Stabilisation of μ -peroxido bridged Fe(III) intermediates with non-symmetric bidentate N-donor ligands

József S. Pap,^{*a*} Apparao Draksharapu,^{*b*} Michel Giorgi,^{*c*} Wesley R. Browne,^{*b*,*} József Kaizer^{*a*,*} and Gábor Speier^{*a*,*}

Materials

All syntheses were done under an argon atmosphere unless stated otherwise. Solvents used for the synthesis and reactions were purified by standard methods and stored under argon. The ligands 2-(2'-pyridyl)-N-methylbenzimidazole (L¹), 2-(2'-pyridyl)benzimidazole (L²), 2-(2'-pyridyl)benzthiazole (L³) and 2-(2'-pyridyl)benzoxazole (L⁴) were synthesized according to published procedures [S1-S3]. Fe(II)(CF₃SO₃)₂ was purchased from commercial source.

Synthesis

 $[\mathbf{Fe}^{II}(\mathbf{L}^1)_3](\mathbf{CF}_3\mathbf{SO}_3)_2\cdot \mathbf{3H}_2\mathbf{O}, \mathbf{1}(\mathbf{CF}_3\mathbf{SO}_3)_2\cdot \mathbf{3H}_2\mathbf{O}$. To a stirred solution of dry Fe^{II}(CF₃SO₃)₂ (0.354 g, 1 mmol) in acetonitrile (20 mL) L¹ (0.585 g, 3 mmol) was added. After stirring for 4 hours at room temperature the wine-red solution was filtered and layered carefully with equal amount of diethyl ether in a Schlenk-tube. After complete diffusion the solvent was removed with a cannula together with a minor amount of brown powdery precipitate on the bottom of the Schlenk. The crystalline product was carefully collected, washed with a minimal amount of diethyl ether and dried in vacuo. Yield: 0.71 g (68.6%). Anal. Calcd for C₄₁H₃₉F₆FeN₉O₉S₂: C, 47.54; H, 3.80; N, 12.17. Found: C, 47.22; H, 3.86; N, 12.02. FT–IR bands (KBr pellet, cm⁻¹) 3440, 3109, 3070, 2963, 2930, 1604, 1482, 1440, 1424, 1262, 1221, 1153, 1030, 788, 746, 631, 516. UV/vis absorption (CH₃CN) [λ_{max} , nm (log ε)] 530 (3.595). Single crystals were obtained by re-crystallisation from acetonitrile.

 $[Fe^{II}(L^2)_3](CF_3SO_3)_2 \cdot 2H_2O, 2(CF_3SO_3)_2 \cdot 2H_2O.$ Synthesis was analogously done to that of $1(CF_3SO_3)_2 \cdot 3H_2O$, but the red microcrystalline product was obtained by slow evaporation of the mother liquor, washed with diethyl ether and dried under vacuum. Yield: 0.78 g (80.0%). Anal. Calcd for $C_{38}H_{31}F_6FeN_9O_8S_2$: C, 46.78; H, 3.20; N, 12.92. Found: C, 46.33; H, 3.12; N, 12.69. FT–IR bands (KBr pellet, cm⁻¹) 3441, 3066, 1601, 1479, 1455, 1442, 1279, 1253, 1225, 1164, 1029, 978, 795, 746, 636, 572, 516. UV/vis absorption (CH₃CN) [λ_{max} , nm (log ε)] 494 (3.237).

[**Fe^{II}**(L^3)₂(**CF**₃**SO**₃)₂], **3.** Synthesis was analogously done to that of **1**(CF₃SO₃)₂·3H₂O. The orange crystalline product was washed with diethyl ether and dried under vacuum. Yield: 0.69 g (89.0%). Anal. Calcd for C₂₆H₁₆F₆FeN₄O₆S₄: C, 40.11; H, 2.07; N, 7.20. Found: C, 39.72; H, 1.97; N, 6.93. FT–IR bands (KBr pellet, cm⁻¹) 3096, 3064, 3029, 1606, 1560, 1489, 1475, 1425, 1310, 1235, 1211, 1159, 1032, 787, 758, 728, 637, 571, 515.

