Supporting Information

Over or under: Hydride attack at the metal versus the coordinated nitrosyl ligand in ferric nitrosyl porphyrins

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Contents:

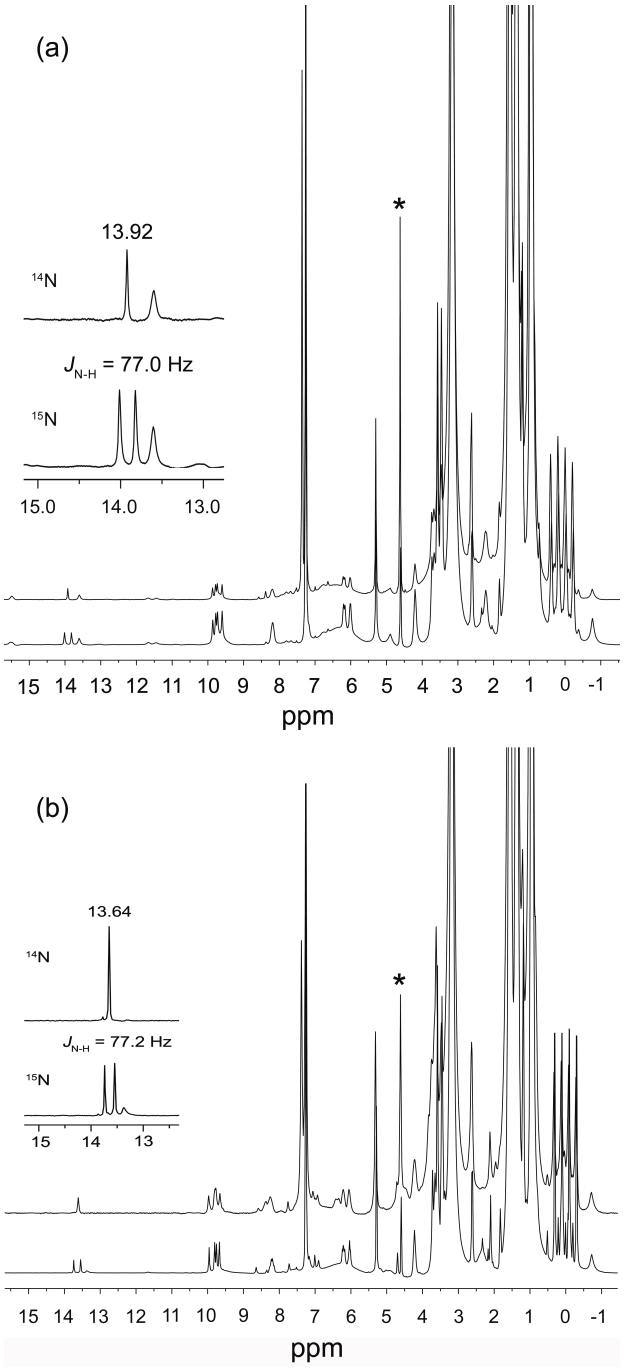


Figure S1. (a) ^{1}H NMR spectra of, (*top*) the product mixture from the reaction of [(PPDME)Fe(NO)(5-MeIm)]OTf with $[NBu_4]BH_4$, (*bottom*) the product mixture from the analogous reaction employing the ^{15}N-labeled precursor [(PPDME)Fe(^{15}NO)(5-MeIm)]OTf. (b) ^{1}H NMR spectra of, (*top*) the product mixture from the reaction of [(PPDME)Fe(NO)(1-MeIm)]OTf with $[NBu_4]BH_4$, (*bottom*) the product mixture from the analogous reaction employing the ^{15}N-labeled precursor [(PPDME)Fe(^{15}NO)(1-MeIm)]OTf. The peak at 4.62 ppm (labeled *) observed in both reactions is assigned to H_2 gas (see also Figure S3). The downfield (*Inset)* regions of the spectra focus on the ^{15}N-isotope-sensitive Fe-*H*NO signals; these HNO signals were integrated against a C_6H_6 internal standard. The product mixtures also contain the final paramagnetic (PPDME)Fe(NO) products.

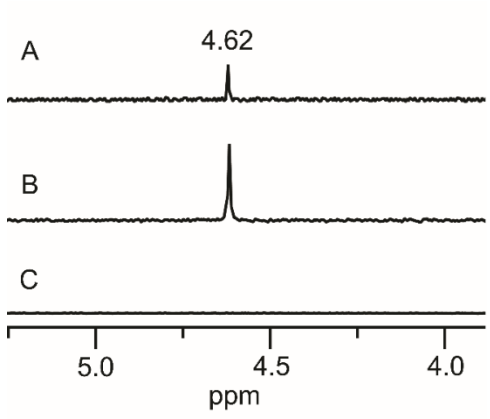
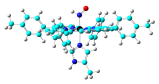
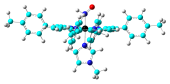
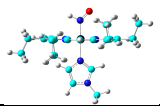


Figure S2. ^{1}H NMR spectroscopic detection of the H_2 (in $CDCl_3$) byproduct from the decomposition of (PPDME)Fe(HNO)(1-MeIm). (A) Spectrum of the reaction headspace. (B) Spectrum of an authentic H_2/N_2 mixture. (C) Spectrum of the blank $CDCl_3$ solvent.

Table S1. NO Vibrational Frequencies and ^{1}H NMR Chemical Shifts

System[a]			δ_H (ppm)	ν_{NO} (cm^{-1})
Fe(TTP)(5-MeIm)(HNO)	Expt		14.26	1381
	Calc		14.60	1371
Fe(TTP)(1-MeIm)(HNO)	Expt		14.02	1389
	Calc		14.55	1369
Fe(OEP)(5-MeIm)(HNO)	Expt		13.99	1383
	Calc		13.91	1369
Fe(OEP)(1-MeIm)(HNO)	Expt		13.72	1388
	Calc		13.92	1371

a) The orientation of the NO moiety of HNO is *cis* to imidazole Me substituent, which was found to be slightly more favorable than the *trans* isomer, as reported previously.[2]

Table S2. Relative Energies with Respect to Reactants (in kcal/mol)

Pathway	System	ΔE_{SCF}	$\Delta E_{SCF+ZPE}$	ΔH	ΔG
	R1+R2	0.00	0.00	0.00	0.00
	I-1$_N$	-12.22	-10.71	-10.62	-1.33
N-Pathway	**TS$_N$**	-12.08	-11.04	-11.39	-1.08
	I-2$_N$	-49.69	-45.51	-46.25	-33.91
	P-1$_N$ + P2	-87.46	-79.42	-81.17	-69.04
H-Pathway	**R1+R2**	0.00	0.00	0.00	0.00
	I-1$_H$/I-2$_H$	-30.30	-28.58	-28.79	-18.90
	TS$_H$	-30.13	-28.78	-29.41	-18.51
	P-1$_H$+ P2	-59.92	-54.39	-55.98	-44.72

Table S3**.** Selected DFT-Calculated Geometric Parameters

Pathway	R_{Fe-NO} (Å)	R_{N-O} (Å)	R_{B-H} (Å)	R_{N-H} (Å)	R_{Fe-H} (Å)	∠FeNO (°)	∠HNO (°)	∠NFeH (°)
N-Pathway								
R1	1.601	1.120				179.9		
R2			1.232					
I-1$_N$	1.615	1.111	1.230	2.984		174.5	73.4	
TS$_N$	1.624	1.113	1.235	2.441		167.3	90.2	
I-2$_N$	1.743	1.209	1.213	1.042		130.9	114.2	
P-1$_N$	1.736	1.214		1.036		131.5	113.1	
P2 [a)]			1.313/ 1.188					
H-pathway								
I-1$_H$/ I-2$_H$	1.671	1.128	1.327		1.594	174.0		169.8
TS$_H$	1.670	1.128	1.330		1.592	175.2		172.0
P-1$_H$	1.769	1.152			1.477	155.2		165.4

[a)] Bridging/terminal B-H bond lengths respectively.

