Supporting Information

Elucidating the light-induced charge accumulation in an artificial analogue of methane monooxygenase enzymes using time-resolved x-ray absorption spectroscopy

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Materials and Methods

Sample Preparation. $[Fe^{III}_2(N\text{-EtHPTB})(H_2O)_2(CH_3O)(CH_3OH)](ClO_4^-)_4$ was synthesized as previously described[1] and matched all reported characterization.

Time-resolved XAS measurements. Time-resolved X-ray absorption spectra were collected at 11 ID-D[2] beamlines at the Advanced Photon Source using undulator radiation at electron energy 8.3 keV. The experiments were carried out using the 24 bunch timing mode of APS (in top up mode with a constant 102 mA ring current) which consists of a train of X-rays separated by 153 ns. This mode easily allows for gateable detectors that selects X-ray pulses. This timing mode was suitable for this type of experiments in which a fresh sample was required for every incoming X-ray pulse as well as for the time resolution of the avalanche Photodiode (APD) detectors.

The sample was pumped at 527 nm wavelength using a regenerative amplified laser with 1.6 kHz repetition rate 5ps-FWHM pulse length and laser power of 630 mW. The solutions mixtures in acetonitrile was circulated through a stainless steel nozzle into a free-flowing 550 μm cylindrical jet inside an airtight aluminium chamber, and continuously degassed with nitrogen. The X-ray and laser beam was spatially overlapped with an X-ray spot size of 100 μm(V) x 450 μm(H) and laser spot size of 170 μm(V) x 550 μm. With a liquid flow speed of 3 m/s, the pumped laser volume was calculated to move out of the FWHM region in around 30 μs. This temporal range ensured that the excited state volume was probed more at the center and less at the edges where the excitation fraction would be less, due to movement of the sample. Beamline 11 ID-D has an automated data digitization system which allows for all X-ray pulses after laser excitation to be collected. Such a system, together with the larger X-ray beam spot size, was very useful for our experiments, as multiple X-ray pulses after laser excitation were averaged to monitor the dynamics for the formation and decay of the reduced Fe(II,II) state in the ns-μs time regime. In addition, by averaging multiple pulses, we obtained a better resolution of the main features in the pre-edge and edge regions of the transient signals.

The delay between the laser and X-ray pulses was adjusted by a programmable delay line (PDL-100A-20NS, Colby Instruments) and the X-ray fluorescence signals were collected with two APDs positioned at 90˚ on both sides of the liquid jet. Moreover, a combination of Z-1 filters and soller slits with conical geometry were used to reduce the background from elastically scattered X-rays. The rise and decay kinetics of the differous state were determined by recording the intensity of the laser (on-off) signal at the peak energy of the transient signal. An Fe metal foil was placed between two ionization chambers downstream to the X-ray beam, and its transmission recorded with each scan for energy calibration. The energy was calibrated by using an Fe foil standard with the first inflection point being at 7111 eV.

The ternary mixture consisting of $[Ru(bpy)_3]^{2+}$ (10 mM), Fe(III,III) (1 mM) with triethylamine as the sacrificial electron donor (660 mM) in acetonitrile under continuous pumping condition was fitting with the following sets of differential equations:

$$\frac{d[Fe(III,III)]}{dt} = -k_1[Fe(III,III)] \quad \text{(Under continous pumping)} \qquad \text{(Eq. 1)}$$

$$\frac{d[Fe(II,II)]}{dt} = k_1[Fe(III,III)] - k_2[Fe(II,II)] \qquad \text{(Eq.2)}$$

(The term $k_1[Fe(III,III)]$ is due to continuous pumping while the term $k_2[Fe(II,II)]$ is caused by degradation pathways leading to the Fe(II,II) state's decay.

EXAFS data analysis. Athena software[3] was used for data processing. The energy scale for each scan was normalized using iron metal standard. Data in energy space were pre-edge corrected, normalized, and background corrected. The processed data were next converted to the photoelectron wave vector (k) space and weighted by k^2. The electron wave number is defined as $k = [2m(E - E_0)/\hbar^2]^{1/2}$, E_0 is the energy origin or the threshold energy. K-space data were truncated near the zero crossings (k = 2.621 to 10.55 Å^{-1}) in Fe EXAFS before Fourier transformation. The k-space data were transferred into the Artemis Software for curve fitting. In order to fit the data, the Fourier peaks were isolated separately, grouped together, or the entire (unfiltered) spectrum was used. The individual Fourier peaks were isolated by applying a Hanning window to the first and last 15% of the chosen range, leaving the middle 70% untouched. Curve fitting was performed using *ab initio*-calculated phases and amplitudes from the FEFF8[4] program from the University of Washington *Ab initio*-calculated phases and amplitudes were used in the EXAFS equation[5]

$$\chi(k) = S_0^2 \sum_j \frac{N_j}{kR_j^2} f_{eff_j}(\pi, k, R_j) e^{-2\sigma_j^2 k^2} e^{\frac{-2R_j}{\lambda_j(k)}} \sin(2kR_j + \phi_{ij}(k)) \qquad \text{Eq. (2)}$$

where N_j is the number of atoms in the j^{th} shell; R_j the mean distance between the absorbing atom and the atoms in the j^{th} shell; $f_{eff_j}(\pi, k, R_j)$ is the *ab initio* amplitude function for shell *j*, and the Debye-Waller term $e^{-2\sigma_j^2 k^2}$ accounts for damping due to static and thermal disorder in absorber-backscatterer distances. The mean free path term $e^{\frac{-2R_j}{\lambda_j(k)}}$ reflects losses due to inelastic scattering, where $\lambda_j(k)$, is the electron mean free path. The oscillations in the EXAFS spectrum are reflected in the sinusoidal term $\sin(2kR_j + \phi_{ij}(k))$, where $\phi_{ij}(k)$ is the *ab initio* phase function for shell *j*. This sinusoidal term shows the direct relation between the frequency of the EXAFS oscillations in k-space and the absorber-back scatterer distance. S_0^2 is an amplitude reduction factor.

The EXAFS equation (Eq. 1) was used to fit the experimental Fourier isolated data (q-space) as well as unfiltered data (k-space) and Fourier transformed data (R-space) using N, S_0^2, E_0, R, and σ^2 as variable parameters**.** N refers to the number of coordination atoms surrounding Fe for each shell. The quality of fit was evaluated by R-factor and the reduced Chi^2 value. The deviation in E_0 ought to be less than or equal to 10 eV. R-factor less than 2% denotes that the fit is good enough[5] whereas R-factor between 2 and 5% denotes that the fit is correct within a consistently broad model. The reduced Chi^2 value is used to compare fits as more absorber-backscatter shells are included to fit the data. A smaller reduced Chi^2 value implies a better fit. The Fe-O-Fe was additionally determined by creating a model in FEFF which accounts for the backscattering amplitude and phase shift of the Fe-O-Fe three atom system. The fitting of the entire spectrum was carried out to optimize the Fe-O distance , Fe-O-Fe bond angle and Debye-Waller factors, The experimental data was fitted from 110-150 degrees with 1 degree steps and the best fit was determined to be the one with Fe-O-Fe coordination number to 1 and least reduced chi-square value.

