Supporting Information for

Modulation of Heme Peroxo Nucleophilicities with Axial Ligands Reveal Key Insights into the Mechanistic Landscape of Nitric Oxide Synthase

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Experimental Section

1. Materials and Methods

All commercially available chemicals were purchased at the highest available purity and used as received unless otherwise stated. Air-sensitive compounds were handled either under an argon atmosphere using standard Schlenk techniques, or in an MBraun Unilab Pro SP (<0.1 ppm O_2, <0.1 ppm H_2O) nitrogen-filled glovebox. All organic solvents were purchased at HPLC-grade or better and degassed (bubbling argon gas for 40 min at room temperature) and dried (passing through a 60 cm alumina column) using an Inert Pure Solv MD 5 (2018) solvent purification system. These solvents were then stored in dark glass bottles inside the glovebox over 4 Å molecular sieves at least for 72 hrs prior to use. Benchtop UV-vis experiments were carried out using Agilent Cary 60 spectrophotometer equipped with a liquid nitrogen chilled Unisoku CoolSpek UV USP-203-B cryostat. A 2 mm path length quartz cell cuvette modified with an extended glass neck with a female 14/19 joint and stopcock was used to perform all UV–vis experiments. Low-temperature ^{2}H NMR spectroscopic studies were carried out on a Bruker AV 360 MHz NMR Spectrometer. ^{1}H NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer. All spectra were recorded in 5-mm (outer diameter) NMR tubes. The chemical shifts were reported as δ (ppm) values calibrated to natural abundance deuterium or proton solvent peaks. For LC-MS analysis, Spectra were obtained in Waters Xevo G2-XS QTOF instrument and Bruker Rapiflex instrument. GC-FID analyses were performed on a Agilent Technologies 8860 GC, using an Agilent DB-1701 (30 m, 0.32 mm, 1.0 µm) column. GC-MS was carried out using an Agilent Technologies 6890N GC, using an Agilent DB-5ms (30 m, 0.25 mm, 0.25 µm) column. The yield determinations were conducted with the GC-FID using calibration curves with n-dodecane as an internal standard. CW EPR experiments were performed at the UA EPR facility using a Bruker ELEXSYS E540 X-band spectrometer (Bruker-Biospin Billerica, MA). Cryogenic measurements were made using a ColdEdge Stinger closed-loop liquid helium cryosystem inserted into an Oxford ESR900 cryostat. A LakeShore 336 temperature controller was used to regulate sample temperature. EPR simulations were calculated using SpinCount developed by Professor Michael Hendrich at Carnegie Mellon University by utilizing the general spin Hamiltonian as shown in Equation **A**.[1-3]

Eq. A $$\hat{H} = \boldsymbol{D}\left(\hat{S}_Z^2 - \frac{\hat{S}^2}{3}\right) + \boldsymbol{E}\left(\hat{S}_X^2 - \hat{S}_Y^2\right) + \beta_e \boldsymbol{S_c} \cdot \boldsymbol{g} \cdot \mathbf{B}$$

In this expression, $\boldsymbol{g}$ is the *g*-tensor for the coupled spin-system ($\boldsymbol{S_c}$), and the axial and rhombic zero-field splitting (*zfs*) parameters are represented by $\boldsymbol{D}$ and $\boldsymbol{E}$, respectively. This program computes the powder pattern for a uniform spherical distribution of the magnetic field vector $\boldsymbol{B}$, and the transition intensities are calculated using '*Fermi's golden rule*'.[4] All simulations were generated with consideration of all intensity factors, both theoretical and experimental, to allow for determination of species concentration. The only unknown factor relating the spin concentration to signal intensity was an instrumental factor that is specific to the microwave detection system. However, this was determined by the spin standard, 1 mM Cu(EDTA), prepared from a copper atomic absorption standard solution purchased from Sigma-Aldrich. Resonance Raman spectra were collected using a setup described previously.[5] All resonance Raman spectra were collected at 77 K on samples held within a liquid nitrogen finger dewar. Raman spectra were collected using 457 nm excitation from a Cobolt Twist diode laser. The excitation beam was focused onto the sample using a 100 mm focal length UV plano-convex lens (Thorlabs), and the scattered light was collected using a UV-fused aspheric lens (Edmund Physics). Elastic scattering of the Rayleigh line was rejected using the corresponding long-pass edge filter (Semrock RazorEdge). The Raman scattered light was imaged onto a spectrograph (Princeton Instruments Isoplane) furnished with an 1800 gr/mm 500-nm blazed grating and measured with a Peltier-cooled CCD detector (Princeton Instruments Pixis 100B). 5,10,15,20 tetraphenylporphyrin iron(III) chloride, [(TPP)Fe^{III}Cl], 4-Methylimidazole (4-MeIm), 4-Dimethylaminopyridine (DMAP), 1,5-Dicyclohexylimidazole (DCHIm), Sodium thiophenolate (ArS-) was purchased from commercial sources. The syntheses of $H_2(F_{20}TPP)$,[6] H_2(TPP-d_8),[7] H_2(F_{20}TPP-d_8),[8] naked [(TPP)Fe^{III}]SbF_6,[9] Sodium 3,5-dimethoxyphenolate (ArO^-),[10] Tetrabutylammonium thiophenolate,[11] were carried out according to previously published methods. Metalation of the porphyrinates to generate [(F_{20}TPP)Fe^{III}Cl], and [(TPP-d_8)Fe^{III}Cl], and the subsequent reduction to [$(THF)_2$(Por)Fe^{II}] complexes were carried out by following previously reported procedures.[12] Formation of the heme peroxo [(B)(Por)Fe^{III}(O_2^{2-})]$^-$ complexes, where Por = the porphyrinate supporting ligand: (where Por = TPP, F_{20}TPP) and B = axial ligands, was carried out following a previously reported procedure.[13, 14]

2. Formation of axial ligated heme peroxo, $[(B)(Por)Fe^{III}(O_2^{2-})]^-$ complexes, where Por = porphyrinate supporting ligand, and B = axial ligands: Generation of the heme peroxo complexes, $[(Por)Fe^{III}(O_2^{2-})]^-$, was carried out following a literature-adapted procedure.[13, 14] In a typical experiment, a 50 µM THF solution (1 mL) of $[(THF)_2(Por)Fe^{II}]$ was added into a 2 mm pathlength Schlenk cuvette inside the glovebox and was sealed using a rubber septum. Upon cooling down inside the UV-vis cryostat stabilized at –40 ºC, this solution was bubbled with dry dioxygen gas using a needle, and excess O_2(g) was removed by three vacuum/Ar purge cycles. The complete formation of the superoxide complexes, $[(Por)Fe^{III}(O_2^{-\bullet})]$, was monitored by UV–vis spectroscopy (Figure 2A). Subsequently, 1 equiv of cobaltocene (in 50 µL of DCM) was added to generate the peroxo complex $[(Por)Fe^{III}(O_2^{2-})]^-$. To which 2 equiv of axial ligand (in 50 µL of DCM) was added to form the axial ligated heme peroxo complex, $[(B)(Por)Fe^{III}(O_2^{2-})]^-$ (Scheme 1.) (Figure 2A). Due to solubility issues, 2 equiv of 15-crown-5 was added to sodium 3,5-dimethoxyphenolate and sodium thiophenolate.

3. Resonance Raman and EPR sample preparation: In a typical resonance Raman sample preparation, 100 µL of the ferrous heme complex, $[(THF)_2(TPP)Fe^{II}]$ (4 mM in 9:1 DCM:THF), was placed in a 250 mm EPR tube (4 mm O.D.) and was sealed with a rubber septum inside the glovebox. Following cooling to −40 °C (using liquid nitrogen/acetone cold bath), dry O_2(g) (or $^{18}O_2$(g)) was bubbled through the solution using a three-way gastight syringe to generate the corresponding superoxo complex, $[(TPP)Fe^{III}(O_2^{-\bullet})]$. Subsequently, 1 equiv of cobaltocene (50 µL) was added in, and the reaction mixture was quickly homogenized with dry Ar bubbling to generate the corresponding $[(TPP)Fe^{III}(O_2^{2-})]^-$ complexes. To which 2 equiv of 4-MeIm (50 µL) (or other axial ligands) was added to form the axial ligated heme peroxo complex, $[(4\text{-}MeIm)(TPP)Fe^{III}(O_2^{2-})]^-$. Immediately following the generation of the complexes, the final mixtures were frozen in liquid N_2. EPR sample preparation was also carried out using the same methodology. Tetrabutylammonium thiophenolate/phenolate was used to overcome solubility issues in EPR/rR sample preparation.

4. Low-temperature ^2H NMR spectroscopic studies: For a typical ^2H NMR experiment, $[(THF)_2(TPP\text{-}d_8)Fe^{II}]$ (15 mg, 0.023 mmol) was dissolved in 0.4 mL of 9:1 DCM:THF, and was sealed in a 5 mm (outer diameter) NMR tube within the glovebox. This tube was then stabilized at –40 °C using a liquid nitrogen/acetone cold bath, followed by the addition of O_2(g) by means of a 9” needle to generate the [(TPP-d_8)Fe^{III}($O_2^{-\bullet}$)] complex. Subsequently, 1 equiv of cobaltocene (50 µL) was added using a Hamilton gas-tight syringe, and was quickly mixed with Ar bubbling to form the corresponding [(TPP-d_8)Fe^{III}(O_2^{2-})]$^-$ complex. To which 2 equiv of 4-MeIm (50 µL) (or other axial ligands) was added to form the axial ligated heme peroxo complex, [(4-MeIm)(TPP-d_8)Fe^{III}(O_2^{2-})]$^-$. The tube was then immediately transferred into the cryostat of the NMR spectrometer held at –40 °C.

5. Spectroscopic reactivity and kinetic studies of [(B)(Por)Fe^{III}(O_2^{2-})]$^-$ with oxime substrates: For each kinetic experiment, 50 µM 9:1 DCM:THF solution of [(B)(Por)Fe^{III}(O_2^{2-})]$^-$ complex (1 mL) was generated in a 2 mm pathlength Schlenk cuvette as previously described (*vide supra*). Subsequently, 200-500 equiv of acetophenone oxime substrates (50 µL in DCM) was added into the cuvette using a gas-tight syringe, and the reaction mixture was quickly mixed with dry argon bubbling. The reaction was monitored by the progression of Soret band spectral changes centered at 436 nm (for [(B)(TPP)Fe^{III}(O_2^{2-})]$^-$) or 432 nm ([(B)(F_{20}TPP)Fe^{III}(O_2^{2-})]$^-$) until plateaued. Kinetic studies were carried out, under pseudo-first-order conditions, by the addition of 200–500 equiv of acetophenone oxime to a 50 µM 1 mL 9:1 DCM:THF solution of [(B)(TPP)Fe^{III}(O_2^{2-})]$^-$ at –40 °C and 500 equiv of acetophenone Oxime was used for [(F_{20}TPP)Fe^{III}(O_2^{2-})]$^-$. Kinetic experiments at variable temperatures (at –30, –40, –50, -60 °C) were performed using [(TPP)Fe^{III}(O_2^{2-})]$^-$ and variable temperatures (at –40, –50, –60, -70 °C) for [(ArO^-)(TPP)Fe^{III}(O_2^{2-})]$^{2-}$ for acetophenone oxime substrate (200–500 equiv) following the same procedure as described, allowing the cuvette to achieve thermal equilibrium (10 min) in the cryostat, prior to the addition of the substrate. The pseudo first-order rate constants, k_{obs} were calculated from plots of ln[(A–A_f)/(A_i–A_f)] vs time(s), where A_i and A_f are initial and final absorbances, respectively. The second-order rate constants (k_2) were obtained from the slope of the best-fit line from a plot of k_{obs} values vs substrate concentration.

6. Bulk oxidation reactions and characterization of organic products: The bulk oxidation reaction of acetophenone oxime substrates using [(4-MeIm)(TPP)Fe^{III}(O_2^{2-})]$^-$ was carried out by a generalized procedure as follows: A 100 mL Schlenk flask, equipped with a magnetic stir bar, containing $[(THF)_2(TPP)Fe^{II}]$ (200 mg, 0.3 mmol) in 9:1 DCM:THF (25 mL) was cooled in a liquid N_2/ acetone bath adjusted to −40 °C. Upon temperature equilibration, dioxygen gas ($O_2(g)$) was bubbled through to form $[(THF)(TPP)Fe^{III}(O_2^{-\bullet})]$. Subsequently, 1 equiv of cobaltocene (in 1 mL DCM) was added to form $[(THF)(TPP)Fe^{III}(O_2^{2-})]^-$. To which 2 equiv of 4-MeIm (1 mL) was added to form the axial ligated heme peroxo complex, $[(4\text{-MeIm})(TPP)Fe^{III}(O_2^{2-})]^-$. Then acetophenone oxime (2 g, 15 mmol; in 5 mL of DCM) was added to it, and the reaction mixture was stirred for another 2 hr at –40 °C before it was dried in vacuum. The final (organic) product, acetophenone, was purified by silica gel column chromatography using DCM:hexane (1:1) as an eluent. GC-FID analysis for yield quantification of acetophenone was conducted using 1.5 mM solutions of $[(B)(TPP)Fe^{III}(O_2^{2-})]^-$ (B= 4-DMAP, ArO^-) complexes. The nitroxyl (NO^-) identification experiment was carried out following the above procedure using $[(4\text{-MeIm})(TPP)Fe^{III}(O_2^{2-})]^-$ and acetophenone oxime as a substrate in the presence of 50 equiv PPh_3. The final reaction mixture was dried in a vacuum, and the phosphorus-containing products were characterized using LC-MS spectroscopy. Yield quantification of triphenylphosphine oxide (TPPO) was performed with a 0.5 mM concentration of $[(4\text{-MeIm})(TPP)Fe^{III}(O_2^{2-})]^-$, which was further diluted for LC-MS analysis.

Acetophenone yield: 14 mg (34%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98-7.96 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 2.61 (s, 3H); GC-MS: *m*/*z* = 120.04 (calc. 120.0).

7. Computational Studies:

All calculations were performed with the package of Gaussian 16, revision C.01.7.[15] Geometry optimizations were carried out using uB97D within the spin-unrestricted formalism.[16, 17] The basis set was def2-TZVP for all atoms.[18] Counter ions (in phenolate and thiophenolate) were removed and not included in the calculations. Vibrational frequencies were obtained for all optimized geometries to ensure the latter did not lead to any imaginary frequencies. Complexes $[(THF)(TPP)Fe^{III}(O_2^{2-})]$, $[(4\text{-MeIm})(TPP)Fe^{III}(O_2^{2-})]$ were optimized as charge -1 and sextet, quartet and doublet spin multiplicities while $[(ArO^-)(TPP)Fe^{III}(O_2^{2-})]$ and $[(ArS^-)(TPP)Fe^{III}(O_2^{2-})]$ were optimized as -2 charge and all possible spin multiplicities. A solvent correction (self-consistent reaction field) using the continuum polarized conductor model with a dielectric constant mimicking dichloromethane and zero-point energies has been included in the energy comparison of different spin states.[19] Bonding and orbital analysis were done by using Chemcraft software.[20] The natural charges of the atoms were calculated using natural bond orbital (NBO) analysis.[21]

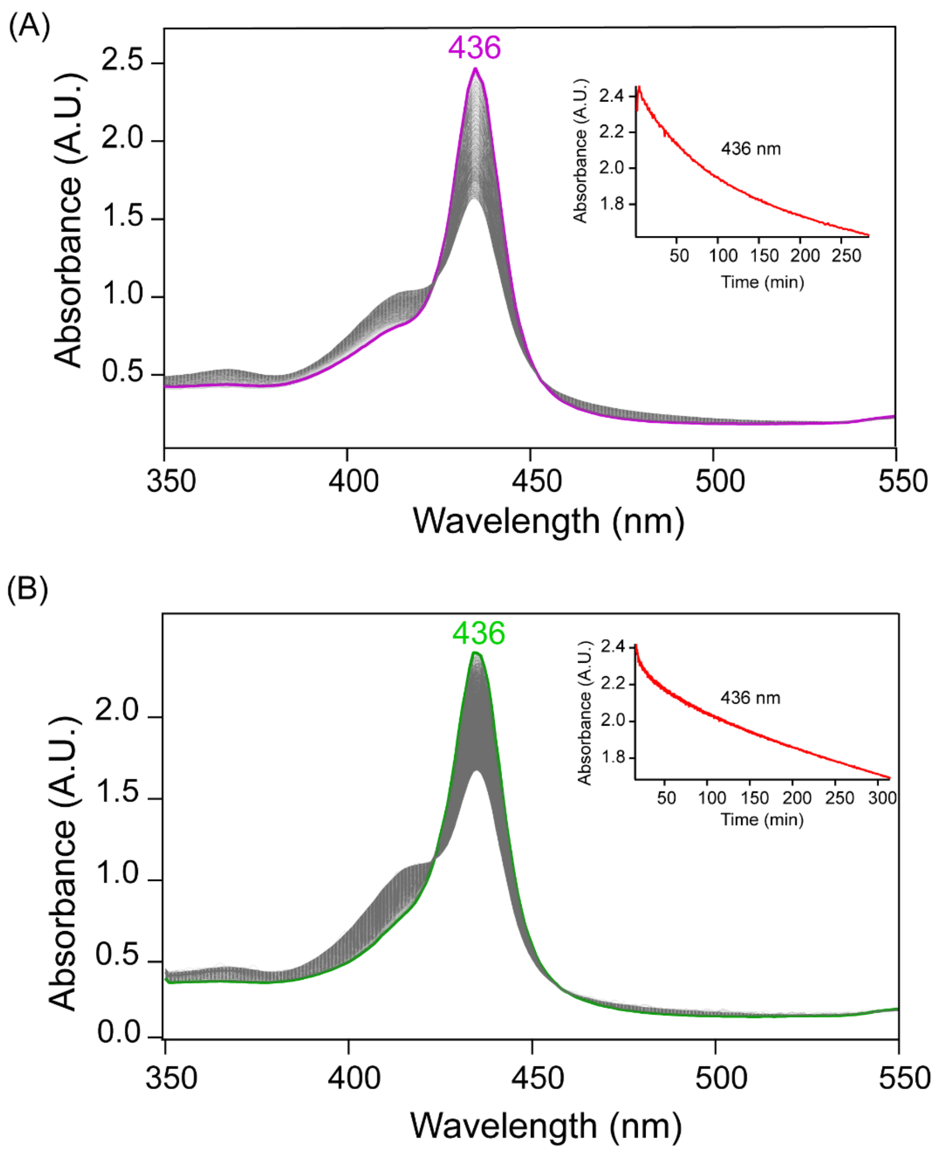


Figure S1. Electronic absorption spectral changes (in 9:1 DCM:THF at –40 ^{o}C) of the self-decay of (A) parent heme-PO complex $[(THF)(TPP)Fe^{III}(O_2^{2-})]^{-}$ (Purple) and (B) thiophenolate ligated $[(ArS^{-})(TPP)Fe^{III}(O_2^{2-})]^{2-}$ (Green). Insets show the kinetic time traces at 436 nm.