Table S4**.** Charges of Selected Atoms and Groups (Unit: 'e')

Pathway	Q_{Fe}	Q_{BH3}	Q_H	Q_N	Q_O	Q_{Por}
R1	0.999			0.101	0.063	-0.163
R2		-0.705	-0.295			
TS-1$_N$	1.123	-0.710	-0.154	0.182	0.051	-0.493
TS-1$_H$	-0.020	-0.469	0.121	0.261	0.020	0.087

Table S5. Bond Strength Energies (in kcal/mol)

Ligand	Bond	ΔE_{SCF}	$\Delta E_{SCF+ZPE}$	ΔH	ΔG
None	Fe-NHO	11.52	7.98	8.80	-4.25
	H-NO	56.76	48.91	50.43	41.54
5-MeIm	Fe-NHO	16.86	11.37	12.90	-3.30
	H-NO	62.25	54.34	55.87	46.95

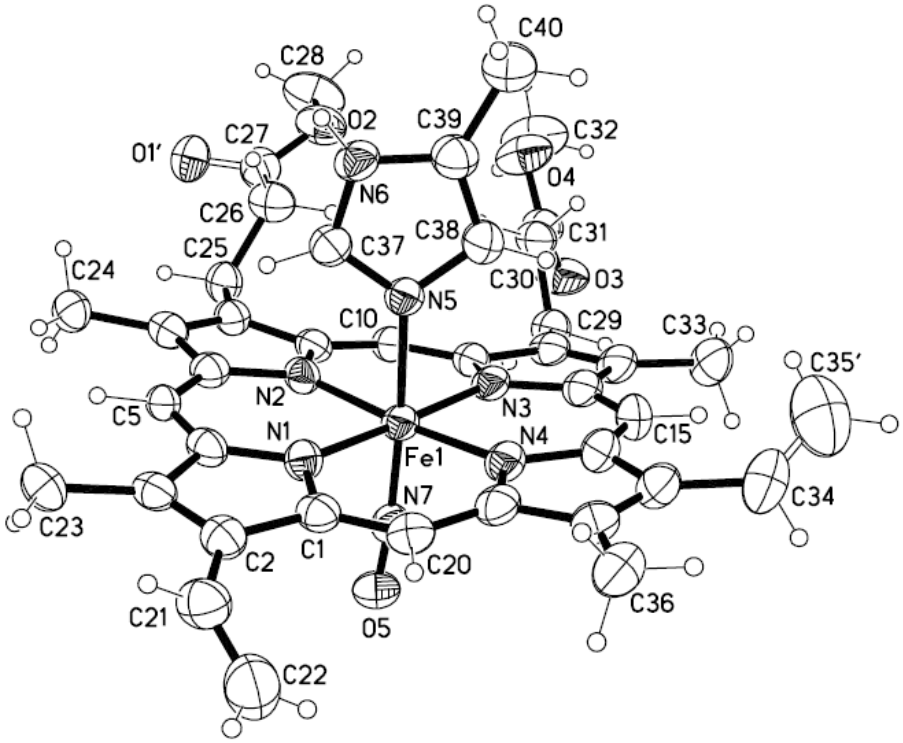


Figure S3. Molecular structure and atom labeling of the cation of [(PPDME)Fe(NO)(5-MeIm)]SbF_6

Experimental for X-ray structural determination of [(PPDME)Fe(NO)(5-MeIm)]SbF_6

The sample was twinned by a 2-fold rotation about the [1 -1 0] axis. The twin ratio refined to 0.4655(12). Both the anion at Sb1B and the free organic cation were located on inversion centers. Oxygen O1 was disordered with refined occupancies of 0.67(6) and 0.33(6) for the unprimed and primed atoms. Atom C35 was disordered with refined occupancies of 0.649(17) and 0.351(17) for the unprimed and primed atoms. Both anion sites were disordered with refined occupancies of 0.705(9) and 0.295(9) for the A site atoms and 0.678(7) and 0.322(7) for the B site atoms. Restraints on the positions of all disordered atoms and the displacement parameters of all non-hydrogen atoms were required. The displacement ellipsoids were drawn at the 50% probability level.

A purple, block-shaped crystal of dimensions 0.20 x 0.08 x 0.06 mm was selected for

structural analysis. Intensity data for this compound were collected using a diffractometer with a Bruker APEX ccd area detector (1) and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The sample was cooled to 100(2) K. Cell parameters were determined from a non-linear least squares fit of 9985 peaks in the range $2.43 < \theta < 24.17°$. A total of 68484 data were measured in the range $1.384 < \theta < 25.902°$ using ϕ and ω oscillation frames. The data were corrected for absorption by the empirical method (2) giving minimum and maximum transmission factors of 0.779 and 0.925. The data were merged to form a set of 16006 independent data with R(int) = 0.0417 and a coverage of 100.0 %. The triclinic space group $P\bar{1}$ was determined by statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 (3). The positions of hydrogens bonded to carbons and imidazolium nitrogens were initially determined by geometry and were refined using a riding model. The hydrogen bonded to N6 was located on a difference map, and its position was refined independently. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 (1.5 for methyl) times the isotropic equivalent displacement parameters of the bonded atoms. A total of 751 parameters were refined against 1337 restraints and 16006 data to give $wR(F^2) = 0.1854$ and S = 1.010 for weights of $w = 1/[\sigma^2 (F^2) + (0.1100 P)^2 + 1.4500 P]$, where $P = [F_o^2 + 2F_c^2] / 3$. The final R(F) was 0.0646 for the 11046 observed, [$F > 4\sigma(F)$], data. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 1.234 and -0.560 e/Å^3, respectively.

Acknowledgment

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References

(1) (a) Data Collection: APEX2 (2007) Bruker AXS Inc., Madison, Wisconsin, USA. (b) Data Reduction: SAINT (2007) Bruker AXS Inc., Madison, Wisconsin, USA.
(2) L. Krause, R. Herbst-Irmer, G. M. Sheldrick, and D. Stalke (2015). *J. Appl. Cryst., 48*, 3-10.
(3) (a) G. M. Sheldrick. *Acta Cryst.* **2015***, A71*, 3-8. (b) G. M. Sheldrick. *Acta Cryst.* **2015***, C71*, 3-8.

Deposition of the crystal structure with the CCDC

CCDC 1484724 contains the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via http;//www.ccdc.cam.ac.uk/conts/retrieving.html

Table S6. Crystal data and structure refinement for [(PPDME)Fe(NO)(5-MeIm)]SbF_6•0.5[$C_4H_7H_2$]SbF_6.