Electronic structure Simulations. Ground state energies and geometry optimization of diiron complexes, Fe(II)/Fe(II) and Fe(III)/Fe(III), where performed with Density Functional Theory with the exchange-correlation functionals gradient corrected approximation (GGA) PBE. We used the wavelet basis code BigDFT[6] and norm conserving Hartwigsen-Goedecker-Hutter (HGH)[7] pseudopotentials with a nonlinear core corrections (NLCC).[8] Calculations including dispersion effects were also carried out with Gaussian09 program package.[9] In this case, B3LYP functional with empirical dispersion D3 correction of Grimme (B3LYP-D3) [10-13] was used. We chose the following basis sets in the calculations: 6-31G* [14-16] for C, N, O and H and LANL2DZ for Fe atoms, including the associated pseudopotential of this basis. [17-19] All geometry optimizations were performed without symmetry restrictions and confirming the nature of the minima through vibrational frequency calculations (no imaginary frequencies). For the calculation of the solvent groups dissociation energy from the Fe(II)/Fe(II) species, single point calculations were carried out using the optimized structures and including solvent effects with the SMD model for the experimental solvent acetonitrile, ε= 35.688. Free energy was calculated using the corrections at 298.15 K and 105 Pa pressure, including zero point energy corrections (ZPE). A correction term of 1.9 kcal/mol (at 298 K) was added to account for the standard state concentration of 1 M.

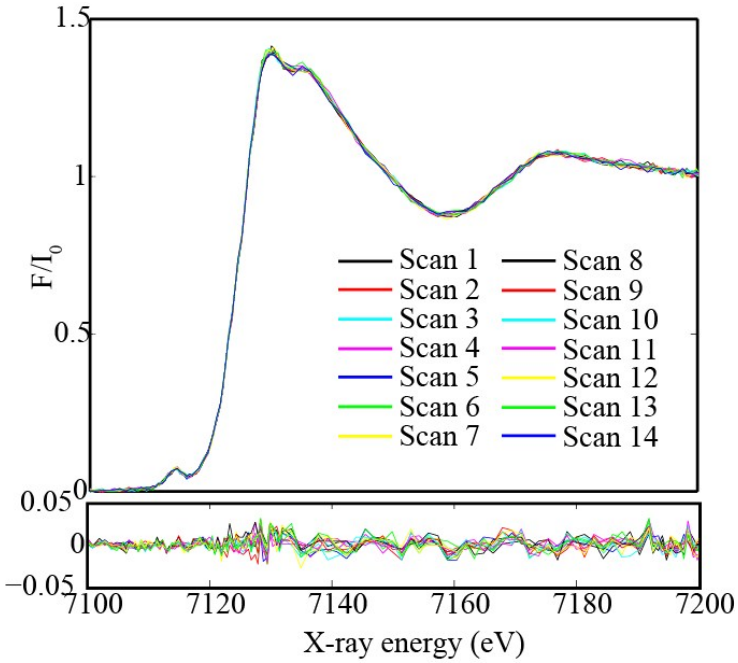

Figure S1. Normalized Fe K-edge XANES upon irradiation in acetonitrile over a total of 14 scans and 4.7 hours. The difference between scan 1-scan 2 , scan 1-scan 3, scan 1-scan 4 etc is also shown in the bottom inset of the figure.

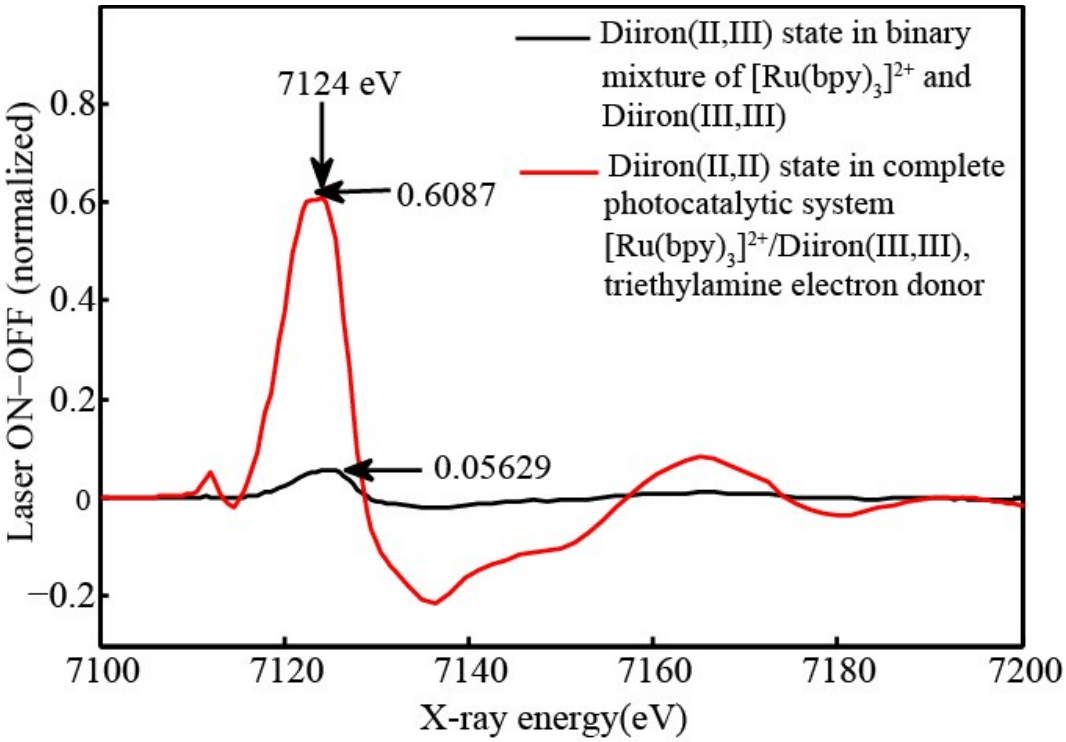

Figure S2. Difference spectrum corresponding to the **(1)** diiron(II,III) reduced state's transient signal in a binary mixture of the photosensitizer $[Ru(bpy)_3]^{2+}$ (10 mM) and diiron(III,III) (1 mM) in acetonitrile **(II)** the diiron(II,II) reduced state in a ternary mixture of $[Ru(bpy)_3]^{2+}$ (10 mM), diiron(III,III) (1 mM) with the triethylamine electron donor (660 mM) in acetonitrile . Since only a maximum relative shift in energy of ~0.32 eV for the reduced iron(II) species was observed in the binary mixture, the presence of the diiron(II,III) dimer is naturally dominated in the latter case. Comparison of the peak energy of the transient signal at 7124 eV in both cases shows that the diiron(II,III) state in a binary mixture shows the presence of 9.2 % pure diiron(II,II) or 18.4 % diiron(II,III). This shows the favored recombination of the diiron(II,III) state with $[Ru(bpy)_3]^{3+}$ in the binary mixture as illustrated in scheme of processes shown in Figure 1 A.

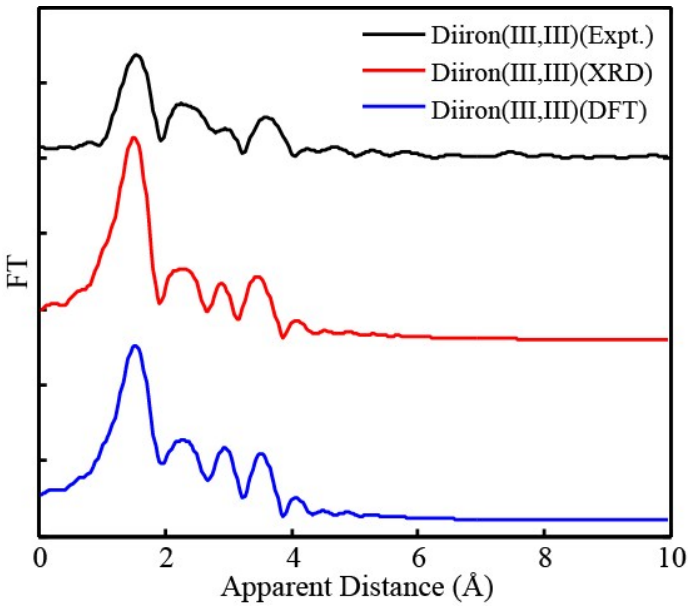

Figure S3. Fourier transforms of k^2-weighted EXAFS of the starting diiron(III,III) complex in acetonitrile (black) in acetonitrile, Simulated EXAFS spectra. Atomic coordinates were obtained from single crystal XRD structure of diiron(III,III) complex (red) and from DFT simulations (blue)

Scheme S1. Solvent molecules dissociation from the Diiron(II,II) species with the calculated energy for this process, using acetonitrile as solvent.