[Fe^{II}(L⁴)₂(CF₃SO₃)₂], 4. Synthesis was analogously done to that of $1(CF_3SO_3)_2 \cdot 3H_2O$. The orange crystalline product was washed with diethyl ether and dried under vacuum. Crystals suitable for X-ray analysis were selected from the bulk product prior to washing with diethyl ether. Yield: 0.61 g (81.7%). Anal. Calcd for C₂₆H₁₆F₆FeN₄O₈S₂: C, 41.84; H, 2.16; N, 7.51. Found: C, 41.85; H, 2.50; N, 7.45. FT–IR bands (KBr pellet, cm⁻¹) 3109, 3076, 1603, 1546, 1476, 1436, 1384, 1315, 1241, 1212, 1162, 1030, 810, 576, 744, 635, 515.

Kinetic studies

Kinetic studies were carried under thermostated (± 0.5 °C) conditions in 1 cm (3 mL volume) quartz cuvettes with stirring under air. During a typical run, a solution of H₂O₂ (diluted from a stock solution to 1.5 mL in acetonitrile and pre-thermostated to the required temperature) was added with an automated pipette to 1.5 mL of a solution of the respective complex (in the presence or absence of co-ligand). Changes in the UV/vis absorption spectra were monitored using a diode-array spectrophotometer between 400 and 1000 nm at a minimum of 1 s time-intervals. The initial reaction rates (V_i) were calculated from the ΔA at the λ_{max} for the intermediates formed. V_i is defined as - {d[complex]/dt}_0 = 2{d[adduct]/dt}_0, where d[adduct]/dt was calculated as $dA_{\lambda max}/(\varepsilon_{\lambda max}dt)$. After determination of the partial orders from the correlation of V_i with either [Fe]₀ or [H₂O₂]₀ the following rate equation was established:

$$-\frac{d[\text{complex}]}{dt}_{0} = k \text{ complex}^{1} \text{ H}_{2}\text{O}_{2}^{1}$$

Analytical and physical measurements

Infrared spectra were recorded on an Avatar 330 FT–IR Thermo Nicolet instrument. UV/vis absorption spectra were recorded on an Agilent 8453 diode–array spectrophotometer using quartz cells. Microanalyses were carried out by the Microanalytical Service of the University of Pannonia. Cyclic voltammograms (CV) were recorded using a VoltaLab 10 potentiostat with VoltaMaster 4 software for data processing or a CHInstruments CH760C, with glassy carbon (working), Pt (auxiliary), and Ag/AgCl in 3 M KCl or SCE (reference) electrodes. Scan rates were 100 mV s⁻¹. The potentials were calibrated against the Fc⁺/Fc redox couple (+437 mV in acetonitrile). Raman spectra were recorded at λ_{exc} 785 nm using a Perkin Elmer Raman Station at room temperature. Raman spectra were obtained at 473 (50 mW at source, Cobolt Lasers) and 355 nm (10 mW, Cobolt Lasers) with a 2.5 cm diameter plano-convex lens (f = 7.5 cm) in a 180° backscattering arrangement. The collimated Raman scattering was

