Supplementary information for manuscript titled

Sulfur K-edge XAS and DFT Calculations on P450 Model Complexes: Effects of Hydrogen Bonding on Electronic Structure and Redox Potentials .

Fig. S1 XAS absorption and 2nd derivatives for SPh,L1,L2 complexes

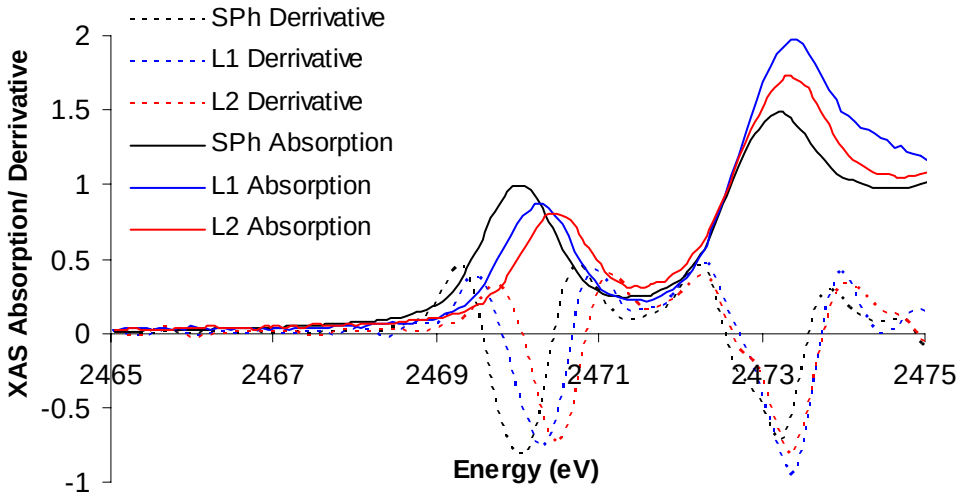


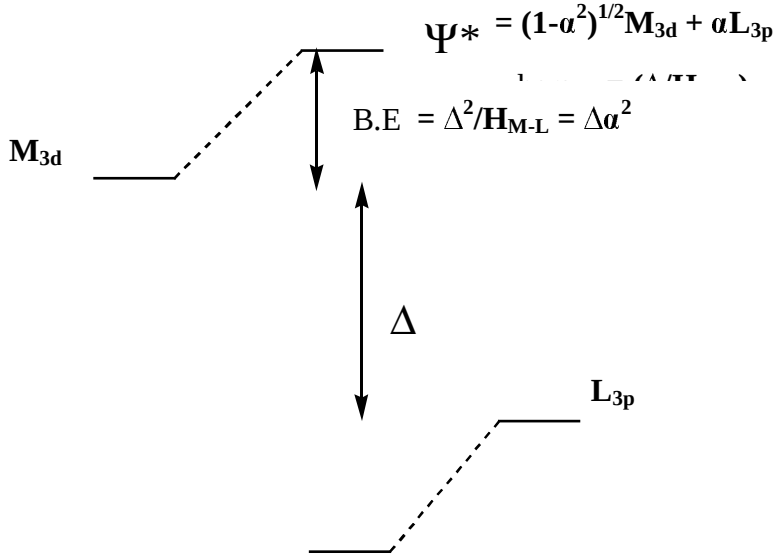
Table S1: The estimated –I effect of the substituent ligands from charges on α and β carbon of a substituted ethylene.

R	q (β-carbon)	q (α-carbon)
CF_3CONH-	-0.1089	0.0130
CH_3CONH-	-0.1306	0.0054
CF_3COO	-0.0946	0.0335
HCOO-	-0.1078	0.02

Table S2: 1s orbital energy shifts calculated from DFT calculations on the free ligands		
	charge	ΔE_{1s} (eV)
SPh	-0.55	0.00
L2	-0.333	-1.22
L2-ester	-0.4926	-0.52
SPh-H2O	-0.2704	-0.72

