An Oxidized Active Site Model for the FeFe Hydrogenase: Reduction with Hydrogen Gas.

Supporting Information

Steven L Matthews and D. Michael Heinekey

Department of Chemistry, University of Washington, Seattle WA, 98195-1700
heinekey@chem.washington.edu

Experimental details

All manipulations were conducted in an air-free manner unless otherwise stated. NMR spectra recorded at 500 MHz using Bruker Avance systems. Elemental analyses were carried out by Columbia Analytical Services of Tuscon, Arizona. The following were used as received: 1,3-propanedithiol (Aldrich), $Fe_3(CO)_{12}$ (Strem), $Li[B(C_6F_5)_4]$ (Strem), $SbCl_5$ (Aldrich), $N(C_6H_5)_3$ (Aldrich), $LiHBEt_3$ (Aldrich), $HSiEt_3$ (Aldrich), Br_2 (Aldrich). Solvents were dried on a solvent drying system using alumina columns and stored in teflon screw capped vessels over an appropriate drying agent under vacuum. Fluorobenzene was prepared for use by adding to vacuum-heated silica (200 °C, 20 millitorr, 5 hours) under argon followed by vacuum transfer to CaH_2 for storage. Complex **1** was prepared according to literature procedures.

Syntheses

$N(Ar^{2,4\text{-}Br})_3$

5.05 g triphenyl amine (20.6 mmol) was added to a 100 mL RB flask with 20 mL of chloroform. Over one hour, 7.0 mL Br_2 (138.3 mmol, 6.7 equiv.) in 7.0 mL chloroform was added dropwise with stirring. The solution was stirred at room temperature for 72 hours. The product was precipitated by addition of ethanol, and recrystallized twice from chloroform/ethanol to afford colorless crystals. Yield: 12.60 g (86%).
^{1}H NMR (δ, $CDCl_3$) 7.84 (1H, d, 2.2 Hz), 7.54 (1H, dd, 2.2, 8.6 Hz), 7.90 (1H, d, 8.6 Hz)

$[N(Ar^{2,4\text{-}Br})_3][SbCl_6]$

3.57 g $N(Ar^{2,4\text{-}Br})_3$ (5.4 mmol) was added to a Schlenk tube with a stir bar. Dichloromethane (20 mL) was added by vacuum transfer from CaH_2 and the solution stirred until the solid dissolved. Under a flow of argon, neat $SbCl_5$ (1 mL, 7.8 mmol) was added dropwise by syringe over 20 minutes. The solution becomes dark green and a dark green precipitate forms. The dark green solid was collected by cannula filtration, washed with diethyl ether and dried under vacuum overnight. Yield: 4.18 g (80 %) This material was used without further characterization.

$[Fe_2Cl(\mu\text{-}S_2C_3H_6)(CO)_6][B(C_6F_5)_4]$ (2)

300 mg of complex **1** (0.78 mmol) and 1.09 g $[N(Ar^{2,4\text{-}Br})_3][SbCl_6]$ (1.03 mmol, 1.33 equiv.) were added to a 100 mL Schlenk flask with a stir bar in a glove box. Approximately 50 mL dichloromethane was added by vacuum transfer from CaH_2 and

the solution stirred vigorously while warming to room temperature. The green color fades to give an orange solution. A solution of $Li[B(C_6F_5)_4]$ in dichloromethane (10 mL) was added to the orange solution by cannula transfer under argon. This mixture was stirred for an hour at room temperature. The solution was then cannula transferred into a flask of vigorously-stirred hexanes (~50 mL), to give a yellow precipitate and a green solution. The yellow solid was collected by cannula filtration and dried under vacuum. Yield: 674 mg.

Recrystallization of **2**: 300 mg of the collected solid was added to a Schlenk flask and dissolved in 8 mL of dichloromethane. This solution is then filtered away from a small amount of yellow precipitate and reduced in volume to ~2 mL and placed in a freezer at -26 °C. Orange crystals (144 mg) are collected by decanting the solution with a pipette. Additional product can be collected by reducing the solvent volume further and returning to the freezer (total 179 mg). ^{1}H NMR spectrum: δ 2.46 (t, 4H, 7 Hz, -CH_2-), 1.90 (qi, 2H, 7 Hz, S-CH_2-). ^{13}C NMR spectrum: δ 201.6 (1C, $^{13}CO_{apical}$, J_{CC} = 8.4 Hz), 194.3 (2C, $^{13}CO_{basal}$, J_{CC} = 8.4 Hz), 25.2 (2C, S-CH_2-), 25.7 (1C, -CH_2-) IR (KBr) 2142, 2125, 2094, 2059, 2046 cm^{-1} UV-Vis /λ_{max}(ε) (CH_2Cl_2): 235 (13000), 309 (2400), 360 (1800), 415 (800). Anal. Calcd. for $C_{33}H_6BClFe_2F_{20}O_6S_2$: C 36.02, H 0.55. Found: 36.00, 0.41.

$[Fe_2(\mu\text{-}C_6F_5)(\mu\text{-}S_2C_3H_6)(CO)_6][B(C_6F_5)_4]$ (3)

10 mg of complex **2** was dissolved in 5 mL of flourobenzene. After heating to 70°C for 72 h, the solution was returned to room temperature and concentrated to approximately half the starting volume and filtered to remove a small amount of solid. After layering with pentane, standing at room temperature for 24h affords orange-red crystals of **3**. Yield: 5 mg(43%). The crystals of **3** contain one half molecule of solvent (C_6H_5F) for each cation. ^{1}H NMR spectrum: δ 2.40 (t, 4H, 7 Hz, -CH_2-), 2.01 (qi, 2H, 7 Hz, S-CH_2-). IR (KBr) 2117, 2082, 2062 cm^{-1} Anal. Calcd. for $C_{84}H_{17}B_2Fe_4F_{51}O_{12}S_4$: C 39.40, H 0.66. Found: 39.1, 0.68.

NMR spectra

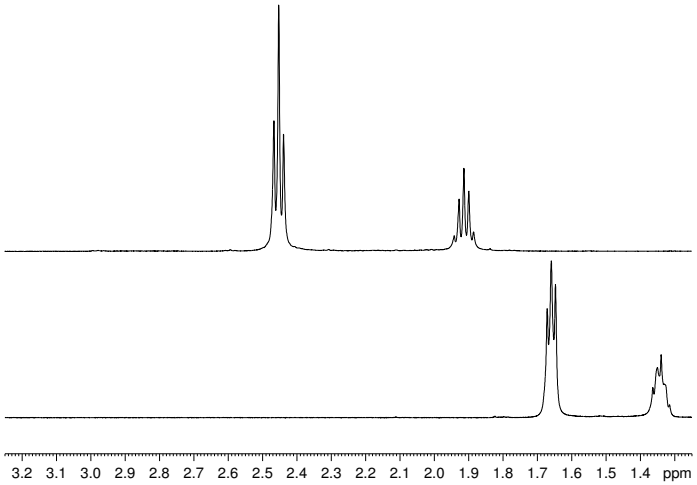

Figure S1 - ^{1}H NMR spectrum of **1** (bottom) and **2** (top). (500 MHz, C_6H_5F, 298 K)

