Electronic Supplementary Material (ESI) for Dalton Transactions.

Spin state and reactivity of iron(IV)oxido complexes with tetradentate bispidine ligands

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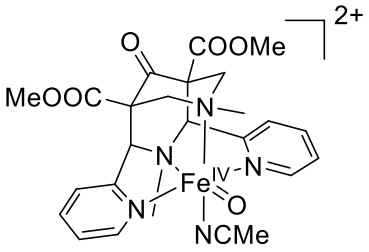
For the bispidine-acetonitrile-iron(IV)-oxido complex [(bispidine)Fe^{IV}=O(MeCN)]$^{2+}$ (Chart S1), there is a preliminary Mössbauer spectrum with an isotope shift that supports an *S*=1 electronic ground state (Figure S1). The sample was prepared from a 4 mM solution of ^{57}Fe-labeled [(bispidine)Fe^{II}(MeCN)$_2$](OTf)$_2$ in MeCN with addition of an ^{s}PhIO suspension in MeCN (20 mM) at 238 K and freezing of the resulting solution in liquid nitrogen after 30 seconds.



[(bispidine)Fe^{IV}=O(MeCN)]$^{2+}$

Chart S1. Structure of the bispidine-acetonitrile-iron(IV)-oxido complex

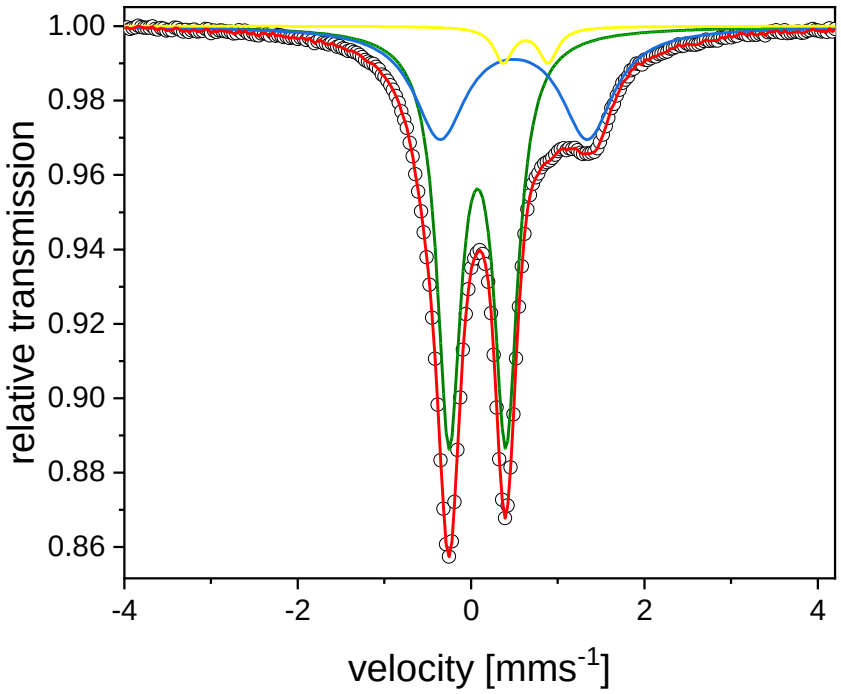


Figure S1. Mössbauer spectrum of in-situ-prepared [(bispidine)$^{57}Fe^{IV}$=O(MeCN)]$^{2+}$ (approx. 4 mM in MeCN) at 80 K (measured by Dr. E. Bill at the Max-Planck Institute for Chemical Energy Conversion in Mülheim, Germany).

The spectrum consist of 3 species with that in green assigned to [(bispidine)Fe^{IV}=O(MeCN)]$^{2+}$; the blue and yellow minor components are tentatively assigned to the unreacted iron(II) precursor and an iron(III) decay product. The isotope shift δ = 0.07 mm s^{-1} and the quadrupole splitting ΔE_Q = 0.66 mm s^1 of [(bispidine)Fe^{IV}=O(MeCN)]$^{2+}$ are as expected for *S* = 1 Fe^{IV}=O. This assignment supports the analysis given in the main text, based on electronic spectroscopy.

The computational methods and program packages used are described in detail in the Experimental Section of the publication. The DLPNO-CCSD(T) protocol used involves the optimization of the structure with B3LYP/def2-TZVP (PCM solvation, MeCN), followed by single point gas phase DLPNO-CCSD(T) calculations to determine the electronic ground state of the optimized geometries. The experimental setup and protocol used is slightly different to that in a recent publication also dealing with ferryl complexes.[1] Correlation consistent basis sets were used.[2, 3] These provide the advantages that it is relatively easy to extrapolate the energy to the complete basis set limit (CBS) and that they provide a large basis for the iron center. Moreover, HF orbitals were taken as starting point for the DLPNO-CCSD(T) calculations, and a well-established protocol was used for the extrapolation of the calculated energies to the energies at the complete basis set limit (CBS).[4] Coupled cluster calculations depend heavily on the size of the basis set, and care was taken to increase the size of the basis set such that convergence of the relative energies was reached. The DLPNO-CCSD(T) energies also strongly depend on a number of other factors, including the choice of PNO localization and the wavefunction optimizer. Therefore, the CBS procedure could not be applied rigorously and was used mainly as an indicator for the stability of the calculations rather than a true extrapolation to the basis set limit.

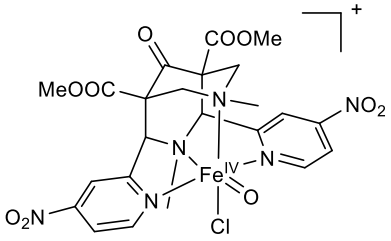
Table S1 gives an overview of the computational results and is an extension of the data tabulated in the main text (Table 1), i.e. it also includes gas-phase DFT calculations for comparison with the DLPNO-CCSD(T) data, which are derived from gas-phase calculations. Moreover, Table S1 also includes CBS data where appropriate. In addition, we have also done a preliminary analysis of two derivatives of [(bispidine)Fe^{IV}=O(Cl)]$^{+}$ with para-substituted pyridines in the bispidine backbone (see Chart 2) that are predicted to lead to a lower ligand field and hence to a smaller quintet-triplet energy gap. Indeed, the data indicate that, at least for the para-nitro-substituted ligand, this might be the case.

Table S2 and Figure S2 include the data of the bench-marking of the DLPNO-CCSD(T) protocol used in this study.