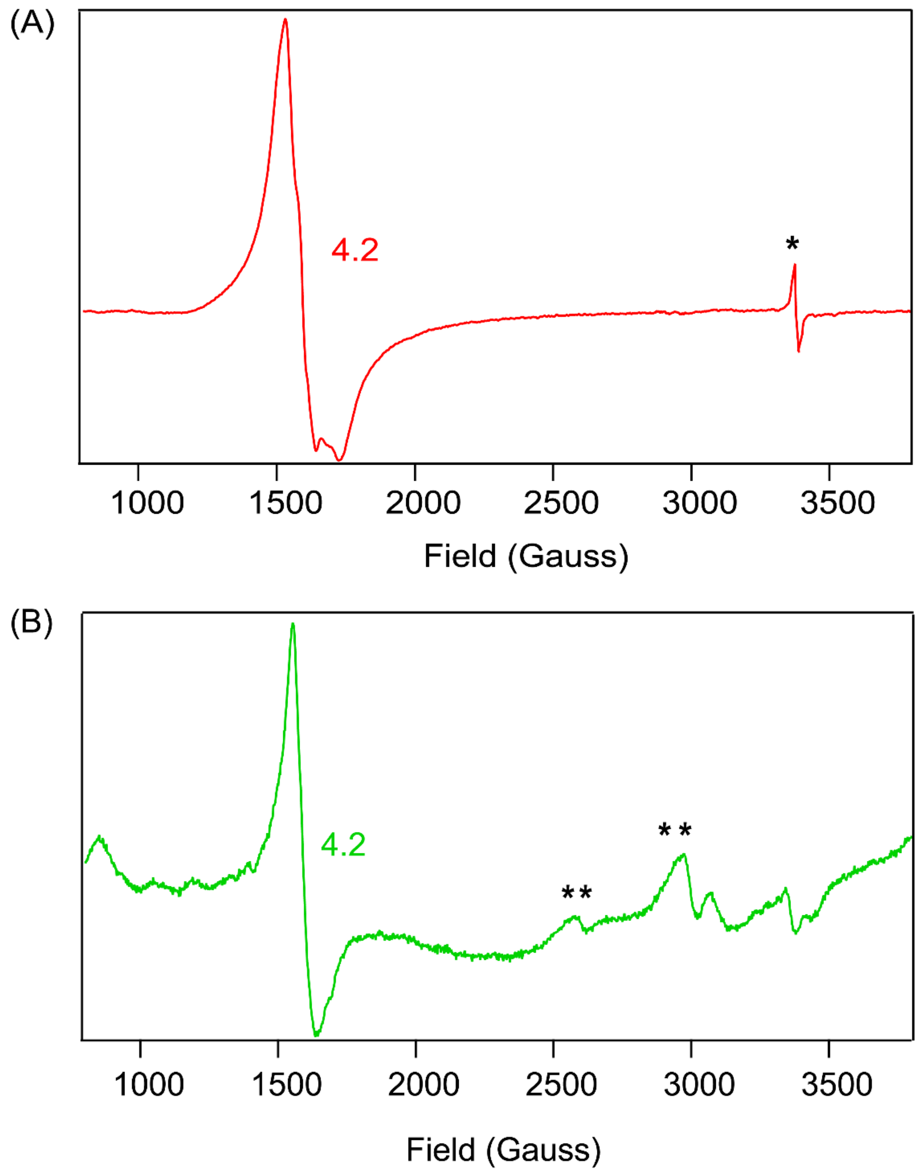
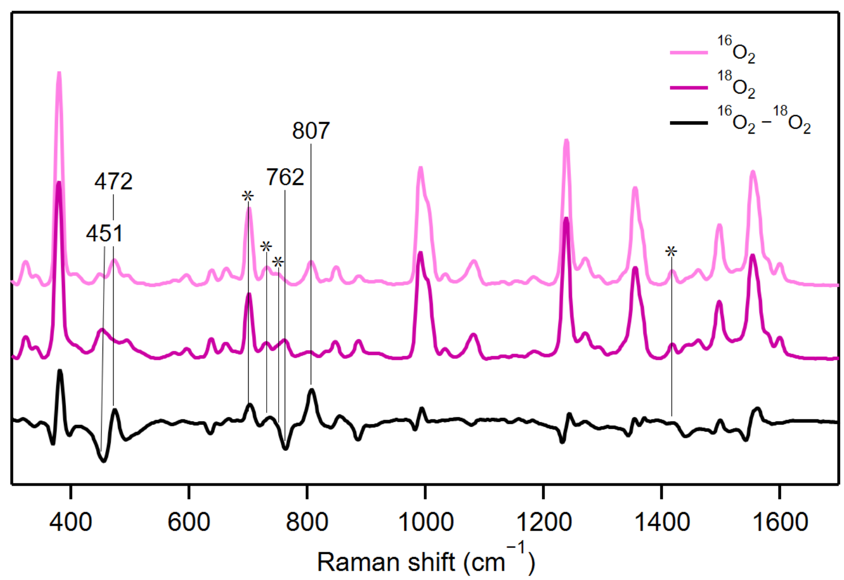


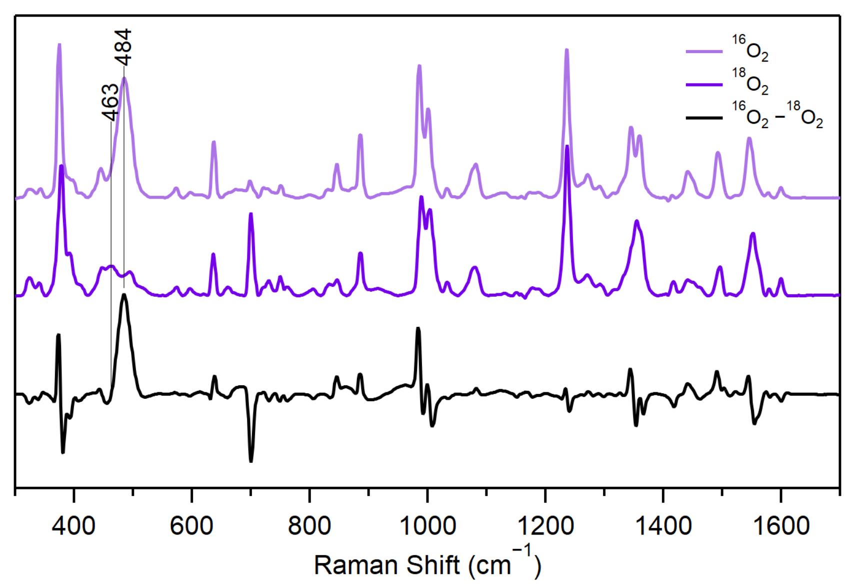
Figure S2. EPR spectral features (in frozen 9:1 DCM:THF at 7 K) for 2 mM solutions of (A) $[(THF)(TPP)Fe^{III}(O_2^{2-})]^-$, *feature (g = 1.99) corresponds to an excess of cobaltocene, and (B) $[(4\text{-}MeIm)(TPP)Fe^{III}(O_2^{2-})]^-$ (g = 4.2); **features (g = 2.6, 2.1) corresponds to the ferric bis-imidazole complex.

(A)



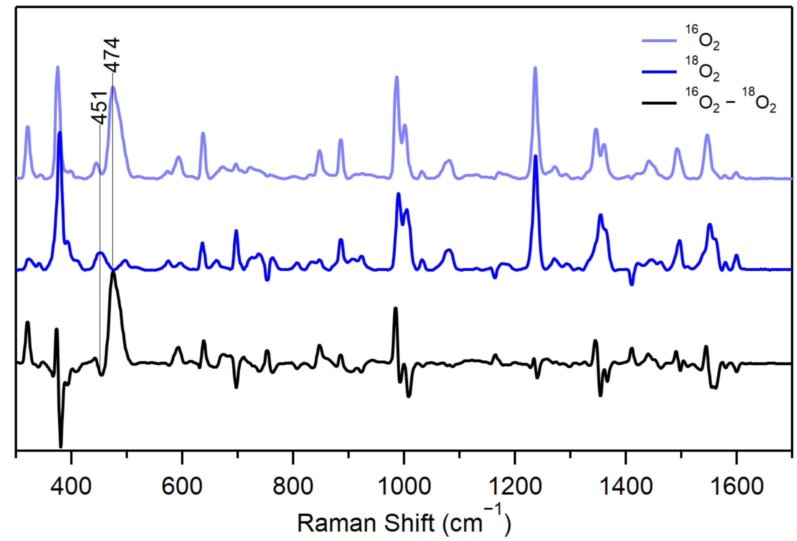
$^{16}O_2$
$^{18}O_2$
$^{16}O_2 - ^{18}O_2$
807
472
762
451
*
400
600
800
1000
1200
1400
1600
Raman shift (cm^{-1})

(B)



$^{16}O_2$
$^{18}O_2$
$^{16}O_2 - ^{18}O_2$
484
463
400
600
800
1000
1200
1400
1600
Raman Shift (cm^{-1})

(C)



(D)

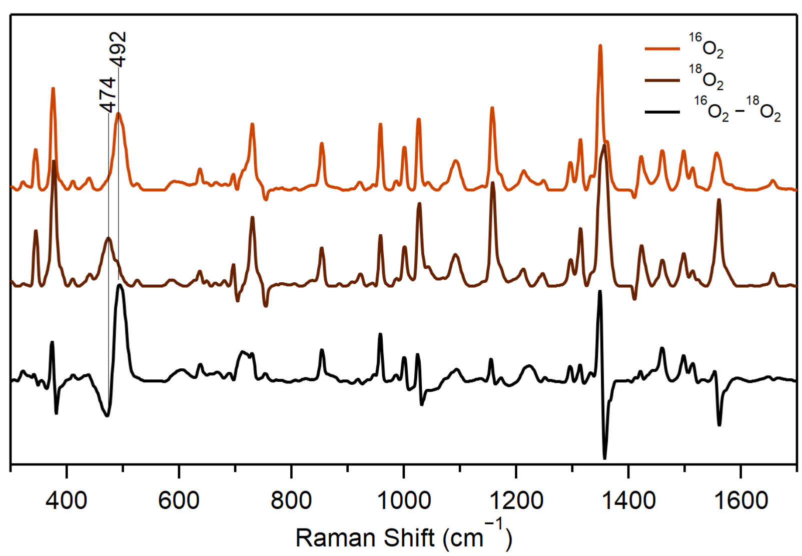


Figure S3. Resonance Raman spectra (λ_{ex}= 457 nm) collected from 2 mM frozen solution samples in 9:1 DCM:THF of (A) $[(THF)(TPP)Fe^{III}(O_2^{2-})]^{-}$ (B) $[(ArS^{-})(TPP)Fe^{III}(O_2^{2-})]^{2-}$ (C) $[(ArO^{-})(TPP)Fe^{III}(O_2^{2-})]^{2-}$ (D)$[(ArO^{-})(F_{20}TPP)Fe^{III}(O_2^{2-})]^{2-}$ prepared with $^{16}O_2$(g) (light color) and $^{18}O_2$(g) (dark color); difference spectrum is shown in black.

Table S1. Spectroscopic characterization details of axially ligated ferric heme peroxo complexes.

Heme-PO Complex	UV-vis (Soret) (nm)	UV-vis (Q-Bands) (nm)	rR ν(Fe–O) (cm^{-1})	rR ν(O–O) (cm^{-1})	Binding Mode	EPR (g)	Ref
$[(THF)(TPP)Fe^{III}(O_2^{2-})]^-$	436 (-40 °C; 9:1 DCM:THF)	564 (-40 °C; 9:1 DCM:THF)	472 ($\Delta^{18}O_2$ = –21)	807 ($\Delta^{18}O_2$ = –45)	Side-on	4.2	This work
$[(THF)(F_{20}TPP)Fe^{III}(O_2^{2-})]^-$	432 (-80 °C; THF)	557 (-80 °C; THF)	469 ($\Delta^{18}O_2$ = –15)	808 ($\Delta^{18}O_2$ = –41)	Side-on	4.2	22
$[(4\text{-MeIm})(TPP)Fe^{III}(O_2^{2-})]^-$	436 (-40 °C; 9:1 DCM:THF)	565 (-40 °C; 9:1 DCM:THF)	479 ($\Delta^{18}O_2$ = –23)	803 ($\Delta^{18}O_2$ = –47)	Side-on	4.2	This work
$[(ArS^-)(TPP)Fe^{III}(O_2^{2-})]^{2-}$	436 (-40 °C; 9:1 DCM:THF)	564 (-40 °C; 9:1 DCM:THF)	484 ($\Delta^{18}O_2$ = –21)	-	Side-on	4.2 & 2.28, 2.13,1.97	This work
$[(ArO^-)(TPP)Fe^{III}(O_2^{2-})]^{2-}$	436 (-40 °C; 9:1 DCM:THF)	565 (-40 °C; 9:1 DCM:THF)	474 ($\Delta^{18}O_2$ = –21)	-	Side-on	-	This work
$[(ArO^-)(F_{20}TPP)Fe^{III}(O_2^{2-})]^{2-}$	432 (-40 °C; 9:1 DCM:THF)	556 (-40 °C; 9:1 DCM:THF)	492 ($\Delta^{18}O_2$ = –18)	-	Side-on	-	This work
$[(TMPIm)Fe^{III}(O_2^{2-})]^-$	440 (-30 °C; 1:4 MeCN:THF)	574 (-30 °C; 1:4 MeCN:THF)	475 ($\Delta^{18}O_2$ = –20)	807 ($\Delta^{18}O_2$ = –49)	Side-on	4.2	23
$[(DMSO)(TMP)Fe^{III}(O_2^{2-})]^-$	-	-	476 ($\Delta^{18}O_2$ = –21)	807 ($\Delta^{18}O_2$ = –45)	Side-on	-	23
$[(F_8TPPIm)Fe^{III}(O_2^{2-})]^-$	424 (-80 °C; THF)	535 & 567 (-80 °C; THF)	578 ($\Delta^{18}O_2$ = –26)	810 ($\Delta^{18}O_2$ = –34)	End-on	2.25, 2.14 & 1.95	24
$[(TMP_{Im}^{Xan})Fe^{III}(O_2^{2-})]^-$	430 (-70 °C; 1:4 MeCN:THF)	568 (-70 °C; 1:4 MeCN:THF)	585 ($\Delta^{18}O_2$ = –25)	808 ($\Delta^{18}O_2$ = –37)	End-on	2.27, 2.16 & 1.96	25
$[(THF)(F_{20}TPP)Fe^{III}(OOH)]$	415 (-80 °C; THF)	530, 553 (-80 °C; THF)	597 ($\Delta^{18}O_2$ = –30)	-	End-on	2.26, 2.15, 1.96	22

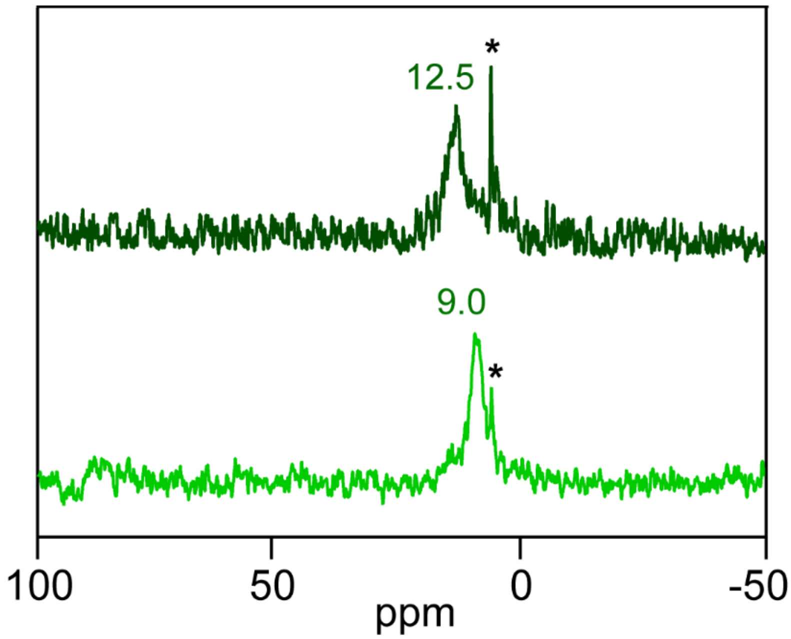


Figure S4. ^{2}H NMR spectra (in 9:1 DCM:THF at −40 °C) for [(4-DMAP)(TPP-d_8)Fe^{III}(O_2^{2-})]$^{-}$ (dark green, top), and (B) [(DCHIm)(TPP-d_8)$Fe^{III}O_2^{2-}$)]$^{-}$ (light green, bottom). *peaks correspond to the solvent.

(A)

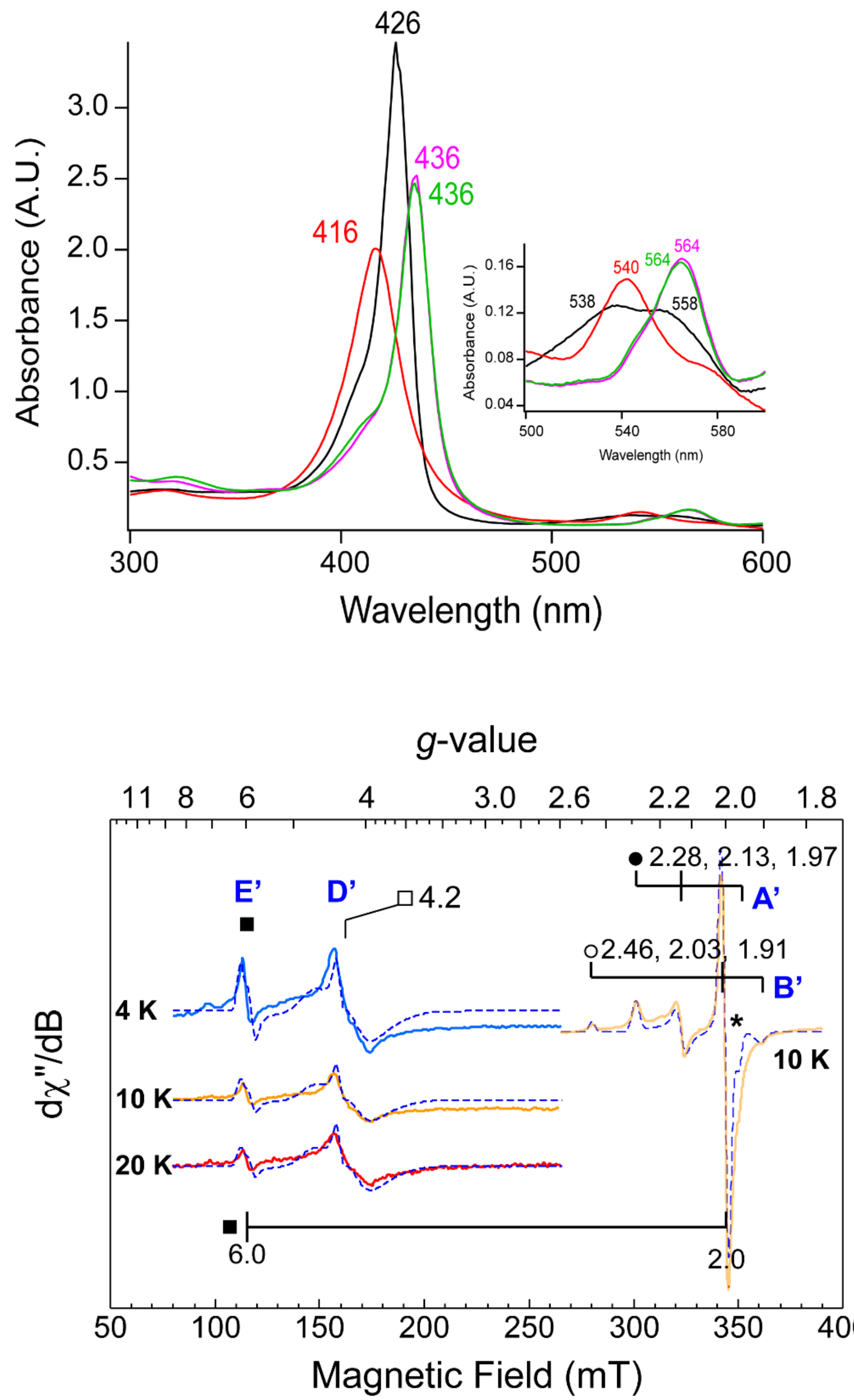


Figure S5. (A) UV−vis spectra (in 9:1 DCM:THF at −40 °C) for 50 μM solutions of $[(THF)_2(TPP)Fe^{II}]$ (black), $[(THF)(TPP)Fe^{III}(O_2^{-\bullet})]$ (red), $[(THF)(TPP)Fe^{III}(O_2^{2-})]^-$ (Pink), $[(ArS^-)(TPP)Fe^{III}(O_2^{2-})]^{2-}$ (Green). Inset shows the expanded Q-band region. (B) X-band CW EPR spectra for a 2 mM solution of $[(ArS^-)(TPP)Fe^{III}(O_2^{2-})]^{2-}$ (in frozen 9:1 DCM:THF) samples at selected temperatures, 4 K (blue), 10 K (orange), and 20 K (red). The axial zero field splitting parameter (*D*) for **E'** (■) and **D'** (□) was determined by matching the experimental and simulated (*blue dashed lines*) signal intensity. Within this temperature regime (4 – 20 K), a single set of spectroscopic parameters (provided in **Table S2**) was used to match experimental signal intensity for species **E'** and **D'**. Low-spin (S = 1/2) ferric sites **A'** and **B'** follow Curie law behavior. *Instrumental parameters*: microwave frequency, 9.631 GHz, microwave power, 67 mW (4K) – 670 mW (20 K); modulation amplitude, 0.92 mT.