Table S3: DFT calculated H-bonding energies for oxidized and reduced heme-thiolate systems and shifts in redox potentials using different functional and solvation models.				
	BP86/PCM (CH_2Cl_2)	PBE/PCM (CH_2Cl_2)	B3LYP/PCM (CH_2Cl_2)	BP86/COSMO (CH_2Cl_2)
H-bonding energy (oxidized)	-1 kcal/mole	-5 kcal/mole	-10 kcal/mole	-1 kcal/mole
H-bonding energy (reduced)	-7 kcal/mole	-11 kcal/mole	-15 kcal/mole	-6 kcal/mole
Shift in redox Potential	+260 mV	+260 mV	+210 mV	+220 mV

Scheme S1: VBCI modeling of M-L bonding interaction.



Scheme S1 represents VBCI modeling of the metal-ligand interaction in a system. The VBCI parameters Δ and H_{M-L} represents the energy separation between the metal 3d and the ligand 3p orbitals when there is no interaction between them and the interaction matrix element, respectively. Bond energy (B.E) can be expressed as $B.E = (\Delta)\alpha^2$.

Now according to Scheme 1a and 1b, the difference in redox potential between the H-Bonding and the non H-bonding complexes can be expressed as difference in their B.E. in the oxidized and the reduced forms i.e

$\Delta E_{redox} = {}^{ox}(BE_L - BE_{L'}) - {}^{red}(BE_L - BE_{L'})$ where subscripts L and L' represents non H-bonding and H-Bonding ligands, respectively and superscripts *ox* and *red* indicates the formal oxidation states of the metal (Fe) in these complexes. We can substitute the BE with the expression obtained from VBCI modeling above to get;

$$\Delta E_{redox} = ({}^{ox}\Delta_L {}^{ox}\alpha^2{}_L - {}^{ox}\Delta_{L'} {}^{ox}\alpha^2{}_{L'}) - ({}^{red}\Delta_L {}^{red}\alpha^2{}_L - {}^{red}\Delta_{L'} {}^{red}\alpha^2{}_{L'}) \quad \text{i}$$

where the superscripts and the subscripts have same implications as above.

We introduce two parameters k_M and k_L to represent the difference in the orbital energies of the oxidized and the reduced Fe ions and the difference between the orbital energies of the H-bonding and non H-bonding ligand donor orbitals, respectively, such that;

$${}^{ox}\Delta_L = {}^{red}\Delta_L - k_M \text{ (where } k_M \text{ is positive)} \quad \text{ii}$$

and, $${}^{red}\Delta_{L'} = {}^{red}\Delta_L - k_L \text{ (where } k_L \text{ is positive)} \quad \text{iii}$$

hence, $${}^{ox}\Delta_{L'} = {}^{red}\Delta_L - k_M - k_L \quad \text{iv}$$

Substituting i with ii, iii and iv and rearranging we get,

$$\Delta E_{redox} = {}^{red}\Delta_L\{({}^{ox}\alpha^2{}_L - {}^{ox}\alpha^2{}_{L'}) - ({}^{red}\alpha^2{}_L - {}^{red}\alpha^2{}_{L'})\} - k_M({}^{ox}\alpha^2{}_L - {}^{ox}\alpha^2{}_{L'}) - k_L({}^{ox}\alpha^2{}_{L'} - {}^{red}\alpha^2{}_{L'})$$

now, for simplicity we replace ${}^{red}\Delta_L$ by Δ and difference between covalencies within the same oxidation state for ligand L and L' as ${}^{ox/red}(\Delta\alpha^2)_{L\rightarrow L'}$

$$\Delta E_{redox} = \Delta\{{}^{ox}(\Delta\alpha^2)_{L\rightarrow L'} - {}^{red}(\Delta\alpha^2)_{L\rightarrow L'}\} - k_M {}^{ox}(\Delta\alpha^2)_{L\rightarrow L'} - k_L({}^{ox}\alpha^2{}_{L'} - {}^{red}\alpha^2{}_{L'})$$

$$\Delta E_{redox} = {}^{ox}(\Delta\alpha^2)_{L\rightarrow L'}[\Delta(1-\upsilon) - k_M] - k_L {}^{ox\rightarrow red}(\Delta\alpha^2)_L \quad \text{v}$$

