Supporting Information for

Roles of carboxylate donors in O-O bond scission of peroxodiiron(III) to high-spin oxodiiron(IV) with a new carboxylate-containing dinucleating ligand

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Product Analysis

Table S11. Oxidation of Alkenes with H_2O_2 Catalyzed by **2b**.

DFT studies

X-ray Structure Report

for

$[Fe_2(\mu\text{-}O)(H_2O)_2(BPG_2E)](ClO_4)_2 \cdot 3H_2O$ (**2a**).

Experimental

Data Collection

A red block crystal of $C_{30}H_{40}Cl_2Fe_2N_6O_{18}$ having approximate dimensions of 0.286 x 0.151 x 0.090 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using multi-layer mirror monochromated Mo-Kα radiation.

The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive triclinic cell with dimensions:

a = 11.4730(4) Å α = 113.070(8)^o
b = 12.9171(4) Å β = 100.094(7)^o
c = 14.4931(4) Å γ = 90.982(6)^o
V = 1936.75(17) Å^3

For Z = 2 and F.W. = 955.28, the calculated density is 1.638 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P-1 (#2)

The data were collected at a temperature of -180 $\pm$ 1^{o}C to a maximum 2θ value of 54.9^o. A total of 44 oscillation images were collected. A sweep of data was done using w scans from 130.0 to 190.0^o in 5.00^o step, at χ=45.0^o and ϕ = 0.0^o. The exposure rate was 60.0 [sec./^{o}]. A second sweep was performed using w scans from 0.0 to 160.0^o in 5.00^o step, at χ=45.0^o and ϕ = 180.0^o. The exposure rate was 60.0 [sec./^{o}]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 19147 reflections were collected, where 8757 were unique (R_{int} = 0.0180); equivalent reflections were merged.

The linear absorption coefficient, μ, for Mo-Kα radiation is 9.705 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.736 to 0.916. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[2] on F^2 was based on 8757 observed reflections and 599 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0281$$

$$wR2 = [\, \Sigma \, (\, w \, (Fo^2 - Fc^2)^2 \,) / \, \Sigma \, w(Fo^2)^2]^{1/2} = 0.0757$$

The standard deviation of an observation of unit weight[3] was 1.06. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.50 and -0.39 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[4]. Anomalous dispersion effects were included in Fcalc[5]; the values for Δf' and Δf'' were those of Creagh and McAuley[6]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[7]. All calculations were performed using the CrystalStructure[8] crystallographic software package except for refinement, which was performed using SHELXL-97[9].

References

(1) SIR2004: M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna (2005)

(2) Least Squares function minimized: (SHELXL97)

$\Sigma w(F_o^2 - F_c^2)^2$ where w = Least Squares weights.

(3) Standard deviation of an observation of unit weight:

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

where: N_o = number of observations
N_v = number of variables

(4) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

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(8) CrystalStructure 4.1: Crystal Structure Analysis Package, Rigaku Corporation (2000-2013). Tokyo 196-8666, Japan.

(9) SHELX97: Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Table S1. Summary of Crystal Data, Data Collection Parameters, and Structure Refinement for **2a**.

A. Crystal Data

Empirical Formula	$C_{30}H_{40}Cl_2Fe_2N_6O_{18}$
Formula Weight	955.28
Crystal Color, Habit	red, block
Crystal Dimensions	0.286 X 0.151 X 0.090 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 11.4730(4) Å b = 12.9171(4) Å c = 14.4931(4) Å α = 113.070(8) ^{o} β = 100.094(7) ^{o} γ = 90.982(6) ^{o} V = 1936.75(17) Å^3
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.638 g/cm^3
F_{000}	984.00
μ(MoKα)	9.705 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoKα (λ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	50kV, 24mA
Temperature	-180.0°C
Detector Aperture	280 x 256 mm
Data Images	44 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	130.0 - 190.0°
Exposure Rate	60.0 sec./°
ω oscillation Range (χ=45.0, ϕ=180.0)	0.0 - 160.0°
Exposure Rate	60.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	54.9°
No. of Reflections Measured	Total: 19147 Unique: 8757 (R_{int} = 0.0180)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.736 - 0.916)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\ w\ (Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\ \sigma^2(Fo^2) + (0.0370 \cdot P)^2 + 1.3514 \cdot P\ ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	54.9^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	8757
No. Variables	599
Reflection/Parameter Ratio	14.62
Residuals: R1 ($I>2.00\sigma(I)$)	0.0281
Residuals: R (All reflections)	0.0333
Residuals: wR2 (All reflections)	0.0757
Goodness of Fit Indicator	1.060
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.50 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.39 $e^-/Å^3$

Table S2. Fractional Atomic Coordinates Including Hydrogen Atoms and Isotropic Thermal Parameters of **2a**.

atom	x	y	z	B_{eq}	occ
Fe1	0.812106(19)	0.287435(18)	0.183206(16)	0.889(5)	1
Fe2	0.614594(18)	0.112766(18)	0.238188(16)	0.816(5)	1
Cl1	0.76767(4)	-0.30482(4)	0.07362(3)	1.831(7)	1
Cl2	0.75806(8)	0.18779(12)	0.63523(12)	1.745(19)	0.756(4)
Cl2a	0.7497(3)	0.2222(4)	0.6760(4)	2.14(6)	0.244(4)
O1	0.71998(9)	0.20492(9)	0.22153(8)	1.098(17)	1
O2	0.96508(10)	0.26345(10)	0.26249(9)	1.305(18)	1
O3	1.16279(10)	0.27334(10)	0.29240(9)	1.504(19)	1
O4	0.68430(10)	0.34115(11)	0.09693(9)	1.252(18)	1
O5	0.59538(10)	-0.01861(9)	0.10178(8)	1.098(17)	1
O6	0.48917(10)	-0.17698(10)	-0.01066(8)	1.365(18)	1
O7	0.46054(10)	0.16010(10)	0.17474(9)	1.231(17)	1
O8	0.66378(13)	-0.28832(13)	0.11950(12)	2.79(3)	1
O9	0.87258(13)	-0.27705(12)	0.15200(11)	2.48(2)	1
O10	0.76926(16)	-0.23651(15)	0.01646(14)	3.54(3)	1
O11	0.76507(15)	-0.42310(13)	0.00634(11)	3.31(3)	1
O12	0.81037(17)	0.17612(16)	0.54945(14)	2.34(4)	0.756(4)
O12a	0.6902(10)	0.2318(7)	0.7534(8)	6.9(3)	0.244(4)
O13	0.8169(2)	0.1224(3)	0.6865(2)	4.15(6)	0.756(4)
O13a	0.8535(9)	0.1701(9)	0.6840(8)	4.6(2)	0.244(4)
O14	0.6345(3)	0.1496(5)	0.6011(5)	3.35(10)	0.756(4)
O14a	0.6624(15)	0.1452(14)	0.5824(13)	5.7(4)	0.244(4)
O15	0.7730(4)	0.3076(4)	0.7030(3)	3.96(10)	0.756(4)
O15a	0.7702(14)	0.3293(14)	0.6776(13)	4.7(4)	0.244(4)
O16	0.37957(12)	0.35263(11)	0.28154(10)	1.69(2)	1
O17	0.36314(12)	0.51567(13)	0.19413(11)	2.12(2)	1
O18	0.60467(13)	0.54234(12)	0.19271(11)	1.90(2)	1
N1	0.94949(12)	0.36992(11)	0.13249(10)	1.12(2)	1
N2	0.83982(12)	0.15941(11)	0.04219(10)	1.06(2)	1
N3	0.83336(12)	0.46169(11)	0.29652(10)	1.23(2)	1
N4	0.50408(12)	-0.01884(11)	0.26136(10)	1.07(2)	1
N5	0.74570(12)	0.03683(11)	0.30769(10)	1.07(2)	1
N6	0.55754(12)	0.20313(11)	0.38270(10)	1.09(2)	1
C1	1.06882(14)	0.34568(14)	0.17366(13)	1.36(3)	1
C2	1.06666(14)	0.29060(13)	0.24952(12)	1.16(2)	1
C3	0.92279(15)	0.31925(14)	0.01921(12)	1.30(2)	1
C4	0.89687(14)	0.19295(14)	-0.01705(12)	1.18(2)	1

Table S2. Atomic coordinates and B_{iso}/B_{eq} and occupancy (continued).

atom	x	y	z	B_{eq}	occ
C5	0.92706(15)	0.11608(15)	-0.10568(13)	1.50(3)	1
C6	0.89507(15)	0.00165(15)	-0.13543(13)	1.52(3)	1
C7	0.83540(14)	-0.03275(14)	-0.07490(12)	1.34(2)	1
C8	0.81002(14)	0.04840(13)	0.01344(12)	1.21(2)	1
C9	0.93652(15)	0.49239(13)	0.17621(13)	1.37(3)	1
C10	0.91486(14)	0.52874(13)	0.28355(12)	1.26(2)	1
C11	0.96902(16)	0.62821(14)	0.36198(14)	1.81(3)	1
C12	0.93669(17)	0.66125(15)	0.45671(14)	2.01(3)	1
C13	0.84643(17)	0.59745(15)	0.46786(14)	1.83(3)	1
C14	0.79412(15)	0.49803(14)	0.38544(13)	1.43(3)	1
C15	0.68843(15)	0.43260(14)	0.39318(13)	1.43(3)	1
C16	0.72054(15)	0.35584(14)	0.45013(13)	1.43(3)	1
C17	0.60689(15)	0.30290(14)	0.45854(12)	1.36(3)	1
C18	0.55147(16)	0.35774(14)	0.54061(13)	1.59(3)	1
C19	0.44779(16)	0.30849(15)	0.54786(13)	1.65(3)	1
C20	0.39943(15)	0.20504(15)	0.47183(13)	1.55(3)	1
C21	0.45631(14)	0.15498(13)	0.39046(12)	1.12(2)	1
C22	0.40598(14)	0.04299(14)	0.30573(12)	1.22(2)	1
C23	0.46014(15)	-0.11170(14)	0.16024(12)	1.43(3)	1
C24	0.51953(14)	-0.10233(13)	0.07743(12)	1.06(2)	1
C25	0.57803(14)	-0.05733(14)	0.33483(13)	1.34(2)	1
C26	0.70915(14)	-0.04444(13)	0.33521(12)	1.15(2)	1
C27	0.78871(15)	-0.10787(14)	0.36894(12)	1.41(3)	1
C28	0.90950(15)	-0.08419(15)	0.37791(13)	1.53(3)	1
C29	0.94729(15)	0.00144(14)	0.35138(13)	1.46(3)	1
C30	0.86345(14)	0.05891(14)	0.31552(12)	1.27(2)	1

$$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$$

Table S2a. Atomic coordinates and B_{iso} involving hydrogen atoms of **2a**.

atom	x	y	z	B_{iso}	occ
H1A	1.12127	0.41726	0.20806	1.629	1
H1B	1.10337	0.29504	0.11599	1.629	1
H2	0.6593(19)	0.4033(19)	0.1272(16)	1.5025	1
H3A	0.99160	0.33603	-0.00711	1.559	1
H3B	0.85313	0.35146	-0.00657	1.559	1
H4	0.633(2)	0.2957(19)	0.0687(17)	1.5025	1
H5	0.96885	0.14119	-0.14533	1.799	1
H6	0.91369	-0.05253	-0.19638	1.825	1
H7	0.81257	-0.11053	-0.09397	1.608	1
H8	0.77022	0.02501	0.05523	1.454	1
H9A	0.86907	0.50948	0.13324	1.643	1
H9B	1.00964	0.53482	0.17702	1.643	1
H10	0.615(2)	0.577(2)	0.1661(19)	2.2747	1
H11	1.02732	0.67320	0.35130	2.170	1
H12	0.97603	0.72676	0.51304	2.414	1
H13	0.82016	0.62094	0.53100	2.190	1
H14	0.541(2)	0.537(2)	0.1915(18)	2.2747	1
H15A	0.64425	0.38563	0.32323	1.713	1
H15B	0.63463	0.48690	0.42858	1.713	1
H16A	0.76818	0.29626	0.41234	1.712	1
H16B	0.76832	0.40058	0.51920	1.712	1
H17	0.4699(19)	0.1597(18)	0.1199(17)	1.4773	1
H18	0.58521	0.42924	0.59171	1.904	1
H19	0.41019	0.34499	0.60413	1.982	1
H20	0.32848	0.16895	0.47533	1.856	1
H21	0.4367(19)	0.2200(19)	0.2047(17)	1.4773	1
H22A	0.36284	-0.00221	0.33292	1.463	1
H22B	0.34907	0.05530	0.25201	1.463	1
H23A	0.37315	-0.11097	0.14060	1.714	1
H23B	0.47502	-0.18481	0.16517	1.714	1
H24	0.370(2)	0.391(2)	0.2499(18)	2.0237	1
H25A	0.55307	-0.13777	0.31673	1.608	1
H25B	0.56399	-0.01303	0.40449	1.608	1
H26	0.312(2)	0.3283(19)	0.2809(17)	2.0237	1
H27	0.76077	-0.16672	0.38565	1.686	1
H28	0.96558	-0.12581	0.40180	1.837	1
H29	1.02965	0.02001	0.35790	1.749	1