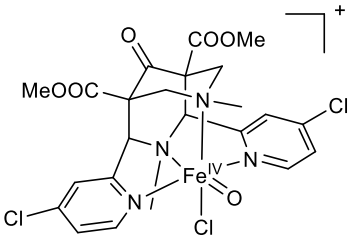
Table S1. Quintet-triplet energy gap in kJ/mol (gas phase energies calculated by a single point calculation: $\Delta E_{gas} = E_{quintet} - E_{triplet}$, *i.e*. a negative entry indicates a quintet ground state. The CASPT2/CC and aug-cc-PVTZ values are taken from the literature.[1]

	DFT (B3LYP) gas phase‡	DFT (B3LYP) PCM (MeCN)‡	DLPNO-CCSD(T)						CASPT2/CC[1]
Basis set	def2-TZVP		cc-PVDZ	cc-PVTZ	cc-PVQZ	cc-PV5Z	CBS	aug-cc-PVTZ†	
TMC (*S*=1)	5.6	10.3	48.3	40.2	41.0	42.0	43.6	-2.1	42.7
TMC-S (*S*=1)	-20.3	-16.4	21.0	17.0#	17.8	-	24.0	-15.1	23.0
NHC (*S*=1)	101.7	108.4	154.0	157.7	185.5	-	-	91.1	123.9
TMG3tren (*S*=2)	-90.5	-96.5	-137.3	-109.0	-107.6	-114.4	-	-	-
bispidine / Cl (*S*=1)	-9.4	-12.1	22.2	11.4	5.7	0.0	-	-	-
bispidine / MeCN (*S*=1)	-10.0	-2.6	22.7	-29.3 (83.3*)	75.7		-	-	-
bispidine-NO_2 / Cl	-		-	-	0.4	-	-	-	-
bispidine-Cl / Cl	-		-	-	6.3	-	-	-	-

loose criteria for the DLPNO-CCSD(T) calculation (the default criteria for the DLPNO-CCSD(T) calculation is NormalPNO.)
* cc-PVQZ basis set on Fe
‡ optimization with the PCM solvent model (MeCN)



bispidine-NO_2



bispidine-Cl

Chart S2. Structure of bispidine-chlorido-iron(IV)-oxido complexes with modified tetradentate bispidine ligands (see additional entries in Table S1).

Table S2. T1 diagnostic obtained from the DLPNO-CCSD(T) calculations with ORCA 4.0.1.2 [5]

T1 Diagnostic		TMC	TMC-S	NHC	TMGTREN	bisp-Cl	bisp-MeCN
cc-PVDZ	S=1	0.03	0.03	0.03	0.04	0.03	0.02
	S=2	0.06	0.05	0.08	0.06	0.03	0.08
cc-PVTZ	S=1	0.02	0.03	0.02	0.02	0.02	0.02
	S=2	0.04	0.04	0.06	0.02	0.03	0.03
cc-PVQZ	S=1	0.02	0.03	0.02	0.02	0.02	0.02
	S=2	0.02	0.03	0.04	0.02	0.02	0.03
cc-PV5Z	S=1	0.02	-	-	0.04	0.03	-
	S=2	0.04	-	-	0.03	0.02	-

