). A mixture of 3-bromopropionic acid (98 %, 2.529 g, 16.2 mmol), triethylamine (3.312 g, 32.4 mmol), and bis(6-methyl-2-pyridyl)amine (3.684 g, 16.2 mmol) in ethanol (200 mL) was stirred at 70 °C for 18 hours. Then the mixture was concentrated to 1/3 volume under reduced pressure and the resulting solution was cooled in an ice bath to give triethylamine hydrobromide as white microcrystals. After filtration, the resulting ethanol solution was concentrated under a reduced pressure to give a green oil, which was dissolved in hot acetonitrile (10 mL). The mixture was cooled in an ice bath to afford a white powder. Yield: 2.65 g (59 %). Anal. Calcd for $C_{17}H_{22}N_3O_{2.5}$: C, 66.21; H, 7.19; N, 13.63 %. Found: C, 66.49; H, 7.22; N, 13.69 %. ¹H NMR (D₂O): δ (ppm) = 2.43 (6H, s, CH₃), 2.64 (2H, t, CH₂CO₂), 3.40 (2H, t, NCH₂), 4.29 (4H, s, pyCH₂), 7.24 (4H, d, py), 7.73 (2H, t, py). ESI-TOF/MS (acetonitrile containing a small amount of formic acid): *m*/*z* (accurate mass) = 150.6246 [MH₂]²⁺ (150.5890), 300.1744 [MH]⁺ (300.1712).

Synthesis of Complexes. $[Fe_2(6Me_2-BPP)_2(O)(OH)](OTf) \cdot 3.5H_2O$ (1). An aqueous solution (10 mL) of Fe(NO₃)₃·9H₂O (0.404 g, 1.0 mmol) was added to an aqueous solution (20 mL) containing $6Me_2$ -BPPH·0.5H₂O (0.308 g, 1.0 mmol) and sodium acetate trihydrate (2.45 g, 18 mmol) to give a red solution, to which was added sodium trifluoromethanesulfonate (98 %) (0.176 g, 1.0 mmol) to afford a red powder. Recrystallization from methanol gave single crystals suitable for X-ray analysis. Yield: 0.62 g (64 %). Anal. Calcd for $C_{35}H_{48}N_6F_3Fe_2O_{16.5}S$: C, 44.09; H, 5.07; N, 8.81 %. Found: C, 44.06; H, 5.04; N, 9.05 %. IR (KBr, cm⁻¹): 3444 (OH), 1608 (C=C), 1224 (CF₃SO₃), 1155 (CF₃SO₃), 1031 (CF₃SO₃), 640 (CF₃SO₃). Mössbauer at 80 K: δ = 0.44 mm s⁻¹ and ΔE_{ϱ} = 1.56 mm s⁻¹. ESI-TOF/MS (acetonitrile): *m/z* (accurate mass) = 741.1784 [M]⁺ (741.1788). UV-vis [λ_{max}/nm (ε/M^{-1} cm⁻¹)] in methanol at –40 °C: 521 (650), 721 (70). Reflectance spectrum at ~-110 °C (λ_{max}/nm): 507, 737.

[Fe₂(6Me₂-BPP)₂(OH)(O₂)](OTf) (2·OTf). Reaction of 30% hydrogen peroxide (0.29 mL, 2.5 mmol) with complex 1 (0.024 g, 0.025 mmol) in 2 mL of methanol at -40 °C produced a blue solution, which was quickly cooled to -80 °C to prevent thermal decomposition. Diethyl ether (2 mL) was added to the solution. The resulting solution was allowed to stand for two weeks at -80 °C to afford blue microcrystals. Mössbauer at 80 K: $\delta = 0.51$ mm s⁻¹ and $\Delta E_{\varrho} = 1.30$ mm s⁻¹. ESI-TOF/MS (acetone at -40 °C): m/z (accurate mass) = 757.1775 [M]⁺ (757.1737). UV-vis [λ_{max} /nm

 $(\varepsilon/M^{-1} \text{ cm}^{-1})]$ in methanol at -80 °C: 644 (3000). Reflectance spectrum at ~-110 °C (λ_{max}/nm): 631.