Table S2. EPR simulation parameters for **Figure S5**.

Species	Spin	$g_{1,2,3}$	D (cm^{-1})	E/D	[X] (%)
A' (●)	1/2	2.28, 2.13, 1.97	-	-	40 ± 3
B' (○)	1/2	2.46, 2.03, 1.91	-	-	20 ± 2
C' (*)	1/2	2.00, 2.00, 2.00	-	-	4 ± 2
D' (□)	5/2	2.0, 2.0, 2.0	0.9 ± 0.1	0.27	32 ± 4
E' (■)	5/2	2.0, 2.0, 2.0	8.0 ± 1.0	0.005	4 ± 2

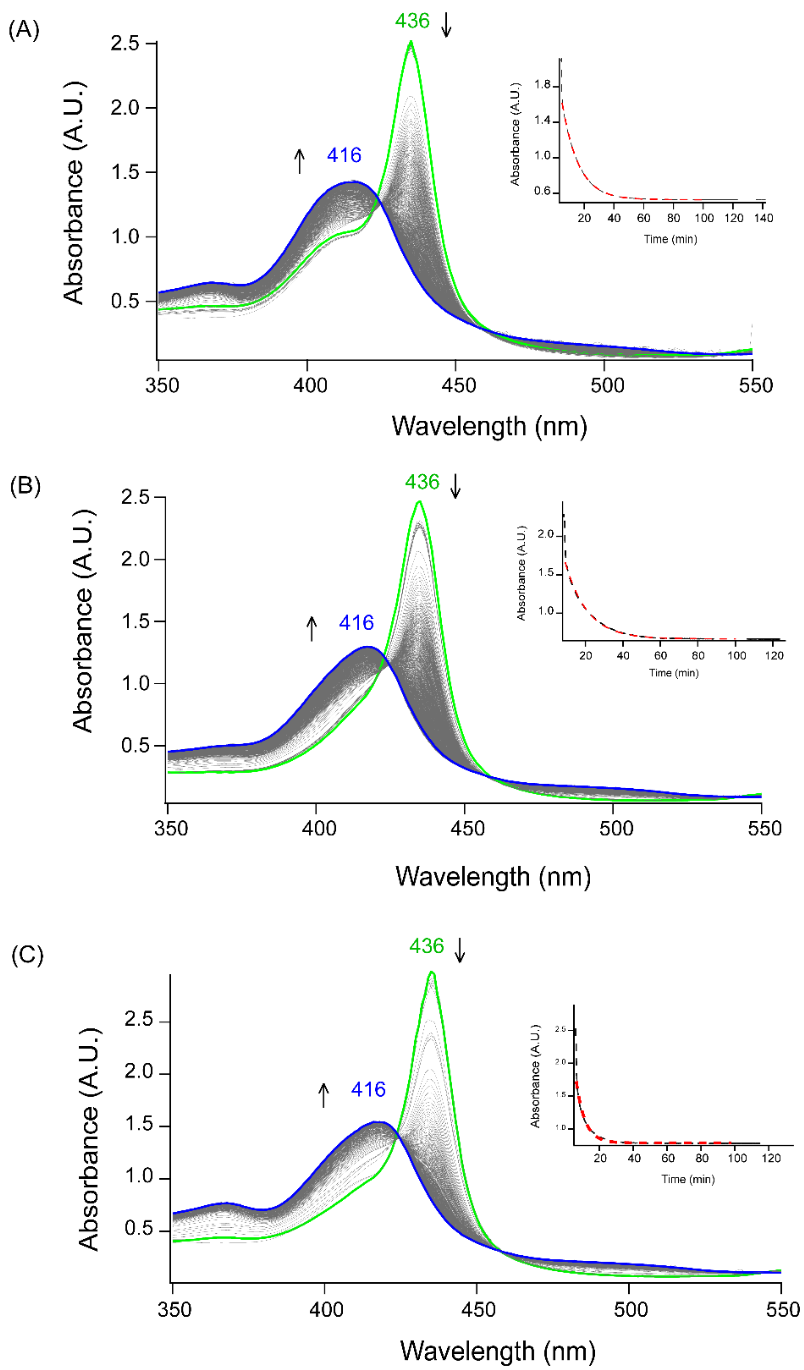


Figure S6. Electronic absorption spectral changes observed (in 9:1 DCM: THF at –40 ºC) during the reaction of a 50 µM solution of (A) $[(DCHIm)(TPP)Fe^{III}(O_2^{2-})]^-$ (B) $[(ArO^-)(TPP)Fe^{III}(O_2^{2-})]^{2-}$ (C) $[(ArS^-)(TPP)Fe^{III}(O_2^{2-})]^{2-}$ with 200 equiv of acetophenone oxime (green: initial $[(B)(TPP)Fe^{III}(O_2^{2-})]^-$ complex; blue: final ferric product). Insets show the kinetic time traces (black) at 436 nm overlaid with the exponential fits (red).

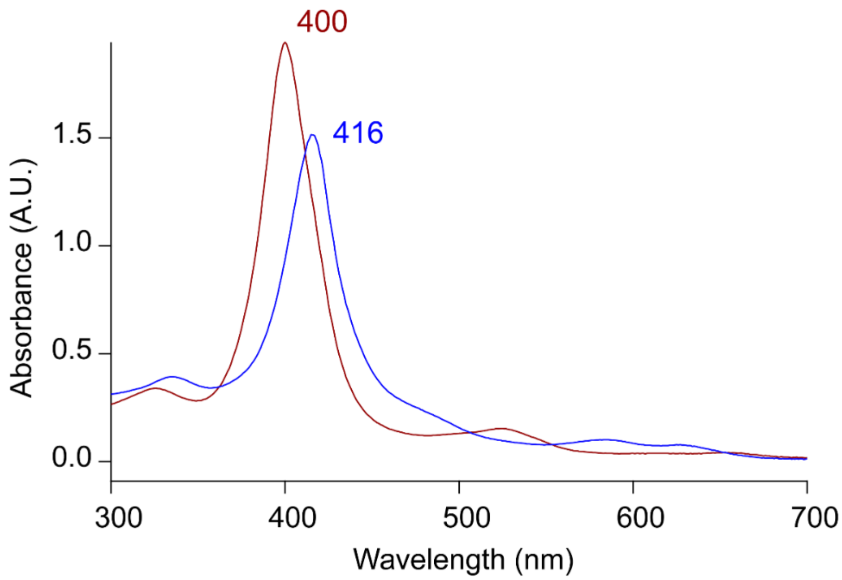


Figure S7. UV−vis spectra (in 9:1 DCM:THF at −40 °C) of naked [(TPP)Fe^{III}]SbF_6 (brown) and upon addition of 1 equiv of TBAOH to form [(TPP)Fe^{III}(OH)] (blue).

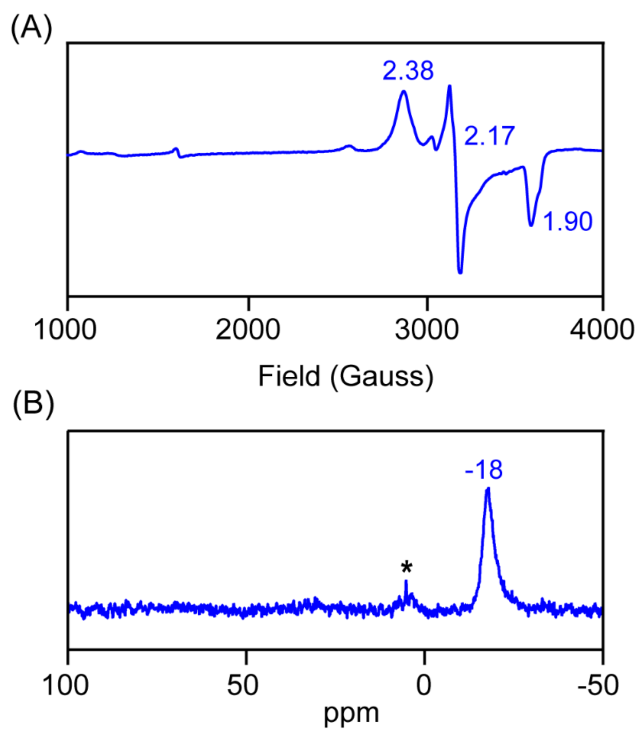


Figure S8. (A) EPR spectral features (in frozen 9:1 DCM:THF at 7 K) (g = 2.38, 2.17 & 1.90) and (B) ^{2}H NMR spectra (in 9:1 DCM:THF at −40 °C) of the final product from the reaction between [(4-MeIm)(TPP-d_8) Fe^{III}(O_2^{2-})]$^-$ and acetophenone oxime.

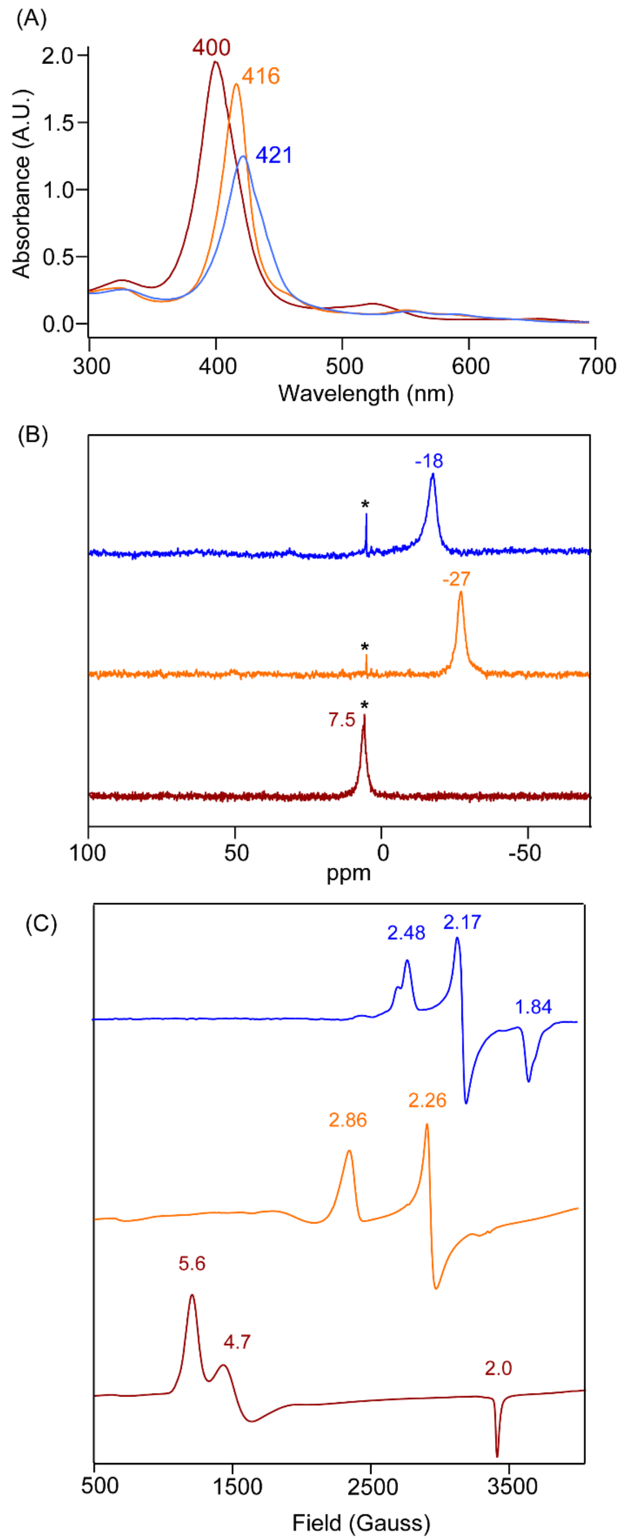


Figure S9. (A) UV−vis (−40 °C), (B) ^{2}H NMR (−40 °C), and (C) EPR (in 7 K) for naked [(TPP-d_8)Fe^{III}]SbF_6 (brown), [(4-MeIm)$_2$(TPP-d_8)Fe^{III}]$^+$ (orange), and [(4-MeIm)(TPP-d_8)Fe^{III}(OH)] (blue) in 9:1 DCM:THF; *peaks correspond to the solvent.

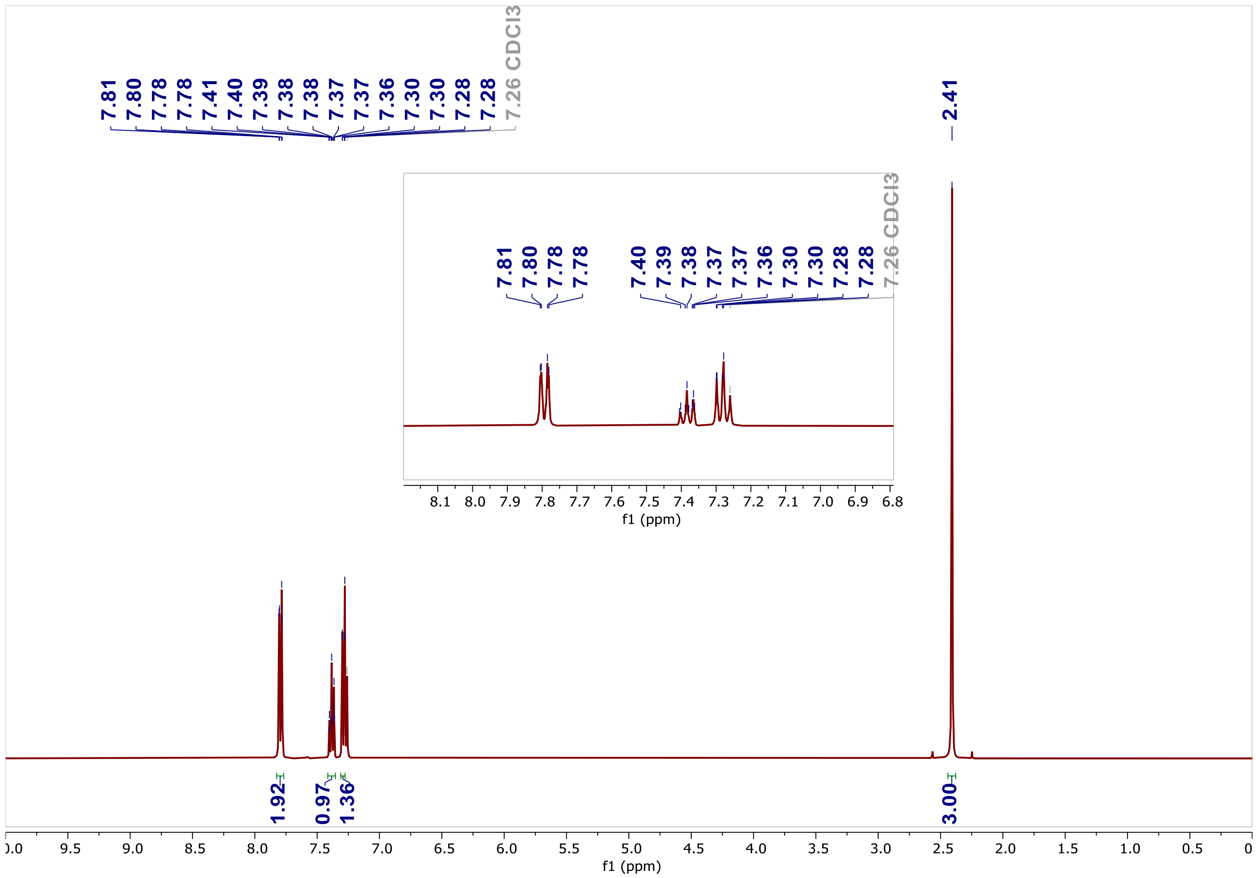
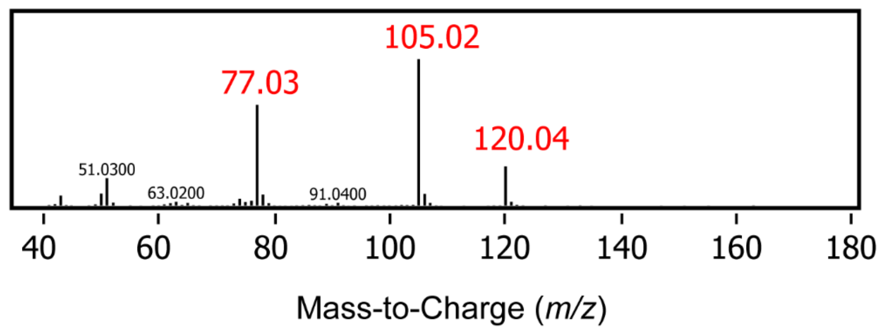


Figure S10. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) of the acetophenone product resulted from a reaction between $[(4\text{-MeIm})(TPP)Fe^{III}(O_2^{2-})]^-$ and acetophenone oxime.

