Supporting Information

Oxidation states from wavefunction analysis

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Table S1: EOS, last occupied and first unoccupied eff-AOs and C(%) values for the $FeCl_6^{4-}$ complex.

Atomic definition	Atom	EOS	$\lambda^{\alpha}_{LO}/\lambda^{\alpha}_{FU}$	$\lambda^{\beta}_{LO}/\lambda^{\beta}_{FU}$	$R_{\alpha}(\%)/R_{\beta}(\%)$
Mulliken	Fe	2	0.995 / 0.040	0.992 / 0.057	100 / 100
	Cl	-1	0.953 / -	0.931 / -	
Löwdin	Fe	2	0.992 / 0.221	0.994 / 0.209	100 / 100
	Cl	-1	0.901 / -	0.884 / -	
Becke	Fe	2	0.957 / 0.156	0.968 / 0.143	100 / 100
	Cl	-1	0.810 / -	0.786 / -	
Hirshfeld	Fe	2	0.939 / 0.119	0.946 / 0.107	100 / 100
	Cl	-1	0.845 / -	0.823 / -	
Hirshfeld-Iterative	Fe	2	0.912 / 0.079	0.912 / 0.077	100 / 100
	Cl	-1	0.873 / 0.013	0.852 / 0.010	
QTAIM	Fe	2	0.970 / 0.141	0.983 / 0.128	100 / 100
	Cl	-1	0.935 / 0.019	0.915 / 0.014	
TFVC	Fe	2	0.938 / 0.101	0.953 / 0.090	100 / 100
	Cl	-1	0.898 / 0.014	0.876 / 0.011	

Table S2: EOS, last occupied and first unoccupied eff-AOs and C(%) values for the $FeCl_6^{3-}$ complex.

Atomic definition	Atom	EOS	$\lambda^{\alpha}_{LO}/\lambda^{\alpha}_{FU}$	$\lambda^{\beta}_{LO}/\lambda^{\beta}_{FU}$	$R_{\alpha}(\%)/R_{\beta}(\%)$
Mulliken	Fe	3	0.998 / 0.085	1.000 / 0.245	100 / 100
	Cl	-1	0.916 / -	0.805 / -	
Löwdin	Fe	3	0.995 / 0.264	0.996 / 0.292	100 / 100
	Cl	-1	0.887 / -	0.809 / -	
Becke	Fe	3	0.964 / 0.191	0.995 / 0.300	100 / 91
	Cl	-1	0.796 / -	0.711 / -	
Hirshfeld	Fe	3	0.948 / 0.149	0.989 / 0.279	100 / 97
	Cl	-1	0.832 / -	0.746 / -	
Hirshfeld-Iterative	Fe	3	0.918 / 0.086	0.978 / 0.250	100 / 100
	Cl	-1	0.883 / 0.015	0.797 / 0.011	
QTAIM	Fe	3	0.975 / 0.177	0.999 / 0.292	100 / 100
	Cl	-1	0.923 / 0.018	0.837 / 0.013	
TFVC	Fe	3	0.951 / 0.137	0.994 / 0.274	100 / 100
	Cl	-1	0.881 / 0.013	0.793 / 0.010	

Table S3: EOS, last occupied and first unoccupied eff-AOs and C(%) values for the high-spin $Fe(H_2O)_6^{2+}$ complex.

Atomic definition	Atom	EOS	$\lambda^{\alpha}_{LO}/\lambda^{\alpha}_{FU}$	$\lambda^{\beta}_{LO}/\lambda^{\beta}_{FU}$	$R_{\alpha}(\%)/R_{\beta}(\%)$
	Fe	2	0.986 / 0.035	0.979 / 0.036	
Mulliken	O	-2	0.534 / -	0.535 / -	89 / 89
	H	1	- / 0.148	- / 0.143	
	Fe	2	0.981 / 0.194	0.986 / 0.186	
Löwdin	O	-2	0.693 / -	0.693 / -	90 / 90
	H	1	- / 0.294	- / 0.291	
	Fe	2	0.973 / 0.183	0.977 / 0.174	
Becke	O	-2	0.565 / -	0.565 / -	80 / 80
	H	1	- / 0.265	- / 0.262	
	Fe	2	0.930 / 0.094	0.931 / 0.088	
Hirshfeld	O	-2	0.536 / -	0.536 / -	86 / 86
	H	1	- / 0.178	- / 0.176	
	Fe	2	0.880 / 0.046	0.867 / 0.053	
Hirshfeld-Iterative	O	-2	0.675 / 0.013	0.675 / -	100 / 100
	H	1	- / 0.081	- / 0.081	
	Fe	2	0.958 / 0.103	0.971 / 0.095	
QTAIM	O	-2	0.785 / 0.015	0.785 / -	100 / 100
	H	1	- / 0.182	- / 0.180 /	
	Fe	2	0.923 / 0.071	0.933 / 0.065	
TFVC	O	-2	0.754 / 0.013	0.754 / -	100 / 100
	H	1	- / 0.156	- / 0.154	

Table S4: EOS, last occupied and first unoccupied eff-AOs and C(%) values for high-spin $Fe(H_2O)_6^{3+}$ complex.