[Fe₂(6Me₂-BPP)₂(OH)(O₂)]B(3-CIPh)₄·6.5CH₃OH (2·B(3-CIPh)₄). This complex was synthesized in the same way to that of 2·OTf by addition of an acetone solution (2mL) of ammonium tetra(3-chlorophenyl)borate (95 %) (0.013 g, 0.025 mmol) into a blue methanol solution. Single crystals suitable for X-ray crystallography were obtained by addition of diethylether (1 mL) at -80 °C. Mössbauer at 80 K: $\delta = 0.50$ mm s⁻¹ and $\Delta E_{\varrho} = 1.31$ mm s⁻¹. ESI-TOF/MS (acetonitrile at -40 °C): *m/z* (accurate mass) = 757.1688 [M]⁺ (757.1737). UV-vis [λ_{max} /nm (ε /M⁻¹ cm⁻¹)] in acetone at -80 °C: 647 (3050). Reflectance spectrum at ~-110 °C (λ_{max} /nm): 644.

[Fe₂(6Me₂-BPP)₂(O)(O₂)]1.5CH₃OH·6H₂O (3). The complex was synthesized by a similar way to that of 2 except for addition of base. To a methanol solution (2 mL) prepared from 1 (0.024 g, 0.025 mmol) and 30% hydrogen peroxide (0.29 mL, 2.5 mmol) at -40 °C was added triethylamine (0.026 g, 0.25 mmol) and the resulting purple solution was quickly cooled to -80 °C. After addition of diethyl ether (2.5 mL), the mixture was allowed to stand for 1 week at -80 °C to afford purple crystals suitable for X-ray crystallography. It was found that a solid sample of **3** gradually converts into **2** for a few days even at -80 °C (Figure S8), whereas it is stable at least 1 week in a matrix of DBU (1,8-diazabicyclo[5,4,0]-7-undecene) at -80 °C. This was confirmed by reflectance spectral measurement at ~-110 °C. Mössbauer spectrum of a polycrystalline sample of **3** was measured in a matrix of DBU. For UV-vis and reflectance spectral measurements, freshly prepared samples were used. Mössbauer at 80 K: $\delta = 0.50$ mm s⁻¹ and $\Delta E_Q = 1.46$ mm s⁻¹. UV-vis [λ_{max}/nm (ε/M⁻¹ cm⁻¹)] in methanol at -80 °C: 462 (1100), 577 (1500), 750 (200). Reflectance spectrum at ~-110 °C (λ_{max}/nm): 467, 576, 750.

[Fe₂(6Me₂-BPP)₂(OH)₂](NO₃)₂·4.5H₂O (4). An aqueous solution (10 mL) of Fe(NO₃)₃·9H₂O (0.404 g, 1.0 mmol) was added to an aqueous solution (20 mL) containing 6Me₂-BPPH·0.5H₂O (0.308 g, 1.0 mmol) and triethylamine (0.101 g, 1.0 mmol) to give an orange-yellow solution, which was allowed to stand for several days at ambient temperature to give yellow crystals. Yield: 0.54 g (57 %). Anal. Calcd for C₃₄H₅₁N₈Fe₂O_{16.5}: C, 43.10; H, 5.43; N, 11.82 %. Found: C, 43.00; H, 5.36; N, 11.84 %. IR (KBr, cm⁻¹): 3444 (OH), 1612 (C=C), 1380 (NO₃). Mössbauer at 80 K: δ = 0.42 mm s⁻¹ and ΔE_Q = 1.16 mm s⁻¹. ESI-TOF/MS (acetonitrile/H₂O): *m/z* (accurate mass) = 371.0945 [M]²⁺ (371.0927).

Determination of the molar extinction coefficients of the peroxo complexes $2 \cdot B(3 - ClPh)_4$, 2·OTf, and 3. Since it was difficult to weigh the amounts of $2 \cdot B(3 - ClPh)_4$, 2·OTf, and 3 due to their thermal instability, the molar extinction coefficients (ε) of the isolated complexes were determined as follows. Typically, appropriate amount of 2·OTf was dissolved into 20 mL of methanol at -80°C and then UV-vis spectrum was measured. After warming to ambient temperature, 1,10-phenanthroline (30 mg, 0.15 mmol) and ascorbic acid (99 %) (30 mg, 0.17 mmol) was added to the solution to generate [Fe^{II}(Phen)₃]²⁺, and then the volume of the resulting solution was adjusted to 25 mL in a volumetric flask by addition of water. A portion (3 mL) was taken up and was diluted to an appropriate concentration for electronic spectral measurement by addition of water, where pH was adjusted at ca. 5 by addition of acetic acid. The iron concentration was determined spectrophotometrically from the absorbance at 510 nm (the molar extinction coefficient of [Fe^{II}(Phen)₃]²⁺ is $1.14 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at pH = 5).