$$\Delta E_{redox} = {}^{ox}(\Delta\alpha^2)_{L\rightarrow L'}[\Delta(1-\upsilon) - k_M] - k_L {}^{ox\rightarrow red}(\Delta\alpha^2{}_{L'})$$

where ${}^{ox}(\Delta\alpha^2)_{L\rightarrow L'}$ represents the decrease in covalency due to H-bonding within a given oxidation state (superscripted as *ox* and *red*), $\upsilon = {}^{red}(\Delta\alpha^2)_{L\rightarrow L'}/{}^{ox}(\Delta\alpha^2)_{L\rightarrow L'}$ and ${}^{ox\rightarrow red}(\Delta\alpha^2{}_{L'})$ is the difference in the covalency of the H-bonded ligand L'-Fe bond between the oxidized and reduced states. The first term in the expression above is linear with

covalency and is dominated by k_M.[1] Since k_M is significantly greater than k_L the first term will dominate over the second.[2] Thus the above expression indicates that in a series of complexes where the change in energy of the ligand donor orbitals is significantly smaller than the energy difference between the oxidized and reduced metal 3d orbitals in the complexes (i.e. $k_L << k_M$) , *E^o will vary approximately linearly with covalency* ($\Delta\alpha^2$) as observed experimentally.

Optimized geometries for the complexes (the charge on Fe is +3 unless otherwise stated)

FeOEPSPh

Fe	1.340066	13.242007	4.180558
C	1.726332	11.372076	6.666425
C	2.279793	11.368543	7.999765
C	2.998603	12.523479	8.137331
C	2.898567	13.231203	6.883175
C	3.556383	14.426168	6.588697
C	3.591580	15.065663	5.349149

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[1] DFT calculations indicate on the FeOEPL series that ν is close to 1. Though the absolute values of the oxidized covalencies are larger than those of the reduced complexes, the H-bonding interaction is stronger in the reduced form leading to a greater change in the covalency.

[2] In the limit where the H-bonding is weak ${}^{ox\rightarrow red}(\Delta\alpha^2_{L'})$ may be greater than ${}^{ox}(\Delta\alpha^2)_{L\rightarrow L'}$ however at this limit k_L will be small. In the strong H-bonding limit k_L (the ligand donor orbital stabilization by H-bonding) and ${}^{ox}(\Delta\alpha^2)_{L\rightarrow L'}$ will be high, but the absolute covalencies of the L'-Fe bond will be small in both oxidation states hence ${}^{ox\rightarrow red}(\Delta\alpha^2_{L'})$ will be small.

C	4.375680	16.241129	5.041489
C	4.194894	16.499856	3.710700
C	3.291050	15.489970	3.205668
C	2.845982	15.395081	1.886674
C	1.971502	14.436031	1.374785
C	1.530776	14.368165	0.000866
C	0.685436	13.297575	-0.094528
C	0.616336	12.698348	1.217803
C	-0.092884	11.537132	1.532203
C	-0.086712	10.869626	2.757918
C	-0.721084	9.595916	3.015983
C	-0.412479	9.252461	4.302771
C	0.399189	10.322676	4.839539
C	0.930045	10.359282	6.128851
N	2.111079	12.517539	6.004556
N	2.931962	14.633962	4.220497
N	1.400163	13.411854	2.098549
N	0.579396	11.296774	3.884550
S	-0.455244	14.449144	4.973940
C	-0.727741	15.685480	3.717612
C	-1.675309	15.459135	2.702951
C	-1.895662	16.424394	1.717965
C	-1.180204	17.627793	1.734188
C	-0.250653	17.864066	2.753731
C	-0.024519	16.903127	3.743039
H	4.140565	14.875412	7.391945
H	3.215034	16.145355	1.187671
H	-0.666739	11.079757	0.726379
H	0.712037	9.509881	6.776588
H	-2.228144	14.520063	2.692625