Empirical formula	$(C_{40}H_{42}FeN_7O_5)^+ 0.5(C_4H_7N_2)^+ 1.5(SbF_6)^-$	
	$C_{42}\ H_{45.5}\ F_9\ Fe\ N_8\ O_5\ Sb_{1.5}$	
Formula weight	1151.84	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 12.0388(10) Å	α= 67.9924(14)°
	b = 14.0169(12) Å	β= 68.7999(14)°
	c = 16.3482(14) Å	γ= 64.7066(14)°
Volume	2244.7(3) Å^3	
Z, Z'	2, 1	
Density (calculated)	1.704 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	1154	
Absorption coefficient	1.311 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.925 and 0.779	
Theta range for data collection	1.384 to 25.902°	
Reflections collected	68484	
Independent reflections	16006 [R(int) = 0.0417]	
Data / restraints / parameters	16006 / 1337 / 751	
$wR(F^2$ all data)	$wR2$ = 0.1854	
$R(F$ obsd data)	$R1$ = 0.0646	
Goodness-of-fit on F^2	1.010	
Observed data [I > 2σ(I)]	11046	
Largest and mean shift / s.u.	0.000 and 0.000	
Largest diff. peak and hole	1.234 and -0.560 e/Å^3	

$wR2 = \{\Sigma\ [w(F_o^2 - F_c^2)^2] / \Sigma\ [w(F_o^2)^2]\ \}^{1/2}$

$R1 = \Sigma\ ||F_o| - |F_c|| / \Sigma\ |F_o|$

Table S7. Bond lengths [Å] and angles [°] for [(PPDME)Fe(NO)(5-MeIm)]1.5SbF_6.0.5$(C_4H_7H_2)^+$.

Fe(1)-N(7)	1.654(5)	C(10)-C(11)	1.375(9)
Fe(1)-N(5)	1.990(5)	C(10)-H(10)	0.9500
Fe(1)-N(3)	1.996(5)	C(11)-C(12)	1.449(8)
Fe(1)-N(2)	1.998(5)	C(12)-C(13)	1.339(9)
Fe(1)-N(4)	1.999(5)	C(12)-C(29)	1.518(9)
Fe(1)-N(1)	2.007(5)	C(13)-C(14)	1.454(9)
O(1)-C(27)	1.227(10)	C(13)-C(33)	1.501(9)
O(1')-C(27)	1.225(10)	C(14)-C(15)	1.373(9)
O(2)-C(27)	1.313(8)	C(15)-C(16)	1.378(9)
O(2)-C(28)	1.436(8)	C(15)-H(15)	0.9500
O(3)-C(31)	1.211(8)	C(16)-C(17)	1.445(9)
O(4)-C(31)	1.320(8)	C(17)-C(18)	1.374(9)
O(4)-C(32)	1.446(8)	C(17)-C(34)	1.472(10)
O(5)-N(7)	1.133(6)	C(18)-C(19)	1.441(9)
N(1)-C(4)	1.368(7)	C(18)-C(36)	1.480(9)
N(1)-C(1)	1.373(7)	C(19)-C(20)	1.373(8)
N(2)-C(9)	1.361(7)	C(20)-H(20)	0.9500
N(2)-C(6)	1.392(7)	C(21)-C(22)	1.272(10)
N(3)-C(14)	1.376(8)	C(21)-H(21)	0.9500
N(3)-C(11)	1.381(8)	C(22)-H(22A)	0.9500
N(4)-C(16)	1.378(7)	C(22)-H(22B)	0.9500
N(4)-C(19)	1.382(8)	C(23)-H(23A)	0.9800
N(5)-C(37)	1.311(7)	C(23)-H(23B)	0.9800
N(5)-C(38)	1.382(8)	C(23)-H(23C)	0.9800
N(6)-C(37)	1.334(8)	C(24)-H(24A)	0.9800
N(6)-C(39)	1.364(8)	C(24)-H(24B)	0.9800
N(6)-H(6)	0.85(7)	C(24)-H(24C)	0.9800
C(1)-C(20)	1.382(8)	C(25)-C(26)	1.522(9)
C(1)-C(2)	1.448(8)	C(25)-H(25A)	0.9900
C(2)-C(3)	1.359(9)	C(25)-H(25B)	0.9900
C(2)-C(21)	1.467(9)	C(26)-C(27)	1.492(9)
C(3)-C(4)	1.450(8)	C(26)-H(26A)	0.9900
C(3)-C(23)	1.499(8)	C(26)-H(26B)	0.9900
C(4)-C(5)	1.389(8)	C(28)-H(28A)	0.9800
C(5)-C(6)	1.394(8)	C(28)-H(28B)	0.9800
C(5)-H(5)	0.9500	C(28)-H(28C)	0.9800
C(6)-C(7)	1.435(8)	C(29)-C(30)	1.526(8)
C(7)-C(8)	1.372(8)	C(29)-H(29A)	0.9900
C(7)-C(24)	1.495(8)	C(29)-H(29B)	0.9900
C(8)-C(9)	1.452(8)	C(30)-C(31)	1.498(9)
C(8)-C(25)	1.496(8)	C(30)-H(30A)	0.9900
C(9)-C(10)	1.387(8)	C(30)-H(30B)	0.9900

C(32)-H(32A)	0.9800	Sb(1')-F(6A')	1.838(6)
C(32)-H(32B)	0.9800	Sb(1')-F(5A')	1.840(6)
C(32)-H(32C)	0.9800	Sb(1')-F(2A')	1.884(7)
C(33)-H(33A)	0.9800	Sb(1')-F(3A')	1.885(7)
C(33)-H(33B)	0.9800	Sb(1')-F(1A')	1.886(7)
C(33)-H(33C)	0.9800	Sb(1B)-F(1B')#1	1.818(12)
C(34)-C(35')	1.254(12)	Sb(1B)-F(1B')	1.818(12)
C(34)-C(35)	1.261(12)	Sb(1B)-F(2B)#1	1.856(4)
C(34)-H(34)	0.9500	Sb(1B)-F(2B)	1.856(4)
C(34)-H(34')	0.9500	Sb(1B)-F(2B')#1	1.856(14)
C(35)-H(35A)	0.9500	Sb(1B)-F(2B')	1.856(14)
C(35)-H(35B)	0.9500	Sb(1B)-F(3B')	1.857(14)
C(35')-H(35C)	0.9500	Sb(1B)-F(3B')#1	1.857(14)
C(35')-H(35D)	0.9500	Sb(1B)-F(1B)#1	1.860(3)
C(36)-H(36A)	0.9800	Sb(1B)-F(1B)	1.860(3)
C(36)-H(36B)	0.9800	Sb(1B)-F(3B)#1	1.863(4)
C(36)-H(36C)	0.9800	Sb(1B)-F(3B)	1.863(4)
C(37)-H(37)	0.9500	N(1C)-C(5C)	1.33(2)
C(38)-C(39)	1.359(9)	N(1C)-C(2C)	1.39(2)
C(38)-H(38)	0.9500	N(1C)-H(1C)	0.8800
C(39)-C(40)	1.500(9)	C(2C)-N(3C)	1.31(2)
C(40)-H(40A)	0.9800	C(2C)-H(2C)	0.9500
C(40)-H(40B)	0.9800	N(3C)-C(4C)	1.33(3)
C(40)-H(40C)	0.9800	N(3C)-H(3C)	0.8800
Sb(1A)-F(3A)	1.859(3)	C(4C)-C(5C)	1.41(3)
Sb(1A)-F(4A)	1.859(3)	C(4C)-H(4C)	0.9500
Sb(1A)-F(1A)	1.861(3)	C(5C)-C(6C)	1.51(2)
Sb(1A)-F(5A)	1.862(3)	C(6C)-H(6CA)	0.9800
Sb(1A)-F(2A)	1.862(3)	C(6C)-H(6CB)	0.9800
Sb(1A)-F(6A)	1.866(3)	C(6C)-H(6CC)	0.9800
Sb(1')-F(4A')	1.837(6)		