focused by a second 2.5 cm diameter plano convex lens (f = 10 cm) through an appropriate long pass edge filter (Semrock) into a Shamrock300i spectrograph (Andor Technology at 473 nm) with a 1200 L/mm grating blazed at 500 nm and Newton EMCCD detector (Andor Technology), or into a Shamrock500i spectrograph (Andor Technology at 355 nm) 2400 L/mm blazed at 300 nm and acquired with an DV420A-BU2 CCD camera (Andor Technology). The spectral slit width was set to 10 or 20 μ m. Data were recorded and processed using Solis (Andor Technology) with spectral calibration performed using the Raman spectrum of acetonitrile/toluene 50:50 (v:v). Samples were held in quartz 10 mm path length cuvettes. ¹H NMR spectra were recorded using a Varian Mercury Plus (400 MHz) spectrometer. Chemical shifts are denoted in ppm relative to the residual solvent signal (1.94 ppm). EPR spectra (X-band, 9.46 GHz) were recorded on a Bruker ECS106 spectrometer in liquid nitrogen (77 K). Samples for measurement were transferred (250 μ L) to EPR tubes, which were frozen in liquid nitrogen immediately.

X-ray crystallography

Determination of single crystal structures and intensity data collection were performed on a Bruker–Nonius Kappa CCD single–crystal diffractometer ($1(CF_3SO_3)_2 \cdot 0.5H_2O$ and 4) using Mo K α radiation ($\lambda = 0.71070$ Å) at 293(2), and 225(2) K, respectively. Details of the structure determination are given in Table S1. Selected bond lengths and angles are listed in the captions of Figs. S1 and S2. SHELX–97 [S4] was used for structure solution and full matrix least squares refinement on F^2 . CIF files are available in the CCDC database: CCDC 955599 ($1(CF_3SO_3)_2 \cdot 0.5H_2O$) and 955600 (4).

Table S1	. Crystal	structure	details	for	1.0	.5H ₂ O	and 4
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Compound reference	1 [.] 0.5H ₂ O	4
Chemical formula	$C_{82}H_{68}F_{12}Fe_2N_{18}O_{13}S_4$	$C_{39}H_{24}F_9Fe_{1.5}N_6O_{12}S_3$
Formula Mass	1981.48	465.34
Crystal system	orthorhombic	monoclinic
a/Å	19.5327(3)	33.061(1)
b/Å	10.9126(1)	13.4974(6)
c/Å	39.6368(8)	19.732(1)
α/°	90	90
β/°	90	95.911(4)
γ/°	90	90
Unit cell volume/Å ³	8448.7(2)	8758.3(6)
Temperature/K	293(2)	225(2)
Space group	Pna2 ₁	C2/c
Number of formula units per unit cell, Z	4	8
Radiation type	ΜοΚα	ΜοΚα
Absorption coefficient, μ/mm^{-1}	0.544	0.755
No. of reflections measured	14563	46858
No. of independent reflections	14563	10531
R _{int}	0.0963	0.048
Final R1 values $(I > 2\sigma(I))$	0.0695	0.0626
Final wR values $(I > 2\sigma(I))$	0.1510	0.1766
Final R1 values (all data)	0.1967	0.0999
Goodness of fit	0.939	1.123
CCDC number	955599	955600



Figure S1. X-ray structure of $[Fe^{II}(L^1)_3](OTf)_2.0.5H_2O$ - the asymmetric unit. Thermal ellipsoids are at 30% probability level. Selected bond distances (Å) and angles (deg): Fe1–N1 2.047(8), Fe1–N2 1.989(3), Fe1–N4 2.029(8), Fe1–N5 1.941(8), Fe1–N7 2.021(7), Fe1–N8 2.000(7), N1–Fe1–N2 80.1(3), N1–Fe1–N4 93.6(3), N1–Fe1–N5 91.3(3), N1–Fe1–N8 94.0(3), N1–Fe1–N7 173.6(3), N2–Fe1–N4 173.7(3), N5–Fe1–N8 170.7(3), Fe2–N10 2.011(8), Fe2–N11 1.988(6), Fe2–N13 1.992(7), Fe2–N14 2.038(7), Fe2–N16 2.038(8), Fe2–N17 1.997(7); N10–Fe2–N13 173.7(3), N11–Fe2–N17 170.5(3), N14–Fe2–N16 175.5(3), N10–Fe2–N11 80.2(3), N10–Fe2–N16 90.5(3), N10–Fe2–N17 93.5(3) and N14–Fe2–N17 98.5(3). The asymmetric unit contains two molecules of the complex.



