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

Supporting information: TD-DFT Study of the Light-induced Spin Crossover of Fe(III) Complexes

Sergi Saureu,[a] Coen de Graaf[a,b]

[a]Departament de Química Física i Inorgànica,
Universitat Rovira i Virgili, Marcel·lí Domingo s/n,
43007 Tarragona, Spain. E-mail: coen.degraaf@urv.cat

[b]Institució Catalana de Recerca i Estudis Avançats (ICREA)
Passeig Lluis Companys 23, 08010 Barcelona, Spain

November 27, 2015

Contents

S1 $[Fe(qsal)_2]^+$: complete active space orbitals, CAS(13,14).

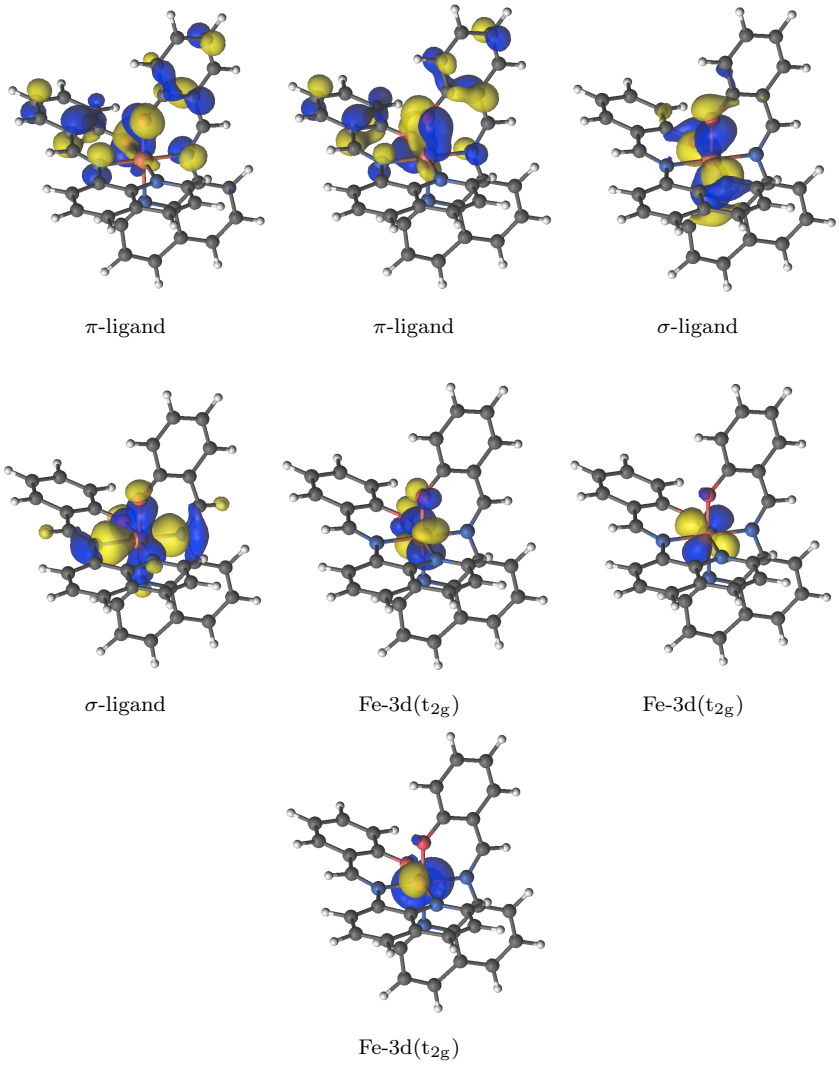

Figure S1.1: CAS(13,14) orbitals. For CAS(9,12) the π orbitals are not included in the active space.

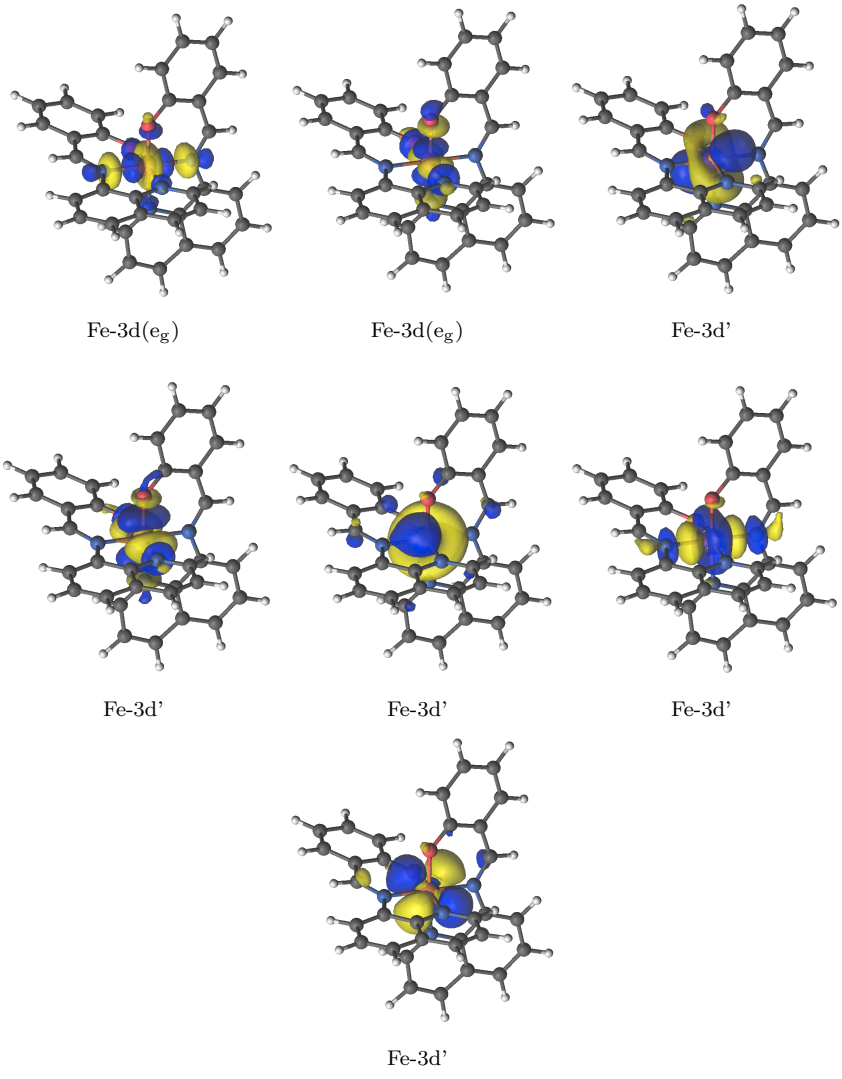

Figure S1.1: (*Continued*) CAS(13,14) orbitals. For CAS(9,12) the π orbitals are not included in the active space.