Physical measurements. Electronic spectra were measured on an Otsuka Electronics MCPD-2000 spectrophotometer with an Otsuka Electronics optical glass fiber attachment. The temperatures were controlled with an EYELA low temp. pairstirrer PSL-1800. The reflectance spectra were obtained with an Otsuka Electronics MCPD-2000 spectrophotometer with an Otsuka

Electronics optical glass fiber attachment. The crystalline samples were finely ground and spread on a white filter paper attached on a hand-made cold copper plate immersed inside a liquid N₂ Dewar vessel at ~-110 °C. IR spectra were obtained on the KBr disks with a Horiba FT-200 spectrophotometer. ¹H NMR spectra were measured with a JEOL JNM-LA400 spectrometer using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS in D₂O) as an internal standard. Mössbauer spectra were measured with S-600 constant-acceleration spectrometer (Austin Science Associates) at 80K. Temperature was controlled with a temperature controller (ITC502, Oxford Instruments) within a variable temperature cryostat (DN1726, Oxford Instruments). The crystalline samples $2 \cdot B(3-ClPh)_4$, $2 \cdot OTf$, and 3 were finely ground on a hand-made cold copper plate immersed inside a liquid N₂ Dewar vessel at ~-110 °C and the powder was loaded in a sample holder cooled on dryice. The data were stored in a 1024-channel analyzer (IT-5200, Inotech Inc.). A 10 mCi cobalt-57 source diffused into a palladium foil was used. The spectra were fitted by a Lorentzian line shape using software of IGOR Pro (WaveMetrics, Inc.) on a personal computer. The velocity scales and isomer shifts were normalized to iron foil at room temperature. Resonance Raman spectra were obtained with a liquid nitrogen cooled CCD detector (Model LN/CCD-1340 × 400PB, Princeton Instruments) attached to a 1 m-single polychromator (Model MC-100DG, Ritsu Oyo Kogaku). A dye laser (600 and 580 nm) (Model 375B Spectra Physics) with rhodamine-6G dye pumped by an Ar^+ laser was used as the exciting source. The laser power used were ~30 mW at the sample points. All measurements were carried out with a spinning cell (1000 rpm) keeping at ~-80 °C. Raman shifts were calibrated with indene and the accuracy of the peak positions of the Raman bands was ± 1 cm⁻¹. ESI-TOF/MS spectra were measured with a Micromass LCT spectrometer. Accurate masses (in m/z) are referenced to the {CH₃(CH₂)₉}₄N⁺ (m/z = 578.6604 in positive ion detection) as an internal standard.

X-ray Crystallography. General Procedures. X-ray diffraction studies for 1, $2 \cdot B(3-ClPh)_4$, and 3 were made on a Rigaku/MSC Mercury diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71070$ Å). The data were collected at $-150 \pm 1^{\circ}$ C to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected. A first sweep of data was done using ω scans from -80.0 to 100.0° in 0.50° step, at $\chi = 45.0^{\circ}$ and $\phi = 0.0^{\circ}$. A second sweep of data was made using ω scans from -80.0 to 100.0° in 0.50° step, at $\chi = 45.0^{\circ}$ and $\phi = 90.0^{\circ}$. Crystal-to-detector distances were 35 mm and detector swing angles were 10° for 1, $2 \cdot B(3-ClPh)_4$, and 3. Exposure rates were $36.0, 20.0, and 30.0 \sec/^{\circ}$ for 1, $2 \cdot B(3-ClPh)_4$, and 3, respectively. The data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied.

The structures were solved by a direct method $(SIR92)^1$ and expanded using a Fourier technique.² The structures were refined by a full-matrix least-squares method by using the teXsan crystallographic software package (Molecular Structure Corporation).³ The structure refinement of **1** and **2**·B(3-ClPh)₄ was carried out by the observations ($I > 3.0\sigma(I)$). The refinement of **3** was carried out by the observations ($I > 0.0\sigma(I)$) to raise the reflection/parameter ratio. ORTEP views (50% probability) of the complex molecules **1**, **2**·B(3-ClPh)₄, and **3** with a full numbering scheme of atoms are shown in Figures S2-S4, respectively. Summary of selected bond distances (Å) and angles (deg) for **1** and **2**·B(3-ClPh)₄ is listed in Table S1.

