Supporting Information belonging to the manuscript:

Biological Activity of Fe(III) *acquo*-complexes towards Ferric Chelate Reductase (FCR)

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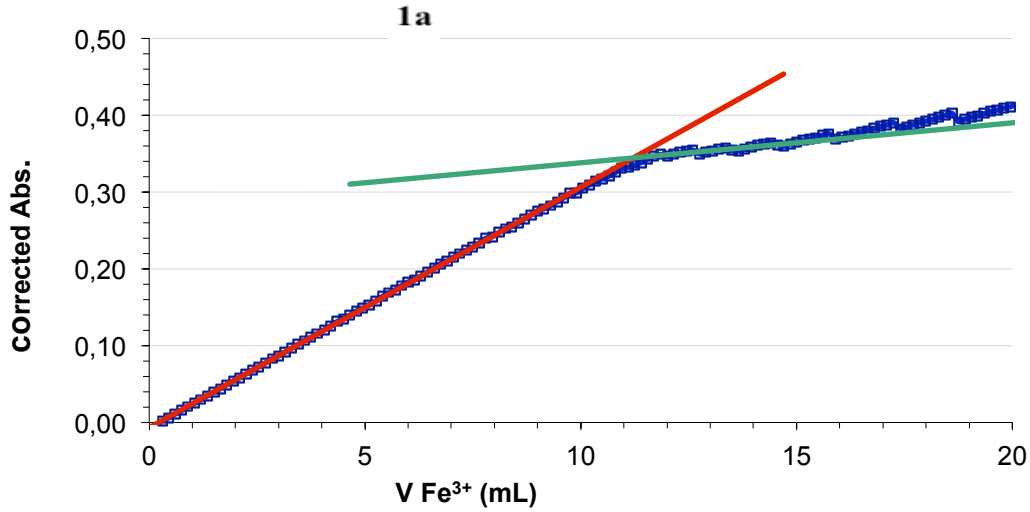
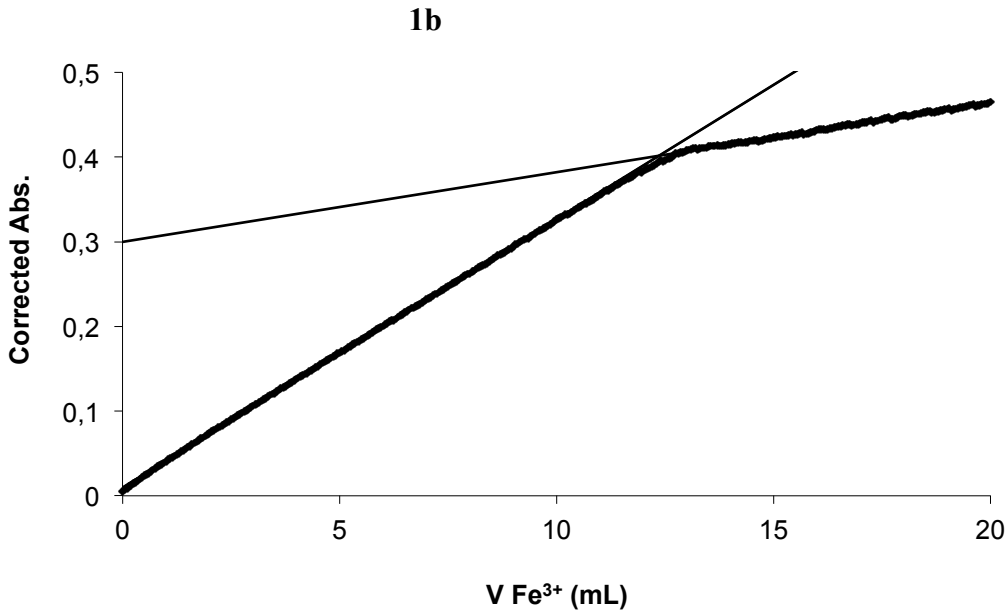
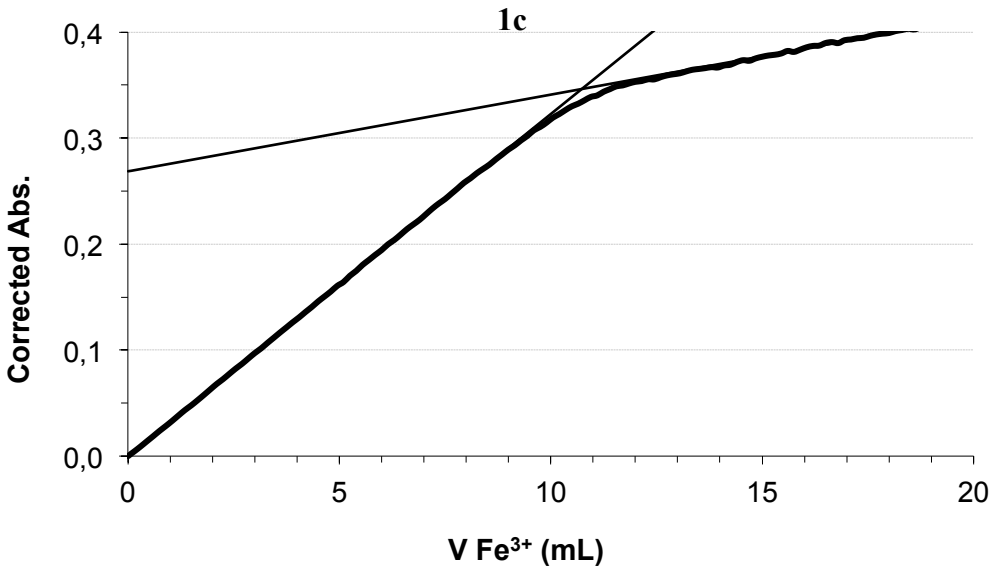
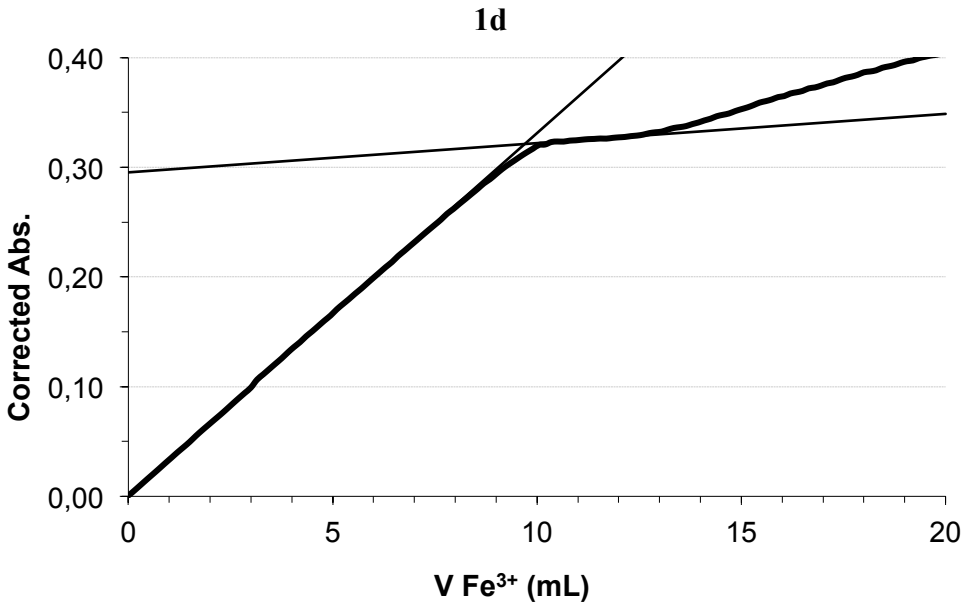
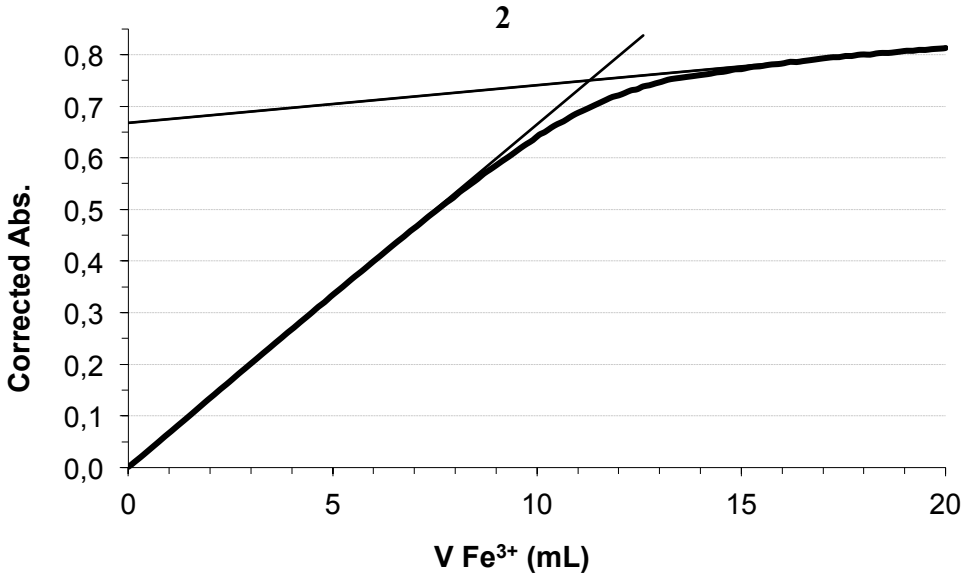
1S. Fe(III) Complexing ability of the chelating agents 1a-d and 2