(A)



(B)

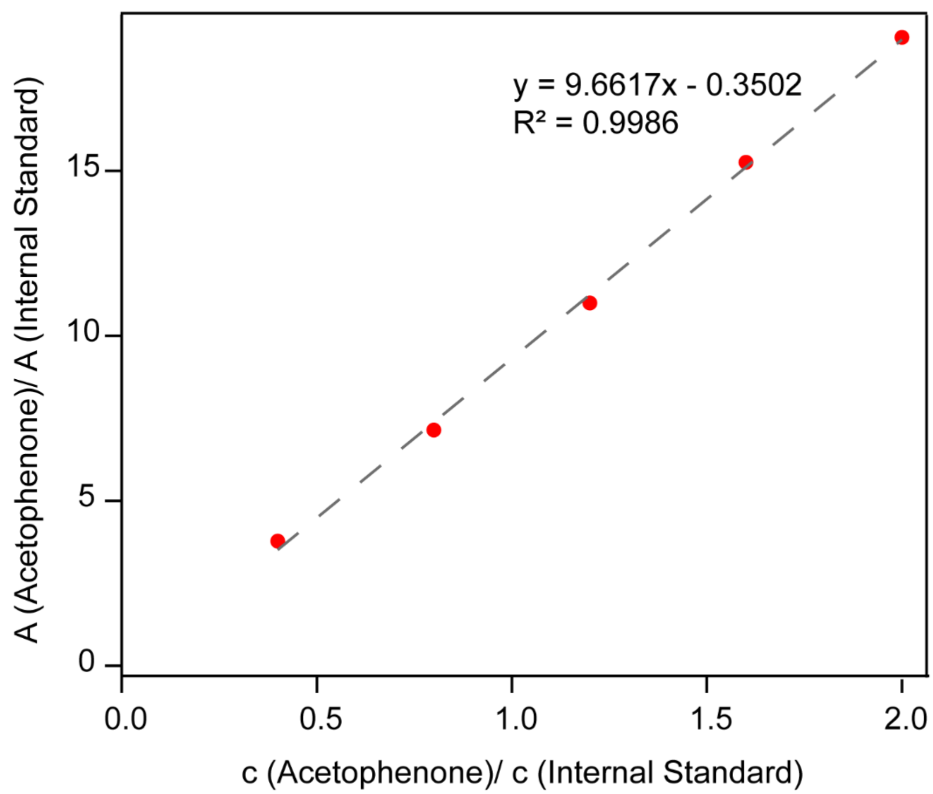
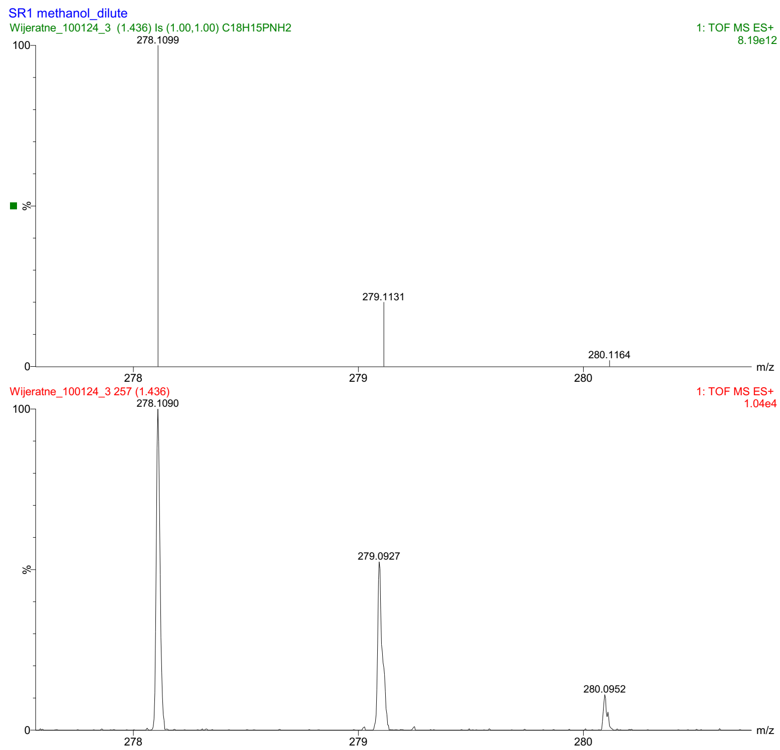
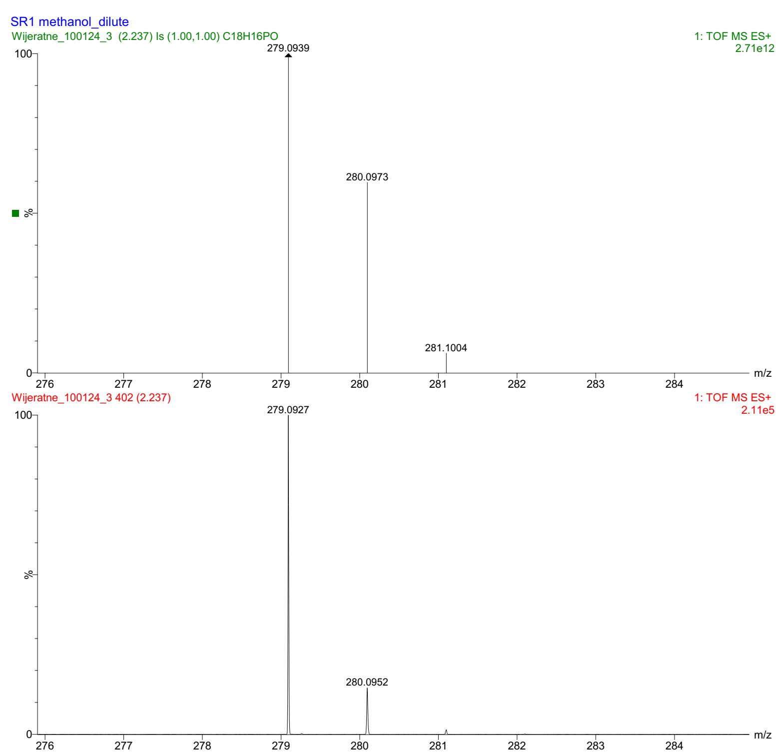


Figure S11. (A) GC-MS data for the acetophenone product resulted from a reaction between [(4-MeIm) (TPP)Fe^{III} (O_2^{2-})]$^-$ and acetophenone oxime showing $[M]^+$ m/z = 120.04 (calc. 120.0). (B) GC-FID generated calibration curve for acetophenone using n-dodecane as an internal standard.

(A)


SR1 methanol_dilute
Wijeratne_100124_3 (1.436) Is (1.00,1.00) C18H15PNH2
1: TOF MS ES+
8.19e12
278.1099
279.1131
280.1164
Wijeratne_100124_3 257 (1.436)
1: TOF MS ES+
1.04e4
278.1090
279.0927
280.0952
%
m/z

(B)


SR1 methanol_dilute
Wijeratne_100124_3 (2.237) Is (1.00,1.00) C18H16PO
1: TOF MS ES+
2.71e12
279.0939
280.0973
281.1004
Wijeratne_100124_3 402 (2.237)
1: TOF MS ES+
2.11e5
279.0927
280.0952
%
m/z

(C)

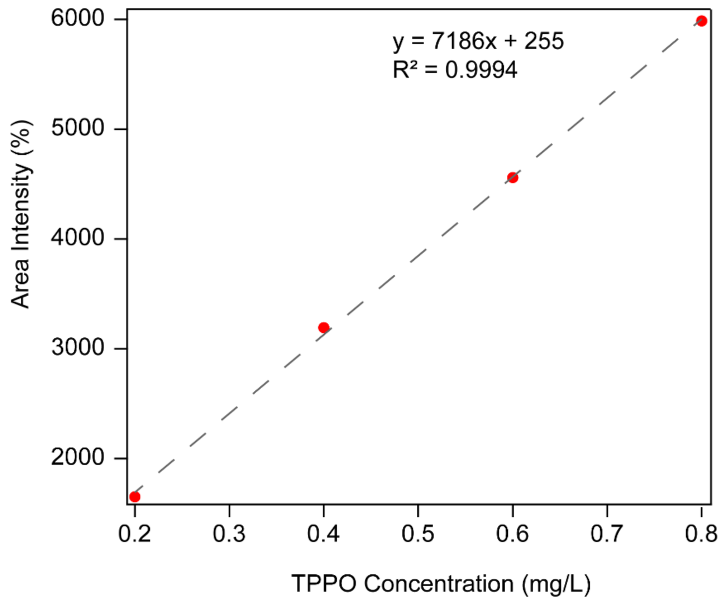


Figure S12. LC-MS data for (A) Ph_3P=NH showing [M+H]+ *m*/*z* = 278.10 (calc. 278.10), and (B) Ph_3P=O showing [M+H]+ *m*/*z* = 279.09 (calc. 279.09) obtained from the reaction between [(4-MeIm)(TPP)Fe^{III}(O_2^{2-})]$^-$ and acetophenone oxime in presence of 50 equiv. of PPh_3.(C) LC-MS generated calibration curve for Ph_3P=O in MeCN/H_2O (70/30). Control experiments indicate <1% yield when heme is not present.

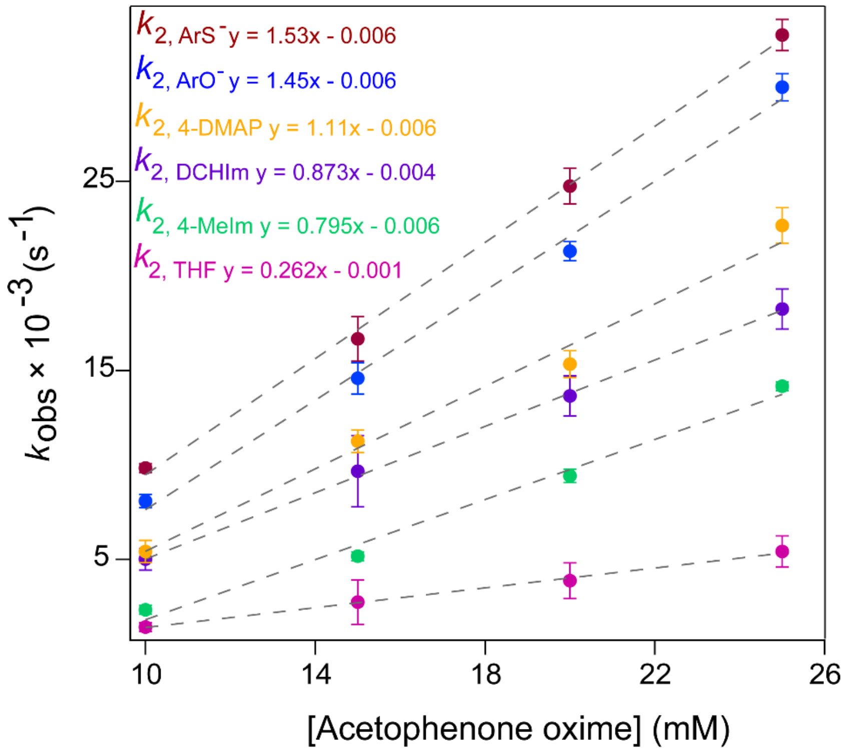


Figure S13. The dependence of pseudo-first-order rate constants (k_{obs}) on the acetophenone oxime concentration for a 50 µM $[(B)[(TPP)Fe^{III}(O_2^{2-})]^-$ in 9:1 DCM:THF at −40 °C. B = ArS^- (brick red), ArO^- (blue), 4-DMAP (orange), DCHIm (purple), 4-MeIm (green) or THF (magenta).

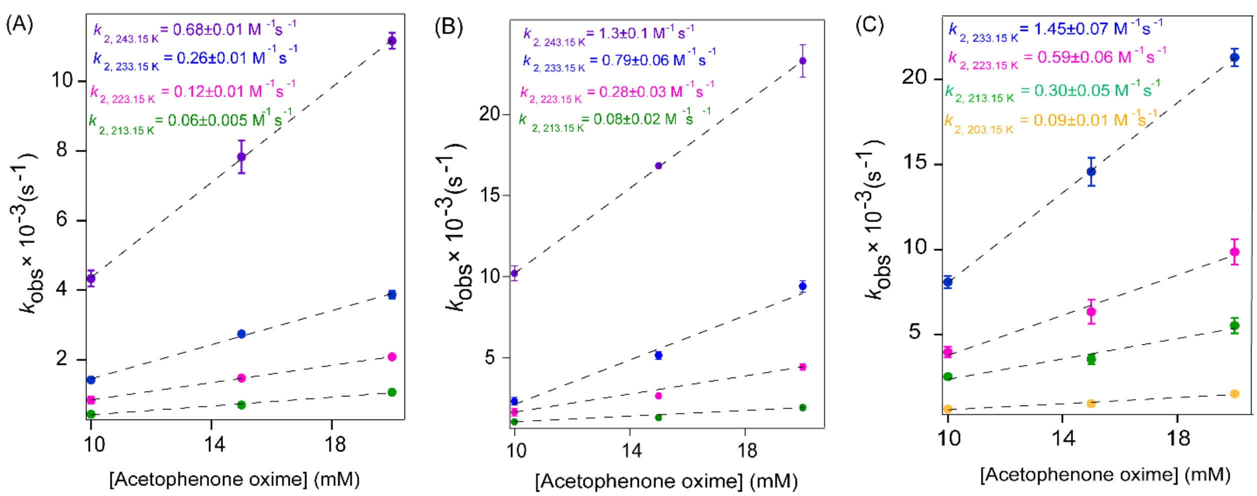


Figure S14. Variable-temperature kinetic plots showing the dependence of pseudo-first-order rate constants (k_{obs}) on acetophenone oxime concentration (with best fit lines) resulting from a 50 µM solution of (A) $[(THF)(TPP)Fe^{III}(O_2^{2-})]^-$, (B) $[(4\text{-}MeIm)(TPP)Fe^{III}(O_2^{2-})]^-$, and (C) $[(ArO^-)(TPP)Fe^{III}(O_2^{2-})]^{2-}$ in 9:1 DCM:THF.

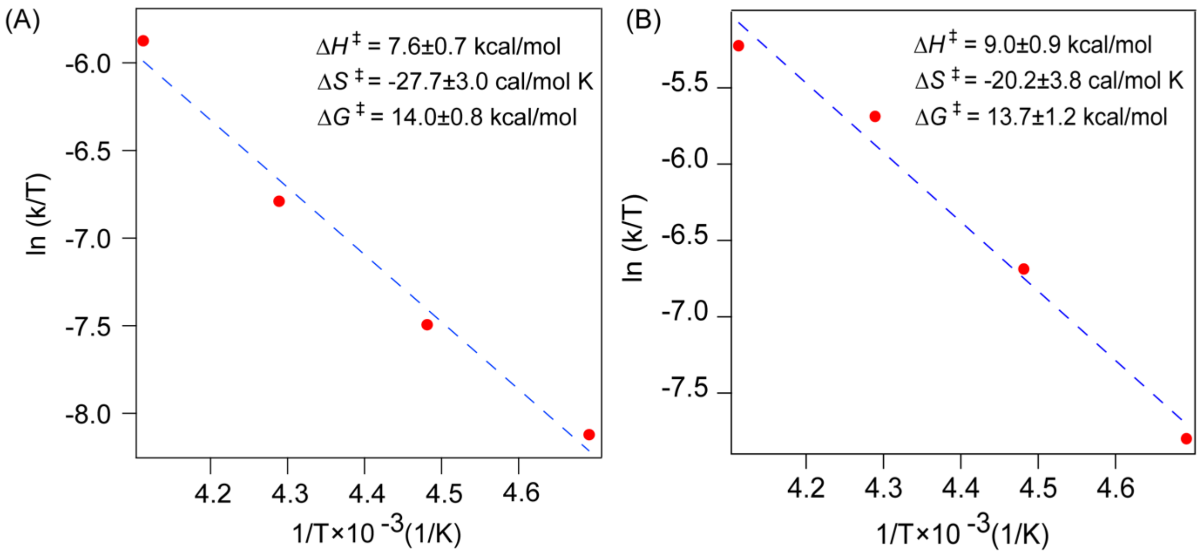


Figure S15. Eyring plot showing ln(k/T) versus 1/T for the reaction of a 50 μM solution of (A) $[(THF)(TPP)Fe^{III}(O_2^{2-})]^-$ and (B) $[(4\text{-MeIm})(TPP)Fe^{III}(O_2^{2-})]^-$ with acetophenone oxime substrate resulting from the data shown in Figure S18 (solvent = 9:1 DCM:THF).

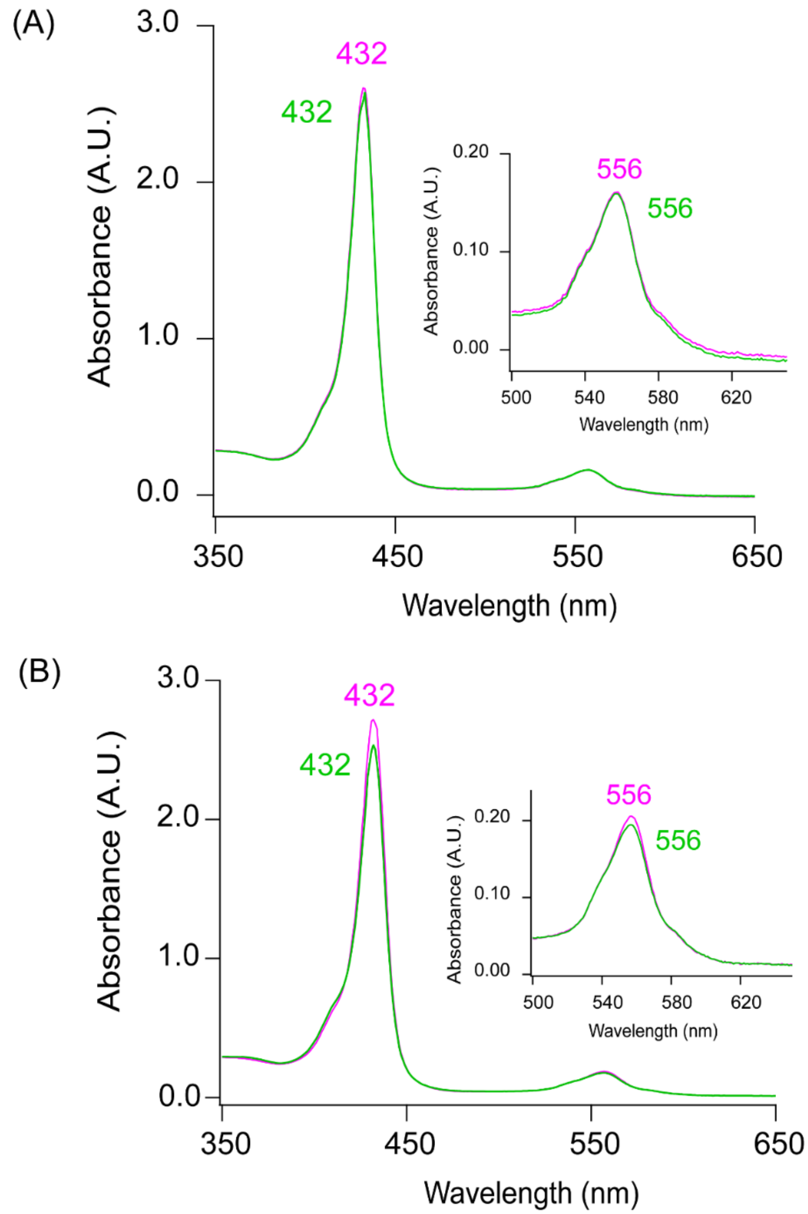


Figure S16. (A) UV−vis spectra (in 9:1 DCM:THF at −40 °C) for 50 μM solutions of $[(THF)(F_{20}TPP)Fe^{III}(O_2^{2-})]^-$ (Purple) and (A) $[(4\text{-MeIm})(F_{20}TPP)Fe^{III}(O_2^{2-})]^-$ (Green) and (B) $[(ArS^-)(F_{20}TPP)Fe^{III}(O_2^{2-})]^{2-}$ (Green). Inset shows the expanded Q-band region.