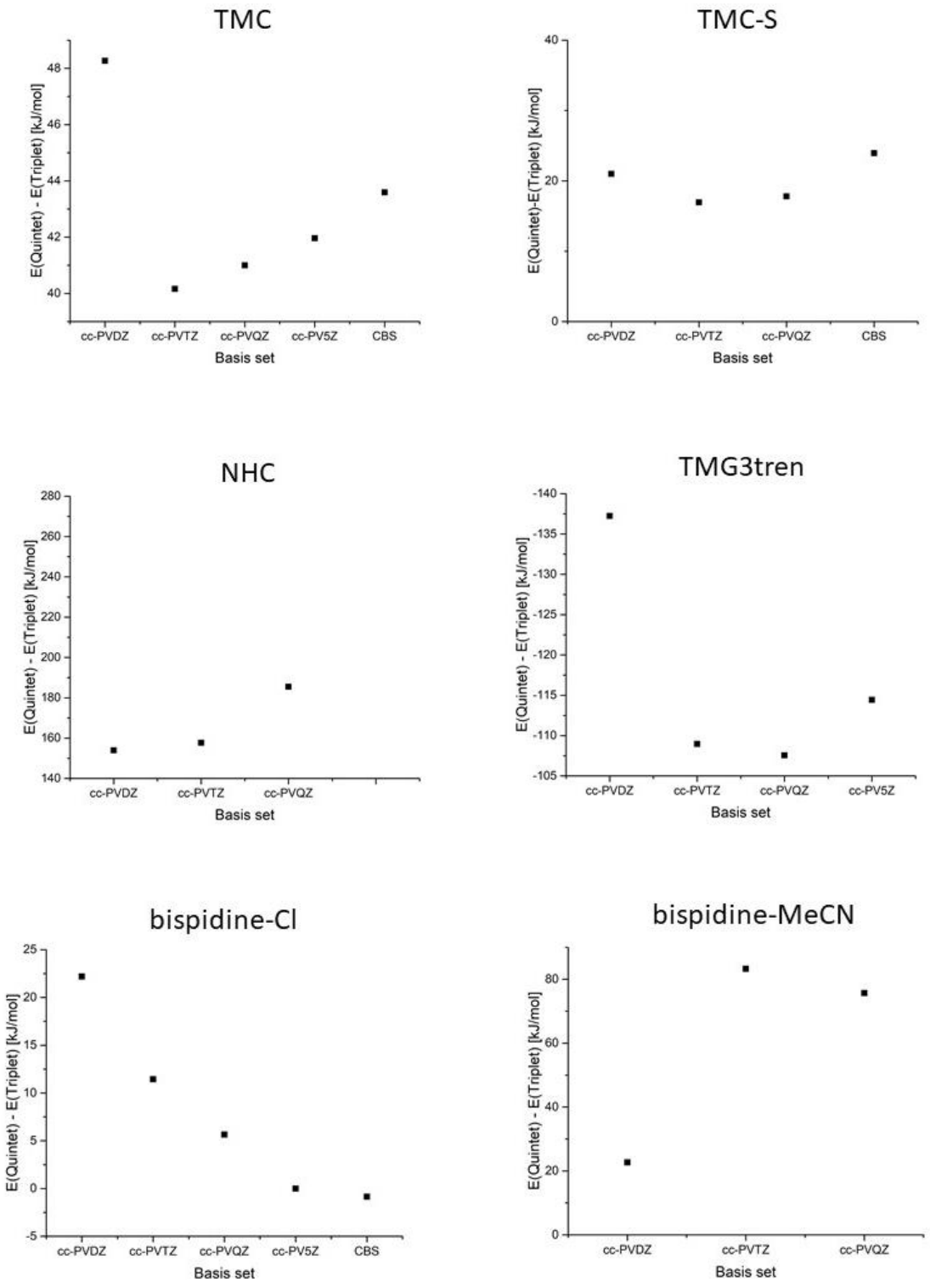


Figure S2. Illustration of the DLPNO-CCSD (T) energies of the complexes as a function of the base set used in the calculation obtained with the ORCA 4.0.1.2 package.[5] CBS extrapolation was performed using the implementation of V. Vasilyev.[4, 6]

References

1. Q. M. Phung, C. Martín-Fernández, J. N. Harvey and M. Feldt, *J. Chem. Theory Comput.*, 2019, **15**, 4297-4304.
2. T. H. Dunning Jr, *J. Chem. Phys.* , 1989,, **90**, 1007-1023.
3. D. E. Woon and T. H. Dunning Jr., *J. Chem. Phys.* , 1993, **98**.
4. A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper and J. Olsen, *Chem. Phys. Lett.*, 1999, **302**, 437-446.
5. F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* , 2012, **2**, 73-78.
6. V. Vasilyev, *Comput. Theor. Chem.* , 2017, **1115**, 1-3.

Cartesian coordinates

Table S3: Cartesian coordinates of the geometry optimization of $[(TMC)Fe^{IV}(O)(MeCN)]^{2+}$, S=1.

Fe	0.002998	-0.007344	0.001515	H	0.553252	-3.857800	0.873763
O	-0.001116	-0.000277	1.630175	H	0.614242	-2.465696	1.965300
N	2.095349	-0.004573	0.097607	C	2.205440	-2.505017	0.533023
N	0.200201	2.113135	-0.058476	H	2.388950	-2.712817	-0.527779
N	-2.125671	0.063743	-0.055342	H	2.833076	-3.216745	1.083469
N	-0.262696	-2.083062	0.099258	C	2.659448	-1.112064	0.930432
N	0.026185	-0.040306	-2.037309	H	2.362521	-0.920766	1.964913
C	2.379856	1.274701	0.818064	H	3.753447	-1.034356	0.876226
H	3.461553	1.463693	0.822094	C	2.786221	-0.008352	-1.220068
H	2.049737	1.148041	1.850453	H	3.867100	0.090132	-1.060877
C	1.658766	2.417051	0.153944	H	2.444812	0.817981	-1.841283
H	2.100939	2.625540	-0.822455	H	2.587643	-0.943763	-1.744176
H	1.760378	3.331135	0.750396	C	-0.183566	2.845719	-1.297287
C	-0.596737	2.654593	1.093961	H	0.021608	3.914507	-1.157466
H	-0.443295	3.742414	1.111828	H	-1.238959	2.729346	-1.523970
H	-0.170268	2.236737	2.007879	H	0.403174	2.484394	-2.141228
C	-2.096782	2.377084	1.031942	C	-2.804306	0.535065	-1.294551
H	-2.530900	2.871230	1.910687	H	-3.890506	0.472572	-1.152725
H	-2.547214	2.886931	0.172889	H	-2.524644	-0.09781	-2.136085
C	-2.560266	0.924003	1.096929	H	-2.550379	1.564826	-1.526693
H	-2.195902	0.450687	2.010641	C	-0.349394	-2.770800	-1.217076
H	-3.658578	0.907687	1.118175	H	-0.583090	-3.830433	-1.055842
C	-2.609979	-1.345025	0.159227	H	0.602407	-2.693001	-1.743597
H	-3.529677	-1.331319	0.755585	H	-1.127677	-2.329378	-1.837385
H	-2.872130	-1.758179	-0.816866	C	0.023227	-0.048464	-3.186690
C	-1.565990	-2.202307	0.823511	C	0.016192	-0.058200	-4.631548
H	-1.889548	-3.251614	0.831694	H	-1.003427	0.121007	-4.993410
H	-1.395726	-1.887484	1.854313	H	0.364485	-1.032499	-4.993982
C	0.766571	-2.782101	0.930227	H	0.679608	0.729029	-5.008050

Table S4: Cartesian coordinates of the geometry optimization of $[(TMC)Fe^{IV}(O)(MeCN)]^{2+}$, S=2.

Fe	0.002998	-0.007344	0.001515	H	0.553252	-3.857800	0.873763
O	-0.001116	-0.000277	1.630175	H	0.614242	-2.465696	1.965300
N	2.095349	-0.004573	0.097607	C	2.205440	-2.505017	0.533023
N	0.200201	2.113135	-0.058476	H	2.388950	-2.712817	-0.527779
N	-2.125671	0.063743	-0.055342	H	2.833076	-3.216745	1.083469
N	-0.262696	-2.083062	0.099258	C	2.659448	-1.112064	0.930432
N	0.026185	-0.040306	-2.037309	H	2.362521	-0.920766	1.964913
C	2.379856	1.274701	0.818064	H	3.753447	-1.034356	0.876226
H	3.461553	1.463693	0.822094	C	2.786221	-0.008352	-1.220068
H	2.049737	1.148041	1.850453	H	3.867100	0.090132	-1.060877
C	1.658766	2.417051	0.153944	H	2.444812	0.817981	-1.841283
H	2.100939	2.625540	-0.822455	H	2.587643	-0.943763	-1.744176
H	1.760378	3.331135	0.750396	C	-0.183566	2.845719	-1.297287
C	-0.596737	2.654593	1.093961	H	0.021608	3.914507	-1.157466
H	-0.443295	3.742414	1.111828	H	-1.238959	2.729346	-1.523970
H	-0.170268	2.236737	2.007879	H	0.403174	2.484394	-2.141228
C	-2.096782	2.377084	1.031942	C	-2.804306	0.535065	-1.294551
H	-2.530900	2.871230	1.910687	H	-3.890506	0.472572	-1.152725
H	-2.547214	2.886931	0.172889	H	-2.524644	-0.097810	-2.136085
C	-2.560266	0.924003	1.096929	H	-2.550379	1.564826	-1.526693
H	-2.195902	0.450687	2.010641	C	-0.349394	-2.770800	-1.217076
H	-3.658578	0.907687	1.118175	H	-0.583090	-3.830433	-1.055842
C	-2.609979	-1.345025	0.159227	H	0.602407	-2.693001	-1.743597
H	-3.529677	-1.331319	0.755585	H	-1.127677	-2.329378	-1.837385
H	-2.872130	-1.758179	-0.816866	C	0.023227	-0.048464	-3.186690
C	-1.565990	-2.202307	0.823511	C	0.016192	-0.058200	-4.631548
H	-1.889548	-3.251614	0.831694	H	-1.003427	0.121007	-4.993410
H	-1.395726	-1.887484	1.854313	H	0.364485	-1.032499	-4.993982
C	0.766571	-2.782101	0.930227	H	0.679608	0.729029	-5.008050