S2 $[Fe(qsal)_2]^+$: Selected B3LYP* angles.

Table S2.1: B3LYP*/def2-TZVP optimized angles. The experimental distances in parenthesis are taken from [Hayami *et al.*, *J. Am. Chem. Soc.* **2001**, 123, 11644–11650].

angle	LS	HS	$\Delta \measuredangle$
O(1)–Fe(1)–O(2)	93.4 (93.8)	96.7 (98.2)	3.3 (4.4)
O(1)–Fe(1)–N(1)	93.7 (94.7)	86.3 (97.1)	7.4 (2.4)
O(1)–Fe(1)–N(2)	175.0 (175.7)	161.3 (165.2)	13.7 (10.5)
O(1)–Fe(1)–N(3)	87.1 (85.3)	103.6 (89.1)	16.5 (3.8)
O(1)–Fe(1)–N(4)	89.2 (90.4)	90.0 (89.8)	0.8 (0.6)
O(2)–Fe(1)–N(1)	87.1 (86.6)	103.6 (89.1)	16.5 (2.5)
O(2)–Fe(1)–N(2)	89.2 (89.9)	89.9 (89.8)	0.7 (0.1)
O(2)–Fe(1)–N(3)	93.7 (94.5)	86.3 (97.1)	7.4 (2.6)
O(2)–Fe(1)–N(4)	175.0 (175.1)	161.3 (165.2)	13.7 (9.9)
N(1)–Fe(1)–N(2)	82.2 (83.3)	75.2 (95.5)	7.0 (12.2)
N(1)–Fe(1)–N(3)	178.9 (179.0)	165.3 (170.5)	13.6 (8.5)
N(1)–Fe(1)–N(4)	96.9 (95.6)	94.2 (77.4)	2.7 (18.2)
N(2)–Fe(1)–N(3)	96.9 (96.6)	94.1 (77.4)	2.8 (19.2)
N(2)–Fe(1)–N(4)	88.5 (86.0)	89.1 (85.4)	0.6 (0.6)
N(3)–Fe(1)–N(4)	82.2 (83.3)	75.2 (95.5)	7.0 (12.2)

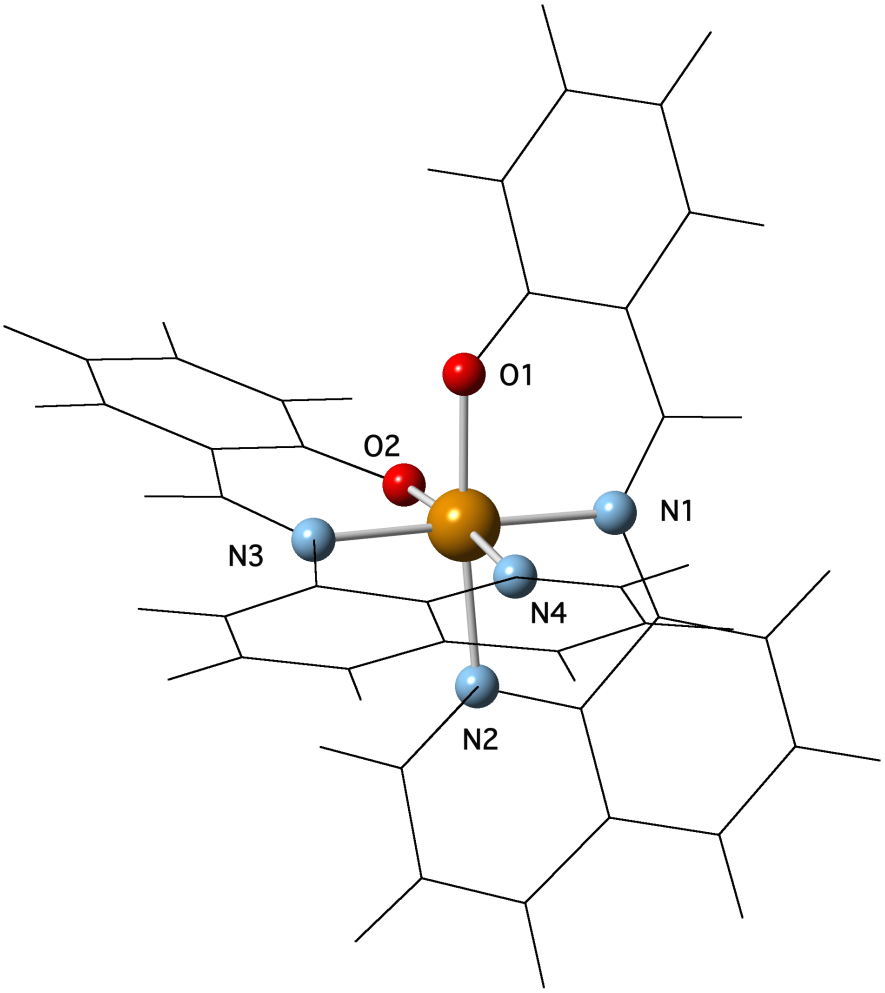

Figure S2.1: Atom numbering of the $[Fe(qsal)_2]^+$used in Table S2.1.

S3 $[Fe(qsal)_2]^+$: Selected PBE0 distances, angles, energies and vibrations.