H	-2.628320	16.231159	0.932472
H	-1.349377	18.376511	0.958652
H	0.308491	18.801295	2.780383
H	0.700737	17.085112	4.536520
H	2.143054	10.574205	8.727945
H	3.566973	12.860325	8.999557
H	4.995370	16.781091	5.751800
H	4.635360	17.296099	3.117653
H	1.831599	15.056694	-0.783105
H	0.160519	12.934559	-0.973224
H	-1.307388	9.033992	2.294748
H	-0.697645	8.354640	4.843700

FeOEPL1

Fe	2.077129	5.096144	3.600082
S	3.690708	3.913810	2.399082
F	1.199087	0.806842	0.949921
F	0.573004	-1.107171	1.832475
F	2.227781	-1.052998	0.394798
O	3.006659	-1.268789	3.209337
N	3.109926	1.021133	2.802286
N	2.732296	7.085888	3.400622
N	0.789124	5.486867	1.997083
N	0.714057	3.621626	4.203954
N	2.667158	5.215295	5.603136
C	3.613144	7.735820	4.238112
C	2.612940	7.870239	2.274807
C	0.941562	6.484162	1.056834
C	-0.162307	4.620388	1.498620
C	-0.227692	3.013915	3.401628

C	0.807561	2.855423	5.345962
C	2.484913	4.238390	6.559193
C	3.556152	6.124069	6.137167
C	4.065171	8.961098	3.619345
C	3.445170	9.045139	2.403714
C	0.069750	6.233788	-0.066893
C	-0.613394	5.081235	0.207567
C	-0.734167	1.826864	4.051928
C	-0.091123	1.727027	5.254303
C	3.289114	4.534574	7.720870
C	3.951339	5.702780	7.460222
C	1.795001	7.580909	1.181884
C	-0.629780	3.478035	2.148894
C	1.635107	3.138553	6.432575
C	3.999470	7.284188	5.500076
C	4.438767	2.861501	3.621629
C	4.084457	1.487062	3.707027
C	4.699686	0.660002	4.660289
C	5.663937	1.190655	5.519302
C	6.030661	2.537926	5.433205
C	5.420592	3.362926	4.488921
C	2.676927	-0.250830	2.607456
C	1.655230	-0.391135	1.434940
H	2.722864	1.763793	2.205777
H	4.414590	-0.387118	4.705650
H	6.136034	0.540345	6.256764
H	6.790989	2.948877	6.097548
H	5.697855	4.413541	4.405441
H	1.808997	8.289344	0.354153
H	-1.385217	2.890700	1.627996

H	1.604789	2.440323	7.268619
H	4.704432	7.906839	6.050551
H	-0.009002	6.865249	-0.947108
H	-1.363645	4.585604	-0.401782
H	4.761762	9.664450	4.066384
H	3.535558	9.829026	1.657368
H	-1.478835	1.156641	3.633165
H	-0.206490	0.958795	6.013346
H	3.335560	3.923020	8.617218
H	4.644719	6.237629	8.102911

FeOEPL2

Fe	0.823789	4.008126	1.427057
S	2.457452	5.582642	0.719978
F	5.599144	2.748125	0.607877
F	6.563345	1.714380	2.294073
F	7.647368	3.275807	1.200022
F	-0.270894	8.751632	0.057608
F	-1.369659	9.962725	1.530701
F	0.314420	10.836370	0.430307
O	6.579113	4.152764	3.728835
O	0.968427	10.063386	3.126781
N	4.815322	4.657142	2.292066
N	-0.524855	4.203085	-0.166755
N	1.472537	8.106922	1.965073
N	1.480015	2.246453	0.485240
N	1.481496	3.159550	3.218556
N	-0.541137	5.105445	2.571811
C	-1.538742	5.135720	-0.269024
C	-2.055092	5.152691	-1.615720