Table S5: Cartesian coordinates of the geometry optimization of $[(TMC\text{-}S)Fe^{IV}(O)(MeCN)]^{2+}$, S=1.

Fe	-0.018637	0.084878	-0.071360
O	-0.121339	0.323399	-1.708152
N	1.463151	-1.343727	-0.463411
N	-1.441410	-1.573629	-0.253180
N	-1.583886	1.491370	0.277903
N	1.269930	1.803759	-0.062364
C	0.718529	-2.360244	-1.270576
H	1.336490	-3.253457	-1.399228
H	0.551589	-1.919406	-2.248279
C	-0.601799	-2.750027	-0.653353
H	-0.439126	-3.354815	0.233588
H	-1.157345	-3.372691	-1.359510
C	-2.381308	-1.192561	-1.354719
H	-3.054868	-2.039458	-1.525229
H	-1.790966	-1.036667	-2.251897
C	-3.234487	0.044216	-1.067449
H	-3.882100	0.170100	-1.939240
H	-3.918898	-0.146500	-0.240434
C	-2.536752	1.390802	-0.878470
H	-1.978518	1.642874	-1.774536
H	-3.308151	2.153285	-0.728564
C	-0.940298	2.847151	0.262950
H	-1.643190	3.582476	-0.135577
H	-0.742176	3.128435	1.294424
C	0.335905	2.865081	-0.538330
H	0.811561	3.846542	-0.450137
H	0.134278	2.676439	-1.588279
C	2.365697	1.679735	-1.067272
H	2.980736	2.582551	-1.001106
H	1.900704	1.661344	-2.049728
C	3.242063	0.447994	-0.911455
H	3.664650	0.376821	0.091200
H	4.098508	0.583797	-1.576361
C	2.566530	-0.842072	-1.347279
H	2.138033	-0.688027	-2.334231
H	3.309891	-1.641113	-1.427315
C	-2.252262	-2.036490	0.906143
H	-2.741531	-2.979332	0.645593
H	-3.023671	-1.321316	1.156687
H	-1.618450	-2.172804	1.774558
C	-2.346640	1.409528	1.551225
H	-3.070132	2.228609	1.594034
H	-1.667193	1.488404	2.393959
H	-2.878433	0.472218	1.630701
C	1.865119	2.216558	1.233753
H	2.395966	3.163137	1.097519
H	2.552233	1.457692	1.588576
H	1.099638	2.336765	1.991041
C	2.097736	-1.932651	0.767284
H	2.947242	-1.300901	1.011762
H	2.488096	-2.923320	0.511980
C	1.200715	-1.993265	1.987340
H	0.497171	-2.823146	1.940230
H	1.829151	-2.170261	2.861150
S	0.317943	-0.413077	2.220113

Table S6: Cartesian coordinates of the geometry optimization of $[(TMC\text{-}S)Fe^{IV}(O)(MeCN)]^{2+}$, S=2.

Fe	0.020805	0.082414	-0.055777
O	-0.085327	0.312102	-1.697701
N	1.384107	-1.529240	-0.470400
N	-1.616153	-1.551789	-0.229199
N	-1.516000	1.657729	0.278576
N	1.435252	1.835978	-0.079981
C	0.526380	-2.446682	-1.280178
H	1.050220	-3.394433	-1.437740
H	0.390242	-1.971510	-2.246734
C	-0.833362	-2.748939	-0.661824
H	-0.707619	-3.388815	0.207261
H	-1.411539	-3.327431	-1.389323
C	-2.521869	-1.063103	-1.309269
H	-3.271817	-1.839789	-1.503042
H	-1.926123	-0.937584	-2.209010
C	-3.263853	0.242143	-0.994912
H	-3.944166	0.401625	-1.836103
H	-3.919965	0.110669	-0.133962
C	-2.476992	1.551533	-0.867671
H	-1.909688	1.723968	-1.777845
H	-3.202600	2.366133	-0.760483
C	-0.770650	2.955116	0.197334
H	-1.417884	3.720890	-0.238894
H	-0.557421	3.270020	1.216363
C	0.523668	2.886838	-0.599587
H	1.009122	3.867688	-0.554407
H	0.318106	2.659877	-1.641531
C	2.505215	1.538782	-1.076250
H	3.232109	2.358023	-1.047182
H	2.045273	1.539397	-2.061591
C	3.238641	0.212261	-0.868446
H	3.587745	0.112950	0.160268
H	4.147146	0.266777	-1.473454
C	2.504984	-1.044258	-1.341522
H	2.084869	-0.851772	-2.325444
H	3.222547	-1.864875	-1.441995
C	-2.424596	-1.956752	0.943286
H	-3.025663	-2.839166	0.698738
H	-3.099185	-1.163625	1.241784
H	-1.776485	-2.178765	1.784695
C	-2.257321	1.651128	1.562055
H	-2.950641	2.497384	1.598464
H	-1.560091	1.726248	2.391607
H	-2.820933	0.734009	1.678065
C	2.053888	2.270714	1.189566
H	2.646284	3.176236	1.021479
H	2.693173	1.486848	1.581858
H	1.296853	2.476593	1.939754
C	1.959430	-2.178345	0.750771
H	2.884315	-1.655785	0.980381
H	2.218814	-3.215120	0.511129
C	1.062824	-2.108662	1.972819
H	0.255129	-2.836930	1.931178
H	1.656448	-2.347832	2.855990
S	0.383523	-0.423804	2.195096

Table S7: Cartesian coordinates of the geometry optimization of $[(NHC)Fe^{IV}(O)(MeCN)]^{2+}$, S=1.