Table S3.1: PBE0/def2-TZVP optimized bond lengths in Å of complex $[Fe(qsal)_2]^+$. The B3LYP* distances are taken from this work and experimental distances from [Hayami *et al.*, *J. Am. Chem. Soc.* **2001**, 123, 11644–11650].

distance	HS	LS	Δr
		PBE0	
Fe–O	1.91	1.86	0.05
Fe–N_1	2.19	2.00	0.19
Fe–N_2	2.13	1.95	0.18
		B3LYP*	
Fe–O	1.91	1.88	0.03
Fe–N_1	2.21	2.02	0.19
Fe–N_2	2.18	1.97	0.21
		Experimental	
Fe–O	1.88	1.88	0.00
Fe–N_1	2.12	1.97	0.15
Fe–N_2	2.09	1.94	0.25

Table S3.2: PBE0/def2-TZVP optimized angles. B3LYP* values in parenthesis are given for comparison.

angle	LS	HS	$\Delta \measuredangle$
O(1)–Fe(1)–O(2)	94.4 (93.4)	97.3 (96.7)	2.9 (3.3)
O(1)–Fe(1)–N(1)	93.6 (93.7)	86.3 (103.5)	7.3 (7.4)
O(1)–Fe(1)–N(2)	174.3 (175.0)	161.2 (161.3)	13.1 (13.7)
O(1)–Fe(1)–N(3)	86.6 (87.1)	101.1 (86.3)	14.5 (16.5)
O(1)–Fe(1)–N(4)	89.3 (89.2)	90.4 (90.0)	1.1 (0.8)
O(2)–Fe(1)–N(1)	86.6 (87.1)	100.6 (86.3)	14 (16.5)
O(2)–Fe(1)–N(2)	89.3 (89.2)	90.9 (89.9)	1.6 (0.7)
O(2)–Fe(1)–N(3)	93.6 (93.7)	86.4 (103.6)	7.2 (7.4)
O(2)–Fe(1)–N(4)	174.3 (175.0)	161.4 (161.3)	12.9 (13.7)
N(1)–Fe(1)–N(2)	82.3 (82.2)	75.5 (94.2)	6.8 (7)
N(1)–Fe(1)–N(3)	178.9 (178.9)	169.1 (165.3)	9.8 (13.6)
N(1)–Fe(1)–N(4)	97.5 (96.9)	96.7 (75.2)	0.8 (2.7)
N(2)–Fe(1)–N(3)	97.5 (96.9)	96.7 (75.2)	0.8 (2.8)
N(2)–Fe(1)–N(4)	87.4 (88.5)	87.0 (89.1)	0.4 (0.6)
N(3)–Fe(1)–N(4)	82.3 (82.2)	75.5 (94.1)	6.8 (7)

Table S3.3: Adiabatic HS-LS energy difference (ΔE_{HL}) and difference in zero-point energy (ΔZPE) at PBE0/def2-TZVP level. Energies in cm^{-1}. B3LYP* values are given for comparison.

	$[Fe(qsal)_2]^+$	
	PBE0	B3LYP*
ΔE_{HL}	-1380	2166
ΔZPE	-590	-670
ΔH_{HL}	-1970	1496

Table S3.4: Frequencies in cm^{-1} of the Fe-L bending and stretching modes for the LS and HS states of $[Fe(qsal)_2]^+$at PBE0 level. The labels of the stretching modes are approximate due to the non-ideal octahedral symmetry. B3LYP* values are given for comparison.

	$[Fe(qsal)_2]^+$			
	PBE0		B3LYP*	
Character	LS	HS	LS	HS
Bending				
	166	138	164	133
	186	147	184	141
	201	186	200	185
	224	195	224	193
	235	212	233	210
Stretching				
e_g	223	218	218	222
e_g	261	225	256	239
a_g	263	230	259	226
t_{1u}	350	265	342	260
t_{1u}	361	275	353	261
t_{1u}	397	317	385	308

S4 $[Fe(pap)_2]^+$: complete active space orbitals, CAS(13,14).

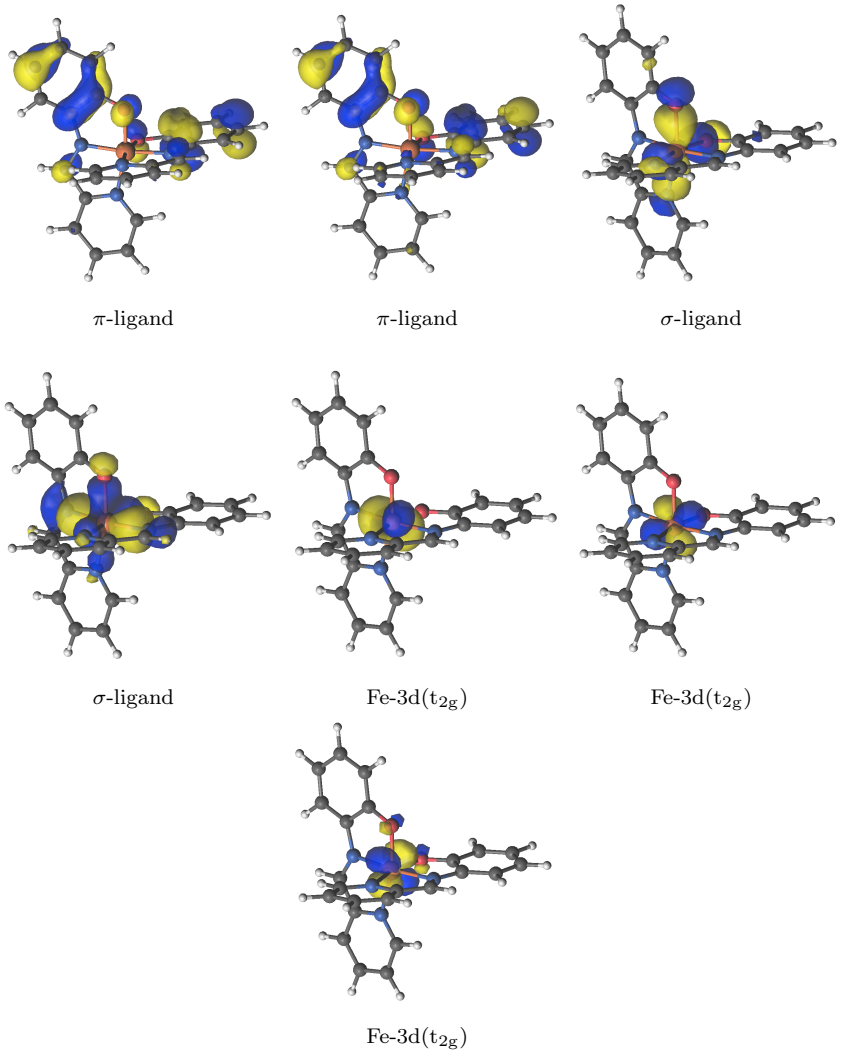

Figure S4.1: CAS(13,14) orbitals. For CAS(9,12) the π orbitals are not included in the active space.

