Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Water binding to Fe^{III} Hemes studied in cooled ion traps, characterization of a strong 'weak 'ligand

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Contents

1) The spin projection method applied to correct the spin contaminated energies:

In this method the spin projected energy *E*s is calculated by subtracting the energy contribution of the higher spin state *E*s+1 from the spin contaminated energy E_C with subsequent renormalization using the following equations:

$$E_S = \frac{E_C - aE_{S+1}}{1 - a}$$

$$a = \frac{\langle S^2 \rangle_C - S(S+1)}{2(S+1)}$$

Where $\langle S^2 \rangle_C$ is the expectation value of S^2 obtained from the spin contaminated wave function and S is the total spin.

2) ELF (Electron Localisation Function) and AIM (Atoms in Molecules) analysis:

To analyze the electron distribution resulting from the ligation with H_2O, the ELF and AIMS functions were used. The ELF function (denoted as η) can be interpreted as a measure of the Pauli repulsion in the atomic or molecular space. At a given point in space, the function reflects the probability of finding a localized electron or a localized pair of electrons, therefore providing meanings to electron localization. Topologically, the ELF isosurfaces partition the molecular space into chemically intuitive regions such as bonds, lone pairs, etc. In fact, the topological analysis of ELF function allows one to distinguish between core basins and valence basins. The core basins denoted as C(X) with X being a nucleus. The valence basins split into bonding basins connected to more than one atomic center, denoted as V(X, Y,.. , with X, Y,.. being nuclei) and non-bonding basins (lone pairs) connected to only one atomic center (labelled V(X)). Accordingly, the existence of a bonding valence basin in the region between two interacting atoms exhibits sharing of electrons and covalence bond.

In QTAIM (Quantum Theory of Atoms in Molecules), Bader's theory allows one to study the concept of chemical bond by exploiting the topological features of the electron density at a Bond Critical Point (BCP) of two interacting atoms and thereby offering a definition of chemical bonding and its strength. Chemical bonding interactions could be characterized according to the topological

properties of electron density at BCP (ρ_{BCP}) namely, its Laplacian ($\nabla^2\rho_{BCP}$), the electronic kinetic energy density (G_{BCP}), the electronic potential energy density (V_{BCP}) and the total electronic energy densities (H_{BCP}). The electron density and its Laplacian stand for the power of the interaction, hence, the stronger interactions exhibit greater ρ_{BCP} and $\nabla^2\rho_{BCP}$ values. The Laplacian of electron density indicates the charge concentration and depletion of electron distribution, so that $\nabla^2\rho_{BCP} < 0$ and $\nabla^2\rho_{BCP} > 0$ belong to a covalent and closed-shell type bonding, respectively. This is despite of strongly polar interactions in where Laplacian can have both signs.

Basically, the definition of a covalent bond was suggested based on two conditions[1-3] :

a) The existence of a BCP in the inter-nuclear region (necessary condition) and b) $H_{BCP}<0$ (sufficient condition). Analogously, the term partially covalent has been recently given for systems verifying $|V_{BCP}|<2G_{BCP}$ and $|V_{BCP}|>G_{BCP}$. Based on this fact there are three possibilities: I) $|V_{BCP}|/G_{BCP}<1$ and ($H_{BCP}>0$), II) $1<|V_{BCP}|/G_{BCP}<2$ ($-G_{BCP}<H_{BCP}<0$), and III) $|V_{BCP}|/G_{BCP}>2$ and ($H_{BCP}<-G_{BCP}$). The I and II associate with the pure ionic character and ionic-covalent (or partially covalent) character and III indicates to the classical covalent nature of the interaction, respectively[1-3].

The values of ρ_{BCP} and $\nabla^2\rho_{BCP}$ at BCP of Fe−O bond are calculated to be 0.043 and 0.145 which are both relatively substantial and lie in the range of strong interactions. Interestingly, the calculated value of V_{BCP} dominates the G_{BCP} value, and results in the overall negative value of the total energy density, ($H_{BCP}=-0.010$ a.u.). Importantly, the ratio of $|V_{BCP}|/G_{BCP}$ is 1.217 falling in $1<|V_{BCP}|/G_{BCP}<2$ range (class II). Based on the standard definition for the $1<|V_{BCP}|/G_{BCP}<2$, and considering other QTAIM parameters, it can be realized that topological properties at BCPs predicts a mixed, ionic/covalent component character for Fe^{III}–H_2O interaction, confirming the results derived from ELF analysis.

References:

1. S. J. Grabowski*, Chem. Rev.*, 2011, **111**, 2597.
2. E. Espinosa, I. Alkorta, J. Elguero and E. Molins*, J. Chem. Phys.*, 2002, **117**, 5529.
3. I. Cukrowski, J. H. de Lange and M. Mitoraj*, J. Phys. Chem. A*, 2014, **118**, 623.

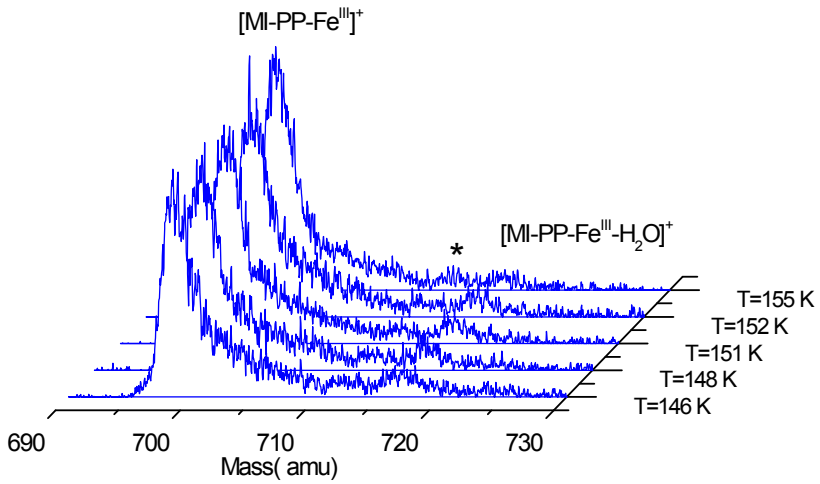


Figure S0: Evolution of the formation of [MI- PP-Fe^{III}–(H$_2$O)]$^+$as a function of temperature. * is an impurity and does not change in intensity with temperature.

