

# Spin-forbidden Ligand Binding to the Ferrous Heme

## Group: *ab initio* and DFT Studies

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## Supporting Information

RELATIVE SPIN-STATE ENERGIES OF MODELS 1 AND 2, CALCULATED BY CCSD.

**Table S1.** CCSD energies (kcal mol<sup>-1</sup>, relative to the quintet state) of triplet and singlet states of model heme compounds.

Basis Set		Model 1		Model 2	
Fe	Amidines	<sup>3</sup> [Fe]	<sup>1</sup> [Fe]	<sup>3</sup> [Fe]	<sup>1</sup> [Fe]
cc-pVTZ	cc-pVDZ	24.8	47.2	13.0	33.0
cc-pVTZ	cc-pVTZ	25.8	48.4	- <sup>a</sup>	- <sup>a</sup>
cc-pVQZ	cc-pVDZ	22.8	44.8	10.8	29.6
cc-pVQZ	cc-pVTZ	24.5	46.3	- <sup>a</sup>	- <sup>a</sup>

<sup>a</sup> Calculations too large to be feasible.

## VARIATION OF BOND LENGTHS AND ANGLES WITH FUNCTIONAL FOR DEOXY AND LIGATED-HAEM GEOMETRIES OPTIMIZED WITH DFT

Gas-phase quintet deoxy-FeP(Im), FeP(Im)(CO), FeP(Im)(NO) and FeP(Im)(O<sub>2</sub>) heme systems have been optimized using the B3LYP, B3PW91, B3P86, BLYP and BP86 DFT functionals. For these models Fe is in the +2 oxidation state, Im is an imidazole group and P is a porphine ring. The optimizations have been carried out using the method and basis set described for FeP(Im) complexes in the computational details. The key bond lengths, bond angles for these structures and related crystal structures are shown below in Tables S1 to S4. In all cases distances are in angstroms (Å) and angles are in degrees (°). The iron out-of-plane distance, d(Fe oop), refers to the distance of the iron atom below the plane of best fit through the four porphyrin nitrogens, with a negative value indicating it is on the proximal side of the haem group and a positive value indicating it is on the distal side of the haem group.  $r(\text{Fe-N}_p)$  is the average iron to porphyrin nitrogen distance, Jawsizes is half the average porphyrin cross-ring N-N distance and  $r(\text{Fe-N}_{\text{Im}})$  is the iron to imidazole bond length.

**Table S2.** Calibration of quintet state deoxy-FeP(Im) geometries against haem model and Mb crystal structures

Structures and method	d(Fe oop)	r(Fe-N <sub>p</sub> )	r(Fe-N <sub>Im</sub> )
<sup>5</sup> FeP(Im) DFT geometries:			
BP86	-0.272	2.089	2.168
BLYP	-0.288	2.103	2.215
B3PW91	-0.281	2.087	2.194
B3P86	-0.272	2.081	2.172
B3LYP	-0.287	2.095	2.214
Crystal Structures:			
Fe(TpivPP)(2-MeIm) <sup>a</sup>	-0.399	2.072	2.095
expt: Mb (1BZN) <sup>b</sup>	-0.290	2.057	2.15
expt: Mb (1A6N) <sup>c</sup>	-0.363	2.070	2.14

<sup>a</sup> Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. S. *Journal of the American Chemical Society* **1980**, 102, 3224. <sup>b</sup> Vojtechovsky, J.; Chu, K.; Berendzen, J.; Sweet, R. M.; Schlichting, I. *Biophysical Journal* **1999**, 77, 2153. <sup>c</sup> Kachalova, G. S.; Popov, A. N.; Bartunik, H. D. *Science* **1999**, 284, 473.

**Table S3.** Bond lengths and angles of our DFT calculated FeP(Im)(CO) systems and similar haem models and Mb crystal structures

Structures and method	$\angle$ Fe-C-O	r(Fe-C)	d(Fe oop)	r(Fe-N <sub>p</sub> )	r(Fe-N <sub>Im</sub> )
FeP(Im)(CO) DFT geometries:					
BP86	180.0	1.753	+0.052	2.020	2.060
BLYP	179.9	1.773	+0.054	2.038	2.110
B3PW91	179.9	1.781	+0.040	2.014	2.047
B3P86	180.0	1.778	+0.042	2.010	2.033
B3LYP	180.0	1.806	+0.039	2.028	2.075
Crystal Structures:					
Fe(TPP)(CO)(Py) <sup>a</sup>	179	1.77	+0.02	2.02	2.10
Fe(TPP)(CO)(1-MeIm) <sup>b</sup>	179.3	1.793	-	2.003	2.071
Fe(OC <sub>3</sub> OPor)(CO)(1-MeIm) <sup>c</sup>	173.9	1.748	+0.06	1.996	2.027
Fe(OC <sub>3</sub> OPor)(CO)(1,2-Me <sub>2</sub> Im) <sup>c</sup>	180.0	1.713	-0.10	2.00	2.102
Myoglobin (1BZP) <sup>d</sup>	172.6	1.73	+0.015	2.005	2.12
Myoglobin (1 <sup>a</sup> 6G) <sup>e</sup>	171.0	1.82	-0.001	1.98	2.06

<sup>a</sup> TPP = 5,10,15,20-tetraphenylporphyrin dianion, Py = pyridine. Peng, S. M.; Ibers, J. A. *Journal of the American Chemical Society* **1976**, 98, 8032. <sup>b</sup> Crystal structure. 1-MeIm = imidazole bound for Fe through  $\epsilon$ -nitrogen and with a methyl group bound to  $\delta$ -nitrogen. Salzmann, R.; Ziegler, C. J.; Godbout, N.; McMahon, M. T.; Suslick, K. S.; Oldfield, E. *Journal of the American Chemical Society* **1998**, 120, 11323. <sup>c</sup> Slebodnick, C.; Duval, M. L.; Ibers, J. A. *Inorganic Chemistry* **1996**, 35, 3607.. <sup>d</sup> Kachalova, G. S.; Popov, A. N.; Bartunik, H. D. *Science* **1999**, 284, 473. <sup>e</sup> Vojtechovsky, J.; Chu, K.; Berendzen, J.; Sweet, R. M.; Schlichting, I. *Biophysical Journal* **1999**, 77, 2153.

**Table S4.** Calibration of ground state FeP(Im)(NO) geometries against haem model and Mb crystal structures

Structures and method	$\angle$ Fe-N-O	r(Fe-N)	d(Fe oop)	r(Fe-N <sub>p</sub> )	r(Fe-N <sub>Im</sub> )
FeP(Im)(NO) DFT geometries:					
BP86	140.0	1.735	+0.086	2.023	2.162
BLYP	139.8	1.750	+0.095	2.040	2.237
B3PW91	140.3	1.783	+0.033	2.013	2.037
B3P86	140.1	1.777	+0.036	2.008	2.025
B3LYP	140.2	1.812	+0.031	2.026	2.061
Crystal Structures:					
Fe(TPP)(NO)(1-MeIm) <sup>a</sup>	142.1/138.3	1.743	+0.07	2.008	2.18
MbNO <sup>b</sup> (1HJT)	112	1.89	0.00	-	2.18
HbNO $\beta$ 37E mutant <sup>c</sup> (1RQA)	135/126	1.71/1.76	-0.15/-0.02	-	2.24/2.19

<sup>a</sup> TPP = 5,10,15,20-tetraphenylporphyrin dianion, 1-MeIm is an axial imidazole group with an methyl group bound to the  $\delta$ -nitrogen. Scheidt, W. R.; Piciulo, P. L. *Journal of the American Chemical Society* **1976**, 98, 1913. <sup>b</sup> 1.7 Å resolution sperm-whale myoglobin. Brucker, E. A.; Olson, J. S.; Ikeda-Saito, M.; Phillips, G. N. *Proteins-Structure Function and Bioinformatics* **1998**, 30, 352. <sup>c</sup> 2.11 Å resolution. First value is average of  $\alpha$ -chains and second value is average of  $\beta$ -chains. Chan, N. L.; Kavanaugh, J. S.; Rogers, P. H.; Arnone, A. *Biochemistry* **2004**, 43, 118.