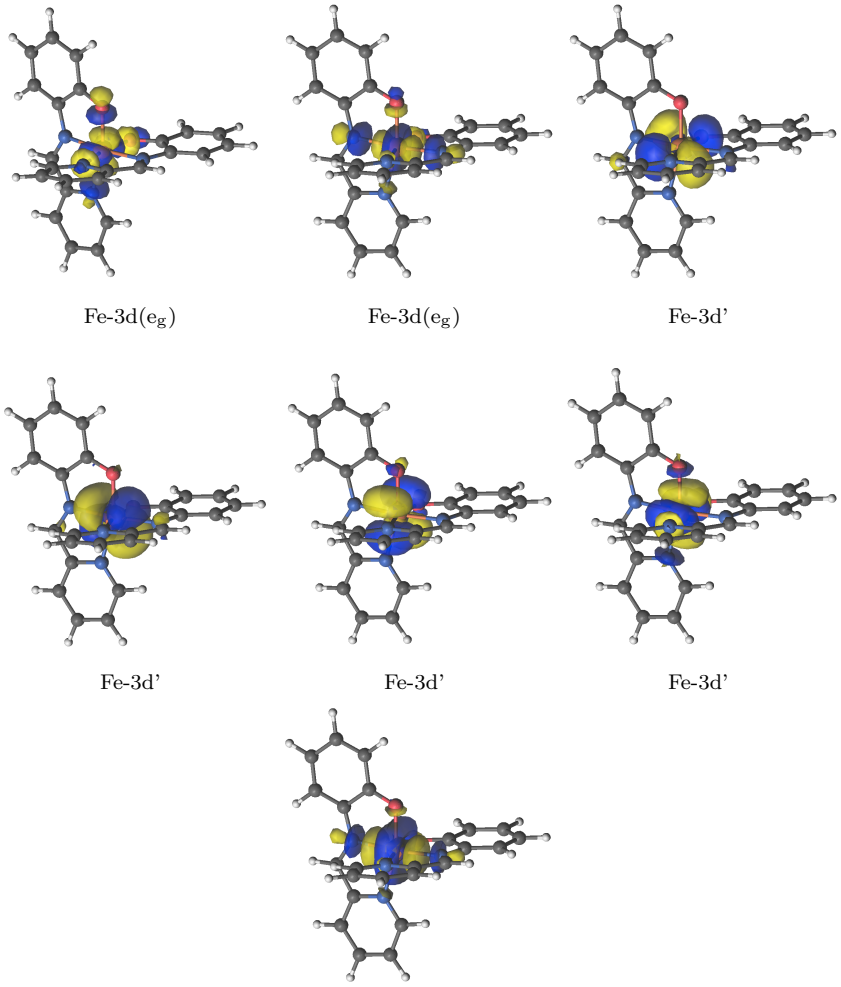

Figure S4.1: (*Continued*) CAS(13,14) orbitals. For CAS(9,12) the π orbitals are not included in the active space.

S5 $[Fe(pap)_2]^+$: Selected B3LYP* angles.

Table S5.1: B3LYP*/def2-TZVP optimized angles. The experimental distances in parenthesis are taken from [Hayami *et al.*, *Chem. Eur. J.* **2009**, 15, 3497–3508].

angle	LS	HS	$\Delta \measuredangle$
O(1)–Fe(1)–O(2)	94.8 (93.6)	101.1 (96.0)	6.3 (2.4)
O(1)–Fe(1)–N(1)	84.9 (85.7)	77.6 (79.0)	7.3 (6.7)
O(1)–Fe(1)–N(2)	166.1 (166.4)	150.3 (152.8)	15.8 (13.6)
O(1)–Fe(1)–N(3)	90.8 (92.0)	114.2 (110.9)	23.4 (18.9)
O(1)–Fe(1)–N(4)	89.8 (90.5)	91.0 (94.3)	1.2 (3.8)
O(2)–Fe(1)–N(1)	90.3 (91.6)	102.2 (115.1)	11.9 (23.5)
O(2)–Fe(1)–N(2)	87.9 (90.0)	89.9 (92.0)	2.0 (2.0)
O(2)–Fe(1)–N(3)	85.0 (85.7)	77.4 (79.2)	7.6 (6.5)
O(2)–Fe(1)–N(4)	165.7 (166.4)	150.7 (152.7)	15.0 (13.7)
N(1)–Fe(1)–N(2)	81.4 (81.0)	73.1 (74.1)	8.3 (6.9)
N(1)–Fe(1)–N(3)	173.4 (176.4)	168.2 (162.3)	5.2 (14.1)
N(1)–Fe(1)–N(4)	103.7 (101.7)	95.0 (91.7)	8.7 (10.0)
N(2)–Fe(1)–N(3)	103.0 (101.4)	106.5 (96.1)	3.5 (5.3)
N(2)–Fe(1)–N(4)	90.9 (89.0)	92.5 (90.4)	1.6 (1.4)
N(3)–Fe(1)–N(4)	81.3 (81.1)	73.2 (73.5)	8.1 (7.6)