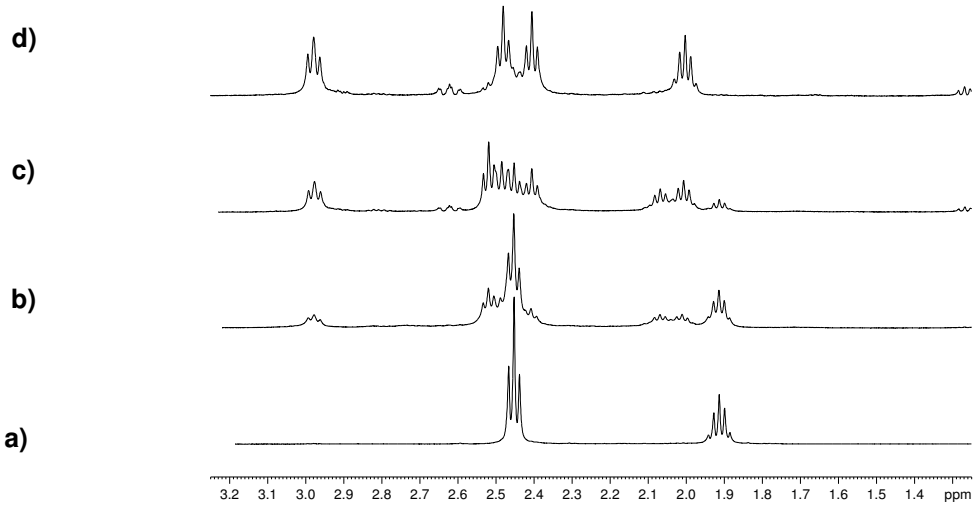

Figure S2 - Partial ^{1}H NMR spectrum (500 MHz, C_6H_5F, 298 K) of (a) Complex **2** after heating at 70 °C for 2 hrs under 1 atm. CO gas, (b) The same sample after being degassed by 3 freeze-pump-thaw cycles, backfilled with argon and heated at 70 °C for an additional 2 hrs, (c) continued heating of b for 16 hours, (d) continued heating of d for ~72 hours.

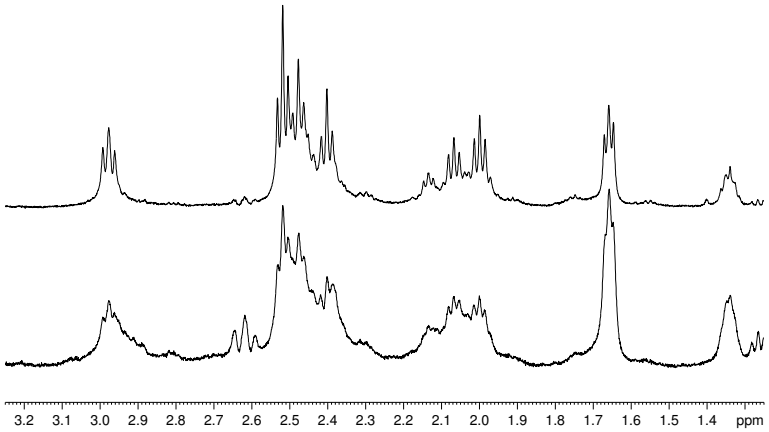

Figure S3 - Partial ^{1}H NMR spectrum (500 MHz, C_6H_5F, 298 K) of (top) Complex **2** after heating under H_2, (bottom) after heating under argon for 48 hours followed by degassing by 3 freeze pump thaw cycles, backfill with H_2 and returned to heat for an additional 24 hours.

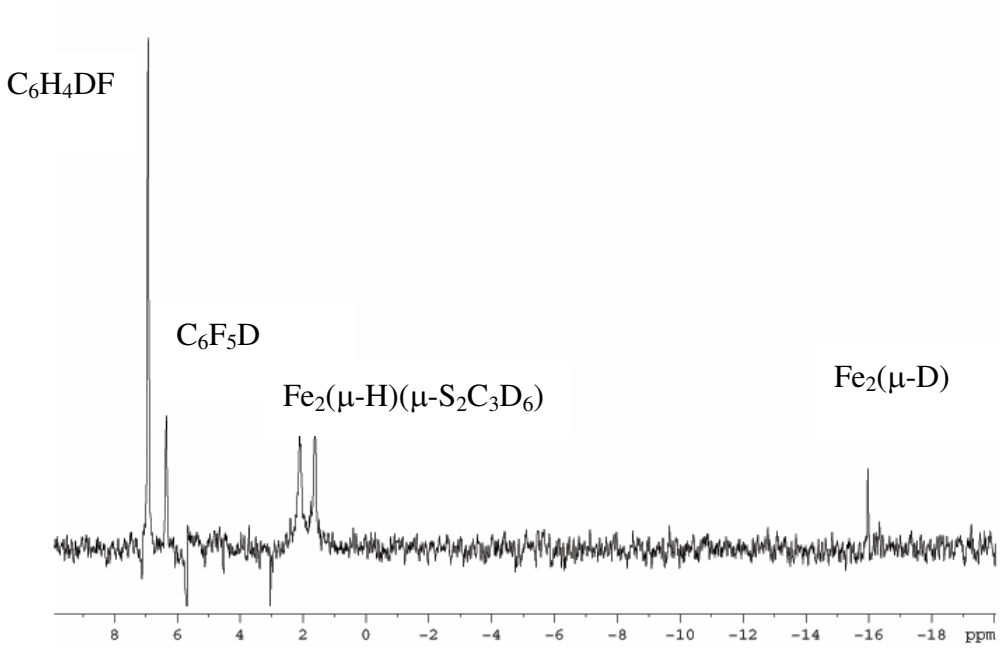

Figure S4 - ^{2}H difference NMR spectrum (final spectrum subtract starting spectrum) of the products of heating complex **2** in C_6H_5F under 1 atm D_2 (note: artifact from transmitter frequency at ~5.8 ppm).

IR spectra

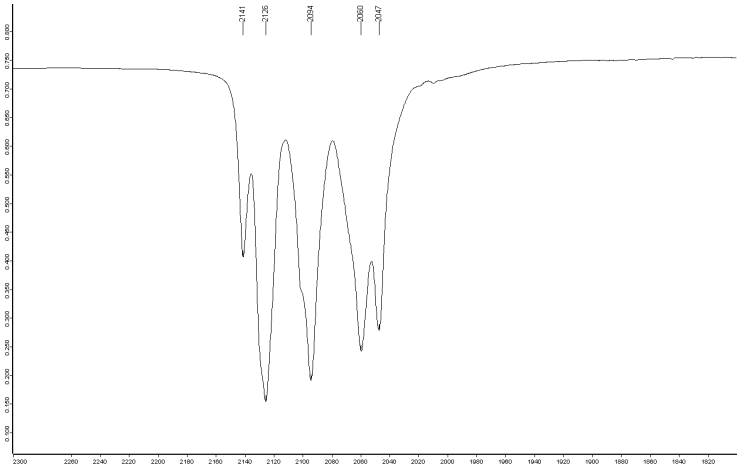

Figure S5 – Partial (carbonyl region) IR spectrum (KBr) of complex **2**.