**Table S5.** Calibration of ground state FeP(Im)(O<sub>2</sub>) geometries against haem model and Mb crystal structures

Structures and method	$\angle \text{Fe-O-O}^a$	$r(\text{Fe-O})^b$	$d(\text{Fe oop})^c$	$r(\text{Fe-N}_p)$	$r(\text{Fe-N}_{\text{Im}})^e$
FeP(Im)(O <sub>2</sub> ) DFT geometries:					
BP86	119.9	1.839	+0.024	2.015	2.080
BLYP	120.1	1.870	+0.024	2.032	2.134
B3PW91	118.7	1.920	+0.007	2.010	2.108
B3P86	118.1	1.867	+0.016	2.004	2.068
B3LYP	118.5	1.899	+0.017	2.020	2.119
Crystal Structures:					
Fe(TpivPP)(O <sub>2</sub> )(Im) <sup>a</sup>	133/129	1.745	+0.030	1.98	2.07
Fe(TpivPP)(O <sub>2</sub> )(2-MeIm) <sup>b</sup>	129.0	1.898	-0.086	1.996	2.107
expt: Mb (1A6M) <sup>c</sup>	122	1.81		2.01	2.06

<sup>a</sup> TpivPP = tetrakis(pivalamidophenyl)porphyrin. Jameson, G. B.; Rodley, G. A.; Robinson, W. T.; Gagne, R. R.; Reed, C. A.; Collman, J. P. *Inorganic Chemistry* **1978**, *17*, 850. <sup>b</sup> Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. S. *Journal of the American Chemical Society* **1980**, *102*, 3224. <sup>c</sup> 1.2 Å resolution. Vojtechovsky, J.; Chu, K.; Berendzen, J.; Sweet, R. M.; Schlichting, I. *Biophysical Journal* **1999**, *77*, 2153.

# Coordinates for FeP(Im), model 1 and model 2 complexes, predicted by B3LYP

Singlet deoxy-FeP(Im)				H	-5.0832	-1.3353	-0.1249	C	1.1017	-2.8653	-0.0768
N	-2.0114	0.0001	0.0007	C	-4.2223	0.6938	-0.0421	C	0.6784	-4.2466	-0.1489
C	-2.8450	-1.0918	-0.0438	H	-5.0658	1.3734	-0.0563	H	1.3441	-5.0994	-0.1997
C	-2.8376	1.0976	0.0024	N	-0.0129	-2.0182	-0.0044	C	-0.6872	-4.2460	-0.1517
C	-4.2277	-0.6723	-0.0702	C	-1.1091	-2.8441	-0.0535	H	-1.3537	-5.0985	-0.2046
H	-5.0767	-1.3434	-0.1156	C	1.0825	-2.8439	-0.0008	N	2.0928	-0.0003	0.0362
C	-4.2226	0.6880	-0.0396	C	0.6666	-4.2264	-0.0437	C	2.8946	-1.1047	-0.0422
H	-5.0665	1.3666	-0.0549	H	1.3410	-5.0740	-0.0539	C	2.8972	1.1014	-0.0481
N	-0.0059	-2.0122	-0.0007	C	-0.6945	-4.2269	-0.0785	C	4.2811	-0.6855	-0.1396
C	-1.1005	-2.8423	-0.0469	H	-1.3680	-5.0740	-0.1233	H	5.1304	-1.3535	-0.2190
C	1.0889	-2.8419	-0.0003	N	2.0184	0.0001	0.0044	C	4.2825	0.6784	-0.1438
C	0.6750	-4.2254	-0.0454	C	2.8379	-1.1002	0.0043	H	5.1336	1.3438	-0.2268
H	1.3505	-5.0719	-0.0626	C	2.8511	1.0915	-0.0490	N	0.0032	2.0580	-0.0362
C	-0.6854	-4.2260	-0.0762	C	4.2229	-0.6925	-0.0407	C	-1.1022	2.8652	-0.0769
H	-1.3594	-5.0727	-0.1234	H	5.0666	-1.3718	-0.0533	C	1.1085	2.8650	-0.0839
N	2.0112	0.0001	0.0007	C	4.2315	0.6684	-0.0755	C	0.6860	4.2465	-0.1573
C	2.8374	-1.0972	0.0030	H	5.0824	1.3369	-0.1218	H	1.3520	5.0992	-0.2132
C	2.8443	1.0916	-0.0441	N	0.0130	2.0181	-0.0044	C	-0.6795	4.2465	-0.1522
C	4.2227	-0.6875	-0.0384	C	-1.0817	2.8444	-0.0002	H	-1.3457	5.0989	-0.2034
H	5.0667	-1.3660	-0.0520	C	1.1093	2.8435	-0.0526	C	-2.4400	-2.4234	-0.0732
C	4.2273	0.6725	-0.0698	C	0.6956	4.2267	-0.0769	C	-2.4336	2.4254	-0.0654
H	5.0758	1.3441	-0.1132	H	1.3698	5.0733	-0.1197	C	2.4394	2.4241	-0.0780
N	0.0061	2.0120	-0.0007	C	-0.6652	4.2270	-0.0425	C	2.4334	-2.4265	-0.0669
C	-1.0885	2.8418	0.0013	H	-1.3391	5.0751	-0.0521	H	-3.2014	-3.1977	-0.1281
C	1.1004	2.8415	-0.0469	C	-2.4327	-2.4177	-0.0694	H	-3.1941	3.2009	-0.1168
C	0.6858	4.2256	-0.0745	C	-2.4069	2.4234	0.0180	H	3.2008	3.1982	-0.1373
H	1.3603	5.0718	-0.1192	C	2.4325	2.4172	-0.0701	H	3.1934	-3.2025	-0.1202
C	-0.6742	4.2257	-0.0425	C	2.4077	-2.4224	0.0183	Fe	-0.0027	0.0008	0.2869
H	-1.3496	5.0723	-0.0569	H	-3.2027	-3.1833	-0.1106	N	0.0316	-0.0013	2.5003
C	-2.4247	-2.4174	-0.0572	H	-3.1726	3.1945	0.0151	C	1.1198	-0.1073	3.2356
C	-2.4120	2.4201	0.0192	H	3.2026	3.1827	-0.1101	N	0.8059	-0.0835	4.5548
C	2.4242	2.4168	-0.0593	H	3.1736	-3.1933	0.0162	C	-0.5662	0.0455	4.6632
C	2.4124	-2.4196	0.0185	Fe	0.0002	0.0002	0.1284	C	-1.0287	0.0944	3.3762
H	-3.1941	-3.1841	-0.0940	N	-0.0171	-0.0034	2.4343	H	2.1258	-0.2012	2.8526
H	-3.1793	3.1895	0.0183	C	-0.9396	-0.5621	3.1870	H	1.4615	-0.1492	5.3200
H	3.1934	3.1835	-0.0948	C	0.5102	0.3461	4.5913	H	-1.0650	0.0886	5.6194
H	3.1800	-3.1888	0.0170	N	-0.6641	-0.3772	4.5052	H	-2.0415	0.1901	3.0137
Fe	0.0006	0.0007	0.1423	C	0.8934	0.5670	3.2953	FeP(Im)(CO)			
N	-0.0021	-0.0020	2.1062	H	-1.8050	-1.0984	2.8244	N	-2.0278	-0.0002	-0.0002
C	-0.7332	-0.7867	2.8752	H	-1.2193	-0.7083	5.2808	C	-2.8536	-1.0918	-0.0449
N	-0.4857	-0.5207	4.1817	H	0.9450	0.6243	5.5392	C	-2.8422	1.0991	0.0460
C	0.4545	0.4886	4.2436	H	1.7578	1.0947	2.9194	C	-4.2370	-0.6695	-0.0210
C	0.7452	0.8002	2.9437	Quintet deoxy-FeP(Im)				H	-5.0879	-1.3392	-0.0449
H	-1.4294	-1.5335	2.5257	N	-2.0925	-0.0003	0.0362	C	-4.2297	0.6897	0.0403
H	-0.9180	-0.9848	4.9666	C	-2.8973	-1.1011	-0.0434	H	-5.0737	1.3675	0.0740
H	0.8188	0.8800	5.1805	C	-2.8939	1.1039	-0.0385	N	-0.0105	-2.0275	0.0002
H	1.4295	1.5338	2.5479	C	-4.2834	-0.6779	-0.1346	C	-1.1063	-2.8478	-0.0436
Triplet deoxy-FeP(Im)				H	-5.1349	-1.3434	-0.2119	C	1.0846	-2.8473	0.0478
N	-2.0185	0.0001	0.0044	C	-4.2815	0.6852	-0.1306	C	0.6680	-4.2325	0.0431
C	-2.8517	-1.0916	-0.0498	H	-5.1306	1.3539	-0.2044	H	1.3418	-5.0795	0.0777
C	-2.8376	1.1011	0.0032	N	-0.0035	-2.0575	-0.0362	C	-0.6912	-4.2333	-0.0185
C	-4.2317	-0.6676	-0.0767	C	-1.1090	-2.8642	-0.0804	H	-1.3650	-5.0809	-0.0418