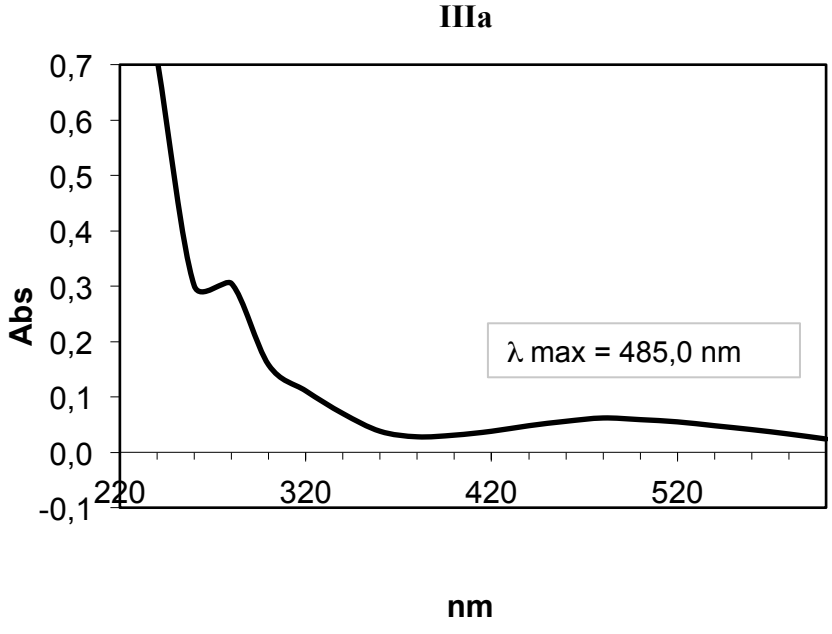




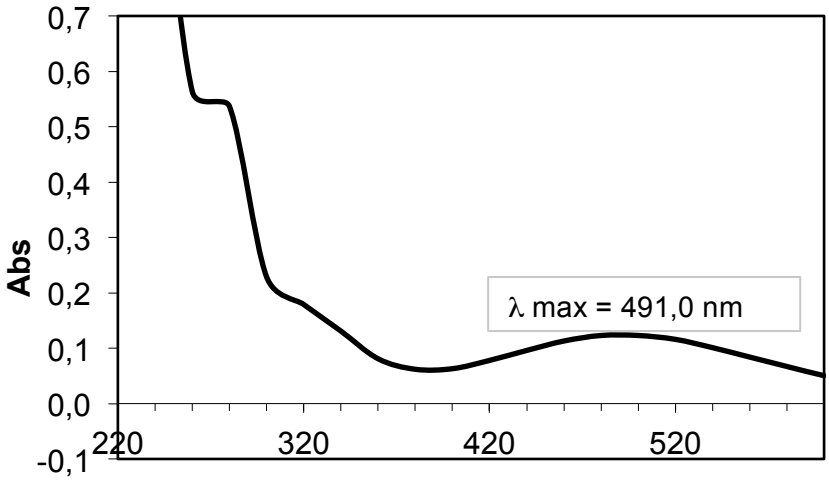




2S. UV-visible spectra

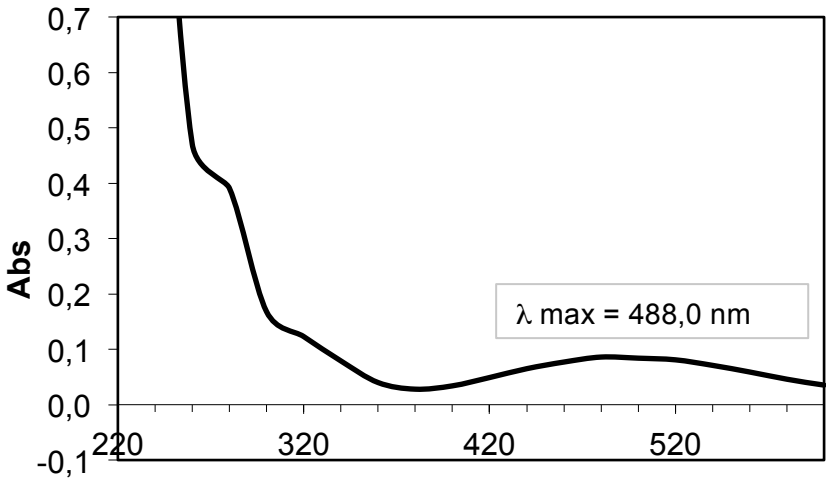


IIIc



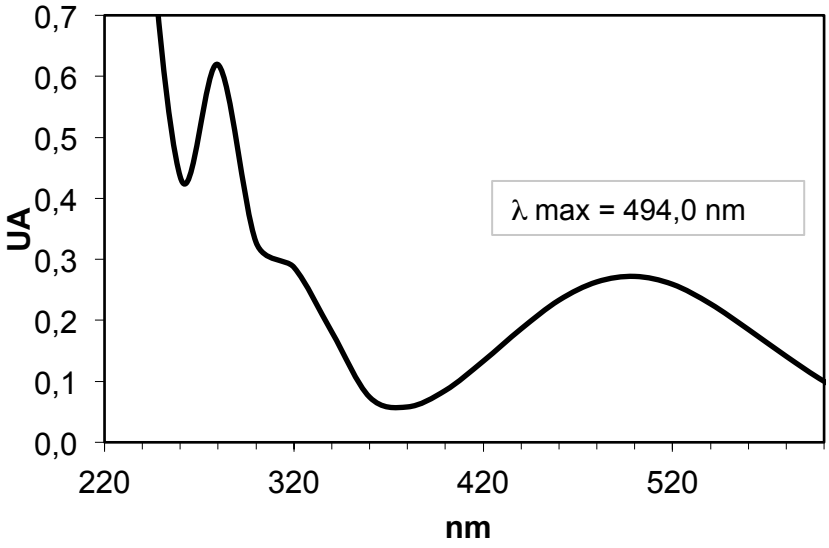
nm

IIId



nm

IV



3S. Electrochemistry

Cyclic voltammetric experiments were performed at room temperature in 0.1 M phosphate buffer. A Metrohm 6.084.010 glassy carbon electrode (GCE) was used as working electrode. A BAS MF 2063 Ag/AgCl 3 M reference and a Pt wire counter electrode were employed. All voltammetric measurements were carried out using a PGSTAT 12 potentiostat from Autolab. The electrochemical software was the General Purpose Electrochemical System (GPES) (EcoChemie B.V.).

3S.1. Redox properties of the ligands 1a-d and 2.

Cyclic voltammograms of 1 mM water solutions of the ligands at pH values ranging from 5.0 to 10.

Table S1

	1a	**1b**	**1c**	**1d**	**2**	***o,o*-EDDHA (I)**
pH	E_{pa}	E_{pa}	E_{pa}	E_{pa}	E_{pa}	E_{pa}
5,0	1.10	0.97	1.31	1.07	0.75	0.93
6,0	0.85	0.89	0.92	1.11	0.75	0.80
7.0	0.83	0.85	0.88	1.11	0.66	0.73
8,0	0.76	0.71	0.74	1.07	0.60	0.78
9,0	0.72	0.68	0.78	1.08	0.53	0.75
10.0	0.70	0.67	0.72	1.09	0.49	0.67