Figure S2. X-ray structure of $Fe^{II}(L^4)_2(OTf)_2 - 4$ the two non-identical complexes within the asymmetric unit, Fe2 extended with symmetry equivalent ligands. Thermal ellipsoids are at 30% probability level. Selected bond distances (Å) and angles (deg): Fe1–N1 2.177(3), Fe1–N2 2.202(3), Fe1–N3 2.154(3), Fe1–N4 2.223(3), Fe1–O4 2.148(3), Fe1–O7 2.098(3), Fe2–N5 2.147(3), Fe2–N6 2.198(3), Fe2–O10 2.171(3), Fe2–N5 2.147(3), Fe2–O10 2.171(3), Fe2–N6 2.198(3), O4–Fe1–N1 99.30(11); N3–Fe1–N1 164.22(12), O7–Fe1–N2 167.58(11), N1–Fe1–N2 75.96(11), O4–Fe1–N4 161.86(10), N1–Fe1–N4 97.35(11), O4–Fe1–N4 161.86(10), N1–Fe1–N4 97.35(11), O4–Fe1–N4 161.86(10), N5–Fe2–N5 166.51(18), N5–Fe2–O10 91.40(11), N5–Fe2–N6 76.59(13), O10–Fe2–N6 167.02(11), N5–Fe2–N6 94.36(12) and O10–Fe2–N6 167.02(11). There is a disordered triflate at Fe1 of 0.5 occupancy that has not been plotted for clarity. The configuration of the donor atoms is *OC*-6-33. The asymmetric unit consists of one and a half molecules of the complex due to symmetry equivalence at Fe2 and there is a difference between the two molecules in the orientation of the triflate anions (Fig. S2).



¹H NMR spectroscopy

Figure S3 1 H NMR (400 MHz) spectra of **1** and **2** in CD₃CN at 298 K



UV/vis spectroscopy and the reaction of complexes 1 and 2 with H_2O_2

Figure S4 Changes in the visible absorption spectrum of 2 (0.5 mM in CH₃CN) upon addition of H₂O₂ (10 eq.) at 20 °C in the (a) absence and (b) in the presence of ligand L² (2 mM).



Figure S5 Changes in absorption of **2** (0.5 mM in CH₃CN) upon addition of H₂O₂ (10 eq.) at 20 °C in the absence 492 nm (dashed black) and 720 nm (solid black) and in the presence 494 nm (dashed red) and 750 nm (solid red) of ligand L^2 (2 mM).

Exp. entry	$[H_2O_2]_0$	[1]	<i>Т</i> (°С)	V_i^{a}	k
	(10 ⁻³ M)	(10 ⁻³ M)		(10 ⁻⁶ M s ⁻¹)	$(M^{-1} s^{-1})$
1	0.5	0.50	20	1.64±0.01	6.56±0.06
2	1.5	0.50	20	4.86±0.02	6.48±0.29
3	2	0.50	20	7.08±0.14	7.08±0.14
4	3	0.50	20	9.78±0.42	6.52±0.28
5	4	0.50	20	13.4±0.8	6.70±0.39
6	5	0.50	20	16.4±1.5	6.56±0.59
7	10	0.50	20	31.6±2.4	6.32±0.48
8	10	0.33	20	18.4±0.9	5.58±0.27
9	10	0.75	20	45.2±3.3	6.03±0.44
10	10	1.00	20	62.4±5.4	6.24±0.54
					avg. 6.60±0.10
11	10	0.50	15	19.1±0.6	3.83±0.11
12	10	0.50	23	38.1±2.8	7.62±0.56
13	10	0.50	25	43.6±1.8	8.71±0.36
14	10	0.50	28	54.9±4.9	10.98±0.98

Table S2. Kinetic data for the reaction of H_2O_2 with $\boldsymbol{1}.$

^adefined as $-\{d[1]/dt\}_0 = 2\{d[1a]/dt\}_0$; the initial rate method was applied to minimize the effect of thermal decay on the calculated k values. **1a** = species absorbing in the NIR.