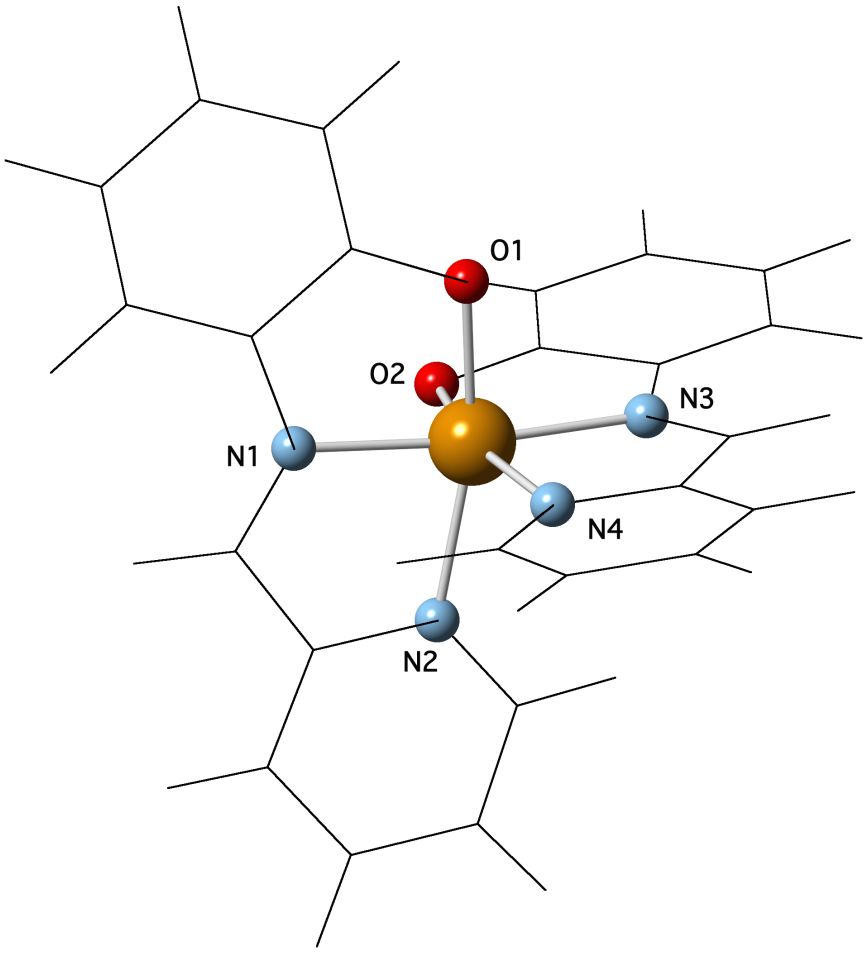

Figure S5.1: Atom numbering of the $[Fe(pap)_2]^+$used in Table S5.1.

S6 Optimized XYZ coordinates.

S6.1 $[Fe(qsal)_2]^+$: B3LYP*/def2-TZVP LS geometry.

Fe -0.000115 0.000096 -0.000017
N 1.442446 1.404755 0.012291
N 0.019250 0.343410 1.933642
N 1.442537 -1.404589 -0.012431
N 0.018962 -0.343534 -1.933639
O -1.288011 -1.360607 0.132881
O -1.287985 1.360773 -0.132984
C 3.065181 3.129867 2.855428
C 3.408016 3.349481 0.389383
C -3.178060 -2.468423 0.932800
C -0.930580 -0.049708 2.739398
C 1.758848 1.814433 1.275561
C -4.081093 -2.730943 1.937797
C 1.376597 1.570841 3.642298
C -2.109856 -1.559928 1.125666
C 2.388935 2.520936 3.886298
C 3.051232 2.940791 -0.870455
C -2.939304 -1.235105 3.420715
C 2.765488 2.785817 1.516932
C -1.987464 -0.933837 2.410774
C 2.061169 1.953206 -1.018558
C 1.033185 1.228955 2.346386
C -3.969099 -2.113253 3.198726
C 3.065132 -3.129558 -2.855742
C 3.408120 -3.349270 -0.389727
C -3.179040 2.467265 -0.932387
C -0.931481 0.048716 -2.739064
C 1.758862 -1.814249 -1.275730
C -4.082942 2.728621 -1.936918
C 1.376359 -1.570659 -3.642436

C -2.110556 1.559148 -1.125393
C 2.388767 -2.520653 -3.886546
C 3.051380 -2.940665 0.870147
C -2.941384 1.232461 -3.419686
C 2.765519 -2.785574 -1.517209
C -1.988682 0.932386 -2.410216
C 2.061335 -1.953078 1.018356
C 1.033036 -1.228849 -2.346487
C -3.971534 2.110147 -3.197506
H 3.835674 3.866050 3.055835
H 4.176752 4.101858 0.532846
H -3.267470 -2.938417 -0.039453
H -0.930521 0.328241 3.761985
H -4.894318 -3.424872 1.751453
H 0.876469 1.112674 4.487287
H 2.633950 2.774808 4.911626
H 3.518270 3.358166 -1.753641
H -2.835270 -0.753120 4.388166
H 1.769781 1.605393 -2.002230
H -4.686301 -2.332626 3.980457
H 3.835665 -3.865679 -3.056230
H 4.176865 -4.101625 -0.533261
H -3.268010 2.937829 0.039629
H -0.931776 -0.329715 -3.761476
H -4.896424 3.422211 -1.750435
H 0.876098 -1.112500 -4.487352
H 2.633737 -2.774470 -4.911899
H 3.518462 -3.358083 1.753289
H -2.837753 0.749930 -4.386908
H 1.770032 -1.605296 2.002061
H -4.689447 2.328580 -3.978851

Total Energy: -2864.16942645 Hartree

S6.2 $[Fe(qsal)_2]^+$: B3LYP*/def2-TZVP IS geometry.

Fe	0.457434	0.000107	-0.000124
N	1.956339	1.446225	0.164722
N	0.584375	0.300954	2.124339
N	1.956787	-1.445384	-0.165046
N	0.584224	-0.300623	-2.124492
O	-0.785540	-1.346013	0.345874
O	-0.786101	1.345735	-0.345712
C	3.739660	2.946458	3.044401
C	3.986852	3.312268	0.589805
C	-2.918139	-2.052116	1.002711
C	-0.441913	0.074041	2.890705
C	2.332562	1.757140	1.440379
C	-3.919003	-2.129011	1.949328
C	2.047706	1.390555	3.813324
C	-1.727158	-1.344434	1.262661
C	3.093424	2.299404	4.070183
C	3.567871	3.003079	-0.679139
C	-2.634143	-0.803070	3.476505
C	3.373205	2.689902	1.701683
C	-1.584033	-0.700226	2.533107
C	2.544953	2.053158	-0.849675
C	1.639713	1.132580	2.517301
C	-3.784375	-1.503877	3.199914
C	3.740059	-2.945333	-3.044915
C	3.987593	-3.311075	-0.590342
C	-2.919239	2.050630	-1.002084
C	-0.442299	-0.074149	-2.890673
C	2.332932	-1.756255	-1.440744
C	-3.920379	2.126962	-1.948457
C	2.047664	-1.389821	-3.813661
C	-1.727916	1.343641	-1.262319
C	3.093558	-2.298441	-4.070632

C	3.568702	-3.001935	0.678645
C	-2.635101	0.801828	-3.475972
C	3.373719	-2.688820	-1.702157
C	-1.584718	0.699553	-2.532820
C	2.545636	-2.052195	0.849294
C	1.639792	-1.131904	-2.517590
C	-3.785684	1.501950	-3.199095
H	4.540094	3.648717	3.249367
H	4.782339	4.031997	0.753655
H	-3.020678	-2.530923	0.036093
H	-0.477922	0.538428	3.879857
H	-4.825849	-2.677274	1.716545
H	1.566298	0.888094	4.644967
H	3.389624	2.487099	5.096309
H	4.009710	3.469092	-1.550843
H	-2.516294	-0.309067	4.436233
H	2.199062	1.783578	-1.841156
H	-4.578810	-1.571028	3.933478
H	4.540607	-3.647439	-3.249962
H	4.783181	-4.030675	-0.754269
H	-3.021832	2.529342	-0.035426
H	-0.478275	-0.538537	-3.879825
H	-4.827494	2.674669	-1.715427
H	1.566006	-0.887521	-4.645256
H	3.389664	-2.486104	-5.096791
H	4.010715	-3.467868	1.550304
H	-2.517188	0.307912	-4.435738
H	2.199800	-1.782675	1.840809
H	-4.580336	1.568637	-3.932465

Total Energy: -2864.14382875 Hartree

S6.3 $[Fe(qsal)_2]^+$: B3LYP*/def2-TZVP HS geometry.