 $[Fe_2(6Me_2-BPP)_2(O)(OH)](OTf)\cdot 10H_2O$ (1). Crystal data for 1; $C_{35}H_{61}F_3Fe_2N_6O_{19}S$, monoclinic, space group C2/c with Z = 4, a = 20.576(4), b = 10.621(2), c = 21.728(4) Å, $\beta = 99.871(4)^\circ$, V = 4678(1) Å³, $\rho_{calcd} = 1.520$ g cm⁻³, R = 0.057, $R_w = 0.086$ for 3621 data with $I > 3\sigma(I)$. A single crystal with dimensions of $0.20 \times 0.20 \times 0.10$ mm was picked up from the solution by a nylon loop (Hampton Research Co.) on a hand–made cold copper plate mounted inside a liquid N₂ Dewar vessel at ca. -80 °C. Then the crystal was mounted on a goniometer head in a N₂ cryostream. There are a half of $[Fe_2(6Me_2-BPP)_2(O)(OH)]^+$ cation, a trifluoromethanesulfonate anion with a half occupation, and 5 water molecules in an asymmetric unit, indicating that the bridging hydroxide and oxide are disordered with each other. Non-hydrogen atoms, except for the counter anion, were refined with anisotropic displacement parameters. Hydrogen atoms were positioned at calculated positions (0.95 Å). They were included, but not refined, in the final least-squares cycles. The maximum peak on a final difference Fourier map was 1.00 eÅ⁻³.

[Fe₂(6Me₂-BPP)₂(OH)(O₂)]B(3-CIPh)₄·6.5CH₃OH (2·B(3-CIPh)₄). Crystal data for 2·B(3-CIPh)₄; C_{64.5}H₉₁BCl₄Fe₂N₆O_{13.5}, monoclinic, space group $P2_1/c$ with Z = 4, a = 14.863(3), b = 21.036(4), c = 21.788(4) Å, $\beta = 90.732(5)^{\circ}$, V = 6811(2) Å³, $\rho_{calcd} = 1.395$ g cm⁻³, R = 0.057, $R_w = 0.078$ for 7654 data with $I > 3\sigma(I)$. A single crystal with dimensions of 0.30 × 0.10 × 0.10 mm was picked up from the solution by a nylon loop (Hampton Research Co.) on a hand–made cold copper plate mounted inside a liquid N₂ Dewar vessel at ca. $-80 \,^{\circ}$ C, and dipped quickly in liquid nitrogen. Then the dipped crystal was mounted on a goniometer head in a N₂ cryostream. There are [Fe₂(6Me₂-BPP)₂(OH)(O₂)]⁺ cation, one tetra(3-chlorophenyl)borate, and 6.5 methanol molecules in an asymmetric unit. Non-hydrogen atoms, except for 1.5 disordered methanol molecules, were refined with anisotropic displacement parameters. The positions of the 1.5 disordered methanol molecules, were included positions (0.95 Å). They were included, but not refined, in the final least-squares cycles. The maximum peak on a final difference Fourier map (1.24 eÅ⁻³) was observed in the neighborhood of a disordered methanol molecule.

[**Fe**₂(**6Me**₂-**BPP**)₂(**0**)(**O**₂)]**1.5CH**₃**OH**·**6H**₂**O** (3). Crystal data for **3**; C_{35.5}H₅₈Fe₂N₆O_{14.5}, monoclinic, space group *C*2/c with *Z* = 4, *a* = 15.920(4), *b* = 15.912(4), *c* = 21.288(5) Å, β = 93.770(6)°, *V* = 5381(2) Å³, ρ_{calcd} = 1.126 g cm⁻³, *R* = 0.165, *R_w* = 0.155 for 5992 data with *I* > 0 σ (*I*) (*R*₁ = 0.100 for 3030 data with *I* > 2.0 σ (*I*)). A single crystal with dimensions of 0.30 × 0.06 × 0.06 mm was picked up from the solution by a nylon loop (Hampton Research Co.) on a hand–made cold copper plate mounted inside a liquid N₂ Dewar vessel at ca. –80 °C, and dipped quickly in liquid nitrogen. Then the dipped crystal was mounted on a goniometer head in a N₂ cryostream. There are a half of [Fe₂(6Me₂-BPP)₂(O)(O₂)], 0.75 methanol molecule, and three water molecules in an asymmetric unit. The bridging oxide and peroxide in the Fe₂(O)(O₂) core are disordered over two positions as shown in Figure S4. Non-hydrogen atoms, except for an oxygen atom of 0.5 disordered water molecule, were refined with anisotropic displacement parameters. Hydrogen atoms were positioned at calculated positions (0.95 Å). They were included, but not refined, in the final leastsquares cycles. The maximum peak on a final difference Fourier map was 0.90 eÅ⁻³.