Fe	-0.013635	-0.000870	-0.262855	C	-0.740868	-2.974221	-1.788855
O	-0.054472	-0.002628	-1.906074	H	-0.459914	-2.153273	-2.444635
N	1.535046	2.731348	-0.668270	H	-1.264665	-3.726841	-2.373868
N	2.718796	1.198580	0.227067	C	-1.510226	-1.328079	-0.106939
N	2.714834	-1.208487	0.229779	C	-2.913821	-3.040063	-0.511225
N	1.526041	-2.739162	-0.662386	H	-3.240631	-3.958203	-0.964653
N	-1.686171	-2.464915	-0.799940	C	-3.524833	-2.228055	0.377394
N	-2.646779	-1.181555	0.611630	H	-4.485515	-2.296936	0.854458
N	-2.642903	1.189930	0.609321	C	-2.945953	0.005402	1.395795
N	-1.678387	2.467412	-0.804957	H	-2.370586	0.005233	2.316122
N	0.120109	0.003061	1.861942	H	-4.003123	0.007322	1.639126
C	1.461042	1.457054	-0.211425	C	-1.506083	1.331313	-0.109876
C	2.812904	3.246663	-0.507787	C	-3.517481	2.238973	0.373384
H	3.068971	4.244090	-0.815769	H	-4.477790	2.312013	0.850594
C	3.561175	2.281839	0.056445	C	-2.903996	3.047248	-0.516937
H	4.596995	2.263665	0.342880	H	-3.227814	3.965638	-0.971976
C	3.132074	-0.004884	0.917492	C	-0.731362	2.971938	-1.794700
H	4.215920	-0.006559	0.972702	H	-1.252676	3.725275	-2.381007
H	2.734986	-0.003256	1.929872	H	-0.453056	2.148961	-2.449051
C	1.456220	-1.463667	-0.208208	C	0.487769	3.627656	-1.184205
C	3.553574	-2.294935	0.061630	H	0.960493	4.230883	-1.957767
H	4.589388	-2.279672	0.348231	H	0.188724	4.300081	-0.378291
C	2.802122	-3.258439	-0.500619	C	0.238747	0.008117	3.002409
H	3.054867	-4.257368	-0.806473	C	0.392176	0.015199	4.441628
C	0.476138	-3.632910	-1.177429	H	-0.482183	0.476251	4.901201
H	0.175064	-4.303552	-0.370791	H	1.281480	0.585295	4.710817
H	0.947106	-4.238382	-1.950311	H	0.494238	-1.007410	4.804256

Table S8: Cartesian coordinates of the geometry optimization of $[(NHC)Fe^{IV}(O)(MeCN)]^{2+}$, S=2.

Fe	0.009433	0.031275	-0.180005	C	0.301058	-3.155521	-1.608184
O	0.024497	0.054840	-1.820272	H	0.424069	-2.307822	-2.279004
N	0.703811	3.127062	-0.495858	H	0.061165	-4.031105	-2.206461
N	2.387241	1.954591	0.123512	C	-1.128554	-1.743891	-0.130058
N	3.138959	-0.367041	0.110567	C	-1.898350	-3.808511	-0.570214
N	2.421572	-2.258903	-0.561109	H	-1.881844	-4.797536	-0.991110
N	-0.868204	-2.901467	-0.761209	C	-2.830451	-3.187599	0.185723
N	-2.338788	-1.919001	0.443929	H	-3.781309	-3.528103	0.554227
N	-3.119362	0.345689	0.420177	C	-3.049073	-0.881882	1.189458
N	-2.474153	1.977526	-0.790358	H	-2.537945	-0.695795	2.129634
N	0.070223	0.014564	1.936111	H	-4.054903	-1.232845	1.393962
C	1.054886	1.882861	-0.106207	C	-2.010717	0.969505	-0.034217
C	1.809425	3.966074	-0.505326	C	-4.272935	0.958136	-0.047012
H	1.740643	5.001499	-0.785132	H	-5.260009	0.614387	0.204974
C	2.869238	3.230472	-0.116947	C	-3.861492	1.998099	-0.806963
H	3.904120	3.492480	0.008460	H	-4.425284	2.738435	-1.345599
C	3.190625	0.922590	0.768942	C	-1.610526	2.870198	-1.562955
H	4.221184	1.261662	0.773010	H	-2.263488	3.564705	-2.085818
H	2.857121	0.812904	1.798837	H	-1.073965	2.281689	-2.306138
C	1.998769	-1.074677	-0.072535	C	-0.644250	3.685093	-0.708327
C	4.261484	-1.097072	-0.250014	H	-0.483452	4.639578	-1.203084
H	5.260403	-0.706667	-0.174810	H	-1.089808	3.891375	0.265217
C	3.805336	-2.293992	-0.671863	C	0.146515	0.019366	3.079626
H	4.333625	-3.155333	-1.038885	C	0.239337	0.023529	4.523582
C	1.593705	-3.437129	-0.847188	H	-0.718383	0.320886	4.950717
H	1.380316	-3.959774	0.086100	H	1.008159	0.729072	4.838451
H	2.206718	-4.096072	-1.458125	H	0.498374	-0.974514	4.876631

Table S9: Cartesian coordinates of the geometry optimization of $[(TMG_3tren)Fe^{IV}(O)]^{2+}$, S=1.