$[\mu(\text{N-EtHPTB})Fe^{II}(OH_2)_2Fe^{II}(MeO)(MeOH)] \rightarrow [\mu(\text{N-EtHPTB})Fe^{II}Fe^{II}] + 2\ H_2O + MeO^- + MeOH$

$\Delta G^0 = 71.06\ kcal \cdot mol^{-1}$

Calculation of the free energy for the MeOH/MeO-/H_2O ligands dissociation from the diiron(II,II) species resulted being an endothermic process confirming that the methanol ligands survive unchanged in acetonitrile after conversion from diiron(III,III) to diiron(II,II).

Table S1. EXAFS Fits parameters for diiron(III,III) and diiron(II,II)

Sample	Fit	Peak	Shell,N	R, Å	E_0	ss.^{2} (10^{-3})	R-factor	Reduced Chi-square
Diiron(III,III)	1	1	Fe-N/O,6	2.04	-7.8	15.7	0.0264	33002
	2	1,2	Fe-N/O,6 Fe-C,6 Fe-C,3	2.05 2.99 3.27	-3.7	16.2 14.5 14.5	0.0337	1630
	3	all	Fe-N/O,6 Fe-C,6 Fe-C,3 Fe-O-Fe,1	2.05 2.99 3.27 3.72	-3.7	16.2 14.5 14.5 14.1	0.0402	556
Diiron(II,II)	4	1	Fe-N/O,6	2.02	-10.4	10.5	0.0298	71212
	5	1,2	Fe-N/O,6 Fe-C,6 Fe-C,3	2.04 3.01 3.33	-5.8	10.9 9.5 9.5	0.0251	3382
	6	all	Fe-N/O,6 Fe-C,6 Fe-C,3 Fe-O-Fe,1	2.04 3.01 3.33 3.58	-5.8	10.9 9.5 9.5 18.5	0.0332	807

- The amplitude reduction factor, S_0^2 was fixed to 1. The debye waller factor for the 2 sets of carbon within the 2nd coordination shell was fitted as one parameter. Peak I refers to the region between 1-2.05, 1-3.2 Å, all to 1-4 Å.

Table S2. Comparison of structural parameters from EXAFS, DFT and XRD data of diiron(III,III) and diiron(II,II) complexes

Species, Fit number in Table S1	EXAFS Shell: N x distance in Å	XRD[1] bond distances (Å)	DFT optimized coordinates, B3LYP, in gas phase, (Å)
Diiron(III,III), Fit 3	Fe-N/O: 6 x 2.05 Fe-C: 6 x 2.99 Fe-C: 3 x 3.27 Fe-Fe: 3.72 Fe-O-Fe: 130˚	Fe-N: 2.06, 2.07, 2.07, 2.07, 2.24, 2.28 Fe-O (methanolate/methanol groups): 1.87, 2.07 Fe-O (aqua groups): 1.94, 2.04 Fe-O in Fe-O-Fe bridge: 1.98, 2.03 Fe-Fe: 3.65 Fe-O-Fe: 131˚	Fe-N:2.05, 2.06, 2.07, 2.08, 2.27, 2.35 Fe-O (Methanolate/methanol groups): 1.87, 2.20 Fe-O(aqua groups): 2.05, 2.20 Fe-O in Fe-O-Fe bridge: 2.03, 2.08 Fe-Fe: 3.72 Fe-O-Fe: 130˚
Diiron(II,II), Fit 6	Fe-N/O: 6 x 2.04 Fe-C: 6 x 3.01 Fe-C: 3 x 3.33 Fe-Fe: 3.58 Fe-O-Fe: 123˚		Fe-N: 2.10, 2.12, 2.39, 2.20, 2.20, 2.52 Fe-O (methanolate/methanol groups): 1.92, 2.25 Fe-O(aqua groups): 2.11, 2.34 Fe-O in Fe-O-Fe bridge: 2.06, 2.16 Fe-Fe: 3.69 Fe-O-Fe: 121˚

Table S3: DFT optimized coordinates for Diiron(III,III), Diiron(III,II) and Diiron(II,II) species

Optimized structures with B3LYP-D3

H_2O

E= -76.4089619876 H

O	0.18585100	1.75848300	0.00000000
H	1.15309900	1.80762100	0.00000000
H	-0.09070800	2.68665800	0.00000000

MeOH

E= -115.715528078 H

C	-0.87230900	1.36904000	-0.01747600
H	-0.49810000	1.86719300	0.88156700
H	-0.51415400	1.93339700	-0.89364300
H	-1.97313900	1.41728500	-0.00038500
O	-0.37931500	0.03802500	0.01866300
H	-0.70350700	-0.41769600	-0.77242300

MeO^-

E= -115.072912438 H

C	-0.82465300	1.26388000	0.00000000
H	-0.51968900	1.94629800	0.89184300
H	-0.51968900	1.94629800	-0.89184300
H	-1.97652200	1.43171000	0.00000000
O	-0.38727800	0.02892200	0.00000000

Diiron(III,III)

E= -2920.59506578 H

C	9.33884700	-1.12712000	6.64328800
H	8.71606100	-1.41705200	7.49315200
H	10.33473000	-1.56580600	6.79074700
C	8.67135400	-1.69111400	5.37662300

H	9.29646300	-1.48263600	4.49573300
C	8.48434000	-3.20278500	5.55225900
H	9.44878400	-3.72365500	5.62131800
H	7.92944100	-3.36728900	6.47899800
C	10.60532700	0.89226500	5.93819100
H	11.47517700	0.23492600	6.06279800
H	10.87768700	1.85601800	6.38191700
C	10.27263400	1.10274600	4.48973600
C	9.04215500	1.45693900	2.70930400
C	10.39521800	1.54018000	2.32327400
C	10.77888100	1.83132500	1.01245200
H	11.81956400	1.91386900	0.71741000
C	9.74770900	2.04211400	0.09792700
H	9.99628200	2.29306300	-0.92835100
C	8.39071200	1.95816400	0.47740300
H	7.62383700	2.13631000	-0.26778500
C	8.01451000	1.65838600	1.78323000
H	6.97511900	1.58380700	2.07938600
C	12.62160700	1.39454000	3.56570700
H	13.01768700	0.92908900	2.65931100
H	12.95112700	0.78350600	4.41017100
C	13.09245200	2.84291800	3.70196800
H	12.75528400	3.45009700	2.85671600
H	14.18578400	2.86956200	3.72495100
H	12.72354900	3.29707900	4.62790800
C	9.25078700	0.91268100	8.01261100
H	9.51925400	1.97285400	7.98753000
H	9.90898900	0.41723100	8.73709700
C	7.80251100	0.77875300	8.38390900
C	5.88249600	0.52746100	9.45323500
C	4.84462300	0.36835300	10.37471800
H	5.02069300	0.32854900	11.44443200
C	3.55540600	0.27262900	9.85382400
H	2.71846500	0.15695100	10.53480700
C	3.30727000	0.33904700	8.46564600
H	2.28142100	0.28624500	8.11416700
C	4.34482400	0.50368000	7.54827100
H	4.16848200	0.60930600	6.48265300
C	5.64519300	0.60153100	8.06408400
C	7.96249700	0.70921000	10.92387600
H	8.99186500	0.37356400	10.77492500
H	7.47748500	-0.02260500	11.57505300
C	7.91012500	2.11582200	11.52031100
H	8.42274900	2.83970000	10.87796200
H	8.40717900	2.11500600	12.49476200
H	6.87779700	2.44724200	11.66661400