(1) Sheldrick, G. M. SHELXS-86. A Program for Crystal Structure Determination. University of Göttingen, FRG, 1986.

(2) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 program system (1994), Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

Analyses of Fermi Resonance. Fermi resonance was analyzed by the method reported previously.¹

The observed Fermi doublet $(v^{(\pm)})$ can be expressed by eq. (1), where v_{Oi} and γ are defined by eqs. (2)–(4). The v_{Oi}^{0} , v_i^{0} , and W_{Oi} are the intrinsic frequencies of the O–O stretching and an overtone of some interacting vibration, and the magnitude of their interaction, respectively:

$v^{(\pm)} = v_{\rm Oi} \pm \gamma/2$	(1)
$v_{\rm Oi} = (v_{\rm O-O}^{0} + v_{\rm i}^{0})/2$	(2)
$\gamma = [(4W_{\rm Oi}^2 + \delta^2)]^{1/2}/2$	(3)
$\delta = \nu_{0-0}^{0} - \nu_i^{0}$	(4)

The vibrational wave functions (Ψ_0 and Ψ_i) of the resultant mixed modes are written by the unperturbed wave functions (Ψ_0^0 and Ψ_i^0) as

$$\Psi_{\rm o} = a\Psi_{\rm o}^{\ 0} + b\Psi_{\rm i}^{\ 0}$$
(5a)
$$\Psi_{\rm i} = -b\Psi_{\rm o}^{\ 0} + a\Psi_{\rm i}^{\ 0}$$
(5b)

where

$$a = [(\gamma + \delta)/2\gamma]^{1/2}$$
 and $b = [(\gamma - \delta)/2\gamma]^{1/2}$ (6)

The intensity ratio, R, of the two resultant bands can be expressed by

$$R = (a/b)^{2} = (\gamma + \delta)/(\gamma - \delta)$$
(7)

We fitted the doublets observed at 800–900 cm⁻¹ for the ¹⁶O₂ and ¹⁸O₂ samples of **2** with two Gaussian functions. By using eqs. 1–4 and 7, and the values of $v^{(+)} = 919$ cm⁻¹, $v^{(-)} = 896$ cm⁻¹, and R = 1.1 obtained from Gaussian analyses for a ¹⁶O₂ sample of **2**, the v_{O-O}^{0} , v_i^{0} , and W_{Oi} were estimated to be 908 cm⁻¹, 907 cm⁻¹, and 11.5 cm⁻¹, respectively. In the same way, we obtained the parameters for a ¹⁸O₂ sample as follows: $v^{(+)} = 881$ cm⁻¹, $v^{(-)} = 850$ cm⁻¹, R = 1.8, $v_{O-O}^{0} = 861$ cm⁻¹, $v_i^{0} = 870$ cm⁻¹, and $W_{Oi} = 14.8$ cm⁻¹. We also estimated the parameters of the doublet observed at 450–470 cm⁻¹ for a ¹⁶O₂ sample as follows: $v^{(+)} = 473$ cm⁻¹, $v^{(-)} = 456$ cm⁻¹, R = 3.0, $v_{Fe-O}^{0} = 460$ cm⁻¹, $v_i^{0} = 469$ cm⁻¹, and $W_{Oi} = 7.4$ cm⁻¹.

The intrinsic v(O-O) frequencies (v_{O-O}^{0}) are 908 for the ¹⁶O₂ sample and 861 cm⁻¹ for the ¹⁸O₂ sample and its isotopic shift is -47 cm⁻¹, which is in reasonable agreement with the expected value. The intrinsic overtone frequency (v_i^{0}) of the ¹⁶O₂ sample is 907 cm⁻¹ $(v_i^{0}/2 = 454 \text{ cm}^{-1})$, which is in good agreement with a fundamental observed at 456 cm⁻¹. The v_i^{0} of the ¹⁸O₂ sample is 870 cm⁻¹ $(v_i^{0}/2 = 435 \text{ cm}^{-1})$. However, since no corresponding band at 435 cm⁻¹ is observed in the resonance Raman spectrum, the fundamental at 435 cm⁻¹ may be a Raman inactive vibration. The intrinsic $v(Fe-O_{O-O}$: vide infra) frequency (v_{Fe-O}^{0}) and intrinsic overtone frequency (v_i^{0}) are 460 and 469 cm⁻¹ $(v_i^{0}/2 = 235 \text{ cm}^{-1})$, respectively. Since there is no band around 235 cm⁻¹, this fundamental may also be a Raman inactive vibration.