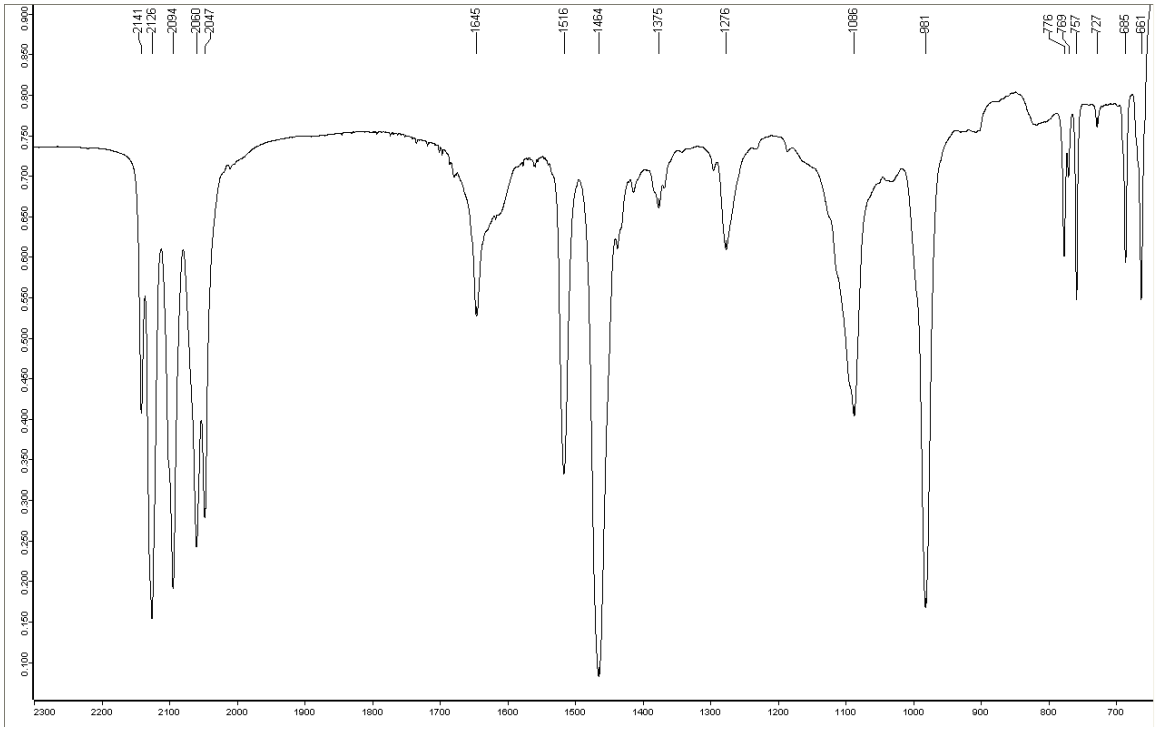

Figure S6 – IR spectrum (KBr) of complex **2.**

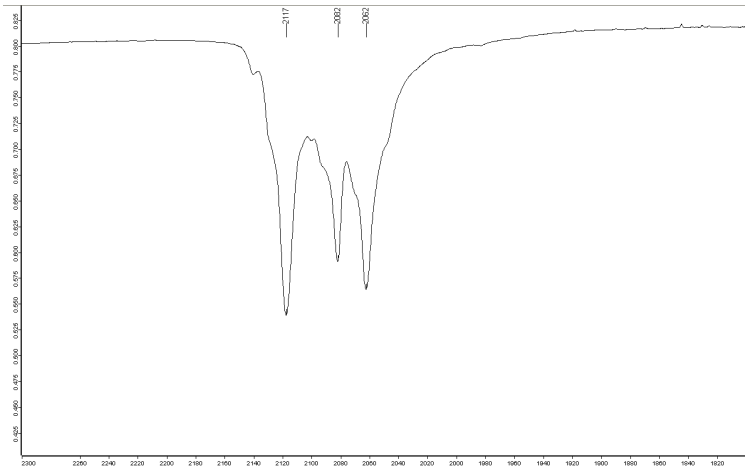

Figure S7 - Partial (carbonyl region) IR spectrum (KBr) of complex **3**.

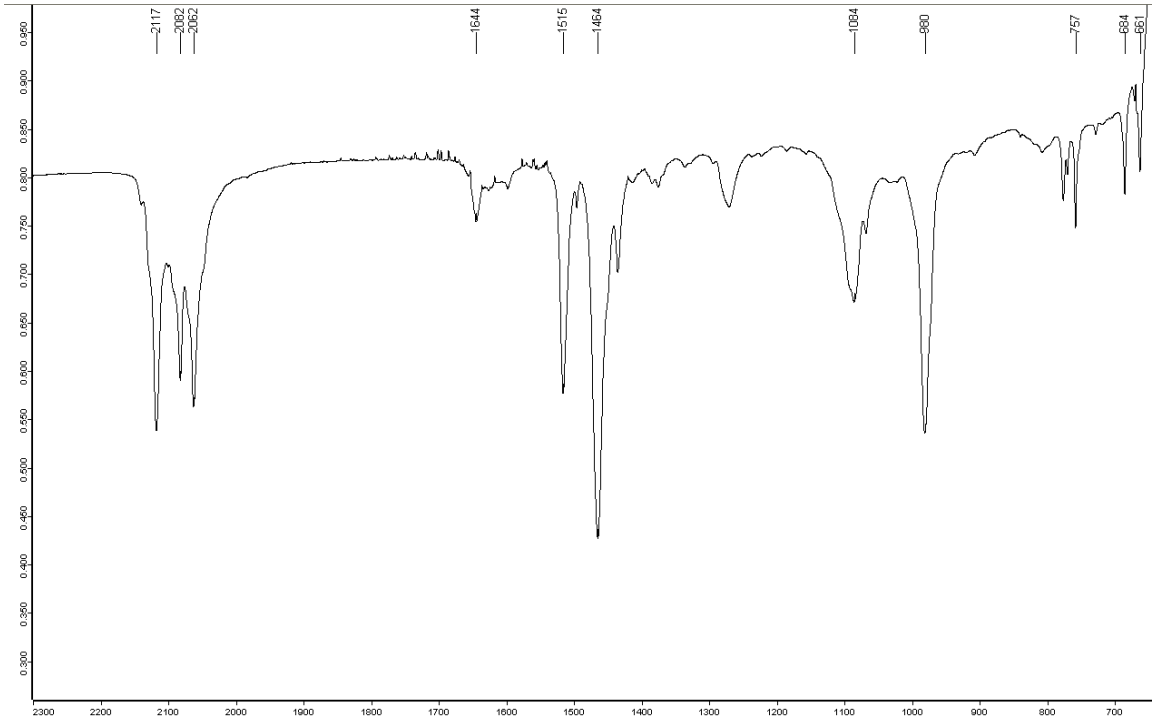

Figure S8 - IR spectrum (KBr) of complex **3**.