C	8.36654500	-3.78931400	3.13953600
H	9.44222100	-3.65038000	3.29711600
H	8.24858400	-4.78427600	2.69459400
C	7.82688600	-2.77434500	2.16748100
C	6.43975600	-1.36010500	1.23336900
C	7.44653600	-1.65945100	0.29368100
C	7.44545700	-1.13206600	-0.99583300
H	8.21555700	-1.36878700	-1.72222300
C	6.37827200	-0.28877000	-1.32366000
H	6.32501000	0.12880600	-2.32413900
C	5.36478500	0.01710700	-0.39429400
H	4.54821200	0.66362800	-0.69957600
C	5.37716400	-0.50939600	0.89685700
H	4.58895500	-0.29674600	1.60912200
C	9.57274300	-3.07046600	0.35572000
H	9.38579500	-3.27803900	-0.70079900
H	9.80158300	-4.02812600	0.83069500
C	10.70797000	-2.06092900	0.53783500
H	10.45572000	-1.10084900	0.07741900
H	11.61965400	-2.44277700	0.06935800
H	10.91177200	-1.88812800	1.60153300
C	7.03995200	-5.06924500	4.80343700
H	6.90957100	-5.10377100	5.88994700
H	7.69492900	-5.90512600	4.53500700
C	5.69120300	-5.16489100	4.14943200
C	3.77651900	-4.45358900	3.35393200
C	2.68107200	-3.71217900	2.88514800
H	2.68033800	-2.62717700	2.92280500
C	1.60718000	-4.42447100	2.35177100
H	0.73985800	-3.88856700	1.98050900
C	1.62541300	-5.82996100	2.27870900
H	0.77151500	-6.35089100	1.85775800
C	2.72282600	-6.57987200	2.72966700
H	2.72584200	-7.66237300	2.65845200
C	3.78916400	-5.86034700	3.26289600
C	5.44910400	-7.68650200	3.92012900
H	5.13033800	-8.20108400	3.01001200
H	6.54140400	-7.71281200	3.93922300
C	4.84824400	-8.32943400	5.17128000
H	5.19269700	-7.82861300	6.08212500
H	5.15858600	-9.37726700	5.22049800
H	3.75502600	-8.30056500	5.14706200
C	5.31147600	2.57945800	4.18630800
H	4.70308700	2.95248900	5.01769800
H	4.67740100	2.46294500	3.30139600
H	6.10232500	3.30061700	3.96189100

C	7.20907400	3.96649400	6.75217400
H	6.62025400	3.37463400	7.45089700
H	6.54729800	4.56725200	6.12436200
H	7.90693400	4.61117900	7.29168600
N	9.41234500	0.36021700	6.64047000
N	7.64949000	-3.75169400	4.45251300
N	8.99920700	1.18245900	4.07765900
N	11.14680400	1.29473300	3.48186300
N	6.86946800	0.76870500	7.42459100
N	7.26990800	0.63597400	9.61569900
N	6.71310100	-2.06744000	2.40081200
N	8.31080700	-2.56264000	0.92770800
N	4.97415400	-4.04381800	3.92336800
N	5.03268400	-6.27209900	3.77021100
O	7.40207700	-1.08466600	5.18320600
O	5.31931500	-2.49453200	6.38730300
H	5.32284000	-1.68800800	6.94104300
H	4.51789800	-2.99401000	6.62202000
O	4.56333800	-0.76197200	4.02631300
H	3.70290600	-0.75650500	4.47766800
H	5.03544100	0.15355600	4.19584600
O	7.95525000	3.01057800	5.93900000
H	8.41392600	3.48087200	5.22215700
O	5.88499200	1.31357800	4.53080600
Fe	5.93745500	-2.26487700	4.28889000
Fe	7.46695600	0.92411300	5.44361900

Diiron(II,II)

E= -2921.46229827 H

C	9.46190900	-0.95569900	6.55770200
H	9.00607100	-1.32124900	7.48432400
H	10.50144200	-1.31543700	6.54038500
C	8.64405900	-1.54959700	5.39501600
H	9.13651000	-1.30373400	4.44141300
C	8.58637800	-3.07984900	5.55679300
H	9.59661000	-3.52026300	5.52857300
H	8.14463700	-3.29900100	6.53331900
C	10.57879100	1.16579700	5.95121600
H	11.52495500	0.66058100	6.19777900
H	10.65974100	2.19321300	6.32405500
C	10.37002200	1.22717100	4.46224900
C	9.35503800	1.38608600	2.54817600
C	10.73849300	1.51263900	2.29563200
C	11.24420400	1.73570700	1.01268700

H	12.30640400	1.84622800	0.82016500
C	10.30847000	1.83005300	-0.01549700
H	10.65370900	2.01696600	-1.02767900
C	8.92462900	1.69484800	0.22645100
H	8.23146300	1.76604200	-0.60406200
C	8.42592700	1.46353200	1.50521700
H	7.36574200	1.34112200	1.69407500
C	12.79824400	1.57101700	3.78127000
H	13.32687900	1.13598800	2.92842900
H	13.07519500	0.98018600	4.65877300
C	13.16751300	3.04383900	3.96509400
H	12.88310800	3.62812100	3.08451500
H	14.24714000	3.14523100	4.11185900
H	12.66272000	3.46975000	4.83933400
C	9.14167700	1.03824100	7.95542300
H	9.32979300	2.11607900	7.95873600
H	9.78485700	0.58482800	8.72177900
C	7.68073700	0.81825800	8.24004800
C	5.74903900	0.17766300	9.11650900
C	4.68838600	-0.35463200	9.85738600
H	4.83393000	-0.81287500	10.83009200
C	3.42121000	-0.27048000	9.28401000
H	2.56966700	-0.67128300	9.82453500
C	3.20968200	0.34646600	8.02783000
H	2.19689100	0.41859000	7.64246400
C	4.26711000	0.88432500	7.29905000
H	4.13726400	1.38490800	6.34480800
C	5.54868300	0.77560600	7.85398400
C	7.78858000	-0.19155100	10.58365200
H	8.81152100	-0.49086300	10.34092300
H	7.27259400	-1.08832400	10.93883800
C	7.76898200	0.91359900	11.64014200
H	8.30916600	1.79956200	11.29009000
H	8.24651200	0.56041300	12.55921300
H	6.74212400	1.20844400	11.87723600
C	8.28757000	-3.68760000	3.18162600
H	9.37016300	-3.51101600	3.23780200
H	8.16620300	-4.68529700	2.73991200
C	7.64608600	-2.68615200	2.25400600
C	6.22681100	-1.27027900	1.41773100
C	7.16002900	-1.56541400	0.40361300
C	7.07965500	-0.99585000	-0.86851700
H	7.79947500	-1.22007500	-1.64883100
C	6.02299400	-0.11580900	-1.09066200
H	5.91492300	0.34463700	-2.06795600
C	5.08267600	0.18457400	-0.08086700