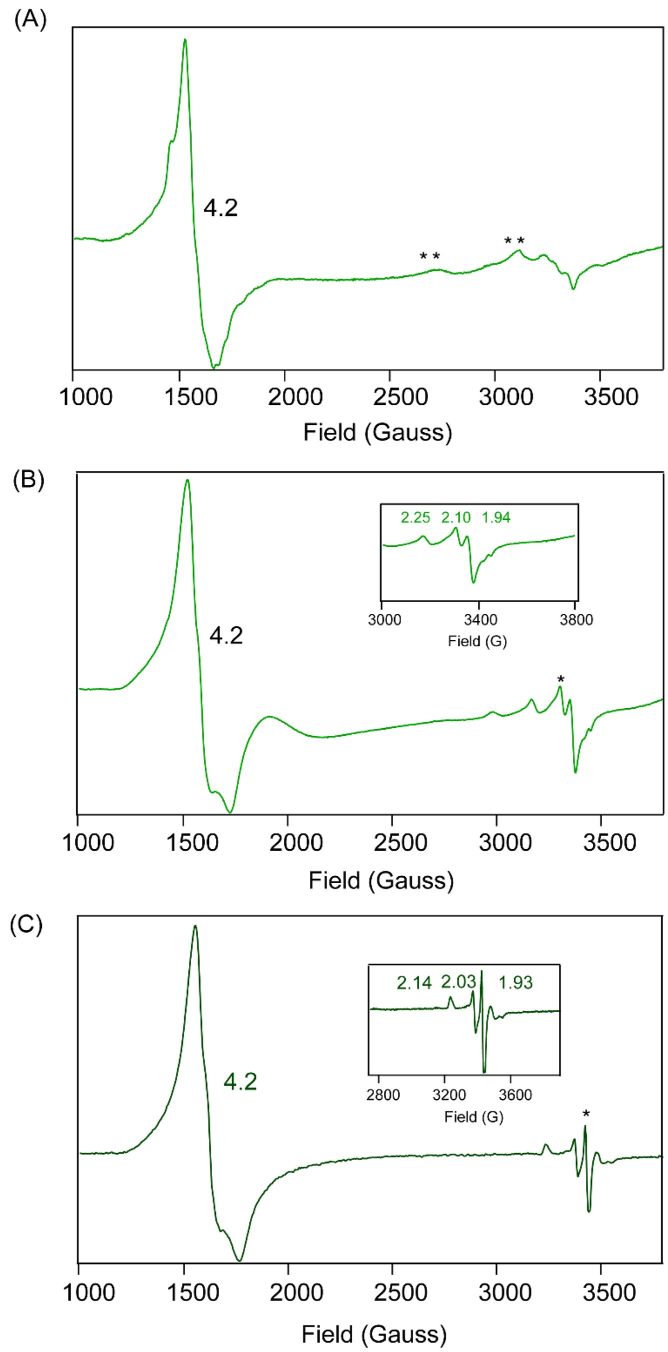


Figure S17. EPR spectral features (in frozen 9:1 DCM:THF at 7 K) for 2 mM solutions of (A) $[(4\text{-MeIm})(F_{20}TPP)Fe^{III}(O_2^{2-})]^-$ (**low spin Fe feature (g = 2.4, 2.1) corresponds to decay product), (B) $[(4\text{-DMAP})(F_{20}TPP)Fe^{III}(O_2^{2-})]^-$ and (C) $[(DCHIm)(F_{20}TPP)Fe^{III}(O_2^{2-})]^-$ (* feature (g = 1.99) corresponds to an excess of cobaltocene).

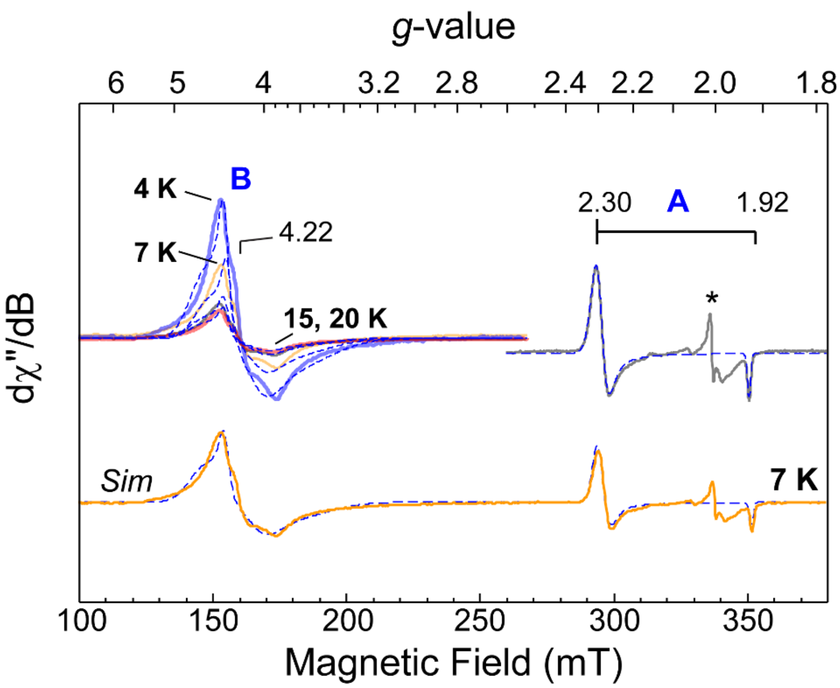


Figure S18. X-band CW EPR spectra of $[(ArS^{-})(F_{20}TPP)Fe^{III}(O_2^{2-})]^{2-}$ samples at selected temperatures, 4 K (blue), 7 K (orange), 10 K, (black), and 20 K (red). The axial zero field splitting parameter (*D*) for the high-spin species **B** was determined by matching the experimental and simulated (*blue dashed lines*) signal. Within this temperature regime (4 – 20 K), a single set of spectroscopic parameters was used to match the experimental signal intensity. The low-spin (S = 1/2) follows the Curie–Weiss law behavior and thus only a single spectrum collected under non-saturating conditions (7 K, 67 mW) was used for simulation. *Instrumental parameters*: microwave frequency, 9.626 GHz, microwave power, 21 mW (4K) – 211 mW (20 K); modulation amplitude, 0.92 mT. Simulation parameters and analytical quantitation of species are provided in **Table S3**. The sharp signal observed at $g \sim 2$ (*) is attributed to residual cobaltocene.

Table S3. EPR simulation parameters for **Figure S18**.

Species	Spin	$g_{1,2,3}$	D (cm^{-1})	E/D	[X] (%)
A	1/2	2.31, 2.29, 1.92	-	-	18 ± 2
B	5/2	2.0, 2.0, 2.0	0.6 ± 0.1	0.24	82 ± 7

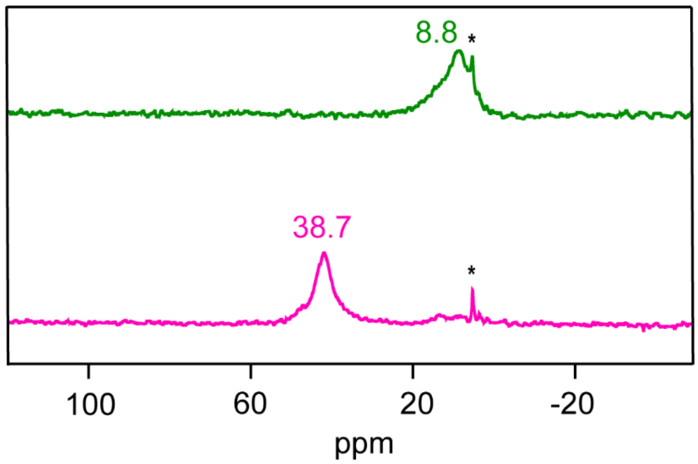


Figure S19. ^{2}H NMR spectra (in 9:1 DCM:THF at −40 °C) for $[(F_{20}TPP\text{-}d_8)\ Fe^{III}(O_2^{2-})]^-$ (pink), and $[(4\text{-}MeIm)(\ F_{20}TPP\text{-}d_8)Fe^{III}(O_2^{2-})]^-$ (green); *peaks correspond to the solvent.

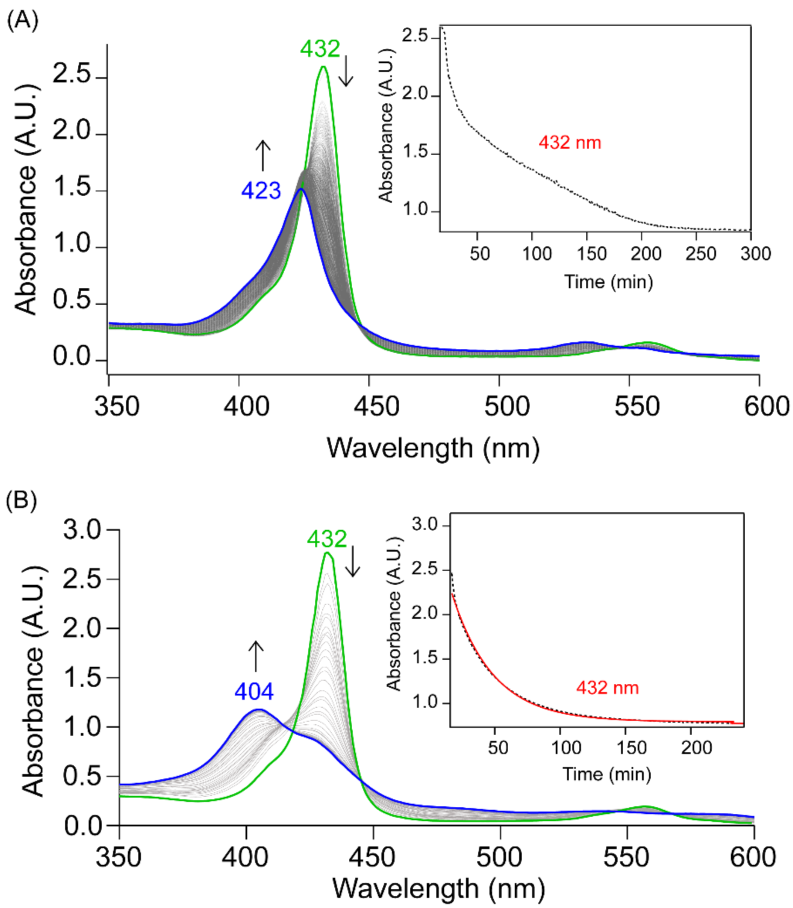


Figure S20. Electronic absorption spectral changes (in 9:1 DCM:THF at –40 ºC) in the presence of 500 equiv of acetophenone oxime (A) $[(DCHIm)(F_{20}TPP)Fe^{III}(O_2^{2-})]^-$ and (B) $[(ArS^-)(F_{20}TPP)Fe^{III}(O_2^{2-})]^{2-}$ (green: initial $[(B)(F_{20}TPP)Fe^{III}(O_2^{2-})]^-$ and blue: final heme product). Insets show the kinetic time traces at 432 nm (red line shows the exponential fit).

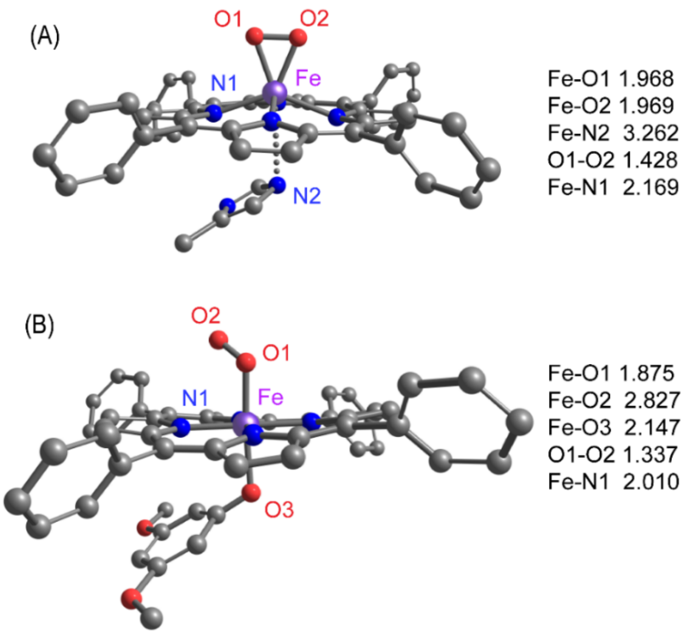


Figure S21. Optimized geometries of (A) $[(4\text{-MeIm})(TPP)Fe^{III}(O_2^{2-})]^-$, (B) $[(ArO^-)(TPP)Fe^{III}(O_2^{2-})]^{2-}$; key bond lengths are shown next to each structure in Å.

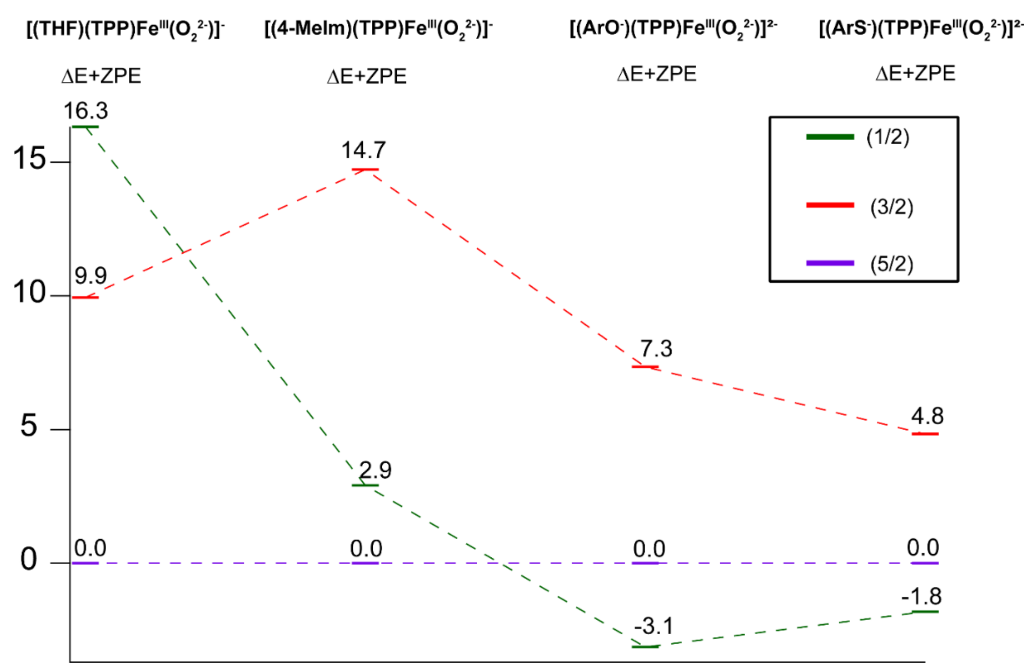


Figure S22. Sextet (purple)/quartet (red)/doublet (green) spin-state energies for the heme-PO complexes with different axial ligands. All energies are presented with respect to the sextet spin state in kcal mol^{-1}.

Table S4. Bond lengths (Å) and bond angles (degree) of the optimized heme-PO structures.

	[(THF)(TPP)Fe^{III}(O_2^{2-})]$^-$	**[(4-MeIm)(TPP)Fe^{III}(O_2^{2-})]$^-$**	**[(ArO$^-$)(TPP)Fe^{III}(O_2^{2-})$^{2-}$**	**[(ArS$^-$)(TPP)Fe^{III}(O_2^{2-})$^{2-}$**
Fe-O1[a]	1.980	1.968	1.875	1.898
Fe-O2[a]	1.977	1.969	2.827	2.845
O1-O2[a]	1.427	1.428	1.337	1.331
Fe-N_{Por}[b]	2.159	2.169	2.010	2.004
Fe-L[c]	4.446	3.262	2.147	2.549
Fe-O1-O2[d]	68.72	68.74	122.45	122.53

[a]bond distances in Å; [b]average value; [c]bond distances between Fe and axially coordinating atom of the ligand in Å; [d]value of the angle ∠Fe-O_{peroxo}-O_{peroxo}.

Table S5. *ν*(Fe-O) and ν(O-O) frequencies, and natural charges for the optimized heme-PO structures.

	[(THF)(TPP)Fe^{III}(O_2^{2-})]$^-$	[(4-MeIm)(TPP)Fe^{III}(O_2^{2-})]$^-$	[(ArO$^-$)(TPP)Fe^{III}(O_2^{2-})]$^{2-}$	[(ArS$^-$)(TPP)Fe^{III}(O_2^{2-})]$^{2-}$
ν(Fe-O) /cm^{-1}	407 (Δ^{18}O = 14)[a]	414 (Δ^{18}O =15)[a]	505 (Δ^{18}O =17)[a]	465 (Δ^{18}O =14)[a]
ν(O-O) /cm^{-1}	899 (Δ^{18}O = 52)[a]	896 (Δ^{18}O = 51)[a]	1003 (Δ^{18}O = 64)[a]	1015 (Δ^{18}O = 63)[a]
Natural Atomic Charge-Fe	0.937	0.929	0.214	0.047
Natural Atomic Charge-O1	-0.417	-0.411	-0.152	-0.149
Natural Atomic Charge-O2	-0.418	-0.410	-0.439	-0.420

[a]Isotopic substitution Δ^{18}O is included in the brackets.