Fe	0.092436	0.002965	0.000133
N	1.664713	1.546310	0.110486
N	0.371738	0.362824	2.133577
N	1.664089	-1.542287	-0.108397
N	0.372410	-0.359310	-2.132640
O	-1.179972	-1.328868	0.517732
O	-1.177819	1.336393	-0.519246
C	3.300917	3.345513	2.900011
C	3.573750	3.550745	0.438056
C	-2.655859	-2.809265	1.584490
C	-0.322253	-0.240886	3.064088
C	1.997376	1.953653	1.365969
C	-3.212727	-3.300919	2.746293
C	1.694643	1.741349	3.746873
C	-1.687292	-1.782180	1.623819
C	2.670516	2.734119	3.955649
C	3.205465	3.132418	-0.814609
C	-1.897436	-1.795326	4.070491
C	2.975337	2.967350	1.578502
C	-1.295929	-1.263508	2.901535
C	2.240612	2.117625	-0.931935
C	1.335240	1.339287	2.470956
C	-2.836776	-2.795881	4.004376
C	3.302396	-3.341897	-2.896524
C	3.573330	-3.546967	-0.434396
C	-2.657474	2.811622	-1.588131
C	-0.324118	0.240709	-3.063638
C	1.997597	-1.949953	-1.363569
C	-3.217146	3.298642	-2.750530
C	1.697012	-1.737564	-3.744701
C	-1.687934	1.785366	-1.625829
C	2.672963	-2.730399	-3.952691

C	3.204238	-3.128391	0.817934
C	-1.902956	1.789912	-4.072196
C	2.975714	-2.963668	-1.575303
C	-1.298574	1.262740	-2.902588
C	2.239444	-2.113431	0.934426
C	1.336272	-1.335733	-2.469095
C	-2.843182	2.789712	-4.007659
H	4.046335	4.115588	3.065359
H	4.318389	4.329301	0.569304
H	-2.948136	-3.191986	0.613541
H	-0.154746	0.041868	4.104824
H	-3.956288	-4.089227	2.687233
H	1.229921	1.301130	4.619974
H	2.920077	3.018880	4.971666
H	3.639587	3.563972	-1.707775
H	-1.598364	-1.393394	5.033927
H	1.931670	1.764022	-1.909069
H	-3.284912	-3.191908	4.907267
H	4.047986	-4.111944	-3.061227
H	4.318009	-4.325590	-0.565034
H	-2.948334	3.197305	-0.617934
H	-0.158408	-0.045521	-4.103708
H	-3.961442	4.086349	-2.692707
H	1.233473	-1.296850	-4.618192
H	2.923545	-3.014960	-4.968512
H	3.637748	-3.559794	1.711469
H	-1.605355	1.385013	-5.034846
H	1.930139	-1.759525	1.911319
H	-3.293427	3.182273	-4.911020

Total Energy: -2864.15817369 Hartree

S6.4 $[Fe(qsal)_2]^+$: PBE0/def2-TZVP LS geometry.

Fe	0.057088	-0.000195	0.000034
N	1.505298	1.375215	0.025904
N	0.051476	0.336703	1.917808
N	1.505643	-1.375306	-0.026089
N	0.051166	-0.337193	-1.917726
O	-1.211731	-1.358728	0.126997
O	-1.211966	1.358114	-0.126815
C	3.169719	3.013837	2.895798
C	3.512365	3.268503	0.426378
C	-3.204097	-2.350666	0.820430
C	-0.979904	0.053497	2.667980
C	1.833146	1.756451	1.289413
C	-4.213049	-2.489787	1.749427
C	1.441273	1.475587	3.654745
C	-2.115409	-1.469230	1.046200
C	2.478664	2.398555	3.916740
C	3.140013	2.886734	-0.841870
C	-3.135882	-0.938409	3.231157
C	2.861073	2.700567	1.549164
C	-2.074757	-0.768676	2.298892
C	2.125427	1.920401	-1.001339
C	1.088580	1.170978	2.350014
C	-4.194132	-1.774622	2.967415
C	3.169894	-3.013501	-2.896328
C	3.513023	-3.268178	-0.426971
C	-3.204959	2.349181	-0.819696
C	-0.980593	-0.054550	-2.667584
C	1.833340	-1.756453	-1.289664
C	-4.214401	2.487609	-1.748272
C	1.440998	-1.475590	-3.654928
C	-2.116054	1.468079	-1.045693
C	2.478552	-2.398317	-3.917133

C	3.140835	-2.886500	0.841353
C	-3.137259	0.936271	-3.230063
C	2.861419	-2.700344	-1.549627
C	-2.075653	0.767233	-2.298228
C	2.126093	-1.920365	1.001028
C	1.088444	-1.171141	-2.350125
C	-4.195758	1.772090	-2.966054
H	3.963413	3.731946	3.111761
H	4.304335	4.005994	0.581613
H	-3.224144	-2.891126	-0.127125
H	-1.018287	0.487470	3.676841
H	-5.046648	-3.162313	1.529792
H	0.923623	1.003518	4.492115
H	2.735726	2.628983	4.953285
H	3.619431	3.313618	-1.723692
H	-3.094536	-0.388033	4.175062
H	1.813668	1.586510	-1.994013
H	-5.004498	-1.891802	3.688850
H	3.963706	-3.731432	-3.112450
H	4.305109	-4.005511	-0.582361
H	-3.224791	2.889899	0.127716
H	-1.019159	-0.488738	-3.676347
H	-5.048185	3.159841	-1.528439
H	0.923089	-1.003586	-4.492177
H	2.735502	-2.628641	-4.953729
H	3.620502	-3.313300	1.723080
H	-3.096096	0.385665	-4.173841
H	1.814475	-1.586540	1.993767
H	-5.006528	1.888684	-3.687130

Total Energy: -2864.279546306 Hartree

S6.5 $[Fe(qsal)_2]^+$: PBE0/def2-TZVP IS geometry.