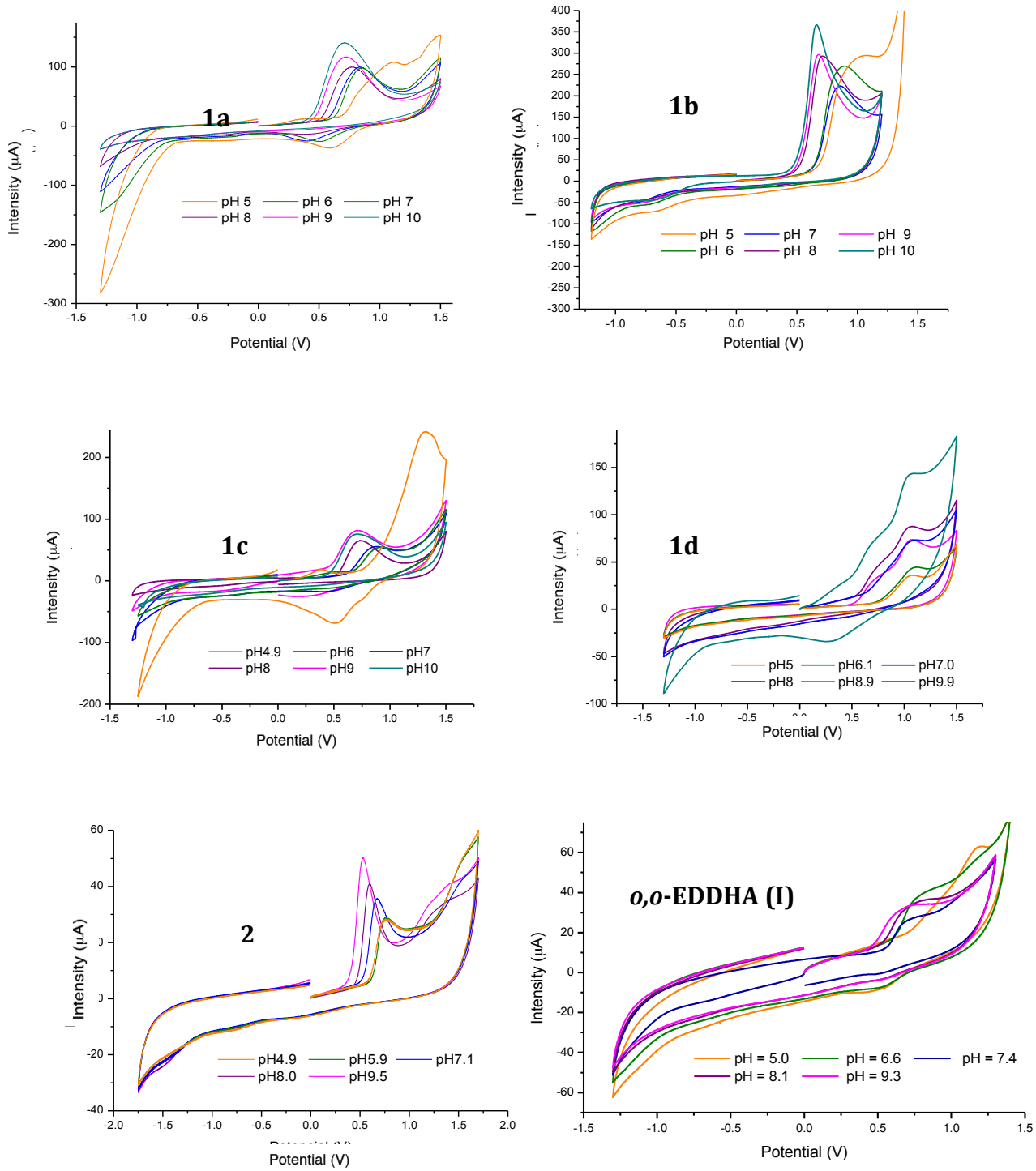


Figure S1. Cyclic voltammograms of the chelating agents **1a-d**, **2** and the reference compound ***o,o*-EDDHA (I)**.

3S.2. Redox properties of the Fe(III) complexes IIIa-d and IV.

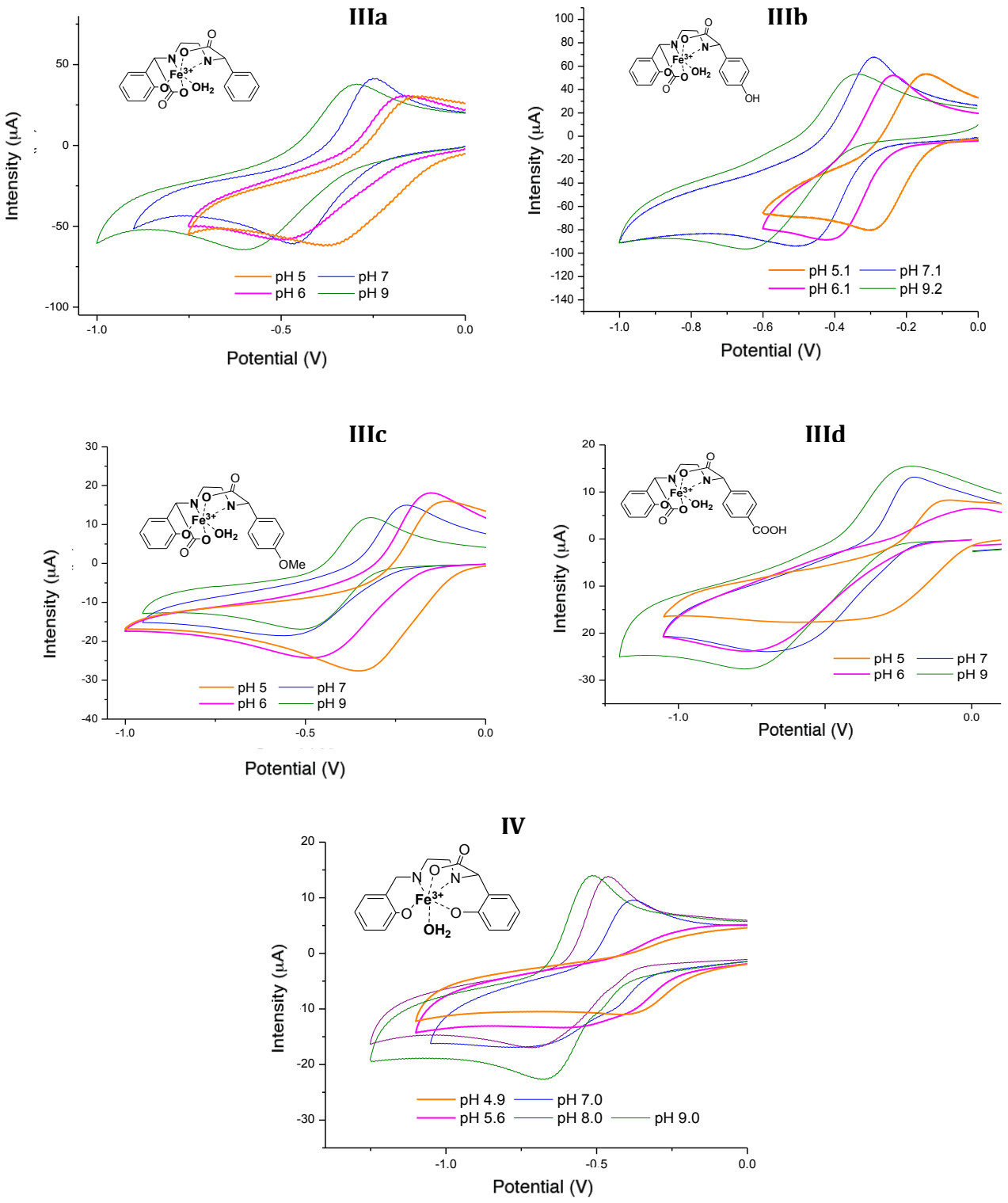


Figure S2. Cyclic voltammograms of the *acquo* complexes **IIIa-d** and **IV**.

Preparation of solid samples of Fe(III) complexes

A solution of the corresponding aminoacid in 5 mL water, at pH 8 (NaOH 1.75 M) was stirred for 10 min at room temperature and then a solution the equimolar amount of $Fe(NO_3)_3.9H_2O$ in 1 mL water was added slowly. During the addition the pH was maintained between 6.5-7.5 with NaOH 1M. After the addition, the pH was adjusted to 7 and the purple solution was kept at 0˚C for 12 h. After removal of the solids by filtration, the solvent was eliminated under vacuum to yield the complexes as purple solids.

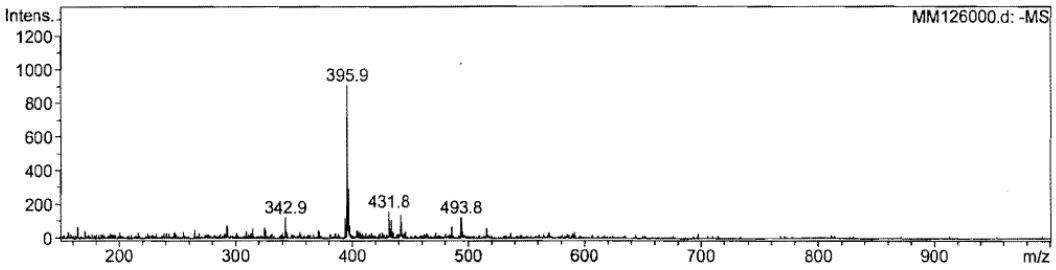
Fe(III) complex of 1a

IR (KBr) ν **:** 3426 ,1632, 1477, 1456, 1384, 1266 $cm.^{-1}$

ESI-MS *m/z* (H_2O/MeOH) 396 $[M-H]^-$, 432 $[M-Cl]^-$,

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	n/a
Mass Range Mode	Std/Normal	Scan Begin	150.00 m/z	Scan End	1000.00 m/z
Capillary Exit	-13.6 Volt	Skim 1	-7.3 Volt	Trap Drive	48.3
Accumulation Time	88000 µs	Averages	14 Spectra	Auto MS/MS	Off