Atomic definition	Atom	EOS	$\lambda^{\alpha}_{LO}/\lambda^{\alpha}_{FU}$	$\lambda^{\beta}_{LO}/\lambda^{\beta}_{FU}$	$R_{\alpha}(\%)/R_{\beta}(\%)$
	Fe	3	0.993 / 0.035	1.000 / 0.116	
Mulliken	O	-2	0.575 / -	0.573 / -	96 / 96
	H	1	- / 0.117	- / 0.113	
	Fe	3	0.987 / 0.223	0.991 / 0.217	
Löwdin	O	-2	0.712 / -	0.710 / -	94 / 94
	H	1	- / 0.274	- / 0.271	
	Fe	3	0.977 / 0.218	0.997 / 0.227	
Becke	O	-2	0.581 / -	0.570 / -	84 / 83
	H	1	- / 0.246	- / 0.243	
	Fe	3	0.935 / 0.111	0.981 / 0.160	
Hirshfeld	O	-2	0.549 / -	0.547 / -	88 / 88
	H	1	- / 0.167	- / 0.165	
	Fe	3	0.887 / 0.059	0.959 / 0.131	
Hirshfeld-Iterative	O	-2	0.701 / 0.012	0.698 / -	100 / 100
	H	1	- / 0.068	- / 0.067	
	Fe	3	0.961 / 0.119	0.996 / 0.160	
QTAIM	O	-2	0.809 / 0.018	0.807 / -	100 / 100
	H	1	- / 0.159	- / 0.157	
	Fe	3	0.931 / 0.088	0.987 / 0.145	
TFVC	O	-2	0.778 / 0.013	0.776 / -	100 / 100
	H	1	- / 0.137	- / 0.135	

Table S5: EOS, last occupied and first unoccupied eff-AOs and C(%) values for the low-spin $Fe(H_2O)_6^{2+}$ complex.

Atomic definition	Atom	EOS	$\lambda_{LO}/\lambda_{FU}$	R(%)
	Fe	2	0.974 / 0.052	
Mulliken	O	-2	0.538 / -	90
	H	1	- / 0.142	
	Fe	2	0.982 / 0.192	
Löwdin	O	-2	0.692 / -	90
	H	1	- / 0.290	
	Fe	2	0.969 / 0.185	
Becke	O	-2	0.560 / -	80
	H	1	- / 0.260	
	Fe	2	0.908 / 0.093	
Hirshfeld	O	-2	0.532 / -	86
	H	1	- / 0.174	
	Fe	2	0.849 / 0.072	
Hirshfeld-Iterative	O	-2	0.671 / 0.011	100
	H	1	- / 0.078	
	Fe	2	0.958 / 0.105	
QTAIM	O	-2	0.785 / 0.012	100
	H	1	- / 0.177	
	Fe	2	0.897 / 0.074	
TFVC	O	-2	0.752 / 0.014	100
	H	1	- / 0.154	

Table S6: EOS, last occupied and first unoccupied eff-AOs and C(%) values for low-spin $Fe(H_2O)_6^{3+}$ complex.

Atomic definition	Atom	EOS	$\lambda^{\alpha}_{LO}/\lambda^{\alpha}_{FU}$	$\lambda^{\beta}_{LO}/\lambda^{\beta}_{FU}$	$R_{\alpha}(\%)/R_{\beta}(\%)$
	Fe	3	0.984 / 0.151	0.982 / 0.136	
Mulliken	O	-2	0.571 / -	0.571 / -	92 / 93
	H	1	- / 0.114	- / 0.114	
	Fe	3	0.984 / 0.228	0.984 / 0.215	
Löwdin	O	-2	0.707 / -	0.707 / -	94 / 94
	H	1	- / 0.271	- / 0.271	
	Fe	3	0.972 / 0.266	0.971 / 0.250	
Becke	O	-2	0.561 / -	0.568 / -	80 / 82
	H	1	- / 0.242	- / 0.243	
	Fe	3	0.912 / 0.193	0.909 / 0.178	
Hirshfeld	O	-2	0.543 / -	0.543 / -	85 / 87
	H	1	- / 0.164	- / 0.164	
	Fe	3	0.858 / 0.164	0.854 / 0.150	
Hirshfeld-Iterative	O	-2	0.698 / 0.011	0.699 / 0.011	100 / 100
	H	1	- / 0.065	- / 0.065	
	Fe	3	0.960 / 0.200	0.959 / 0.185	
QTAIM	O	-2	0.804 / 0.012	0.806 / 0.012	100 / 100
	H	1	- / 0.157	- / 0.157	
	Fe	3	0.913 / 0.173	0.910 / 0.160	
TFVC	O	-2	0.774 / 0.013	0.775 / 0.013	100 / 100
	H	1	- / 0.135	- / 0.136	

Table S7: EOS, last occupied and first unoccupied eff-AOs and C(%) values for the $Fe(CN)_6^{4-}$ complex.