Fe	-0.022569	-0.373784	0.235976
O	0.095200	-0.625015	-1.340043
N	1.822201	-1.051064	0.693607
N	-1.983596	-0.881310	0.510485
N	-0.112713	-0.224572	2.429413
N	-0.093928	1.595219	0.374125
C	2.226484	-0.858241	2.092305
C	0.992267	-1.068433	2.947210
H	2.651831	0.131703	2.275041
H	2.991861	-1.582531	2.378459
H	1.187861	-0.843183	4.000116
H	0.677151	-2.108836	2.873452
C	-2.074354	-1.555982	1.814514
C	-1.443884	-0.703181	2.893183
H	-1.535925	-2.507833	1.741496
H	-3.103059	-1.802475	2.076326
H	-1.339674	-1.256956	3.828633
H	-2.068821	0.162596	3.096259
C	-0.564374	2.047214	1.688486
C	0.075584	1.208543	2.774335
H	-1.650829	1.935454	1.721298
H	-0.359987	3.104304	1.846105
H	-0.352404	1.422823	3.756650
H	1.139673	1.418658	2.829531
C	0.382121	2.494149	-0.496108
C	2.740606	-1.545844	-0.152302
C	-3.087910	-0.788904	-0.230004
N	-3.063069	-0.989368	-1.569552
N	-4.303281	-0.512688	0.324012
N	0.149200	2.384510	-1.819802
N	1.093182	3.580826	-0.086562
N	2.401057	-2.456131	-1.085715
N	4.045467	-1.182157	-0.072759
C	2.036753	3.552145	1.020101
H	2.257902	2.528195	1.299388
H	1.661502	4.091755	1.893679
H	2.965501	4.029776	0.701633
C	0.914079	4.895766	-0.696712
H	0.067623	4.883860	-1.376043
H	1.808166	5.211398	-1.239248
H	0.715812	5.625057	0.091760
C	1.130646	2.784199	-2.820608
H	0.806696	3.668459	-3.374557
H	1.257297	1.964133	-3.530323
H	2.088187	2.986316	-2.350305
C	-1.100087	1.867475	-2.354700
H	-0.941405	0.921914	-2.870448
H	-1.506741	2.599310	-3.057560
H	-1.807770	1.716113	-1.547209
C	-4.470204	0.386120	1.454810
H	-3.583549	0.999257	1.575207
H	-4.668628	-0.152092	2.385964
H	-5.319065	1.043644	1.257594
C	-5.526527	-1.180543	-0.110101
H	-6.021150	-1.611736	0.763169
H	-5.293397	-1.984392	-0.801258
H	-6.219365	-0.483555	-0.587448
C	-3.955059	-0.290313	-2.486029
H	-4.736067	-0.948265	-2.875902
H	-3.371399	0.074316	-3.333143
H	-4.418886	0.557699	-1.990871
C	-2.265236	-2.043948	-2.180017
H	-1.752668	-2.606778	-1.408599
H	-1.525373	-1.636392	-2.867172
H	-2.934271	-2.71202	-2.730446
C	3.034563	-2.506451	-2.398863
H	3.663803	-1.634855	-2.549782
H	2.251617	-2.504324	-3.159562
H	3.633088	-3.411226	-2.525046
C	1.315439	-3.408465	-0.901101
H	0.961677	-3.379393	0.124288
H	1.688967	-4.410608	-1.124883
H	0.487044	-3.184505	-1.572095
C	5.144446	-2.109438	-0.325179
H	5.672852	-1.873109	-1.251518
H	4.771966	-3.128128	-0.373913
H	5.853741	-2.038482	0.501613
C	4.447519	0.166204	0.304469
H	5.225727	0.503365	-0.382356
H	4.847522	0.203872	1.320511
H	3.601701	0.840895	0.219591

Table S10: Cartesian coordinates of the geometry optimization of $[(TMG_3tren)Fe^{IV}(O)]^{2+}$, S=2.

Fe	-0.007790	-0.253085	0.278004	C	0.642683	2.899890	-2.975185
O	0.115433	-0.376455	-1.339456	H	0.259094	3.778968	-3.497560
N	1.755844	-1.168793	0.684394	H	0.597581	2.048180	-3.657075
N	-1.902331	-1.014462	0.597733	H	1.679623	3.068413	-2.701686
N	-0.034394	-0.076053	2.434599	C	-1.486809	2.081080	-2.066532
N	-0.012827	1.789824	0.399741	H	-1.443208	1.098922	-2.534449
C	2.209706	-0.984593	2.071677	H	-1.990200	2.778784	-2.739976
C	0.981814	-1.029022	2.955010	H	-2.050901	2.012405	-1.142069
H	2.747212	-0.044965	2.218382	C	-4.317767	0.547600	1.302690
H	2.893485	-1.784698	2.362403	H	-3.400495	1.127318	1.322287
H	1.224086	-0.790117	3.994379	H	-4.544058	0.187555	2.309934
H	0.550159	-2.028296	2.927560	H	-5.129737	1.207137	0.990511
C	-2.037411	-1.436429	2.001530	C	-5.469273	-1.177719	-0.010939
C	-1.396969	-0.418814	2.924536	H	-5.999879	-1.430917	0.909701
H	-1.539624	-2.404760	2.111388	H	-5.287304	-2.094084	-0.564067
H	-3.077729	-1.592319	2.286115	H	-6.107877	-0.518876	-0.604011
H	-1.340673	-0.790064	3.951054	C	-3.837498	-0.749751	-2.468284
H	-1.987566	0.492972	2.937597	H	-4.623813	-1.434068	-2.795222
C	-0.280786	2.276346	1.761110	H	-3.220083	-0.505273	-3.334555
C	0.319729	1.328759	2.778802	H	-4.290740	0.163774	-2.095876
H	-1.365435	2.338223	1.896967	C	-2.120141	-2.417327	-1.923102
H	0.100849	3.282291	1.931286	H	-1.712680	-2.955014	-1.074396
H	-0.020916	1.561492	3.791157	H	-1.302176	-2.021071	-2.524393
H	1.403168	1.418822	2.768713	H	-2.713895	-3.104078	-2.530641
C	0.342317	2.676311	-0.540753	C	2.856013	-2.677874	-2.428659
C	2.637833	-1.685782	-0.185517	H	3.492878	-1.817904	-2.611164
C	-3.008054	-0.964525	-0.155260	H	2.059688	-2.685175	-3.175077
N	-2.988541	-1.351943	-1.447073	H	3.441501	-3.592853	-2.543828
N	-4.204774	-0.537625	0.339667	C	1.179614	-3.544803	-0.859864
N	-0.149773	2.586355	-1.792188	H	0.787227	-3.415587	0.143037
N	1.197990	3.702424	-0.283146	H	1.579210	-4.557133	-0.965047
N	2.246445	-2.586321	-1.107105	H	0.377556	-3.415541	-1.582932
N	3.953147	-1.356273	-0.143824	C	5.018184	-2.319359	-0.410176
C	2.289768	3.598048	0.672793	H	5.531374	-2.109474	-1.351171
H	2.423202	2.565574	0.976177	H	4.615540	-3.327320	-0.436944
H	2.113304	4.213555	1.558602	H	5.747829	-2.259926	0.399469
H	3.210976	3.942707	0.198203	C	4.405654	-0.017466	0.208427
C	1.057997	5.015826	-0.904487	H	5.169011	0.292257	-0.507479
H	0.108913	5.085632	-1.426896	H	4.841632	0.015376	1.209751
H	1.871333	5.222067	-1.603967	H	3.577000	0.680588	0.147731
H	1.079503	5.776046	-0.120860				

Table S11: Cartesian coordinates of the geometry optimization of $[(L_1)Fe^{IV}(O)(MeCN)]^{2+}$, S=1.