N(7)-Fe(1)-N(5)	176.4(2)	N(2)-Fe(1)-N(1)	89.75(19)
N(7)-Fe(1)-N(3)	92.2(2)	N(4)-Fe(1)-N(1)	90.4(2)
N(5)-Fe(1)-N(3)	89.99(19)	C(27)-O(2)-C(28)	116.4(6)
N(7)-Fe(1)-N(2)	89.8(2)	C(31)-O(4)-C(32)	116.4(6)
N(5)-Fe(1)-N(2)	87.27(19)	C(4)-N(1)-C(1)	106.3(5)
N(3)-Fe(1)-N(2)	90.4(2)	C(4)-N(1)-Fe(1)	127.2(4)
N(7)-Fe(1)-N(4)	95.1(2)	C(1)-N(1)-Fe(1)	126.4(4)
N(5)-Fe(1)-N(4)	87.8(2)	C(9)-N(2)-C(6)	106.1(5)
N(3)-Fe(1)-N(4)	89.3(2)	C(9)-N(2)-Fe(1)	126.4(4)
N(2)-Fe(1)-N(4)	175.05(19)	C(6)-N(2)-Fe(1)	127.5(4)
N(7)-Fe(1)-N(1)	90.1(2)	C(14)-N(3)-C(11)	105.7(5)
N(5)-Fe(1)-N(1)	87.71(19)	C(14)-N(3)-Fe(1)	127.9(4)
N(3)-Fe(1)-N(1)	177.69(19)	C(11)-N(3)-Fe(1)	125.8(4)

C(16)-N(4)-C(19)	106.4(5)	C(11)-C(12)-C(29)	124.6(6)
C(16)-N(4)-Fe(1)	127.5(4)	C(12)-C(13)-C(14)	106.8(6)
C(19)-N(4)-Fe(1)	126.1(4)	C(12)-C(13)-C(33)	129.0(6)
C(37)-N(5)-C(38)	106.1(5)	C(14)-C(13)-C(33)	124.1(6)
C(37)-N(5)-Fe(1)	125.6(4)	C(15)-C(14)-N(3)	124.7(6)
C(38)-N(5)-Fe(1)	128.3(4)	C(15)-C(14)-C(13)	125.2(6)
C(37)-N(6)-C(39)	108.5(5)	N(3)-C(14)-C(13)	110.1(6)
C(37)-N(6)-H(6)	128(5)	C(14)-C(15)-C(16)	125.5(6)
C(39)-N(6)-H(6)	123(5)	C(14)-C(15)-H(15)	117.2
O(5)-N(7)-Fe(1)	174.8(5)	C(16)-C(15)-H(15)	117.2
N(1)-C(1)-C(20)	124.9(6)	N(4)-C(16)-C(15)	124.8(6)
N(1)-C(1)-C(2)	110.0(5)	N(4)-C(16)-C(17)	109.8(5)
C(20)-C(1)-C(2)	124.8(6)	C(15)-C(16)-C(17)	125.4(6)
C(3)-C(2)-C(1)	106.7(5)	C(18)-C(17)-C(16)	107.1(6)
C(3)-C(2)-C(21)	126.4(6)	C(18)-C(17)-C(34)	129.1(6)
C(1)-C(2)-C(21)	126.9(6)	C(16)-C(17)-C(34)	123.8(6)
C(2)-C(3)-C(4)	106.7(5)	C(17)-C(18)-C(19)	106.5(6)
C(2)-C(3)-C(23)	129.1(5)	C(17)-C(18)-C(36)	128.7(6)
C(4)-C(3)-C(23)	124.1(6)	C(19)-C(18)-C(36)	124.8(6)
N(1)-C(4)-C(5)	126.4(5)	C(20)-C(19)-N(4)	125.8(6)
N(1)-C(4)-C(3)	110.1(5)	C(20)-C(19)-C(18)	123.9(6)
C(5)-C(4)-C(3)	123.5(6)	N(4)-C(19)-C(18)	110.2(6)
C(4)-C(5)-C(6)	123.9(5)	C(19)-C(20)-C(1)	125.3(6)
C(4)-C(5)-H(5)	118.1	C(19)-C(20)-H(20)	117.3
C(6)-C(5)-H(5)	118.1	C(1)-C(20)-H(20)	117.3
N(2)-C(6)-C(5)	125.0(5)	C(22)-C(21)-C(2)	128.0(7)
N(2)-C(6)-C(7)	109.8(5)	C(22)-C(21)-H(21)	116.0
C(5)-C(6)-C(7)	125.1(6)	C(2)-C(21)-H(21)	116.0
C(8)-C(7)-C(6)	107.2(5)	C(21)-C(22)-H(22A)	120.0
C(8)-C(7)-C(24)	128.4(5)	C(21)-C(22)-H(22B)	120.0
C(6)-C(7)-C(24)	124.4(5)	H(22A)-C(22)-H(22B)	120.0
C(7)-C(8)-C(9)	106.1(5)	C(3)-C(23)-H(23A)	109.5
C(7)-C(8)-C(25)	129.1(6)	C(3)-C(23)-H(23B)	109.5
C(9)-C(8)-C(25)	124.8(5)	H(23A)-C(23)-H(23B)	109.5
N(2)-C(9)-C(10)	125.5(6)	C(3)-C(23)-H(23C)	109.5
N(2)-C(9)-C(8)	110.6(5)	H(23A)-C(23)-H(23C)	109.5
C(10)-C(9)-C(8)	123.8(6)	H(23B)-C(23)-H(23C)	109.5
C(11)-C(10)-C(9)	125.0(6)	C(7)-C(24)-H(24A)	109.5
C(11)-C(10)-H(10)	117.5	C(7)-C(24)-H(24B)	109.5
C(9)-C(10)-H(10)	117.5	H(24A)-C(24)-H(24B)	109.5
C(10)-C(11)-N(3)	125.1(5)	C(7)-C(24)-H(24C)	109.5
C(10)-C(11)-C(12)	125.0(6)	H(24A)-C(24)-H(24C)	109.5
N(3)-C(11)-C(12)	109.7(6)	H(24B)-C(24)-H(24C)	109.5
C(13)-C(12)-C(11)	107.6(6)	C(8)-C(25)-C(26)	111.9(5)
C(13)-C(12)-C(29)	127.7(6)	C(8)-C(25)-H(25A)	109.2