#	m/z	I	FWHM	S/N
1	342.9	124	0.4	24.6
2	393.8	120	0.4	23.8
3	394.9	19	0.4	3.8
4	395.9	907	0.4	179.8
5	396.9	294	0.4	58.3
6	397.9	77	0.3	15.3
7	398.8	20	0.3	4.0
8	431.8	158	0.3	31.3
9	433.9	104	0.3	20.6
10	441.9	138	0.4	27.3
11	493.8	124	0.4	24.6

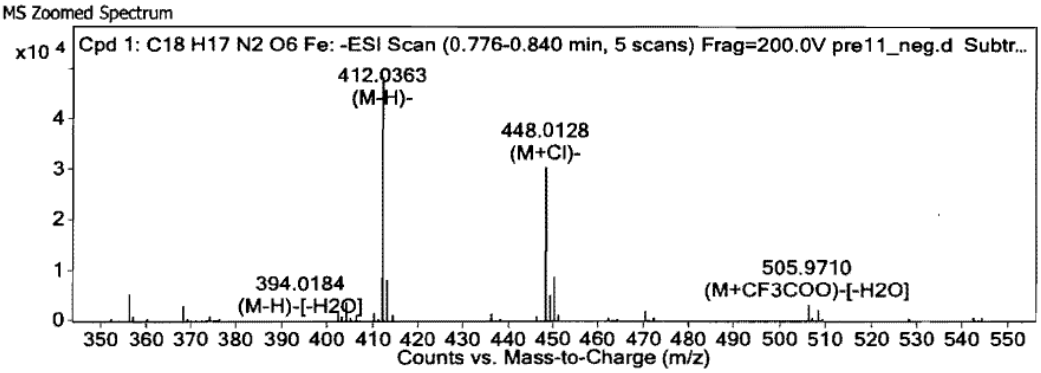
Fe(III) complex of 1b

IR (KBr) ν **:** 3408,1635, 1477, 1453, 1349, 1266 cm^{-1}.

ESI-MS *m/z* (H_2O/MeOH) 412 $[M-H]^-$.

Compound Label	RT	Algorithm	Mass
Cpd 1: C18 H17 N2 O6 Fe	0.808	Find By Formula	411.0481

MS Zoomed Spectrum



MS Spectrum Peak List

m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
394.0184	394.0258	-18.79	1	133	C18 H14 Fe N2 O5	(M-H)-[-H2O]
412.0363	412.0363	-0.16		48255	C18 H16 Fe N2 O6	(M-H)-
413.0394	413.0392	0.38		8353	C18 H16 Fe N2 O6	(M-H)-
440.0292	440.0313	-4.78	1	146	C19 H16 Fe N2 O7	(M+HCOO)-[-H2O]
448.0128	448.0131	-0.68	1	30632	C18 H17 Cl Fe N2 O6	(M+Cl)-
449.0157	449.0159	-0.63	1	5219	C18 H17 Cl Fe N2 O6	(M+Cl)-
450.0111	450.0109	0.28	1	8831	C18 H17 Cl Fe N2 O6	(M+Cl)-
472.051	472.0575	-13.76	1	758	C20 H20 Fe N2 O8	(M+CH3COO)-
473.9635	473.9521	23.99	1	183	C18 H15 Br Fe N2 O5	(M+Br)-[-H2O]
505.971	506.0233	-103.31	1	3490	C20 H15 F3 Fe N2 O7	(M+CF3COO)-[-H2O]

--- End Of Report ---

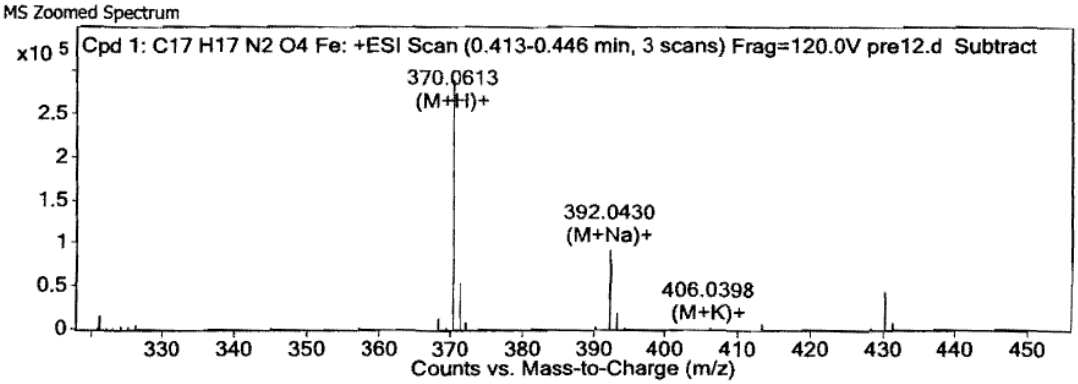
Fe(III) complex of 2

IR (KBr) ν **:** 3396, 3260, 1625, 1599, 1478, 1449, 1356, 1271 cm^{-1}.

ESI-MS *m/z* (H_2O/MeOH) 370 $[M+H]^+$.

Compound Label	RT	Algorithm	Mass
Cpd 1: C17 H17 N2 O4 Fe	0.446	Find By Formula	367.0587

MS Zoomed Spectrum

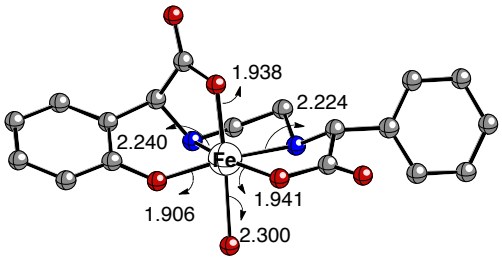


MS Spectrum Peak List

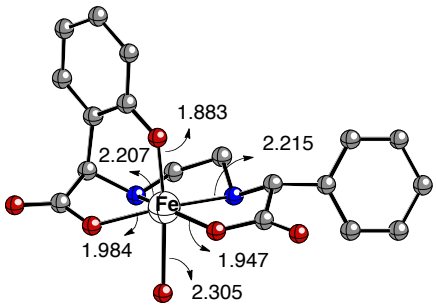
m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
368.064	368.0848	-56.44		14508	C17 H19 Fe N3 O3	(M+NH4)+[-H2O]
370.0613	370.0611	0.73		290217	C17 H18 Fe N2 O4	(M+H)+
371.0644	371.0639	1.18		54635	C17 H18 Fe N2 O4	(M+H)+
372.0661	372.0658	0.78		8652	C17 H18 Fe N2 O4	(M+H)+
374.0117	374.0324	-55.56		95	C17 H15 Fe N2 Na O3	(M+Na)+[-H2O]
385.0945	385.0923	5.81	1	823	C17 H21 Fe N3 O4	(M+NH4)+
390.0451	390.0064	99.22	1	5063	C17 H15 Fe K N2 O3	(M+K)+[-H2O]
392.043	392.043	0.08	1	92365	C17 H17 Fe N2 Na O4	(M+Na)+
393.0457	393.0459	-0.4	1	20107	C17 H17 Fe N2 Na O4	(M+Na)+
406.0398	406.0216	44.79	1	3270	C17 H17 Fe K N2 O4	(M+K)+

4S. Cartesian coordinates

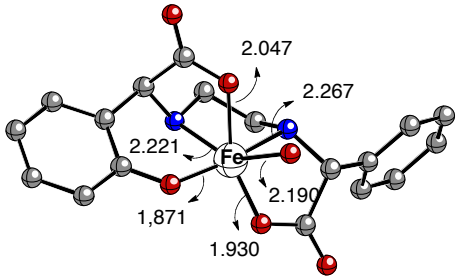
Cartesian coordinates (in Å) and total energies (in a. u., non corrected zero-point vibrational energies included) of all the stationary points discussed in the text. All calculations have been performed at the B3LYP/6-311+G(d) + DZPVE level of theory.