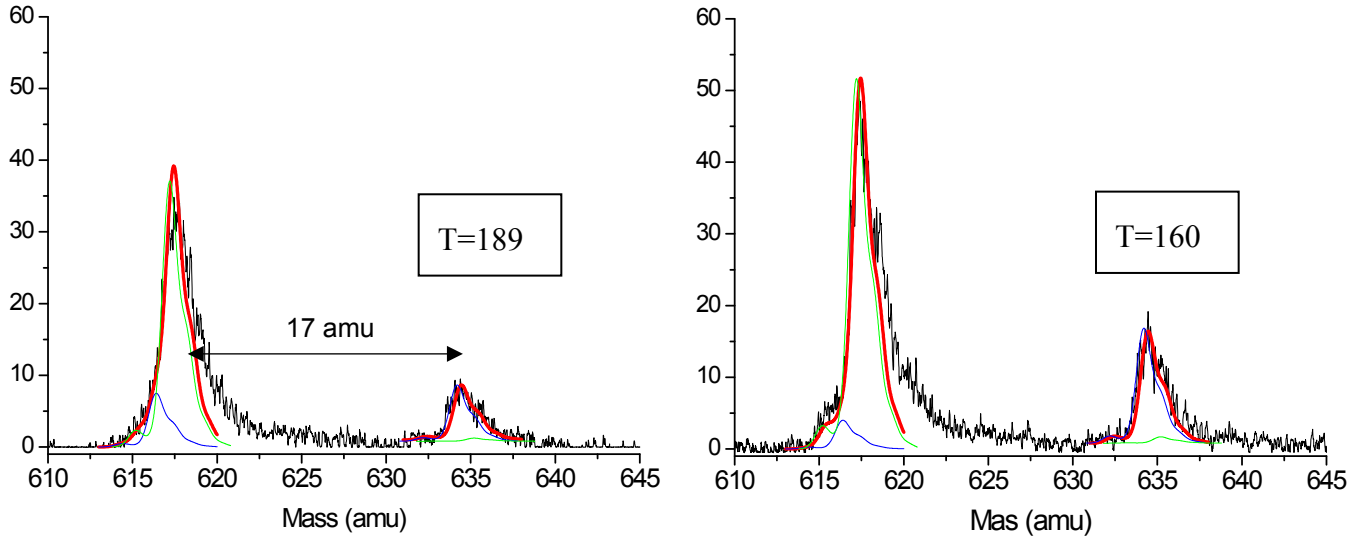


Figure S1 : complexation of free ferric heme and protonated heme at two temperatures 189 and 160 K . Black experimental spectrum , Red fitting curve blue ferric heme in 1/1 complexation at 190 and 4/1 at 160K. Green protonated heme1/70 at 189 K to 1/45 at 160 K

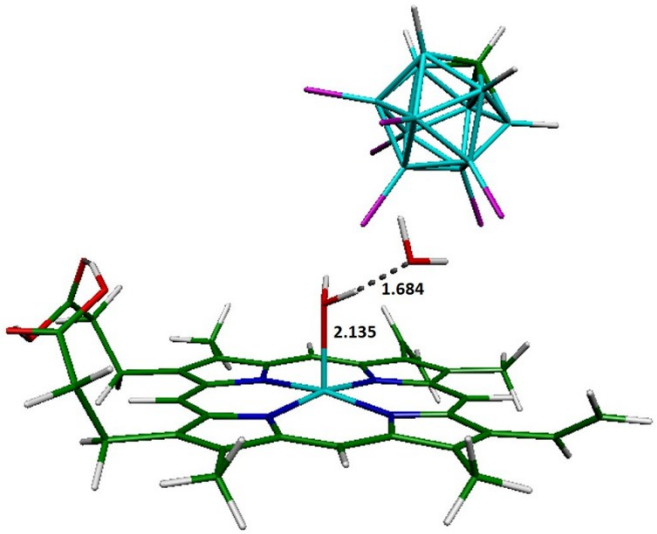


Figure S2: The optimized [heme-FeIII–(H2O)2]+ accompanied with a counter ion.

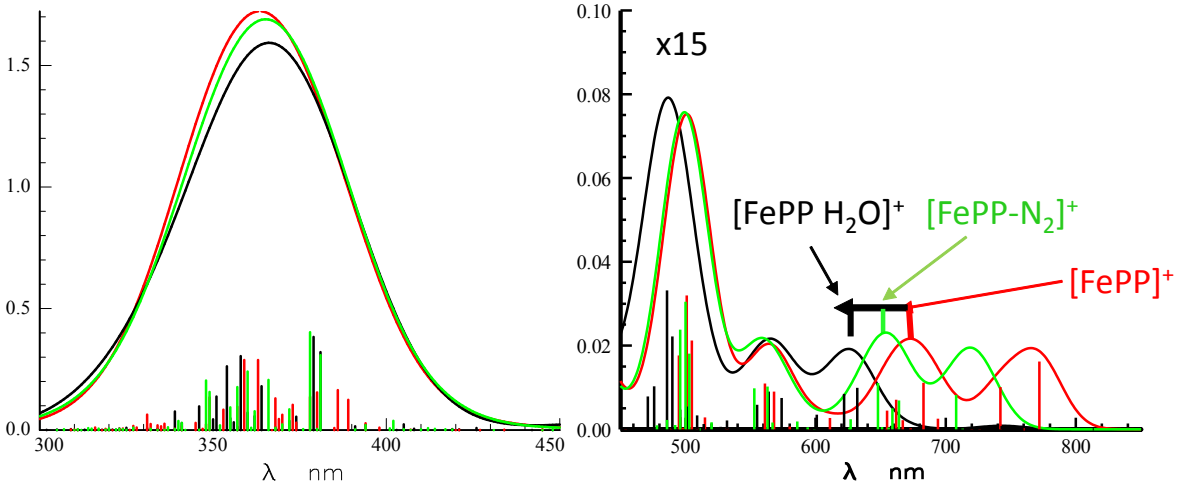


Figure S3 A: Simulated spectra of [PP Fe^{III}]$^+$ (red) and [PP Fe^{III}–H_2O]$^+$ (black), [PP Fe^{III}–N_2]$^+$ (green) complexes (S=3/2), sticks and convolution with a Gaussian of 40 nm width FWMH. Within the arrow , evolving charge transfer bands.

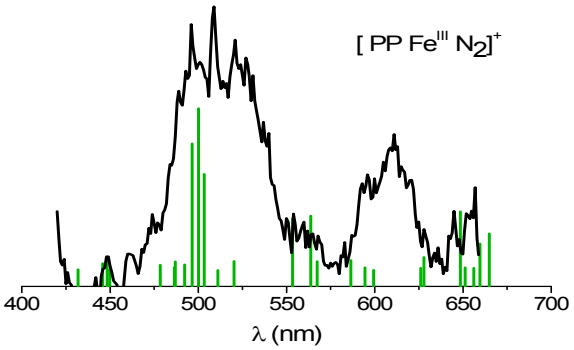


Figure S3 B: Experimental spectrum of [PP Fe^{III} N$_2$]$^+$ (black) and calculated [PP Fe^{III}–N$_2$]$^+$ complex (S=3/2) (green Sticks) .