Fe	-1.056350	1.117186	0.595939	H	2.322463	-0.498979	2.100776
C	2.055064	-0.264598	-0.025199	H	-0.997257	-1.802030	1.877959
C	1.727160	-1.749301	-0.227202	H	0.676376	-2.140455	2.225902
C	0.263726	-2.042225	0.117337	H	1.678755	0.355170	-2.038122
C	0.039499	-3.570155	0.064906	H	-3.543616	4.650061	-2.112212
C	3.556773	-0.069600	-0.338722	H	-4.499932	4.491727	-0.623104
C	-0.090789	-5.463292	-1.348380	H	-4.806963	3.406494	-1.995973
C	5.749837	-0.406224	0.487759	H	0.763945	-0.447638	3.789229
C	1.717221	0.110584	1.429144	H	-0.934336	-0.015099	3.490112
C	0.016490	-1.576934	1.564659	H	0.314165	1.227191	3.390514
C	1.222205	0.540273	-1.066277	H	-0.294853	0.054895	-3.223021
C	-0.615364	-1.290029	-0.924014	H	-0.601863	1.665522	-2.550138
C	1.280740	2.020422	-0.741074	H	-1.850863	0.419918	-2.453687
C	1.330907	4.613691	0.152282	H	2.921988	2.541276	-2.007155
C	0.407619	3.696794	0.626694	H	-0.505287	-1.812178	-1.873508
C	-2.061534	-1.318456	-0.472267	H	-2.681366	-3.054649	-1.557214
C	-3.616750	-0.347391	0.967732	H	-3.814174	0.449653	1.670300
C	-4.560246	-1.313607	0.658518	H	-4.957163	-3.053766	-0.539454
C	-2.967566	-2.298737	-0.840534	H	-5.529826	-1.286192	1.134102
C	-3.065585	3.008052	-0.911787	H	2.959690	4.909162	-1.219790
C	-4.035475	3.943287	-1.443533	H	1.328196	5.623186	0.537043
C	0.092672	0.182121	3.203278	H	-0.331965	3.952805	1.371788
C	-0.781721	0.603734	-2.414933	N	0.277248	-0.120336	1.750198
C	-4.235504	-2.295866	-0.267087	N	-0.234857	0.157266	-1.100667
C	2.215536	2.894973	-1.271123	N	0.387096	2.432079	0.183787
C	2.237799	4.210768	-0.818978	N	-2.397989	-0.355375	0.411197
H	0.830979	-5.888618	-0.961453	N	-2.299276	2.270610	-0.485347
H	-0.173452	-5.624727	-2.416899	O	-0.059425	-4.015391	-1.181020
H	-0.942879	-5.879687	-0.817831	O	4.306333	-0.413989	0.691537
H	6.003997	-1.102286	-0.306701	O	2.514713	-2.566919	-0.602344
H	6.170550	-0.723380	1.434571	O	-0.003041	-4.237766	1.060386
H	6.078930	0.596150	0.228100	O	3.949539	0.319711	-1.406659
H	1.961349	1.148608	1.633284	O	-1.645910	1.813305	1.942698

Table S12: Cartesian coordinates of the geometry optimization of $[(L_1)Fe^{IV}(O)(MeCN)]^{2+}$, S=2

Fe	-1.530901	0.325078	0.636340	H	2.337963	0.921590	2.100398
C	1.882546	0.944661	-0.006816	H	0.291109	-2.063965	1.920116
C	2.446343	-0.464765	-0.232488	H	1.895533	-1.451061	2.226270
C	1.416148	-1.538574	0.131503	H	1.172359	1.227015	-2.000711
C	2.095174	-2.924106	0.030046	H	-5.985590	1.891899	-1.974231
C	3.001867	1.950684	-0.365009	H	-6.544351	1.183678	-0.444029
C	3.035049	-4.517316	-1.446196	H	-6.310222	0.150280	-1.869632
C	5.025229	2.924181	0.384380	H	1.033597	0.035621	3.875151
C	1.455405	1.052604	1.470670	H	-0.609195	-0.570086	3.570797
C	1.009384	-1.313409	1.601966	H	-0.284936	1.160103	3.474739
C	0.709216	1.140151	-1.018060	H	-0.313409	-0.103780	-3.157447
C	0.237407	-1.406291	-0.881745	H	-1.474055	1.042963	-2.458448
C	-0.069987	2.406492	-0.713520	H	-1.792824	-0.688041	-2.366237
C	-1.510661	4.599125	0.104567	H	1.034234	3.740277	-1.967468
C	-1.775142	3.330949	0.590946	H	0.616048	-1.745727	-1.845127
C	-0.928104	-2.275155	-0.451402	H	-0.389225	-4.043297	-1.529559
C	-2.805137	-2.401986	0.932092	H	-3.452010	-1.872920	1.617691
C	-3.000489	-3.733590	0.608605	H	-2.268616	-5.370606	-0.576514
C	-1.081784	-3.597758	-0.830708	H	-3.819408	-4.280243	1.052953
C	-4.554213	0.783714	-0.930156	H	-0.282951	5.731413	-1.248971
C	-5.928579	1.015876	-1.327975	H	-2.089378	5.440942	0.455902
C	0.126653	0.174006	3.281877	H	-2.553872	3.140015	1.315791
C	-1.014679	0.067507	-2.339146	N	0.438661	0.034899	1.833926
C	-2.132591	-4.335774	-0.293178	N	-0.285406	0.002738	-1.034502
C	0.231066	3.646741	-1.252118	N	-1.071952	2.264150	0.182641
C	-0.502280	4.755219	-0.838174	N	-1.793159	-1.694891	0.408326
H	4.043445	-4.350382	-1.078005	N	-3.465591	0.600137	-0.613624
H	3.035008	-4.670877	-2.519105	O	2.239715	-3.314810	-1.231021
H	2.585107	-5.358451	-0.925574	O	3.845674	2.105867	0.636823
H	5.603543	2.481589	-0.421804	O	3.551769	-0.689941	-0.628923
H	5.580284	2.914016	1.314888	O	2.459200	-3.526195	1.000766
H	4.722623	3.933406	0.119070	O	3.075309	2.478157	-1.444140
H	1.055219	2.040633	1.685894	O	-2.421359	0.563623	1.967896

Table S13: Cartesian coordinates of the geometry optimization of $[(L_1)Fe^{IV}(O)(Cl)]^+$, S=1.