XRD data

Table 1: Crystallographic data for **2**

Empirical Formula	C24 B F20, C9 H6 Cl Fe2 O6 S2
Formula Weight	1100.46
Temperature K	130(2)
Wavelength Å	0.71073
Habit/color	Prism / orange
Crystal System, space group	Triclinic, P $\bar{1}$ (No.2)
Unit Cell Dimensions	
a, Å	9.8081(4)
b, Å	13.6899(7)
c, Å	14.1130(7)
α, (deg.)	93.981(2)
β, (deg.)	96.589(3)
γ, (deg.)	100.781(3)
Volume ($Å^3$)	1841.20(15)
Density Mg/m^3	1.985
Reflections Collected/Unique	14221 / 8706
R_{int}	0.0976
ϑm / completeness	25° / 100%
Final R indices [I>2σ(I)]	
R1, wR2	0.0463, 0.1069
R indices (all data)	
R1,wR2	0.0706, 0.1172

Table 2: Crystallographic data for **3**.

Empirical Formula	C84 H17 B2 F51 Fe4 O12 S4
Formula Weight	2560.24
Temperature K	110(2) K
Wavelength Å	0.71073 Å
Habit/color	Prism / orange
Crystal System, space group	Triclinic, P $\bar{1}$ (No.2)
Unit Cell Dimensions	
a, Å	9.0235(4)
b, Å	13.5721(6)
c, Å	18.2507(9)
α, (deg.)	99.901(3)
β, (deg.)	102.990(3)
γ, (deg.)	97.502(3)
Volume ($Å^3$)	2111.89(17)
Density Mg/m^3	2.013
Reflections Collected/Unique	49264 / 10406
Rint	0.0498
ϑm / completeness	25o / 99.3%
Final R indices [I>2σ(I)]	
R1, wR2	0.0428, 0.0980
R indices (all data)	
R1,wR2	0.0720, 0.1103

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe1	0.34920(4)	0.10667(3)	-0.31106(3)	0.01513(11)
Fe2	0.37269(4)	0.23945(3)	-0.12885(2)	0.01361(11)
Cl1	0.23335(7)	0.08378(5)	-0.17674(4)	0.01875(16)
S1	0.30737(7)	0.26714(5)	-0.28547(4)	0.01589(16)
S2	0.53942(7)	0.17351(5)	-0.19947(4)	0.01433(15)
F1	-0.10273(17)	0.17130(12)	0.13980(11)	0.0232(4)
F2	-0.25247(17)	0.27054(13)	0.02750(11)	0.0264(4)
F3	-0.17920(18)	0.47222(13)	0.02888(12)	0.0290(4)
F4	0.05787(19)	0.57154(13)	0.14080(14)	0.0347(5)
F5	0.21952(19)	0.47369(13)	0.24305(13)	0.0335(5)
F6	0.32991(17)	0.34595(13)	0.11952(10)	0.0243(4)
F7	0.60274(17)	0.39947(13)	0.13089(11)	0.0268(4)
F8	0.77265(16)	0.38481(13)	0.29493(11)	0.0245(4)
F9	0.65277(18)	0.32369(15)	0.45108(11)	0.0327(5)
F10	0.37931(18)	0.26827(14)	0.44241(10)	0.0297(5)
F11	0.2505(2)	0.42603(13)	0.42942(13)	0.0369(5)
F12	0.1227(2)	0.45055(15)	0.58119(14)	0.0483(6)
F13	-0.1067(2)	0.31654(15)	0.61125(12)	0.0350(5)
F14	-0.20551(18)	0.15404(14)	0.48096(11)	0.0287(4)
F15	-0.08161(18)	0.12764(12)	0.32818(11)	0.0257(4)
F16	0.1888(2)	0.08877(13)	0.39135(10)	0.0285(4)
F17	0.1784(2)	-0.10008(13)	0.33015(12)	0.0346(5)
F18	0.14113(18)	-0.15975(12)	0.13911(11)	0.0235(4)
F19	0.13870(19)	-0.01974(13)	0.01122(11)	0.0272(4)
F20	0.14614(19)	0.16857(12)	0.06889(10)	0.0234(4)
O1	0.4111(3)	-0.09567(16)	-0.29134(16)	0.0364(6)
O2	0.0685(2)	0.06357(17)	-0.42558(14)	0.0309(6)
O3	0.4923(2)	0.10749(16)	-0.48147(14)	0.0277(5)
O4	0.5493(2)	0.43749(15)	-0.07915(13)	0.0236(5)
O5	0.4607(2)	0.16109(16)	0.05458(13)	0.0244(5)
O6	0.1247(2)	0.30818(16)	-0.06657(14)	0.0259(5)

C1	0.4485(3)	0.3594(2)	-0.32114(19)	0.0206(7)
H1A	0.4147	0.3811	-0.3835	0.025
H1B	0.468	0.4186	-0.2736	0.025
C2	0.5853(3)	0.3246(2)	-0.33032(19)	0.0201(7)
H2A	0.5696	0.2758	-0.3875	0.024
H2B	0.6549	0.383	-0.3431	0.024
C3	0.6501(3)	0.2776(2)	-0.24714(18)	0.0176(6)
H3A	0.6851	0.3307	-0.194	0.021
H3B	0.7325	0.2535	-0.2671	0.021
C4	0.3846(3)	-0.0204(2)	-0.30134(19)	0.0212(7)
C5	0.1764(3)	0.0744(2)	-0.38477(19)	0.0209(7)
C6	0.4399(3)	0.1138(2)	-0.41474(19)	0.0182(6)
C7	0.4819(3)	0.3606(2)	-0.09813(17)	0.0183(6)
C8	0.4268(3)	0.1931(2)	-0.01358(19)	0.0193(6)
C9	0.2185(3)	0.2831(2)	-0.08890(18)	0.0181(6)
C10	0.0709(3)	0.3158(2)	0.19636(17)	0.0138(6)
C11	-0.0538(3)	0.2704(2)	0.14051(18)	0.0149(6)
C12	-0.1355(3)	0.3201(2)	0.08271(18)	0.0165(6)
C13	-0.0993(3)	0.4222(2)	0.08220(19)	0.0190(6)
C14	0.0203(3)	0.4718(2)	0.1387(2)	0.0228(7)
C15	0.1013(3)	0.4186(2)	0.19185(19)	0.0192(6)
C16	0.3357(3)	0.30443(19)	0.28120(17)	0.0137(6)
C17	0.4042(3)	0.3388(2)	0.20489(17)	0.0151(6)
C18	0.5469(3)	0.3671(2)	0.20885(18)	0.0175(6)
C19	0.6328(3)	0.3617(2)	0.29117(19)	0.0170(6)
C20	0.5716(3)	0.3295(2)	0.36938(18)	0.0184(6)
C21	0.4285(3)	0.3016(2)	0.36220(18)	0.0179(6)
C22	0.0957(3)	0.2735(2)	0.37024(18)	0.0146(6)
C23	0.1380(3)	0.3548(2)	0.4381(2)	0.0216(7)
C24	0.0734(3)	0.3700(2)	0.5184(2)	0.0272(8)
C25	-0.0427(3)	0.3022(2)	0.53374(19)	0.0231(7)
C26	-0.0917(3)	0.2218(2)	0.46834(19)	0.0189(6)
C27	-0.0233(3)	0.2098(2)	0.38938(18)	0.0157(6)
C28	0.1598(3)	0.1399(2)	0.23373(18)	0.0137(6)
C29	0.1727(3)	0.0664(2)	0.29489(18)	0.0190(6)
C30	0.1667(3)	-0.0321(2)	0.26578(19)	0.0195(6)

C31	0.1515(3)	-0.0636(2)	0.16925(19)	0.0172(6)
C32	0.1467(3)	0.0068(2)	0.10549(18)	0.0181(6)
C33	0.1523(3)	0.1046(2)	0.13804(18)	0.0162(6)
B1	0.1653(3)	0.2584(2)	0.2699(2)	0.0139(6)

Table 4. Bond lengths [Å] and angles [°] for **2**.