N	2.0280	-0.0002	-0.0002	C	0.6765	4.2296	-0.1515	H	3.1981	3.1999	-0.1442
C	2.8424	-1.1000	0.0454	H	1.3499	5.0751	-0.2245	H	3.1981	-3.1999	-0.1443
C	2.8544	1.0918	-0.0452	C	-0.6850	4.2297	-0.1507	Fe	-0.0012	0.0000	0.0996
C	4.2296	-0.6907	0.0385	H	-1.3587	5.0750	-0.2223	N	0.0029	0.0000	2.3194
H	5.0736	-1.3686	0.0701	C	-2.4178	-2.4217	-0.0747	C	-1.0841	0.0001	3.1666
C	4.2373	0.6690	-0.0221	C	-2.4243	2.4207	-0.0759	C	-0.6540	0.0002	4.4655
H	5.0887	1.3380	-0.0479	C	2.4177	2.4219	-0.0793	N	0.7258	0.0001	4.3954
N	0.0103	2.0278	0.0002	C	2.4240	-2.4208	-0.0802	C	1.0751	0.0000	3.0835
C	-1.0854	2.8477	0.0447	H	-3.1835	-3.1904	-0.1418	H	-2.0898	0.0001	2.7758
C	1.1063	2.8486	-0.0445	H	-3.1910	3.1878	-0.1426	H	-1.1802	0.0002	5.4074
C	0.6905	4.2338	-0.0224	H	3.1829	3.1905	-0.1518	H	1.3634	0.0002	5.1776
H	1.3639	5.0818	-0.0485	H	3.1903	-3.1879	-0.1520	O	-0.1162	0.0014	-3.3497
C	-0.6692	4.2328	0.0371	Fe	-0.0015	0.0001	0.0831	C	-0.0388	0.0005	-2.2235
H	-1.3431	5.0802	0.0678	N	0.0009	-0.0005	2.2757	H	2.0946	0.0000	2.7292
C	-2.4306	-2.4183	-0.0786	C	-1.0853	0.0002	3.1238	<sup>3,5</sup> MECP FeP(lm)(CO)			
C	-2.4100	2.4216	0.0747	C	-0.6580	0.0002	4.4248	N	-2.0460	-0.0000	0.0249
C	2.4310	2.4187	-0.0765	N	0.7216	0.0009	4.3550	C	-2.8548	-1.1047	-0.0112
C	2.4094	-2.4223	0.0765	C	1.0714	-0.0002	3.0419	C	-2.8656	1.0972	-0.0136
H	-3.2003	-3.1844	-0.1136	H	-2.0933	-0.0007	2.7406	C	-4.2415	-0.6917	-0.0527
H	-3.1761	3.1915	0.1077	H	-1.1859	-0.0008	5.3673	H	-5.0874	-1.3664	-0.0918
H	3.2009	3.1848	-0.1123	H	1.3589	0.0019	5.1386	C	-4.2484	0.6714	-0.0539
H	3.1750	-3.1926	0.1107	O	-0.0605	0.0007	-3.5861	H	-5.1006	1.3381	-0.0942
Fe	-0.0009	-0.0009	-0.0390	C	-0.0300	-0.0004	-2.4584	N	0.0111	-2.0587	-0.0249
N	0.0003	-0.0035	2.0358	H	2.0924	0.0008	2.6953	C	-1.0904	-2.8730	-0.0447
C	-0.7886	-0.7573	2.8791	<sup>1,5</sup> MECP FeP(lm)(CO)			C	1.1133	-2.8729	-0.0533	
C	-0.4759	-0.4670	4.1789	N	-2.0910	-0.0000	0.0222	C	0.6942	-4.2575	-0.0934
N	0.5243	0.4834	4.1130	C	-2.8928	-1.1038	-0.0465	H	1.3567	-5.1141	-0.1232
C	0.7787	0.7318	2.8044	C	-2.8928	1.1038	-0.0466	C	-0.6702	-4.2568	-0.0882
H	-1.5184	-1.4489	2.4890	C	-4.2801	-0.6812	-0.1326	H	-1.3342	-5.1122	-0.1123
H	-0.8588	-0.8361	5.1175	H	-5.1325	-1.3477	-0.2013	N	2.0476	-0.0000	0.0249
H	0.9881	0.9195	4.8962	C	-4.2800	0.6813	-0.1327	C	2.8668	-1.0980	-0.0282
O	0.0030	-0.0002	-2.9854	H	-5.1324	1.3479	-0.2015	C	2.8555	1.1060	-0.0260
C	0.0008	-0.0003	-1.8452	N	-0.0000	-2.0697	-0.0222	C	4.2486	-0.6712	-0.0883
H	1.5184	1.4365	2.4560	C	-1.1057	-2.8733	-0.0671	H	5.1013	-1.3371	-0.1454
<sup>1,3</sup> MECP FeP(lm)(CO)			C	1.1053	-2.8734	-0.0714	C	4.2412	0.6919	-0.0873	
N	-2.0270	0.0001	0.0049	C	0.6821	-4.2559	-0.1431	H	5.0866	1.3669	-0.1433
C	-2.8481	-1.0979	-0.0564	H	1.3476	-5.1103	-0.1979	N	-0.0127	2.0588	-0.0249
C	-2.8515	1.0960	-0.0573	C	-0.6829	-4.2559	-0.1403	C	-1.1149	2.8732	-0.0466
C	-4.2311	-0.6832	-0.1444	H	-1.3488	-5.1099	-0.1923	C	1.0886	2.8732	-0.0513
H	-5.0758	-1.3574	-0.2165	N	2.0911	-0.0000	0.0222	C	0.6683	4.2571	-0.0927
C	-4.2333	0.6785	-0.1446	C	2.8928	-1.1041	-0.0561	H	1.3320	5.1129	-0.1214
H	-5.0796	1.3506	-0.2168	C	2.8929	1.1042	-0.0561	C	-0.6959	4.2578	-0.0889
N	0.0032	-2.0259	-0.0049	C	4.2787	-0.6814	-0.1558	H	-1.3589	5.1139	-0.1138
C	-1.0921	-2.8475	-0.0599	H	5.1304	-1.3478	-0.2365	C	-2.4152	-2.4314	-0.0307
C	1.0993	-2.8476	-0.0628	C	4.2787	0.6815	-0.1557	C	-2.4382	2.4278	-0.0343
C	0.6849	-4.2298	-0.1515	H	5.1303	1.3478	-0.2365	C	2.4143	2.4315	-0.0451
H	1.3587	-5.0750	-0.2245	N	-0.0001	2.0697	-0.0222	C	2.4370	-2.4278	-0.0484
C	-0.6765	-4.2296	-0.1500	C	-1.1057	2.8734	-0.0673	H	-3.1870	-3.1967	-0.0570
H	-1.3499	-5.0753	-0.2212	C	1.1054	2.8735	-0.0714	H	-3.2144	3.1884	-0.0610
N	2.0274	0.0001	0.0049	C	0.6820	4.2561	-0.1432	H	3.1839	3.1993	-0.0829
C	2.8521	-1.0965	-0.0638	H	1.3475	5.1104	-0.1980	H	3.2115	-3.1903	-0.0866
C	2.8489	1.0983	-0.0631	C	-0.6829	4.2558	-0.1404	Fe	-0.0005	0.0000	0.1568
C	4.2329	-0.6790	-0.1619	H	-1.3488	5.1100	-0.1926	N	-0.0059	-0.0014	2.4656
H	5.0783	-1.3505	-0.2450	C	-2.4352	-2.4266	-0.0734	C	-1.0843	0.0016	3.3249
C	4.2306	0.6835	-0.1618	C	-2.4352	2.4267	-0.0736	C	-0.6474	0.0021	4.6219
H	5.0747	1.3571	-0.2449	C	2.4346	2.4271	-0.0819	N	0.7312	0.0003	4.5411
N	-0.0036	2.0258	-0.0049	C	2.4349	-2.4269	-0.0820	C	1.0695	-0.0022	3.2262
C	-1.0992	2.8476	-0.0612	H	-3.1987	-3.1995	-0.1286	H	-2.0975	0.0019	2.9477
C	1.0923	2.8473	-0.0619	H	-3.1987	3.1994	-0.1289	H	-1.1656	0.0019	5.5689