Table S2a. Atomic coordinates and B_{iso} involving hydrogens/B_{eq} and occupancy (continued).

atom	x	y	z	B_{eq}	occ
H30	0.88926	0.11595	0.29563	1.521	1
H31	0.327(2)	0.573(2)	0.2278(19)	2.5456	1
H32	0.331(2)	0.491(2)	0.136(2)	2.5456	1

Table S3. Anisotropic Thermal Parameters for Non-hydrogen Atoms in **2a**.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe1	0.01143(11)	0.01033(10)	0.01173(11)	-0.00149(8)	0.00331(8)	0.00379(8)
Fe2	0.01059(11)	0.01012(10)	0.01052(11)	-0.00042(8)	0.00301(8)	0.00406(8)
Cl1	0.0276(2)	0.0219(2)	0.0260(2)	0.00856(16)	0.01267(17)	0.01252(17)
Cl2	0.0133(3)	0.0293(5)	0.0300(6)	0.0001(3)	0.0015(3)	0.0197(5)
Cl2a	0.0230(11)	0.0281(18)	0.036(2)	0.0073(11)	0.0101(12)	0.0173(16)
O1	0.0139(5)	0.0132(5)	0.0143(5)	-0.0026(4)	0.0049(4)	0.0044(4)
O2	0.0150(5)	0.0191(6)	0.0176(6)	-0.0015(4)	0.0026(4)	0.0100(5)
O3	0.0148(6)	0.0249(6)	0.0170(6)	0.0019(5)	0.0021(4)	0.0084(5)
O4	0.0139(6)	0.0121(5)	0.0193(6)	-0.0004(4)	0.0012(4)	0.0048(5)
O5	0.0153(5)	0.0124(5)	0.0131(5)	-0.0017(4)	0.0034(4)	0.0040(4)
O6	0.0206(6)	0.0150(5)	0.0130(6)	-0.0038(4)	0.0005(4)	0.0036(4)
O7	0.0160(6)	0.0176(6)	0.0153(6)	0.0041(4)	0.0046(4)	0.0080(5)
O8	0.0294(8)	0.0422(9)	0.0512(9)	0.0114(6)	0.0213(7)	0.0305(8)
O9	0.0307(7)	0.0275(7)	0.0310(8)	-0.0025(6)	0.0063(6)	0.0064(6)
O10	0.0519(10)	0.0552(10)	0.0607(11)	0.0292(8)	0.0371(9)	0.0467(9)
O11	0.0559(10)	0.0278(8)	0.0253(8)	0.0148(7)	-0.0096(7)	-0.0003(6)
O12	0.0298(10)	0.0294(10)	0.0253(10)	-0.0074(7)	0.0052(7)	0.0067(8)
O12a	0.100(8)	0.047(5)	0.110(8)	-0.018(5)	0.087(7)	-0.002(5)
O13	0.0229(12)	0.087(2)	0.0846(19)	0.0067(13)	0.0045(11)	0.0756(19)
O13a	0.042(5)	0.064(6)	0.097(7)	0.030(4)	0.022(5)	0.056(5)
O14	0.0147(10)	0.057(2)	0.077(3)	-0.0025(11)	0.0007(13)	0.054(2)
O14a	0.117(15)	0.034(5)	0.034(6)	-0.004(8)	-0.042(9)	0.007(4)
O15	0.0334(16)	0.049(3)	0.0417(19)	0.0032(17)	0.0178(14)	-0.0134(18)
O15a	0.025(4)	0.068(7)	0.099(11)	-0.006(4)	-0.006(5)	0.054(7)
O16	0.0164(6)	0.0227(6)	0.0260(7)	0.0028(5)	0.0046(5)	0.0106(5)
O17	0.0258(7)	0.0317(7)	0.0200(7)	0.0013(6)	0.0023(5)	0.0081(6)
O18	0.0222(7)	0.0215(7)	0.0321(7)	0.0039(5)	0.0095(6)	0.0129(6)
N1	0.0148(6)	0.0135(6)	0.0147(7)	0.0000(5)	0.0037(5)	0.0062(5)
N2	0.0141(6)	0.0138(6)	0.0130(6)	0.0010(5)	0.0046(5)	0.0053(5)

N3	0.0161(7)	0.0127(6)	0.0157(7)	-0.0022(5)	0.0031(5)	0.0033(5)
N4	0.0140(6)	0.0145(6)	0.0132(6)	0.0006(5)	0.0039(5)	0.0063(5)
N5	0.0147(6)	0.0133(6)	0.0127(6)	0.0007(5)	0.0030(5)	0.0050(5)
N6	0.0155(6)	0.0146(6)	0.0124(6)	0.0019(5)	0.0039(5)	0.0061(5)
C1	0.0134(7)	0.0197(8)	0.0213(8)	0.0005(6)	0.0043(6)	0.0108(7)
C2	0.0158(7)	0.0120(7)	0.0123(7)	0.0009(6)	0.0025(6)	0.0008(6)
C3	0.0192(8)	0.0173(8)	0.0147(8)	-0.0004(6)	0.0055(6)	0.0077(6)
C4	0.0143(7)	0.0173(8)	0.0143(7)	-0.0001(6)	0.0029(6)	0.0075(6)

Table S3. Anisotropic displacement parameters (continued).

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C5	0.0203(8)	0.0226(8)	0.0154(8)	-0.0007(6)	0.0066(6)	0.0079(7)
C6	0.0207(8)	0.0203(8)	0.0135(8)	0.0006(6)	0.0056(6)	0.0024(6)
C7	0.0165(8)	0.0142(7)	0.0174(8)	-0.0000(6)	0.0028(6)	0.0037(6)
C8	0.0141(7)	0.0161(7)	0.0167(8)	0.0001(6)	0.0047(6)	0.0068(6)
C9	0.0190(8)	0.0132(7)	0.0217(8)	-0.0017(6)	0.0062(6)	0.0083(6)
C10	0.0142(7)	0.0134(7)	0.0196(8)	0.0001(6)	0.0031(6)	0.0060(6)
C11	0.0210(9)	0.0148(8)	0.0286(10)	-0.0054(6)	0.0043(7)	0.0048(7)
C12	0.0248(9)	0.0164(8)	0.0251(9)	-0.0052(7)	0.0001(7)	-0.0001(7)
C13	0.0296(9)	0.0179(8)	0.0174(8)	-0.0007(7)	0.0045(7)	0.0026(7)
C14	0.0203(8)	0.0150(7)	0.0182(8)	0.0020(6)	0.0030(6)	0.0059(6)
C15	0.0189(8)	0.0169(8)	0.0171(8)	0.0035(6)	0.0044(6)	0.0050(6)
C16	0.0196(8)	0.0171(8)	0.0151(8)	0.0005(6)	0.0013(6)	0.0048(6)
C17	0.0211(8)	0.0156(7)	0.0159(8)	0.0029(6)	0.0043(6)	0.0071(6)
C18	0.0277(9)	0.0173(8)	0.0145(8)	0.0037(7)	0.0065(6)	0.0045(6)
C19	0.0254(9)	0.0251(9)	0.0167(8)	0.0103(7)	0.0107(7)	0.0101(7)
C20	0.0182(8)	0.0253(9)	0.0202(8)	0.0055(7)	0.0094(6)	0.0118(7)
C21	0.0150(7)	0.0165(7)	0.0141(8)	0.0032(6)	0.0032(6)	0.0091(6)
C22	0.0126(7)	0.0181(8)	0.0169(8)	-0.0000(6)	0.0047(6)	0.0077(6)
C23	0.0206(8)	0.0147(7)	0.0167(8)	-0.0051(6)	0.0053(6)	0.0035(6)
C24	0.0131(7)	0.0132(7)	0.0145(8)	0.0014(6)	0.0011(5)	0.0068(6)
C25	0.0167(8)	0.0195(8)	0.0203(8)	0.0028(6)	0.0064(6)	0.0127(7)
C26	0.0160(8)	0.0154(7)	0.0118(7)	0.0010(6)	0.0045(6)	0.0044(6)
C27	0.0223(8)	0.0171(8)	0.0172(8)	0.0037(6)	0.0073(6)	0.0089(6)
C28	0.0205(8)	0.0210(8)	0.0176(8)	0.0070(6)	0.0035(6)	0.0086(7)
C29	0.0147(8)	0.0215(8)	0.0183(8)	0.0018(6)	0.0026(6)	0.0073(7)
C30	0.0158(8)	0.0162(7)	0.0161(8)	-0.0008(6)	0.0033(6)	0.0065(6)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S4. Fragment Analysis of **2a**.

fragment: 1

Fe(1)	Fe(2)	O(1)	O(2)	O(3)
O(4)	O(5)	O(6)	O(7)	N(1)
N(2)	N(3)	N(4)	N(5)	N(6)
C(1)	C(2)	C(3)	C(4)	C(5)
C(6)	C(7)	C(8)	C(9)	C(10)
C(11)	C(12)	C(13)	C(14)	C(15)
C(16)	C(17)	C(18)	C(19)	C(20)
C(21)	C(22)	C(23)	C(24)	C(25)
C(26)	C(27)	C(28)	C(29)	C(30)

fragment: 2

Cl(1)	O(8)	O(9)	O(10)	O(11)

fragment: 3

Cl(2)	O(12)	O(13)	O(14)	O(15)

fragment: 4

Cl(2a)	O(12a)	O(13a)	O(14a)	O(15a)

fragment: 5

O(16)

fragment: 6

O(17)

fragment: 7

O(18)

Table S5. Bond Distances and Bond Angles of **2a**.

Bond Distances (Å)

atom	atom	distance	atom	atom	distance
Fe1	O1	1.7869(13)	Fe1	O2	2.0217(12)
Fe1	O4	2.0657(14)	Fe1	N1	2.2632(16)
Fe1	N2	2.1471(13)	Fe1	N3	2.1833(12)
Fe2	O1	1.7932(13)	Fe2	O5	2.0105(10)
Fe2	O7	2.0619(12)	Fe2	N4	2.2656(16)
Fe2	N5	2.1291(15)	Fe2	N6	2.1837(14)
Cl1	O8	1.4435(17)	Cl1	O9	1.4333(14)
Cl1	O10	1.429(2)	Cl1	O11	1.4514(15)
Cl2	O12	1.430(3)	Cl2	O13	1.435(4)
Cl2	O14	1.427(4)	Cl2	O15	1.460(4)
Cl2a	O12a	1.380(14)	Cl2a	O13a	1.387(11)
Cl2a	O14a	1.504(15)	Cl2a	O15a	1.39(2)
O2	C2	1.277(2)	O3	C2	1.237(2)
O5	C24	1.270(2)	O6	C24	1.2445(16)
N1	C1	1.484(2)	N1	C3	1.481(2)
N1	C9	1.477(2)	N2	C4	1.354(3)
N2	C8	1.346(2)	N3	C10	1.350(2)
N3	C14	1.349(2)	N4	C22	1.483(2)
N4	C23	1.4776(17)	N4	C25	1.488(2)
N5	C26	1.345(3)	N5	C30	1.352(2)
N6	C17	1.3551(18)	N6	C21	1.351(2)
C1	C2	1.529(3)	C3	C4	1.511(2)
C4	C5	1.387(2)	C5	C6	1.390(3)
C6	C7	1.393(3)	C7	C8	1.383(2)
C9	C10	1.506(3)	C10	C11	1.3819(19)
C11	C12	1.389(3)	C12	C13	1.383(3)
C13	C14	1.399(2)	C14	C15	1.511(3)
C15	C16	1.532(3)	C16	C17	1.508(3)
C17	C18	1.393(2)	C18	C19	1.379(3)
C19	C20	1.383(2)	C20	C21	1.386(2)
C21	C22	1.5049(19)	C23	C24	1.522(3)
C25	C26	1.510(2)	C26	C27	1.388(3)
C27	C28	1.386(2)	C28	C29	1.391(3)
C29	C30	1.378(3)			

Bond lengths involving hydrogens (Å)

O4	H2	0.83(2)	O4	H4	0.76(2)
O7	H17	0.82(3)	O7	H21	0.80(2)
O16	H24	0.79(3)	O16	H26	0.82(3)
O17	H31	0.87(2)	O17	H32	0.79(3)
O18	H10	0.72(3)	O18	H14	0.73(3)
C1	H1A	0.990	C1	H1B	0.990
C3	H3A	0.990	C3	H3B	0.990
C5	H5	0.950	C6	H6	0.950
C7	H7	0.950	C8	H8	0.950
C9	H9A	0.990	C9	H9B	0.990
C11	H11	0.950	C12	H12	0.950
C13	H13	0.950	C15	H15A	0.990
C15	H15B	0.990	C16	H16A	0.990
C16	H16B	0.990	C18	H18	0.950
C19	H19	0.950	C20	H20	0.950
C22	H22A	0.990	C22	H22B	0.990
C23	H23A	0.990	C23	H23B	0.990
C25	H25A	0.990	C25	H25B	0.990
C27	H27	0.950	C28	H28	0.950
C29	H29	0.950	C30	H30	0.950

Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
O1	Fe1	O2	94.30(6)	O1	Fe1	O4	100.31(5)
O1	Fe1	N1	170.64(5)	O1	Fe1	N2	99.54(5)
O1	Fe1	N3	108.27(5)	O2	Fe1	O4	165.23(6)
O2	Fe1	N1	78.56(6)	O2	Fe1	N2	92.18(5)
O2	Fe1	N3	87.63(5)	O4	Fe1	N1	87.14(6)
O4	Fe1	N2	87.59(5)	O4	Fe1	N3	85.72(5)
N1	Fe1	N2	74.94(5)	N1	Fe1	N3	77.72(5)
N2	Fe1	N3	152.13(6)	O1	Fe2	O5	99.55(5)
O1	Fe2	O7	98.66(6)	O1	Fe2	N4	171.59(5)
O1	Fe2	N5	94.73(6)	O1	Fe2	N6	108.72(5)
O5	Fe2	O7	85.36(5)	O5	Fe2	N4	78.13(5)
O5	Fe2	N5	91.99(5)	O5	Fe2	N6	151.03(5)
O7	Fe2	N4	89.25(5)	O7	Fe2	N5	166.60(6)
O7	Fe2	N6	84.28(5)	N4	Fe2	N5	77.35(6)
N4	Fe2	N6	74.76(5)	N5	Fe2	N6	91.89(5)
O8	Cl1	O9	109.52(9)	O8	Cl1	O10	109.91(11)

O8	Cl1	O11	109.24(10)	O9	Cl1	O10	110.76(10)
O9	Cl1	O11	107.66(9)	O10	Cl1	O11	109.72(10)
O12	Cl2	O13	109.34(17)	O12	Cl2	O14	109.6(3)
O12	Cl2	O15	107.3(2)	O13	Cl2	O14	110.0(3)
O13	Cl2	O15	110.7(2)	O14	Cl2	O15	109.8(3)
O12a	Cl2a	O13a	111.6(8)	O12a	Cl2a	O14a	102.0(9)
O12a	Cl2a	O15a	108.3(9)	O13a	Cl2a	O14a	109.0(8)
O13a	Cl2a	O15a	112.6(9)	O14a	Cl2a	O15a	112.9(11)
Fe1	O1	Fe2	170.43(6)	Fe1	O2	C2	121.75(13)
Fe2	O5	C24	120.81(11)	Fe1	N1	C1	108.06(12)
Fe1	N1	C3	106.66(10)	Fe1	N1	C9	106.37(11)
C1	N1	C3	111.42(13)	C1	N1	C9	111.05(11)
C3	N1	C9	112.93(15)	Fe1	N2	C4	117.36(10)
Fe1	N2	C8	123.49(13)	C4	N2	C8	119.03(14)
Fe1	N3	C10	113.53(10)	Fe1	N3	C14	125.59(12)
C10	N3	C14	119.13(12)	Fe2	N4	C22	103.81(11)
Fe2	N4	C23	107.94(12)	Fe2	N4	C25	109.09(10)
C22	N4	C23	111.99(12)	C22	N4	C25	110.75(14)
C23	N4	C25	112.80(13)	Fe2	N5	C26	118.29(11)
Fe2	N5	C30	122.46(14)	C26	N5	C30	118.89(16)
Fe2	N6	C17	127.39(13)	Fe2	N6	C21	113.68(9)
C17	N6	C21	118.74(14)	N1	C1	C2	113.40(15)
O2	C2	O3	124.56(19)	O2	C2	C1	117.43(15)
O3	C2	C1	117.99(16)	N1	C3	C4	108.55(16)
N2	C4	C3	115.30(13)	N2	C4	C5	121.87(16)
C3	C4	C5	122.82(18)	C4	C5	C6	118.80(19)
C5	C6	C7	119.29(15)	C6	C7	C8	118.79(16)
N2	C8	C7	122.21(18)	N1	C9	C10	109.99(16)
N3	C10	C9	115.60(12)	N3	C10	C11	122.19(17)
C9	C10	C11	122.07(17)	C10	C11	C12	118.82(18)
C11	C12	C13	119.05(14)	C12	C13	C14	119.47(18)
N3	C14	C13	120.85(18)	N3	C14	C15	118.91(12)
C13	C14	C15	120.17(17)	C14	C15	C16	114.32(15)
C15	C16	C17	108.42(14)	N6	C17	C16	118.60(15)
N6	C17	C18	120.78(16)	C16	C17	C18	120.57(13)
C17	C18	C19	120.16(14)	C18	C19	C20	118.90(17)
C19	C20	C21	118.84(17)	N6	C21	C20	122.51(13)
N6	C21	C22	117.01(14)	C20	C21	C22	120.48(15)
N4	C22	C21	109.45(12)	N4	C23	C24	112.47(14)
O5	C24	O6	124.06(18)	O5	C24	C23	118.38(12)
O6	C24	C23	117.56(15)	N4	C25	C26	112.51(17)
N5	C26	C25	116.43(16)	N5	C26	C27	121.82(16)
C25	C26	C27	121.61(18)	C26	C27	C28	119.11(19)
C27	C28	C29	118.97(18)	C28	C29	C30	118.98(16)

N5	C30	C29	122.19(19)

Bond angles involving hydrogens (º)

atom	atom	atom	angle	atom	atom	atom	angle
Fe1	O4	H2	116.8(15)	Fe1	O4	H4	111(2)
H2	O4	H4	111(2)	Fe2	O7	H17	107.1(15)
Fe2	O7	H21	120.7(15)	H17	O7	H21	106(3)
H24	O16	H26	106(3)	H31	O17	H32	109(3)
H10	O18	H14	108(3)	N1	C1	H1A	108.9
N1	C1	H1B	108.9	C2	C1	H1A	108.9
C2	C1	H1B	108.9	H1A	C1	H1B	107.7
N1	C3	H3A	110.0	N1	C3	H3B	110.0
C4	C3	H3A	110.0	C4	C3	H3B	110.0
H3A	C3	H3B	108.4	C4	C5	H5	120.6
C6	C5	H5	120.6	C5	C6	H6	120.4
C7	C6	H6	120.4	C6	C7	H7	120.6
C8	C7	H7	120.6	N2	C8	H8	118.9
C7	C8	H8	118.9	N1	C9	H9A	109.7
N1	C9	H9B	109.7	C10	C9	H9A	109.7
C10	C9	H9B	109.7	H9A	C9	H9B	108.2
C10	C11	H11	120.6	C12	C11	H11	120.6
C11	C12	H12	120.5	C13	C12	H12	120.5
C12	C13	H13	120.3	C14	C13	H13	120.3
C14	C15	H15A	108.7	C14	C15	H15B	108.7
C16	C15	H15A	108.7	C16	C15	H15B	108.7
H15A	C15	H15B	107.6	C15	C16	H16A	110.0
C15	C16	H16B	110.0	C17	C16	H16A	110.0
C17	C16	H16B	110.0	H16A	C16	H16B	108.4
C17	C18	H18	119.9	C19	C18	H18	119.9
C18	C19	H19	120.5	C20	C19	H19	120.6
C19	C20	H20	120.6	C21	C20	H20	120.6
N4	C22	H22A	109.8	N4	C22	H22B	109.8
C21	C22	H22A	109.8	C21	C22	H22B	109.8
H22A	C22	H22B	108.2	N4	C23	H23A	109.1
N4	C23	H23B	109.1	C24	C23	H23A	109.1
C24	C23	H23B	109.1	H23A	C23	H23B	107.8
N4	C25	H25A	109.1	N4	C25	H25B	109.1
C26	C25	H25A	109.1	C26	C25	H25B	109.1
H25A	C25	H25B	107.8	C26	C27	H27	120.4
C28	C27	H27	120.4	C27	C28	H28	120.5
C29	C28	H28	120.5	C28	C29	H29	120.5
C30	C29	H29	120.5	N5	C30	H30	118.9

C29	C30	H30	118.9

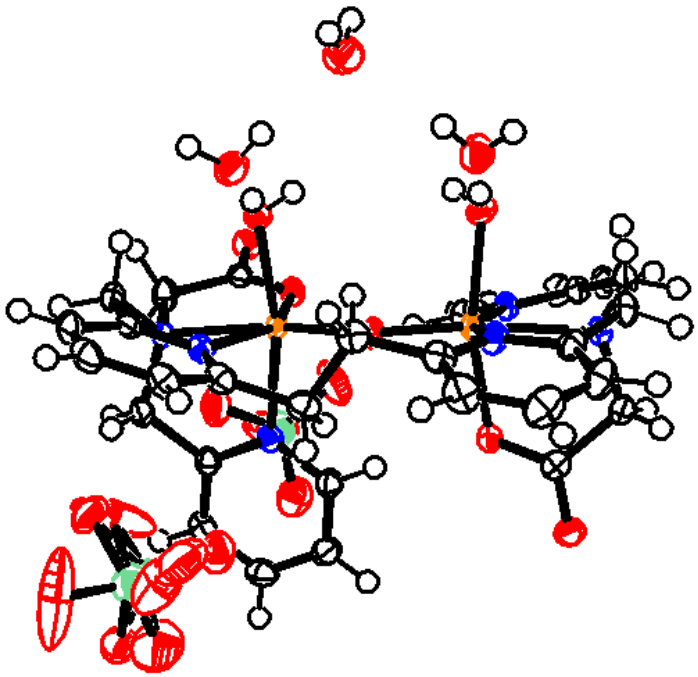


Figure S1. ORTEP view of $[Fe_2(\mu\text{-}O)(H_2O)_2(BPG_2E)](ClO_4)_2 \cdot 3H_2O$ (**2a**).

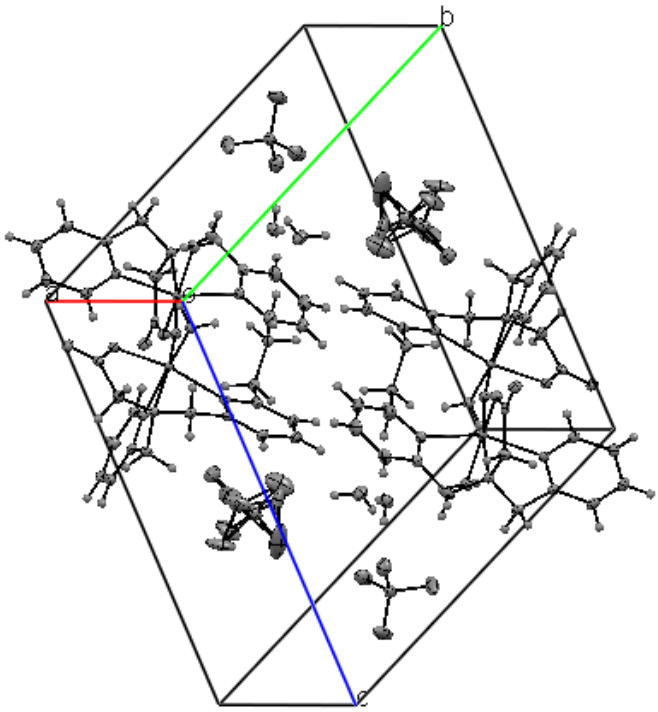


Figure S2. Crystal structure of the unit cell of **2a**.

X-ray Structure Report

for

$[Fe_2(\mu\text{-}O)(H_2O)_2(BPG_2E)](TfO)_2 \cdot 2H_2O$ **(2b)**.

Experimental

Data Collection

A red block crystal of $C_{32}H_{38}F_6Fe_2N_6O_{15}S_2$ having approximate dimensions of 0.389 x 0.145 x 0.122 mm was mounted in a loop. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using multi-layer mirror monochromated Mo-Kα radiation.

The crystal-to-detector distance was 127.00 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive triclinic cell with dimensions:

a = 11.5827(3) Å α = 114.729(8)°
b = 13.4954(3) Å β = 99.954(7)°
c = 14.5372(3) Å γ = 90.485(6)°
V = 2024.60(17) Å^3

For Z = 2 and F.W. = 1036.49, the calculated density is 1.700 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P-1 (#2)

The data were collected at a temperature of -180 ± 1°C to a maximum 2θ value of 54.9°. A total of 44 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0° in 5.00° step, at χ=45.0° and ϕ = 0.0°. The exposure rate was 60.0 [sec./°]. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.00° step, at χ=45.0° and ϕ = 180.0°. The exposure rate was 60.0 [sec./°]. The crystal-to-detector distance was 127.00 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 20161 reflections were collected, where 9218 were unique (R_{int} = 0.0303); equivalent reflections were merged.