C	0.466363	2.581678	-1.730964
C	-1.351580	4.218375	-2.324941
C	-0.405540	3.622411	-1.412843
C	2.783338	1.267323	2.331320
C	1.323152	1.927165	-0.847537
C	2.143706	0.786584	-1.180155
C	0.450113	4.744889	4.795445
C	2.786530	0.410386	-0.033856
C	2.366646	1.323002	1.002304
C	-2.012214	5.925500	0.777660
C	2.369561	2.111805	3.360267
C	2.788272	2.006205	4.736941
C	1.318647	3.701932	4.477584
C	2.140730	2.992546	5.427474
C	-0.429043	5.380376	3.919260
C	-1.388277	6.390849	4.295748
C	-1.559726	5.907285	2.095797
C	-2.090977	6.713961	3.168175
C	3.069975	6.318203	2.218071
C	4.187400	5.763570	2.897715
C	4.651569	6.330446	4.093430
C	4.023582	7.468912	4.597296
C	2.964787	8.077597	3.924949
C	2.496188	7.513160	2.729374
C	5.929564	3.993239	2.700622
C	6.429551	2.921288	1.682059
C	0.843107	9.293487	2.180083
C	-0.131511	9.705165	1.032049
H	4.383791	4.372719	1.405340
H	1.235731	7.582248	1.115144

H	0.447125	2.219311	-2.758283
H	3.488544	0.479933	2.594115
H	0.430060	5.069335	5.835114
H	-2.822106	6.615789	0.545864
H	5.500160	5.877257	4.596030
H	4.385352	7.908222	5.527133
H	2.501271	8.986442	4.295211
H	-2.859361	5.793319	-1.965355
H	-1.467213	3.943444	-3.369347
H	2.205509	0.330008	-2.163624
H	3.481541	-0.412073	0.106997
H	3.489056	1.269910	5.119052
H	2.206503	3.222009	6.486738
H	-1.507187	6.793808	5.297032
H	-2.898600	7.432215	3.065346

FeOEPSPh+ $2H_2O$

Fe	0.823800	4.008100	1.427100
S	2.457500	5.582600	0.720000
N	-0.524900	4.203100	-0.166800
N	1.480000	2.246500	0.485200
N	1.481500	3.159500	3.218600
N	-0.541100	5.105400	2.571800
C	-1.538700	5.135700	-0.269000
C	-2.055100	5.152700	-1.615700
C	0.466400	2.581700	-1.731000
C	-1.351600	4.218400	-2.324900
C	-0.405500	3.622400	-1.412800
C	2.783300	1.267300	2.331300
C	1.323200	1.927200	-0.847500
C	2.143700	0.786600	-1.180200

C	0.450100	4.744900	4.795400
C	2.786500	0.410400	-0.033900
C	2.366600	1.323000	1.002300
C	-2.012200	5.925500	0.777700
C	2.369600	2.111800	3.360300
C	2.788300	2.006200	4.736900
C	1.318600	3.701900	4.477600
C	2.140700	2.992500	5.427500
C	-0.429000	5.380400	3.919300
C	-1.388300	6.390800	4.295700
C	-1.559700	5.907300	2.095800
C	-2.091000	6.714000	3.168200
C	3.070000	6.318200	2.218100
C	4.187400	5.763600	2.897700
C	4.651600	6.330400	4.093400
C	4.023600	7.468900	4.597300
C	2.964800	8.077600	3.924900
C	2.496200	7.513200	2.729400
H	0.447100	2.219300	-2.758300
H	3.488500	0.479900	2.594100
H	0.430100	5.069300	5.835100
H	-2.822100	6.615800	0.545900
H	5.500200	5.877300	4.596000
H	4.385400	7.908200	5.527100
H	2.544000	8.907600	4.291000
H	-2.859400	5.793300	-1.965400
H	-1.467200	3.943400	-3.369300
H	2.205500	0.330000	-2.163600
H	3.481500	-0.412100	0.107000
H	3.489100	1.269900	5.119100

H	2.206500	3.222000	6.486700
H	-1.507200	6.793800	5.297000
H	-2.898600	7.432200	3.065300
H	1.750600	7.956400	2.231800
H	4.647800	4.960500	2.519500
O	0.675297	8.359366	-0.206829
H	1.059187	7.469353	-0.030010
H	1.363198	8.788472	-0.745658
O	5.303608	3.722648	0.268750
H	5.791565	4.400164	-0.231622
H	4.390795	4.090442	0.300339