H	4.26905100	0.86736000	-0.30570500
C	5.16558200	-0.38923300	1.18454400
H	4.43975800	-0.18538900	1.96312100
C	9.29573200	-2.94673200	0.34903200
H	9.09999300	-3.07374100	-0.71918100
H	9.52369600	-3.94036900	0.74620400
C	10.44940500	-1.96970100	0.58713500
H	10.20709600	-0.97907300	0.19237400
H	11.35828400	-2.33070300	0.09548100
H	10.65539700	-1.86260300	1.65866100
C	7.10531600	-4.97193500	4.92830700
H	7.02813500	-4.99185400	6.02017500
H	7.73223600	-5.82476400	4.63402100
C	5.71555100	-5.07881400	4.35766400
C	3.73907000	-4.43980800	3.70412100
C	2.59723800	-3.71833300	3.34031900
H	2.58031600	-2.63578900	3.42389700
C	1.51259100	-4.44858300	2.86750600
H	0.60503200	-3.93004300	2.57453700
C	1.56206000	-5.85565200	2.75609000
H	0.69125500	-6.38654700	2.38465300
C	2.69717300	-6.58092000	3.10785900
H	2.72551900	-7.66194700	3.01837100
C	3.78552900	-5.84248400	3.57957300
C	5.52931600	-7.60614300	4.12232800
H	5.12479600	-8.15853600	3.26938900
H	6.61780100	-7.61549400	4.01796200
C	5.09401900	-8.23725600	5.44579700
H	5.52354700	-7.69852100	6.29741100
H	5.42838800	-9.27822000	5.49258300
H	4.00428100	-8.22034900	5.54372200
C	5.41604700	2.51833100	3.45090900
H	4.58410000	3.06851400	3.91558200
H	5.10579400	2.21879300	2.44024000
H	6.26177800	3.21413900	3.34185200
C	7.10276500	4.22634300	6.16065000
H	6.70615500	3.73525200	7.04836400
H	6.28089400	4.44847700	5.47320600
H	7.62283000	5.14759500	6.44045400
N	9.42484800	0.52764900	6.59697300
N	7.69902000	-3.67549500	4.53906900
N	9.16346400	1.21208900	3.91533700
N	11.36280200	1.38401700	3.53717100
N	6.77459900	1.15166900	7.33525100
N	7.12621800	0.21681100	9.33741200
N	6.56839600	-1.98536500	2.55870000

N	8.05297600	-2.47854600	0.96782200
N	4.95868900	-4.00166200	4.20093200
N	5.06762400	-6.21940000	3.99128800
O	7.35259700	-1.00607600	5.42131000
O	5.59851700	-2.32132600	6.87326000
H	6.27785600	-1.61096300	6.85079600
H	4.81927300	-1.93469400	7.30612400
O	4.35677400	-0.66887400	4.41498600
H	3.80977000	-0.55274600	5.20790900
H	4.86749900	0.23376700	4.28118500
O	8.02639900	3.28294200	5.57208300
H	8.37987600	3.64859800	4.74480100
O	5.78234600	1.39372700	4.22013100
Fe	5.86556900	-2.13817000	4.55090100
Fe	7.40127200	1.14660300	5.22458100

Diiron(II,II) (without H_2O, MeO^- and MeOH groups coordinated)

E= -2537.27679581 H

C	8.82762700	-2.35763500	6.39755500
H	8.21119000	-2.97768500	7.05252200
H	9.87230900	-2.67434700	6.51346700
C	8.34340700	-2.58180900	4.95194800
H	8.98288300	-2.01459300	4.26265000
C	8.39493200	-4.07113100	4.57852600
H	9.42341900	-4.45380000	4.64435700
H	7.77117700	-4.63047700	5.28327300
C	9.80705000	-0.05357300	6.51871400
H	10.75370800	-0.57971600	6.69576900
H	9.77595300	0.78837500	7.22020800
C	9.74073300	0.50315700	5.11909500
C	8.89303400	1.20156200	3.22500600
C	10.26837800	1.50856000	3.21746200
C	10.88017600	2.16406200	2.14629400
H	11.93455800	2.41904600	2.14824900
C	10.05745300	2.49665500	1.07262600
H	10.48411400	3.02187500	0.22400300
C	8.68188500	2.17848100	1.06512800
H	8.07923700	2.45324600	0.20655100
C	8.07880200	1.52385600	2.13484300
H	7.02103400	1.28071100	2.12225200
C	12.15859700	1.25616400	4.90578500
H	12.81241600	1.12304300	4.03985700
H	12.40521300	0.46110200	5.61459500

C	12.33643600	2.64035700	5.53086800
H	12.08585100	3.42907800	4.81540300
H	13.37765500	2.77444100	5.83837800
H	11.70046500	2.76150800	6.41441900
C	8.14701700	-0.75522500	8.20463400
H	8.96788000	-0.58166500	8.91043700
H	7.64905100	-1.67824500	8.51792500
C	7.14429700	0.37175300	8.23439100
C	5.80392200	2.00053100	8.91145000
C	5.10265100	2.98247600	9.61504200
H	5.27133900	3.17205300	10.66956500
C	4.16955600	3.71522000	8.88825800
H	3.59864000	4.48955100	9.39008800
C	3.94590400	3.47923700	7.51398700
H	3.20715700	4.07810500	6.99137800
C	4.64784600	2.49995300	6.81984500
H	4.47259000	2.31859500	5.76313500
C	5.58620100	1.75723100	7.54238100
C	7.37551900	1.03036200	10.67027500
H	7.73072000	0.01026800	10.83768400
H	6.55319100	1.19450500	11.37118500
C	8.48862300	2.05976300	10.86461400
H	9.32662000	1.87087700	10.18363500
H	8.86463700	2.00735600	11.89048800
H	8.12076700	3.07446400	10.68589600
C	8.64827600	-3.75758800	2.11326400
H	9.57450000	-3.32895200	2.51277700
H	8.96123600	-4.56445000	1.44142900
C	7.89168600	-2.70124300	1.34181600
C	6.32594400	-1.28616500	0.75973100
C	7.38742300	-1.14510400	-0.15342000
C	7.34820400	-0.22708700	-1.20476200
H	8.16366300	-0.12178600	-1.91211200
C	6.19800500	0.55100000	-1.30577100
H	6.11550900	1.27104800	-2.11366400
C	5.12858100	0.41913400	-0.39231300
H	4.24781300	1.04019700	-0.51969400
C	5.17330900	-0.50164300	0.65028900
H	4.34044700	-0.62134400	1.33775500
C	9.70345300	-2.19567700	-0.34791100
H	9.59337100	-2.04818900	-1.42504200
H	10.04244700	-3.22546400	-0.20522200
C	10.68375600	-1.18926400	0.25648500
H	10.32756300	-0.16464200	0.11927200
H	11.66069400	-1.28690800	-0.22606400
H	10.81342500	-1.36058400	1.33193400