Atomic definition	Atom	EOS	$\lambda_{LO}/\lambda_{FU}$	R(%)
Mulliken	Fe	2	0.826 / 0.199	74
	C	2	0.789 / 0.253	
	N	-3	0.491 / -	
Löwdin	Fe	2	0.862 / 0.319	60
	C	2	0.705 / 0.448	
	N	-3	0.543 / 0.031	
Becke	Fe	2	0.853 / 0.312	56
	C	2	0.626 / 0.349	
	N	-3	0.412 / -	
Hirshfeld	Fe	2	0.780 / 0.243	64
	C	2	0.617 / 0.283	
	N	-3	0.423 / -	
Hirshfeld-Iterative	Fe	2	0.773 / 0.238	67
	C	2	0.597 / 0.259	
	N	-3	0.433 / -	
QTAIM	Fe	2	0.846 / 0.259	98
	C	2	0.794 / 0.271	
	N	-3	0.747 / 0.026	
TFVC	Fe	2	0.786 / 0.223	99
	C	2	0.732 / 0.230	
	N	-3	0.719 / 0.024	

Table S8: EOS, last occupied and first unoccupied eff-AOs and C(%) values for the $Fe(CN)_6^{3-}$ complex

Atomic definition	Atom	EOS	$\lambda^{\alpha}_{LO}/\lambda^{\alpha}_{FU}$	$\lambda^{\beta}_{LO}/\lambda^{\beta}_{FU}$	$R_{\alpha}(\%)/R_{\beta}(\%)$
Mulliken	Fe	3	0.896 / 0.327	0.871 / 0.283	63 / 66
	C	2	0.701 / 0.263	0.737 / 0.280	
	N	-3	0.453 / -	0.442 / -	
Löwdin	Fe	3	0.920 / 0.420	0.900 / 0.378	59 / 59
	C	2	0.672 / 0.448	0.687 / 0.450	
	N	-3	0.538 / 0.029	0.539 / 0.030	
Becke	Fe	3	0.905 / 0.432	0.886 / 0.393	47 / 51
	C	2	0.596 / 0.350	0.607 / 0.364	
	N	-3	0.406 / -	0.407 / -	
Hirshfeld	Fe	3	0.832 / 0.358	0.812 / 0.319	56 / 60
	C	2	0.584 / 0.288	0.596 / 0.299	
	N	-3	0.418 / -	0.419 / -	
Hirshfeld-Iterative	Fe	3	0.823 / 0.349	0.802 / 0.310	58 / 62
	C	2	0.577 / 0.272	0.590 / 0.283	
	N	-3	0.425 / -	0.426 / -	
QTAIM	Fe	3	0.900 / 0.384	0.881 / 0.343	84 / 85
	C	2	0.762 / 0.278	0.777 / 0.293	
	N	-3	0.728 / 0.021	0.692 / 0.022	
TFVC	Fe	3	0.848 / 0.344	0.827 / 0.305	85 / 86
	C	2	0.694 / 0.235	0.709 / 0.245	
	N	-3	0.701 / 0.020	0.665 / 0.021	

Table S9: EOS, last occupied and first unoccupied eff-AOs and R(%) values for the $Fe(CO)_6^{2+}$ complex

Atomic definition	Atom	EOS	$\lambda_{LO}/\lambda_{FU}$	R(%)
	Fe	2	0.813 / 0.215	
Mulliken	C	2	0.752 / 0.230	69
	O	-2	0.424 / -	
	Fe	2	0.849 / 0.315	
Löwdin	C	2	0.705 / 0.413	67
	O	-2	0.579 / 0.025	
	Fe	2	0.836 / 0.330	
Becke	C	2	0.608 / 0.331	61
	O	-2	0.445 / -	
	Fe	2	0.753 / 0.256	
Hirshfeld	C	2	0.600 / 0.240	74
	O	-2	0.497 / -	
	Fe	2	0.760 / 0.260	
Hirshfeld-Iterative	C	2	0.600 / 0.237	74
	O	-2	0.504 / -	
	Fe	2	0.832 / 0.281	
QTAIM	C	2	0.775 / 0.219	99
	O	-2	0.807 / 0.029	
	Fe	2	0.768 / 0.241	
TFVC	C	2	0.714 / 0.191	97
	O	-2	0.777 / 0.025	

Table S10: EOS, last occupied and first unoccupied eff-AOs and R(%) values for the $Fe(CO)_6^{3+}$ complex

Atomic definition	Atom	EOS	$\lambda^{\alpha}_{LO}/\lambda^{\alpha}_{FU}$	$\lambda^{\beta}_{LO}/\lambda^{\beta}_{FU}$	$R_{\alpha}(\%)/R_{\beta}(\%)$
Mulliken	Fe	3	0.913 / 0.308	0.894 / 0.263	60 / 65
	C	2	0.690 / 0.243	0.723 / 0.242	
	O	-2	0.410 / -	0.412 / -	
Löwdin	Fe	3	0.933 / 0.398	0.918 / 0.353	66 / 66
	C	2	0.693 / 0.414	0.709 / 0.415	
	O	-2	0.576 / 0.024	0.412 / 0.025	
Becke	Fe	3	0.919 / 0.414	0.905 / 0.372	53 / 57
	C	2	0.601 / 0.330	0.614 / 0.333	
	O	-2	0.441 / -	0.442 / -	
Hirshfeld	Fe	3	0.850 / 0.342	0.835 / 0.302	65 / 69
	C	2	0.599 / 0.245	0.613 / 0.252	
	O	-2	0.493 / -	0.494 / -	
Hirshfeld-Iterative	Fe	3	0.854 / 0.343	0.838 / 0.302	66 / 70
	C	2	0.609 / 0.246	0.623 / 0.254	
	O	-2	0.499 / -	0.499 / -	
QTAIM	Fe	3	0.912 / 0.362	0.898 / 0.319	91 / 95
	C	2	0.768 / 0.215	0.784 / 0.221	
	O	-2	0.794 / 0.026	0.773 / 0.027	
TFVC	Fe	3	0.862 / 0.326	0.846 / 0.285	88 / 94
	C	2	0.705 / 0.189	0.720 / 0.194	
	O	-2	0.762 / 0.022	0.740 / 0.023	

Table S11: EOS and R(%) values for a set of organic and inorganic molecules.