Fe1-C6	1.797(3)
Fe1-C5	1.844(3)
Fe1-C4	1.847(3)
Fe1-S2	2.2989(8)
Fe1-S1	2.3207(9)
Fe1-Cl1	2.3295(7)
Fe2-C7	1.793(3)
Fe2-C8	1.844(3)
Fe2-C9	1.857(3)
Fe2-S2	2.2986(8)
Fe2-S1	2.3069(7)
Fe2-Cl1	2.3161(7)
S1-C1	1.833(2)
S2-C3	1.840(2)
F1-C11	1.351(3)
F2-C12	1.347(3)
F3-C13	1.336(3)
F4-C14	1.343(3)
F5-C15	1.356(3)
F6-C17	1.354(3)
F7-C18	1.350(3)
F8-C19	1.343(3)
F9-C20	1.340(3)
F1-C21	1.356(3)
F11-C23	1.352(3)
F12-C24	1.342(3)
F13-C25	1.343(3)
F14-C26	1.349(3)
F15-C27	1.360(3)

F16-C29	1.359(3)
F17-C30	1.356(3)
F18-C31	1.337(3)
F19-C32	1.344(3)
F20-C33	1.360(3)
O1-C4	1.123(4)
O2-C5	1.124(4)
O3-C6	1.129(3)
O4-C7	1.130(3)
O5-C8	1.126(3)
O6-C9	1.110(4)
C1-C2	1.521(4)
C1-H1A	0.99
C1-H1B	0.99
C2-C3	1.511(4)
C2-H2A	0.99
C2-H2B	0.99
C3-H3A	0.99
C3-H3B	0.99
C10-C11	1.389(4)
C10-C15	1.390(4)
C10-B1	1.649(4)
C11-C12	1.379(4)
C12-C13	1.377(4)
C13-C14	1.373(4)
C14-C15	1.371(4)
C16-C21	1.385(4)
C16-C17	1.397(3)
C16-B1	1.658(4)
C17-C18	1.374(4)
C18-C19	1.369(4)
C19-C20	1.375(3)
C20-C21	1.374(4)
C22-C23	1.385(4)
C22-C27	1.386(4)
C22-B1	1.658(4)

C23-C24	1.383(4)
C24-C25	1.376(4)
C25-C26	1.361(4)
C26-C27	1.381(4)
C28-C29	1.384(4)
C28-C33	1.392(4)
C28-B1	1.655(4)
C29-C30	1.370(4)
C30-C31	1.383(4)
C31-C32	1.366(4)
C32-C33	1.374(4)

C6-Fe1-C5	92.42(12)
C6Fe1-C4	88.48(13)
C5-Fe1-C4	99.07(13)
C6-Fe1-S2	97.05(9)
C5-Fe1-S2	166.19(10)
C4-Fe1-S2	91.23(9)
C6-Fe1-S1	102.78(9)
C5-Fe1-S1	87.31(10)
C4-Fe1-S1	166.88(9)
S2-Fe1-S1	80.82(3)
C6-Fe1-Cl1	175.31(9)
C5-Fe1-Cl1	87.77(8)
C4-Fe1-Cl1	86.86(9)
S2-Fe1-Cl1	83.61(3)
S1-Fe1-Cl1	81.92(3)
C7-Fe2-C8	93.64(12)
C7-Fe2-C9	91.94(13)
C8-Fe2-C9	95.00(12)
C7-Fe2-S2	94.45(9)
C8-Fe2-S2	91.12(10)
C9-Fe2-S2	170.86(9)
C7-Fe2-S1	94.81(8)
C8-Fe2-S1	168.95(10)
C9-Fe2-S1	91.84(9)

S2-Fe2-S1	81.13(3)
C7-Fe2-Cl1	177.03(8)
C8-Fe2-Cl1	88.88(9)
C9-Fe2-Cl1	89.41(9)
S2-Fe2-Cl1	83.92(3)
S1-Fe2-Cl1	82.50(3)
Fe2-Cl1-Fe1	80.59(2)
C1-S1-Fe2	107.61(9)
C1-S1-Fe1	110.89(11)
Fe2-S1-Fe1	80.97(3)
C3-S2-Fe2	106.68(10)
C3-S2-Fe1	109.65(9)
Fe2-S2-Fe1	81.62(3)
C2-C1-S1	116.0(2)
C2-C1-H1A	108.3
S1-C1-H1A	108.3
C2-C1-H1B	108.3
S1-C1-H1B	108.3
H1A-C1-H1B	107.4
C3-C2-C1	118.2(2)
C3-C2-H2A	107.8
C1-C2-H2A	107.8
C3-C2-H2B	107.8
C1-C2-H2B	107.8
H2A-C2-H2B	107.1
C2-C3-S2	117.86(19)
C2-C3-H3A	107.8
S2-C3-H3A	107.8
C2-C3-H3B	107.8
S2-C3-H3B	107.8
H3A-C3-H3B	107.2
O1-C4-Fe1	176.4(3)
O2-C5-Fe1	172.9(3)
O3-C6-Fe1	172.6(2)
O4-C7-Fe2	179.0(3)
O5-C8-Fe2	176.9(3)

O6-C9-Fe2	178.6(3)
C11-C10-C15	112.6(3)
C11-C10-B1	124.6(2)
C15-C10-B1	122.5(2)
F1-C11-C12	115.3(2)
F1-C11-C10	120.5(3)
C12-C11-C10	124.2(2)
F2-C12-C13	119.0(3)
F2-C12-C11	121.0(2)
C13-C12-C11	120.0(2)
F3-C13-C14	120.6(3)
F3-C13-C12	121.0(2)
C14-C13-C12	118.4(3)
F4-C14-C15	120.5(3)
F4-C14-C13	120.0(3)
C15-C14-C13	119.5(3)
F5-C15-C14	115.2(2)
F5-C15-C10	119.5(3)
C14-C15-C10	125.2(3)
C21-C16-C17	112.1(2)
C21-C16-B1	124.5(2)
C17-C16-B1	122.9(2)
F6-C17-C18	115.2(2)
F6-C17-C16	120.3(2)
C18-C17-C16	124.5(2)
F7-C18-C19	119.8(2)
F7-C18-C17	119.8(2)
C19-C18-C17	120.3(2)
F8-C19-C18	121.1(2)
F8-C19-C20	120.9(2)
C18-C19-C20	118.0(2)
F9-C20-C21	120.8(2)
F9-C20-C19	119.5(2)
C21-C20-C19	119.7(3)
F10-C21-C20	115.0(2)
F10-C21-C16	119.7(2)