Fe	0.049292	-1.760313	0.430505	H	-2.224809	0.235510	1.603670
C	-1.333551	1.453703	0.035779	H	-1.407373	1.673364	2.185040
C	-0.097514	2.345316	-0.077027	H	1.941820	0.410433	1.889548
C	1.180163	1.559516	0.209302	H	0.942604	1.774151	2.341105
C	2.367107	2.542393	0.210490	H	-1.464015	0.860519	-2.015538
C	-2.565954	2.340076	-0.237482	H	-0.288543	0.474478	3.806280
C	3.796258	3.856941	-1.139740	H	0.687032	-0.959358	3.398896
C	-4.131422	3.819265	0.735060	H	-1.073244	-1.035678	3.282812
C	-1.347985	0.860183	1.459690	H	0.223794	-0.059755	-3.260344
C	1.043661	0.958352	1.622300	H	-0.632236	-1.535198	-2.743495
C	-1.246011	0.359432	-1.073046	H	1.119581	-1.461215	-2.620612
C	1.334560	0.476978	-0.903847	H	-3.842506	0.102300	-2.026947
C	-2.280698	-0.719699	-0.820799	H	1.618425	0.998315	-1.816509
C	-4.059046	-2.676705	-0.105276	H	4.043670	0.453156	-1.534122
C	-2.757089	-2.664585	0.365175	H	2.527755	-3.201777	1.344332
C	2.422209	-0.506390	-0.518647	H	5.726786	-1.168043	-0.675571
C	2.919430	-2.404958	0.729663	H	4.962887	-3.020867	0.822487
C	4.266151	-2.296967	0.425635	H	-5.466491	-1.676593	-1.385429
C	3.749512	-0.357240	-0.883172	H	-4.731747	-3.462821	0.205485
C	-0.206431	-0.396202	3.150885	H	-2.374240	-3.425618	1.028681
C	0.207413	-0.879758	-2.539047	N	-0.129148	0.057933	1.734959
C	4.685197	-1.265741	-0.401659	N	0.088594	-0.319286	-1.159878
C	-3.560799	-0.688958	-1.348358	N	-1.894903	-1.705462	0.012950
C	-4.462376	-1.681993	-0.983790	N	2.024786	-1.525479	0.267731
Cl	0.226365	-3.583161	-0.962548	O	2.739925	2.872954	-1.018579
H	3.482254	4.791103	-0.679416	O	-3.015076	2.906159	0.871771
H	3.946834	3.983527	-2.206411	O	-0.133624	3.520589	-0.324665
H	4.701668	3.490007	-0.661437	O	2.859886	2.970396	1.222623
H	-3.851260	4.649405	0.090386	O	-3.024610	2.511891	-1.338644
H	-4.340918	4.165415	1.741410	O	0.007194	-2.709466	1.746713
H	-4.989121	3.295257	0.319288				

Table S14: Cartesian coordinates of the geometry optimization of $[(L_1)Fe^{IV}(O)(Cl)]^+$, S=2.

Fe	0.074963	-1.878865	0.447190	H	-2.229322	0.266077	1.653169
C	-1.346800	1.453068	0.056731	H	-1.453277	1.742901	2.195610
C	-0.119186	2.353963	-0.064838	H	1.931230	0.472987	1.933117
C	1.162741	1.580605	0.228672	H	0.954454	1.864605	2.354537
C	2.345466	2.569068	0.194743	H	-1.430917	0.835468	-1.987063
C	-2.580318	2.326452	-0.253458	H	-0.300367	0.545201	3.886647
C	3.733498	3.881974	-1.199683	H	0.686989	-0.874693	3.465334
C	-4.194717	3.788243	0.661907	H	-1.072179	-0.965090	3.348010
C	-1.362675	0.904157	1.500906	H	0.217938	-0.127944	-3.208218
C	1.033357	1.021378	1.662019	H	-0.621573	-1.603610	-2.667165
C	-1.245299	0.338159	-1.035358	H	1.129531	-1.508912	-2.547900
C	1.319377	0.480466	-0.871506	H	-3.812456	0.126279	-2.074426
C	-2.307202	-0.718500	-0.809291	H	1.557832	1.001907	-1.797428
C	-4.147047	-2.639259	-0.147542	H	3.997191	0.549116	-1.612372
C	-2.862897	-2.645918	0.368675	H	2.746071	-3.113501	1.382625
C	2.455746	-0.455062	-0.515130	H	5.773040	-0.994288	-0.801895
C	3.077370	-2.310905	0.739197	H	5.146068	-2.849659	0.754527
C	4.405208	-2.159775	0.377532	H	-5.487451	-1.619135	-1.482563
C	3.760258	-0.260456	-0.937719	H	-4.846015	-3.410574	0.141527
C	-0.210886	-0.316109	3.217146	H	-2.520802	-3.412237	1.049515
C	0.211332	-0.936138	-2.474443	N	-0.138412	0.137788	1.808800
C	4.748262	-1.126127	-0.482369	N	0.088473	-0.355735	-1.100550
C	-3.567461	-0.665502	-1.382524	N	-1.969955	-1.705975	0.040113
C	-4.498656	-1.640679	-1.044882	N	2.130543	-1.475032	0.299492
Cl	0.280538	-3.752931	-0.973474	O	2.684355	2.895056	-1.046119
H	3.428302	4.817500	-0.736197	O	-3.075126	2.886333	0.839197
H	3.856031	4.003660	-2.270532	O	-0.165924	3.529247	-0.312028
H	4.652473	3.521023	-0.743058	O	2.864739	3.004960	1.189893
H	-3.900130	4.620666	0.026658	O	-3.002379	2.496200	-1.369893
H	-4.443251	4.133052	1.659818	O	0.034717	-2.783312	1.788411
H	-5.032024	3.255710	0.216457				