Molecule	EOS	R(%)
LiF	$Li^{1+}\ F^{1-}$	100
CO	$C^{2+}\ O^{2-}$	100
CN^-	$C^{2+}\ N^{3-}$	97
NO^+	$N^{3+}\ O^{2-}$	94
CO_2	$C^{4+}\ (O^{2-})_2$	100
SO_2	$S^{4+}\ (O^{2-})_2$	100
SO_3	$S^{6+}\ (O^{2-})_3$	94
LiH	$Li^{1+}\ H^{1-}$	100
BeH_2	$Be^{2+}\ (H^{1-})_2$	100
MgH_2	$Mg^{2+}\ (H^{1-})_2$	100
AlH_3	$Al^{3+}\ (H^{1-})_3$	100
BH_3	$B^{3+}\ (H^{1-})_3$	100
B_2H_6	$(B^{3+})_2(H^{1-})_6$	100
SiH_4	$Si^{4+}\ (H^{1+})_4$	100
NH_3	$N^{3-}\ (H^{1+})_3$	81
PH_3	$P^{3-}\ (H^{1+})_3$	100
H_2O	$(H^{1+})_2O^{2-}$	100
H_2S	$(H^{1-})_2S^{2+}$	55
HF	$H^{1+}\ F^{1-}$	100
HCl	$H^{1+}\ Cl^{1-}$	78
HCNO	$H^{1+}\ C^{2+}\ N^{1-}O^{2-}$	60
$HCONH_2$	$H^{1-}\ C^{4+}\ O^{2-}N^{3-}\ (H^{1+})_2$	52
CH_4	$C^{4+}\ (H^{1-})_4$	45
CH_4	$C^{4-}\ (H^{1+})_4$	42
C_2H_6	$(C^{3-})_2(H^{1+})_6$	41
C_2H_4	$(C^{2+})_2(H^{1-})_4$	52
C_6H_6	$(C^{1+})_6(H^{1-})_6$	54
C_2H_2	$(C^{1-})_2(H^{1+})_2$	57