C20-C21-C16	125.3(2)
C23-C22-C27	112.4(2)
C23-C22-B1	124.9(2)
C27-C22-B1	122.2(2)
F11-C23-C24	115.0(2)
F11-C23-C22	120.5(2)
C24-C23-C22	124.5(3)
F12-C24-C25	119.9(3)
F12-C24-C23	120.5(3)
C25-C24-C23	119.7(3)
F13-C25-C26	121.2(3)
F13-C25-C24	120.1(3)
C26-C25-C24	118.7(3)
F14-C26-C25	120.3(2)
F14-C26-C27	120.2(2)
C25-C26-C27	119.5(2)
F15-C27-C26	114.7(2)
F15-C27-C22	120.2(2)
C26-C27-C22	125.1(3)
C29-C28-C33	112.3(3)
C29-C28-B1	124.2(2)
C33-C28-B1	123.4(2)
F16-C29-C30	114.9(2)
F16-C29-C28	120.4(3)
C30-C29-C28	124.7(2)
F17-C30-C29	121.2(2)
F17-C30-C31	118.6(3)
C29-C30-C31	120.2(3)
F18-C31-C32	121.0(2)
F18-C31-C30	121.2(2)
C32-C31-C30	117.8(3)
F19-C32-C31	119.9(3)
F19-C32-C33	120.2(2)
C31-C32-C33	119.9(2)
F20-C33-C32	115.4(2)
F20-C33-C28	119.7(2)

C32-C33-C28	125.0(2)
C10-B1-C28	114.2(2)
C10-B1-C22	101.2(2)
C28-B1-C22	113.4(2)
C10-B1-C16	113.8(2)
C28-B1-C16	101.4(2)
C22-B1-C16	113.4(2)

Table 5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-2994(3)	7385(2)	1644(2)	21(1)
C(2)	-2354(3)	6578(2)	1183(2)	20(1)
C(3)	-1092(3)	6131(2)	1626(2)	19(1)
C(4)	824(3)	9980(2)	1988(2)	19(1)
C(5)	-22(3)	8313(2)	987(2)	21(1)
C(6)	2672(4)	8541(2)	1907(2)	22(1)
C(7)	-675(3)	8704(2)	4006(2)	17(1)
C(8)	-1667(3)	6926(2)	3244(2)	19(1)
C(9)	1283(3)	7377(2)	3914(2)	20(1)
C(10)	1751(3)	9148(2)	3327(2)	12(1)
C(11)	3295(4)	9011(2)	3539(2)	23(1)
C(12)	4487(4)	9772(2)	3960(2)	26(1)
C(13)	4191(4)	10722(2)	4209(2)	29(1)
C(14)	2696(4)	10904(2)	4028(2)	26(1)
C(15)	1531(3)	10128(2)	3589(2)	22(1)
C(16)	7498(3)	2856(2)	2874(2)	15(1)
C(17)	7585(3)	2102(2)	3300(2)	18(1)
C(18)	8583(3)	2224(2)	4017(2)	19(1)
C(19)	9563(3)	3130(2)	4350(2)	19(1)
C(20)	9501(3)	3922(2)	3970(2)	18(1)
C(21)	8481(3)	3766(2)	3257(2)	15(1)
C(22)	5454(3)	1652(2)	1564(2)	17(1)
C(23)	3896(4)	1339(2)	1197(2)	20(1)
C(24)	3284(4)	361(2)	765(2)	27(1)
C(25)	4231(5)	-332(2)	663(2)	31(1)
C(26)	5787(4)	-46(2)	994(2)	27(1)
C(27)	6353(4)	919(2)	1432(2)	22(1)
C(28)	5064(3)	3522(2)	2273(2)	13(1)
C(29)	4082(3)	3177(2)	2701(2)	16(1)
C(30)	3045(3)	3708(2)	2964(2)	18(1)

C(31)	2949(3)	4658(2)	2812(2)	19(1)
C(32)	3906(3)	5051(2)	2405(2)	18(1)
C(33)	4927(3)	4484(2)	2151(2)	14(1)
C(34)	7197(3)	3207(2)	1401(2)	14(1)
C(35)	6339(3)	3368(2)	713(2)	15(1)
C(36)	6962(3)	3617(2)	130(2)	18(1)
C(37)	8526(3)	3693(2)	211(2)	20(1)
C(38)	9436(3)	3528(2)	873(2)	19(1)
C(39)	8767(3)	3285(2)	1443(2)	16(1)
C(40)	5310(4)	5875(3)	4749(2)	33(1)
C(41)	5898(4)	5035(3)	4477(2)	31(1)
C(42)	5568(4)	4147(3)	4726(2)	31(1)
O(1)	913(3)	10803(2)	1969(1)	28(1)
O(2)	-422(3)	8189(2)	338(1)	30(1)
O(3)	3856(3)	8445(2)	1827(1)	34(1)
O(4)	-1089(3)	9157(2)	4480(1)	27(1)
O(5)	-2683(2)	6360(2)	3268(1)	25(1)
O(6)	2123(2)	7035(2)	4310(1)	25(1)
B(1)	6299(4)	2812(2)	2031(2)	14(1)
F(1)	3674(2)	8095(1)	3329(1)	27(1)
F(2)	5927(2)	9584(2)	4146(1)	37(1)
F(3)	5332(2)	11460(2)	4631(1)	42(1)
F(4)	2386(2)	11814(1)	4281(1)	33(1)
F(5)	112(2)	10362(1)	3419(1)	27(1)
F(6)	6656(2)	1178(1)	3027(1)	22(1)
F(7)	8599(2)	1455(1)	4398(1)	24(1)
F(8)	10569(2)	3238(1)	5039(1)	25(1)
F(9)	10441(2)	4819(1)	4280(1)	23(1)
F(10)	8484(2)	4572(1)	2911(1)	18(1)
F(11)	2876(2)	1968(1)	1235(1)	23(1)
F(12)	1757(2)	104(2)	432(1)	37(1)
F(13)	3647(3)	-1272(1)	247(1)	44(1)
F(14)	6748(3)	-704(1)	874(1)	39(1)
F(15)	7892(2)	1148(1)	1727(1)	26(1)
F(16)	4126(2)	2247(1)	2880(1)	20(1)
F(17)	2148(2)	3315(1)	3374(1)	24(1)

F(18)	1954(2)	5198(1)	3065(1)	29(1)
F(19)	3869(2)	5992(1)	2266(1)	26(1)
F(20)	5829(2)	4952(1)	1763(1)	18(1)
F(21)	4787(2)	3263(1)	576(1)	19(1)
F(22)	6061(2)	3759(1)	-526(1)	27(1)
F(23)	9152(2)	3906(1)	-362(1)	29(1)
F(24)	10966(2)	3608(1)	958(1)	27(1)
F(25)	9756(2)	3118(1)	2062(1)	22(1)
F(26)	5556(6)	6714(4)	4460(3)	56(1)
S(1)	-1629(1)	8479(1)	2293(1)	16(1)
S(2)	611(1)	7005(1)	2241(1)	16(1)
Fe(1)	716(1)	8607(1)	2012(1)	15(1)
Fe(2)	-105(1)	7892(1)	3244(1)	15(1)

Table 6. Bond lengths [Å] and angles [°] for **3**.