H	1.3742	0.0037	5.3206	H	-5.0810	-1.3568	0.0780	H	-1.3725	-5.0712	-0.1593
O	-0.1662	0.0043	-4.0692	C	-4.2354	0.6780	0.0076	N	2.0201	0.0015	0.0009
C	-0.0467	0.0008	-2.9477	H	-5.0848	1.3498	-0.0038	C	2.8369	-1.1013	0.0127
H	2.0899	-0.0038	2.8697	N	0.0022	-2.0234	-0.0012	C	2.8572	1.0923	-0.0187
FeP(lm)(OC)				C	-1.0923	-2.8470	0.0236	C	4.2231	-0.6964	0.0005
N	-2.0193	-0.0001	-0.0001	C	1.0955	-2.8465	-0.0692	H	5.0644	-1.3781	0.0032
C	-2.8483	-1.0921	-0.0421	C	0.6803	-4.2336	-0.0846	C	4.2364	0.6656	-0.0207
C	-2.8413	1.0973	0.0221	H	1.3529	-5.0810	-0.1397	H	5.0897	1.3318	-0.0388
C	-4.2323	-0.6726	-0.0459	C	-0.6787	-4.2337	-0.0236	N	0.0147	2.0164	-0.0009
H	-5.0814	-1.3439	-0.0791	H	-1.3536	-5.0807	-0.0197	C	-1.0805	2.8453	0.0266
C	-4.2279	0.6872	-0.0030	N	2.0235	-0.0001	0.0012	C	1.1133	2.8439	-0.0148
H	-5.0732	1.3644	0.0045	C	2.8474	-1.0925	-0.0646	C	0.7000	4.2264	-0.0029
N	-0.0065	-2.0194	0.0001	C	2.8460	1.0948	0.0270	H	1.3753	5.0726	-0.0149
C	-1.1010	-2.8451	-0.0419	C	4.2343	-0.6764	-0.0768	C	-0.6620	4.2270	0.0245
C	1.0882	-2.8448	0.0222	H	5.0821	-1.3488	-0.1299	H	-1.3347	5.0754	0.0394
C	0.6738	-4.2303	-0.0028	C	4.2334	0.6825	-0.0165	C	-2.4343	-2.4157	-0.0884
H	1.3484	-5.0777	0.0046	H	5.0803	1.3579	-0.0112	C	-2.4072	2.4254	0.0397
C	-0.6859	-4.2303	-0.0457	N	-0.0021	2.0236	-0.0012	C	2.4380	2.4190	-0.0246
H	-1.3598	-5.0774	-0.0788	C	-1.0992	2.8511	-0.0230	C	2.4053	-2.4240	0.0213
N	2.0195	-0.0001	-0.0001	C	1.0953	2.8491	0.0400	H	-3.2036	-3.1806	-0.1419
C	2.8415	-1.0979	0.0223	C	0.6794	4.2332	0.0390	H	-3.1711	3.1974	0.0500
C	2.8492	1.0923	-0.0388	H	1.3528	5.0810	0.0636	H	3.2072	3.1855	-0.0370
C	4.2279	-0.6879	-0.0002	C	-0.6818	4.2352	-0.0036	H	3.1706	-3.1947	0.0223
H	5.0731	-1.3653	0.0064	H	-1.3537	5.0848	-0.0183	Fe	-0.0005	-0.0042	0.1226
C	4.2329	0.6723	-0.0406	C	-2.4176	-2.4214	0.0620	O	0.1187	0.5136	-3.0571
H	5.0824	1.3432	-0.0729	C	-2.4250	2.4225	-0.0377	H	-0.5277	1.0173	-2.5501
N	0.0063	2.0196	0.0001	C	2.4190	2.4196	0.0610	H	0.9549	0.6516	-2.5984
C	-1.0888	2.8450	0.0226	C	2.4204	-2.4178	-0.0984	N	0.0079	-0.0127	2.4351
C	1.1012	2.8458	-0.0385	H	-3.1848	-3.1910	0.0862	C	-0.8522	-0.6726	3.1795
C	0.6858	4.2308	-0.0399	H	-3.1939	3.1906	-0.0509	N	-0.5811	-0.4989	4.5000
H	1.3594	5.0783	-0.0719	H	3.1877	3.1876	0.0842	C	0.5243	0.3248	4.5969
C	-0.6744	4.2301	0.0005	H	3.1885	-3.1851	-0.1518	C	0.8725	0.6143	3.3038
H	-1.3491	5.0775	0.0075	Fe	0.0059	-0.0058	0.0611	H	-1.6689	-1.2755	2.8088
C	-2.4256	-2.4181	-0.0635	O	-0.0321	0.0328	-2.0457	H	-1.0959	-0.9013	5.2700
C	-2.4131	2.4203	0.0448	H	-0.9695	-0.1335	-2.2112	H	0.9419	0.6151	5.5485
C	2.4263	2.4188	-0.0569	H	0.1144	0.9740	-2.2088	H	1.6823	1.2272	2.9363
C	2.4126	-2.4209	0.0445	N	0.0128	-0.0137	2.0687	Quinet FeP(lm)(OH <sub>2</sub> )			
H	-3.1950	-3.1849	-0.0962	C	0.7481	-0.7999	2.8303	N	-2.0911	0.0009	0.0148
H	-3.1804	3.1897	0.0606	N	0.5100	-0.5440	4.1415	C	-2.8863	-1.1147	0.0156
H	3.1958	3.1857	-0.0877	C	-0.4315	0.4636	4.2151	C	-2.9052	1.1005	0.0422
H	3.1797	-3.1906	0.0601	C	-0.7291	0.7810	2.9178	C	-4.2770	-0.7018	0.0462
Fe	-0.0009	-0.0009	0.0732	H	1.4436	-1.5442	2.4739	H	-5.1271	-1.3730	0.0489
N	0.0009	0.0013	2.0556	H	0.9479	-1.0123	4.9208	C	-4.2885	0.6640	0.0625
C	-0.7759	-0.7695	2.8954	H	-0.7906	0.8487	5.1568	H	-5.1506	1.3201	0.0809
C	-0.4733	-0.4682	4.1949	H	-1.4170	1.5166	2.5320	N	0.0167	-2.0836	-0.0148
N	0.5057	0.5036	4.1311	Triplet FeP(lm)(OH <sub>2</sub> )				C	-1.0875	-2.8865	-0.0353
C	0.7618	0.7573	2.8240	N	-2.0206	0.0015	0.0009	C	1.1223	-2.8802	-0.0727
H	-1.4883	-1.4771	2.5023	C	-2.8535	-1.0895	-0.0627	C	0.7020	-4.2677	-0.1252
H	-0.8519	-0.8437	5.1327	C	-2.8395	1.1031	0.0112	H	1.3687	-5.1200	-0.1790
H	0.9565	0.9516	4.9150	C	-4.2338	-0.6648	-0.0865	C	-0.6628	-4.2721	-0.0997
C	-0.0026	-0.0016	-3.3372	H	-5.0848	-1.3321	-0.1406	H	-1.3261	-5.1281	-0.1322
O	-0.0016	-0.0012	-2.2085	C	-4.2246	0.6964	-0.0384	N	2.0951	0.0009	0.0148
H	1.4865	1.4767	2.4750	H	-5.0673	1.3764	-0.0446	C	2.9013	-1.0954	-0.0653
Singlet FeP(lm)(OH <sub>2</sub> )				N	-0.0141	-2.0194	-0.0009	C	2.8859	1.1124	-0.0362
N	-2.0237	-0.0001	0.0012	C	-1.1101	-2.8424	-0.0666	C	4.2866	-0.6617	-0.1469
C	-2.8484	-1.0979	0.0452	C	1.0800	-2.8452	-0.0029	H	5.1438	-1.3202	-0.2213
C	-2.8519	1.0963	-0.0176	C	0.6633	-4.2281	-0.0597	C	4.2778	0.7015	-0.1271
C	-4.2331	-0.6831	0.0500	H	1.3370	-5.0756	-0.0757	H	5.1249	1.3742	-0.1842
				C	-0.6974	-4.2266	-0.1017	N	-0.0207	2.0817	-0.0148

C	-1.1272	2.8864	0.0302
C	1.0887	2.8858	-0.0024
C	0.6650	4.2700	0.0354
H	1.3293	5.1257	0.0467
C	-0.7017	4.2703	0.0561
H	-1.3644	5.1270	0.0869
C	-2.4185	-2.4381	-0.0083
C	-2.4553	2.4300	0.0503
C	2.4193	2.4357	-0.0228
C	2.4501	-2.4231	-0.0881
H	-3.1815	-3.2131	-0.0179
H	-3.2251	3.1977	0.0762
H	3.1818	3.2109	-0.0416
H	3.2186	-3.1901	-0.1483
Fe	0.0146	-0.0121	0.1394
O	-0.1700	0.1863	-2.3333
H	-1.1222	0.0416	-2.2628
H	-0.0400	1.1390	-2.2416
N	-0.0246	-0.0120	2.4171
C	-1.0630	-0.3169	3.1662
N	-0.7407	-0.2503	4.4836
C	0.5876	0.1202	4.5748
C	1.0125	0.2624	3.2811
H	-2.0431	-0.5856	2.7991
H	-1.3622	-0.4398	5.2566
H	1.0855	0.2429	5.5243
H	1.9866	0.5408	2.9074