(1) Y. Hayashi, T. Kayatani, H. Sugimoto, M. Suzuki, K. Inomata, A. Uehara, Y. Mizutani, T. Kitagawa, and Y. Maeda, *J. Am. Chem. Soc.* **1995**, *117*, 11220-11229.

Normal coordinate analyses. Normal coordinate analyses (NCAs) were performed using the values (the intrinsic v(O-O) frequency (v_{O-O}^{0}) and the intrinsic $v(Fe-O_{O-O})$ frequency (v_{Fe-O}^{0}) for **2**) obtained by the above Fermi resonance analyses. We have also carried out NCA of **2** under the assumption that the bands at 473 and 456 cm⁻¹ are not a Fermi doublet, but independent vibrations. However, no satisfactory fitting was obtained. The analyses were carried out by the Wilson GF matrix method using a Urey–Bradley force field (Vibratz program, version 1.1). The vibrational data of **2** and **3** were analyzed for the ring models of the Fe₂(OH)(O₂) (C_1) and Fe₂(O)(O₂) (C_s) cores obtained from the X-ray data. The atom numbering scheme of the Fe₂(O(H))(O₂) core is

shown in Figure S9.

In a first set of calculation of **2**, the O_{OH} -H stretching, bending, and torsion force constants were fixed at the values listed in Table S2 and the O–O, Fe–O_{O–O}, and Fe–O_{OH} force constants were refined, where suitable Urey–Bradley nonbonded interaction constants were also included for the two Fe–O_{OH}–H bending modes using a f' = –0.1f model. The starting values of the force constants are selected from those of the (μ -oxo), bis(μ -oxo), and (μ -peroxo)diiron(III) complexes.^{1–3} However, these sets of the parameters did not give a good fit for v_{as} (Fe–O_{O–O}) and v_s (Fe–O_{O–O}) values. In order to improve the fittings, three types of the stretch–stretch interaction force constants *F*(Fe–O_{OH} + Fe–O_{O–O}), *F*(Fe–O_{OH} + Fe–O_{OH}), and *F*(O–O + Fe–O_{O–O}) were introduced. These interaction force constants gave reasonable fit. The same analysis was performed for **3**. The force constants obtained are given in Table S2. The results of NCA for **2** and **3** are listed in Tables S3 and S4, respectively, with the observed data. Displacement coordinates for **2** and **3** are shown in Figures S10 and S11, respectively.

The *K*(O–O) and *K*(Fe–O_{0–O}) obtained are 3.55 and 2.18 mdyn/Å for **2**, and 3.25 and 1.84 mdyn/Å for **3**, respectively. These vales are similar to those obtained from the (μ -peroxo)diiron(III) complexes [Fe₂{HB(3,5-^{iPr2}pz)₃}₂(O₂)(PhCO₂)₂] (*K*(O–O) = 3.07 and *K*(Fe–O) = 1.99 mdyn/Å) and [Fe₂(*N*-Et-hptb)(O₂)(OPPh₃)₂]³⁺ (*K*(O–O) = 3.26 and *K*(Fe–O) = 2.36 mdyn/Å).¹ The stretch–stretch interaction force constants used for **2** and **3** fall in the range reported for the (μ -oxo)-, bis(μ -oxo)-, and (μ -peroxo)diiron(III) complexes.²⁻⁴ Introduction of the stretch–stretch interaction force constant reflects the strong π -bonding interaction force constants are generally smaller than 10% of the force constant *K*, but can be somewhat larger for a stronger π -bonding system.⁵

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Table S1.Selected Bond Distances (Å) and Angles (deg) for $[Fe_2(6Me_2 - BPP)_2(O)(OH)](OTf) \cdot 10H_2O$ (1) and $[Fe_2(6Me_2 - BPP)_2(OH)(O_2)]B(3-ClPh)_4 \cdot 6.5CH_3OH$ (2·B(3-ClPh)₄).