Cartesian coordinates of optimized geometries

[(THF)(TPP)$Fe^{III}(O_2^{2-})]^-$ (uB97D-def2-TZVP) Charge: -1, Multiplicity: 6

26	-0.067379000	0.021975000	-0.991756000
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6	-2.491997000	-1.868931000	-0.175986000
6	-3.926839000	-1.869488000	0.036313000
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6	0.164824000	3.074173000	-0.284685000
6	1.574052000	3.056111000	-0.249757000
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6	3.825918000	1.902213000	-0.246404000
6	4.222488000	0.598604000	-0.283195000
6	3.014706000	-0.204120000	-0.301797000
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1	-3.352216000	-4.202165000	-1.988903000
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6	4.714267000	-3.090018000	-1.443270000
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6	6.773681000	-3.676969000	-0.307178000
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1	4.096916000	7.823096000	-0.004540000
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[(THF)(TPP)$Fe^{III}(O_2^{2-})]^-$ (uB97D-def2-TZVP) Charge: -1, Multiplicity: 4

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7	-0.959677000	1.863960000	-0.438604000
6	2.196618000	-2.110083000	-0.432791000
6	2.426648000	-3.538662000	-0.342272000
6	1.202097000	-4.133698000	-0.293938000
6	0.217720000	-3.070328000	-0.336252000
6	-1.165043000	-3.261625000	-0.190490000
6	-2.127693000	-2.231951000	-0.129348000
6	-3.527801000	-2.441471000	0.130121000
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6	1.063060000	3.265404000	-0.264237000
6	2.022470000	2.228112000	-0.235207000
6	3.448419000	2.460923000	-0.239532000
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6	2.984841000	0.254438000	-0.296897000
6	3.207083000	-1.138201000	-0.382222000
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6	-5.175307000	2.319905000	1.002971000
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6	-7.407255000	2.477934000	0.070559000
1	-6.830386000	3.286817000	1.989747000
1	-7.672024000	1.562987000	-1.869307000
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1	-3.530928000	-7.009375000	-1.668396000
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6	4.618394000	-1.619319000	-0.364502000
6	5.433951000	-1.410031000	0.760624000
6	5.157443000	-2.305572000	-1.465329000
6	6.752253000	-1.872391000	0.784895000
1	5.022082000	-0.884927000	1.619356000
6	6.476479000	-2.767733000	-1.444735000
1	4.533290000	-2.470992000	-2.340626000
6	7.279113000	-2.552772000	-0.318978000
1	7.366678000	-1.706038000	1.667655000
1	6.878178000	-3.292564000	-2.309363000
1	8.305787000	-2.912662000	-0.301483000
6	1.561326000	4.668327000	-0.171415000
6	2.220633000	5.117969000	0.985239000
6	1.374919000	5.571358000	-1.231090000
6	2.680077000	6.434031000	1.081367000
1	2.365938000	4.425799000	1.811598000
6	1.835056000	6.888040000	-1.138702000
1	0.868334000	5.230823000	-2.131308000
6	2.489268000	7.324534000	0.018521000
1	3.182954000	6.765671000	1.987771000
1	1.685933000	7.571714000	-1.972209000
1	2.847136000	8.349444000	0.091831000
1	3.926008000	3.431853000	-0.231127000
1	5.105262000	1.013319000	-0.312776000
1	3.397971000	-4.013545000	-0.292439000
1	0.979626000	-5.189525000	-0.211308000
1	-3.989982000	-3.403201000	0.310130000
1	-5.173177000	-0.979603000	0.271770000
1	-3.501353000	4.029571000	-0.210836000
1	-1.078312000	5.195802000	-0.162546000
8	-0.621642000	0.192290000	3.378950000
6	-0.056237000	-1.039075000	2.884464000
6	0.262399000	1.221742000	2.892519000
6	1.480062000	-0.872081000	2.961052000
1	-0.445219000	-1.853561000	3.507394000
6	1.681469000	0.664187000	3.090465000
1	0.071535000	1.402330000	1.825516000
1	0.056218000	2.133977000	3.465103000
1	2.371561000	1.054667000	2.336502000
1	2.059421000	0.922458000	4.087101000
1	1.951520000	-1.264464000	2.056554000
1	1.896030000	-1.396679000	3.828846000
1	-0.367064000	-1.196026000	1.842377000

[(THF)(TPP)$Fe^{III}(O_2^{2-})]^-$ (uB97D-def2-TZVP) Charge: -1, Multiplicity: 2

26	0.071795000	0.025009000	-0.724770000
7	-1.160758000	-1.532757000	-0.183101000
7	-1.496390000	1.246217000	-0.559009000

7	1.280567000	1.572162000	-0.123732000
7	1.636126000	-1.202052000	-0.518736000
6	-2.830082000	0.893467000	-0.638016000
6	-3.659522000	2.079094000	-0.682629000
6	-2.829017000	3.146662000	-0.558507000
6	-1.485584000	2.623428000	-0.436366000
6	-0.376110000	3.405984000	-0.123926000
6	0.916519000	2.887551000	0.054844000
6	2.070628000	3.685281000	0.365576000
6	3.154134000	2.853337000	0.295197000
6	2.654242000	1.549410000	-0.043611000
6	3.471024000	0.434628000	-0.296637000
6	2.973021000	-0.848346000	-0.512442000
6	3.803650000	-2.031301000	-0.581310000
6	2.969769000	-3.101839000	-0.523636000
6	1.620042000	-2.582799000	-0.455929000
6	0.497733000	-3.371296000	-0.208219000
6	-0.802217000	-2.856197000	-0.063206000
6	-1.972390000	-3.678023000	0.072389000
6	-3.052392000	-2.846075000	-0.030193000
6	-2.537516000	-1.518198000	-0.213750000
6	-3.338930000	-0.395121000	-0.483654000
8	-0.330758000	-0.510730000	-2.556247000
8	0.532646000	0.569480000	-2.538996000
6	4.949419000	0.640606000	-0.271643000
6	5.736908000	0.113369000	0.764152000
6	5.576938000	1.386389000	-1.282286000
6	7.119213000	0.320549000	0.786905000
1	5.256288000	-0.458409000	1.554695000
6	6.959193000	1.593844000	-1.263357000
1	4.972008000	1.801408000	-2.085412000
6	7.735226000	1.061046000	-0.228006000
1	7.713955000	-0.092408000	1.599346000
1	7.429899000	2.169820000	-2.057691000
1	8.811062000	1.222856000	-0.211397000
6	-0.569590000	4.875034000	0.057863000
6	-1.285071000	5.369666000	1.159914000
6	-0.033778000	5.788688000	-0.863338000
6	-1.463645000	6.744766000	1.336741000
1	-1.699658000	4.666567000	1.878934000
6	-0.212041000	7.164358000	-0.690223000
1	0.522619000	5.412134000	-1.718702000
6	-0.927774000	7.646967000	0.411121000
1	-2.017987000	7.111273000	2.198529000
1	0.205616000	7.858745000	-1.416628000
1	-1.066407000	8.717555000	0.547128000
6	-4.817293000	-0.576214000	-0.536700000
6	-5.537227000	-0.958212000	0.607462000
6	-5.521206000	-0.351290000	-1.730800000
6	-6.925015000	-1.114283000	0.559089000
1	-4.999382000	-1.126997000	1.537538000
6	-6.909456000	-0.506744000	-1.781977000
1	-4.969906000	-0.055012000	-2.620483000
6	-7.616503000	-0.889387000	-0.636814000
1	-7.467249000	-1.405711000	1.456546000
1	-7.438129000	-0.332236000	-2.717044000
1	-8.697104000	-1.010348000	-0.675391000
6	0.682448000	-4.844494000	-0.072369000
6	0.450301000	-5.479443000	1.158913000
6	1.089963000	-5.625092000	-1.166036000
6	0.623147000	-6.859488000	1.294921000
1	0.135337000	-4.880222000	2.010384000
6	1.263778000	-7.005702000	-1.032788000
1	1.266951000	-5.140922000	-2.123778000
6	1.030987000	-7.627974000	0.198641000
1	0.443690000	-7.334036000	2.257702000
1	1.576454000	-7.595783000	-1.892048000
1	1.165798000	-8.702548000	0.303193000
1	-1.967025000	-4.753561000	0.187567000
1	-4.101119000	-3.110109000	-0.013074000
1	-4.739427000	2.075319000	-0.747945000
1	-3.089608000	4.195676000	-0.512165000
1	2.052224000	4.744052000	0.587729000
1	4.196976000	3.096545000	0.450924000
1	4.884969000	-2.027014000	-0.611716000
1	3.231015000	-4.151163000	-0.493182000
8	0.539578000	0.201581000	3.437784000
6	-0.549515000	0.997133000	2.925162000
6	0.287885000	-1.131138000	2.954357000
6	-1.802276000	0.087415000	2.934032000
1	-0.639328000	1.882291000	3.566258000
6	-1.223800000	-1.340990000	3.129115000
1	0.564747000	-1.204335000	1.891659000
1	0.905693000	-1.820057000	3.542691000
1	-1.621677000	-2.053158000	2.400587000
1	-1.438766000	-1.709709000	4.139490000
1	-2.339550000	0.174858000	1.986141000
1	-2.486352000	0.350898000	3.748629000
1	-0.321153000	1.311733000	1.898557000

[(4-MeIm)(TPP)Fe^{III}(O_2^{2-})]$^-$ (uB97D-def2-TZVP) Charge: -1, Multiplicity: 6

7	1.695974000	1.372491000	-0.129074000
7	-1.183741000	1.610546000	-0.477590000
6	3.032703000	1.057225000	-0.086437000
6	3.822507000	2.268037000	-0.050816000
6	2.945646000	3.313164000	-0.092628000
6	1.615983000	2.743791000	-0.134707000
6	0.421280000	3.487495000	-0.177460000
6	-0.874262000	2.933582000	-0.272888000
6	-2.086867000	3.694544000	-0.072231000
6	-3.125157000	2.813143000	-0.151020000
6	-2.552292000	1.509948000	-0.400621000
6	3.562943000	-0.244878000	-0.059882000
6	0.523926000	4.971807000	-0.083788000
6	1.088477000	5.587718000	1.046315000
6	1.176472000	6.979434000	1.133486000
6	0.702261000	7.780617000	0.088767000
6	0.137488000	7.179087000	-1.041445000
6	0.047491000	5.787288000	-1.124660000
6	5.047099000	-0.375768000	0.064283000
6	5.631980000	-0.804201000	1.265941000
6	7.020284000	-0.921661000	1.381194000
6	7.844157000	-0.609716000	0.294129000
6	7.270380000	-0.180509000	-0.907579000
6	5.881687000	-0.065147000	-1.020442000
1	4.903232000	2.309497000	-0.007526000
1	3.175665000	4.370481000	-0.098634000
1	-2.131152000	4.754951000	0.138249000
1	-4.179357000	3.016937000	-0.017599000
1	1.610478000	7.438246000	2.019660000
1	-0.230495000	7.793607000	-1.860644000
1	7.458073000	-1.252979000	2.320760000
1	7.903215000	0.061855000	-1.759030000
6	-3.308947000	0.321131000	-0.452758000
6	2.808661000	-1.432550000	-0.130278000
6	-2.773950000	-0.981076000	-0.470813000
6	-4.793635000	0.457633000	-0.425131000
7	1.450656000	-1.518081000	-0.324603000
6	3.369097000	-2.758230000	0.009218000
7	-1.443263000	-1.292710000	-0.413277000
6	-3.563552000	-2.195157000	-0.554120000
6	-5.474307000	1.112442000	-1.465068000
6	-5.539927000	-0.054161000	0.649937000
6	1.131992000	-2.854066000	-0.288977000
6	2.329717000	-3.637528000	-0.078767000
1	4.415314000	-2.980631000	0.173322000
6	-1.357292000	-2.658120000	-0.434870000
6	-2.684175000	-3.235986000	-0.533366000
1	-4.642258000	-2.239390000	-0.627698000
6	-6.864986000	1.247084000	-1.435195000
6	-6.929967000	0.082734000	0.683941000
6	-0.163604000	-3.402956000	-0.373771000
1	2.364122000	-4.715652000	0.006615000
1	-2.906520000	-4.293812000	-0.584303000
6	-7.598005000	0.732856000	-0.359852000
1	-7.376171000	1.751083000	-2.253027000
1	-7.490732000	-0.313762000	1.528094000
6	-0.278718000	-4.890508000	-0.356118000
6	0.244971000	-5.662410000	-1.406202000
6	-0.906689000	-5.547695000	0.715011000
6	0.140082000	-7.055953000	-1.389221000
6	-1.009943000	-6.941156000	0.735667000
6	-0.487774000	-7.700359000	-0.317531000
1	0.545910000	-7.637924000	-2.214333000
1	-1.494170000	-7.434043000	1.576373000
1	8.924758000	-0.700151000	0.382931000
1	-8.680548000	0.838973000	-0.334837000
1	-0.568658000	-8.785273000	-0.302771000
1	0.771158000	8.864383000	0.155387000
26	0.165089000	0.044438000	-1.026517000
1	-4.903684000	1.511400000	-2.300592000
1	-5.018937000	-0.552323000	1.463597000
1	4.990655000	-1.043918000	2.111301000
1	5.433856000	0.266948000	-1.954494000
1	-1.306706000	-4.956526000	1.535594000
1	0.731382000	-5.160203000	-2.239355000
1	-0.390043000	5.318976000	-2.003267000
1	1.451798000	4.965186000	1.860565000
8	0.862319000	0.535240000	-2.801131000
8	-0.223763000	-0.386312000	-2.907551000
6	0.246216000	-1.042167000	2.716083000
6	-1.137346000	0.667341000	2.598920000
6	-1.707391000	-0.356057000	3.322306000
7	-0.825667000	-1.423679000	3.395062000
1	1.130097000	-1.638063000	2.527995000
1	-1.511950000	1.631777000	2.288280000
6	-3.070268000	-0.406810000	3.940463000
1	-3.621300000	0.518228000	3.733418000
1	-3.651516000	-1.249709000	3.539061000
1	-3.015800000	-0.539453000	5.030875000
7	0.111948000	0.219338000	2.231162000
1	0.741506000	0.679464000	1.571056000

[(4-MeIm)(TPP)Fe^{III}(O_2^{2-})]$^-$ (uB97D-def2-TZVP) Charge: -1, Multiplicity: 4

7	-0.950518000	-1.771837000	-0.324895000
7	1.761349000	-0.872075000	-0.395425000
6	-2.303165000	-2.004900000	-0.381893000
6	-2.568182000	-3.414141000	-0.277359000
6	-1.353067000	-4.036371000	-0.161218000
6	-0.354275000	-3.003338000	-0.196962000
6	1.034088000	-3.236001000	-0.170994000
6	1.998262000	-2.236739000	-0.295527000
6	3.421056000	-2.492655000	-0.300970000
6	4.043172000	-1.290136000	-0.422556000
6	3.009897000	-0.280607000	-0.463465000
6	-3.298830000	-1.011643000	-0.473024000
6	1.490917000	-4.648831000	-0.020805000
6	1.280375000	-5.339457000	1.183976000
6	1.700399000	-6.664324000	1.333145000
6	2.338291000	-7.322434000	0.275465000
6	2.551294000	-6.645370000	-0.930417000
6	2.129396000	-5.320414000	-1.075879000
6	-4.716242000	-1.465155000	-0.574423000
6	-5.633497000	-1.213312000	0.459309000
6	-6.958968000	-1.647031000	0.363765000
6	-7.389957000	-2.344250000	-0.770316000
6	-6.484948000	-2.603918000	-1.805848000
6	-5.160434000	-2.168958000	-1.706359000
1	-3.551510000	-3.866041000	-0.287694000
1	-1.151325000	-5.095863000	-0.071016000
1	3.873561000	-3.471483000	-0.213141000
1	5.105896000	-1.087788000	-0.447162000
1	1.533044000	-7.181459000	2.276100000
1	3.041996000	-7.150179000	-1.760425000
1	-7.653646000	-1.444774000	1.176858000
1	-6.811353000	-3.142201000	-2.693667000
6	3.273156000	1.089256000	-0.423866000
6	-3.037575000	0.357493000	-0.439884000
6	2.279242000	2.070517000	-0.272705000
6	4.696757000	1.529345000	-0.486544000
7	-1.788737000	0.951144000	-0.311876000
6	-4.064288000	1.374370000	-0.497651000
7	0.919420000	1.832080000	-0.237674000
6	2.538165000	3.476454000	-0.146045000
6	5.449331000	1.349207000	-1.658614000
6	5.321062000	2.115963000	0.626828000
6	-2.028120000	2.311542000	-0.232306000
6	-3.444341000	2.575977000	-0.357349000
1	-5.120403000	1.179709000	-0.629209000

6	0.321815000	3.069399000	-0.098855000
6	1.322979000	4.094670000	-0.015739000
1	3.519579000	3.931834000	-0.153302000
6	6.788793000	1.745177000	-1.718437000
6	6.659674000	2.514054000	0.570557000
6	-1.063153000	3.310347000	-0.088441000
1	-3.890973000	3.561709000	-0.355805000
1	1.123424000	5.150744000	0.108832000
6	7.399188000	2.329957000	-0.603367000
1	7.354473000	1.599996000	-2.636850000
1	7.127183000	2.962236000	1.445328000
6	-1.531700000	4.719715000	0.054523000
6	-1.277498000	5.672649000	-0.945920000
6	-2.248480000	5.120938000	1.194110000
6	-1.725127000	6.989887000	-0.811212000
6	-2.697818000	6.437446000	1.332666000
6	-2.437031000	7.377656000	0.329711000
1	-1.522840000	7.712242000	-1.599775000
1	-3.248413000	6.729567000	2.224930000
1	-8.421310000	-2.682641000	-0.846328000
1	8.441636000	2.638634000	-0.648197000
1	-2.786157000	8.402811000	0.435456000
1	2.665762000	-8.353775000	0.389834000
26	-0.010405000	0.042844000	-0.349333000
1	4.973878000	0.894548000	-2.525000000
1	4.748234000	2.253609000	1.540981000
1	-5.297624000	-0.673596000	1.341956000
1	-4.456828000	-2.370246000	-2.511028000
1	-2.451085000	4.389222000	1.973222000
1	-0.727799000	5.370339000	-1.834318000
1	2.291724000	-4.794730000	-2.014180000
1	0.784938000	-4.826921000	2.005786000
8	-0.252985000	-0.300583000	-2.602572000
8	0.192438000	0.743829000	-3.252246000
6	-1.326718000	-0.342413000	2.594233000
6	0.147501000	-0.469969000	4.238571000
6	0.794549000	-0.246639000	3.042150000
7	-0.143934000	-0.169195000	2.031507000
1	-2.275232000	-0.346646000	2.074617000
1	0.512677000	-0.587944000	5.249364000
6	2.259909000	-0.108020000	2.781835000
1	2.633332000	-0.944269000	2.177442000
1	2.468106000	0.806317000	2.213732000
1	2.814959000	-0.078661000	3.726958000
7	-1.199616000	-0.529448000	3.933171000
1	-1.953872000	-0.678862000	4.587876000

[(4-MeIm)(TPP)Fe^{III}(O_2^{2-})]$^{-}$ (uB97D-def2-TZVP) Charge: -1, Multiplicity: 2