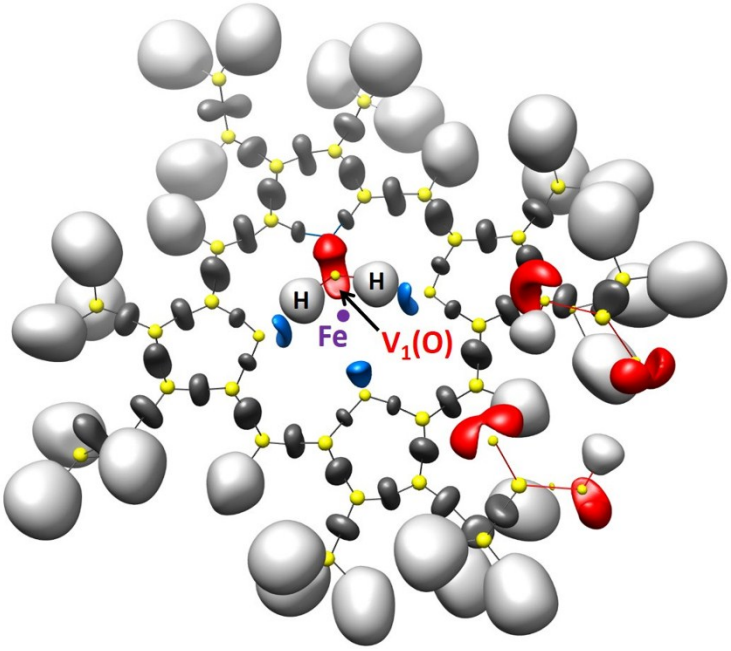
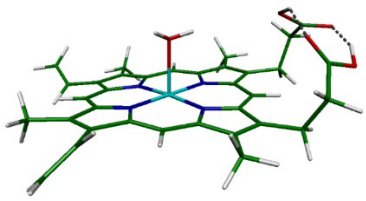
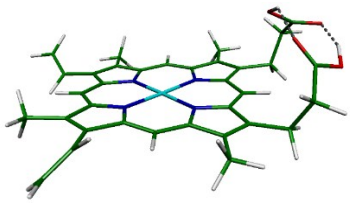
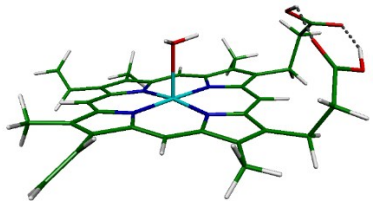
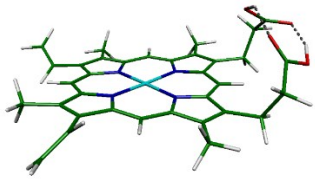
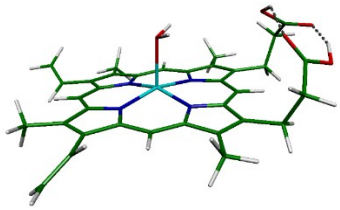
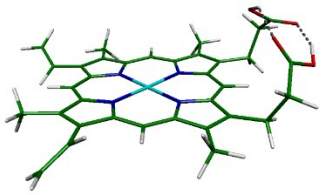


Figure S4: Topological Electron Localized Function (ELF) determined by the TopMode algorithm based on the OPBX-PBE optimized geometry of the [PP Fe^{III}-H$_2$O]$^+$ complex.

Table S1: Relative spin state energies of the ferric Heme complex with/without H_2O ligand (in $kcalmol^{-1}$) determined at the OPTX-PBE level.

Spin state	$[PP\text{-}Fe^{III}]^+$	$[PP\text{-}Fe^{III}\text{–}H_2O]^+$
1/2	18.58	25.44
3/2	**0.00**	**0.00**
5/2	11.93	7.55

Table S2: The optimized [heme-Fe^{III}]$^{+}$ systems:

Spin	[heme-Fe^{III} $-H_2O$]$^{+}$	[heme-Fe^{III}]$^{+}$
1/2		
3/2		
5/2		

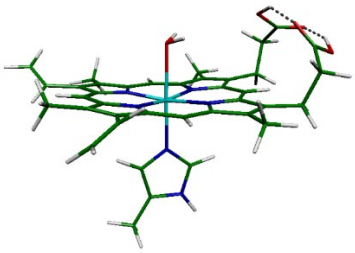
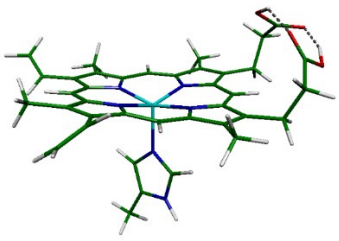
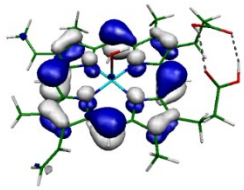
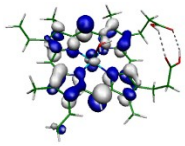
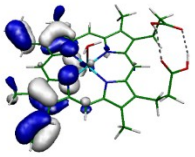
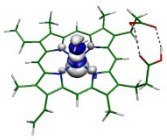
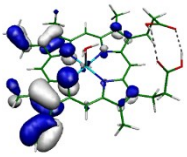
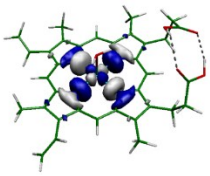
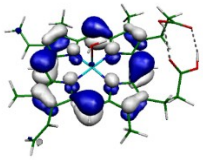
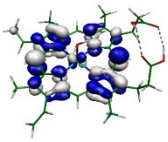
[MI-heme-Fe^{III} $-(H_2O)$]$^{+}$	[MI-heme-Fe^{III}]$^{+}$
	

Table S3A: Electronic transition energies and the contributed MOs in transitions, obtained at the B3LYP/cc-pVDZ (TZVP for Fe) level of theory for the $[Fe^{III}$ PP-$H_2O]^+$ complex (S=3/2) using the geometry optimized at OPTX-PBE level. H and L stand for HOMO and LUMO respectively

Vertical			Contributed orbitals	Weight (%)	Shape	
nm	eV	Oscillator strengths			Initial orb. Cutoff=0.03	Final orb. Cutoff=0.03
486.650	2.548	0.033	H-1 (b) → L+3 (b) dz^2 (2%) → d_π (15%)	28.2%		
490.050	2.530	0.022	H-3 (b) → L+2 (b) d_π (5%) → dz^2 (81%)	24.6%		
			H-3 (a) → L (a) d_π (3%) → dx^2-y^2 (40%)	15.6%		
			H-1 (b) → L+4 (b) dz^2 (2%) → d_π (15%)	13.1%		