	1	$2 \cdot B(3-ClPh)_4$							
Distances (Å)									
FeFe	2.969(1)	3.396(1)							
0–0		1.396(5)							
Fe–O (peroxo)		1.867(4) (O1)							
		1.887(4) (O2)							
Fe–O (OH or O)	1.967(3) (O3)	2.006(4) (O3)							
	1.903(3) (O3*)	1.943(4) (O3)							
Fe-O (carboxylato)	1.979(3) (O1)	1.986(4) (O4)							
		1.999(4) (O6)							
Fe-N (amine)	2.175(3) (N1)	2.208(4) (N1)							
		2.183(5) (N4)							
Fe–N (py)	2.215(3) (N2)	2.232(5) (N2)							
	2.200(3) (N3)	2.204(4) (N3)							
		2.193(5) (N5)							
		2.221(5) (N6)							
	Angles (°)								
Fe–O–Fe	100.2(1)	118.6(2)							
Fe-O-O		123.1(3)							
		120.4(3)							
Fe-O-O-Fe		-14.5 (4)							

	Fe ₂ (OH)	(O_2) core (2)	$\overline{Fe_2(O)(O_2) \operatorname{core} (3)}$					
Internal coordinate	core geometry ^a foce constant ^b core		core geometry ^a	foce constant ^b				
bond stretch		K (stretching)		K (stretching)				
Fe1–O3 (OH or O)	2.006	2.00	1.719	2.54				
Fe2–O3 (OH or O)	1.943	2.00	1.743	2.54				
Fe1-O1 (peroxo)	1.867	2.18	2.065	1.84				
Fe2–O2 (peroxo)	1.887	2.18	2.102	1.84				
01–02	1.396	3.55	1.41	3.25				
О3–Н	0.95	5.00 ^c						
angle bending		H (bending)		H (bending)				
Fe1–O3–Fe2	118.6	0.25 ^c	132.7	0.30 ^c				
O1-Fe1-O3	87.4	0.25 ^c	89.3	0.25 ^c				
O2-Fe2-O3	89.2	0.25 ^c	88.0	0.25 ^c				
Fe1O1O2	123.1	0.30 ^c	115.2	0.15 ^c				
Fe2O2O1	120.4	0.30 ^c	114.8	0.15 ^c				
Fe1O3H	120.2	0.20 ^{c, d}						
Fe2–O3–H	121.2	0.20 ^{c, d}						
		<i>F</i> (stretch–stretch)		F (stretch–stretch)				
Fe1–O3 + Fe2–O3		0.36		0.25				
Fe1–O1 + Fe1–O3		0.23		0.19				
Fe1–O1 + O1–O2		0.10		0.12				
Fe2–O2 + Fe2–O3		0.23		0.19				
Fe2–O2 + O1–O2		0.10		0.12				
torsion angle		au (torsion)						
Fe1-O1-O2-Fe2	-14.5	0.25 °						

Table S2. Data Used for NCA of the $Fe_2(OH)(O_2)$ Core (2) and $Fe_2(O)(O_2)$ Core (3)

a) Based on X-ray data of **2** and **3**. b) *K* and *F* in mdyn/Å, *H* and τ in mdyn·Å/rad². c) Values are fixed. d) Urey-Bradley force field, f' = -0.1f.