C(26)-C(25)-H(25A)	109.2	C(13)-C(33)-H(33C)	109.5
C(8)-C(25)-H(25B)	109.2	H(33A)-C(33)-H(33C)	109.5
C(26)-C(25)-H(25B)	109.2	H(33B)-C(33)-H(33C)	109.5
H(25A)-C(25)-H(25B)	107.9	C(35')-C(34)-C(17)	130.1(17)
C(27)-C(26)-C(25)	112.8(6)	C(35)-C(34)-C(17)	126.7(9)
C(27)-C(26)-H(26A)	109.0	C(35)-C(34)-H(34)	116.6
C(25)-C(26)-H(26A)	109.0	C(17)-C(34)-H(34)	116.6
C(27)-C(26)-H(26B)	109.0	C(35')-C(34)-H(34')	114.9
C(25)-C(26)-H(26B)	109.0	C(17)-C(34)-H(34')	114.9
H(26A)-C(26)-H(26B)	107.8	C(34)-C(35)-H(35A)	120.0
O(1')-C(27)-O(2)	124.8(11)	C(34)-C(35)-H(35B)	120.0
O(1)-C(27)-O(2)	119.2(10)	H(35A)-C(35)-H(35B)	120.0
O(1')-C(27)-C(26)	115.2(14)	C(34)-C(35')-H(35C)	120.0
O(1)-C(27)-C(26)	126.4(8)	C(34)-C(35')-H(35D)	120.0
O(2)-C(27)-C(26)	113.2(7)	H(35C)-C(35')-H(35D)	120.0
O(2)-C(28)-H(28A)	109.5	C(18)-C(36)-H(36A)	109.5
O(2)-C(28)-H(28B)	109.5	C(18)-C(36)-H(36B)	109.5
H(28A)-C(28)-H(28B)	109.5	H(36A)-C(36)-H(36B)	109.5
O(2)-C(28)-H(28C)	109.5	C(18)-C(36)-H(36C)	109.5
H(28A)-C(28)-H(28C)	109.5	H(36A)-C(36)-H(36C)	109.5
H(28B)-C(28)-H(28C)	109.5	H(36B)-C(36)-H(36C)	109.5
C(12)-C(29)-C(30)	114.5(5)	N(5)-C(37)-N(6)	110.7(6)
C(12)-C(29)-H(29A)	108.6	N(5)-C(37)-H(37)	124.6
C(30)-C(29)-H(29A)	108.6	N(6)-C(37)-H(37)	124.6
C(12)-C(29)-H(29B)	108.6	C(39)-C(38)-N(5)	109.1(6)
C(30)-C(29)-H(29B)	108.6	C(39)-C(38)-H(38)	125.5
H(29A)-C(29)-H(29B)	107.6	N(5)-C(38)-H(38)	125.5
C(31)-C(30)-C(29)	111.4(5)	C(38)-C(39)-N(6)	105.5(6)
C(31)-C(30)-H(30A)	109.4	C(38)-C(39)-C(40)	132.7(7)
C(29)-C(30)-H(30A)	109.4	N(6)-C(39)-C(40)	121.8(6)
C(31)-C(30)-H(30B)	109.4	C(39)-C(40)-H(40A)	109.5
C(29)-C(30)-H(30B)	109.4	C(39)-C(40)-H(40B)	109.5
H(30A)-C(30)-H(30B)	108.0	H(40A)-C(40)-H(40B)	109.5
O(3)-C(31)-O(4)	122.6(6)	C(39)-C(40)-H(40C)	109.5
O(3)-C(31)-C(30)	125.2(6)	H(40A)-C(40)-H(40C)	109.5
O(4)-C(31)-C(30)	112.2(5)	H(40B)-C(40)-H(40C)	109.5
O(4)-C(32)-H(32A)	109.5	F(3A)-Sb(1A)-F(4A)	90.85(18)
O(4)-C(32)-H(32B)	109.5	F(3A)-Sb(1A)-F(1A)	90.38(19)
H(32A)-C(32)-H(32B)	109.5	F(4A)-Sb(1A)-F(1A)	178.7(2)
O(4)-C(32)-H(32C)	109.5	F(3A)-Sb(1A)-F(5A)	89.71(18)
H(32A)-C(32)-H(32C)	109.5	F(4A)-Sb(1A)-F(5A)	90.18(19)
H(32B)-C(32)-H(32C)	109.5	F(1A)-Sb(1A)-F(5A)	90.36(19)
C(13)-C(33)-H(33A)	109.5	F(3A)-Sb(1A)-F(2A)	89.98(18)
C(13)-C(33)-H(33B)	109.5	F(4A)-Sb(1A)-F(2A)	89.86(19)
H(33A)-C(33)-H(33B)	109.5	F(1A)-Sb(1A)-F(2A)	89.61(18)

F(5A)-Sb(1A)-F(2A)	179.7(2)
F(3A)-Sb(1A)-F(6A)	179.1(2)
F(4A)-Sb(1A)-F(6A)	89.52(18)
F(1A)-Sb(1A)-F(6A)	89.25(17)
F(5A)-Sb(1A)-F(6A)	89.49(18)
F(2A)-Sb(1A)-F(6A)	90.82(18)
F(4A')-Sb(1')-F(6A')	91.7(4)
F(4A')-Sb(1')-F(5A')	91.5(4)
F(6A')-Sb(1')-F(5A')	91.2(4)
F(4A')-Sb(1')-F(2A')	90.0(2)
F(6A')-Sb(1')-F(2A')	90.0(2)
F(5A')-Sb(1')-F(2A')	178.1(5)
F(4A')-Sb(1')-F(3A')	90.0(2)
F(6A')-Sb(1')-F(3A')	177.9(5)
F(5A')-Sb(1')-F(3A')	90.0(2)
F(2A')-Sb(1')-F(3A')	88.7(4)
F(4A')-Sb(1')-F(1A')	178.0(5)
F(6A')-Sb(1')-F(1A')	89.9(2)
F(5A')-Sb(1')-F(1A')	89.8(2)
F(2A')-Sb(1')-F(1A')	88.7(4)
F(3A')-Sb(1')-F(1A')	88.3(4)
F(1B')#1-Sb(1B)-F(1B')	180.0
F(2B)#1-Sb(1B)-F(2B)	180.0(7)
F(1B')#1-Sb(1B)-F(2B')#1	91.6(6)
F(1B')-Sb(1B)-F(2B')#1	88.4(6)
F(1B')#1-Sb(1B)-F(2B')	88.4(6)
F(1B')-Sb(1B)-F(2B')	91.6(6)
F(2B')#1-Sb(1B)-F(2B')	180.0
F(1B')#1-Sb(1B)-F(3B')	88.6(6)
F(1B')-Sb(1B)-F(3B')	91.4(6)
F(2B')#1-Sb(1B)-F(3B')	89.7(5)
F(2B')-Sb(1B)-F(3B')	90.3(5)
F(1B')#1-Sb(1B)-F(3B')#1	91.4(6)
F(1B')-Sb(1B)-F(3B')#1	88.6(6)
F(2B')#1-Sb(1B)-F(3B')#1	90.3(5)
F(2B')-Sb(1B)-F(3B')#1	89.7(5)
F(3B')-Sb(1B)-F(3B')#1	180.0(12)
F(2B)#1-Sb(1B)-F(1B)#1	90.6(4)
F(2B)-Sb(1B)-F(1B)#1	89.4(4)
F(2B)#1-Sb(1B)-F(1B)	89.4(4)
F(2B)-Sb(1B)-F(1B)	90.6(4)
F(1B)#1-Sb(1B)-F(1B)	180.0(6)
F(2B)#1-Sb(1B)-F(3B)#1	88.2(5)
F(2B)-Sb(1B)-F(3B)#1	91.8(5)
F(1B)#1-Sb(1B)-F(3B)#1	90.7(4)
F(1B)-Sb(1B)-F(3B)#1	89.3(4)
F(2B)#1-Sb(1B)-F(3B)	91.8(5)
F(2B)-Sb(1B)-F(3B)	88.2(5)
F(1B)#1-Sb(1B)-F(3B)	89.3(4)
F(1B)-Sb(1B)-F(3B)	90.7(4)
F(3B)#1-Sb(1B)-F(3B)	180.0
C(5C)-N(1C)-C(2C)	107.5(16)
C(5C)-N(1C)-H(1C)	126.3
C(2C)-N(1C)-H(1C)	126.3
N(3C)-C(2C)-N(1C)	111.8(15)
N(3C)-C(2C)-H(2C)	124.1
N(1C)-C(2C)-H(2C)	124.1
C(2C)-N(3C)-C(4C)	103.7(17)
C(2C)-N(3C)-H(3C)	128.1
C(4C)-N(3C)-H(3C)	128.1
N(3C)-C(4C)-C(5C)	113(2)
N(3C)-C(4C)-H(4C)	123.6
C(5C)-C(4C)-H(4C)	123.6
N(1C)-C(5C)-C(4C)	103.6(16)
N(1C)-C(5C)-C(6C)	130.8(18)
C(4C)-C(5C)-C(6C)	125.6(18)
C(5C)-C(6C)-H(6CA)	109.5
C(5C)-C(6C)-H(6CB)	109.5
H(6CA)-C(6C)-H(6CB)	109.5
C(5C)-C(6C)-H(6CC)	109.5
H(6CA)-C(6C)-H(6CC)	109.5
H(6CB)-C(6C)-H(6CC)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+2, -y+1, -z+2