The linear absorption coefficient, μ, for Mo-Kα radiation is 9.227 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.682 to 0.894. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[2] on F^2 was based on 9218 observed reflections and 592 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0257$$

$$wR2 = [\, \Sigma \, (\, w \, (Fo^2 - Fc^2)^2 \,) / \, \Sigma \, w(Fo^2)^2]^{1/2} = 0.0814$$

The standard deviation of an observation of unit weight[3] was 1.10. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.54 and -0.41 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[4]. Anomalous dispersion effects were included in Fcalc[5]; the values for Δf' and Δf'' were those of Creagh and McAuley[6]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[7]. All calculations were performed using the CrystalStructure[8] crystallographic software package except for refinement, which was performed using SHELXL-97[9].

References

(1) SIR2004: M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna (2005)

(2) Least Squares function minimized: (SHELXL97)

$\Sigma w(F_o^2 - F_c^2)^2$ where w = Least Squares weights.

(3) Standard deviation of an observation of unit weight:

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

where: N_o = number of observations
N_v = number of variables

(4) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(5) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(6) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(7) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(8) CrystalStructure 4.1: Crystal Structure Analysis Package, Rigaku Corporation (2000-2013). Tokyo 196-8666, Japan.

(9) SHELX97: Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Table S6. Summary of Crystal Data, Data Collection Parameters, and Structure Refinement for **2b**.

A. Crystal Data

Empirical Formula	$C_{32}H_{38}F_6Fe_2N_6O_{15}S_2$
Formula Weight	1036.49
Crystal Color, Habit	red, block
Crystal Dimensions	0.389 X 0.145 X 0.122 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 11.5827(3) Å b = 13.4954(3) Å c = 14.5372(3) Å α = 114.729(8) ^{o} β = 99.954(7) ^{o} γ = 90.485(6) ^{o} V = 2024.60(17) Å^3
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.700 g/cm^3
F_{000}	1060.00
μ(MoKα)	9.227 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoKα (λ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	50kV, 24mA
Temperature	-180.0°C
Detector Aperture	280 x 256 mm
Data Images	44 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	130.0 - 190.0°
Exposure Rate	60.0 sec./°
ω oscillation Range (χ=45.0, ϕ=180.0)	0.0 - 160.0°
Exposure Rate	60.0 sec./°
Detector Position	127.00 mm
Pixel Size	0.100 mm
$2\theta_{max}$	54.9°
No. of Reflections Measured	Total: 20161 Unique: 9218 (R_{int} = 0.0303)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.682 - 0.894)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\ w\ (Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\ \sigma^2(Fo^2) + (0.0415 \cdot P)^2 + 0.8127 \cdot P\ ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	54.9^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	9218
No. Variables	592
Reflection/Parameter Ratio	15.57
Residuals: R1 ($I>2.00\sigma(I)$)	0.0257
Residuals: R (All reflections)	0.0281
Residuals: wR2 (All reflections)	0.0814
Goodness of Fit Indicator	1.098
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Diff. Map	0.54 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.41 $e^-/Å^3$

Table S7. Fractional Atomic Coordinates Including Hydrogen Atoms and Isotropic Thermal Parameters of **2b**.

atom	x	y	z	B_{eq}
Fe1	0.388055(17)	0.380488(15)	0.754242(15)	0.731(5)
Fe2	0.193960(17)	0.217699(15)	0.811441(15)	0.744(5)
S1	0.73343(3)	0.07060(3)	0.96735(3)	1.268(6)
S2	0.23509(3)	0.34776(3)	0.38376(3)	1.076(6)
F1	0.66289(10)	0.23844(9)	1.11353(8)	2.57(2)
F2	0.84314(11)	0.20755(10)	1.15061(9)	3.34(3)
F3	0.79494(11)	0.28216(9)	1.04543(10)	3.22(2)
F4	0.24822(10)	0.13694(8)	0.27657(8)	2.55(2)
F5	0.10642(9)	0.20369(8)	0.21099(7)	1.822(16)
F6	0.28405(10)	0.23692(10)	0.19920(8)	2.74(2)
O1	0.28258(9)	0.29472(8)	0.77087(8)	0.970(16)
O2	0.40253(9)	0.51045(8)	0.89335(8)	1.059(16)
O3	0.50390(9)	0.66618(8)	1.00845(8)	1.216(17)
O4	0.54039(9)	0.33840(9)	0.82114(9)	1.144(17)
O5	0.04137(9)	0.23831(8)	0.73300(8)	1.073(16)
O6	-0.15399(9)	0.23526(9)	0.71280(8)	1.211(17)
O7	0.32368(10)	0.17622(9)	0.90027(9)	1.106(17)
O8	0.67810(11)	0.00660(10)	1.00880(10)	2.00(2)
O9	0.65488(11)	0.08721(10)	0.88648(9)	1.96(2)
O10	0.84914(10)	0.04405(9)	0.94774(9)	1.713(19)
O11	0.16622(11)	0.31457(9)	0.44120(9)	1.709(19)
O12	0.36042(10)	0.36575(9)	0.42236(9)	1.531(18)
O13	0.18668(10)	0.42891(9)	0.35120(10)	1.715(19)
O14	0.63549(11)	0.15353(10)	0.72540(9)	1.588(18)
O15	0.42055(11)	-0.01458(10)	0.82481(10)	1.79(2)
N1	0.50152(11)	0.50460(10)	0.73587(9)	0.974(18)
N2	0.26165(11)	0.45695(10)	0.68855(9)	0.955(18)
N3	0.44445(11)	0.28919(10)	0.60860(9)	0.937(18)
N4	0.06240(11)	0.14066(9)	0.86498(9)	0.890(18)
N5	0.16368(10)	0.34583(10)	0.95412(9)	0.911(18)
N6	0.17698(11)	0.04625(10)	0.69906(9)	0.948(18)
C1	0.54739(13)	0.59212(12)	0.84000(11)	1.24(2)
C2	0.47925(12)	0.58986(11)	0.91983(11)	0.94(2)
C3	0.43040(13)	0.54616(12)	0.66586(12)	1.21(2)
C4	0.30047(13)	0.53606(12)	0.66505(11)	1.09(2)
C5	0.22300(15)	0.59989(13)	0.63469(12)	1.43(2)
C6	0.10287(15)	0.57947(13)	0.62563(12)	1.62(3)

Table S7. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
C7	0.06335(14)	0.49637(13)	0.64843(12)	1.50(2)
C8	0.14499(13)	0.43759(12)	0.68013(11)	1.22(2)
C9	0.59632(13)	0.44270(12)	0.68714(11)	1.20(2)
C10	0.54452(13)	0.33459(12)	0.60023(11)	1.07(2)
C11	0.59919(14)	0.28447(13)	0.51681(12)	1.40(2)
C12	0.54998(14)	0.18460(13)	0.43848(12)	1.52(2)
C13	0.44685(14)	0.13836(12)	0.44621(11)	1.33(2)
C14	0.39428(13)	0.19268(12)	0.53109(11)	1.06(2)
C15	0.28411(13)	0.14169(12)	0.54129(11)	1.11(2)
C16	0.31768(13)	0.07030(12)	0.59985(11)	1.12(2)
C17	0.21533(13)	0.00822(12)	0.60887(11)	1.09(2)
C18	0.16508(15)	-0.09024(13)	0.52683(12)	1.51(2)
C19	0.07652(15)	-0.15111(13)	0.53826(13)	1.78(3)
C20	0.04363(14)	-0.11576(12)	0.63384(12)	1.46(2)
C21	0.09679(13)	-0.01763(11)	0.71292(11)	1.05(2)
C22	0.07616(13)	0.02168(11)	0.82159(11)	1.08(2)
C23	-0.05661(12)	0.16288(12)	0.82569(11)	1.07(2)
C24	-0.05760(13)	0.21571(11)	0.75057(10)	0.92(2)
C25	0.09112(13)	0.19225(11)	0.97943(11)	0.99(2)
C26	0.11336(12)	0.31438(11)	1.01619(11)	0.95(2)
C27	0.08608(13)	0.38967(12)	1.10769(11)	1.18(2)
C28	0.11294(13)	0.50068(12)	1.13710(12)	1.31(2)
C29	0.16490(13)	0.53280(12)	1.07367(12)	1.21(2)
C30	0.18883(13)	0.45354(12)	0.98271(11)	1.09(2)
C31	0.75971(15)	0.20690(14)	1.07477(14)	1.91(3)
C32	0.21828(14)	0.22522(13)	0.26176(11)	1.40(2)

$$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$$

Table S7a. Atomic coordinates and B_{iso} involving hydrogen atoms of **2b**.

atom	x	y	z	B_{iso}
H1A	0.54294	0.66415	0.83738	1.484
H1B	0.63121	0.58365	0.86147	1.484
H2	0.56133	0.27982	0.78952	1.373
H3A	0.44419	0.50451	0.59485	1.454
H3B	0.45701	0.62406	0.68819	1.454
H4	0.53130	0.34471	0.87963	1.373
H5	0.25200	0.65688	0.62031	1.716
H6	0.04860	0.62162	0.60420	1.943
H7	-0.01839	0.48033	0.64230	1.799
H8	0.11806	0.38145	0.69662	1.464
H9A	0.65367	0.42999	0.73920	1.443
H9B	0.63837	0.48576	0.66019	1.443
H10	0.37300	0.22338	0.93200	1.327
H11	0.66963	0.31819	0.51335	1.680
H12	0.58614	0.14852	0.38062	1.830
H13	0.41199	0.06959	0.39359	1.593
H14	0.34837	0.12113	0.87758	1.327
H15A	0.23677	0.09600	0.47195	1.330
H15B	0.23614	0.19975	0.57939	1.330
H16A	0.37156	0.01724	0.56415	1.349
H16B	0.36130	0.11805	0.67016	1.349
H17	0.69955	0.17567	0.72440	1.906
H18	0.19167	-0.11543	0.46323	1.810
H19	0.03873	-0.21607	0.48169	2.132
H20	-0.01410	-0.15800	0.64470	1.749
H21	0.64768	0.13310	0.76766	1.906
H22A	0.00433	-0.01851	0.82172	1.292
H22B	0.14353	0.00704	0.86484	1.292
H23A	-0.09060	0.21190	0.88497	1.283
H23B	-0.10758	0.09311	0.79038	1.283
H24	0.48586	0.00315	0.83380	2.151
H25A	0.16196	0.16287	1.00397	1.191
H25B	0.02488	0.17588	1.00725	1.191
H26	0.40266	-0.03196	0.87060	2.151
H27	0.04966	0.36585	1.14958	1.417
H28	0.09590	0.55381	1.19984	1.574
H29	0.18385	0.60824	1.09238	1.450

Table S7a. Atomic coordinates and B_{iso} involving hydrogens/B_{eq} (continued).