$v_{s}(\text{Fe-O}_{oxo}) + \delta (\text{Fe-O}_{oxo}-\text{Fe})$	$v_{\rm as}({\rm Fe-O_{0-0}}) + \delta ({\rm Fe-O-0})$	$v_{as}(\text{Fe-O}_{oxo})$	v(0-0)	assignment		 a) Potential energy distributio Table S4. Experimental Frequencies 		$v_{s}(Fe-O_{0-0})$	$v_{\rm s}({\rm Fe-O}_{\rm OH})$	$v_{\rm as}({\rm Fe-O}_{\rm OH}) + v_{\rm as}({\rm Fe-O}_{\rm O-O})$	$v_{\rm as}({\rm Fe-O}_{\rm O-O}) + v_{\rm as}({\rm Fe-O}_{\rm OH})$		v(0-0)	assignment		Table S3. Experimental Frequencies
		695	847	$^{16}O_2$	exp	n (PED), (uencies an	(473, 4	460 ^t	498	548		(919, 8	₁ 806	¹⁶ O ₂		uencies an
		693	814	$^{18}O_2$	eriment	contribu d NCA	56)	J				96) (J		exp	d NCA
		2	33	∇_{8l-9l}	al	tions (%) Results o		447	493	536		881, 850)	861 ^b	${}^{18}O_2$	erimental	Results o
507 ^b	570 ^b	695	848	${}^{16}O_2$. b) Assia f [Fe ₂ (6N	10	12	5	12			47	16-18		f [Fe ₂ (6N
507 ^b	542 ^b	694	799	$^{18}O_2$	calcd	gned as a Ie ₂ -BPP					-			Δ		Ie ₂ -BPP
0	28	1	49	Λ^{16-18}		a Fermi () ₂ (O)(O ₂		461	499	548	503°		907	¹⁶ O ₂) ₂ (OH)(C
0	0	0	94.7	0-0		loublet. c) r)] (3) (Freq	-	444	496	535	588°		856	$^{18}O_2$	calcd	$(2)^{+}(2)$ (Fr
1.0	70.0	1.4	7.9	Fe-O		not observe	1.1	17	З	13	15		51	Δ^{16-18}		equencies i
	0			90		d. 2m ⁻¹)		0 7	1.7	0	0		88.6	0-0		n cm ⁻¹)
56.7	4.8	107.0	0	Fe-O _{oxo}	PED ^a			74	8	31	53		13	Fe-(PE	
32		-	_	Fe-O			į	در ا	.4	.2	3.0		3.1	O_{0-0}	Da	
7.7	0	0	0	_{oxo} –Fe			10.0	103	55.8	76.4	31.7		0	Fe–O _{OH}		
0	28.9	0	0	Fe-0-0												

 $v_s(\text{Fe-O}_{0-0})$ 46544619465447a) Potential energy distribution (PED), contributions (%). b) not observed.

18

4.2

87.1

2.0

1.3

0



Figure S1. Tetradentate tripodal ligand (6Me₂-BPP).



Figure S2. ORTEP view (50% probability) of the complex cation of $[Fe_2(6Me_2-BPP)_2(O)(OH)](OTf)\cdot 10H_2O$ (1) with a full numbering scheme of atoms. Hydrogen atoms are omitted for clarity.



Figure S3. ORTEP view (50% probability) of the complex cation of $[Fe_2(6Me_2-BPP)_2(OH)(O_2)]B(3-CIPh)_4\cdot 6.5CH_3OH (2\cdot B(3-CIPh)_4)$ with a full numbering scheme of atoms. Hydrogen atoms are omitted for clarity.



Figure S4. ORTEP view (50% probability) of the complex molecule of $[Fe_2(6Me_2-BPP)_2(O)(O_2)]1.5CH_3OH \cdot 6H_2O$ (3) with a full numbering scheme of atoms. Hydrogen atoms are omitted for clarity.



Figure S5. Electronic spectral changes of 2·OTf in CH₃OH at -80 °C. (a) 2·OTf, (b) addition of 1 eq. Et₃N to (a), (c) addition of 1 eq. HClO₄ to (b), and (d) addition of 1 eq. Et₃N to (c).



Figure S6. Resonance Raman spectral changes of **2** (**a**) prepared from the reaction of **1** with $H_2^{16}O_2$, (**b**) addition of 1.5 eq. Et₃N to (**a**), (**c**) addition of 0.5 eq. Et₃N to (**b**), (**d**) addition of 0.5 eq. HClO₄ to (**c**), and (**e**) addition of 0.5 eq. HClO₄ to (**d**) in CH₃OH (ca. 10 mM) at -80 °C with a 600 nm laser excitation (laser power: ~30 mW).



Figure S7. Mössbauer spectra of polycrystalline samples of 4 (a), 1 (b), $2 \cdot B(3-ClPh)_4$ (c), $2 \cdot OTf$ (d), and 3 (e) at 80 K. Mössbauer spectrum of 3 was measured in a matrix of DBU (1,8-diazabicyclo[5,4,0]-7-undecene) to prevent the protonation to the oxo group.



Figure S8. Reflectance spectral change of 3 (a), after 1 day (b), 2 days (c), and 3 days (d), and $2 \cdot OTf(e)$ at ~-110°C.



Figure S9. Atom numbering scheme of the $Fe_2(OH \text{ or } O)(O_2)$ core used for NCA of 2 and 3.



Figure S10. Atomic displacement vectors for the normal modes calculated for 2.



Figure S11. Atomic displacement vectors for the normal modes calculated for 3.