C(1)-C(2)	1.520(4)
C(1)-S(1)	1.840(3)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.501(4)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-S(2)	1.822(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-O(1)	1.118(3)
C(4)-Fe(1)	1.862(3)
C(5)-O(2)	1.134(4)
C(5)-Fe(1)	1.794(3)
C(6)-O(3)	1.131(4)
C(6)-Fe(1)	1.830(3)
C(7)-O(4)	1.134(3)
C(7)-Fe(2)	1.832(3)
C(8)-O(5)	1.130(3)
C(8)-Fe(2)	1.795(3)
C(9)-O(6)	1.128(3)
C(9)-Fe(2)	1.840(3)
C(10)-C(15)	1.390(4)
C(10)-C(11)	1.405(4)
C(10)-Fe(2)	2.188(2)
C(10)-Fe(1)	2.318(3)
C(11)-F(1)	1.348(3)
C(11)-C(12)	1.371(4)
C(12)-F(2)	1.337(4)
C(12)-C(13)	1.372(5)
C(13)-F(3)	1.329(4)
C(13)-C(14)	1.380(5)
C(14)-F(4)	1.330(3)
C(14)-C(15)	1.377(4)

C(15)-F(5)	1.341(3)
C(16)-C(17)	1.387(4)
C(16)-C(21)	1.393(4)
C(16)-B(1)	1.656(4)
C(17)-F(6)	1.358(3)
C(17)-C(18)	1.381(4)
C(18)-F(7)	1.351(3)
C(18)-C(19)	1.372(4)
C(19)-F(8)	1.347(3)
C(19)-C(20)	1.376(4)
C(20)-F(9)	1.341(3)
C(20)-C(21)	1.378(4)
C(21)-F(10)	1.354(3)
C(22)-C(27)	1.387(4)
C(22)-C(23)	1.388(4)
C(22)-B(1)	1.649(4)
C(23)-F(11)	1.340(3)
C(23)-C(24)	1.393(4)
C(24)-F(12)	1.347(4)
C(24)-C(25)	1.368(5)
C(25)-F(13)	1.340(3)
C(25)-C(26)	1.372(5)
C(26)-F(14)	1.349(4)
C(26)-C(27)	1.377(4)
C(27)-F(15)	1.345(4)
C(28)-C(33)	1.378(4)
C(28)-C(29)	1.395(4)
C(28)-B(1)	1.649(4)
C(29)-F(16)	1.360(3)
C(29)-C(30)	1.373(4)
C(30)-F(17)	1.339(3)
C(30)-C(31)	1.374(4)
C(31)-F(18)	1.341(3)
C(31)-C(32)	1.373(4)
C(32)-F(19)	1.347(3)
C(32)-C(33)	1.382(4)

C(33)-F(20)	1.358(3)
C(34)-C(35)	1.387(4)
C(34)-C(39)	1.391(4)
C(34)-B(1)	1.668(4)
C(35)-F(21)	1.349(3)
C(35)-C(36)	1.381(4)
C(36)-F(22)	1.346(3)
C(36)-C(37)	1.374(4)
C(37)-F(23)	1.349(3)
C(37)-C(38)	1.371(4)
C(38)-F(24)	1.342(3)
C(38)-C(39)	1.379(4)
C(39)-F(25)	1.346(3)
C(40)-C(42)#1	1.375(5)
C(40)-C(41)	1.382(5)
C(40)-H(40)	0.9500
C(41)-C(42)	1.380(5)
C(41)-H(41)	0.9500
C(42)-C(40)#1	1.375(5)
C(42)-H(42)	0.9500
S(1)-Fe(1)	2.2796(8)
S(1)-Fe(2)	2.2863(8)
S(2)-Fe(1)	2.2775(8)
S(2)-Fe(2)	2.2791(8)
Fe(1)-Fe(2)	2.8032(6)

C(2)-C(1)-S(1)	118.4(2)
C(2)-C(1)-H(1A)	107.7
S(1)-C(1)-H(1A)	107.7
C(2)-C(1)-H(1B)	107.7
S(1)-C(1)-H(1B)	107.7
H(1A)-C(1)-H(1B)	107.1
C(3)-C(2)-C(1)	116.7(2)
C(3)-C(2)-H(2A)	108.1
C(1)-C(2)-H(2A)	108.1
C(3)-C(2)-H(2B)	108.1

C(1)-C(2)-H(2B)	108.1
H(2A)-C(2)-H(2B)	107.3
C(2)-C(3)-S(2)	117.69(19)
C(2)-C(3)-H(3A)	107.9
S(2)-C(3)-H(3A)	107.9
C(2)-C(3)-H(3B)	107.9
S(2)-C(3)-H(3B)	107.9
H(3A)-C(3)-H(3B)	107.2
O(1)-C(4)-Fe(1)	178.7(3)
O(2)-C(5)-Fe(1)	175.2(3)
O(3)-C(6)-Fe(1)	176.3(3)
O(4)-C(7)-Fe(2)	175.9(3)
O(5)-C(8)-Fe(2)	176.0(3)
O(6)-C(9)-Fe(2)	178.0(3)
C(15)-C(10)-C(11)	113.8(2)
C(15)-C(10)-Fe(2)	117.7(2)
C(11)-C(10)-Fe(2)	119.29(19)
C(15)-C(10)-Fe(1)	111.76(19)
C(11)-C(10)-Fe(1)	111.22(19)
Fe(2)-C(10)-Fe(1)	76.88(8)
F(1)-C(11)-C(12)	116.2(3)
F(1)-C(11)-C(10)	120.2(3)
C(12)-C(11)-C(10)	123.5(3)
F(2)-C(12)-C(11)	120.2(3)
F(2)-C(12)-C(13)	120.0(3)
C(11)-C(12)-C(13)	119.8(3)
F(3)-C(13)-C(12)	120.3(3)
F(3)-C(13)-C(14)	120.1(3)
C(12)-C(13)-C(14)	119.6(3)
F(4)-C(14)-C(15)	120.6(3)
F(4)-C(14)-C(13)	120.3(3)
C(15)-C(14)-C(13)	119.1(3)
F(5)-C(15)-C(14)	116.1(3)
F(5)-C(15)-C(10)	119.8(3)
C(14)-C(15)-C(10)	124.1(3)
C(17)-C(16)-C(21)	113.0(2)