atom	x	y	z	B_{eq}
H30	0.22402	0.47576	0.93918	1.307

Table S8. Anisotropic Thermal Parameters for Non-hydrogen Atoms in **2b**.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe1	0.00812(10)	0.01063(10)	0.00908(10)	-0.00074(7)	0.00125(8)	0.00446(8)
Fe2	0.00886(10)	0.00984(10)	0.00899(10)	-0.00148(7)	0.00107(8)	0.00374(8)
S1	0.01464(18)	0.01883(18)	0.01720(18)	0.00156(13)	0.00397(14)	0.00975(15)
S2	0.01250(17)	0.01435(16)	0.01452(17)	-0.00070(13)	0.00142(13)	0.00710(14)
F1	0.0324(6)	0.0373(6)	0.0289(6)	0.0186(5)	0.0132(5)	0.0120(5)
F2	0.0377(7)	0.0383(6)	0.0278(6)	0.0149(5)	-0.0096(5)	-0.0024(5)
F3	0.0454(7)	0.0199(5)	0.0559(8)	-0.0000(5)	0.0169(6)	0.0125(5)
F4	0.0440(7)	0.0185(5)	0.0242(5)	0.0083(4)	-0.0059(5)	0.0041(4)
F5	0.0197(5)	0.0272(5)	0.0191(5)	-0.0062(4)	-0.0057(4)	0.0105(4)
F6	0.0305(6)	0.0489(7)	0.0195(5)	-0.0062(5)	0.0104(4)	0.0076(5)
O1	0.0122(5)	0.0124(5)	0.0119(5)	-0.0011(4)	0.0033(4)	0.0045(4)
O2	0.0134(5)	0.0135(5)	0.0118(5)	-0.0030(4)	0.0015(4)	0.0043(4)
O3	0.0176(5)	0.0145(5)	0.0113(5)	-0.0038(4)	-0.0004(4)	0.0041(4)
O4	0.0131(5)	0.0190(5)	0.0130(5)	0.0034(4)	0.0024(4)	0.0084(4)
O5	0.0121(5)	0.0168(5)	0.0131(5)	-0.0011(4)	0.0010(4)	0.0080(4)
O6	0.0133(5)	0.0186(5)	0.0137(5)	0.0021(4)	0.0009(4)	0.0071(4)
O7	0.0117(5)	0.0116(5)	0.0159(5)	-0.0018(4)	-0.0017(4)	0.0048(4)
O8	0.0239(6)	0.0297(6)	0.0313(6)	0.0018(5)	0.0101(5)	0.0199(6)
O9	0.0238(6)	0.0319(7)	0.0224(6)	0.0030(5)	0.0013(5)	0.0164(5)
O10	0.0170(6)	0.0223(6)	0.0249(6)	0.0026(4)	0.0072(5)	0.0080(5)
O11	0.0255(6)	0.0224(6)	0.0170(5)	-0.0054(5)	0.0063(5)	0.0077(5)
O12	0.0142(5)	0.0207(6)	0.0206(5)	-0.0009(4)	-0.0024(4)	0.0085(5)
O13	0.0159(5)	0.0212(6)	0.0330(6)	0.0031(4)	0.0030(5)	0.0169(5)
O14	0.0149(6)	0.0264(6)	0.0222(6)	0.0023(5)	0.0028(5)	0.0138(5)
O15	0.0195(6)	0.0257(6)	0.0240(6)	0.0031(5)	0.0051(5)	0.0113(5)
N1	0.0112(6)	0.0152(6)	0.0105(5)	-0.0008(4)	0.0017(5)	0.0055(5)
N2	0.0119(6)	0.0138(6)	0.0105(5)	0.0010(4)	0.0015(5)	0.0053(5)
N3	0.0118(6)	0.0142(6)	0.0107(5)	0.0018(4)	0.0022(5)	0.0063(5)
N4	0.0114(6)	0.0113(6)	0.0106(5)	-0.0008(4)	0.0002(5)	0.0050(5)
N5	0.0099(5)	0.0132(6)	0.0111(5)	-0.0004(4)	0.0007(5)	0.0053(5)
N6	0.0115(6)	0.0119(6)	0.0121(6)	-0.0003(4)	0.0012(5)	0.0050(5)
C1	0.0148(7)	0.0163(7)	0.0127(7)	-0.0052(5)	0.0010(6)	0.0039(6)
C2	0.0106(6)	0.0129(6)	0.0126(6)	0.0007(5)	-0.0006(5)	0.0070(5)
C3	0.0159(7)	0.0172(7)	0.0159(7)	-0.0012(5)	0.0022(6)	0.0103(6)
C4	0.0163(7)	0.0152(7)	0.0094(6)	0.0014(5)	0.0028(5)	0.0047(5)
C5	0.0241(8)	0.0177(7)	0.0162(7)	0.0049(6)	0.0050(6)	0.0102(6)
C6	0.0218(8)	0.0238(8)	0.0173(7)	0.0092(6)	0.0035(6)	0.0100(6)

Table S8. Anisotropic displacement parameters (continued).

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C7	0.0140(7)	0.0246(8)	0.0170(7)	0.0050(6)	0.0027(6)	0.0076(6)
C8	0.0139(7)	0.0179(7)	0.0136(7)	0.0004(5)	0.0018(6)	0.0062(6)
C9	0.0111(7)	0.0199(7)	0.0157(7)	-0.0005(5)	0.0044(6)	0.0079(6)
C10	0.0117(7)	0.0184(7)	0.0135(7)	0.0027(5)	0.0025(5)	0.0097(6)
C11	0.0151(7)	0.0240(8)	0.0190(7)	0.0045(6)	0.0080(6)	0.0120(6)
C12	0.0222(8)	0.0234(8)	0.0170(7)	0.0097(6)	0.0096(6)	0.0106(6)
C13	0.0211(8)	0.0158(7)	0.0136(7)	0.0049(6)	0.0039(6)	0.0061(6)
C14	0.0148(7)	0.0141(7)	0.0124(6)	0.0031(5)	0.0013(5)	0.0071(6)
C15	0.0143(7)	0.0146(7)	0.0114(6)	0.0003(5)	0.0000(5)	0.0047(5)
C16	0.0143(7)	0.0151(7)	0.0138(6)	0.0022(5)	0.0038(6)	0.0062(6)
C17	0.0145(7)	0.0137(7)	0.0131(7)	0.0027(5)	0.0019(6)	0.0058(6)
C18	0.0226(8)	0.0175(7)	0.0134(7)	-0.0002(6)	0.0034(6)	0.0030(6)
C19	0.0249(8)	0.0159(7)	0.0172(7)	-0.0051(6)	0.0001(6)	-0.0004(6)
C20	0.0175(7)	0.0154(7)	0.0194(7)	-0.0043(6)	0.0015(6)	0.0052(6)
C21	0.0126(7)	0.0121(6)	0.0147(7)	0.0001(5)	0.0017(5)	0.0057(6)
C22	0.0148(7)	0.0106(6)	0.0150(7)	-0.0021(5)	0.0022(6)	0.0054(5)
C23	0.0096(6)	0.0178(7)	0.0148(7)	-0.0004(5)	0.0004(5)	0.0092(6)
C24	0.0136(7)	0.0102(6)	0.0084(6)	0.0001(5)	0.0012(5)	0.0015(5)
C25	0.0144(7)	0.0138(6)	0.0095(6)	-0.0012(5)	0.0006(5)	0.0056(5)
C26	0.0097(6)	0.0150(7)	0.0113(6)	-0.0001(5)	-0.0003(5)	0.0063(5)
C27	0.0156(7)	0.0175(7)	0.0121(6)	0.0007(5)	0.0030(6)	0.0065(6)
C28	0.0166(7)	0.0168(7)	0.0133(7)	0.0022(6)	0.0025(6)	0.0036(6)
C29	0.0138(7)	0.0135(7)	0.0170(7)	0.0005(5)	0.0018(6)	0.0054(6)
C30	0.0119(7)	0.0147(7)	0.0153(7)	-0.0006(5)	0.0015(5)	0.0073(6)
C31	0.0218(8)	0.0228(8)	0.0261(8)	0.0072(6)	0.0041(7)	0.0086(7)
C32	0.0181(7)	0.0214(7)	0.0129(7)	-0.0005(6)	0.0002(6)	0.0075(6)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S9. Fragment Analysis of **2b**.

fragment: 1					
	Fe(1)	Fe(2)	O(1)	O(2)	O(3)
	O(4)	O(5)	O(6)	O(7)	N(1)
	N(2)	N(3)	N(4)	N(5)	N(6)
	C(1)	C(2)	C(3)	C(4)	C(5)
	C(6)	C(7)	C(8)	C(9)	C(10)
	C(11)	C(12)	C(13)	C(14)	C(15)
	C(16)	C(17)	C(18)	C(19)	C(20)
	C(21)	C(22)	C(23)	C(24)	C(25)
	C(26)	C(27)	C(28)	C(29)	C(30)
fragment: 2					
	S(1)	F(1)	F(2)	F(3)	O(8)
	O(9)	O(10)	C(31)		
fragment: 3					
	S(2)	F(4)	F(5)	F(6)	O(11)
	O(12)	O(13)	C(32)		
fragment: 4					
	O(14)				
fragment: 5					
	O(15)				

Table S10. Bond Distances and Bond Angles of **2b**.

Bond Distances (Å)

atom	atom	distance	atom	atom	distance
Fe1	O1	1.7897(12)	Fe1	O2	2.0259(9)
Fe1	O4	2.0658(12)	Fe1	N1	2.2500(15)
Fe1	N2	2.1183(14)	Fe1	N3	2.1764(12)
Fe2	O1	1.7849(13)	Fe2	O5	2.0195(11)
Fe2	O7	2.0461(13)	Fe2	N4	2.2514(15)
Fe2	N5	2.1625(11)	Fe2	N6	2.1863(11)
S1	O8	1.4420(17)	S1	O9	1.4540(14)
S1	O10	1.4355(12)	S1	C31	1.8269(15)
S2	O11	1.4392(16)	S2	O12	1.4421(12)
S2	O13	1.4457(15)	S2	C32	1.8274(13)
F1	C31	1.335(2)	F2	C31	1.331(2)
F3	C31	1.340(3)	F4	C32	1.335(2)
F5	C32	1.3384(18)	F6	C32	1.338(2)
O2	C2	1.2676(18)	O3	C2	1.2489(15)
O5	C24	1.278(2)	O6	C24	1.2377(18)
N1	C1	1.4779(16)	N1	C3	1.491(2)
N1	C9	1.481(2)	N2	C4	1.345(2)
N2	C8	1.349(2)	N3	C10	1.354(2)
N3	C14	1.3552(16)	N4	C22	1.4809(18)
N4	C23	1.4813(19)	N4	C25	1.4830(18)
N5	C26	1.354(2)	N5	C30	1.348(2)
N6	C17	1.350(2)	N6	C21	1.358(2)
C1	C2	1.522(2)	C3	C4	1.508(2)
C4	C5	1.391(3)	C5	C6	1.389(2)
C6	C7	1.390(3)	C7	C8	1.380(2)
C9	C10	1.5052(17)	C10	C11	1.384(2)
C11	C12	1.3844(19)	C12	C13	1.386(3)
C13	C14	1.393(2)	C14	C15	1.503(2)
C15	C16	1.543(3)	C16	C17	1.501(2)
C17	C18	1.3956(18)	C18	C19	1.383(3)
C19	C20	1.391(3)	C20	C21	1.3864(17)
C21	C22	1.505(2)	C23	C24	1.532(3)
C25	C26	1.509(2)	C26	C27	1.3862(19)
C27	C28	1.391(2)	C28	C29	1.386(3)
C29	C30	1.385(2)			

Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
O4	H2	0.796	O4	H4	0.844
O7	H10	0.775	O7	H14	0.758
O14	H17	0.802	O14	H21	0.765
O15	H24	0.764	O15	H26	0.848
C1	H1A	0.990	C1	H1B	0.990
C3	H3A	0.990	C3	H3B	0.990
C5	H5	0.950	C6	H6	0.950
C7	H7	0.950	C8	H8	0.950
C9	H9A	0.990	C9	H9B	0.990
C11	H11	0.950	C12	H12	0.950
C13	H13	0.950	C15	H15A	0.990
C15	H15B	0.990	C16	H16A	0.990
C16	H16B	0.990	C18	H18	0.950
C19	H19	0.950	C20	H20	0.950
C22	H22A	0.990	C22	H22B	0.990
C23	H23A	0.990	C23	H23B	0.990
C25	H25A	0.990	C25	H25B	0.990
C27	H27	0.950	C28	H28	0.950
C29	H29	0.950	C30	H30	0.950

Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
O1	Fe1	O2	98.00(5)	O1	Fe1	O4	99.21(5)
O1	Fe1	N1	172.12(5)	O1	Fe1	N2	95.26(5)
O1	Fe1	N3	108.95(5)	O2	Fe1	O4	85.03(4)
O2	Fe1	N1	78.31(5)	O2	Fe1	N2	89.72(4)
O2	Fe1	N3	152.54(5)	O4	Fe1	N1	87.48(5)
O4	Fe1	N2	165.16(5)	O4	Fe1	N3	85.55(5)
N1	Fe1	N2	77.86(5)	N1	Fe1	N3	75.55(5)
N2	Fe1	N3	92.90(5)	O1	Fe2	O5	94.02(5)
O1	Fe2	O7	99.22(5)	O1	Fe2	N4	171.05(5)
O1	Fe2	N5	100.10(5)	O1	Fe2	N6	108.10(5)
O5	Fe2	O7	166.76(5)	O5	Fe2	N4	79.16(5)
O5	Fe2	N5	91.18(4)	O5	Fe2	N6	88.95(4)
O7	Fe2	N4	87.69(5)	O7	Fe2	N5	86.75(5)
O7	Fe2	N6	86.74(5)	N4	Fe2	N5	74.48(5)
N4	Fe2	N6	77.79(5)	N5	Fe2	N6	151.73(6)