<sup>1,3</sup>MECP FeP(lm)(OH<sub>2</sub>)

N	-2.0233	-0.0003	0.0027
C	-2.8586	-1.0894	0.0759
C	-2.8363	1.1056	0.0343
C	-4.2359	-0.6584	0.1445
H	-5.0876	-1.3228	0.2173
C	-4.2220	0.7035	0.1131
H	-5.0609	1.3867	0.1546
N	-0.0235	-2.0238	-0.0027
C	-1.1171	-2.8470	0.0566
C	1.0706	-2.8451	-0.0192
C	0.6573	-4.2313	0.0191
H	1.3332	-5.0768	0.0130
C	-0.7023	-4.2333	0.0734
H	-1.3736	-5.0815	0.1219
N	2.0230	-0.0003	0.0027
C	2.8339	-1.1031	-0.0147
C	2.8581	1.0849	0.0589
C	4.2246	-0.7040	0.0243
H	5.0637	-1.3877	0.0220
C	4.2399	0.6556	0.0767
H	5.0932	1.3199	0.1282
N	0.0239	2.0244	-0.0027
C	-1.0721	2.8490	0.0301
C	1.1211	2.8461	0.0760
C	0.7063	4.2291	0.1435
H	1.3794	5.0739	0.2188
C	-0.6546	4.2308	0.1089
H	-1.3290	5.0770	0.1484
C	-2.4400	-2.4172	0.1090
C	-2.3974	2.4266	0.0363
C	2.4429	2.4131	0.1095

C	2.3959	-2.4236	-0.0295
H	-3.2095	-3.1800	0.1947
H	-3.1599	3.1992	0.0875
H	3.2137	3.1738	0.1988
H	3.1589	-3.1969	-0.0227
Fe	0.0034	-0.0024	0.0333
O	-0.0505	0.0624	-2.3086
H	-0.9822	-0.1000	-2.5015
H	0.1161	0.9959	-2.4886
N	0.0071	-0.0029	2.2838
C	-0.9079	-0.5547	3.0583
N	-0.6059	-0.3826	4.3702
C	0.5781	0.3248	4.4376
C	0.9408	0.5494	3.1343
H	-1.7892	-1.0839	2.7170
H	-1.1498	-0.7112	5.1534
H	1.0341	0.5923	5.3802
H	1.8087	1.0668	2.7556

1,5MECP FeP(lm)(OH<sub>2</sub>)

N	-2.0690	-0.0009	0.0043
C	-2.8850	-1.0990	0.0880
C	-2.8747	1.1071	0.0250
C	-4.2702	-0.6695	0.1570
H	-5.1231	-1.3341	0.2336
C	-4.2635	0.6953	0.1091
H	-5.1095	1.3720	0.1373
N	-0.0089	-2.0639	-0.0043
C	-1.1109	-2.8722	0.0782
C	1.0951	-2.8713	0.0074
C	0.6775	-4.2580	0.0766
H	1.3496	-5.1079	0.0915
C	-0.6875	-4.2584	0.1283
H	-1.3554	-5.1096	0.1934
N	2.0699	-0.0009	0.0043
C	2.8758	-1.1039	-0.0005
C	2.8839	1.0973	0.0325
C	4.2689	-0.6917	0.0250
H	5.1152	-1.3681	0.0279
C	4.2740	0.6722	0.0501
H	5.1275	1.3396	0.0789
N	0.0080	2.0657	-0.0043
C	-1.0917	2.8720	0.0063
C	1.1100	2.8690	0.0377
C	0.6919	4.2603	0.0748
H	1.3641	5.1092	0.1181
C	-0.6719	4.2623	0.0492
H	-1.3437	5.1129	0.0651
C	-2.4382	-2.4251	0.1266
C	-2.4205	2.4304	0.0083
C	2.4375	2.4225	0.0592
C	2.4237	-2.4273	-0.0058
H	-3.2049	-3.1920	0.2091
H	-3.1856	3.2018	0.0217
H	3.2054	3.1906	0.0990
H	3.1897	-3.1977	0.0008
Fe	0.0087	0.0065	0.0530
O	-0.0539	0.0061	-2.2276
H	0.1169	-0.9077	-2.4890
H	-0.9812	0.1912	-2.4221

N	0.0116	0.0238	2.2650
C	-0.9022	-0.5158	3.0416
N	-0.5954	-0.3201	4.3523
C	0.5869	0.3917	4.4057
C	0.9483	0.5950	3.0988
H	-1.7804	-1.0464	2.7047
H	-1.1383	-0.6415	5.1424
H	1.0455	0.6771	5.3414
H	1.8086	1.1121	2.7023

3,5MECP FeP(lm)(OH<sub>2</sub>)

N	-2.0521	0.0002	0.0028
C	-2.8753	-1.0970	0.0915
C	-2.8612	1.1076	0.0525
C	-4.2551	-0.6670	0.1796
H	-5.1150	-1.3220	0.2504
C	-4.2464	0.6959	0.1492
H	-5.1000	1.3620	0.1890
N	-0.0170	-2.0536	-0.0028
C	-1.1152	-2.8693	0.0683
C	1.0830	-2.8672	-0.0107
C	0.6652	-4.2538	0.0384
H	1.3278	-5.1110	0.0241
C	-0.6961	-4.2556	0.0955
H	-1.3569	-5.1131	0.1398
N	2.0528	0.0002	0.0028
C	2.8594	-1.1049	-0.0066
C	2.8766	1.0928	0.0701
C	4.2505	-0.6963	0.0430
H	5.1040	-1.3637	0.0315
C	4.2614	0.6638	0.0982
H	5.1230	1.3188	0.1436
N	0.0163	2.0533	-0.0028
C	-1.0847	2.8707	0.0485
C	1.1191	2.8668	0.0913
C	0.7010	4.2489	0.1767
H	1.3634	5.1030	0.2495
C	-0.6625	4.2516	0.1435
H	-1.3224	5.1101	0.1806
C	-2.4405	-2.4254	0.1275
C	-2.4127	2.4321	0.0604
C	2.4435	2.4212	0.1272
C	2.4107	-2.4287	-0.0184
H	-3.2089	-3.1883	0.2306
H	-3.1773	3.2029	0.1252
H	3.2124	3.1834	0.2317
H	3.1764	-3.2006	-0.0049
Fe	0.0067	-0.0052	0.0285
O	-0.0446	0.0556	-2.3770
H	-0.9906	-0.0909	-2.4994
H	0.1106	1.0018	-2.4886
N	0.0106	-0.0069	2.3387
C	-0.9022	-0.5592	3.1060
N	-0.6001	-0.3898	4.4192
C	0.5870	0.3198	4.4858
C	0.9463	0.5451	3.1840
H	-1.7800	-1.0847	2.7530
H	-1.1424	-0.7225	5.2027
H	1.0443	0.5861	5.4272
H	1.8082	1.0623	2.7900

# Doublet FeP(lm)(NO)

N	-2.0276	-0.0009	-0.0003
C	-2.8424	-1.1002	0.0372
C	-2.8527	1.0903	-0.0521
C	-4.2296	-0.6919	0.0169
H	-5.0740	-1.3699	0.0377
C	-4.2359	0.6679	-0.0428
H	-5.0865	1.3373	-0.0785
N	0.0121	-2.0260	0.0003
C	-1.0844	-2.8458	0.0400
C	1.1071	-2.8468	-0.0503
C	0.6909	-4.2315	-0.0371
H	1.3642	-5.0792	-0.0692
C	-0.6687	-4.2306	0.0242
H	-1.3431	-5.0776	0.0491
N	2.0257	-0.0009	-0.0003
C	2.8521	-1.0914	-0.0517
C	2.8395	1.0999	0.0390
C	4.2342	-0.6678	-0.0397
H	5.0851	-1.3367	-0.0725
C	4.2264	0.6917	0.0219
H	5.0700	1.3704	0.0462
N	-0.0102	2.0278	0.0003
C	-1.1061	2.8471	-0.0508
C	1.0847	2.8487	0.0385
C	0.6686	4.2337	0.0197
H	1.3421	5.0816	0.0415
C	-0.6913	4.2328	-0.0400
H	-1.3652	5.0801	-0.0749
C	-2.4094	-2.4221	0.0680
C	-2.4306	2.4174	-0.0820
C	2.4090	2.4227	0.0682
C	2.4312	-2.4181	-0.0837
H	-3.1744	-3.1933	0.0948
H	-3.2006	3.1831	-0.1236
H	3.1761	3.1917	0.0951
H	3.2010	-3.1835	-0.1258
Fe	0.0051	-0.0046	-0.0437
O	0.6110	-0.5795	-2.7110
N	0.0468	-0.0455	-1.8441
N	0.0100	-0.0091	2.0613
C	-0.7548	0.7426	2.8265
N	-0.5031	0.4963	4.1362
C	0.4811	-0.4707	4.2056
C	0.7869	-0.7720	2.9066
H	-1.4828	1.4579	2.4753
H	-0.9583	0.9441	4.9180
H	0.8591	-0.8414	5.1456
H	1.5047	-1.4772	2.5182