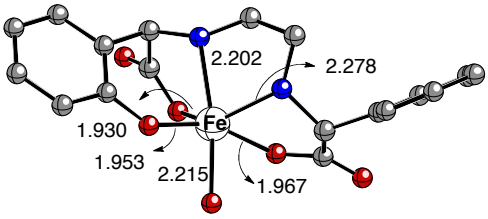
IIIa1 (*S* = 5/2), E_{rel} **= +1.7**



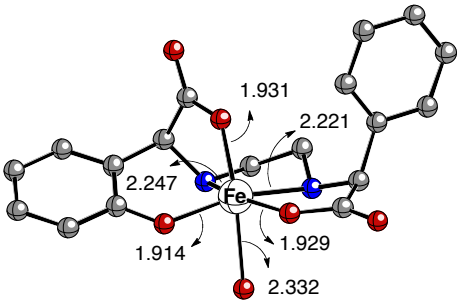
IIIa2 (*S* = 5/2), E_{rel} **= + 3.8**



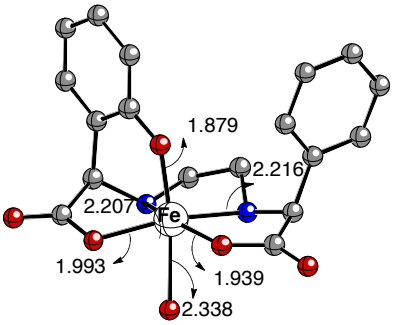
IIIa3 (*S* = 5/2), E_{rel} **= 0.0**



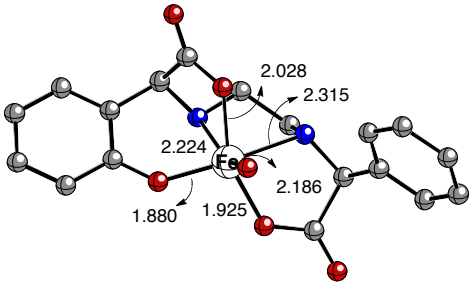
IIIa4(*S* = 5/2), E_{rel} **= +13.0**



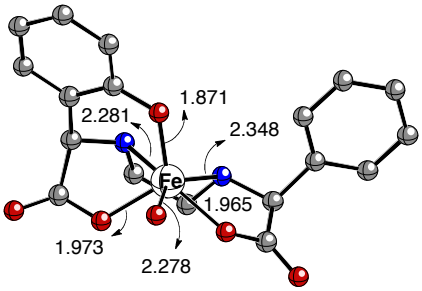
IIIa5 (*S* = 5/2), E_{rel} **= +4.7**



IIIa6 (*S* = 5/2), E_{rel} **= +7.2**



IIIa7(*S* = 5/2), E_{rel} **= +0.1**



IIIa8(*S* = 5/2), E_{rel} **= +8.9**

Figure S3. Minimum energy geometries calculated considering a high spin state (S = 5/2) for the Fe(III) in **IIIa.**

IIIa1 (S =5/2) E = -2520.656583

C	4.151810	2.548470	1.251777
C	3.817535	1.355178	0.589552
C	4.629465	0.228364	0.784576
C	5.745283	0.285613	1.625984
C	6.061712	1.474985	2.286328
C	5.262198	2.607516	2.095239
C	2.576064	1.263621	-0.270901
C	2.407584	2.417526	-1.311692
O	1.165874	2.559105	-1.723310
Fe	-0.276629	1.466396	-1.019233
O	0.027465	-0.346846	-1.633546
C	-0.780763	-1.299306	-1.229245
O	-0.727360	-2.463894	-1.546454
O	-2.021611	1.766062	-1.726655
C	-3.070070	0.942305	-1.758649
C	-4.211005	1.319967	-2.499562
C	-5.329012	0.494050	-2.570263
C	-5.345806	-0.731655	-1.893851
C	-4.231171	-1.112412	-1.146107
C	-3.091578	-0.299903	-1.057890
C	-1.891177	-0.785651	-0.262920
N	-1.345702	0.313551	0.577514
C	-0.433973	-0.059607	1.677908
C	1.035229	-0.060348	1.238395
N	1.312934	1.184395	0.510569
O	-0.821114	3.475985	-0.043780
O	3.348563	3.072316	-1.690080
H	2.612677	0.339124	-0.871244
H	-4.235995	-2.069207	-0.616650
H	-6.219925	-1.384197	-1.946696
H	-6.194802	0.807359	-3.159762
H	-4.176528	2.275392	-3.027742
H	-2.196889	-1.640272	0.362203
H	1.685683	-0.187191	2.121846
H	1.240190	-0.898823	0.558555
H	-0.697011	-1.043556	2.105213
H	-0.569507	0.685842	2.478405
H	-0.189803	4.000350	-0.567577
H	-1.651121	3.510835	-0.554513
H	-2.124618	0.859848	0.945148
H	1.267948	1.979883	1.152944
H	4.391816	-0.703767	0.263623
H	6.369790	-0.601052	1.761450
H	6.934922	1.524139	2.941799
H	5.514235	3.546015	2.595569

H	3.557019	3.449786	1.083018

IIIa2 (S =5/2) E = -2520.653168

C	0.815849	4.319330	-1.934550
C	0.823481	3.596595	-0.729515
C	0.280004	4.196008	0.416062
C	-0.265721	5.482723	0.362791
C	-0.276170	6.187118	-0.843217
C	0.267909	5.601735	-1.991896
C	1.350238	2.179016	-0.675967
C	2.746581	1.965873	-1.350123
O	2.976571	0.712535	-1.667253
Fe	1.630834	-0.670034	-1.401677
O	1.851500	-2.562151	-1.958680
C	0.927303	-3.415874	-1.582176
O	0.968759	-4.617146	-1.697711
O	1.530712	-0.957573	0.457121
C	0.799337	-1.797901	1.178867
C	0.957742	-1.822196	2.582228
C	0.200749	-2.683671	3.371192
C	-0.740055	-3.537875	2.782617
C	-0.912457	-3.516422	1.397096
C	-0.163493	-2.660597	0.578303
C	-0.322184	-2.728053	-0.925793
N	-0.449750	-1.388266	-1.565824
C	-1.453373	-0.412406	-1.086790
C	-0.781805	0.829127	-0.470686
N	0.414759	1.175933	-1.251618
O	1.691759	-0.574059	-3.704455
O	3.512770	2.885112	-1.514588
H	-1.192569	-3.361859	-1.158914
H	1.494878	1.881088	0.375857
H	0.148547	1.476156	-2.193334
H	-1.506642	1.660560	-0.416857
H	-0.448254	0.611339	0.552844
H	-2.127400	-0.870947	-0.347040
H	-2.075121	-0.110124	-1.945396
H	-0.565771	-1.531310	-2.568360
H	-1.640010	-4.187509	0.932167
H	-1.334544	-4.216489	3.398130
H	0.345902	-2.691572	4.454723
H	1.701499	-1.152716	3.019595
H	2.500415	-0.037552	-3.771902
H	1.989319	-1.501520	-3.763045
H	0.292631	3.653128	1.365787
H	-0.679478	5.935636	1.267360
H	-0.698630	7.194113	-0.888008
H	0.278149	6.154069	-2.935006

H	1.270616	3.888976	-2.830239

IIIa3 (S =5/2) E = -2520.659232

C	-3.773334	0.771611	-0.352218
C	-4.838395	-0.117225	-0.514202
C	-4.583400	-1.493223	-0.565130
C	-3.281526	-1.972632	-0.449535
C	-2.197971	-1.085429	-0.268429
C	-2.454585	0.316310	-0.232292
O	-0.969143	-1.570363	-0.148239
Fe	0.709252	-0.768053	0.054229
O	1.475523	-1.725638	1.869482
C	-1.322143	1.300178	-0.018868
C	-0.810323	1.246548	1.460082
O	-1.366910	1.894976	2.316850
N	-0.180134	1.004133	-0.926383
C	0.825806	2.079550	-1.031970
C	2.214762	1.490762	-1.262673
N	2.533655	0.560187	-0.170611
C	3.662266	-0.379230	-0.399906
C	3.138568	-1.549889	-1.287078
O	1.853364	-1.757798	-1.144082
O	3.883899	-2.203137	-1.981003
O	0.212688	0.449396	1.623841
H	-0.531056	0.745263	-1.851018
H	2.659926	1.076030	0.701374
H	1.118432	-2.606118	2.058452
H	0.994455	-1.087005	2.439370
H	3.838622	-0.847854	0.583234
C	4.952726	0.285106	-0.845077
H	0.571541	2.792313	-1.835487
H	0.817652	2.647635	-0.088722
H	2.961441	2.297593	-1.362609
H	2.229434	0.924647	-2.208169
H	-1.701617	2.320625	-0.188740
H	-3.965820	1.847282	-0.310974
H	-3.061239	-3.041534	-0.487368
H	-5.858953	0.261340	-0.603809
H	-5.408328	-2.198262	-0.698139
C	5.805680	0.828838	0.129380
C	6.969419	1.513345	-0.230730
C	7.300226	1.662098	-1.580436
C	6.464016	1.117832	-2.559938
C	5.300790	0.433635	-2.197204
H	5.559729	0.707540	1.189326
H	7.621984	1.923544	0.544264
H	8.212082	2.191739	-1.867880
H	6.723988	1.216741	-3.617029