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Exp. entry	$[H_2O_2]_0$	[2]	[L]	<i>Т</i> (°С)	V_i^{a}	k
	(10 ⁻³ M)	(10 ⁻³ M)	(10 ⁻³ M)		(10 ⁻⁶ M s ⁻¹)	$(M^{-1} s^{-1})$
1	1	0.50	0	20	2.88±0.12	5.76±0.24
2	2	0.50	0	20	5.65±0.38	5.66±0.38
3	3	0.50	0	20	8.28±0.58	5.52±0.38
4	4	0.50	0	20	10.5±1.4	5.26±0.68
5	5	0.50	0	20	12.5±1.4	5.00±0.54
6	10	0.50	0	20	25.8±5.0	5.14±1.00
7	10	0.33	0	20	15.7±3.3	4.76±0.98
8	10	0.75	0	20	39.8±6.0	4.70±0.78
9	10	1.00	0	20	48.8±5.8	4.88±0.58
10	10	1.50	0	20	72.0±15.0	4.80±1.00
						avg. 5.38±0.15
11	10	0.50	1	20	16.8±1.3	-
12	10	0.50	2	20	15.9±1.3	-
13	10	0.50	5	20	13.5±1.0	-
14	10	0.50	0	15	17.4±2.6	3.48±0.26
15	10	0.50	0	24	35.2±5.0	7.04±0.50
16	10	0.50	0	26	40.6±0.6	8.12±0.06
17	10	0.50	0	28	45.4±2.2	9.08±0.23

Table S3. Kinetic data for the reaction of H_2O_2 with **2**.

^adefined as $-\{d[\mathbf{2}]/dt\}_0 = 2\{d[\mathbf{2a}]/dt\}_0$; the initial rate method was applied to minimize the effect of thermal decay on the calculated k values. **2a** = species absorbing in the NIR.



Figure S6. Hammett plot of log of the relative rate of reaction of **2** with H_2O_2 in the presence of various para-substituted pyridines (conditions: 1 mM complex, 10 mM H_2O_2 and 10 mM of 4-R-py at 20°C).





Figure S7. Raman spectra of complexes **1** and **2** in the solid state at λ_{exc} 785 nm. A multipoint baseline correction has been applied. * spectral artefact.



Figure S8 Raman spectra of complexes **1** and **2** (10 mM) in CH₃CN at λ_{exc} 785 nm. Solvent contributions have been removed by subtraction and a multipoint baseline correction has been applied. # imperfect solvent subtraction, * spectral artefact.



Figure S9 Raman spectra of complexes **1** and **2** at both 1 mM (black/green) and 0.1 mM (blue/red) in CH₃CN at λ_{exc} 355 nm. Solvent contributions have been removed by subtraction and a multipoint baseline correction has been applied. # imperfect solvent subtraction.



Figure S10 Raman spectra of (a) **1** (6.5 mM) in CH₃CN, (b) 210 s and (c) 420 s after two eq. of $H_2^{18}O_2$ was added, followed by (d) 180 s and (e) 390 s after addition of a 2nd two eq. of $H_2^{16}O_2$. The expected shift for v(O-O) is 50 cm⁻¹; observed 50 cm⁻¹, for v(Fe-O) is 20 cm⁻¹; observed 18 cm⁻¹. Spectra are normalised to the solvent band at 919 cm⁻¹. (Expansion of 300-100 cm⁻¹ region of spectra shown in Fig. 3).



Figure S11 Raman spectra of **1** (6.5 mM) in CH₃CN (black), 420 s (red) after two eq. of $H_2^{18}O_2$ was added. Spectra are normalised to the solvent band at 919 cm⁻¹. (Expansion of 1000-1700 cm⁻¹ region of spectra shown in Fig. 3).