O8	S1	O9	113.65(8)	O8	S1	O10	115.69(8)
O8	S1	C31	102.91(9)	O9	S1	O10	115.29(8)
O9	S1	C31	103.52(8)	O10	S1	C31	103.44(7)
O11	S2	O12	115.79(8)	O11	S2	O13	115.29(8)
O11	S2	C32	102.47(7)	O12	S2	O13	114.42(8)
O12	S2	C32	103.75(7)	O13	S2	C32	102.49(8)
Fe1	O1	Fe2	169.12(6)	Fe1	O2	C2	119.94(10)
Fe2	O5	C24	120.89(11)	Fe1	N1	C1	107.57(11)
Fe1	N1	C3	109.19(9)	Fe1	N1	C9	104.62(10)
C1	N1	C3	112.78(12)	C1	N1	C9	112.17(11)
C3	N1	C9	110.13(13)	Fe1	N2	C4	118.07(10)
Fe1	N2	C8	122.35(13)	C4	N2	C8	119.18(15)
Fe1	N3	C10	113.75(8)	Fe1	N3	C14	127.42(12)
C10	N3	C14	118.75(13)	Fe2	N4	C22	107.04(10)
Fe2	N4	C23	107.90(11)	Fe2	N4	C25	106.83(9)
C22	N4	C23	111.36(10)	C22	N4	C25	111.90(13)
C23	N4	C25	111.52(11)	Fe2	N5	C26	116.99(9)
Fe2	N5	C30	124.07(12)	C26	N5	C30	118.91(12)
Fe2	N6	C17	125.44(12)	Fe2	N6	C21	113.40(9)
C17	N6	C21	119.08(11)	N1	C1	C2	112.35(12)
O2	C2	O3	123.89(16)	O2	C2	C1	118.52(11)
O3	C2	C1	117.58(13)	N1	C3	C4	112.48(16)
N2	C4	C3	116.55(15)	N2	C4	C5	121.34(15)
C3	C4	C5	121.97(17)	C4	C5	C6	119.35(18)
C5	C6	C7	118.93(17)	C6	C7	C8	118.80(15)
N2	C8	C7	122.38(17)	N1	C9	C10	109.84(12)
N3	C10	C9	117.09(13)	N3	C10	C11	122.37(12)
C9	C10	C11	120.53(15)	C10	C11	C12	119.20(16)
C11	C12	C13	118.63(15)	C12	C13	C14	120.05(12)
N3	C14	C13	120.95(15)	N3	C14	C15	118.63(13)
C13	C14	C15	120.32(12)	C14	C15	C16	109.32(13)
C15	C16	C17	114.69(13)	N6	C17	C16	118.95(11)
N6	C17	C18	120.79(16)	C16	C17	C18	120.18(14)
C17	C18	C19	119.91(16)	C18	C19	C20	119.00(13)
C19	C20	C21	118.66(17)	N6	C21	C20	122.13(15)
N6	C21	C22	115.27(11)	C20	C21	C22	122.47(16)
N4	C22	C21	109.90(14)	N4	C23	C24	113.57(13)
O5	C24	O6	124.73(16)	O5	C24	C23	117.62(13)
O6	C24	C23	117.64(14)	N4	C25	C26	108.46(14)
N5	C26	C25	115.28(12)	N5	C26	C27	121.95(14)
C25	C26	C27	122.77(16)	C26	C27	C28	118.86(17)
C27	C28	C29	119.15(13)	C28	C29	C30	119.17(15)
N5	C30	C29	121.96(17)	S1	C31	F1	111.64(11)
S1	C31	F2	110.30(13)	S1	C31	F3	111.43(13)

F1	C31	F2	107.72(16)	F1	C31	F3	107.68(15)
F2	C31	F3	107.91(14)	S2	C32	F4	111.71(11)
S2	C32	F5	110.96(11)	S2	C32	F6	111.73(11)
F4	C32	F5	107.04(13)	F4	C32	F6	108.07(14)
F5	C32	F6	107.09(13)				

Bond angles involving hydrogens (º)

atom	atom	atom	angle	atom	atom	atom	angle
Fe1	O4	H2	117.3	Fe1	O4	H4	107.2
H2	O4	H4	110.1	Fe2	O7	H10	112.6
Fe2	O7	H14	120.1	H10	O7	H14	111.9
H17	O14	H21	103.4	H24	O15	H26	113.7
N1	C1	H1A	109.1	N1	C1	H1B	109.1
C2	C1	H1A	109.1	C2	C1	H1B	109.1
H1A	C1	H1B	107.9	N1	C3	H3A	109.1
N1	C3	H3B	109.1	C4	C3	H3A	109.1
C4	C3	H3B	109.1	H3A	C3	H3B	107.8
C4	C5	H5	120.3	C6	C5	H5	120.3
C5	C6	H6	120.5	C7	C6	H6	120.5
C6	C7	H7	120.6	C8	C7	H7	120.6
N2	C8	H8	118.8	C7	C8	H8	118.8
N1	C9	H9A	109.7	N1	C9	H9B	109.7
C10	C9	H9A	109.7	C10	C9	H9B	109.7
H9A	C9	H9B	108.2	C10	C11	H11	120.4
C12	C11	H11	120.4	C11	C12	H12	120.7
C13	C12	H12	120.7	C12	C13	H13	120.0
C14	C13	H13	120.0	C14	C15	H15A	109.8
C14	C15	H15B	109.8	C16	C15	H15A	109.8
C16	C15	H15B	109.8	H15A	C15	H15B	108.3
C15	C16	H16A	108.6	C15	C16	H16B	108.6
C17	C16	H16A	108.6	C17	C16	H16B	108.6
H16A	C16	H16B	107.6	C17	C18	H18	120.0
C19	C18	H18	120.0	C18	C19	H19	120.5
C20	C19	H19	120.5	C19	C20	H20	120.7
C21	C20	H20	120.7	N4	C22	H22A	109.7
N4	C22	H22B	109.7	C21	C22	H22A	109.7
C21	C22	H22B	109.7	H22A	C22	H22B	108.2
N4	C23	H23A	108.9	N4	C23	H23B	108.9
C24	C23	H23A	108.8	C24	C23	H23B	108.8
H23A	C23	H23B	107.7	N4	C25	H25A	110.0
N4	C25	H25B	110.0	C26	C25	H25A	110.0
C26	C25	H25B	110.0	H25A	C25	H25B	108.4

C26	C27	H27	120.6	C28	C27	H27	120.6
C27	C28	H28	120.4	C29	C28	H28	120.4
C28	C29	H29	120.4	C30	C29	H29	120.4
N5	C30	H30	119.0	C29	C30	H30	119.0

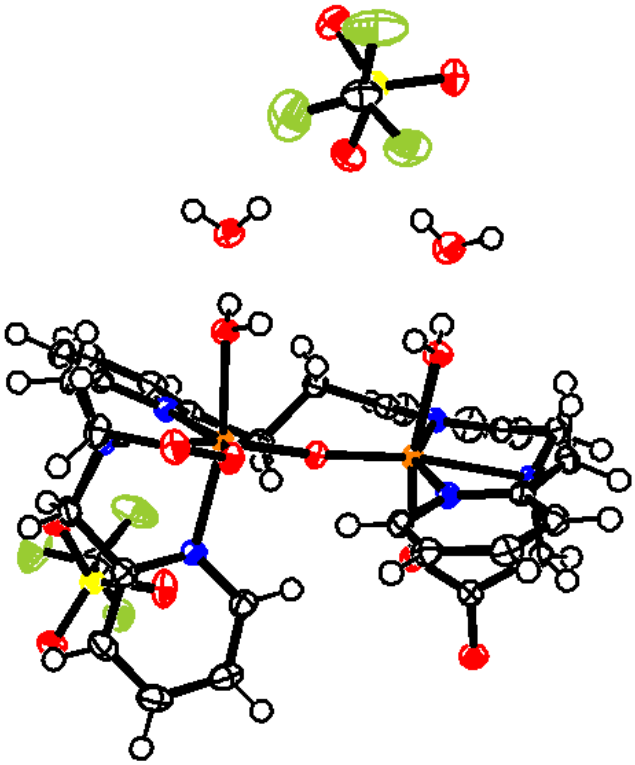


Figure S3. ORTEP view of **2b**.

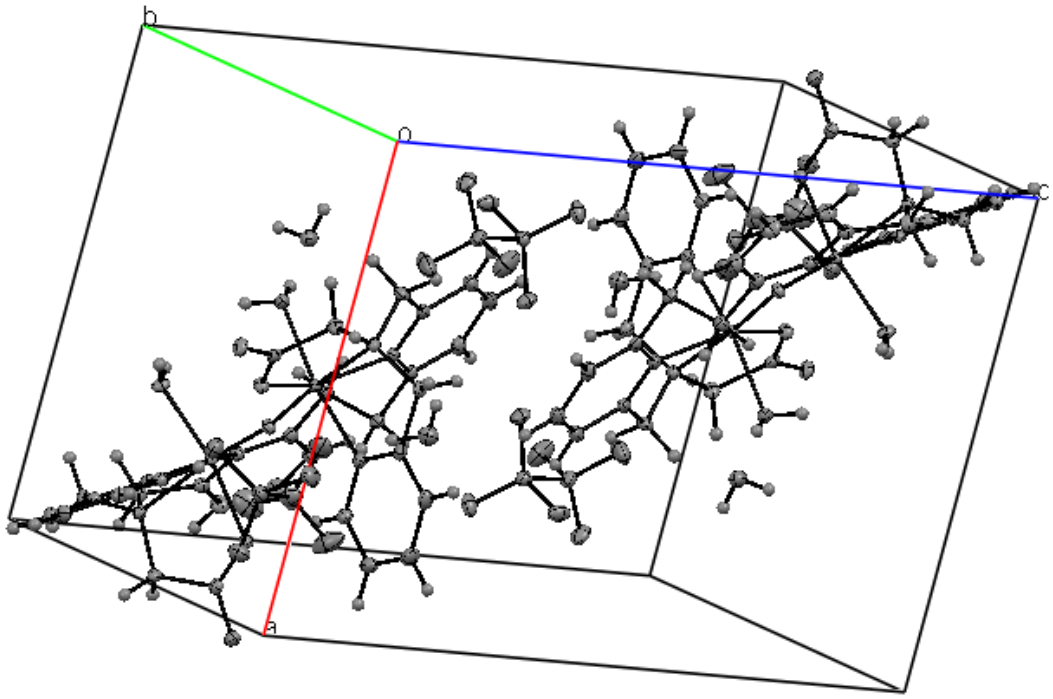


Figure S4. Crystal structure of the unit cell of **2b**.

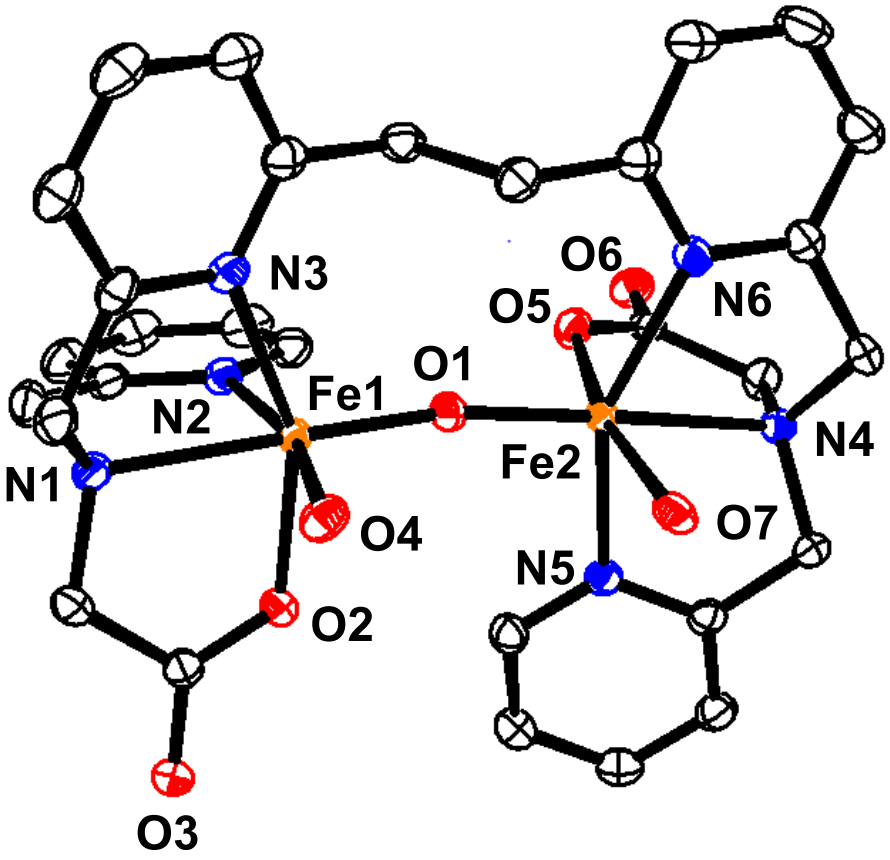
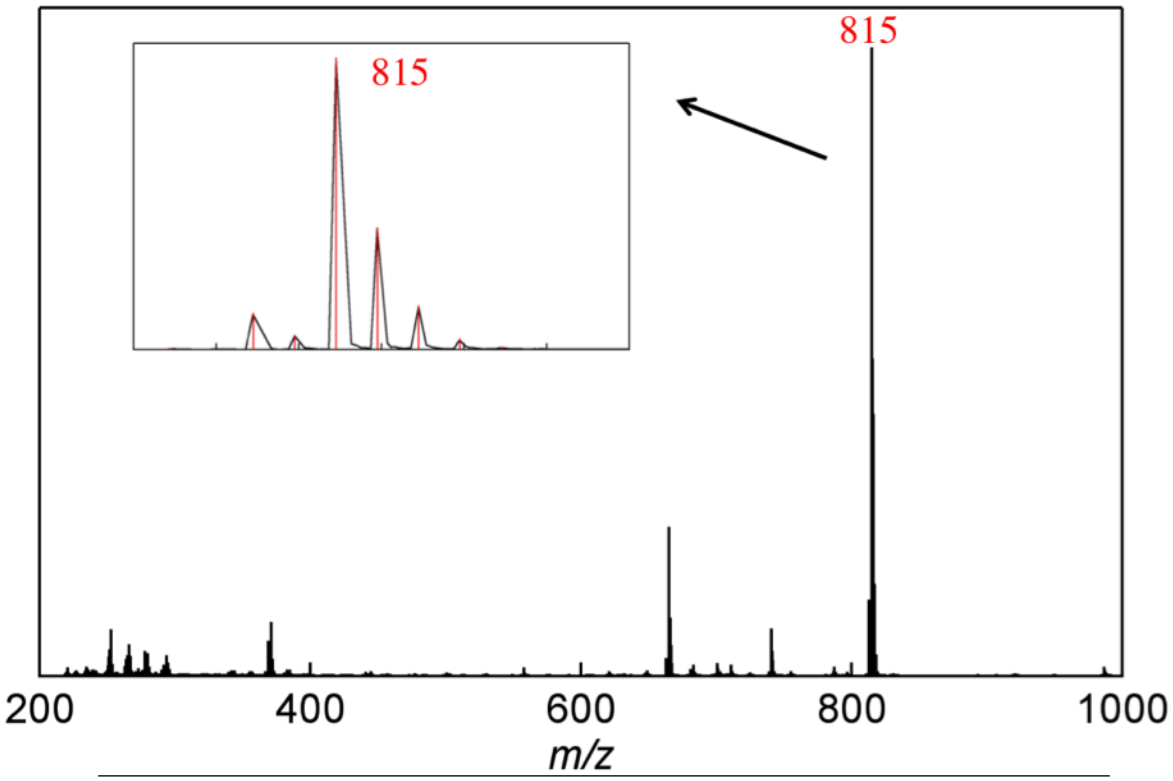