# Quartet FeP(lm)(NO)

N	-2.0178	0.0005	-0.0025
C	-2.8351	-1.1016	-0.0010
C	-2.8528	1.0900	-0.0505
C	-4.2206	-0.6968	-0.0412
H	-5.0629	-1.3777	-0.0517
C	-4.2320	0.6644	-0.0735
H	-5.0840	1.3315	-0.1155
N	0.0154	-2.0185	0.0025

C	-1.0797	-2.8445	0.0017
C	1.1122	-2.8435	-0.0503
C	0.6979	-4.2262	-0.0786
H	1.3719	-5.0720	-0.1256
C	-0.6629	-4.2265	-0.0434
H	-1.3368	-5.0743	-0.0562
N	2.0193	0.0005	-0.0025
C	2.8530	-1.0894	-0.0549
C	2.8366	1.1018	-0.0023
C	4.2327	-0.6647	-0.0852
H	5.0842	-1.3321	-0.1328
C	4.2220	0.6961	-0.0495
H	5.0644	1.3768	-0.0623
N	-0.0169	2.0175	0.0025
C	-1.1136	2.8440	-0.0452
C	1.0794	2.8435	0.0050
C	0.6631	4.2256	-0.0314
H	1.3372	5.0734	-0.0403
C	-0.6985	4.2264	-0.0639
H	-1.3720	5.0732	-0.1046
C	-2.4045	-2.4234	0.0156
C	-2.4372	2.4171	-0.0646
C	2.4049	2.4233	0.0168
C	2.4353	-2.4157	-0.0754
H	-3.1701	-3.1942	0.0121
H	-3.2082	3.1816	-0.1033
H	3.1697	3.1950	0.0141
H	3.2056	-3.1803	-0.1220
Fe	-0.0011	0.0007	0.1007
O	1.1522	-1.1688	-3.1768
N	0.4335	-0.4487	-2.6344
N	0.0103	-0.0065	2.4065
C	-0.6887	0.8173	3.1562
N	-0.4749	0.5682	4.4749
C	0.4183	-0.4824	4.5648
C	0.7058	-0.8226	3.2698
H	-1.3479	1.5918	2.7906
H	-0.8944	1.0631	5.2487
H	0.7517	-0.8731	5.5141
H	1.3616	-1.5954	2.8966

# Sextet FeP(lm)(NO)

N	-2.0882	0.0005	0.0383
C	-2.8918	-1.1047	-0.0430
C	-2.8941	1.1024	-0.0480
C	-4.2781	-0.6846	-0.1409
H	-5.1274	-1.3525	-0.2211
C	-4.2794	0.6789	-0.1444
H	-5.1301	1.3446	-0.2275
N	0.0028	-2.0598	-0.0383
C	-1.1024	-2.8677	-0.0800
C	1.1078	-2.8667	-0.0839
C	0.6863	-4.2477	-0.1561
H	1.3526	-5.1002	-0.2093
C	-0.6801	-4.2484	-0.1533
H	-1.3460	-5.1014	-0.2048
N	2.0872	0.0005	0.0383
C	2.8933	-1.1016	-0.0430
C	2.8915	1.1042	-0.0303
C	4.2797	-0.6780	-0.1284

H	5.1303	-1.3442	-0.2046
C	4.2791	0.6846	-0.1200
H	5.1288	1.3529	-0.1894
N	-0.0018	2.0588	-0.0383
C	-1.1083	2.8674	-0.0818
C	1.1039	2.8683	-0.0633
C	0.6811	4.2488	-0.1287
H	1.3471	5.1023	-0.1682
C	-0.6853	4.2480	-0.1409
H	-1.3510	5.1012	-0.1908
C	-2.4338	-2.4262	-0.0703
C	-2.4385	2.4251	-0.0776
C	2.4347	2.4266	-0.0524
C	2.4387	-2.4234	-0.0758
H	-3.1952	-3.2004	-0.1262
H	-3.2008	3.1982	-0.1356
H	3.1967	3.2006	-0.0979
H	3.2014	-3.1962	-0.1317
Fe	0.0001	-0.0016	0.2729
O	1.3860	1.5142	-3.3104
N	0.4173	0.9825	-2.9924
N	-0.0078	-0.0015	2.4837
C	-1.0893	-0.0520	3.2346
N	-0.7563	-0.0337	4.5491
C	0.6215	0.0323	4.6376
C	1.0678	0.0517	3.3440
H	-2.1038	-0.1010	2.8664
H	-1.4033	-0.0632	5.3239
H	1.1350	0.0584	5.5862
H	2.0781	0.0994	2.9664
N	-2.0229	0.0002	-0.0003
C	-2.8383	-1.1025	0.0422
C	-2.8538	1.0901	-0.0498
C	-4.2252	-0.6957	0.0287
H	-5.0674	-1.3740	0.0602
C	-4.2353	0.6661	-0.0335
H	-5.0854	1.3337	-0.0641
N	0.0134	-2.0220	0.0003
C	-1.0799	-2.8450	0.0537
C	1.1109	-2.8464	-0.0241
C	0.6977	-4.2300	0.0172
H	1.3719	-5.0772	0.0144
C	-0.6626	-4.2285	0.0698
H	-1.3369	-5.0752	0.1140
N	2.0233	0.0002	-0.0003
C	2.8538	-1.0911	-0.0266
C	2.8402	1.1000	0.0505
C	4.2356	-0.6701	0.0107
H	5.0862	-1.3388	0.0070
C	4.2265	0.6919	0.0621
H	5.0694	1.3688	0.1030
N	-0.0139	2.0216	0.0003
C	-1.1097	2.8446	-0.0467
C	1.0820	2.8442	0.0476
C	0.6649	4.2274	0.0409
H	1.3375	5.0755	0.0793
C	-0.6954	4.2279	-0.0240
H	-1.3708	5.0742	-0.0525
C	-2.4062	-2.4243	0.0780

C	-2.4338	2.4162	-0.0793
C	2.4080	2.4225	0.0792
C	2.4350	-2.4180	-0.0518
H	-3.1700	-3.1967	0.1113
H	-3.2037	3.1825	-0.1162
H	3.1739	3.1931	0.1129
H	3.2053	-3.1841	-0.0766
Fe	-0.0035	0.0041	0.0351
O	0.7230	-0.6731	-3.0283
N	0.0857	-0.0804	-2.2636
N	0.0065	-0.0050	2.2460
C	-0.7858	0.7219	3.0049
N	-0.5352	0.4884	4.3180
C	0.4804	-0.4457	4.3947
C	0.8018	-0.7382	3.0973
H	-1.5352	1.4121	2.6429
H	-1.0108	0.9230	5.0971
H	0.8660	-0.8029	5.3374
H	1.5425	-1.4180	2.7032

#### 2,4MECP FeP(lm)(NO)

N	-2.0229	0.0002	-0.0003
C	-2.8383	-1.1025	0.0422
C	-2.8538	1.0901	-0.0498
C	-4.2252	-0.6957	0.0287
H	-5.0674	-1.3740	0.0602
C	-4.2353	0.6661	-0.0335
H	-5.0854	1.3337	-0.0641
N	0.0134	-2.0220	0.0003
C	-1.0799	-2.8450	0.0537
C	1.1109	-2.8464	-0.0241
C	0.6977	-4.2300	0.0172
H	1.3719	-5.0772	0.0144
C	-0.6626	-4.2285	0.0698
H	-1.3369	-5.0752	0.1140
N	2.0233	0.0002	-0.0003
C	2.8538	-1.0911	-0.0266
C	2.8402	1.1000	0.0505
C	4.2356	-0.6701	0.0107
H	5.0862	-1.3388	0.0070
C	4.2265	0.6919	0.0621
H	5.0694	1.3688	0.1030
N	-0.0139	2.0216	0.0003
C	-1.1097	2.8446	-0.0467
C	1.0820	2.8442	0.0476
C	0.6649	4.2274	0.0409
H	1.3375	5.0755	0.0793
C	-0.6954	4.2279	-0.0240
H	-1.3708	5.0742	-0.0525
C	-2.4062	-2.4243	0.0780
C	-2.4338	2.4162	-0.0793
C	2.4080	2.4225	0.0792
C	2.4350	-2.4180	-0.0518
H	-3.1700	-3.1967	0.1113
H	-3.2037	3.1825	-0.1162
H	3.1739	3.1931	0.1129
H	3.2053	-3.1841	-0.0766
Fe	-0.0035	0.0041	0.0351
O	0.7230	-0.6731	-3.0283
N	0.0857	-0.0804	-2.2636