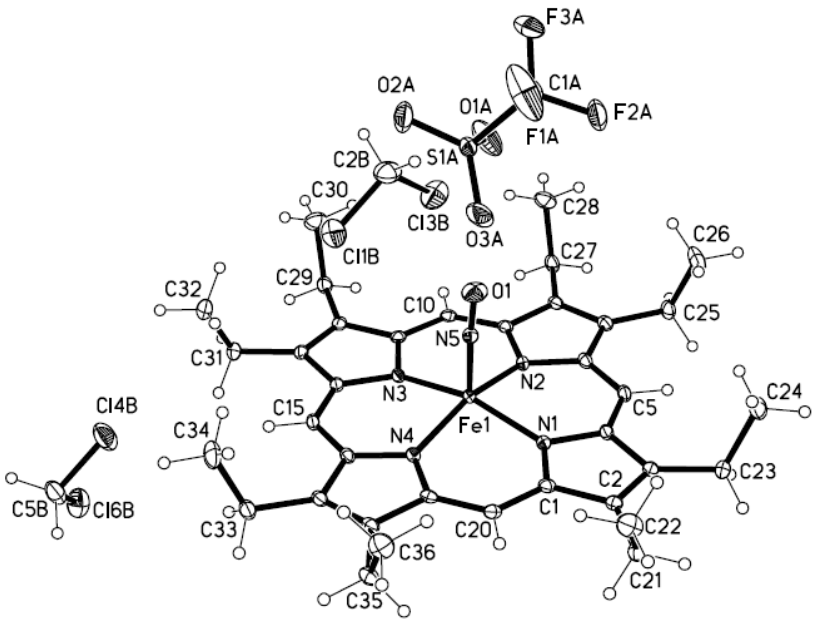

Figure S4. Molecular structure of [(OEP)Fe(NO)]OTf

Experimental for X-ray structural determination of [(OEP)Fe(NO)]OTf

The selected crystal was a 4-component twin. The intensity data were effectively detwinned by the integration and scaling programs. The displacement ellipsoids were drawn at the 50% probability level.

A red block-shaped crystal of dimensions 0.500 x 0.240 x 0.180 mm was selected for structural analysis. Intensity data for this compound were collected using a diffractometer with a Bruker APEX ccd area detector (1) and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The sample was cooled to 100(2) K. Cell parameters were determined from a non-linear least squares fit of 9982 peaks in the range $2.26 < \theta < 27.58°$. A total of 91,295 data were measured in the range $1.570 < \theta < 27.753°$ using ϕ and ω oscillation frames. The data were corrected for absorption by the empirical method (2) giving minimum and maximum transmission factors of 0.714 and 0.881. The data were merged to form a set of 9460 independent data with R(int) = 0.0571 and a coverage of 97.9 %.

The triclinic space group $P\bar{1}$ was determined by statistical tests and verified by

subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 (3). The positions of hydrogens were initially determined by geometry and were refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 (1.5 for methyl) times the isotropic equivalent displacement parameters of the bonded atoms. A total of 514 parameters were refined against 9460 data to give $wR(F^2)$ = 0.0902 and S = 1.000 for weights of $w = 1/[\sigma^2 (F^2) + (0.0360 P)^2]$, where $P = [F_o^2 + 2F_c^2] / 3$. The final $R(F)$ was 0.0358 for the 7049 observed, $[F > 4\sigma(F)]$, data. The largest shift/s.u. was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 0.587 and -0.425 e/Å^3, respectively.

Acknowledgment

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References

(1) (a) Data Collection: APEX2 (2007) Bruker AXS Inc., Madison, Wisconsin, USA. (b) Data Reduction: SAINT (2007) Bruker AXS Inc., Madison, Wisconsin, USA.

(2) SADABS (2002) Bruker AXS Inc., Madison, Wisconsin, USA.

(3) (a) G. M. Sheldrick. *Acta Cryst.* **2015***, A71*, 3-8. (b) G. M. Sheldrick. *Acta Cryst.* **2015***., C71*, 3-8.

Deposition of the crystal structure with the CCDC

CCDC 1484725 contains the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via http;//www.ccdc.cam.ac.uk/conts/retrieving.html

Table S8. Crystal data and structure refinement for [(OEP)Fe(NO)]OTf.2(CH_2Cl_2).

Empirical formula	$(C_{36}H_{44}FeN_5O)^+ (CF_3O_3S)^- 2(CH_2Cl_2)$	
	$C_{39}H_{48}Cl_4F_3FeN_5O_4S$	
Formula weight	937.53	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 12.424(2) Å	α= 100.515(3)°
	b = 13.832(3) Å	β= 112.954(3)°
	c = 15.083(3) Å	γ= 109.155(3)°
Volume	2106.1(7) $Å^3$	
Z, Z'	2, 1	
Density (calculated)	1.478 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	972	
Absorption coefficient	0.721 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.881 and 0.714	
Theta range for data collection	1.570 to 27.753°	
Reflections collected	9460	
Independent reflections	9460 [R(int) = ?]	
Data / restraints / parameters	9460 / 0 / 514	
$wR(F^2$ all data)	$wR2$ = 0.0902	
R(F obsd data)	$R1$ = 0.0358	
Goodness-of-fit on F^2	1.000	
Observed data [I > 2s(I)]	7049	
Largest and mean shift / s.u.	0.001 and 0.000	
Largest diff. peak and hole	0.587 and -0.425 $e/Å^3$	

$wR2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

Table S9. Bond lengths [Å] and angles [°] for [(OEP)Fe(NO)]OTf.2(CH_2Cl_2).