H	4.677134	-0.019114	-2.968943

IIIa4 (S =5/2) E = -2520.638108

C	-4.559412	-1.345684	-0.083912
C	-4.815106	-0.103875	0.509665
C	-3.751037	0.766000	0.751055
C	-2.433611	0.430522	0.411301
C	-2.170731	-0.828472	-0.213462
C	-3.260801	-1.701335	-0.435584
O	-0.953275	-1.220280	-0.586423
Fe	0.720274	-0.213793	-0.595439
O	2.559120	0.211177	-1.151184
C	3.632788	-0.298234	-0.620774
O	4.771008	-0.125876	-1.000944
C	-1.315319	1.427788	0.665930
C	-0.912519	2.101876	-0.679602
O	-1.466735	3.105577	-1.058842
N	-0.158141	0.692072	1.209940
C	1.009292	1.385507	1.755475
C	2.054643	0.310249	2.121930
N	2.017665	-0.836131	1.171107
C	3.313896	-1.261351	0.562208
O	0.020402	1.436309	-1.313518
O	1.070595	-2.010761	-1.843353
H	-3.047563	-2.665301	-0.903654
H	-3.940904	1.739164	1.212139
H	-5.380428	-2.041738	-0.275953
H	-5.832486	0.183132	0.784006
H	-1.665684	2.217690	1.350055
H	-0.496187	-0.017677	1.862636
H	1.598319	-1.640826	1.635614
H	0.771330	2.003504	2.640942
H	1.400405	2.057533	0.975651
H	3.057999	0.756683	2.133744
H	1.871595	-0.060878	3.143503
H	0.127398	-2.251825	-1.916133
H	1.407718	-1.805399	-2.728383
C	4.418756	-1.519292	1.570868
H	3.077014	-2.217129	0.064277
C	5.415270	-0.575405	1.868418
C	6.367862	-0.837796	2.857398
C	6.345343	-2.045196	3.561217
C	5.366456	-2.998451	3.265359
C	4.415819	-2.734689	2.276490
H	5.469492	0.349725	1.293744
H	7.140934	-0.095162	3.070774
H	7.095597	-2.248122	4.329689
H	5.348799	-3.952690	3.798116

H	3.662411	-3.493945	2.040958

IIIa5 (S =5/2) E = -2520.651651

C	-4.824564	1.731087	0.549575
C	-3.606725	1.082090	0.846539
C	-3.650405	-0.237521	1.385625
C	-4.895553	-0.853228	1.579962
C	-6.090345	-0.203753	1.269023
C	-6.046723	1.096968	0.753103
O	-2.461499	1.734185	0.631058
Fe	-0.665451	1.074969	0.701885
O	-0.608168	2.974756	2.053672
C	-2.380958	-1.010211	1.704271
N	-1.417055	-0.144726	2.433499
C	-0.309833	-0.807919	3.155815
C	0.990291	-0.837021	2.340287
N	1.199717	0.496519	1.760151
C	2.366170	0.771678	0.863619
C	1.963284	1.909923	-0.126649
O	2.817902	2.570216	-0.665901
C	2.905370	-0.443854	0.128320
C	4.158655	-0.962633	0.489012
C	4.692968	-2.070995	-0.173701
C	3.975746	-2.676841	-1.208322
C	2.727176	-2.165876	-1.576888
C	2.194869	-1.054373	-0.919296
O	0.665560	2.059406	-0.288979
O	-0.916756	-0.638536	-0.153608
C	-1.727695	-1.520654	0.386776
O	-1.991902	-2.611864	-0.057422
H	-4.921200	-1.870049	1.981449
H	-7.046229	-0.706884	1.429676
H	-6.973924	1.620558	0.505269
H	-4.771092	2.742080	0.139613
H	-2.641253	-1.897431	2.303959
H	3.194694	1.177513	1.464933
H	1.822953	-1.153661	2.994429
H	0.927386	-1.563238	1.520328
H	-0.584569	-1.834191	3.455317
H	-0.139990	-0.238702	4.084651
H	-0.111154	3.551736	1.449211
H	-1.542819	3.108675	1.801054
H	-1.940044	0.449622	3.076235
H	1.217038	1.191217	2.510116
H	4.729257	-0.486328	1.291536
H	5.673141	-2.457514	0.116981
H	4.389944	-3.543664	-1.729602
H	2.158657	-2.633265	-2.384478

H	1.212709	-0.679860	-1.211689

IIIa6 (S =5/2) E = -2520.647710

C	1.218268	-2.680913	2.376270
C	0.907175	-2.390610	1.029715
C	-0.108311	-3.147861	0.377781
C	-0.757430	-4.167338	1.086504
C	-0.434372	-4.451551	2.415030
C	0.558059	-3.700120	3.056602
O	1.551387	-1.410529	0.408292
Fe	1.442910	-0.740786	-1.344188
O	1.180879	-0.252318	-3.616141
C	-0.426810	-2.921775	-1.083919
N	-0.633403	-1.485939	-1.420745
C	-1.591413	-0.656946	-0.656265
C	-0.896051	0.562163	-0.012511
N	0.179020	1.026083	-0.903159
C	1.075517	2.156017	-0.503656
C	2.451495	1.952034	-1.212246
O	3.158874	2.904010	-1.442173
C	0.750520	-3.425974	-1.992251
O	1.613496	-2.483117	-2.298091
O	0.795631	-4.580940	-2.341092
O	2.730814	0.700404	-1.500197
H	-1.310631	-3.523884	-1.348780
C	1.242381	2.325237	0.997560
H	0.665141	3.100404	-0.893838
H	-0.208102	1.255192	-1.821199
H	-1.643859	1.347768	0.198388
H	-0.437869	0.281653	0.943796
H	-2.077051	-1.255575	0.128445
H	-2.386514	-0.318270	-1.341202
H	-0.852047	-1.428510	-2.414815
H	-1.525757	-4.756181	0.577742
H	-0.952458	-5.253609	2.945200
H	0.819713	-3.912856	4.096516
H	1.997429	-2.086525	2.857398
H	1.971896	0.293261	-3.759679
H	1.461533	-1.167819	-3.813139
C	0.535908	3.341533	1.659618
C	0.672423	3.529160	3.037678
C	1.524793	2.701240	3.772748
C	2.238780	1.690561	3.121318
C	2.102025	1.502371	1.743923
H	-0.120958	4.003177	1.087362
H	0.118612	4.329472	3.535007

H	1.639046	2.847997	4.849780
H	2.915221	1.045828	3.688093
H	2.659383	0.705940	1.249225

IIIa7 (S =5/2) E = -2520.659081

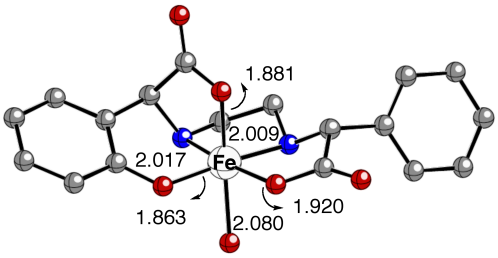
C	3.516415	0.189913	2.748536
C	4.171132	-0.327528	1.621283
C	5.439309	-0.911728	1.784911
C	6.040875	-0.964567	3.041932
C	5.388667	-0.431137	4.159444
C	4.126211	0.143403	4.007847
C	3.566859	-0.302971	0.224605
C	3.124663	-1.738627	-0.214830
O	3.961189	-2.563590	-0.503036
N	2.416460	0.606162	0.101999
C	2.244649	1.186737	-1.236374
C	0.858815	1.811461	-1.347833
N	-0.174534	0.789364	-1.102388
C	-1.422274	1.296392	-0.473809
C	-1.129475	1.611747	1.031088
O	-0.178474	0.873122	1.544110
Fe	0.513448	-0.672010	0.426917
O	1.829478	-1.913927	-0.229901
O	-1.129986	-1.525598	0.103471
C	-2.316908	-1.087636	-0.296137
C	-3.387274	-1.999938	-0.425526
C	-4.649610	-1.566786	-0.822010
C	-4.876068	-0.215547	-1.111544
C	-3.821040	0.693577	-1.006168
C	-2.542358	0.284312	-0.608611
O	0.619705	-1.382558	2.492242
O	-1.774269	2.457633	1.607806
H	-0.400962	0.291859	-1.966216
H	2.461656	1.353424	0.795899
H	0.114047	-2.201548	2.605864
H	0.067046	-0.655995	2.842336
H	4.366218	-0.010040	-0.478545
H	0.727271	2.293370	-2.332278
H	0.747398	2.601466	-0.588566
H	3.025214	1.935918	-1.466555
H	2.348297	0.377119	-1.977296
H	-1.740830	2.242275	-0.940737
H	-3.990282	1.750103	-1.231852
H	-3.190316	-3.049301	-0.195891
H	-5.865675	0.127067	-1.421513
H	-5.465474	-2.289430	-0.908196
H	5.940805	-1.344026	0.916474
H	7.027284	-1.422873	3.149557
H	5.862797	-0.467262	5.143463