N	0.0065	-0.0050	2.2460
C	-0.7858	0.7219	3.0049
N	-0.5352	0.4884	4.3180
C	0.4804	-0.4457	4.3947
C	0.8018	-0.7382	3.0973
H	-1.5352	1.4121	2.6429
H	-1.0108	0.9230	5.0971
H	0.8660	-0.8029	5.3374
H	1.5425	-1.4180	2.7032

#### 2,6MECP FeP(lm)(NO)

N	-2.0698	0.0013	0.0019
C	-2.8792	-1.0997	0.0097
C	-2.8763	1.1056	-0.0438
C	-4.2653	-0.6767	-0.0222
H	-5.1149	-1.3477	-0.0265
C	-4.2636	0.6862	-0.0587
H	-5.1109	1.3579	-0.0996
N	-0.0058	-2.0701	-0.0019
C	-1.1093	-2.8747	0.0112
C	1.0984	-2.8767	-0.0471
C	0.6749	-4.2621	-0.0580
H	1.3423	-5.1127	-0.0968
C	-0.6887	-4.2609	-0.0179
H	-1.3584	-5.1100	-0.0175
N	2.0727	0.0013	0.0019
C	2.8764	-1.1038	-0.0467
C	2.8789	1.1028	0.0112
C	4.2639	-0.6829	-0.0615
H	5.1122	-1.3530	-0.1026
C	4.2655	0.6796	-0.0218
H	5.1154	1.3485	-0.0244
N	0.0030	2.0675	-0.0019
C	-1.1005	2.8760	-0.0423
C	1.1059	2.8747	0.0101
C	0.6858	4.2606	-0.0156
H	1.3567	5.1100	-0.0157
C	-0.6783	4.2615	-0.0513
H	-1.3475	5.1112	-0.0878
C	-2.4359	-2.4267	0.0255
C	-2.4290	2.4322	-0.0638
C	2.4332	2.4294	0.0247
C	2.4264	-2.4303	-0.0742
H	-3.2054	-3.1958	0.0315
H	-3.1974	3.2026	-0.1041
H	3.2027	3.1980	0.0307
H	3.1940	-3.1999	-0.1188
Fe	0.0013	-0.0014	0.0747
O	0.8083	-0.7497	-3.0382
N	0.1992	-0.1312	-2.2793
N	0.0257	-0.0214	2.2284
C	-0.7637	0.7063	2.9900
N	-0.5058	0.4656	4.2991
C	0.5074	-0.4717	4.3699
C	0.8230	-0.7603	3.0688
H	-1.5120	1.3990	2.6340
H	-0.9739	0.8971	5.0819
H	0.8939	-0.8319	5.3078
H	1.5607	-1.4419	2.6741

#### 4,6MECP FeP(lm)(NO)

N	-2.0544	-0.0000	0.0318
C	-2.8692	-1.0977	-0.0364
C	-2.8655	1.0996	-0.0390
C	-4.2513	-0.6794	-0.1194
H	-5.0940	-1.3556	-0.1921
C	-4.2488	0.6842	-0.1217
H	-5.0889	1.3630	-0.1959
N	-0.0035	-2.0401	-0.0318
C	-1.1032	-2.8552	-0.0700
C	1.0963	-2.8537	-0.0731
C	0.6792	-4.2350	-0.1386
H	1.3572	-5.0772	-0.1859
C	-0.6860	-4.2361	-0.1354
H	-1.3622	-5.0798	-0.1806
N	2.0544	-0.0000	0.0318
C	2.8649	-1.0989	-0.0388
C	2.8685	1.0969	-0.0377
C	4.2488	-0.6836	-0.1246
H	5.0883	-1.3630	-0.1986
C	4.2512	0.6789	-0.1232
H	5.0932	1.3557	-0.1964
N	0.0035	2.0402	-0.0318
C	-1.0959	2.8543	-0.0742
C	1.1035	2.8543	-0.0730
C	0.6871	4.2353	-0.1410
H	1.3644	5.0781	-0.1892
C	-0.6781	4.2354	-0.1422
H	-1.3550	5.0782	-0.1902
C	-2.4297	-2.4216	-0.0610
C	-2.4225	2.4219	-0.0663
C	2.4296	2.4205	-0.0645
C	2.4226	-2.4212	-0.0664
H	-3.1966	-3.1908	-0.1085
H	-3.1880	3.1929	-0.1180
H	3.1967	3.1893	-0.1136
H	3.1883	-3.1917	-0.1176
Fe	0.0023	0.0002	0.2087
O	0.1593	-0.2030	-4.4317
N	0.0092	0.0045	-3.3120
N	-0.0203	-0.0015	2.4721
C	-1.1083	0.0095	3.2135
N	-0.7903	0.0048	4.5329
C	0.5876	-0.0115	4.6343
C	1.0457	-0.0141	3.3454
H	-2.1216	0.0220	2.8371
H	-1.4456	0.0111	5.3012
H	1.0917	-0.0192	5.5895
H	2.0629	-0.0256	2.9799

#### Singlet FeP(lm)(O2)

N	-2.0197	0.0003	0.0006
C	-2.8281	-1.1047	0.0243
C	-2.8539	1.0859	-0.0602
C	-4.2156	-0.7050	-0.0094
H	-5.0545	-1.3898	-0.0027
C	-4.2311	0.6547	-0.0662
H	-5.0848	1.3188	-0.1120
N	0.0251	-2.0203	-0.0006
C	-1.0699	-2.8433	0.0234