Fe(1)-N(5)	1.6371(15)	C(18)-C(19)	1.446(2)
Fe(1)-N(2)	1.9864(15)	C(18)-C(35)	1.496(3)
Fe(1)-N(4)	1.9899(15)	C(19)-C(20)	1.376(2)
Fe(1)-N(1)	1.9910(15)	C(20)-H(20)	0.9500
Fe(1)-N(3)	1.9998(15)	C(21)-C(22)	1.527(3)
O(1)-N(5)	1.1473(19)	C(21)-H(21A)	0.9900
N(1)-C(1)	1.387(2)	C(21)-H(21B)	0.9900
N(1)-C(4)	1.387(2)	C(22)-H(22A)	0.9800
N(2)-C(6)	1.384(2)	C(22)-H(22B)	0.9800
N(2)-C(9)	1.386(2)	C(22)-H(22C)	0.9800
N(3)-C(14)	1.385(2)	C(23)-C(24)	1.531(3)
N(3)-C(11)	1.390(2)	C(23)-H(23A)	0.9900
N(4)-C(16)	1.382(2)	C(23)-H(23B)	0.9900
N(4)-C(19)	1.383(2)	C(24)-H(24A)	0.9800
C(1)-C(20)	1.377(3)	C(24)-H(24B)	0.9800
C(1)-C(2)	1.442(3)	C(24)-H(24C)	0.9800
C(2)-C(3)	1.357(3)	C(25)-C(26)	1.525(3)
C(2)-C(21)	1.501(3)	C(25)-H(25A)	0.9900
C(3)-C(4)	1.439(3)	C(25)-H(25B)	0.9900
C(3)-C(23)	1.505(2)	C(26)-H(26A)	0.9800
C(4)-C(5)	1.375(3)	C(26)-H(26B)	0.9800
C(5)-C(6)	1.379(3)	C(26)-H(26C)	0.9800
C(5)-H(5)	0.9500	C(27)-C(28)	1.526(3)
C(6)-C(7)	1.437(3)	C(27)-H(27A)	0.9900
C(7)-C(8)	1.364(3)	C(27)-H(27B)	0.9900
C(7)-C(25)	1.493(3)	C(28)-H(28A)	0.9800
C(8)-C(9)	1.440(2)	C(28)-H(28B)	0.9800
C(8)-C(27)	1.494(2)	C(28)-H(28C)	0.9800
C(9)-C(10)	1.373(2)	C(29)-C(30)	1.532(3)
C(10)-C(11)	1.376(2)	C(29)-H(29A)	0.9900
C(10)-H(10)	0.9500	C(29)-H(29B)	0.9900
C(11)-C(12)	1.437(2)	C(30)-H(30A)	0.9800
C(12)-C(13)	1.352(3)	C(30)-H(30B)	0.9800
C(12)-C(29)	1.500(2)	C(30)-H(30C)	0.9800
C(13)-C(14)	1.439(2)	C(31)-C(32)	1.526(2)
C(13)-C(31)	1.501(2)	C(31)-H(31A)	0.9900
C(14)-C(15)	1.365(3)	C(31)-H(31B)	0.9900
C(15)-C(16)	1.377(2)	C(32)-H(32A)	0.9800
C(15)-H(15)	0.9500	C(32)-H(32B)	0.9800
C(16)-C(17)	1.435(3)	C(32)-H(32C)	0.9800
C(17)-C(18)	1.358(3)	C(33)-C(34)	1.520(3)
C(17)-C(33)	1.500(2)	C(33)-H(33A)	0.9900

C(33)-H(33B)	0.9900	S(1A)-C(1A)	1.816(2)
C(34)-H(34A)	0.9800	F(1A)-C(1A)	1.326(2)
C(34)-H(34B)	0.9800	F(2A)-C(1A)	1.330(2)
C(34)-H(34C)	0.9800	F(3A)-C(1A)	1.325(2)
C(35)-C(36)	1.526(3)	Cl(1B)-C(2B)	1.765(2)
C(35)-H(35A)	0.9900	C(2B)-Cl(3B)	1.756(2)
C(35)-H(35B)	0.9900	C(2B)-H(2B1)	0.9900
C(36)-H(36A)	0.9800	C(2B)-H(2B2)	0.9900
C(36)-H(36B)	0.9800	Cl(4B)-C(5B)	1.768(2)
C(36)-H(36C)	0.9800	C(5B)-Cl(6B)	1.765(2)
S(1A)-O(2A)	1.4206(15)	C(5B)-H(5B1)	0.9900
S(1A)-O(1A)	1.4223(15)	C(5B)-H(5B2)	0.9900
S(1A)-O(3A)	1.4229(15)		

N(5)-Fe(1)-N(2)	98.61(7)	C(4)-C(3)-C(23)	124.27(16)
N(5)-Fe(1)-N(4)	99.50(7)	C(5)-C(4)-N(1)	123.96(17)
N(2)-Fe(1)-N(4)	161.89(6)	C(5)-C(4)-C(3)	124.59(17)
N(5)-Fe(1)-N(1)	97.91(7)	N(1)-C(4)-C(3)	111.45(15)
N(2)-Fe(1)-N(1)	88.92(6)	C(4)-C(5)-C(6)	125.61(17)
N(4)-Fe(1)-N(1)	88.25(6)	C(4)-C(5)-H(5)	117.2
N(5)-Fe(1)-N(3)	101.14(7)	C(6)-C(5)-H(5)	117.2
N(2)-Fe(1)-N(3)	88.14(6)	C(5)-C(6)-N(2)	124.33(16)
N(4)-Fe(1)-N(3)	88.72(6)	C(5)-C(6)-C(7)	124.08(17)
N(1)-Fe(1)-N(3)	160.95(6)	N(2)-C(6)-C(7)	111.55(16)
C(1)-N(1)-C(4)	103.69(14)	C(8)-C(7)-C(6)	106.44(16)
C(1)-N(1)-Fe(1)	127.77(12)	C(8)-C(7)-C(25)	128.13(17)
C(4)-N(1)-Fe(1)	127.44(12)	C(6)-C(7)-C(25)	125.39(17)
C(6)-N(2)-C(9)	104.15(14)	C(7)-C(8)-C(9)	106.69(16)
C(6)-N(2)-Fe(1)	126.81(12)	C(7)-C(8)-C(27)	128.44(17)
C(9)-N(2)-Fe(1)	127.36(12)	C(9)-C(8)-C(27)	124.84(16)
C(14)-N(3)-C(11)	103.72(14)	C(10)-C(9)-N(2)	124.57(16)
C(14)-N(3)-Fe(1)	126.57(12)	C(10)-C(9)-C(8)	124.26(17)
C(11)-N(3)-Fe(1)	127.75(12)	N(2)-C(9)-C(8)	111.17(16)
C(16)-N(4)-C(19)	104.13(14)	C(9)-C(10)-C(11)	125.57(17)
C(16)-N(4)-Fe(1)	126.99(12)	C(9)-C(10)-H(10)	117.2
C(19)-N(4)-Fe(1)	127.68(12)	C(11)-C(10)-H(10)	117.2
O(1)-N(5)-Fe(1)	176.15(15)	C(10)-C(11)-N(3)	123.41(16)
C(20)-C(1)-N(1)	124.08(17)	C(10)-C(11)-C(12)	125.17(17)
C(20)-C(1)-C(2)	124.33(17)	N(3)-C(11)-C(12)	111.42(15)
N(1)-C(1)-C(2)	111.56(15)	C(13)-C(12)-C(11)	106.64(16)
C(3)-C(2)-C(1)	106.43(16)	C(13)-C(12)-C(29)	127.43(17)
C(3)-C(2)-C(21)	129.16(17)	C(11)-C(12)-C(29)	125.91(16)
C(1)-C(2)-C(21)	124.41(17)	C(12)-C(13)-C(14)	106.93(16)
C(2)-C(3)-C(4)	106.83(16)	C(12)-C(13)-C(31)	128.68(17)
C(2)-C(3)-C(23)	128.89(17)	C(14)-C(13)-C(31)	124.34(16)