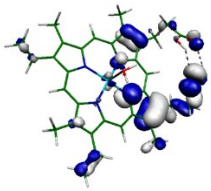
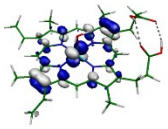
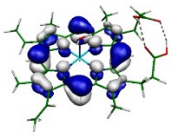
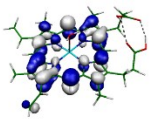
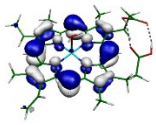
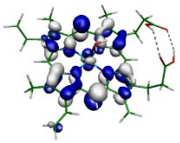
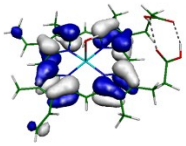
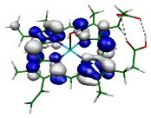
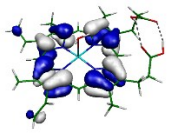
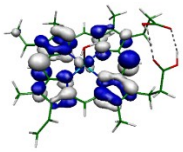
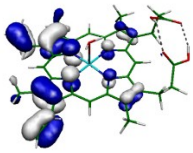
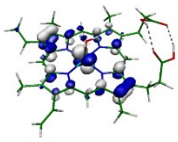
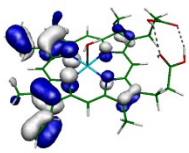
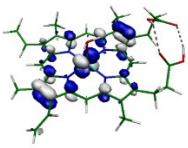
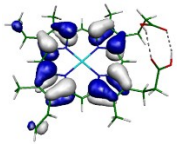
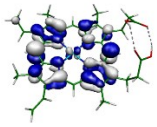
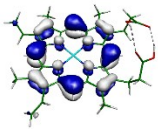
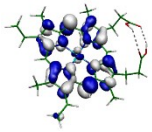
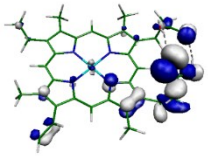
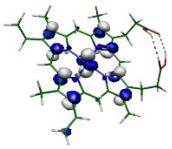
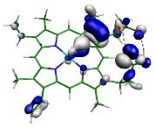
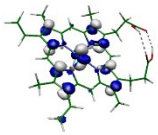
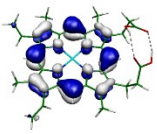
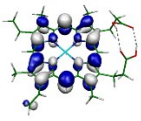
564.102	**2.198**	**0.009**	**H-4 (b) → L (b)** **d_{π} (4%) → d_{yz} (56%)**	**22.5%**		
574.429	**2.158**	**0.008**	**H-1 (a) → L+1 (a)** **dz^2 (1%) → d (0%)**	**17.1%**		
			H-1 (b) → L+3 (b) **dz^2 (2%) → d_{π} (15%)**	**11.9%**		
			H (a) → L+2 (a) **d (0%) → d (0%)**	**11.1%**		
			H (b) → L+4 (b) **d (0%) → d_{π} (15%)**	**10.3%**		
622.168	**1.993**	**0.008**	**H-2 (b) → L+1 (b)** **d_{π} (1%) → d_{xz} (56%)**	**61.6%**		
632.983	**1.959**	**0.010**	**H-2 (b) → L (b)** **d_{π} (1%) → d_{yz} (56%)**	**43.8%**		

Table S3B: Electronic transition energies and the contributed MOs in transitions, obtained at the B3LYP/cc-pVDZ (TZVP for Fe) level of theory for $[Fe^{III}\ PP]^{+}$ complex (S=3/2) using the geometry optimized at OPTX-PBE level. H and L stand for HOMO and LUMO respectively

Vertical			Contributed orbitals	Weight (%)	Shape	
nm	ev	Oscillator strengths			Initial orb. Cutoff=0.03	Final orb. Cutoff=0.03
501.126	2.474	0.032	H (b) → L+4 (b) d (0%) → d_π (10%)	27.0 %		
			H-1 (b) → L+3 (b) d_π (1%) → d_π (10%)	26.9 %		
505.497	2.453	0.021	H-4 (b) → L+3 (b) d_π (2%) → d_π (60%)	22.3 %		
			H-5 (b) → L+3 (b) d_π (5%) → d_π (60%)	16.0 %		
561.871	2.207	0.011	H-1 (a) → L+1 (a) d (1%) → d (0%)	22.4 %		

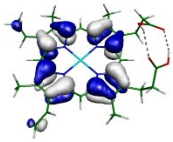
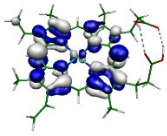
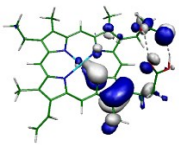
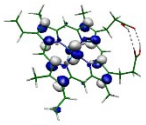
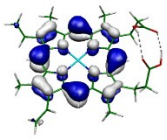
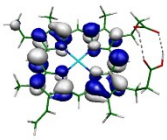
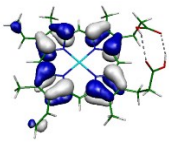
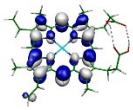
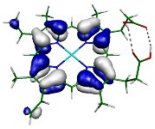
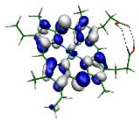
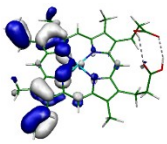
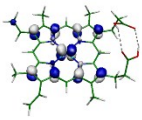
			H (b) → L+4 (b) **d (0%) → d_π (10%)**	**20.2 %**		
			H-6 (b) → L+1 (b) **d_{xz} (6%) → d_π (60%)**	**15.3 %**		
568.788	**2.180**	**0.009**	**H-1 (a) → L+2 (a)** **d (1%) → d_π (1%)**	**35.7 %**		
662.961	**1.870**	**0.007**	**H (a) → L+1 (a)** **d (0%) → d (0%)**	**34.2 %**		
			H (b) → L+3 (b) **d (0%) → d_π (10%)**	**26.3 %**		
683.290	**1.815**	**0.011**	**H-3 (b) → L (b)** **d_π (6%) → d_π (60%)**	**54.0 %**		

Table S4: Single point calculation with two different functionals and cc-pVTZ (C, H, O)//aug-ccpVTZ (Fe, N, O (H_2O)) basis sets, both on the previously OPBE optimized [heme Fe^{III}-H_2O] complex (S=3/2).

Method	E_b	D3(BJ) Dispersion	Eb+D3(BJ)
OPBE	-5.73	-9.21	-14.94
B3LYP	-13.00	-4.94	-17.94

Table S5 Dipole(H_2O)–Charge(Fe) interaction energy. Dipoles and charges obtained from OPBE calculations.