7	-1.125484000	-1.642941000	-0.359623000
7	1.646913000	-1.112506000	-0.332188000
6	-2.488943000	-1.719007000	-0.537031000
6	-2.926823000	-3.093117000	-0.447603000
6	-1.819454000	-3.843858000	-0.184759000
6	-0.698495000	-2.933410000	-0.136686000
6	0.633362000	-3.334591000	0.033928000
6	1.727036000	-2.470582000	-0.109278000
6	3.109050000	-2.891178000	-0.097315000
6	3.859296000	-1.787116000	-0.375302000
6	2.942760000	-0.679241000	-0.503866000
6	-3.357220000	-0.623934000	-0.658602000
6	0.891676000	-4.773876000	0.328433000
6	0.479370000	-5.328997000	1.551485000
6	0.705199000	-6.678070000	1.839534000
6	1.347782000	-7.497768000	0.904974000
6	1.760054000	-6.957439000	-0.318310000
6	1.532248000	-5.607859000	-0.602725000
6	-4.802078000	-0.911371000	-0.891053000
6	-5.769913000	-0.621686000	0.085195000
6	-7.119979000	-0.907596000	-0.136394000
6	-7.526127000	-1.492238000	-1.341288000
6	-6.571151000	-1.789665000	-2.319888000
6	-5.221845000	-1.502490000	-2.094438000
1	-3.951227000	-3.426130000	-0.554142000
1	-1.754374000	-4.915716000	-0.048787000
1	3.450964000	-3.901206000	0.086216000
1	4.936585000	-1.712604000	-0.449135000
1	0.382062000	-7.088298000	2.794491000
1	2.254312000	-7.588468000	-1.054573000
1	-7.854101000	-0.679109000	0.633995000
1	-6.876958000	-2.242781000	-3.260999000
6	3.349784000	0.657485000	-0.605424000
6	-2.953016000	0.708251000	-0.497568000
6	2.487262000	1.744517000	-0.416649000
6	4.802087000	0.917597000	-0.821228000
7	-1.657760000	1.130762000	-0.278034000
6	-3.854371000	1.837365000	-0.472296000
7	1.122947000	1.660462000	-0.227292000
6	2.918658000	3.119296000	-0.318837000
6	5.415389000	0.546852000	-2.029407000
6	5.594749000	1.504025000	0.179550000
6	-1.733027000	2.490250000	-0.073482000
6	-3.102567000	2.936829000	-0.184512000
1	-4.920821000	1.785905000	-0.647640000
6	0.691066000	2.952051000	-0.014033000
6	1.813234000	3.861762000	-0.029467000
1	3.937670000	3.462124000	-0.439512000
6	6.780790000	0.763706000	-2.236569000
6	6.960197000	1.722221000	-0.023840000
6	-0.644951000	3.351518000	0.114352000
1	-3.430007000	3.963665000	-0.084542000
1	1.751497000	4.930017000	0.130383000
6	7.558614000	1.353657000	-1.234120000
1	7.236495000	0.474048000	-3.181542000
1	7.558382000	2.173800000	0.765409000
6	-0.941917000	4.788670000	0.384478000
6	-0.660051000	5.782893000	-0.566800000
6	-1.537139000	5.172073000	1.597578000
6	-0.956787000	7.124506000	-0.310173000
6	-1.835412000	6.512861000	1.858071000
6	-1.544805000	7.494888000	0.904588000
1	-0.734536000	7.879957000	-1.061501000
1	-2.292593000	6.790739000	2.805924000
1	-8.576815000	-1.715431000	-1.515155000
1	8.621690000	1.522504000	-1.393387000
1	-1.776693000	8.538953000	1.105077000
1	1.524109000	-8.548277000	1.127089000
26	-0.004426000	0.020393000	-0.324629000
1	4.810233000	0.086572000	-2.807430000
1	5.131605000	1.782805000	1.123086000
1	-5.453749000	-0.172008000	1.023672000
1	-4.478984000	-1.733779000	-2.854670000
1	-1.764673000	4.407441000	2.337398000
1	-0.209862000	5.493845000	-1.513603000
1	1.847521000	-5.189764000	-1.555889000
1	-0.020794000	-4.691112000	2.277146000
8	0.036347000	0.007075000	-2.207262000
8	-0.178035000	1.108731000	-2.916800000
6	-1.324276000	-0.265862000	2.380020000
6	0.142026000	-0.287023000	4.032297000
6	0.800565000	-0.135546000	2.832422000
7	-0.134892000	-0.121527000	1.809930000
1	-2.268555000	-0.302082000	1.858227000
1	0.505993000	-0.341195000	5.048402000
6	2.272693000	-0.019586000	2.616249000
1	2.667531000	-0.902968000	2.100669000
1	2.510004000	0.847938000	1.992897000
1	2.781922000	0.081279000	3.582133000
7	-1.200657000	-0.369623000	3.724125000
1	-1.960327000	-0.480732000	4.379450000

[(ArO^{-})(TPP)Fe^{III}(O_2^{2-})]$^{2-}$ (uB97D-def2-TZVP) Charge: -2, Multiplicity: 6

7	0.586466000	-2.070519000	-0.538124000
7	2.607390000	0.061348000	-0.157547000
6	-0.509045000	-2.885280000	-0.618870000
6	-0.108686000	-4.246817000	-0.327971000
6	1.241733000	-4.226027000	-0.102749000
6	1.672721000	-2.849638000	-0.249481000
6	3.005519000	-2.385937000	-0.089382000
6	3.427986000	-1.036148000	-0.082165000
6	4.806159000	-0.587500000	0.012373000
6	4.782695000	0.778627000	0.024992000
6	3.391093000	1.182760000	-0.068404000
6	-1.828989000	-2.462474000	-0.918643000
6	4.057473000	-3.427303000	0.095694000
6	4.832470000	-3.476079000	1.268003000
6	5.814053000	-4.455925000	1.441008000
6	6.040638000	-5.409404000	0.441724000
6	5.276332000	-5.373371000	-0.730294000
6	4.295137000	-4.392695000	-0.899001000
6	-2.868138000	-3.525462000	-1.033157000
6	-3.981825000	-3.532361000	-0.174833000
6	-4.955069000	-4.530274000	-0.270171000
6	-4.835468000	-5.541483000	-1.230303000
6	-3.733329000	-5.544642000	-2.093464000
6	-2.759941000	-4.546678000	-1.993563000
1	-0.770058000	-5.103140000	-0.289152000
1	1.881236000	-5.062130000	0.151019000
1	5.675177000	-1.231769000	0.056733000
1	5.629689000	1.450985000	0.079195000
1	6.398215000	-4.478526000	2.359238000
1	5.447501000	-6.106613000	-1.516395000
1	-5.803603000	-4.521567000	0.411700000
1	-3.633683000	-6.322417000	-2.848494000
6	2.922483000	2.518094000	-0.075020000
6	-2.261627000	-1.128299000	-1.088501000
6	1.579073000	2.934102000	-0.265992000
6	3.934677000	3.592070000	0.139918000
7	-1.497728000	-0.004782000	-0.904612000
6	-3.601277000	-0.730239000	-1.481203000
7	0.521905000	2.116917000	-0.578923000
6	1.099519000	4.293479000	-0.133416000
6	4.156175000	4.580422000	-0.836178000
6	4.692158000	3.647046000	1.323738000
6	-2.299256000	1.086388000	-1.114305000
6	-3.625167000	0.634182000	-1.496496000
1	-4.412263000	-1.405774000	-1.721270000
6	-0.601167000	2.898519000	-0.675657000
6	-0.246296000	4.271316000	-0.384885000
1	1.705497000	5.149840000	0.134554000
6	5.103342000	5.588614000	-0.638294000
6	5.639981000	4.654061000	1.525763000
6	-1.908141000	2.437681000	-0.974953000
1	-4.458630000	1.275189000	-1.753521000
1	-0.935307000	5.105874000	-0.357233000
6	5.850139000	5.630055000	0.544825000
1	5.262269000	6.339005000	-1.410677000
1	6.210513000	4.680101000	2.452434000
6	-2.971221000	3.470786000	-1.126446000
6	-2.862153000	4.487162000	-2.093234000
6	-4.110768000	3.459523000	-0.301127000
6	-3.855360000	5.460544000	-2.230184000
6	-5.104819000	4.431789000	-0.434726000
6	-4.982160000	5.437992000	-1.399900000
1	-3.751891000	6.233958000	-2.989222000
1	-5.971995000	4.408333000	0.222920000
1	-5.593258000	-6.318939000	-1.306046000
1	6.587841000	6.414717000	0.700827000
1	-5.755732000	6.196368000	-1.504118000
1	6.804495000	-6.172931000	0.575211000
26	0.569547000	0.024018000	-0.603097000
8	0.878441000	-0.842008000	-3.656250000
8	0.910916000	-0.053030000	-2.589290000
1	3.578604000	4.547207000	-1.757055000
1	4.526093000	2.892007000	2.088601000
1	-4.069045000	-2.754832000	0.578556000
1	-1.905248000	-4.547161000	-2.666048000
1	-4.201796000	2.689240000	0.459573000
1	-1.988758000	4.504391000	-2.740991000
1	3.703284000	-4.362917000	-1.810953000
1	4.653437000	-2.738618000	2.046996000
6	-1.663119000	1.186589000	2.333241000
6	-2.977494000	1.182813000	2.795692000
6	-3.660509000	-0.014717000	3.067893000
6	-2.976550000	-1.225639000	2.868606000
6	-1.660141000	-1.256729000	2.409500000
6	-0.968614000	-0.042132000	2.105183000
1	-1.153270000	2.105720000	2.067531000
1	-4.680654000	-0.004164000	3.441784000

1	-1.148193000	-2.190830000	2.206639000
8	-3.713161000	2.338700000	3.011193000
8	-3.713453000	-2.365928000	3.154679000
6	-3.013963000	-3.612118000	3.143356000
1	-3.744309000	-4.371307000	3.441376000
1	-2.629617000	-3.845930000	2.141077000
1	-2.173787000	-3.596386000	3.854063000
6	-3.009632000	3.580577000	2.926495000
1	-2.612315000	3.747681000	1.916215000
1	-3.742282000	4.358316000	3.164725000
1	-2.178013000	3.608839000	3.647107000
8	0.240458000	-0.052228000	1.629403000

$[(ArO^{-})(TPP)Fe^{III}(O_2^{2-})]^{2-}$ (uB97D-def2-TZVP) Charge: -2, Multiplicity: 4

7	0.969071000	-1.891169000	-0.519462000
7	2.480483000	0.517505000	-0.153232000
6	0.057947000	-2.921379000	-0.451524000
6	0.733829000	-4.145403000	-0.161529000
6	2.083918000	-3.854470000	-0.105446000
6	2.213680000	-2.453274000	-0.332810000
6	3.448545000	-1.749681000	-0.316893000
6	3.544857000	-0.364188000	-0.237829000
6	4.788544000	0.373237000	-0.162808000
6	4.466347000	1.680413000	0.030683000
6	3.018427000	1.769746000	0.039899000
6	-1.337548000	-2.798627000	-0.686343000
6	4.692647000	-2.565004000	-0.329574000
6	5.624901000	-2.506156000	0.722733000
6	6.788663000	-3.281167000	0.699948000
6	7.041981000	-4.139985000	-0.374862000
6	6.118501000	-4.217149000	-1.425712000
6	4.957476000	-3.441372000	-1.398993000
6	-2.173253000	-4.025644000	-0.647134000
6	-3.269610000	-4.111741000	0.232934000
6	-4.075313000	-5.252528000	0.275164000
6	-3.801676000	-6.340123000	-0.561561000
6	-2.713755000	-6.271408000	-1.442023000
6	-1.911320000	-5.128919000	-1.482191000
1	0.255383000	-5.105909000	-0.022913000
1	2.905355000	-4.532727000	0.087347000
1	5.775576000	-0.063271000	-0.243141000
1	5.137838000	2.523322000	0.132820000
1	7.493489000	-3.220293000	1.527485000
1	6.306356000	-4.879123000	-2.269326000
1	-4.912153000	-5.294752000	0.970464000
1	-2.496025000	-7.106876000	-2.105423000
6	2.312297000	2.968582000	0.165783000
6	-1.969227000	-1.586239000	-0.964751000
6	0.916235000	3.087212000	-0.074910000
6	3.074049000	4.195055000	0.520325000
7	-1.408462000	-0.332679000	-0.896032000
6	-3.340390000	-1.477201000	-1.419887000
7	0.095035000	2.072160000	-0.520860000
6	0.170235000	4.299711000	0.032543000
6	3.094973000	5.319634000	-0.327373000
6	3.814011000	4.261367000	1.716896000
6	-2.398534000	0.566722000	-1.243176000
6	-3.596690000	-0.156165000	-1.611854000
1	-4.003554000	-2.314916000	-1.591480000
6	-1.141057000	2.643889000	-0.756634000
6	-1.109456000	4.025618000	-0.411556000
1	0.561869000	5.245466000	0.383358000
6	3.827383000	6.461752000	0.003755000
6	4.550394000	5.401571000	2.051506000
6	-2.301683000	1.953817000	-1.191181000
1	-4.512405000	0.297790000	-1.966518000
1	-1.952417000	4.701738000	-0.471466000
6	4.560115000	6.509599000	1.197076000
1	3.834747000	7.313272000	-0.674717000
1	5.111300000	5.426963000	2.984352000
6	-3.495801000	2.774976000	-1.525535000
6	-3.436703000	3.741932000	-2.546608000
6	-4.705486000	2.632052000	-0.820570000
6	-4.547966000	4.526911000	-2.862660000
6	-5.819983000	3.415366000	-1.133858000
6	-5.747755000	4.366322000	-2.157459000
1	-4.480151000	5.261255000	-3.663526000
1	-6.742900000	3.288669000	-0.570413000
1	-4.426732000	-7.230509000	-0.529330000
1	5.131083000	7.399102000	1.456230000
1	-6.614136000	4.978121000	-2.401421000
1	7.946510000	-4.744873000	-0.393262000
26	0.531115000	0.086572000	-0.540594000
8	0.668920000	-0.768848000	-3.287014000
8	0.846485000	0.161287000	-2.372574000
1	2.533257000	5.283992000	-1.257731000
1	3.804329000	3.403173000	2.385186000
1	-3.475322000	-3.273804000	0.893173000
1	-1.072431000	-5.076417000	-2.171980000
1	-4.759077000	1.906579000	-0.013431000
1	-2.505498000	3.868451000	-3.094214000
1	4.240636000	-3.501973000	-2.214777000
1	5.424895000	-1.847158000	1.564218000
6	-1.814173000	0.931543000	2.098471000
6	-3.079899000	0.773794000	2.665194000
6	-3.515468000	-0.472686000	3.143041000
6	-2.648117000	-1.571420000	3.045539000
6	-1.378015000	-1.443457000	2.479050000
6	-0.949526000	-0.185300000	1.982555000
1	-1.483245000	1.874548000	1.682797000
1	-4.500696000	-0.582422000	3.588106000
1	-0.718250000	-2.292478000	2.344772000
8	-3.992323000	1.802861000	2.788476000
8	-3.151894000	-2.763032000	3.531173000
6	-2.260133000	-3.882022000	3.568375000
1	-2.826956000	-4.701943000	4.020117000
1	-1.939820000	-4.167521000	2.557187000
1	-1.372860000	-3.654937000	4.178166000
6	-3.536810000	3.118339000	2.448435000
1	-3.233778000	3.177434000	1.395626000
1	-4.385835000	3.785012000	2.628471000
1	-2.685256000	3.410561000	3.081358000
8	0.244730000	-0.070249000	1.433492000

$[(ArO^{-})(TPP)Fe^{III}(O_2^{2-})]^{2-}$ (uB97D-def2-TZVP) Charge: -2, Multiplicity: 2

7	-0.184037000	2.024492000	-0.496042000
7	-2.503311000	0.387603000	-0.220743000
6	1.026463000	2.658318000	-0.669323000
6	0.904983000	4.063988000	-0.363777000
6	-0.398048000	4.282998000	-0.028718000
6	-1.078786000	3.014996000	-0.145217000
6	-2.458041000	2.846293000	0.038310000
6	-3.114755000	1.612093000	-0.055919000
6	-4.549043000	1.451519000	-0.003616000
6	-4.801460000	0.116354000	-0.115158000
6	-3.519175000	-0.543416000	-0.218703000
6	2.226317000	2.042473000	-1.044995000
6	-3.283359000	4.052165000	0.336475000
6	-3.973613000	4.163643000	1.555804000
6	-4.751922000	5.289071000	1.841138000
6	-4.856061000	6.326836000	0.907936000
6	-4.175527000	6.227910000	-0.311067000
6	-3.397579000	5.101073000	-0.591940000
6	3.414937000	2.908043000	-1.281550000
6	4.568859000	2.789287000	-0.487171000
6	5.677880000	3.610677000	-0.705727000
6	5.655806000	4.568000000	-1.726572000
6	4.513350000	4.696822000	-2.524886000
6	3.405202000	3.874722000	-2.302360000
1	1.717882000	4.777839000	-0.389804000
1	-0.863288000	5.213731000	0.268965000
1	-5.261989000	2.260174000	0.094248000
1	-5.761548000	-0.382963000	-0.122117000
1	-5.273662000	5.357577000	2.794029000
1	-4.254578000	7.026580000	-1.046442000
1	6.557623000	3.507731000	-0.072813000
1	4.486454000	5.435155000	-3.324382000
6	-3.349506000	-1.934334000	-0.261422000
6	2.371329000	0.658252000	-1.174768000
6	-2.099015000	-2.563973000	-0.353256000
6	-4.558284000	-2.801504000	-0.166279000
7	1.396585000	-0.280934000	-0.913767000
6	3.605920000	0.008984000	-1.548505000
7	-0.891471000	-1.935117000	-0.555167000
6	-1.901999000	-3.987414000	-0.197432000
6	-4.897632000	-3.673688000	-1.215508000
6	-5.380583000	-2.782220000	0.973860000
6	2.014100000	-1.505798000	-1.046366000
6	3.387429000	-1.331745000	-1.456949000
1	4.515915000	0.518852000	-1.835486000
6	0.056500000	-2.936195000	-0.573828000
6	-0.563373000	-4.215298000	-0.320511000
1	-2.687037000	-4.705730000	0.000911000
6	-6.023185000	-4.497987000	-1.131129000
6	-6.507080000	-3.604832000	1.062593000
6	1.421561000	-2.755887000	-0.829214000
1	4.082034000	-2.136267000	-1.660026000
1	-0.038410000	-5.158658000	-0.246042000
6	-6.833910000	-4.466700000	0.009328000
1	-6.269684000	-5.161823000	-1.957884000
1	-7.126407000	-3.577545000	1.957394000
6	2.304649000	-3.955161000	-0.859505000
6	2.106111000	-4.990562000	-1.789211000
6	3.370596000	-4.071353000	0.050300000
6	2.943268000	-6.109833000	-1.807581000
6	4.207753000	-5.189805000	0.036234000
6	3.997969000	-6.214885000	-0.893316000
1	2.775543000	-6.897521000	-2.540000000
1	5.021028000	-5.262678000	0.756170000
1	6.519287000	5.208035000	-1.897552000
1	-7.710405000	-5.108146000	0.077182000
1	4.650013000	-7.086156000	-0.906443000
1	-5.461953000	7.203592000	1.128152000
26	-0.542728000	0.058273000	-0.587324000
8	-0.196436000	0.733183000	-3.311279000
8	-0.951525000	0.086238000	-2.417152000
1	-4.267751000	-3.698109000	-2.101928000
1	-5.124460000	-2.116631000	1.794880000
1	4.581599000	2.057769000	0.316044000
1	2.517355000	3.973284000	-2.922863000
1	3.530315000	-3.278515000	0.775683000
1	1.289459000	-4.907680000	-2.502563000
1	-2.871080000	5.022816000	-1.540321000
1	-3.891598000	3.357329000	2.281160000
6	1.429825000	-1.443148000	2.452679000
6	2.725903000	-1.533231000	2.960857000
6	3.541174000	-0.398580000	3.099818000
6	3.013644000	0.847759000	2.722202000
6	1.720316000	0.970411000	2.217182000
6	0.898609000	-0.182189000	2.047267000
1	0.817116000	-2.322663000	2.289649000
1	4.545569000	-0.479743000	3.506447000
1	1.326974000	1.919923000	1.876143000
8	3.313827000	-2.728244000	3.348497000
8	3.874491000	1.921736000	2.883441000
6	3.327516000	3.227292000	2.674080000
1	4.141559000	3.930574000	2.876606000
1	2.977426000	3.354659000	1.641513000
1	2.487247000	3.412797000	3.360525000
6	2.467786000	-3.879090000	3.411909000
1	2.082604000	-4.148174000	2.418712000
1	3.093435000	-4.692152000	3.793925000
1	1.618778000	-3.704074000	4.089989000
8	-0.301321000	-0.093848000	1.541472000