H	3.601815	0.555493	4.873729
H	2.515835	0.620679	2.671606

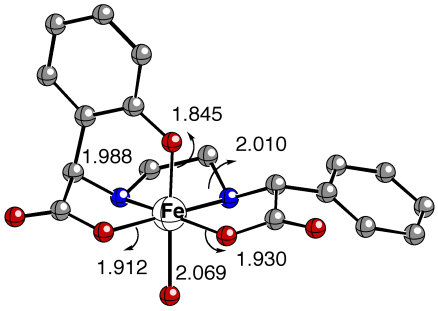
IIIa8 (S =5/2) E = -2520.644956

C	-4.480916	-1.439629	-0.658544
C	-4.806385	-0.464238	0.291476
C	-3.788004	0.299115	0.864142
C	-2.444527	0.121157	0.507507
C	-2.115479	-0.860289	-0.478450
C	-3.155818	-1.635704	-1.035267
O	-0.864746	-1.084316	-0.894106
Fe	0.571322	0.112465	-0.802393
O	2.278547	0.117414	-1.776950
C	3.445426	-0.321408	-1.384336
O	4.496339	-0.177515	-1.962468
C	-1.382550	0.992227	1.167101
C	-1.012025	2.220971	0.281649
O	-1.631322	3.255068	0.360313
N	-0.160679	0.201650	1.357326
C	0.915257	0.715095	2.214875
C	2.283948	0.419909	1.558876
N	2.165460	-0.759328	0.684717
C	3.382791	-1.131356	-0.055627
O	-0.006594	1.979216	-0.528357
O	0.106298	0.836485	-2.912135
H	-2.879709	-2.383257	-1.781726
H	-4.035467	1.060198	1.609142
H	-5.267189	-2.049315	-1.111429
H	-5.844912	-0.301917	0.587966
H	-1.782422	1.387375	2.116065
H	-0.407319	-0.753859	1.610655
H	1.844038	-1.566065	1.223092
H	0.856053	0.260062	3.219319
H	0.796501	1.799753	2.349668
H	2.589110	1.269050	0.926510
H	3.067014	0.290409	2.328238
H	-0.065760	1.761810	-2.664104
H	1.042654	0.821249	-3.184868
H	4.289529	-0.872106	0.515853
C	3.415496	-2.616556	-0.372319
C	4.648156	-3.286531	-0.402039
C	4.713298	-4.640698	-0.735348
C	3.545851	-5.346029	-1.043976
C	2.315119	-4.685246	-1.025490
C	2.247880	-3.326857	-0.699525
H	5.563851	-2.736692	-0.171481
H	5.681277	-5.147787	-0.752924
H	3.596452	-6.406691	-1.302315

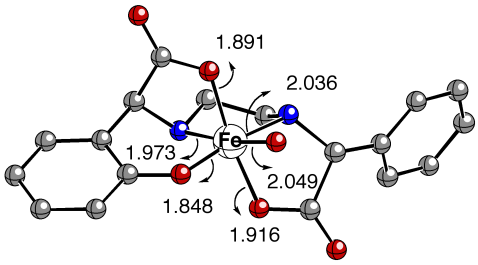
H	1.398033	-5.224460	-1.275577
H	1.274572	-2.828998	-0.714457



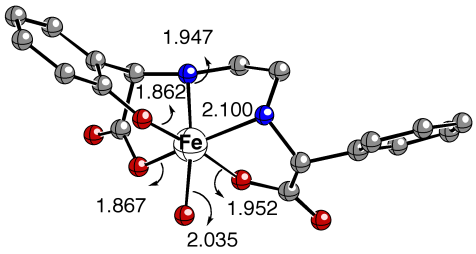
IIIa1 (*S* = 1/2), **E_{rel} = +11.1**



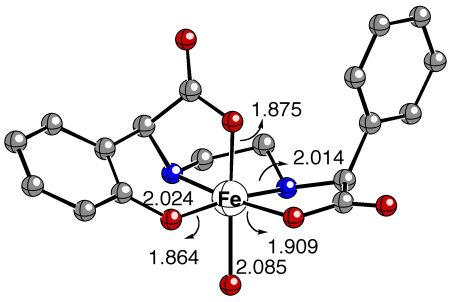
IIIa2 (*S* = 1/2), **E_{rel} = +16.5**



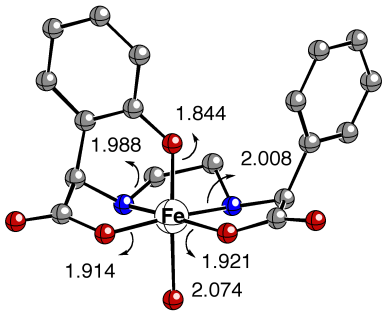
IIIa3 (*S* = 1/2), **E_{rel} = +6.5**



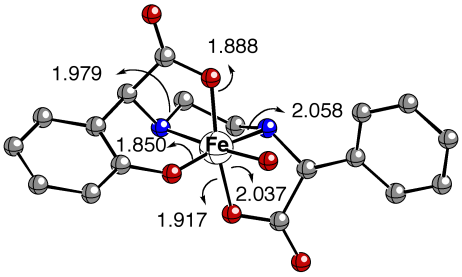
IIIa4 (*S* = 1/2), **E_{rel} = +22.8**



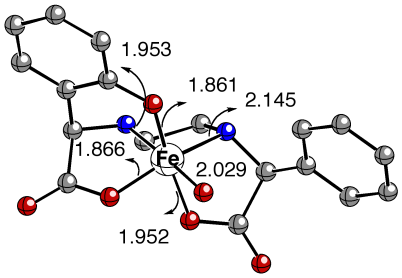
IIIa5 (*S* = 1/2), **E_{rel} = +15.4**



IIIa6 (*S* = 1/2), **E_{rel} = +21.2**



IIIa7 (*S* = 1/2), **E_{rel} = +8.4**



IIIa8 (*S* = 1/2), E_{rel} = +23.5

Figure S4. Minimum energy geometries calculated considering a low spin state (S = 1/2) for the Fe(III) in **IIIa.**

IIIa1 (S = 1/2) E= -2520.641374

C	4.125569	2.559005	1.077985
C	3.718187	1.337404	0.515614
C	4.513392	0.200855	0.726023
C	5.684062	0.276630	1.487219
C	6.072951	1.494447	2.050367
C	5.291254	2.636139	1.842073
C	2.425717	1.228482	-0.258785
C	2.171565	2.355571	-1.310592
O	0.900822	2.521884	-1.588529
Fe	-0.356372	1.459742	-0.599612
O	0.070104	-0.185489	-1.407623
C	-0.690213	-1.204846	-1.095086
O	-0.529997	-2.350138	-1.448241
O	-1.935519	1.835634	-1.515786
C	-2.943230	0.982208	-1.697847
C	-4.005881	1.368558	-2.545044
C	-5.097432	0.532565	-2.756367
C	-5.167934	-0.718123	-2.128322
C	-4.129331	-1.113593	-1.287310
C	-3.019823	-0.286592	-1.055360
C	-1.879424	-0.782149	-0.193958
N	-1.401293	0.318883	0.695427
C	-0.504841	-0.057407	1.823574
C	0.964365	-0.052336	1.391550
N	1.213890	1.187462	0.624317
O	-0.773491	3.346394	0.170226
O	3.085063	2.979484	-1.797702
H	2.401177	0.288181	-0.830149
H	-4.167634	-2.091549	-0.799085
H	-6.022535	-1.377310	-2.294676
H	-5.902661	0.857430	-3.420866
H	-3.933024	2.342659	-3.033517
H	-2.201208	-1.653346	0.397759
H	1.624237	-0.130587	2.271541
H	1.185771	-0.904187	0.736235
H	-0.782776	-1.040290	2.240602
H	-0.658310	0.691038	2.617488
H	-0.134968	3.773852	-0.439876
H	-1.617694	3.400539	-0.324101
H	-2.219227	0.806475	1.064940
H	1.258715	1.983307	1.267775
H	4.219675	-0.752539	0.277318
H	6.295444	-0.617198	1.634699
H	6.989640	1.558038	2.642146

H	5.600353	3.595529	2.264645
H	3.545693	3.465575	0.888205

IIIa2 (S = 1/2): E = -2520.632722

C	1.144985	-1.667722	2.467571
C	0.807381	-1.650764	1.094451
C	-0.090285	-2.638783	0.606553
C	-0.614687	-3.596678	1.487619
C	-0.275027	-3.600030	2.839414
C	0.612539	-2.627803	3.321867
O	1.309784	-0.688845	0.330179
Fe	1.131686	-0.531285	-1.500090
O	1.193956	-0.308756	-3.556414
C	-0.376295	-2.727051	-0.867955
N	-0.662455	-1.388376	-1.481668
C	-1.679405	-0.465593	-0.892500
C	-1.026157	0.821045	-0.347794
N	0.144984	1.190124	-1.178260
C	1.147825	2.112322	-0.592193
C	2.538903	1.836525	-1.219437
O	3.385309	2.698997	-1.230301
C	0.884249	-3.255828	-1.634338
O	1.710222	-2.290620	-1.975902
O	1.030220	-4.433220	-1.855517
O	2.668210	0.620489	-1.697646
H	-1.205611	-3.427670	-1.048628
H	1.224747	1.889267	0.481097
C	0.791428	3.507882	-0.759203
H	-0.161502	1.557366	-2.082904
H	-1.769443	1.636247	-0.305821
H	-0.652541	0.653489	0.668402
H	-2.233162	-0.969122	-0.086290
H	-2.404294	-0.220748	-1.684824
H	-0.910220	-1.556598	-2.457683
H	-1.292558	-4.359571	1.093986
H	-0.691695	-4.354415	3.510040
H	0.893440	-2.621110	4.378554
H	1.842085	-0.908162	2.827717
H	2.009449	0.236637	-3.500852
H	1.533333	-1.211437	-3.725393
C	-0.429893	3.982316	-0.265960
C	-0.774000	5.329754	-0.427211
C	0.103213	6.202758	-1.081704
C	1.324534	5.728324	-1.574947
C	1.668641	4.380886	-1.413696
H	-1.112240	3.303244	0.243142
H	-1.724014	5.698796	-0.043539