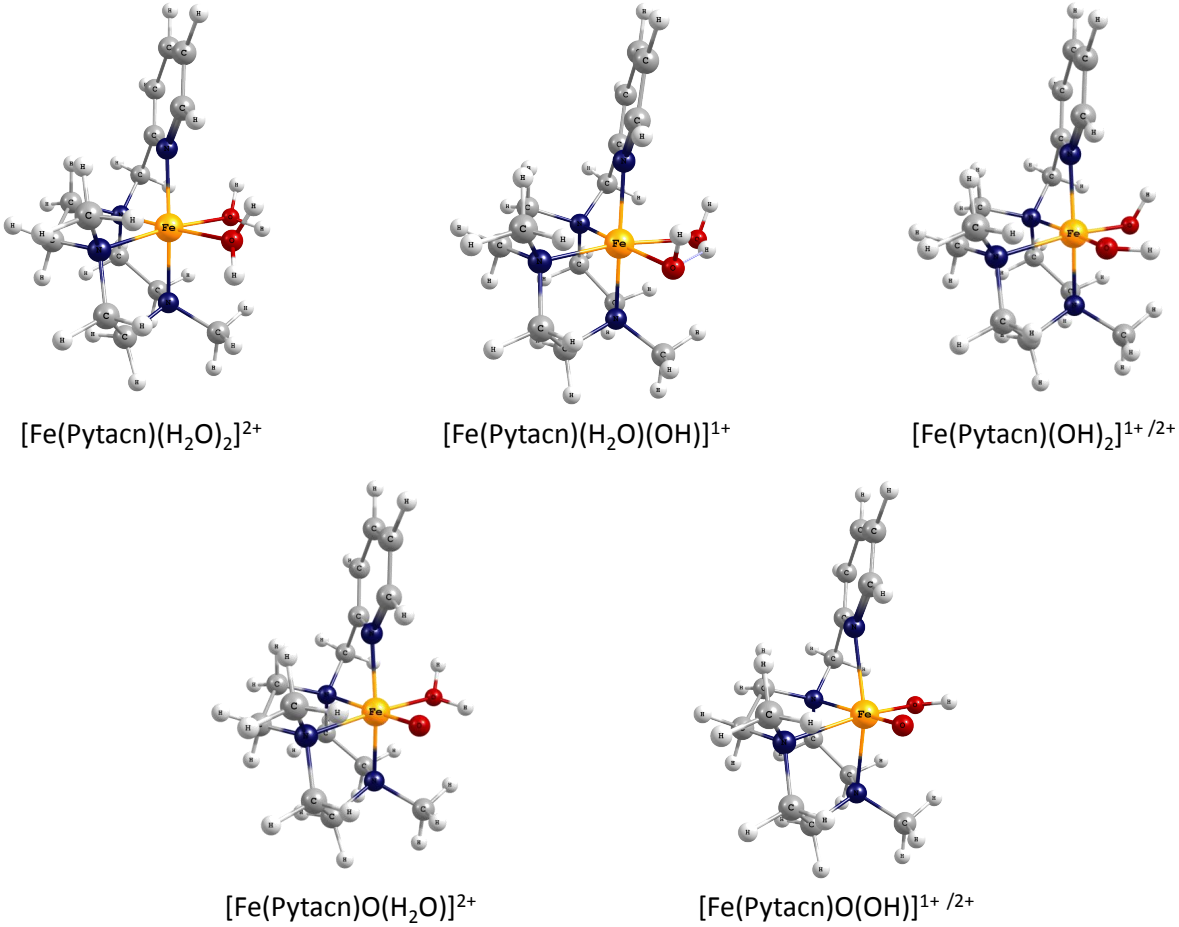

Figure S1: Structure of the [Fe(Pytacn)] active species

Table S12: Cartesian coordinates of Fe^{II}bis aquo complex.
UB3LYP/SDD+6-311G(d,p) Energy = -1043.882312 a.u.

Atom	X	Y	Z
H	0.53357	1.17869	3.21343
H	2.85766	2.076	1.63326
H	1.81471	0.12912	2.64613
C	0.83397	0.52483	2.39231
H	3.20917	-0.33438	1.28211
H	-0.08075	-1.33079	3.04233
C	2.35538	1.59339	0.78769
H	1.83122	-1.92376	1.8447
H	4.05927	0.51968	0.01379
C	0.16217	2.5698	1.23782
C	3.06534	0.29844	0.40804
N	0.92773	1.30854	1.11209
C	-0.16572	-0.60536	2.2282
H	2.36733	2.29385	-0.04933
H	-1.17641	-0.20095	2.23705
C	1.27432	-2.15146	0.93648
H	0.99186	-3.20505	0.98929
H	3.13404	-2.34484	-0.15506
N	0.05518	-1.27938	0.90846
N	2.25023	-0.44517	-0.60893
C	2.14071	-1.90641	-0.29957
H	-1.56572	-2.63179	1.28875
C	2.87361	-0.28672	-1.94537
C	-1.18981	-1.9757	0.49731
H	1.67864	-2.36878	-1.17034
Fe	0.28897	0.16274	-0.46187
H	-0.95693	-2.59467	-0.37173
C	-2.21636	-0.91632	0.14415
N	-1.70314	0.27621	-0.24994
H	-3.9561	-2.09048	0.56697
C	-3.58408	-1.1292	0.23633
C	-2.54498	1.27875	-0.54619
H	-2.09113	2.21966	-0.83061
C	-4.45293	-0.09058	-0.09149
C	-3.92468	1.1366	-0.48363
H	-5.52446	-0.23457	-0.02946
H	-4.56309	1.97358	-0.7329
H	2.2722	-0.80142	-2.69265
H	3.88194	-0.71446	-1.94402
H	2.93757	0.77148	-2.19706
H	-0.86947	2.32956	1.49344
H	0.18155	3.09505	0.28361
H	0.59329	3.207	2.01746
O	-0.13004	-1.02387	-2.14471
O	0.45207	1.65797	-1.87749
H	0.11714	-0.52665	-2.93705
H	-1.05607	-1.2643	-2.28149
H	1.15342	2.31924	-1.88703
H	-0.33565	2.08827	-2.23159

Table S13: Cartesian coordinates of Fe^{II}aquo hydroxo complex.
UB3LYP/SDD+6-311G(d,p) Energy= -1043.418827 a.u.

Atom	X	Y	Z
H	0.52678	1.19714	3.20674
H	2.86044	2.12963	1.55502
H	1.82677	0.16258	2.65339
C	0.84152	0.54277	2.39018
H	3.19872	-0.32183	1.2789
H	-0.0444	-1.32433	3.05873
C	2.34606	1.60198	0.74256
H	1.86651	-1.91239	1.82498
H	4.05983	0.518	0.00688
C	0.16222	2.57241	1.19859
C	3.0616	0.30143	0.39601
N	0.93003	1.31388	1.10671
C	-0.14404	-0.60899	2.2357
H	2.30691	2.23833	-0.14231
H	-1.15999	-0.21686	2.24896
C	1.29213	-2.14738	0.92892
H	1.01999	-3.2043	0.99173
H	3.12015	-2.36243	-0.21534
N	0.07263	-1.28378	0.92017
N	2.25195	-0.44128	-0.61792
C	2.13227	-1.89832	-0.32611
H	-1.54148	-2.66503	1.24577
C	2.85234	-0.24954	-1.95674
C	-1.1617	-1.97563	0.48282
H	1.63385	-2.33542	-1.19156
Fe	0.2912	0.18022	-0.46017
H	-0.91427	-2.55238	-0.41219
C	-2.19879	-0.92247	0.1462
N	-1.69667	0.27549	-0.24355
H	-3.9249	-2.11726	0.56909
C	-3.56448	-1.15061	0.24032
C	-2.55083	1.26677	-0.54196
H	-2.10534	2.20913	-0.83349
C	-4.44618	-0.12175	-0.08538
C	-3.92973	1.1101	-0.47918
H	-5.5163	-0.27688	-0.02228
H	-4.57732	1.93996	-0.73017
H	2.24015	-0.76047	-2.69725
H	3.87303	-0.65115	-1.97582
H	2.86006	0.81608	-2.17938
H	-0.86817	2.33764	1.46639
H	0.18161	3.05033	0.2192
H	0.59354	3.23985	1.95481
O	-0.10155	-0.82273	-2.28586
O	0.48879	1.55885	-1.8871
H	0.05796	0.14953	-2.5484
H	-1.03781	-0.99164	-2.44484
H	-0.26549	2.15461	-1.92881