C	1.1215	-2.8415	-0.0568	N	1.0941	1.6921	0.3291	C	0.0000	2.4741	0.0000
C	0.7075	-4.2243	-0.0604	N	-1.0937	1.6923	0.3291	H	-1.9851	2.2409	0.0000
H	1.3821	-5.0700	-0.1036	N	-1.0941	-1.6921	0.3291	H	0.0000	3.5763	0.0000
C	-0.6529	-4.2255	-0.0063	N	1.0937	-1.6923	0.3291	H	1.9851	2.2409	0.0000
H	-1.3268	-5.0732	0.0014	C	-0.0003	-2.4311	0.3291	H	1.9851	-2.2409	0.0000
N	2.0203	0.0003	0.0006	C	0.0003	2.4311	0.3291	H	0.0000	-3.5763	0.0000
C	2.8553	-1.0856	-0.0536	H	-1.9931	2.1473	0.3291	H	-1.9851	-2.2409	0.0000
C	2.8293	1.1054	0.0263	H	0.0004	3.5302	0.3291	O	0.0000	0.0000	-2.0333
C	4.2328	-0.6544	-0.0536	H	1.9935	2.1469	0.3291	H	-0.7954	0.0000	-2.5659
H	5.0870	-1.3184	-0.0944	H	1.9931	-2.1473	0.3291	H	0.7954	0.0000	-2.5659
C	4.2167	0.7058	0.0003	H	-0.0004	-3.5302	0.3291	Fe	0.0000	0.0000	0.0000
H	5.0557	1.3904	0.0104	H	-1.9935	-2.1469	0.3291	O	0.0000	0.0000	2.0333
N	-0.0257	2.0197	-0.0006	O	0.0000	0.0000	-2.1062	H	-0.7954	0.0000	2.5659
C	-1.1217	2.8402	-0.0628	H	-0.7843	0.0000	-2.6603	H	0.7954	0.0000	2.5659
C	1.0690	2.8420	0.0221	H	0.7843	-0.0000	-2.6603				
C	0.6520	4.2243	-0.0142								
H	1.3261	5.0718	-0.0091	Model 1 Deoxy Quintet				Model 2 Deoxy Singlet			
C	-0.7078	4.2227	-0.0713	Fe	0.0000	0.0000	0.1730	N	-0.2145	1.3893	1.3862
H	-1.3825	5.0680	-0.1189	N	1.1193	1.8167	0.3329	C	-0.2318	1.2302	2.6959
C	-2.3953	-2.4253	0.0506	N	-1.1191	1.8169	0.3329	C	-0.2020	0.0009	3.3619
C	-2.4440	2.4134	-0.0894	N	-1.1193	-1.8167	0.3329	C	-0.2338	-1.2283	2.6959
C	2.3948	2.4255	0.0511	N	1.1191	-1.8169	0.3329	N	-0.2168	-1.3875	1.3862
C	2.4446	-2.4140	-0.0815	C	-0.0002	-2.5197	0.3329	N	-0.2145	1.3893	-1.3862
H	-3.1589	-3.1975	0.0655	C	0.0002	2.5197	0.3329	C	-0.2318	1.2302	-2.6959
H	-3.2160	3.1757	-0.1385	H	-1.9796	2.3456	0.3329	C	-0.2020	0.0009	-3.3619
H	3.1575	3.1988	0.0664	H	0.0002	3.6185	0.3329	C	-0.2338	-1.2283	-2.6959
H	3.2169	-3.1764	-0.1271	H	1.9799	2.3454	0.3329	N	-0.2168	-1.3875	-1.3862
Fe	-0.0064	0.0064	-0.0169	H	1.9796	-2.3456	0.3329	H	-0.2827	2.3680	1.1230
O	-0.7171	0.7118	-2.5765	H	-0.0002	-3.6185	0.3329	H	-0.2903	2.1262	3.3204
O	0.0582	-0.0568	-1.9141	H	-1.9799	-2.3454	0.3329	H	-0.2243	0.0009	4.4450
N	-0.0067	0.0087	2.1022	O	0.0000	0.0000	-2.0747	H	-0.2937	-2.1242	3.3204
C	0.7371	-0.7667	2.8658	H	-0.7864	0.0000	-2.6249	H	-0.2903	2.1262	-3.3204
N	0.4990	-0.5078	4.1737	H	0.7864	0.0000	-2.6249	H	-0.2243	0.0009	-4.4450
C	-0.4535	0.4915	4.2448					H	-0.2937	-2.1242	-3.3204
C	-0.7558	0.7997	2.9470	Model 1 CO-ligated complex				H	-0.2865	-2.3661	-1.1230
H	1.4405	-1.5055	2.5122	Fe	0.0000	0.0000	0.1231	H	-0.2827	2.3680	-1.1230
H	0.9423	-0.9676	4.9558	N	-1.0883	1.7343	0.2142	H	-0.2865	-2.3661	1.1230
H	-0.8142	0.8762	5.1861	N	1.0999	1.7272	0.2142	Fe	-0.0886	0.0008	0.0000
H	-1.4511	1.5270	2.5582	N	1.0883	-1.7343	0.2142	O	1.9297	-0.0000	0.0000
				N	-1.0999	-1.7272	0.2142	H	2.4653	0.7942	0.0000
Model 1 Deoxy Singlet				C	-0.0082	-2.4652	0.2141	H	2.4652	-0.7942	0.0000
Fe	0.0000	0.0000	0.1726	C	0.0082	2.4652	0.2141				
N	1.0980	1.7196	0.2841	H	2.0027	2.1757	0.2142	Model 2 Deoxy Triplet			
N	-1.0978	1.7197	0.2841	H	0.0117	3.5638	0.2141	N	-0.2358	1.3762	1.3767
N	-1.0980	-1.7196	0.2841	H	-1.9882	2.1887	0.2142	C	-0.2518	1.2246	2.6898
N	1.0978	-1.7197	0.2841	H	-2.0027	-2.1757	0.2142	C	-0.2269	-0.0007	3.3583
C	-0.0002	-2.4520	0.2842	H	-0.0117	-3.5638	0.2141	C	-0.2511	-1.2261	2.6898
C	0.0002	2.4520	0.2842	H	1.9882	-2.1887	0.2142	N	-0.2353	-1.3776	1.3767
H	-1.9913	2.1872	0.2841	O	0.0000	0.0000	2.1758	N	-0.2358	1.3762	-1.3767
H	0.0002	3.5519	0.2842	H	0.7953	0.0000	2.7093	C	-0.2518	1.2246	-2.6898
H	1.9916	2.1869	0.2841	H	-0.7953	0.0000	2.7093	C	-0.2269	-0.0007	-3.3583
H	1.9913	-2.1872	0.2841	O	0.0000	0.0000	-2.7957	C	-0.2511	-1.2261	-2.6898
H	-0.0002	-3.5519	0.2842	C	0.0000	0.0000	-1.6529	N	-0.2353	-1.3776	-1.3767
H	-1.9916	-2.1869	0.2841					H	-0.3069	2.3524	1.1077
O	0.0000	0.0000	-1.8335	Model 1 H <sub>2</sub> O-ligated complex				H	-0.3039	2.1255	3.3062
H	-0.7974	0.0000	-2.3640	N	1.1029	1.7504	0.0000	H	-0.2433	-0.0007	4.4413
H	0.7974	0.0000	-2.3640	N	-1.1029	1.7504	0.0000	H	-0.3021	-2.1270	3.3062
				N	-1.1029	-1.7504	0.0000	H	-0.3039	2.1255	-3.3062
Model 1 Deoxy Triplet				N	1.1029	-1.7504	0.0000	H	-0.2433	-0.0007	-4.4413
Fe	0.0000	0.0000	0.2096	C	0.0000	-2.4741	0.0000	H	-0.3021	-2.1270	-3.3062
								H	-0.3055	-2.3538	-1.1077

H	-0.3069	2.3524	-1.1077
H	-0.3055	-2.3538	1.1077
Fe	-0.1322	-0.0008	0.0000
O	2.2169	-0.0000	0.0000
H	2.7752	0.7824	0.0000
H	2.7753	-0.7824	0.0000

Model 2 Deoxy Quintet

N	-0.2318	1.4315	1.5287
C	-0.3040	1.2394	2.8347
C	-0.3069	0.0011	3.4855
C	-0.3058	-1.2372	2.8347
N	-0.2343	-1.4294	1.5287
N	-0.2318	1.4315	-1.5287
C	-0.3040	1.2394	-2.8347
C	-0.3069	0.0011	-3.4855
C	-0.3058	-1.2372	-2.8347
N	-0.2343	-1.4294	-1.5287
H	-0.2916	2.4180	1.2976
H	-0.3818	2.1174	3.4854
H	-0.3675	0.0011	4.5690
H	-0.3847	-2.1153	3.4854
H	-0.3818	2.1174	-3.4854
H	-0.3675	0.0011	-4.5690
H	-0.3847	-2.1153	-3.4854
H	-0.2953	-2.4159	-1.2976
H	-0.2916	2.4180	-1.2976
H	-0.2953	-2.4159	1.2976
Fe	-0.0368	0.0007	0.0000
O	2.1913	-0.0000	0.0000

H	2.7449	0.7851	0.0000
H	2.7447	-0.7851	0.0000

Model 2 CO-ligated complex

N	0.1275	1.3964	1.3954
C	0.2258	1.2308	2.7006
C	0.2918	0.0004	3.3651
C	0.2251	-1.2301	2.7006
N	0.1267	-1.3961	1.3954
N	0.1275	1.3964	-1.3954
C	0.2258	1.2308	-2.7006
C	0.2918	0.0004	-3.3651
C	0.2251	-1.2301	-2.7006
N	0.1267	-1.3961	-1.3954
O	-2.8960	0.0034	0.0000
C	-1.7511	0.0016	0.0000
H	0.0394	2.3712	1.1279
H	0.2565	2.1267	3.3276
H	0.3760	0.0006	4.4479
H	0.2552	-2.1260	3.3276
H	0.2565	2.1267	-3.3276
H	0.3760	0.0006	-4.4479
H	0.2552	-2.1260	-3.3276
H	0.0376	-2.3711	-1.1279
H	0.0394	2.3712	-1.1279
H	0.0376	-2.3711	1.1279
Fe	0.0079	0.0002	0.0000
O	2.1541	0.0000	0.0000
H	2.6977	0.7914	0.0000
H	2.6973	-0.7914	0.0000

Model 2 H<sub>2</sub>O-ligated complex

N	0.0000	1.3974	1.4051
C	0.0000	2.7036	1.2342
C	0.0000	3.3653	0.0000
C	0.0000	2.7036	-1.2342
N	0.0000	1.3974	-1.4051
N	0.0000	-1.3974	1.4051
C	0.0000	-2.7036	1.2342
C	0.0000	-3.3653	0.0000
C	0.0000	-2.7036	-1.2342
N	0.0000	-1.3974	-1.4051
H	0.0000	1.1422	2.3890
H	0.0000	3.3388	2.1259
H	0.0000	4.4489	0.0000
H	0.0000	3.3388	-2.1259
H	0.0000	-3.3388	2.1259
H	0.0000	-4.4489	0.0000
H	0.0000	-3.3388	-2.1259
H	0.0000	-1.1422	-2.3890
H	0.0000	-1.1422	2.3890
H	0.0000	1.1422	-2.3890
Fe	0.0000	0.0000	0.0000
O	-2.0655	0.0000	0.0000
H	-2.6051	0.0000	0.7924
H	-2.6051	0.0000	-0.7924
O	2.0655	0.0000	0.0000
H	2.6051	0.0000	0.7924
H	2.6051	0.0000	-0.7924