FeOEPSMe

Fe	2.081624	5.093943	3.589399
S	3.685299	3.940737	2.415933
N	2.731249	7.090521	3.396029
N	0.780088	5.495791	1.996869
N	0.720549	3.605654	4.201711
N	2.680591	5.199985	5.596241
C	3.610524	7.736264	4.233691
C	2.613360	7.872721	2.271745
C	0.933661	6.490681	1.057479
C	-0.165855	4.625480	1.499977
C	-0.226314	3.006716	3.401471
C	0.805494	2.847699	5.346712
C	2.489797	4.230633	6.558173
C	3.560476	6.117485	6.131473
C	4.065324	8.963024	3.615812
C	3.450949	9.045410	2.397986
C	0.063384	6.238665	-0.068282
C	-0.618697	5.085260	0.206612

C	-0.748378	1.827003	4.059462
C	-0.108513	1.728524	5.263333
C	3.283250	4.537813	7.725330
C	3.944949	5.706593	7.461323
C	1.791897	7.585533	1.180961
C	-0.626381	3.476921	2.148687
C	1.635385	3.132426	6.433377
C	3.996277	7.282488	5.495911
C	4.474111	2.828816	3.637799
H	1.807250	8.294318	0.353258
H	-1.382169	2.892471	1.624592
H	1.592906	2.445550	7.278383
H	4.694547	7.909174	6.050374
H	-0.012133	6.867116	-0.951071
H	-1.363823	4.587069	-0.406393
H	4.755933	9.669158	4.067617
H	3.538811	9.832279	1.654584
H	-1.506918	1.166476	3.650266
H	-0.241266	0.972361	6.031623
H	3.316525	3.940167	8.631805
H	4.625840	6.250511	8.109370
H	5.244378	2.242641	3.119042
H	3.727992	2.146809	4.068737
H	4.940106	3.415145	4.441350

FeOEPSMe+2H_2O

Fe	2.080667	5.097663	3.587851
S	3.746821	3.937062	2.461648
N	2.704168	7.099465	3.407822
N	0.780116	5.493000	1.993472
N	0.716880	3.620336	4.199475

N	2.680391	5.199320	5.590751
C	3.578163	7.753266	4.249197
C	2.577867	7.891200	2.287171
C	0.921248	6.496939	1.059536
C	-0.173931	4.627763	1.497641
C	-0.242064	3.027481	3.405238
C	0.791441	2.864386	5.349538
C	2.489079	4.229886	6.553744
C	3.555373	6.121221	6.130864
C	4.016287	8.988158	3.640722
C	3.399396	9.072929	2.425234
C	0.044147	6.250093	-0.060375
C	-0.635041	5.093947	0.212024
C	-0.779783	1.864121	4.070366
C	-0.140964	1.762518	5.273953
C	3.281366	4.536866	7.720103
C	3.940688	5.707816	7.458347
C	1.764983	7.601130	1.191782
C	-0.641599	3.487534	2.151178
C	1.626683	3.138812	6.432790
C	3.976339	7.294576	5.503856
C	4.494983	2.787308	3.684896
H	1.772878	8.315600	0.369202
H	-1.397815	2.899822	1.632180
H	1.577942	2.453909	7.278794
H	4.676859	7.921084	6.055194
H	-0.041788	6.886318	-0.936453
H	-1.385266	4.598185	-0.397004
H	4.715597	9.688030	4.087829
H	3.489036	9.859431	1.681676

H	-1.544405	1.211674	3.659455
H	-0.284289	1.013049	6.047043
H	3.312878	3.939486	8.626784
H	4.616589	6.254953	8.109170
H	5.276638	2.216433	3.169536
H	3.734092	2.097479	4.067808
H	4.936669	3.350017	4.515375
H	2.216791	2.074464	1.646113
O	1.841452	1.187336	1.446653
H	2.587173	0.718108	1.034690
O	6.379444	6.291519	2.803272
H	6.959065	5.661879	3.265923
H	5.558156	5.771970	2.650523