Complex	$\mu_z(H_2O)$ (Debye)[a)]	$\mu_{Total}(H_2O)$ (Debye) [a)]	q(Fe) (e) [a)]	$E = \frac{1}{4\pi\varepsilon_0} \times \frac{\mu_{Total}(H2O) * q(Fe)}{r_{Fe-OH2}^{\ 2}}$ $(kcal/mol)$
$[PP\text{-}Fe^{III}]^+$	-	-	-	-
$[H\ PP\text{-}Fe]^+$	-	-	-	-
$[PP\text{-}Fe^{II}]$	-	-	-	-
$[PP\text{-}Fe^{III}\text{–}H_2O]^+$	-0.3854	0.5890	1.8097	1.411612
$[H\ PP\text{-}Fe\text{–}H_2O]^+$	-0.2908	0.5775	1.7273	1.255296
$[PP\text{-}Fe^{II}\text{–}H_2O]$	-0.3724	0.5891	1.6400	1.084075
$[PP\text{-}Fe^{III}\text{–}(H_2O)_2]^+$	-0.3422	0.5965	1.8544	1.359292
$[H\ PP\text{-}Fe\text{–}(H_2O)_2]^+$	-0.3916	0.5825	1.7799	1.230028
$[PP\text{-}Fe^{II}\text{–}(H_2O)_2]$	-0.3934	0.6282	1.6722	1.057596

Table S6: The xyz coordinates of the spin state optimized geometry of the ferric Heme complexes investigated in this study at the OPTX-PBE level of theory.

[heme-Fe^{III}]$^{+}$, S=3/2			
C	-3.988082	5.065321	3.309191
C	-4.055404	6.485040	3.553028
C	-5.401580	6.791819	3.673325
C	-6.122350	5.559569	3.515413
N	-5.260917	4.483034	3.305634
C	-7.508086	5.491248	3.562880
H	-8.078914	6.417812	3.727737
C	-8.209690	4.303091	3.426617
C	-8.741700	2.177833	3.253312
C	-9.985733	2.892086	3.355505
N	-7.641161	3.039007	3.288277
C	-9.649322	4.237372	3.465118
C	-8.675155	0.795336	3.139968
H	-9.612981	0.220633	3.129332
C	-7.475929	0.107994	3.024818
C	-5.351831	-0.396961	2.779177
C	-6.061091	-1.647399	2.760067
N	-6.211592	0.690417	2.953652
C	-7.405980	-1.328711	2.915684
C	-3.974747	-0.315342	2.629245
H	-3.412534	-1.246777	2.465530
C	-3.279872	0.885058	2.658414
C	-2.742518	3.010958	2.843877
C	-1.514818	2.299407	2.581742
N	-3.840749	2.145666	2.870543
C	-1.857021	0.960890	2.478498
C	-2.803867	4.379208	3.074748
H	-1.864957	4.955230	3.053696
FE	-5.738690	2.589836	3.107695
C	-0.125804	2.870470	2.446616
H	0.567743	2.213919	3.015674
H	-0.038381	3.867199	2.921196
C	0.400295	2.945551	0.980180
H	1.506924	2.989735	1.003595
H	0.066881	2.057393	0.404355
C	-0.066167	4.217459	0.310560
O	0.586357	5.262751	0.356500
O	-1.267886	4.115314	-0.284306
H	-1.531363	5.028507	-0.540402
C	-2.906110	7.451284	3.690987
H	-1.970984	6.933155	3.983053
H	-3.143884	8.131371	4.536830
C	-2.646955	8.335159	2.435725
H	-3.601031	8.689381	2.000131
H	-2.026236	9.201052	2.748960
C	-1.874490	7.573021	1.378932
O	-2.378102	7.022898	0.399417
O	-0.560045	7.538865	1.674517
H	-0.119021	6.943916	1.018677
C	-0.964518	-0.222575	2.228388
H	-1.031366	-0.945544	3.070054
H	-1.260513	-0.747103	1.294337
H	0.101186	0.065708	2.124909
C	-8.568929	-2.217949	2.986170

H	-9.329989	-1.986588	3.753223
C	-8.777046	-3.274170	2.172141
H	-8.087297	-3.539359	1.354683
H	-9.674028	-3.901827	2.292230
C	-10.523901	5.409184	3.567604
H	-10.254869	6.288241	2.953615
C	-11.611128	5.489730	4.363030
H	-11.916810	4.671902	5.035381
H	-12.225654	6.403710	4.377603
C	-11.346468	2.263034	3.284884
H	-11.418508	1.573739	2.417252
H	-11.553958	1.682160	4.209478
H	-12.140839	3.028796	3.174203
C	-6.039471	8.130104	3.916829
H	-5.290082	8.938283	4.041978
H	-6.689657	8.411369	3.060077
H	-6.664310	8.108076	4.835345
C	-5.412647	-2.997536	2.660042
H	-4.590007	-3.094337	3.399803
H	-6.139734	-3.810794	2.858945
H	-4.992174	-3.154209	1.643215

[heme-Fe^{III}-H_2O]$^+$, S=3/2

C	-6.377266	5.488388	3.559896
C	-7.485618	6.363550	3.862911
C	-8.620144	5.569272	3.842844
C	-8.184590	4.234590	3.529416
N	-6.803252	4.172261	3.376537
C	-9.063628	3.167358	3.377320
H	-10.141552	3.349119	3.508000
C	-8.651248	1.871488	3.093923
C	-7.423983	0.067544	2.814229
C	-8.793700	-0.372402	2.774840
N	-7.329816	1.449711	2.983369
C	-9.570955	0.767334	2.952378
C	-6.344211	-0.805083	2.733515
H	-6.542478	-1.880906	2.613843
C	-5.023431	-0.383521	2.814875
C	-3.210149	0.855117	2.847734
C	-2.756950	-0.511398	2.797774
N	-4.600343	0.939191	2.878659
C	-3.903873	-1.295652	2.776350
C	-2.339946	1.937975	2.825266
H	-1.261377	1.733146	2.747473
C	-2.763529	3.259584	2.892364
C	-3.992032	5.069745	3.147827
C	-2.626020	5.517320	3.007302
N	-4.084090	3.682153	3.030066
C	-1.856226	4.374216	2.865106
C	-5.061955	5.917983	3.416223
H	-4.855141	6.995312	3.519010
FE	-5.708168	2.567083	2.984638
C	-2.114679	6.936184	3.005847
H	-1.178833	6.965965	3.604561
H	-2.811132	7.627971	3.518500
C	-1.778734	7.489082	1.586268
H	-1.063639	8.328364	1.692585
H	-1.334876	6.688403	0.959018
C	-3.012281	8.060985	0.928072
O	-3.347374	9.239132	1.064036
O	-3.736243	7.164400	0.228115
H	-4.574319	7.622638	-0.010846