Fe	0.556823	0.000151	-0.000145
N	2.042366	1.429459	0.200181
N	0.626955	0.292233	2.115471
N	2.042730	-1.428697	-0.200561
N	0.626819	-0.291930	-2.115699
O	-0.693341	-1.325993	0.306059
O	-0.693657	1.326005	-0.306110
C	3.797882	2.880668	3.120708
C	4.068659	3.284375	0.667741
C	-2.935227	-1.821984	0.750528
C	-0.470333	0.167585	2.801239
C	2.406075	1.719702	1.479021
C	-4.040468	-1.744604	1.577731
C	2.082306	1.320044	3.846641
C	-1.713617	-1.213902	1.111603
C	3.135423	2.218223	4.129754
C	3.657891	2.993093	-0.612627
C	-2.795922	-0.468260	3.186325
C	3.445585	2.645317	1.767796
C	-1.644170	-0.522633	2.364064
C	2.632856	2.044133	-0.804135
C	1.690007	1.086557	2.539448
C	-3.981739	-1.060879	2.805695
C	3.798335	-2.879475	-3.121264
C	4.069409	-3.283162	-0.668321
C	-2.935965	1.820686	-0.749925
C	-0.470677	-0.167796	-2.801214
C	2.406398	-1.718866	-1.479437
C	-4.041442	1.742578	-1.576757
C	2.082329	-1.319249	-3.847031
C	-1.714138	1.213265	-1.111339
C	3.135649	-2.217160	-4.130245

C	3.658703	-2.991959	0.612085
C	-2.796695	0.466779	-3.185626
C	3.446098	-2.644232	-1.768315
C	-1.644717	0.521894	-2.363745
C	2.633481	-2.043220	0.803698
C	1.690083	-1.085902	-2.539801
C	-3.982725	1.058762	-2.804662
H	4.604043	3.581136	3.348498
H	4.868477	4.006944	0.850697
H	-2.974824	-2.342821	-0.207406
H	-0.547825	0.673043	3.777593
H	-4.974154	-2.216513	1.261059
H	1.577380	0.802812	4.665959
H	3.425814	2.390342	5.168891
H	4.112428	3.477496	-1.477684
H	-2.732829	0.068211	4.137025
H	2.281853	1.782589	-1.806523
H	-4.863169	-0.995391	3.445676
H	4.604648	-3.579742	-3.349133
H	4.869373	-4.005552	-0.851350
H	-2.975548	2.341586	0.207976
H	-0.548192	-0.673348	-3.777519
H	-4.975301	2.213963	-1.259817
H	1.577194	-0.802132	-4.666294
H	3.426007	-2.389181	-5.169407
H	4.113436	-3.476253	1.477099
H	-2.733610	-0.069784	-4.136274
H	2.282549	-1.781728	1.806123
H	-4.864338	0.992659	-3.444327

Total Energy: -2864.258874143 Hartree

S6.6 $[Fe(qsal)_2]^+$: PBE0/def2-TZVP HS geometry.

Fe	0.119757	0.002303	0.000211
N	1.677948	1.527114	0.098484
N	0.403645	0.341232	2.114429
N	1.678481	-1.523092	-0.096675
N	0.404331	-0.338410	-2.113466
O	-1.146026	-1.325371	0.495521
O	-1.145365	1.330551	-0.496387
C	3.340155	3.315871	2.878130
C	3.592320	3.526252	0.409133
C	-2.692315	-2.755083	1.531436
C	-0.315639	-0.244443	3.037812
C	2.024714	1.927568	1.347484
C	-3.276082	-3.231975	2.688261
C	1.733903	1.705705	3.731245
C	-1.687012	-1.759495	1.582639
C	2.713131	2.700457	3.937072
C	3.204958	3.112598	-0.843657
C	-1.930210	-1.769658	4.035861
C	3.004404	2.939980	1.556121
C	-1.303060	-1.253469	2.870040
C	2.233076	2.098949	-0.951429
C	1.366646	1.307766	2.453829
C	-2.897170	-2.745662	3.956864
C	3.341816	-3.312589	-2.875274
C	3.593257	-3.522191	-0.406190
C	-2.694500	2.755874	-1.534143
C	-0.316296	0.244859	-3.037339
C	2.025624	-1.924029	-1.345433
C	-3.279748	3.229633	-2.691511
C	1.735734	-1.702809	-3.729371
C	-1.687928	1.761492	-1.584012
C	2.715165	-2.697480	-3.934607

C	3.205567	-3.108090	0.846338
C	-1.933241	1.766171	-4.037130
C	3.005544	-2.936360	-1.553494
C	-1.304568	1.253175	-2.870711
C	2.233586	-2.094458	0.953509
C	1.367791	-1.304745	-2.452181
C	-2.901223	2.741238	-3.959428
H	4.091447	4.091171	3.042713
H	4.345508	4.308445	0.536724
H	-2.990652	-3.128880	0.550267
H	-0.158683	0.052134	4.085134
H	-4.050724	-4.000486	2.615731
H	1.269501	1.257339	4.610676
H	2.972082	2.987744	4.958765
H	3.633390	3.552175	-1.745456
H	-1.626381	-1.371724	5.008560
H	1.898743	1.745557	-1.930270
H	-3.371806	-3.137526	4.857727
H	4.093307	-4.087808	-3.039362
H	4.346575	-4.304333	-0.533348
H	-2.992632	3.131274	-0.553531
H	-0.160053	-0.053757	-4.084178
H	-4.055368	3.997249	-2.619976
H	1.271858	-1.254463	-4.609091
H	2.974642	-2.984886	-4.956136
H	3.633857	-3.547261	1.748404
H	-1.629774	1.366458	-5.009215
H	1.899223	-1.740687	1.932188
H	-3.377004	3.130710	-4.860728

Total Energy: -2864.285826012 Hartree

S6.7 $[Fe(pap)_2]^+$: B3LYP*/def2-TZVP LS geometry.