Table S14: Cartesian coordinates of Fe^{III}bis hydroxo complex.
UB3LYP/SDD+6-311G(d,p) Energy= -1042.653487 a.u.

Atom	X	Y	Z
H	0.69783	1.45369	3.12524
H	3.14441	2.06403	1.40578
H	1.88884	0.28109	2.63294
C	0.94799	0.74183	2.33271
H	3.27418	-0.39469	1.31004
H	-0.15654	-0.92893	3.15623
C	2.55202	1.54261	0.64062
H	1.72624	-1.82759	2.01999
H	4.17157	0.29264	-0.01565
C	0.50372	2.78835	1.07026
C	3.16064	0.16407	0.38045
N	1.12699	1.44594	1.03713
C	-0.15398	-0.31317	2.24713
H	2.58207	2.1398	-0.27202
H	-1.12255	0.18316	2.19122
C	1.16093	-2.08008	1.12212
H	0.82483	-3.11199	1.26044
H	3.00385	-2.55505	0.10316
N	-0.01058	-1.15798	1.03491
N	2.33882	-0.63609	-0.57513
C	2.06719	-2.02557	-0.1163
H	-1.63983	-2.44078	1.57338
C	2.98004	-0.66072	-1.91459
C	-1.28036	-1.8503	0.72109
H	1.57768	-2.52612	-0.95038
Fe	0.26502	0.20079	-0.80293
H	-1.09081	-2.52492	-0.11733
C	-2.33455	-0.85081	0.28995
N	-1.87903	0.26746	-0.30362
H	-4.0411	-1.9757	0.95342
C	-3.69613	-1.07283	0.46432
C	-2.74697	1.18993	-0.74644
H	-2.30882	2.06118	-1.21916
C	-4.60022	-0.12055	0.00098
C	-4.12	1.03297	-0.6129
H	-5.66563	-0.2755	0.12315
H	-4.79126	1.79785	-0.98098
H	2.32051	-1.17229	-2.61204
H	3.94847	-1.1728	-1.87148
H	3.13205	0.36268	-2.25799
H	-0.54494	2.69287	1.35617
H	0.55163	3.22575	0.07537
H	1.00676	3.44083	1.79509
O	-0.05176	-1.21149	-2.00219
O	0.44047	1.79047	-1.75156
H	0.41506	1.78248	-2.71345
H	-0.57995	-1.07377	-2.79428

Table S15: Cartesian coordinates of Fe^{IV}bis hydroxo complex.
UB3LYP/SDD+6-311G(d,p) Energy= -1042.272032 a.u.

Atom	X	Y	Z
H	0.56436	1.45906	3.07565
H	2.89382	2.20802	1.37758
H	1.84678	0.38163	2.58667
C	0.85884	0.74195	2.30711
H	3.23162	-0.22595	1.2244
H	-0.044	-1.05441	3.12073
C	2.37083	1.66476	0.58368
H	1.82175	-1.81512	1.95567
H	4.04031	0.5122	-0.13749
C	0.20578	2.72584	1.00493
C	3.05973	0.33626	0.30749
N	0.94169	1.42906	0.97031
C	-0.14132	-0.39632	2.25205
H	2.36169	2.28999	-0.30777
H	-1.15712	-0.00436	2.24965
C	1.26443	-2.08377	1.05898
H	0.95625	-3.12383	1.18289
H	3.12912	-2.34933	-0.01229
N	0.04518	-1.19286	0.98882
N	2.23108	-0.50861	-0.63015
C	2.12788	-1.94633	-0.19394
H	-1.56582	-2.48411	1.55287
C	2.81045	-0.45165	-2.00963
C	-1.22388	-1.92466	0.67741
H	1.6859	-2.48737	-1.02726
Fe	0.28585	0.12677	-0.57738
H	-1.01978	-2.63019	-0.12974
C	-2.24443	-0.90519	0.23006
N	-1.71867	0.21255	-0.32935
H	-4.01994	-1.95952	0.81046
C	-3.61633	-1.06503	0.3518
C	-2.52547	1.18651	-0.78933
H	-2.03934	2.0437	-1.23653
C	-4.45952	-0.06133	-0.12567
C	-3.90656	1.08004	-0.69991
H	-5.5346	-0.17029	-0.04553
H	-4.52952	1.87962	-1.07963
H	2.14984	-0.97068	-2.69851
H	3.79241	-0.93215	-2.00293
H	2.921	0.58922	-2.30869
H	-0.82227	2.55433	1.32205
H	0.21426	3.17066	0.01284
H	0.68591	3.40629	1.71373
O	-0.01228	-1.11434	-1.85586
O	0.45	1.51544	-1.65062
H	0.40913	1.28313	-2.59018
H	-0.88324	-1.06289	-2.27243

Table S16: Cartesian coordinates of Fe^{IV}oxo aquo complex.
UB3LYP/SDD+6-311G(d,p) Energy= -1042.605037 a.u.