Fe^{II}OEPSMe

Fe	2.079128	5.091917	3.589216
S	3.697693	3.892368	2.434777
N	2.738948	7.105469	3.389675
N	0.829196	5.462403	1.942769
N	0.726003	3.584719	4.188967
N	2.757188	5.161889	5.573489
C	3.611372	7.753428	4.234609
C	2.599557	7.896113	2.274856
C	0.934087	6.493217	1.037268
C	-0.149423	4.611300	1.469955
C	-0.238901	3.005099	3.397336
C	0.801534	2.842944	5.342877
C	2.520612	4.216843	6.548791
C	3.589541	6.111963	6.130830
C	4.040906	8.992753	3.633522
C	3.413915	9.082065	2.412400

C	0.016744	6.268150	-0.068634
C	-0.650906	5.105897	0.200269
C	-0.791229	1.856302	4.070345
C	-0.143037	1.751649	5.281104
C	3.271213	4.554831	7.746881
C	3.927363	5.727142	7.487858
C	1.767276	7.603903	1.179342
C	-0.625033	3.479347	2.131430
C	1.646905	3.134126	6.430550
C	4.003498	7.285242	5.500312
C	4.527295	2.793596	3.652576
H	1.753189	8.334487	0.368928
H	-1.407295	2.913658	1.621475
H	1.577596	2.467690	7.291956
H	4.680583	7.928258	6.065943
H	-0.104927	6.927830	-0.925090
H	-1.424297	4.625566	-0.395619
H	4.730004	9.703613	4.084717
H	3.487631	9.881898	1.678984
H	-1.571570	1.210463	3.673004
H	-0.298134	1.009466	6.061020
H	3.267618	3.979565	8.670107
H	4.568649	6.296255	8.157907
H	5.312042	2.217929	3.141319
H	3.801972	2.093796	4.090419
H	4.981321	3.382114	4.461068

Fe^{II}OEPSMe+ $2H_2O$

Fe	2.036775	5.132720	3.628289
S	3.676975	3.867119	2.494574
N	2.683213	7.150523	3.430932

N	0.795166	5.492761	1.972568
N	0.688357	3.637841	4.230284
N	2.726454	5.216014	5.610927
C	3.542115	7.812766	4.278950
C	2.516634	7.952380	2.326453
C	0.879988	6.531533	1.074777
C	-0.176828	4.635870	1.499906
C	-0.266844	3.045626	3.437293
C	0.764401	2.901751	5.388316
C	2.488470	4.273246	6.588154
C	3.552842	6.167807	6.169315
C	3.931250	9.072359	3.691916
C	3.295058	9.159593	2.477202
C	-0.038940	6.303005	-0.028549
C	-0.688941	5.130676	0.234513
C	-0.816636	1.898874	4.116222
C	-0.175801	1.807154	5.329452
C	3.236307	4.613543	7.786702
C	3.890260	5.786077	7.527944
C	1.691016	7.655711	1.228966
C	-0.646686	3.503759	2.164873
C	1.610340	3.194521	6.472868
C	3.952450	7.346617	5.539473
C	4.524278	2.816201	3.748095
H	1.660023	8.396752	0.429041
H	-1.416669	2.924978	1.652694
H	1.540458	2.529804	7.335225
H	4.618766	8.000849	6.104458
H	-0.173765	6.967819	-0.878431
H	-1.457286	4.642952	-0.360790

H	4.597220	9.799215	4.151045
H	3.338845	9.971463	1.755476
H	-1.584985	1.242363	3.715459
H	-0.327071	1.066955	6.111344
H	3.231632	4.039468	8.710257
H	4.527592	6.358137	8.198646
H	5.430257	2.391184	3.297533
H	3.861470	2.002276	4.066269
H	4.807169	3.418025	4.620033
H	2.641155	1.998914	1.450300
O	2.532411	1.133495	0.972664
H	3.366814	1.090298	0.473365
O	6.562648	5.465198	2.431237
H	6.337144	6.080359	3.153402
H	5.681049	5.031618	2.273075