Figure S12 Raman spectra of (a) **2** (6.5 mM) in CH₃CN, (b) 120 s and (c) 300 s after 2 eq. of $H_2^{18}O_2$ was added, followed by (d) 120 s and (e) 300 s after addition of 2 eq of $H_2^{16}O_2$ at room temperature. Expected isotope shift for v(O-O) 50 cm⁻¹; observed 50 cm⁻¹, expected for v(Fe-O) 20 cm⁻¹; observed 18 cm⁻¹. Spectra were normalised 919 cm⁻¹ to the solvent bands.



Figure S13 Raman spectra of **1** (10 mM) in CH₃CN at λ_{exc} 785 nm recorded over 6 min after addition of 2 eq. of H₂O₂ at room temperature. Spectra were normalised 919 cm⁻¹ to the solvent bands. * solvent bands. #spectral artefact.



Figure S14 (upper spectrum) Raman spectrum of **2** (10 mM) in CH₃CN at λ_{exc} 785 nm recorded immediately after addition of 2 eq. of H₂O₂ at room temperature. (lower spectra) Raman spectra of **2** (10 mM) in CH₃CN at λ_{exc} 785 nm recorded over 6 min after addition of a 2nd equivalent of 2 eq. of H₂O₂ at room temperature. Spectra were normalised 919 cm⁻¹ to the solvent bands. * solvent bands.

EPR spectroscopy



Figure S15 X-band EPR spectra of solutions of $\mathbf{1}$ (10 mM) frozen to 77 K 60 s (black) and 240 s (red) after addition of 10 eq. H_2O_2 .



Figure S16 X-band EPR spectra of solutions of **2** (10 mM) frozen to 77 K 60 s (black) and 240 s (red) after addition of 10 eq. H_2O_2 .

 Ligand	$E_{pa}(Fe^{3+/2+})$	$E_{pc}(Fe^{3+/2+})$	$E_{pa}(L^{0/\bullet-})$	$E_{pc}(L^{0/\bullet^{-}})$
	(V)	(∨)	(∨)	(∨)
 L^1	+0.89	+0.81	-1.28	-1.36
L ²	+0.94	+0.85	-	-1.59
L^3	+1.44	+0.32	-0.89	-1.18
L^4	+1.50	+0.42	-0.92	-1.08
				-1.30

Electrochemical properties

Table S4. Redox potentials for complexes 1-4.

^avs. Ag/AgCl reference electrode



Figure S17 Cyclic voltammetry of (lower) 1 and 2 in (0.1 M TBAClO₄) CH₃CN.



Figure S18 Cyclic voltammetry of **1** in (0.1 M TBAPF₆) CH_3CN (black) and with 2 (red) and 5 (blue) vol% water added, vs SCE.



Figure S19 Cyclic voltammetry of **2** in (0.1 M TBAPF₆) CH_3CN (black) and with 2 (red) and 5 (blue) vol% water added vs SCE.



Figure S20 Cyclic voltammetry of **1** and **2** in (0.1 M TBAClO₄) CH₃CN before (black), immediately after (red) and 10 min after (blue, respectively) addition of 10 eq of H_2O_2 .



Figure S21 Cyclic voltammetry of **3** in (0.1 M TBAClO₄) CH₃CN (lower) and with 3 eq of ligand L^3 (upper) added.



Figure S22 Cyclic voltammetry of **1** in (0.1 M TBAClO₄) CH₃CN (black) and with 3 eq of ligand L^4 (red) added.



Figure S21 Comparison of the rate of reaction of **2** with H_2O_2 and the redox potential in the presence of various para-substituted pyridines (conditions for rate determination: 1 mM complex, 10 mM H_2O_2 and 10 mM of 4-R-py at 20°C, conditions for CV measurements: 1 mM complex, 10 mM 4-R-py, 20°C)

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