C(17)-C(16)-B(1)	127.8(2)
C(21)-C(16)-B(1)	119.0(2)
F(6)-C(17)-C(18)	115.4(2)
F(6)-C(17)-C(16)	120.9(2)
C(18)-C(17)-C(16)	123.7(3)
F(7)-C(18)-C(19)	119.3(3)
F(7)-C(18)-C(17)	120.4(3)
C(19)-C(18)-C(17)	120.3(3)
F(8)-C(19)-C(18)	120.2(3)
F(8)-C(19)-C(20)	120.8(3)
C(18)-C(19)-C(20)	119.0(3)
F(9)-C(20)-C(19)	120.5(3)
F(9)-C(20)-C(21)	120.9(3)
C(19)-C(20)-C(21)	118.6(3)
F(10)-C(21)-C(20)	115.7(2)
F(10)-C(21)-C(16)	118.9(2)
C(20)-C(21)-C(16)	125.3(3)
C(27)-C(22)-C(23)	113.9(3)
C(27)-C(22)-B(1)	119.4(3)
C(23)-C(22)-B(1)	126.3(3)
F(11)-C(23)-C(22)	121.6(2)
F(11)-C(23)-C(24)	115.4(3)
C(22)-C(23)-C(24)	123.0(3)
F(12)-C(24)-C(25)	119.8(3)
F(12)-C(24)-C(23)	119.9(3)
C(25)-C(24)-C(23)	120.3(3)
F(13)-C(25)-C(24)	120.5(3)
F(13)-C(25)-C(26)	120.7(3)
C(24)-C(25)-C(26)	118.8(3)
F(14)-C(26)-C(25)	119.7(3)
F(14)-C(26)-C(27)	120.8(3)
C(25)-C(26)-C(27)	119.5(3)
F(15)-C(27)-C(26)	116.0(3)
F(15)-C(27)-C(22)	119.5(3)
C(26)-C(27)-C(22)	124.5(3)
C(33)-C(28)-C(29)	112.9(2)

C(33)-C(28)-B(1)	128.0(2)
C(29)-C(28)-B(1)	119.0(2)
F(16)-C(29)-C(30)	116.1(2)
F(16)-C(29)-C(28)	119.0(2)
C(30)-C(29)-C(28)	124.9(3)
F(17)-C(30)-C(29)	120.7(2)
F(17)-C(30)-C(31)	120.1(3)
C(29)-C(30)-C(31)	119.2(3)
F(18)-C(31)-C(32)	120.6(3)
F(18)-C(31)-C(30)	120.6(3)
C(32)-C(31)-C(30)	118.8(3)
F(19)-C(32)-C(31)	120.1(2)
F(19)-C(32)-C(33)	120.1(3)
C(31)-C(32)-C(33)	119.7(3)
F(20)-C(33)-C(28)	121.0(2)
F(20)-C(33)-C(32)	114.6(2)
C(28)-C(33)-C(32)	124.4(3)
C(35)-C(34)-C(39)	113.4(2)
C(35)-C(34)-B(1)	119.9(2)
C(39)-C(34)-B(1)	126.3(2)
F(21)-C(35)-C(36)	115.8(2)
F(21)-C(35)-C(34)	119.9(2)
C(36)-C(35)-C(34)	124.3(3)
F(22)-C(36)-C(37)	119.3(3)
F(22)-C(36)-C(35)	121.3(3)
C(37)-C(36)-C(35)	119.4(3)
F(23)-C(37)-C(38)	120.5(3)
F(23)-C(37)-C(36)	120.3(3)
C(38)-C(37)-C(36)	119.1(3)
F(24)-C(38)-C(37)	119.5(3)
F(24)-C(38)-C(39)	120.9(3)
C(37)-C(38)-C(39)	119.6(3)
F(25)-C(39)-C(38)	114.9(2)
F(25)-C(39)-C(34)	120.9(2)
C(38)-C(39)-C(34)	124.2(3)
C(42)#1-C(40)-C(41)	121.5(3)

C(42)#1-C(40)-H(40)	119.2
C(41)-C(40)-H(40)	119.2
C(42)-C(41)-C(40)	119.1(3)
C(42)-C(41)-H(41)	120.4
C(40)-C(41)-H(41)	120.4
C(40)#1-C(42)-C(41)	119.3(3)
C(40)#1-C(42)-H(42)	120.3
C(41)-C(42)-H(42)	120.3
C(22)-B(1)-C(28)	112.8(2)
C(22)-B(1)-C(16)	113.9(2)
C(28)-B(1)-C(16)	102.2(2)
C(22)-B(1)-C(34)	101.2(2)
C(28)-B(1)-C(34)	114.4(2)
C(16)-B(1)-C(34)	112.9(2)
C(1)-S(1)-Fe(1)	110.84(10)
C(1)-S(1)-Fe(2)	108.00(10)
Fe(1)-S(1)-Fe(2)	75.75(3)
C(3)-S(2)-Fe(1)	112.52(9)
C(3)-S(2)-Fe(2)	107.83(10)
Fe(1)-S(2)-Fe(2)	75.93(2)
C(5)-Fe(1)-C(6)	90.42(14)
C(5)-Fe(1)-C(4)	88.73(13)
C(6)-Fe(1)-C(4)	95.61(13)
C(5)-Fe(1)-S(2)	99.80(9)
C(6)-Fe(1)-S(2)	87.10(9)
C(4)-Fe(1)-S(2)	171.05(9)
C(5)-Fe(1)-S(1)	96.17(10)
C(6)-Fe(1)-S(1)	169.17(9)
C(4)-Fe(1)-S(1)	93.13(9)
S(2)-Fe(1)-S(1)	83.33(3)
C(5)-Fe(1)-C(10)	174.37(11)
C(6)-Fe(1)-C(10)	88.50(12)
C(4)-Fe(1)-C(10)	85.88(11)
S(2)-Fe(1)-C(10)	85.66(6)
S(1)-Fe(1)-C(10)	85.74(7)
C(5)-Fe(1)-Fe(2)	135.44(9)

C(6)-Fe(1)-Fe(2)	117.41(9)
C(4)-Fe(1)-Fe(2)	119.52(9)
S(2)-Fe(1)-Fe(2)	52.06(2)
S(1)-Fe(1)-Fe(2)	52.23(2)
C(10)-Fe(1)-Fe(2)	49.47(6)
C(8)-Fe(2)-C(7)	87.41(12)
C(8)-Fe(2)-C(9)	91.77(13)
C(7)-Fe(2)-C(9)	94.33(12)
C(8)-Fe(2)-C(10)	175.12(11)
C(7)-Fe(2)-C(10)	87.73(11)
C(9)-Fe(2)-C(10)	88.24(11)
C(8)-Fe(2)-S(2)	96.13(9)
C(7)-Fe(2)-S(2)	174.73(9)
C(9)-Fe(2)-S(2)	89.47(9)
C(10)-Fe(2)-S(2)	88.75(7)
C(8)-Fe(2)-S(1)	91.90(9)
C(7)-Fe(2)-S(1)	92.86(9)
C(9)-Fe(2)-S(1)	172.06(9)
C(10)-Fe(2)-S(1)	88.70(7)
S(2)-Fe(2)-S(1)	83.14(3)
C(8)-Fe(2)-Fe(1)	129.94(9)
C(7)-Fe(2)-Fe(1)	122.75(9)
C(9)-Fe(2)-Fe(1)	120.70(9)
C(10)-Fe(2)-Fe(1)	53.65(7)
S(2)-Fe(2)-Fe(1)	52.01(2)
S(1)-Fe(2)-Fe(1)	52.01(2)