C	-7.434225	7.841027	4.164149
H	-6.432696	8.144500	4.529430
H	-8.128609	8.035033	5.009322
C	-7.864850	8.758502	2.982474
H	-8.766007	8.353728	2.482336
H	-8.076938	9.768970	3.390654
C	-6.752995	8.895507	1.963495
O	-6.643279	8.213899	0.942464
O	-5.866957	9.836951	2.341677
H	-5.107655	9.809788	1.708985
C	-0.365616	4.255391	2.705315
H	0.067953	3.675613	3.548599
H	-0.110958	3.734801	1.757006
H	0.138092	5.243299	2.689165
C	-4.032134	-2.756972	2.737597
H	-4.792477	-3.205952	3.401955
C	-3.307805	-3.574738	1.946008
H	-2.563093	-3.197415	1.226418
H	-3.457859	-4.665082	1.984608
C	-11.030856	0.902525	2.987630
H	-11.464543	1.766412	2.450973
C	-11.867642	0.067139	3.637815
H	-11.509697	-0.789832	4.230665
H	-12.955896	0.234176	3.609819
C	-9.235033	-1.787173	2.531316
H	-8.693287	-2.227359	1.667941
H	-9.033484	-2.414014	3.426611
H	-10.321065	-1.839000	2.312639
C	-10.050751	5.968246	4.078706
H	-10.150874	7.038764	4.350874
H	-10.658842	5.801046	3.162942
H	-10.492386	5.369588	4.903681
C	-1.317564	-0.940101	2.824498
H	-0.772508	-0.429418	3.646033
H	-1.226973	-2.033361	2.987704
H	-0.818165	-0.694453	1.862470
O	-5.870773	2.945908	0.741267
H	-6.805866	2.963484	0.475141
H	-5.544445	3.845612	0.563706

[heme-Fe^{III} $-(H_2O)_2]^+$, S=3/2

C	-6.900443	5.393011	3.361711
C	-8.158656	6.093120	3.498587
C	-9.146805	5.123458	3.456705
C	-8.479207	3.858172	3.294400
N	-7.101278	4.020237	3.247665
C	-9.161136	2.648207	3.187053
H	-10.260618	2.660647	3.231334
C	-8.527342	1.421124	3.017741
C	-7.004104	-0.156700	2.848118
C	-8.280094	-0.820454	2.742854
N	-7.155677	1.215921	3.015690
C	-9.243349	0.175320	2.856813
C	-5.787869	-0.833960	2.796721
H	-5.805671	-1.926202	2.666609
C	-4.549792	-0.206625	2.899768
C	-2.961310	1.308642	3.035513
C	-2.290883	0.034206	2.965344
N	-4.344126	1.161555	3.006009
C	-3.294080	-0.924181	2.874168
C	-2.281643	2.521567	3.108913
H	-1.181805	2.497378	3.111503

C	-2.915667	3.759955	3.161380
C	-4.437577	5.350929	3.242998
C	-3.150750	6.012312	3.234985
N	-4.288980	3.969380	3.177965
C	-2.198146	5.007465	3.201572
C	-5.656737	6.020764	3.333779
H	-5.634675	7.119998	3.399882
FE	-5.723866	2.592274	3.117806
C	-2.873315	7.494592	3.247976
H	-2.032420	7.679465	3.950232
H	-3.727050	8.073439	3.652173
C	-2.455504	8.080346	1.863382
H	-1.913262	9.032157	2.030018
H	-1.803791	7.361310	1.325205
C	-3.671385	8.420620	1.034401
O	-4.216434	9.525203	1.084858
O	-4.131623	7.402053	0.281759
H	-5.001040	7.697418	-0.073834
C	-8.374707	7.575622	3.670714
H	-7.486898	8.069350	4.114657
H	-9.190929	7.710214	4.411384
C	-8.797563	8.320599	2.369218
H	-9.522533	7.715070	1.792159
H	-9.255997	9.289190	2.660615
C	-7.596851	8.624282	1.498818
O	-7.227547	7.938738	0.543066
O	-6.952038	9.723218	1.934543
H	-6.114247	9.808812	1.416031
C	-0.699022	5.126786	3.197063
H	-0.264773	4.603546	4.076305
H	-0.270968	4.674178	2.276517
H	-0.359327	6.181819	3.238398
C	-3.180281	-2.383930	2.784101
H	-3.893814	-2.977880	3.384103
C	-2.290068	-3.041073	2.011749
H	-1.579036	-2.520954	1.349952
H	-2.261555	-4.141992	2.006529
C	-10.705408	0.069050	2.800829
H	-11.237378	0.845011	2.219671
C	-8.465113	-2.289678	2.494373
H	-7.820131	-2.631599	1.657597
H	-8.199902	-2.875271	3.401193
H	-9.516155	-2.525143	2.229725
C	-10.637389	5.295482	3.542197
H	-10.931566	6.353716	3.700235
H	-11.123815	4.954057	2.602607
H	-11.055042	4.702861	4.384439
C	-0.802886	-0.153488	3.046842
H	-0.382668	0.400416	3.913108
H	-0.536336	-1.223069	3.170340
H	-0.311402	0.217331	2.121683
O	-5.756287	2.792275	0.759120
H	-6.501537	3.371321	0.525481
O	-5.701127	2.396552	5.477507
H	-4.937645	1.845034	5.715699
H	-4.976454	3.315112	0.507080
H	-6.464092	1.850131	5.730045
C	-11.434785	-0.887185	3.412703
H	-12.531460	-0.904881	3.311389
H	-10.980926	-1.668401	4.043543
[MI-heme-Fe^{III}]$^{+}$, S=5/2			
C	-7.256709	-2.381651	7.526109

C	-7.937048	-1.696731	8.609079
C	-8.886829	-0.876426	8.013417
C	-8.786094	-1.086221	6.589571
N	-7.828644	-2.045883	6.304548
C	-9.541791	-0.389420	5.638951
H	-10.276819	0.341871	6.012581
C	-9.420757	-0.509195	4.251564
C	-8.825168	-1.208749	2.246643
C	-9.786316	-0.148342	2.031844
N	-8.626807	-1.432025	3.600641
C	-10.178694	0.282489	3.296041
C	-8.211389	-1.926704	1.213640
H	-8.494849	-1.668174	0.181421
C	-7.238894	-2.917792	1.382166
C	-5.705843	-4.214844	2.297902
C	-5.578547	-4.393545	0.870562
N	-6.748135	-3.352444	2.601626
C	-6.548232	-3.576256	0.290494
C	-4.850926	-4.797517	3.239815
H	-4.065061	-5.466594	2.855104
C	-4.875798	-4.568297	4.619723
C	-5.446076	-3.853239	6.630815
C	-4.257130	-4.671765	6.803303
N	-5.810422	-3.801738	5.293955
C	-3.911960	-5.126521	5.540304
C	-6.148241	-3.227554	7.670538
H	-5.776839	-3.394144	8.696603
FE	-7.525552	-2.965629	4.473508
C	-3.511594	-4.979567	8.079743
H	-3.275598	-6.065292	8.085596
H	-4.142691	-4.812422	8.974840
C	-2.167388	-4.202364	8.241250
H	-1.507661	-4.770636	8.925653
H	-1.677952	-4.074718	7.253893
C	-2.409396	-2.861852	8.891922
O	-2.424178	-2.719912	10.118606
O	-2.659721	-1.867338	8.025270
H	-2.956730	-1.092676	8.556861
C	-7.693866	-1.835694	10.094449
H	-7.220073	-2.808092	10.337278
H	-8.686963	-1.851265	10.592568
C	-6.866029	-0.679533	10.722074
H	-7.182364	0.300294	10.315690
H	-7.025219	-0.699287	11.821527
C	-5.380742	-0.850475	10.483157
O	-4.711050	-0.160828	9.714030
O	-4.887163	-1.873894	11.206996
H	-3.933593	-1.988449	10.961509
C	-2.767126	-6.019788	5.144508
H	-3.144967	-6.942213	4.652736
H	-2.094812	-5.494412	4.433307
H	-2.155176	-6.335576	6.013929
C	-6.851591	-3.359488	-1.126876
H	-7.919594	-3.263021	-1.394823
C	-5.935280	-3.241533	-2.110980
H	-4.850411	-3.272640	-1.922273
H	-6.256182	-3.080330	-3.151983
C	-10.195051	0.391413	0.690414
H	-9.314230	0.489500	0.023271
H	-10.930461	-0.285723	0.204562
H	-10.662244	1.393526	0.786063
C	-9.840685	0.082023	8.673812