C	7.37177400	-5.70189800	3.02254600
H	8.05978600	-6.40937300	3.50276100
H	7.38738300	-5.91705100	1.94852800
C	5.95994200	-5.88158400	3.52352700
C	3.89672800	-5.38694400	4.08986200
C	2.68300900	-4.77153500	4.40890800
H	2.57312300	-3.69089300	4.39160400
C	1.61911700	-5.60397800	4.73907800
H	0.65709700	-5.16750100	4.98712000
C	1.75768900	-7.00913900	4.75613000
H	0.90069000	-7.62059400	5.01889600
C	2.96287400	-7.63020300	4.44324600
H	3.06228000	-8.71014700	4.45917900
C	4.02577800	-6.78810900	4.10882700
C	5.93761700	-8.41269000	3.65170200
H	5.18051200	-9.05704600	3.19712500
H	6.77675800	-8.37181800	2.95217900
C	6.36808700	-8.93641900	5.02176800
H	7.14703000	-8.30306000	5.46073900
H	6.76744500	-9.94965800	4.91950400
H	5.52098600	-8.97096600	5.71318900
N	8.64560400	-0.93717500	6.81298000
N	7.81981500	-4.29604100	3.22578900
N	8.59247400	0.57838200	4.43623700
N	10.77798100	1.03557400	4.43361100
N	6.43808200	0.72263000	7.14561200
N	6.79504500	1.09594700	9.31444400
N	6.67224100	-2.26982500	1.68627000
N	8.36155800	-2.06807000	0.24474600
N	5.13015700	-4.84446700	3.71828900
N	5.34828300	-7.06224400	3.73666500
O	7.00108000	-2.08563500	4.82635900
Fe	5.98471200	-3.06335700	3.41387200
Fe	7.01636900	-0.20815100	5.47040000

Diiron(III,II)

E= -2921.08881525 H

C	9.35027500	-1.01365800	6.69182300
H	8.75487300	-1.31655100	7.55712100
H	10.35637900	-1.43846100	6.80971000
C	8.64837500	-1.57284400	5.44110300
H	9.26168300	-1.37717400	4.54871800
C	8.45050400	-3.08732100	5.61820100
H	9.42411200	-3.58916200	5.73002100

H	7.87161000	-3.23875800	6.53277100
C	10.57723500	1.03024700	5.98737000
H	11.47403300	0.41688200	6.14411200
H	10.79653600	2.02233400	6.39635800
C	10.25161900	1.16900300	4.52774100
C	9.03119700	1.42215900	2.72789700
C	10.38363300	1.43257300	2.33209100
C	10.76530900	1.59751300	0.99827400
H	11.80585700	1.62351600	0.69233200
C	9.73358300	1.74487200	0.07380200
H	9.98029000	1.88727000	-0.97351900
C	8.37663000	1.72289500	0.46292500
H	7.60773700	1.82610800	-0.29364200
C	8.00265500	1.55719500	1.79186900
H	6.96446400	1.51442900	2.09712500
C	12.60391100	1.30282800	3.57407600
H	12.97888500	0.75162600	2.70731900
H	12.91800200	0.75083700	4.46387000
C	13.13082400	2.73810200	3.59163800
H	12.80774600	3.28579000	2.70131200
H	14.22453900	2.72927200	3.60988200
H	12.77955000	3.27792500	4.47762900
C	9.23370000	1.02324800	8.06501400
H	9.48060900	2.08843700	8.03902700
H	9.90034700	0.53999800	8.79047200
C	7.78800800	0.86277000	8.43946300
C	5.88356200	0.50747700	9.50978000
C	4.85529100	0.25739700	10.42238500
H	5.04006500	0.14653500	11.48555900
C	3.56752400	0.15896700	9.90091100
H	2.73823700	-0.03108800	10.57437700
C	3.31029500	0.31044500	8.52055200
H	2.28582900	0.24250600	8.16762500
C	4.33648100	0.57049000	7.61373100
H	4.15682100	0.72154900	6.55459900
C	5.63542200	0.67163100	8.13094500
C	7.96961000	0.61805600	10.96794100
H	9.00227000	0.30781200	10.78964500
H	7.50103600	-0.16327700	11.57244600
C	7.90624000	1.97748900	11.66439500
H	8.40226700	2.75090700	11.06846600
H	8.41078400	1.91739000	12.63318300
H	6.87020700	2.28370000	11.83783600
C	8.38024200	-3.69161600	3.21499000
H	9.44334200	-3.46706800	3.37010200
H	8.34561100	-4.70764600	2.80310600

C	7.78386400	-2.74841200	2.20075200
C	6.39046400	-1.38497500	1.22749300
C	7.35720400	-1.74816800	0.26914200
C	7.31748200	-1.27708300	-1.04491000
H	8.06040700	-1.55823500	-1.78391700
C	6.25791400	-0.43381600	-1.37034600
H	6.17485200	-0.05685200	-2.38490700
C	5.28150800	-0.06687800	-0.41818300
H	4.46676400	0.58180500	-0.72463400
C	5.33166800	-0.53351200	0.89214800
H	4.57754000	-0.27638400	1.62798400
C	9.46984800	-3.16749400	0.35521700
H	9.27365600	-3.39463700	-0.69589300
H	9.68415300	-4.12027100	0.84781300
C	10.63483800	-2.18669500	0.50242900
H	10.39862400	-1.23053700	0.02606500
H	11.53492500	-2.59820200	0.03596800
H	10.85101700	-1.99323700	1.56027700
C	7.02624400	-4.96271900	4.85105100
H	6.85561300	-4.97932100	5.93245400
H	7.68270400	-5.81028100	4.61973800
C	5.69698900	-5.07244800	4.15136700
C	3.78020100	-4.43374300	3.32848900
C	2.66601700	-3.72234700	2.87000600
H	2.61048500	-2.64310200	2.97876500
C	1.65428200	-4.45226300	2.25689500
H	0.77181900	-3.93982600	1.88728800
C	1.74749200	-5.85303700	2.09821400
H	0.93293300	-6.38447000	1.61693300
C	2.85674800	-6.56877400	2.53808700
H	2.92047900	-7.64398500	2.40870100
C	3.87181700	-5.82832900	3.15041900
C	5.59207500	-7.59079600	3.77306300
H	5.31034400	-8.08759000	2.84061900
H	6.68474900	-7.57397400	3.80587300
C	5.00897700	-8.31636400	4.98612200
H	5.31756100	-7.83506600	5.92057100
H	5.35997200	-9.35243100	5.00233300
H	3.91560900	-8.32609700	4.94687800
C	5.42577700	2.77190200	4.12657400
H	4.78461700	3.23684600	4.88527900
H	4.84346600	2.63533400	3.20823400
H	6.26728600	3.43909300	3.90844200
C	7.25965300	4.07364200	6.76650300
H	6.72131500	3.50409700	7.52256100
H	6.54594900	4.58810300	6.11862900

H	7.92792400	4.79689300	7.24121000
N	9.40286400	0.47563900	6.69617600
N	7.65673700	-3.66020300	4.51261700
N	8.98666800	1.26613700	4.11245900
N	11.13147400	1.25381000	3.50344500
N	6.84771800	0.90396300	7.49596000
N	7.26844700	0.62758600	9.66854800
N	6.69804500	-2.02172700	2.42699200
N	8.22966200	-2.62347700	0.92249100
N	4.93271400	-3.99488400	3.97193900
N	5.11459400	-6.20144300	3.67435000
O	7.39808400	-0.93078100	5.27772600
O	5.30894900	-2.45729500	6.51416100
H	5.13488400	-1.64646900	7.02866600
H	4.50615800	-3.00222800	6.58141400
O	4.44574200	-0.61563200	4.13007500
H	3.57123500	-0.59470800	4.54710300
H	4.88593000	0.27855200	4.25300900
O	8.03736800	3.10503900	6.01173200
H	8.44796200	3.54218900	5.24715100
O	5.89365500	1.51077300	4.58693700
Fe	5.89072300	-2.15877800	4.35408300
Fe	7.42931500	1.00111900	5.48168200