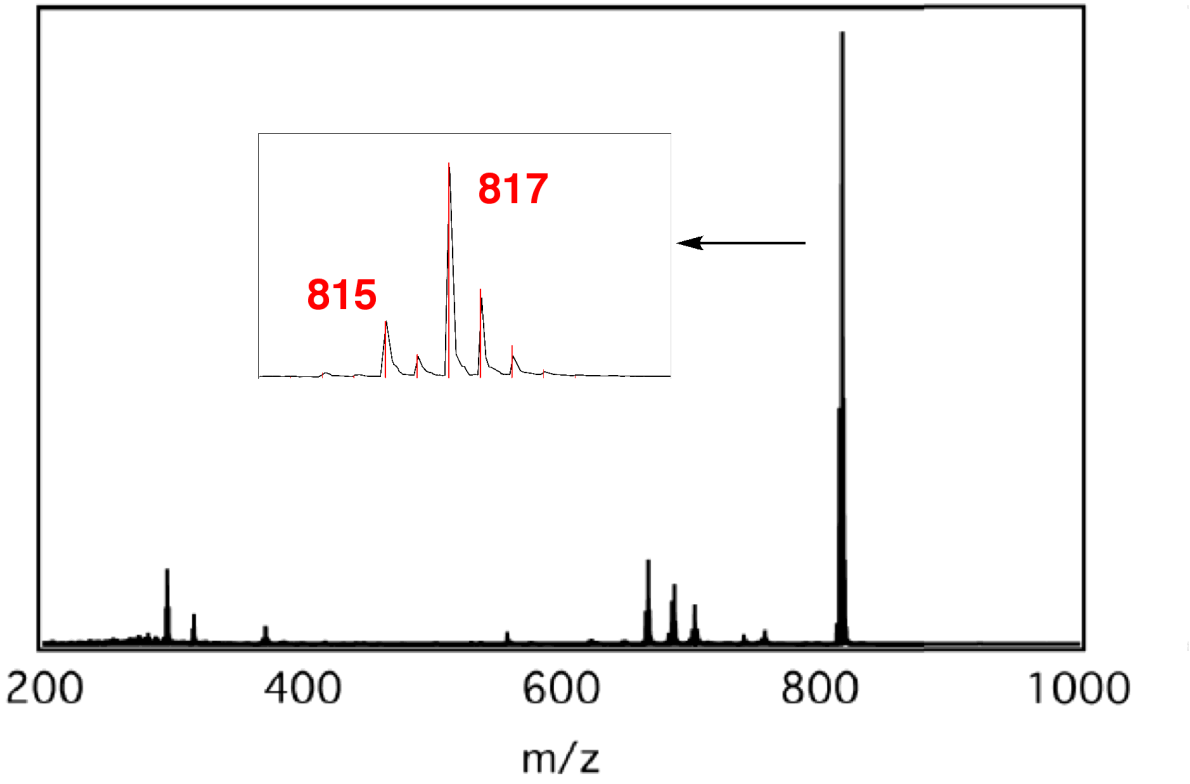
Figure S5. ORTEP view (70% probability) of the cationic portion of **2b**. Selected bond distances [Å] and angle [°]: Fe1···Fe2 3.559 Å, $O_{aq}\cdots O_{aq}$ 3.926 Å, Fe1-O1 1.7897(12), Fe1-O2 2.0259(9), Fe1-O4 2.0658(12), Fe1-N1 2.2500(15), Fe1-N2 2.1183(14), Fe1-N3 2.1764(12), Fe2-O1 1.7849(13), Fe2-O5 2.0195(11), Fe2-O7 2.0461(13), Fe2-N4 2.2514(15), Fe2-N5 2.1625(11), Fe2-N6 2.1863(11); Fe1-O1-Fe2 169.12(6).



m/z	fragment
815	[**2b** – $2H_2O$ – TfO]$^+$

2b = 1000

Figure S6. ESI mass spectrum of $[Fe_2(\mu\text{-}O)(H_2O)_2(BPG_2E)](OTf)_2$ (**2b**) in MeCN/H_2O (10:1, v/v) at room temperature.



m/z	fragment
817	[^{18}O-labeled **2b** – 2H$_2$^{18}O - OTf]$^+$

^{18}O-labeled **2b** = 1006

Figure S7. ESI mass spectrum of [Fe$_2$(μ-^{18}O)(H$_2$^{18}O)$_2$(BPG$_2$E)](OTf)$_2$ (^{18}O-labeled **2b**) in MeCN/H$_2$O (10:1, v/v) at room temperature. Inset shows the isotope pattern of molecular ion peak, where the red line shows theoretical isotope pattern calculated for a 14 : 86 mixture of **2b** and ^{18}O-labeled **2b**.

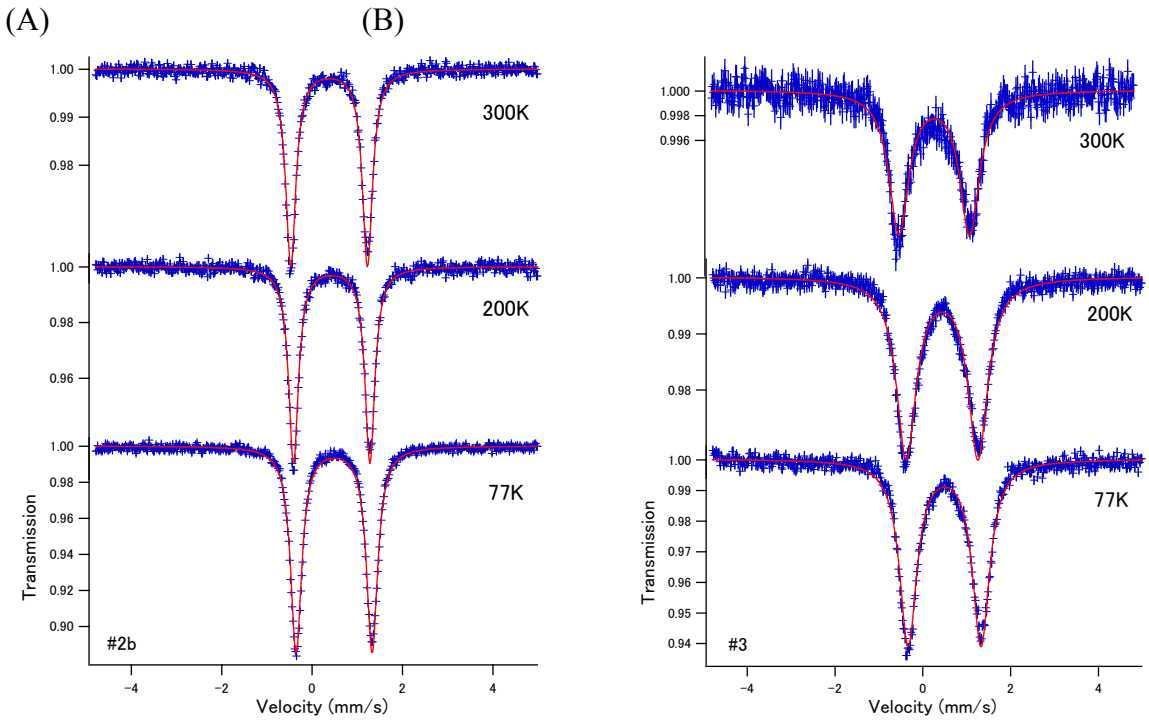


Figure S8. The Mössbauer spectra of starting material **2b** (A) and decomposed product (B) of **3** at 77 K.

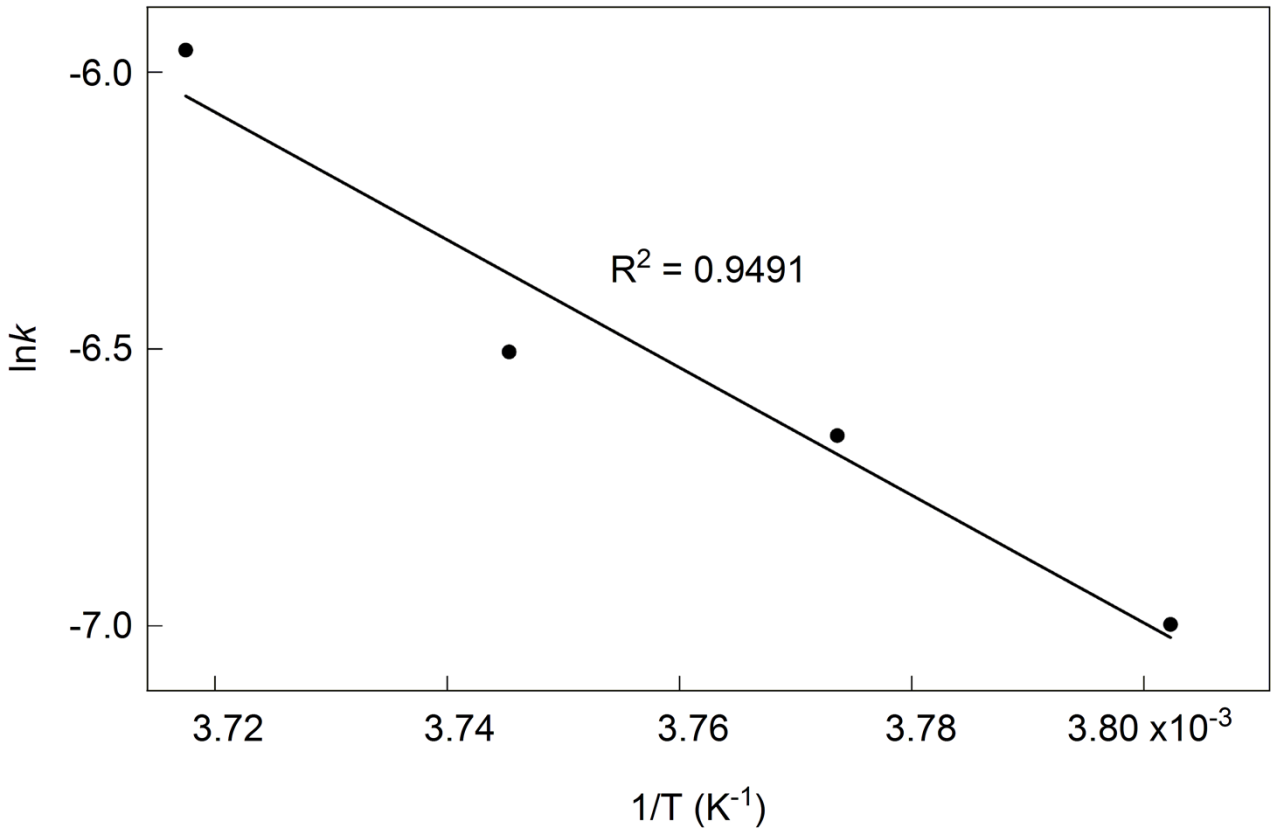


Figure S9. Arrhenius plot for thermal decomposition of **3**.

Table S11. Oxidation of alkenes with H_2O_2 catalyzed by **2b**.

	Yield[a] [%] epoxide	benzaldehyde	turnover number
trans-β-methylstyrene	99	0	9.9 [b]
	99	0	>120 [c]
	70	0	7[d]
	6	98	10.4[e]
cis-β-methylstyrene	37 (*trans*) and 6 (*cis*)	0	4.3[b]
	0.7 (*trans*) and 0.3 (*cis*)	40	4.1[e]
cyclooctene	15	0	1.5[b]

[a] Yield based on the H_2O_2 used. [b] 10 equiv of H_2O_2 were added using syringe pump over 5 h under the conditions described in the experimental section. [c] More than 120 equiv of H_2O_2 were added over 60 h under the conditions described in the experimental section. [d] The reaction was carried out at -10°C under the same conditions as [b]. [e] The reaction was carried out under O_2-atmosphere using 10 equiv of H_2O_2.