Fe	0.003350	-0.001210	-0.001041
N	-0.866777	-1.144288	-1.293742
N	1.199841	0.361395	-1.579160
N	0.670956	1.218837	1.341215
N	1.398865	-1.193628	0.824849
O	-1.273633	-0.672899	1.204623
O	-1.055340	1.450439	-0.556806
C	-2.152435	-1.456923	0.610035
C	-3.263552	-1.991274	1.287852
C	-4.145814	-2.806942	0.605656
C	-3.965673	-3.118434	-0.756298
C	-2.887064	-2.603673	-1.444785
C	-1.979881	-1.773799	-0.767313
C	-0.430635	-1.082389	-2.512421
C	0.730104	-0.244111	-2.709807
C	1.336083	-0.026932	-3.947611
C	2.434560	0.816712	-4.024873
C	2.914201	1.416023	-2.864093
C	2.265024	1.161646	-1.662275
C	-0.934641	2.486076	0.249695
C	-1.696720	3.656762	0.084303
C	-1.520292	4.708558	0.961599
C	-0.592681	4.643191	2.020865
C	0.170241	3.508765	2.202136
C	0.005772	2.430152	1.318400
C	1.564449	0.756412	2.158980
C	2.003749	-0.594466	1.892873
C	2.964680	-1.268120	2.648567
C	3.307996	-2.566919	2.304830
C	2.685640	-3.167500	1.213815
C	1.737790	-2.443932	0.501082
H	-3.411347	-1.742210	2.332171

H -5.002075 -3.216168 1.130856
H -4.678413 -3.758520 -1.262094
H -2.745381 -2.839007 -2.494312
H -0.907670 -1.591526 -3.345879
H 0.937020 -0.512600 -4.830560
H 2.911154 1.009303 -4.979302
H 3.769656 2.079426 -2.883633
H 2.597842 1.620937 -0.738616
H -2.412626 3.707401 -0.727799
H -2.109417 5.610027 0.830590
H -0.478627 5.487081 2.690795
H 0.885694 3.453085 3.015844
H 1.957348 1.320494 3.000747
H 3.429501 -0.770112 3.491267
H 4.049855 -3.107442 2.881607
H 2.927206 -4.178940 0.912294
H 1.226216 -2.878183 -0.350125

Total Energy: -2557.15080505 Hartree

S6.8 $[Fe(pap)_2]^+$: B3LYP*/def2-TZVP IS geometry.

Fe -0.026974 0.048658 0.174363
O -1.427975 -0.815620 1.238632
O -1.005485 1.544103 -0.421500
N -0.884163 -1.138161 -1.277599
N 1.288872 0.349742 -1.710979
N 0.711927 1.296802 1.488093
N 1.412698 -1.162646 0.989425
C -2.240852 -1.597750 0.575716
C -3.357992 -2.218335 1.171262
C -4.177777 -3.028620 0.411301
C -3.926547 -3.252271 -0.955419
C -2.843834 -2.653731 -1.565987

C -1.994771 -1.826791 -0.811150
C -0.446373 -1.078693 -2.490843
C 0.708603 -0.246924 -2.776419
C 1.177658 -0.041995 -4.076676
C 2.256104 0.809076 -4.275317
C 2.849688 1.417178 -3.173900
C 2.329683 1.155031 -1.909660
C -0.856926 2.588740 0.369972
C -1.589099 3.775777 0.184939
C -1.382992 4.835888 1.044099
C -0.456771 4.763424 2.106232
C 0.275475 3.613738 2.308899
C 0.080427 2.526292 1.441424
C 1.596258 0.808157 2.303469
C 2.015997 -0.555373 2.053765
C 2.956648 -1.229128 2.831348
C 3.283777 -2.540319 2.509860
C 2.665428 -3.147661 1.422571
C 1.733714 -2.420321 0.688040
H -3.557205 -2.032696 2.220371
H -5.036398 -3.501437 0.875876
H -4.588500 -3.890015 -1.529005
H -2.657823 -2.825878 -2.620733
H -0.929323 -1.610057 -3.308838
H 0.689736 -0.534341 -4.910560
H 2.630253 0.998667 -5.275161
H 3.694803 2.085257 -3.285330
H 2.763133 1.616247 -1.027329
H -2.303947 3.830465 -0.627648
H -1.947517 5.750679 0.898589
H -0.322196 5.615248 2.762062
H 0.987815 3.551865 3.124651
H 2.002358 1.369001 3.141993

H 3.419899 -0.727488 3.672730

H 4.010781 -3.082531 3.103763

H 2.896202 -4.166588 1.138135

H 1.222904 -2.858517 -0.161507

Total Energy: -2557.12777064 Hartree

S6.9 $[Fe(pap)_2]^+$: B3LYP*/def2-TZVP HS geometry.

Fe -0.311573 -0.031902 0.202910

N -1.065794 -1.274036 -1.421614

N 0.964604 0.408623 -1.606479

N 0.744701 1.353158 1.525069

N 1.319675 -1.200084 1.189622

O -1.652808 -1.094533 1.083416

O -1.270764 1.629228 -0.072447

C -2.392493 -1.922477 0.379541

C -3.454245 -2.656294 0.939311

C -4.193200 -3.506422 0.137940

C -3.909745 -3.657766 -1.232060

C -2.877529 -2.944777 -1.807270

C -2.114792 -2.074927 -1.011771

C -0.590763 -1.095104 -2.604478

C 0.519299 -0.165998 -2.749480

C 1.085714 0.135492 -3.987778

C 2.132001 1.047228 -4.047573

C 2.589719 1.626599 -2.870638

C 1.972576 1.277871 -1.672775

C -0.848696 2.721038 0.513755

C -1.439960 3.978925 0.285689

C -0.938915 5.094402 0.926231

C 0.146622 5.006431 1.820379

C 0.737990 3.785462 2.071282

C 0.253058 2.638319 1.421679

C	1.703682	0.894994	2.253423
C	2.042770	-0.512223	2.106324
C	3.044383	-1.127791	2.858035
C	3.303984	-2.477037	2.659212
C	2.551511	-3.178763	1.723662
C	1.566538	-2.498129	1.013797
H	-3.680351	-2.529762	1.991546
H	-5.011744	-4.068839	0.573936
H	-4.506264	-4.331508	-1.835332
H	-2.660523	-3.060614	-2.864204
H	-0.985319	-1.592769	-3.490202
H	0.700879	-0.336893	-4.884453
H	2.582048	1.305453	-4.999399
H	3.403655	2.341123	-2.871157
H	2.295694	1.718853	-0.736217
H	-2.279782	4.044525	-0.395969
H	-1.392765	6.061436	0.737808
H	0.515690	5.899113	2.310713
H	1.572853	3.718008	2.760884
H	2.264627	1.505658	2.961371
H	3.605248	-0.550856	3.584684
H	4.078261	-2.975940	3.230937
H	2.723099	-4.231538	1.535464
H	0.953618	-3.013623	0.281478

Total Energy: -2557.14092420 Hartree