C(15)-C(14)-N(3)	124.45(17)	C(7)-C(25)-C(26)	113.35(16)
C(15)-C(14)-C(13)	124.26(17)	C(7)-C(25)-H(25A)	108.9
N(3)-C(14)-C(13)	111.28(15)	C(26)-C(25)-H(25A)	108.9
C(14)-C(15)-C(16)	125.54(17)	C(7)-C(25)-H(25B)	108.9
C(14)-C(15)-H(15)	117.2	C(26)-C(25)-H(25B)	108.9
C(16)-C(15)-H(15)	117.2	H(25A)-C(25)-H(25B)	107.7
C(15)-C(16)-N(4)	124.56(16)	C(25)-C(26)-H(26A)	109.5
C(15)-C(16)-C(17)	123.99(17)	C(25)-C(26)-H(26B)	109.5
N(4)-C(16)-C(17)	111.45(16)	H(26A)-C(26)-H(26B)	109.5
C(18)-C(17)-C(16)	106.88(16)	C(25)-C(26)-H(26C)	109.5
C(18)-C(17)-C(33)	129.06(17)	H(26A)-C(26)-H(26C)	109.5
C(16)-C(17)-C(33)	124.05(17)	H(26B)-C(26)-H(26C)	109.5
C(17)-C(18)-C(19)	106.32(16)	C(8)-C(27)-C(28)	112.44(16)
C(17)-C(18)-C(35)	128.56(17)	C(8)-C(27)-H(27A)	109.1
C(19)-C(18)-C(35)	125.11(17)	C(28)-C(27)-H(27A)	109.1
C(20)-C(19)-N(4)	124.36(16)	C(8)-C(27)-H(27B)	109.1
C(20)-C(19)-C(18)	124.39(17)	C(28)-C(27)-H(27B)	109.1
N(4)-C(19)-C(18)	111.21(16)	H(27A)-C(27)-H(27B)	107.8
C(19)-C(20)-C(1)	125.15(17)	C(27)-C(28)-H(28A)	109.5
C(19)-C(20)-H(20)	117.4	C(27)-C(28)-H(28B)	109.5
C(1)-C(20)-H(20)	117.4	H(28A)-C(28)-H(28B)	109.5
C(2)-C(21)-C(22)	114.18(16)	C(27)-C(28)-H(28C)	109.5
C(2)-C(21)-H(21A)	108.7	H(28A)-C(28)-H(28C)	109.5
C(22)-C(21)-H(21A)	108.7	H(28B)-C(28)-H(28C)	109.5
C(2)-C(21)-H(21B)	108.7	C(12)-C(29)-C(30)	113.26(16)
C(22)-C(21)-H(21B)	108.7	C(12)-C(29)-H(29A)	108.9
H(21A)-C(21)-H(21B)	107.6	C(30)-C(29)-H(29A)	108.9
C(21)-C(22)-H(22A)	109.5	C(12)-C(29)-H(29B)	108.9
C(21)-C(22)-H(22B)	109.5	C(30)-C(29)-H(29B)	108.9
H(22A)-C(22)-H(22B)	109.5	H(29A)-C(29)-H(29B)	107.7
C(21)-C(22)-H(22C)	109.5	C(29)-C(30)-H(30A)	109.5
H(22A)-C(22)-H(22C)	109.5	C(29)-C(30)-H(30B)	109.5
H(22B)-C(22)-H(22C)	109.5	H(30A)-C(30)-H(30B)	109.5
C(3)-C(23)-C(24)	114.04(15)	C(29)-C(30)-H(30C)	109.5
C(3)-C(23)-H(23A)	108.7	H(30A)-C(30)-H(30C)	109.5
C(24)-C(23)-H(23A)	108.7	H(30B)-C(30)-H(30C)	109.5
C(3)-C(23)-H(23B)	108.7	C(13)-C(31)-C(32)	113.00(16)
C(24)-C(23)-H(23B)	108.7	C(13)-C(31)-H(31A)	109.0
H(23A)-C(23)-H(23B)	107.6	C(32)-C(31)-H(31A)	109.0
C(23)-C(24)-H(24A)	109.5	C(13)-C(31)-H(31B)	109.0
C(23)-C(24)-H(24B)	109.5	C(32)-C(31)-H(31B)	109.0
H(24A)-C(24)-H(24B)	109.5	H(31A)-C(31)-H(31B)	107.8
C(23)-C(24)-H(24C)	109.5	C(31)-C(32)-H(32A)	109.5
H(24A)-C(24)-H(24C)	109.5	C(31)-C(32)-H(32B)	109.5
H(24B)-C(24)-H(24C)	109.5	H(32A)-C(32)-H(32B)	109.5

C(31)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(17)-C(33)-C(34)	112.62(16)
C(17)-C(33)-H(33A)	109.1
C(34)-C(33)-H(33A)	109.1
C(17)-C(33)-H(33B)	109.1
C(34)-C(33)-H(33B)	109.1
H(33A)-C(33)-H(33B)	107.8
C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(18)-C(35)-C(36)	114.11(15)
C(18)-C(35)-H(35A)	108.7
C(36)-C(35)-H(35A)	108.7
C(18)-C(35)-H(35B)	108.7
C(36)-C(35)-H(35B)	108.7
H(35A)-C(35)-H(35B)	107.6
C(35)-C(36)-H(36A)	109.5
C(35)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(35)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
O(2A)-S(1A)-O(1A)	115.57(11)
O(2A)-S(1A)-O(3A)	114.69(11)
O(1A)-S(1A)-O(3A)	114.94(11)
O(2A)-S(1A)-C(1A)	103.60(10)
O(1A)-S(1A)-C(1A)	102.19(9)
O(3A)-S(1A)-C(1A)	103.33(10)
F(3A)-C(1A)-F(1A)	108.02(19)
F(3A)-C(1A)-F(2A)	106.74(16)
F(1A)-C(1A)-F(2A)	106.09(18)
F(3A)-C(1A)-S(1A)	111.49(15)
F(1A)-C(1A)-S(1A)	112.06(14)
F(2A)-C(1A)-S(1A)	112.12(15)
Cl(3B)-C(2B)-Cl(1B)	111.51(12)
Cl(3B)-C(2B)-H(2B1)	109.3
Cl(1B)-C(2B)-H(2B1)	109.3
Cl(3B)-C(2B)-H(2B2)	109.3
Cl(1B)-C(2B)-H(2B2)	109.3
H(2B1)-C(2B)-H(2B2)	108.0
Cl(6B)-C(5B)-Cl(4B)	110.83(11)
Cl(6B)-C(5B)-H(5B1)	109.5
Cl(4B)-C(5B)-H(5B1)	109.5
Cl(6B)-C(5B)-H(5B2)	109.5
Cl(4B)-C(5B)-H(5B2)	109.5
H(5B1)-C(5B)-H(5B2)	108.1