DFT Studies

(S1) Complete reference of Gaussian09 (Reference 1)

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci,G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian09, Revision C.01*, Gaussian Inc., Wallingford, CT, 2010.

(S2) Cartesian coordinate (in Å) of 3

SCF Energy (ZPE corrected) = -4540.504673 au

Atomic Number	X	Y	Z
26	1.368211000	-0.645561000	-0.184644000
26	-1.662988000	-0.120370000	0.138702000
8	-0.010608000	-0.193771000	0.874609000
8	1.806720000	-2.583411000	0.077799000
8	0.313710000	-0.739556000	-1.730747000
8	-2.570684000	0.602488000	1.765685000
8	-0.949952000	-0.136547000	-1.632876000
7	3.439336000	-0.948157000	-1.178293000
7	2.859503000	-0.148727000	1.423496000
7	2.249702000	1.596165000	-0.813880000
7	-3.994074000	-0.508069000	-0.256332000
7	-2.034845000	-2.297413000	0.183633000
7	-2.603512000	1.934457000	-0.713937000
6	3.201785000	-2.250652000	-1.821361000
6	2.495088000	-3.203539000	-0.830071000
6	4.479945000	-1.046443000	-0.146022000
6	4.152002000	-0.344636000	1.153272000

6	5.148363000	0.002409000	2.065299000
6	4.775748000	0.542074000	3.291799000
6	3.423714000	0.722918000	3.572734000
6	2.494735000	0.366355000	2.602266000
6	3.673273000	0.150812000	-2.110769000
6	3.418999000	1.489638000	-1.461536000
6	4.314627000	2.548738000	-1.571779000
6	3.974292000	3.767218000	-0.990688000
6	2.744803000	3.888546000	-0.358839000
6	1.887973000	2.782429000	-0.299085000
6	0.486256000	2.904850000	0.226783000
6	-0.460262000	3.027975000	-0.984693000
6	-1.933124000	3.092733000	-0.685845000
6	-4.595165000	0.613677000	-0.974377000
6	-4.081825000	-1.764903000	-0.992092000
6	-1.112250000	-3.147587000	0.649805000
1	4.124299000	-2.715601000	-2.195784000
1	2.525965000	-2.095285000	-2.670697000
1	5.448821000	-0.691804000	-0.530721000
1	4.617817000	-2.107998000	0.093919000
1	6.195147000	-0.156416000	1.818070000
1	5.533895000	0.817497000	4.021097000
1	1.420668000	0.478966000	2.738220000
1	2.956038000	0.037898000	-2.932737000
1	4.686888000	0.118051000	-2.543300000
1	5.255156000	2.417299000	-2.099810000
1	4.655605000	4.613269000	-1.042256000
1	2.433466000	4.831396000	0.082525000
1	0.396735000	3.782198000	0.878010000
1	0.228045000	2.009383000	0.804098000
1	-0.185142000	3.923745000	-1.557444000
1	-0.306820000	2.154449000	-1.628577000
1	-4.454792000	0.442047000	-2.049308000
1	-0.252043000	-2.700727000	1.131587000
8	2.619424000	-4.409420000	-0.966084000
1	3.091752000	1.134124000	4.521244000
6	-3.124524000	-2.784853000	-0.429594000
6	-1.223758000	-4.525494000	0.500347000
6	-2.355445000	-5.034998000	-0.123709000
6	-3.329334000	-4.151584000	-0.583243000
1	-0.421766000	-5.165660000	0.853167000
1	-2.483180000	-6.106964000	-0.253336000
1	-4.232299000	-4.512419000	-1.068914000
6	-2.600510000	4.307281000	-0.492113000

6	-3.982075000	4.308692000	-0.360146000
6	-4.673999000	3.105753000	-0.478939000
6	-3.940744000	1.940112000	-0.667104000
1	-2.034834000	5.234853000	-0.461605000
1	-4.520083000	5.238716000	-0.193403000
1	-5.758395000	3.070765000	-0.426105000
1	-5.680494000	0.671693000	-0.794693000
1	-3.786006000	-1.566522000	-2.031138000
1	-5.105176000	-2.176206000	-1.013681000
6	-3.809156000	0.388439000	2.068835000
6	-4.517257000	-0.596649000	1.114538000
8	-4.429196000	0.832328000	3.022268000
1	-5.603655000	-0.433538000	1.145493000
1	-4.322521000	-1.603521000	1.500490000

(S3) Cartesian coordinate (in Å) of $TS_{3\text{-}4}$

SCF Energy (ZPE corrected) = -4540.469824 au

Atomic Number	X	Y	Z
26	1.386313000	-0.595426000	-0.356032000
26	-1.686297000	-0.086860000	-0.052944000
8	-0.030917000	-0.110088000	0.596342000
8	1.700216000	-2.614044000	-0.173189000
8	2.565423000	-4.361032000	-1.316072000
8	0.581265000	-0.546353000	-1.831918000
8	-2.312393000	0.513636000	1.706936000
8	-4.080309000	0.887212000	3.054952000
8	-1.210447000	-0.381529000	-1.639349000
7	3.379271000	-0.898596000	-1.196793000
7	2.563938000	-0.392805000	1.375948000
7	2.387667000	1.683178000	-0.686517000
7	-3.874597000	-0.352589000	-0.314431000
7	-2.120226000	-2.291737000	0.216715000
7	-2.440120000	2.047672000	-0.687609000
6	3.180838000	-2.143867000	-1.966036000
6	2.423693000	-3.169029000	-1.089163000
6	4.343099000	-1.120830000	-0.096381000
6	3.877173000	-0.607905000	1.242480000
6	4.751483000	-0.441854000	2.314877000
6	4.233747000	-0.067217000	3.550244000

6	2.861822000	0.133167000	3.681347000
6	2.057704000	-0.035579000	2.561276000
6	3.757301000	0.247205000	-2.029462000
6	3.573986000	1.549580000	-1.288821000
6	4.537846000	2.554154000	-1.272428000
6	4.238911000	3.741133000	-0.608069000
6	2.989573000	3.891725000	-0.019572000
6	2.068962000	2.839108000	-0.087123000
6	0.649875000	2.979360000	0.389900000
6	-0.256727000	3.078763000	-0.852085000
6	-1.736599000	3.181812000	-0.604578000
6	-2.380613000	4.409273000	-0.410238000
6	-3.766552000	4.446022000	-0.340267000
6	-4.487342000	3.267035000	-0.520531000
6	-3.776364000	2.087439000	-0.703537000
6	-4.426748000	0.776049000	-1.070121000
6	-4.418587000	-0.373599000	1.061311000
6	-3.559083000	0.441789000	2.045171000
6	-4.076854000	-1.627255000	-1.013648000
6	-3.232442000	-2.713396000	-0.395153000
6	-3.548212000	-4.063537000	-0.504550000
6	-2.652316000	-4.999442000	0.007147000
6	-1.485432000	-4.556660000	0.619133000
6	-1.261910000	-3.186178000	0.711661000
1	4.130868000	-2.568373000	-2.317885000
1	2.551402000	-1.910900000	-2.830921000
1	5.323847000	-0.692265000	-0.347517000
1	4.497396000	-2.201722000	0.007333000
1	5.816751000	-0.612273000	2.181972000
1	4.896053000	0.065026000	4.402489000
1	2.418453000	0.418832000	4.630312000
1	0.977443000	0.108615000	2.562355000
1	3.081121000	0.251533000	-2.892476000
1	4.787841000	0.150809000	-2.405820000
1	5.493952000	2.409251000	-1.768296000
1	4.969826000	4.545127000	-0.562152000
1	2.716706000	4.815715000	0.483032000
1	0.544052000	3.866346000	1.025173000
1	0.357379000	2.091363000	0.961843000
1	0.050426000	3.949658000	-1.447047000
1	-0.088938000	2.186018000	-1.464600000
1	-1.793589000	5.320869000	-0.334398000
1	-4.285429000	5.387370000	-0.176730000
1	-5.573652000	3.263117000	-0.522126000

1	-5.519757000	0.834204000	-0.955645000
1	-4.212206000	0.602790000	-2.131927000
1	-4.411719000	-1.405915000	1.425964000
1	-5.458716000	-0.025000000	1.081985000
1	-3.745630000	-1.492433000	-2.051183000
1	-5.138868000	-1.919602000	-1.030730000
1	-4.468956000	-4.373251000	-0.992460000
1	-2.863881000	-6.062592000	-0.077674000
1	-0.746771000	-5.249900000	1.008328000
1	-0.361455000	-2.784848000	1.162646000

(S4) Cartesian coordinate (in Å) of 4.

SCF Energy (ZPE corrected) = -4540.503340 au

Atomic Number	X	Y	Z
26	1.627274000	-0.463262000	-0.832352000
26	-1.809953000	-0.134692000	-0.535297000
8	-0.042311000	-0.132526000	-0.377058000
8	1.836384000	-2.474192000	-0.782347000
8	1.657140000	-0.191954000	-2.424917000
8	-1.849378000	0.245906000	1.432612000
8	-2.079103000	-0.327336000	-2.120863000
7	3.842426000	-0.758396000	-0.823861000
7	2.114596000	-0.587239000	1.306958000
7	2.584689000	1.696965000	-0.400771000
7	-4.014739000	-0.270611000	-0.065291000
7	-2.185441000	-2.267788000	-0.166012000
7	-2.491526000	2.020656000	-0.662027000
6	3.951484000	-1.934783000	-1.706088000
6	2.916539000	-2.994708000	-1.272518000
6	4.364863000	-1.061234000	0.520747000
6	3.392434000	-0.789822000	1.641862000
6	3.807285000	-0.814731000	2.972647000
6	2.859959000	-0.640504000	3.975622000
6	1.529057000	-0.445913000	3.619121000
6	1.196782000	-0.422100000	2.269575000
6	4.408693000	0.461991000	-1.395639000
6	3.891877000	1.696755000	-0.698796000
6	4.718944000	2.785817000	-0.438240000

6	4.159075000	3.920260000	0.139061000
6	2.801619000	3.924453000	0.426987000
6	2.028933000	2.791372000	0.144673000
6	0.547444000	2.795884000	0.399034000
6	-0.241562000	2.954132000	-0.915688000
6	-1.720678000	3.117180000	-0.700448000
6	-4.613603000	0.869684000	-0.756406000
6	-4.437083000	-1.555213000	-0.629081000
6	-1.231560000	-3.183420000	0.029747000
1	4.962438000	-2.362650000	-1.702925000
1	3.696238000	-1.620208000	-2.722408000
1	5.303353000	-0.517755000	0.700814000
1	4.620601000	-2.127877000	0.557743000
1	4.855631000	-0.974747000	3.212631000
1	3.159673000	-0.656651000	5.020938000
1	0.174614000	-0.257733000	1.930227000
1	4.074175000	0.506043000	-2.438446000
1	5.509820000	0.446782000	-1.387058000
1	5.776050000	2.739934000	-0.685623000
1	4.774439000	4.788626000	0.362179000
1	2.329891000	4.794197000	0.875768000
1	0.303599000	3.619378000	1.080732000
1	0.234578000	1.860817000	0.871077000
1	0.125145000	3.836629000	-1.455081000
1	-0.057141000	2.077433000	-1.544371000
1	-4.597405000	0.647233000	-1.830179000
1	-0.204070000	-2.828759000	0.037275000
8	3.169469000	-4.180806000	-1.412051000
1	0.749293000	-0.304879000	4.361566000
6	-3.466107000	-2.648311000	-0.256431000
6	-1.531653000	-4.535810000	0.170891000
6	-2.861879000	-4.934938000	0.116556000
6	-3.848900000	-3.976139000	-0.100902000
1	-0.725449000	-5.248749000	0.313041000
1	-3.132281000	-5.981552000	0.234050000
1	-4.898522000	-4.252028000	-0.162225000
6	-2.287079000	4.390915000	-0.569627000
6	-3.658529000	4.520474000	-0.409028000
6	-4.448100000	3.374792000	-0.420087000
6	-3.823193000	2.141665000	-0.566382000
1	-1.643972000	5.266158000	-0.602058000
1	-4.111774000	5.501976000	-0.293541000
1	-5.529042000	3.431926000	-0.327695000
1	-5.661712000	1.021703000	-0.455653000

1	-4.416475000	-1.459425000	-1.721307000
1	-5.462038000	-1.820189000	-0.326984000
6	-2.928219000	0.269770000	2.142735000
6	-4.189198000	-0.203231000	1.397946000
8	-3.027397000	0.574261000	3.321455000
1	-5.036772000	0.438074000	1.668049000
1	-4.417541000	-1.204553000	1.779656000