$[(ArS^{-})(TPP)Fe^{III}(O_2^{2-})]^{2-}$ (uB97D-def2-TZVP) Charge: -2, Multiplicity: 6

7	-0.949476000	1.985508000	-0.356687000
7	-2.328411000	-0.593033000	-0.227286000
6	-0.112696000	3.073471000	-0.332568000
6	-0.875937000	4.259540000	-0.002852000
6	-2.173897000	3.867913000	0.156229000
6	-2.215728000	2.438701000	-0.076106000
6	-3.377706000	1.642225000	0.001154000
6	-3.418001000	0.233215000	-0.097108000
6	-4.624914000	-0.565754000	-0.062199000
6	-4.240239000	-1.873566000	-0.143966000
6	-2.795473000	-1.884986000	-0.229767000
6	1.280451000	3.048557000	-0.557771000
6	-4.672230000	2.349878000	0.225426000
6	-5.423256000	2.126259000	1.391941000
6	-6.633080000	2.792921000	1.603426000
6	-7.114697000	3.695875000	0.648858000
6	-6.375741000	3.927309000	-0.516727000
6	-5.165141000	3.260662000	-0.724461000
6	1.987995000	4.362108000	-0.566821000
6	2.945046000	4.669588000	0.414708000
6	3.603197000	5.902228000	0.411612000
6	3.315059000	6.850092000	-0.576842000
6	2.362952000	6.555632000	-1.559273000
6	1.704688000	5.322716000	-1.552029000
1	-0.465918000	5.254691000	0.111711000
1	-3.022769000	4.482760000	0.425883000
1	-5.631698000	-0.176284000	0.014011000
1	-4.874902000	-2.750131000	-0.148827000
1	-7.197005000	2.610941000	2.516287000
1	-6.743584000	4.624607000	-1.267041000
1	4.336967000	6.124090000	1.184149000
1	2.134711000	7.284915000	-2.334215000
6	-1.996198000	-3.047391000	-0.292614000
6	2.064852000	1.889365000	-0.738203000
6	-0.590244000	-3.072153000	-0.410324000
6	-2.691204000	-4.363755000	-0.192582000
7	1.605963000	0.597830000	-0.678667000
6	3.489970000	1.882539000	-0.987427000
7	0.220060000	-1.979280000	-0.601356000
6	0.226235000	-4.262911000	-0.295994000
6	-2.631333000	-5.286974000	-1.250286000
6	-3.412315000	-4.712705000	0.962022000
6	2.693523000	-0.225905000	-0.827980000
6	3.878901000	0.575659000	-1.040083000
1	4.109883000	2.762349000	-1.100539000
6	1.516114000	-2.433549000	-0.621549000
6	1.526256000	-3.868616000	-0.424062000
1	-0.148452000	-5.261737000	-0.113329000
6	-3.278617000	-6.522259000	-1.160039000
6	-4.058326000	-5.948221000	1.056115000
6	2.670507000	-1.635346000	-0.772196000
1	4.875654000	0.187407000	-1.202990000
1	2.414204000	-4.484460000	-0.365655000
6	-3.995189000	-6.857552000	-0.005755000
1	-3.226050000	-7.221344000	-1.992501000
1	-4.606440000	-6.202938000	1.961154000
6	3.982497000	-2.342360000	-0.837171000
6	4.275728000	-3.226515000	-1.888765000
6	4.947733000	-2.141459000	0.164176000
6	5.504260000	-3.891112000	-1.941950000
6	6.174905000	-2.807988000	0.114008000
6	6.458952000	-3.684452000	-0.939626000
1	5.716982000	-4.567744000	-2.767512000
1	6.907751000	-2.646188000	0.902590000
1	3.827271000	7.810134000	-0.580874000
1	-4.498607000	-7.819538000	0.066325000
1	7.414894000	-4.203045000	-0.979166000
1	-8.056898000	4.215104000	0.812285000
26	-0.405394000	0.012626000	-0.829209000
8	-0.355065000	0.763528000	-3.840695000
8	-0.627138000	0.104212000	-2.711391000
1	-2.075132000	-5.025022000	-2.147410000
1	-3.455252000	-4.008218000	1.789256000
1	3.162462000	3.935587000	1.186462000
1	0.966443000	5.091313000	-2.316486000
1	4.722336000	-1.467428000	0.987282000
1	3.533557000	-3.385984000	-2.667772000
1	-4.591304000	3.438703000	-1.630997000
1	-5.046136000	1.428227000	2.135667000
6	2.616395000	-1.165511000	3.732474000
6	3.996602000	-0.966614000	3.656929000
6	4.522923000	0.183419000	3.052649000
6	3.630961000	1.122746000	2.516875000
6	2.252046000	0.929290000	2.593457000
6	1.691053000	-0.219956000	3.212778000
1	2.228670000	-2.067821000	4.203793000
1	5.598570000	0.334940000	2.985377000
1	1.583657000	1.664030000	2.150441000
16	-0.043891000	-0.457652000	3.336620000
1	4.015675000	2.008448000	2.014372000
1	4.667799000	-1.721071000	4.067978000

$[(ArS^{-})(TPP)Fe^{III}(O_2^{2-})]^{2-}$ (uB97D-def2-TZVP) Charge: -2, Multiplicity: 4

7	0.809026000	-1.947019000	-0.316911000
7	2.319373000	0.454820000	-0.232452000
6	-0.085483000	-2.998686000	-0.339332000
6	0.582847000	-4.229556000	-0.000381000
6	1.896109000	-3.926052000	0.202861000
6	2.036266000	-2.508176000	-0.019038000
6	3.254775000	-1.821852000	0.041309000
6	3.369936000	-0.433686000	-0.106797000
6	4.626226000	0.272954000	-0.133576000
6	4.332192000	1.599751000	-0.242363000
6	2.896093000	1.710613000	-0.275211000
6	-1.450112000	-2.907210000	-0.638753000
6	4.498018000	-2.610397000	0.277994000
6	5.263347000	-2.411949000	1.439516000
6	6.428437000	-3.150290000	1.664368000
6	6.849902000	-4.101098000	0.727974000
6	6.096383000	-4.307423000	-0.433080000
6	4.930867000	-3.568450000	-0.654134000
6	-2.231909000	-4.174205000	-0.720348000
6	-3.239813000	-4.458749000	0.215516000
6	-3.966543000	-5.650340000	0.144109000
6	-3.696549000	-6.578310000	-0.868089000
6	-2.693743000	-6.305870000	-1.805475000
6	-1.967091000	-5.114236000	-1.729703000
1	0.099197000	-5.194042000	0.082880000
1	2.700617000	-4.592296000	0.484599000
1	5.601051000	-0.193089000	-0.078826000
1	5.019831000	2.433438000	-0.295025000
1	7.004455000	-2.986350000	2.573131000
1	6.418233000	-5.041316000	-1.169554000
1	-4.739809000	-5.856068000	0.881842000
1	-2.478860000	-7.020098000	-2.598092000
6	2.200765000	2.925257000	-0.306703000
6	-2.125501000	-1.696405000	-0.825042000
6	0.804902000	3.019671000	-0.356129000
6	2.986031000	4.191810000	-0.253178000
7	-1.571602000	-0.439785000	-0.691786000
6	-3.530824000	-1.593150000	-1.124018000
7	-0.073353000	1.962085000	-0.505554000
6	0.077930000	4.257794000	-0.233271000
6	2.953646000	5.099391000	-1.325134000
6	3.767122000	4.508698000	0.870822000
6	-2.620617000	0.444896000	-0.832849000
6	-3.839815000	-0.266771000	-1.121804000
1	-4.190800000	-2.432768000	-1.297370000
6	-1.335407000	2.526031000	-0.517617000
6	-1.246846000	3.952212000	-0.325770000
1	0.530561000	5.228374000	-0.078534000
6	3.684682000	6.289645000	-1.277844000
6	4.497211000	5.699249000	0.922245000
6	-2.538531000	1.835677000	-0.705138000
1	-4.801906000	0.197206000	-1.293054000
1	-2.093797000	4.622288000	-0.262733000
6	4.459644000	6.594080000	-0.153080000
1	3.651531000	6.977594000	-2.120546000
1	5.091458000	5.930347000	1.804245000
6	-3.804996000	2.620761000	-0.754437000
6	-4.045876000	3.545609000	-1.783661000
6	-4.783715000	2.445716000	0.238184000
6	-5.236380000	4.277290000	-1.822498000
6	-5.973261000	3.178443000	0.202282000
6	-6.204962000	4.096591000	-0.828442000
1	-5.409189000	4.985507000	-2.630763000
1	-6.717826000	3.034703000	0.983393000
1	-4.262021000	-7.506264000	-0.925248000
1	5.028180000	7.521091000	-0.114267000
1	-7.131526000	4.666709000	-0.857229000
1	7.757128000	-4.676317000	0.901678000
26	0.389886000	0.005494000	-0.599252000
8	0.295748000	-0.831060000	-3.639828000
8	0.617201000	-0.089530000	-2.597365000
1	2.350833000	4.861700000	-2.198643000
1	3.791769000	3.814806000	1.707766000
1	-3.443266000	-3.740030000	1.005217000
1	-1.188158000	-4.899539000	-2.457885000
1	-4.600527000	1.735572000	1.041242000
1	-3.293192000	3.684416000	-2.556545000
1	4.345708000	-3.726919000	-1.557072000
1	4.933314000	-1.675096000	2.168159000
6	-2.587784000	1.105667000	3.776645000
6	-3.979896000	1.030477000	3.693922000
6	-4.601271000	-0.027323000	3.015935000
6	-3.791882000	-1.001426000	2.414941000
6	-2.401576000	-0.932035000	2.499115000
6	-1.746182000	0.121557000	3.190751000
1	-2.125271000	1.937966000	4.305820000
1	-5.685813000	-0.081528000	2.942805000
1	-1.797261000	-1.689836000	2.006417000
16	0.002827000	0.202483000	3.321235000
1	-4.250110000	-1.815787000	1.856416000
1	-4.585095000	1.809900000	4.1574900

$[(ArS^{-})(TPP)Fe^{III}(O_2^{2-})]^{2-}$ (uB97D-def2-TZVP) Charge: -2, Multiplicity: 2

7	1.429902000	-1.646761000	-0.255747000
7	1.993359000	1.134083000	-0.193450000
6	0.970370000	-2.936850000	-0.100055000
6	2.079764000	-3.844420000	0.085322000
6	3.217081000	-3.099289000	-0.005230000
6	2.805523000	-1.729939000	-0.211958000
6	3.698532000	-0.651101000	-0.269885000
6	3.299447000	0.691827000	-0.246245000
6	4.207604000	1.813676000	-0.208652000
6	3.443436000	2.935873000	-0.077845000
6	2.065067000	2.503761000	-0.068075000
6	-0.372372000	-3.330950000	-0.140124000
6	5.156981000	-0.960544000	-0.299929000
6	6.002469000	-0.597260000	0.762276000
6	7.366393000	-0.901600000	0.731382000

6	7.911457000	-1.578968000	-0.365445000
6	7.080126000	-1.949575000	-1.428572000
6	5.716691000	-1.643231000	-1.393618000
6	-0.705902000	-4.769679000	0.058262000
6	-1.503393000	-5.167017000	1.145974000
6	-1.834824000	-6.510452000	1.342110000
6	-1.375053000	-7.485677000	0.449424000
6	-0.584131000	-7.103498000	-0.640227000
6	-0.255182000	-5.758607000	-0.832871000
1	1.992419000	-4.908806000	0.259307000
1	4.243225000	-3.432141000	0.084492000
1	5.286013000	1.744365000	-0.267951000
1	3.772010000	3.965317000	-0.013541000
1	8.002492000	-0.615721000	1.567201000
1	7.493918000	-2.474809000	-2.287525000
1	-2.449114000	-6.796477000	2.194081000
1	-0.228471000	-7.852662000	-1.345403000
6	0.972370000	3.379619000	-0.002557000
6	-1.430372000	-2.449418000	-0.399532000
6	-0.355716000	2.981741000	-0.199940000
6	1.256285000	4.821828000	0.248486000
7	-1.332819000	-1.081280000	-0.504715000
6	-2.781235000	-2.879295000	-0.676674000
7	-0.776735000	1.692883000	-0.448405000
6	-1.480104000	3.889266000	-0.228083000
6	0.996433000	5.800479000	-0.725783000
6	1.808284000	5.231731000	1.474340000
6	-2.602324000	-0.636987000	-0.812960000
6	-3.501613000	-1.756929000	-0.955715000
1	-3.117186000	-3.908174000	-0.680389000
6	-2.131102000	1.780825000	-0.687923000
6	-2.575353000	3.147124000	-0.555241000
1	-1.428052000	4.951882000	-0.030182000
6	1.274913000	7.148556000	-0.482162000
6	2.088062000	6.578596000	1.722377000
6	-2.991078000	0.702333000	-0.926602000
1	-4.547005000	-1.684957000	-1.225500000
1	-3.599277000	3.479863000	-0.666736000
6	1.821708000	7.543516000	0.744178000
1	1.070323000	7.890112000	-1.252366000
1	2.510542000	6.875173000	2.680746000
6	-4.413322000	1.011224000	-1.247052000
6	-4.742751000	1.702570000	-2.425649000
6	-5.453106000	0.641531000	-0.376747000
6	-6.071729000	2.010734000	-2.730816000
6	-6.782806000	0.948685000	-0.678618000
6	-7.098623000	1.633796000	-1.857759000
1	-6.305581000	2.542018000	-3.651735000
1	-7.573125000	0.659299000	0.012107000
1	-1.632206000	-8.532336000	0.600131000
1	2.039179000	8.592599000	0.935068000
1	-8.133887000	1.873447000	-2.092984000
1	8.973030000	-1.817155000	-0.390481000
26	0.325290000	0.014516000	-0.377256000
8	0.432322000	-0.963075000	-3.046912000
8	0.507202000	0.111254000	-2.264327000
1	0.575814000	5.493573000	-1.680614000
1	2.013125000	4.480625000	2.234151000
1	-1.861674000	-4.407845000	1.837540000
1	0.353513000	-5.461468000	-1.683643000
1	-5.203524000	0.126969000	0.547020000
1	-3.944082000	1.995945000	-3.103508000
1	5.069729000	-1.931431000	-2.219244000
1	5.578167000	-0.076588000	1.617555000
6	-2.321629000	1.142155000	2.435231000
6	-3.684260000	1.117113000	2.734450000
6	-4.307675000	-0.072985000	3.132728000
6	-3.539781000	-1.241427000	3.221137000
6	-2.175786000	-1.216938000	2.919890000
6	-1.527007000	-0.024244000	2.524634000
1	-1.858324000	2.067051000	2.101921000
1	-5.372153000	-0.091121000	3.359867000
1	-1.592733000	-2.134140000	2.975777000
16	0.195952000	0.006957000	2.168859000
1	-4.007437000	-2.180457000	3.516868000
1	-4.269207000	2.031355000	2.639051000

References

(1) Petasis, D. T.; Hendrich, M. P., Chapter Eight - Quantitative Interpretation of Multifrequency Multimode EPR Spectra of Metal Containing Proteins, Enzymes, and Biomimetic Complexes. In *Methods in Enzymology*, Qin, P. Z.; Warncke, K., Eds. Academic Press: 2015; Vol. 563, pp 171-208.

(2) Alessandro Bencini, D. G., *Electron Paramagnetic Resonance of Exchange Coupled Systems*. Springer Berlin, Heidelberg: 1990.

(3) Golombek, A. P.; Hendrich, M. P., *J. Magn. Reson.* **2003,** *165*, 33-48.

(4) Cohen-Tannoudji, C.; Diu, B.; Dui, B.; Laloë, F.; Hemley, S. R.; Ostrowsky, N.; Ostrowsky, D. B., *Quantum Mechanics*. Wiley: 1977.

(5) Slater, J. W.; Marguet, S. C.; Cirino, S. L.; Maugeri, P. T.; Shafaat, H. S., *Inorg. Chem.* **2017,** *56*, 3926-3938.

(6) Peters, M. K.; Röhricht, F.; Näther, C.; Herges, R., *Org. Lett.* **2018,** *20*, 7879-7883.

(7) Shirazi, A.; Goff, H. M., *J. Am. Chem. Soc.* **1982,** *104*, 6318-6322.

(8) Muresan, A. Z.; Thamyongkit, P.; Diers, J. R.; Holten, D.; Lindsey, J. S.; Bocian, D. F., *J. Org. Chem.* **2008,** *73*, 6947-6959.

(9) Wang, J.; Schopfer, M. P.; Puiu, S. C.; Sarjeant, A. A. N.; Karlin, K. D., *Inorg. Chem.* **2010,** *49*, 1404-1419.

(10) Ehudin, M. A.; Gee, L. B.; Sabuncu, S.; Braun, A.; Moënne-Loccoz, P.; Hedman, B.; Hodgson, K. O.; Solomon, E. I.; Karlin, K. D., *J. Am. Chem. Soc.* **2019,** *141*, 5942-5960.

(11) Wang, B.; Graskemper, J. W.; Qin, L.; DiMagno, S. G., *Angew. Chem. Int. Ed.* **2010,** *49*, 4079-4083.

(12) Ghiladi, R. A.; Kretzer, R. M.; Guzei, I.; Rheingold, A. L.; Neuhold, Y.-M.; Hatwell, K. R.; Zuberbühler, A. D.; Karlin, K. D., *Inorg. Chem.* **2001,** *40*, 5754-5767.

(13) Chufán, E. E.; Karlin, K. D., *J. Am. Chem. Soc.* **2003,** *125*, 16160-16161.

(14) Mondal, P.; Ishigami, I.; Yeh, S.-R.; Wijeratne, G. B., *Angew. Chem. Int. Ed.* **2022,** *61*, e202211521.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16 Rev. C.01*, Wallingford, CT, 2016.

(16) Grimme, S., *J. Comput. Chem.* **2006,** *27*, 1787-1799.

(17) Ovalle, S.; Malardier-Jugroot, C., *Comput. Theor. Chem.* **2022,** *1213*, 113726.

(18) Weigend, F.; Ahlrichs, R., *Phys. Chem. Chem. Phys.* **2005,** *7*, 3297-3305.

(19) Barone, V.; Cossi, M., *J. Phys. Chem. A* **1998,** *102*, 1995-2001.

(20) https://www.chemcraftprog.com *Chemcraft* Version 1.8, build 682.

(21) E. D. Glendening, A. E. R., J. E. Carpenter, F. Weinhold *NBO Version 3.1*.

(22) Mondal, P.; Ishigami, I.; Gérard, E. F.; Lim, C.; Yeh, S.-R.; de Visser, S. P.; Wijeratne, G. B., *Chem. Sci.* **2021,** *12*, 8872-8883.
(23) Liu, J.-G.; Ohta, T.; Yamaguchi, S.; Ogura, T.; Sakamoto, S.; Maeda, Y.; Naruta, Y., *Angew. Chem. Int. Ed.* **2009,** *48*, 9262-9267.
(24) Kim, H.; Rogler, P. J.; Sharma, S. K.; Schaefer, A. W.; Solomon, E. I.; Karlin, K. D., *Angew. Chem. Int. Ed.* **2021,** *60*, 5907-5912.
(25) Liu, J.-G.; Shimizu, Y.; Ohta, T.; Naruta, Y., *J. Am. Chem. Soc.* **2010,** *132*, 3672-3673.