Optimized structures with PBE

<u>Diiron(II,II)</u>

C 9.3503 -1.0137 6.6918
H 8.7549 -1.3166 7.5571
H 10.3564 -1.4385 6.8097
C 8.6484 -1.5728 5.4411
H 9.2617 -1.3772 4.5487
C 8.4505 -3.0873 5.6182
H 9.4241 -3.5892 5.7300
H 7.8716 -3.2388 6.5328
C 10.5772 1.0302 5.9874
H 11.4740 0.4169 6.1441
H 10.7965 2.0223 6.3964
C 10.2516 1.1690 4.5277
C 9.0312 1.4222 2.7279
C 10.3836 1.4326 2.3321
C 10.7653 1.5975 0.9983
H 11.8059 1.6235 0.6923
C 9.7336 1.7449 0.0738

H 9.9803 1.8873 -0.9735
C 8.3766 1.7229 0.4629
H 7.6077 1.8261 -0.2936
C 8.0027 1.5572 1.7919
H 6.9645 1.5144 2.0971
C 12.6039 1.3028 3.5741
H 12.9789 0.7516 2.7073
H 12.9180 0.7508 4.4639
C 13.1308 2.7381 3.5916
H 12.8077 3.2858 2.7013
H 14.2245 2.7293 3.6099
H 12.7796 3.2779 4.4776
C 9.2337 1.0232 8.0650
H 9.4806 2.0884 8.0390
H 9.9003 0.5400 8.7905
C 7.7880 0.8628 8.4395
C 5.8836 0.5075 9.5098
C 4.8553 0.2574 10.4224
H 5.0401 0.1465 11.4856
C 3.5675 0.1590 9.9009
H 2.7382 -0.0311 10.5744
C 3.3103 0.3104 8.5206
H 2.2858 0.2425 8.1676
C 4.3365 0.5705 7.6137
H 4.1568 0.7215 6.5546
C 5.6354 0.6716 8.1309
C 7.9696 0.6181 10.9679
H 9.0023 0.3078 10.7896
H 7.5010 -0.1633 11.5724
C 7.9062 1.9775 11.6644
H 8.4023 2.7509 11.0685
H 8.4108 1.9174 12.6332
H 6.8702 2.2837 11.8378
C 8.3802 -3.6916 3.2150
H 9.4433 -3.4671 3.3701
H 8.3456 -4.7076 2.8031
C 7.7839 -2.7484 2.2008
C 6.3905 -1.3850 1.2275
C 7.3572 -1.7482 0.2691
C 7.3175 -1.2771 -1.0449
H 8.0604 -1.5582 -1.7839
C 6.2579 -0.4338 -1.3703
H 6.1749 -0.0569 -2.3849
C 5.2815 -0.0669 -0.4182
H 4.4668 0.5818 -0.7246
C 5.3317 -0.5335 0.8921

H 4.5775 -0.2764 1.6280
C 9.4698 -3.1675 0.3552
H 9.2737 -3.3946 -0.6959
H 9.6842 -4.1203 0.8478
C 10.6348 -2.1867 0.5024
H 10.3986 -1.2305 0.0261
H 11.5349 -2.5982 0.0360
H 10.8510 -1.9932 1.5603
C 7.0262 -4.9627 4.8511
H 6.8556 -4.9793 5.9325
H 7.6827 -5.8103 4.6197
C 5.6970 -5.0724 4.1514
C 3.7802 -4.4337 3.3285
C 2.6660 -3.7223 2.8700
H 2.6105 -2.6431 2.9788
C 1.6543 -4.4523 2.2569
H 0.7718 -3.9398 1.8873
C 1.7475 -5.8530 2.0982
H 0.9329 -6.3845 1.6169
C 2.8567 -6.5688 2.5381
H 2.9205 -7.6440 2.4087
C 3.8718 -5.8283 3.1504
C 5.5921 -7.5908 3.7731
H 5.3103 -8.0876 2.8406
H 6.6847 -7.5740 3.8059
C 5.0090 -8.3164 4.9861
H 5.3176 -7.8351 5.9206
H 5.3600 -9.3524 5.0023
H 3.9156 -8.3261 4.9469
C 5.4258 2.7719 4.1266
H 4.7846 3.2368 4.8853
H 4.8435 2.6353 3.2082
H 6.2673 3.4391 3.9084
C 7.2597 4.0736 6.7665
H 6.7213 3.5041 7.5226
H 6.5459 4.5881 6.1186
H 7.9279 4.7969 7.2412
N 9.4029 0.4756 6.6962
N 7.6567 -3.6602 4.5126
N 8.9867 1.2661 4.1125
N 11.1315 1.2538 3.5034
N 6.8477 0.9040 7.4960
N 7.2684 0.6276 9.6685
N 6.6980 -2.0217 2.4270
N 8.2297 -2.6235 0.9225
N 4.9327 -3.9949 3.9719

N 5.1146 -6.2014 3.6744
O 7.3981 -0.9308 5.2777
O 5.3089 -2.4573 6.5142
H 5.1349 -1.6465 7.0287
H 4.5062 -3.0022 6.5814
O 4.4457 -0.6156 4.1301
H 3.5712 -0.5947 4.5471
H 4.8859 0.2786 4.2530
O 8.0374 3.1050 6.0117
H 8.4480 3.5422 5.2472
O 5.8937 1.5108 4.5869
Fe 5.8907 -2.1588 4.3541
Fe 7.4293 1.0011 5.4817

Diiron(III,III)

Fe 5.9424 -2.4379 4.4083
Fe 7.4293 0.7369 5.4656
C 9.2279 -1.3354 6.8414
H 8.5125 -1.5697 7.6406
H 10.2010 -1.7874 7.1046
C 8.6692 -1.8865 5.5347
H 9.3222 -1.5656 4.7020
C 8.5875 -3.4083 5.5507
H 9.6017 -3.8590 5.5629
H 8.0558 -3.7229 6.4573
C 10.5781 0.5648 6.0671
H 11.3846 -0.1810 6.1948
H 10.9569 1.4902 6.5286
C 10.2848 0.8198 4.6174
C 9.1701 1.2203 2.7718
C 10.5494 1.3774 2.4905
C 11.0185 1.7851 1.2440
H 12.0819 1.9278 1.0427
C 10.0586 2.0285 0.2656
H 10.3765 2.3733 -0.7162
C 8.6810 1.8488 0.5216
H 7.9662 2.0477 -0.2734
C 8.2185 1.4374 1.7698
H 7.1564 1.2897 1.9587
C 12.6726 1.2132 3.9161
H 13.1655 0.9718 2.9666
H 12.9646 0.4239 4.6238
C 13.0474 2.6052 4.4246
H 12.7526 3.3855 3.7121
H 14.1315 2.6717 4.5740

H 12.5756 2.8333 5.3917
C 9.1846 0.7669 8.0954
H 9.6075 1.7851 8.0589
H 9.7424 0.2283 8.8849
C 7.7187 0.8549 8.3993
C 5.7939 1.1547 9.4462
C 4.7707 1.3756 10.3642
H 4.9709 1.4709 11.4313
C 3.4807 1.4858 9.8545
H 2.6556 1.6742 10.5382
C 3.2228 1.3768 8.4714
H 2.2008 1.4943 8.1166
C 4.2519 1.1425 7.5599
H 4.0470 1.0819 6.4924
C 5.5556 1.0309 8.0592
C 7.9037 1.2722 10.8810
H 8.8535 0.7215 10.8358
H 7.3150 0.8095 11.6833
C 8.1191 2.7673 11.1058
H 8.7503 3.2105 10.3218
H 8.6139 2.9406 12.0684
H 7.1616 3.3037 11.1179
C 8.4884 -3.6142 3.0826
H 9.5031 -3.2351 3.2842
H 8.6313 -4.5839 2.5827
C 7.7321 -2.6850 2.1750
C 6.1430 -1.3577 1.4360
C 7.0694 -1.5531 0.3862
C 6.9159 -0.9422 -0.8551
H 7.6419 -1.0781 -1.6572
C 5.7929 -0.1330 -1.0235
H 5.6251 0.3534 -1.9803
C 4.8491 0.0492 0.0093
H 3.9702 0.6642 -0.1774
C 5.0092 -0.5612 1.2496
H 4.2669 -0.4427 2.0377
C 9.2629 -2.8366 0.1708
H 8.9416 -3.1211 -0.8397
H 9.6392 -3.7466 0.6538
C 10.3241 -1.7378 0.1418
H 9.9392 -0.8241 -0.3257
H 11.1907 -2.0760 -0.4394
H 10.6703 -1.4759 1.1523
C 7.2828 -5.2340 4.5184
H 7.2691 -5.4940 5.5893
H 7.9740 -5.9552 4.0526