Atom	X	Y	Z
H	0.5465	1.98291	2.74052
H	2.81043	2.4777	0.96405
H	1.82865	0.82337	2.4557
C	0.83954	1.13008	2.12795
H	3.21074	0.05627	1.2579
H	-0.04219	-0.48757	3.25889
C	2.33252	1.78002	0.27123
H	1.86326	-1.36437	2.23342
H	4.03429	0.54748	-0.2086
C	0.11594	2.80256	0.48738
C	3.05259	0.44184	0.2532
N	0.90741	1.55648	0.67995
C	-0.14934	-0.00282	2.28561
H	2.30929	2.21739	-0.72559
H	-1.1657	0.37746	2.20427
C	1.30159	-1.82334	1.42141
H	1.03114	-2.8304	1.74294
H	3.15218	-2.25404	0.37848
N	0.06919	-0.99839	1.18873
N	2.22879	-0.5526	-0.52388
C	2.14529	-1.89435	0.15039
H	-1.54504	-2.18744	1.93743
C	2.81997	-0.7178	-1.88157
C	-1.18011	-1.77884	0.99141
H	1.68778	-2.57076	-0.56852
Fe	0.30726	0.09309	-0.5799
H	-0.96301	-2.61787	0.32718
C	-2.19999	-0.84405	0.37354
N	-1.68009	0.18873	-0.33375
H	-3.96084	-1.82179	1.09527
C	-3.57011	-0.99765	0.51314
C	-2.49023	1.07818	-0.92747
H	-1.9995	1.86049	-1.49001
C	-4.41673	-0.07355	-0.09691
C	-3.87035	0.97994	-0.82536
H	-5.49039	-0.17373	0.00122
H	-4.49624	1.71643	-1.31058
H	2.23555	-1.43774	-2.44998
H	3.84396	-1.08807	-1.78224
H	2.81069	0.24769	-2.38329
H	-0.9058	2.62735	0.82084
H	0.12433	3.06045	-0.56903
H	0.56278	3.60415	1.0813
O	-0.11954	-1.54677	-1.78828
H	0.06287	-1.27926	-2.70163
H	-1.0385	-1.85061	-1.79667
O	0.42497	1.05969	-1.88385

Table S17: Cartesian coordinates of Fe^{IV}oxohydroxo complex.
UB3LYP/SDD+6-311G(d,p) Energy=-1041.988990 a.u.

Atom	X	Y	Z
H	0.66574	1.81564	2.8598
H	3.10539	2.24094	1.13404
H	1.88181	0.6087	2.5347
C	0.93354	1.00571	2.17618
H	3.29088	-0.21453	1.33303
H	-0.11943	-0.60276	3.17327
C	2.55753	1.61588	0.41754
H	1.72696	-1.59379	2.15725
H	4.20848	0.32118	-0.0499
C	0.48184	2.87361	0.6491
C	3.19089	0.22562	0.33997
N	1.11607	1.53924	0.79041
C	-0.14628	-0.07017	2.21485
H	2.60189	2.10062	-0.5586
H	-1.12664	0.39494	2.12931
C	1.17922	-1.93841	1.27923
H	0.8313	-2.94744	1.51622
H	3.03656	-2.51861	0.35084
N	0.00567	-1.02478	1.079
N	2.3849	-0.67324	-0.52425
C	2.10798	-2.00817	0.06074
H	-1.59671	-2.27124	1.75516
C	2.9965	-0.80859	-1.86694
C	-1.26846	-1.75237	0.84663
H	1.63124	-2.58882	-0.72705
Fe	0.27851	0.1595	-0.73549
H	-1.08611	-2.49112	0.063
C	-2.33927	-0.80009	0.35262
N	-1.89994	0.30459	-0.276
H	-4.02799	-1.95456	1.01569
C	-3.69688	-1.06431	0.49474
C	-2.78238	1.16146	-0.80787
H	-2.36309	2.0157	-1.32622
C	-4.61589	-0.17137	-0.05034
C	-4.15348	0.96021	-0.71591
H	-5.67901	-0.35839	0.04314
H	-4.83692	1.67368	-1.15754
H	2.32834	-1.38415	-2.50335
H	3.97082	-1.30858	-1.80475
H	3.12346	0.17937	-2.30822
H	-0.56821	2.80664	0.9349
H	0.54207	3.1846	-0.392
H	0.97941	3.60964	1.29031
O	-0.11187	-1.30289	-1.78194
O	0.43641	1.27743	-1.90161
H	-0.27383	-1.05559	-2.69927

Table S18: Cartesian coordinates of Fe^{V}oxo hydroxo complex.
UB3LYP/SDD+6-311G(d,p) Energy= -1041.604274 a.u.