H	-9.775824	0.048659	9.780794
H	-9.615126	1.122517	8.356824
H	-10.890538	-0.145951	8.389934
C	-4.610460	-5.327317	0.202239
H	-4.610285	-6.320059	0.700456
H	-4.871333	-5.484005	-0.864587
H	-3.580431	-4.913051	0.248085
N	-8.964487	-4.501881	4.676566
C	-9.740928	-4.712914	5.739979
C	-9.284767	-5.484435	3.748959
H	-9.736029	-4.113033	6.650914
C	-10.269298	-6.300987	4.257968
H	-8.785838	-5.533621	2.777562
H	-11.222541	-6.159699	6.171503
C	-10.971021	-7.490111	3.688044
H	-10.813399	-8.393501	4.317873
H	-12.066102	-7.312581	3.605118
H	-10.584790	-7.711609	2.673251
N	-10.536959	-5.787134	5.521402
C	-11.110901	1.351274	3.663048
H	-10.831779	1.960721	4.541175
C	-12.277341	1.632038	3.043311
H	-12.653425	1.046153	2.189571
H	-12.909098	2.461698	3.396721

[MI-heme-Fe^{III} −H_2O]$^+$, S=5/2

C	-7.228887	-2.339317	7.564396
C	-7.931496	-1.660464	8.640869
C	-8.932121	-0.907076	8.040440
C	-8.827783	-1.130837	6.615861
N	-7.799599	-2.012240	6.347332
C	-9.646830	-0.507014	5.658308
H	-10.424013	0.175557	6.035909
C	-9.543532	-0.638357	4.264349
C	-8.876647	-1.272861	2.252821
C	-9.887757	-0.260708	2.040060
N	-8.689477	-1.495204	3.605150
C	-10.325437	0.126579	3.307337
C	-8.177748	-1.925750	1.222170
H	-8.435631	-1.651457	0.188234
C	-7.180445	-2.898450	1.397573
C	-5.693497	-4.239077	2.338161
C	-5.552947	-4.422464	0.909556
N	-6.694000	-3.327088	2.614446
C	-6.476776	-3.563467	0.313569
C	-4.883544	-4.870374	3.297259
H	-4.121224	-5.567800	2.917224
C	-4.914552	-4.657813	4.685873
C	-5.446616	-3.882644	6.693915
C	-4.297660	-4.756186	6.873668
N	-5.798072	-3.834580	5.357841
C	-3.981000	-5.253007	5.616302
C	-6.125119	-3.199358	7.721888
H	-5.754959	-3.349431	8.749920
FE	-7.327268	-2.755180	4.481084
C	-3.543465	-5.051095	8.145802
H	-3.303916	-6.135861	8.163940
H	-4.159372	-4.866612	9.048736
C	-2.194239	-4.275183	8.274460
H	-1.540082	-4.814904	8.987284
H	-1.702455	-4.199678	7.283417
C	-2.427184	-2.905349	8.864571
O	-2.469857	-2.713876	10.082829

O	-2.632571	-1.934857	7.955187
H	-2.931783	-1.143242	8.459772
C	-7.652536	-1.732615	10.120211
H	-7.162330	-2.687762	10.401543
H	-8.628177	-1.728610	10.650661
C	-6.817219	-0.538239	10.670295
H	-7.150260	0.413668	10.214576
H	-6.952484	-0.501811	11.772361
C	-5.339705	-0.728732	10.404381
O	-4.703753	-0.156368	9.516656
O	-4.812259	-1.638071	11.245458
H	-3.877309	-1.806810	10.965247
C	-2.881743	-6.204171	5.231372
H	-3.302166	-7.097098	4.720393
H	-2.167698	-5.714297	4.533903
H	-2.300176	-6.563687	6.105476
C	-6.756144	-3.342128	-1.106324
H	-7.815575	-3.187052	-1.382679
C	-5.827400	-3.279171	-2.084965
H	-4.747282	-3.367273	-1.888860
H	-6.130508	-3.107485	-3.129509
C	-10.301263	0.271434	0.697970
H	-9.410447	0.495775	0.074271
H	-10.922953	-0.476664	0.159271
H	-10.892436	1.204951	0.794076
C	-9.937355	0.001421	8.691174
H	-9.872874	-0.014778	9.799029
H	-9.775734	1.051874	8.364380
H	-10.971794	-0.291319	8.409674
C	-4.610721	-5.392272	0.256094
H	-4.657070	-6.382525	0.756159
H	-4.857683	-5.540770	-0.815319
H	-3.566275	-5.016742	0.320460
O	-5.727172	-0.921624	4.340315
H	-5.915179	-0.339757	5.095320
H	-4.859092	-1.298691	4.559424
N	-8.736533	-4.395847	4.643562
C	-8.943061	-5.176454	5.695186
C	-9.595161	-4.824470	3.647199
H	-8.419769	-5.094418	6.647285
C	-10.339258	-5.889934	4.104493
H	-9.614725	-4.336877	2.668513
H	-10.251614	-6.805237	6.041547
C	-11.401912	-6.723918	3.460341
H	-11.112764	-7.797277	3.437583
H	-12.367817	-6.634899	4.003983
H	-11.558918	-6.385176	2.417354
N	-9.903473	-6.093144	5.407537
C	-11.320725	1.136438	3.673564
H	-11.085070	1.764839	4.552683
C	-12.498718	1.338035	3.044457
H	-12.831128	0.721819	2.194214
H	-13.185911	2.127881	3.386166

[hemeH-Fe^{II}]$^{+}$, S=1

C	-3.270666	4.386210	3.245738
C	-2.865134	5.772447	3.397669
C	-4.029730	6.508112	3.464684
C	-5.114843	5.563475	3.365699
N	-4.653675	4.256714	3.243312
C	-6.446747	5.950660	3.385802
H	-6.658795	7.026556	3.462920