C 5.8954 -5.3126 3.9488
C 3.8865 -4.6278 3.3650
C 2.7234 -3.9129 3.0617
H 2.6671 -2.8314 3.1811
C 1.6377 -4.6328 2.5678
H 0.7166 -4.1113 2.3169
C 1.7124 -6.0277 2.3668
H 0.8393 -6.5557 1.9884
C 2.8832 -6.7423 2.6215
H 2.9461 -7.8167 2.4517
C 3.9633 -6.0167 3.1203
C 5.7868 -7.7801 3.4076
H 5.6236 -8.1222 2.3750
H 6.8753 -7.7223 3.5445
C 5.1247 -8.6846 4.4449
H 5.3092 -8.3292 5.4691
H 5.5207 -9.7026 4.3611
H 4.0389 -8.7306 4.3035
C 5.2726 2.2325 3.9963
H 4.6344 2.6560 4.7844
H 4.6580 2.0459 3.1037
H 6.0575 2.9571 3.7465
C 7.2729 3.8238 6.5536
H 6.1937 3.6540 6.5250
H 7.5063 4.8357 6.1984
H 7.6425 3.6922 7.5752
N 9.3447 0.1421 6.7632
N 7.7832 -3.8416 4.3822
N 9.0348 0.8757 4.1236
N 11.2214 1.0821 3.6812
N 6.7873 0.8360 7.4258
N 7.1759 1.0277 9.6211
N 6.6000 -2.0697 2.5383
N 8.0530 -2.4114 0.8937
N 5.1070 -4.2204 3.8997
N 5.2606 -6.4041 3.4834
O 5.4597 -3.1327 6.4231
H 5.3327 -2.6335 7.2462
H 5.0132 -3.9933 6.5568
O 4.5104 -1.0648 4.3564
H 3.7063 -1.1113 4.8993
H 4.9875 -0.0900 4.4087
O 7.9029 2.8172 5.6937
H 8.5592 3.2364 5.0980
O 5.8620 1.0057 4.4589
O 7.3770 -1.3165 5.3163

Diiron(II,II)

Fe 5.9562 -2.4289 4.4989
Fe 7.4316 0.7470 5.4631
C 9.2343 -1.3665 6.8446
H 8.5131 -1.6132 7.6393
H 10.1923 -1.8583 7.0973
C 8.6602 -1.8973 5.5226
H 9.3603 -1.5959 4.7132
C 8.6028 -3.4334 5.5236
H 9.6305 -3.8450 5.5518
H 8.0663 -3.7727 6.4227
C 10.6017 0.5565 6.0730
H 11.4280 -0.1763 6.1576
H 10.9721 1.4898 6.5268
C 10.3136 0.8382 4.6164
C 9.2250 1.2751 2.7811
C 10.6030 1.4023 2.4834
C 11.0504 1.7998 1.2178
H 12.1046 1.9374 0.9775
C 10.0783 2.0391 0.2509
H 10.3851 2.3693 -0.7444
C 8.7101 1.8723 0.5250
H 7.9805 2.0394 -0.2686
C 8.2644 1.4883 1.7839
H 7.2033 1.3372 1.9788
C 12.7127 1.2272 3.8949
H 13.2299 1.0088 2.9521
H 13.0261 0.4566 4.6136
C 13.0738 2.6191 4.3967
H 12.7705 3.3867 3.6740
H 14.1567 2.6887 4.5460
H 12.5847 2.8264 5.3567
C 9.1902 0.7492 8.1174
H 9.5850 1.7779 8.0624
H 9.7389 0.2329 8.9283
C 7.7182 0.8321 8.4332
C 5.7947 1.1455 9.5094
C 4.7482 1.3810 10.4135
H 4.8933 1.4946 11.4894
C 3.4682 1.4864 9.8746
H 2.6225 1.6847 10.5359
C 3.2361 1.3659 8.4922

H 2.2192 1.4733 8.1117
C 4.2732 1.1314 7.5966
H 4.0963 1.0722 6.5228
C 5.5705 1.0171 8.1166
C 7.8947 1.2802 10.9255
H 8.8506 0.7408 10.8934
H 7.3171 0.8570 11.7559
C 8.1147 2.7732 11.1336
H 8.7414 3.1851 10.3322
H 8.6170 2.9574 12.0899
H 7.1585 3.3112 11.1408
C 8.4969 -3.6481 3.0390
H 9.4928 -3.2047 3.2114
H 8.6901 -4.5928 2.4993
C 7.7055 -2.7289 2.1377
C 6.1519 -1.3961 1.3964
C 7.0809 -1.5719 0.3442
C 6.9122 -0.9581 -0.9017
H 7.6190 -1.0818 -1.7231
C 5.7867 -0.1554 -1.0605
H 5.6310 0.3579 -2.0102
C 4.8573 0.0227 -0.0216
H 3.9883 0.6615 -0.1912
C 5.0179 -0.5904 1.2161
H 4.2933 -0.4431 2.0178
C 9.2745 -2.8420 0.1410
H 8.9892 -3.1201 -0.8822
H 9.6555 -3.7511 0.6216
C 10.3400 -1.7534 0.1178
H 9.9526 -0.8393 -0.3469
H 11.2114 -2.0904 -0.4566
H 10.6679 -1.5047 1.1355
C 7.2811 -5.2715 4.4908
H 7.2473 -5.5051 5.5687
H 7.9196 -6.0429 4.0213
C 5.8807 -5.3375 3.9369
C 3.8815 -4.6718 3.3682
C 2.7200 -3.9459 3.0642
H 2.6607 -2.8681 3.2255
C 1.6437 -4.6544 2.5427
H 0.7150 -4.1334 2.3054
C 1.7138 -6.0399 2.3195
H 0.8367 -6.5649 1.9429
C 2.8666 -6.7711 2.5820
H 2.8879 -7.8409 2.3756
C 3.9529 -6.0608 3.1031

C 5.7656 -7.8251 3.3986
H 5.5851 -8.2179 2.3890
H 6.8517 -7.7797 3.5490
C 5.1322 -8.7303 4.4444
H 5.3518 -8.3620 5.4548
H 5.5379 -9.7444 4.3543
H 4.0470 -8.7901 4.3081
C 5.2254 2.2774 3.9784
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H 4.6090 2.1009 3.0820
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C 7.2473 3.8896 6.5704
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N 5.0955 -4.2620 3.9129
N 5.2466 -6.4522 3.4546
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H 3.7498 -0.9371 5.0462
H 4.9681 -0.0378 4.3894
O 7.9019 2.8968 5.7393
H 8.4670 3.3283 5.0850
O 5.7843 1.0506 4.4519
O 7.3934 -1.3330 5.3096

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