Atom	X	Y	Z
H	0.57246	1.61875	2.97591
H	2.85225	2.3547	1.21744
H	1.86819	0.53649	2.53159
C	0.87093	0.86408	2.24575
H	3.25202	-0.08394	1.20757
H	0.01541	-0.8951	3.17284
C	2.34706	1.74465	0.46147
H	1.8461	-1.72035	2.03608
H	4.04197	0.59389	-0.19865
C	0.15563	2.76067	0.84376
C	3.06788	0.42452	0.26259
N	0.92918	1.4836	0.87357
C	-0.11008	-0.29447	2.26687
H	2.31523	2.31493	-0.467
H	-1.13212	0.08144	2.26696
C	1.29571	-2.0168	1.14322
H	1.01152	-3.06112	1.28825
H	3.18505	-2.26327	0.10389
N	0.06573	-1.15057	1.04769
N	2.24977	-0.48666	-0.62208
C	2.17356	-1.90266	-0.10739
H	-1.55975	-2.40313	1.67236
C	2.8192	-0.48339	-2.00721
C	-1.20911	-1.882	0.77679
H	1.76122	-2.49846	-0.91752
Fe	0.27018	0.10283	-0.61634
H	-1.02627	-2.6169	-0.00907
C	-2.22487	-0.8751	0.28695
N	-1.71285	0.22295	-0.32554
H	-3.99418	-1.9117	0.90725
C	-3.59621	-1.03808	0.40545
C	-2.5241	1.15407	-0.86082
H	-2.0456	1.98153	-1.36842
C	-4.44649	-0.07321	-0.13524
C	-3.90325	1.0374	-0.77588
H	-5.5209	-0.19119	-0.05816
H	-4.53157	1.80216	-1.21389
H	2.20549	-1.10332	-2.654
H	3.83479	-0.8865	-1.97252
H	2.84059	0.53584	-2.38879
H	-0.86432	2.58161	1.18026
H	0.14487	3.154	-0.17072
H	0.62518	3.48903	1.51064
O	-0.04723	-1.28103	-1.71045
O	0.36311	1.26861	-1.74878
H	-0.26709	-0.98695	-2.60711

Table S19: Cartesian coordinates of the TS corresponding to the H-abstraction step of the catalytic hydroxylation of cyclohexane with the [Fe(Pytacn)] complex.
UB3LYP/SDD+6-311G(d,p) Energy=-1277.547735 a.u.

Atom	X	Y	Z
H	-3.47233	-0.59126	2.58233
H	-1.5948	-2.91752	2.58272
H	-3.45034	-1.88145	1.40986
C	-3.05636	-0.88856	1.61768
H	-2.45268	-3.23573	0.29219
H	-4.54981	-0.02373	0.30874
C	-1.0983	-2.38767	1.76267
H	-3.76876	-1.85188	-0.88274
H	-0.91222	-4.05166	0.4083
C	-1.07243	-0.23647	2.91992
C	-1.38619	-3.06912	0.43464
N	-1.55467	-0.96108	1.71105
C	-3.4886	0.0998	0.54637
H	-0.02774	-2.37338	1.96496
H	-3.35451	1.11884	0.90582
C	-3.05941	-1.2806	-1.48143
H	-3.58865	-0.9842	-2.38971
H	-2.15459	-3.13062	-2.1615
N	-2.65781	-0.06418	-0.69117
N	-0.86984	-2.23047	-0.70662
C	-1.84237	-2.12824	-1.85175
H	-3.68547	1.55568	-1.65161
C	0.41879	-2.80237	-1.20351
C	-2.66372	1.20975	-1.46807
H	-1.29458	-1.66949	-2.67167
Fe	-0.66674	-0.28029	-0.10501
H	-2.17402	1.02652	-2.42635
C	-1.86362	2.22708	-0.68901
N	-0.90749	1.70965	0.12095
H	-2.82904	3.9945	-1.42436
C	-2.05322	3.59795	-0.78095
C	-0.11135	2.52328	0.83705
H	0.64339	2.04093	1.44333
C	-1.23347	4.44759	-0.03972
C	-0.25091	3.90238	0.78248
H	-1.364	5.52136	-0.10244
H	0.40312	4.53073	1.37297
H	0.82413	-2.15105	-1.97207
H	0.2351	-3.79817	-1.61606
H	1.1203	-2.8716	-0.37463
H	-1.43865	0.78933	2.90197
H	0.01557	-0.23386	2.92401
H	-1.44178	-0.72744	3.82484
O	-0.05122	0.05399	-1.76581
O	0.8491	-0.38058	0.67193
H	2.25181	-0.20121	0.02942
C	3.36428	-0.13746	-0.36352
H	0.75963	0.58053	-1.75465
C	4.11939	-1.27503	0.29668
H	4.05037	-1.19364	1.38646
H	3.71571	-2.24938	0.00774
C	3.91099	1.23637	-0.02437
H	3.36083	2.03074	-0.53779
H	3.83714	1.41723	1.05353
C	5.62279	-1.20013	-0.11534
H	6.15825	-1.99876	0.40537
H	5.7112	-1.40041	-1.1883
C	5.41433	1.30377	-0.43665
H	5.80488	2.28318	-0.14683
H	5.4894	1.23882	-1.52728
C	6.21074	0.17224	0.21398
H	7.25011	0.21485	-0.1303
H	6.23799	0.31403	1.30041