C	-7.501535	5.052087	3.309748
C	-8.719236	3.207264	3.205524
C	-9.667965	4.239451	3.243632
N	-7.383956	3.688934	3.235035
C	-8.919516	5.465761	3.313606
C	-9.074981	1.848199	3.164865
H	-10.145007	1.598703	3.144163
C	-8.172622	0.812862	3.124502
C	-6.327056	-0.359249	2.989030
C	-7.409747	-1.320964	3.008917
N	-6.779179	0.945760	3.073682
C	-8.573961	-0.582917	3.091686
C	-4.990531	-0.741478	2.884298
H	-4.759468	-1.813554	2.795685
C	-3.944134	0.164431	2.866554
C	-2.760948	2.006525	2.939582
C	-1.816747	0.911428	2.760196
N	-4.068321	1.550758	2.982838
C	-2.565362	-0.242535	2.730113
C	-2.375603	3.334796	3.083211
H	-1.300120	3.571185	3.053711
FE	-5.728712	2.605782	3.140054
C	-0.317110	1.001788	2.626278
H	0.129412	0.197526	3.250121
H	0.081978	1.947925	3.042179
C	0.212029	0.809142	1.171776
H	1.276879	0.507160	1.218624
H	-0.382150	0.031029	0.649117
C	0.169039	2.111079	0.406674
O	1.125752	2.889125	0.375443
O	-1.012601	2.362838	-0.184250
H	-0.970877	3.291804	-0.506941
C	-1.460993	6.312507	3.498056
H	-0.748618	5.535605	3.841083
H	-1.457402	7.087872	4.293833
C	-0.925245	6.975766	2.195129
H	-1.709547	7.596343	1.720643
H	-0.051058	7.605101	2.465497
C	-0.452218	5.933963	1.202876
O	-1.114376	5.513981	0.253500
O	0.781233	5.492681	1.519771
H	0.997820	4.741475	0.913250
C	-2.108657	-1.667795	2.580657
H	-2.418990	-2.272928	3.459996
H	-2.544869	-2.128443	1.667920
H	-1.005613	-1.749961	2.498162
C	-9.965577	-1.042461	3.161782
H	-10.622965	-0.533676	3.889627
C	-10.490328	-2.021121	2.395818
H	-9.908719	-2.542153	1.618370
H	-11.544109	-2.317708	2.516356
C	-9.348513	6.775265	3.371016
H	-8.562419	7.547758	3.416091
C	-10.748901	7.296999	3.378807
H	-11.325579	6.902179	4.242420
H	-10.753385	8.405152	3.437909
C	-11.158019	4.095536	3.219874
H	-11.495251	3.044740	3.151639
H	-11.606826	4.532892	4.137283
H	-11.589259	4.639170	2.352390
C	-4.198299	7.995312	3.610696
H	-3.225556	8.521852	3.693327

H	-4.726043	8.418492	2.728158
H	-4.785777	8.239897	4.522046
C	-7.222312	-2.810591	3.004807
H	-6.491999	-3.115872	3.784082
H	-8.175915	-3.336542	3.212492
H	-6.848020	-3.154961	2.016654
H	-11.297656	6.997715	2.460317

[hemeH-$Fe^{II}-H_2O]^+$, S=1

C	-2.964365	3.903238	3.197821
C	-2.300056	5.182926	3.359864
C	-3.302340	6.120676	3.511169
C	-4.549616	5.401483	3.427979
N	-4.345222	4.040119	3.240694
C	-5.787658	6.028203	3.504289
H	-5.796261	7.118834	3.640977
C	-6.994573	5.350225	3.390721
C	-8.533120	3.775423	3.155801
C	-9.270607	4.967583	3.237339
N	-7.135599	3.995958	3.232860
C	-8.309108	6.022657	3.409688
C	-9.139841	2.509795	3.071891
H	-10.236974	2.471763	3.018270
C	-8.454875	1.316130	3.079231
C	-6.867124	-0.193646	3.060365
C	-8.115621	-0.928150	3.087066
N	-7.065299	1.174758	3.070050
C	-9.117494	0.023495	3.088610
C	-5.625579	-0.825908	3.003496
H	-5.602031	-1.925703	2.980204
C	-4.424607	-0.135425	2.941711
C	-2.917746	1.458938	2.916057
C	-2.196987	0.201951	2.779136
N	-4.286579	1.252403	2.984290
C	-3.146360	-0.795587	2.818188
C	-2.291683	2.698031	3.015367
H	-1.192098	2.726721	2.958966
FE	-5.721969	2.618461	3.090181
C	-0.711224	0.009350	2.601689
H	-0.396957	-0.850032	3.232095
H	-0.131460	0.875360	2.977816
C	-0.281418	-0.310090	1.136616
H	0.717901	-0.788229	1.155224
H	-1.019829	-0.991326	0.664796
C	-0.134055	0.955366	0.325430
O	0.936826	1.557361	0.225282
O	-1.280044	1.393081	-0.234586
H	-1.081099	2.288858	-0.591272
C	-0.816406	5.451615	3.373276
H	-0.242078	4.557742	3.690805
H	-0.618262	6.220379	4.149589
C	-0.250310	5.990686	2.025844
H	-0.940450	6.737819	1.588200
H	0.738372	6.453783	2.228002
C	-0.037262	4.867615	1.032659
O	-0.843345	4.529287	0.163761
O	1.139676	4.249689	1.251793
H	1.178365	3.454846	0.665221
C	-2.961945	-2.286737	2.740987
H	-3.361228	-2.776457	3.655444
H	-3.494813	-2.707096	1.860521
H	-1.894771	-2.575574	2.651465

C	-10.574194	-0.156988	3.117869
H	-11.143913	0.495461	3.803910
C	-11.253414	-1.046036	2.364640
H	-10.757856	-1.699150	1.628116
H	-12.347776	-1.132215	2.454364
C	-8.490495	7.381138	3.578238
H	-7.576251	7.985642	3.701934
C	-9.770964	8.151459	3.623598
H	-10.431289	7.798255	4.444441
H	-9.570802	9.231293	3.783168
C	-10.759703	5.111720	3.165101
H	-11.281348	4.154668	2.979377
H	-11.157539	5.534482	4.112536
H	-11.046282	5.808171	2.349014
C	-3.182124	7.607142	3.709585
H	-2.125257	7.940188	3.755157
H	-3.663711	8.156318	2.871137
H	-3.669947	7.918372	4.658722
C	-8.225025	-2.424797	3.156359
H	-7.584414	-2.826376	3.969855
H	-9.268264	-2.741073	3.358952
H	-7.906114	-2.886005	2.196767
O	-5.681564	2.812876	0.758829
H	-5.143571	3.592398	0.538041
H	-5.152347	2.065209	0.432074
H	-10.344548	8.043192	2.678393