H	-0.164454	7.250872	-1.207135
H	2.006880	6.407396	-2.084049
H	2.618654	4.011844	-1.797368

IIIa3 (S = 1/2): E = -2520.648792

C	-3.715981	0.599238	-0.522163
C	-4.685416	-0.398586	-0.625240
C	-4.309983	-1.735231	-0.436571
C	-2.989579	-2.066981	-0.147299
C	-1.998799	-1.066575	-0.032661
C	-2.380233	0.289472	-0.232908
O	-0.755222	-1.420695	0.266423
Fe	0.736594	-0.332697	0.175093
O	1.467185	-1.648332	1.566864
C	-1.348541	1.382924	-0.085891
C	-0.851291	1.508863	1.387191
O	-1.413239	2.213014	2.190656
N	-0.140636	1.066291	-0.905428
C	0.803845	2.201305	-1.055972
C	2.221407	1.662410	-1.186941
N	2.474448	0.695290	-0.089550
C	3.507188	-0.341320	-0.400891
C	2.813316	-1.346193	-1.371926
O	1.512701	-1.305835	-1.281816
O	3.455165	-2.073296	-2.098623
O	0.211339	0.765808	1.621932
H	-0.411473	0.690946	-1.817948
H	2.701528	1.196437	0.772016
H	0.863493	-2.388933	1.368316
H	1.087523	-1.242777	2.367804
H	3.644117	-0.897732	0.539603
C	4.848396	0.228182	-0.823546
H	0.538244	2.829949	-1.922211
H	0.717997	2.833255	-0.159250
H	2.960480	2.479341	-1.190311
H	2.329807	1.122468	-2.138184
H	-1.787753	2.347896	-0.383571
H	-3.996592	1.647141	-0.662813
H	-2.683325	-3.104722	0.000738
H	-5.721456	-0.138329	-0.852067
H	-5.057281	-2.529213	-0.519114
C	5.717829	0.709262	0.170275
C	6.938098	1.301214	-0.163918
C	7.311719	1.414714	-1.506290
C	6.461298	0.928520	-2.503371
C	5.239240	0.338696	-2.167471
H	5.440697	0.609310	1.224905
H	7.601770	1.664643	0.624781
H	8.268311	1.870945	-1.773481
H	6.754542	0.999039	-3.553958

H	4.602709	-0.074833	-2.950229

IIIa4 (S = 1/2): E= -2520.622734

C	-4.480537	-1.375279	0.312526
C	-4.737914	-0.019218	0.549127
C	-3.672637	0.881104	0.563089
C	-2.355155	0.457668	0.345566
C	-2.088876	-0.923266	0.085819
C	-3.180590	-1.819530	0.087395
O	-0.866659	-1.412504	-0.153377
Fe	0.661052	-0.369233	-0.370140
O	2.334549	0.551674	-0.776783
C	3.462777	0.019651	-0.408892
O	4.568344	0.358820	-0.776750
C	-1.209973	1.458545	0.338062
C	-0.838226	1.722467	-1.147524
O	-1.260993	2.679458	-1.748968
N	-0.083146	0.769616	1.023442
C	1.064045	1.397166	1.689990
C	1.887033	0.199037	2.209682
N	1.920226	-0.930354	1.214184
C	3.251566	-1.169232	0.569824
O	-0.117576	0.745641	-1.650081
O	1.195073	-1.648188	-1.861290
H	-2.968201	-2.873624	-0.105690
H	-3.859883	1.943450	0.742895
H	-5.303781	-2.094813	0.300667
H	-5.757369	0.332083	0.721971
H	-1.493137	2.399466	0.832003
H	-0.515680	0.134892	1.699403
H	1.611699	-1.787094	1.674711
H	0.758423	2.045448	2.530489
H	1.626059	1.992577	0.959813
H	2.907917	0.507183	2.474472
H	1.425390	-0.183125	3.134088
H	0.331778	-2.044127	-2.074634
H	1.396290	-1.035628	-2.591011
C	4.365784	-1.492909	1.548206
H	3.095058	-2.048506	-0.076563
C	5.326296	-0.551495	1.952990
C	6.294382	-0.891289	2.903272
C	6.322450	-2.172513	3.460303
C	5.379569	-3.122553	3.055782
C	4.414529	-2.782913	2.105256
H	5.340724	0.434872	1.488682
H	7.039304	-0.149179	3.201643
H	7.084147	-2.434918	4.198924

H	5.402358	-4.132579	3.472887
H	3.691774	-3.539550	1.781590

IIIa5 (S = 1/2): E = -2520.634595

C	-4.713739	1.770920	0.578436
C	-3.513079	1.120094	0.940076
C	-3.584179	-0.233353	1.376487
C	-4.827901	-0.880818	1.423335
C	-6.003050	-0.225027	1.060548
C	-5.935979	1.109079	0.637244
O	-2.374777	1.811539	0.884275
Fe	-0.664087	1.113921	1.138827
O	-0.506065	2.878972	2.237780
C	-2.322915	-0.999838	1.706821
N	-1.412856	-0.150338	2.531756
C	-0.279043	-0.840352	3.208070
C	0.974635	-0.850244	2.328568
N	1.147293	0.513970	1.785799
C	2.188052	0.793847	0.718299
C	1.602548	1.829452	-0.297671
O	2.327029	2.295272	-1.144022
C	2.789494	-0.432977	0.062616
C	4.056728	-0.877030	0.473047
C	4.647055	-2.001191	-0.110726
C	3.972387	-2.696909	-1.117247
C	2.710698	-2.261075	-1.535082
C	2.121348	-1.135793	-0.954094
O	0.351840	2.163563	-0.091535
O	-0.789064	-0.377876	0.008465
C	-1.571952	-1.353415	0.397886
O	-1.732736	-2.408162	-0.170620
H	-4.865355	-1.925352	1.745444
H	-6.960899	-0.747655	1.104706
H	-6.847975	1.637523	0.346537
H	-4.644583	2.807717	0.242139
H	-2.573358	-1.933808	2.233700
H	3.016151	1.325320	1.212448
H	1.849818	-1.176593	2.915707
H	0.868899	-1.544253	1.488082
H	-0.556564	-1.868614	3.494612
H	-0.075310	-0.286977	4.139404
H	-0.042082	3.336045	1.505061
H	-1.446844	3.099133	2.072583
H	-1.978604	0.332879	3.231393
H	1.344006	1.148384	2.563088
H	4.597158	-0.326978	1.249571
H	5.637727	-2.327381	0.216127
H	4.431123	-3.574807	-1.579479

H	2.176930	-2.799054	-2.322172
H	1.129658	-0.813352	-1.275876

IIIa6 (S = 1/2): E = -2520.625259

C	1.365995	-2.551155	2.172153
C	0.909092	-2.269110	0.863630
C	-0.091511	-3.109608	0.304409
C	-0.596979	-4.183707	1.052219
C	-0.138609	-4.447577	2.341686
C	0.850351	-3.622164	2.894603
O	1.406431	-1.213774	0.229313
Fe	1.078994	-0.720358	-1.517872
O	0.995912	-0.160497	-3.514030
C	-0.515519	-2.915981	-1.125861
N	-0.759749	-1.474893	-1.459590
C	-1.638554	-0.625299	-0.600064
C	-0.853432	0.540924	0.036780
N	0.212374	0.981199	-0.895613
C	1.282730	1.953021	-0.438767
C	2.673799	1.488733	-0.989338
O	3.627018	2.217038	-0.841842
C	0.629894	-3.364930	-2.094455
O	1.490324	-2.400244	-2.339667
O	0.671371	-4.488014	-2.534573
O	2.670784	0.349235	-1.632642
H	-1.405329	-3.527041	-1.340578
C	1.290018	2.247480	1.047666
H	1.084291	2.907600	-0.950562
H	-0.221005	1.384852	-1.728857
H	-1.540060	1.365286	0.293045
H	-0.364944	0.216776	0.959852
H	-2.098244	-1.234659	0.191497
H	-2.454143	-0.239735	-1.232546
H	-1.117983	-1.447822	-2.415273
H	-1.356585	-4.828543	0.600973
H	-0.542555	-5.288726	2.908913
H	1.224415	-3.818448	3.903130
H	2.139956	-1.906629	2.592832
H	1.850720	0.317566	-3.462388
H	1.250140	-1.048687	-3.840532
C	0.562909	3.342910	1.539409
C	0.545901	3.638378	2.905263
C	1.266098	2.840673	3.798229
C	2.001444	1.752380	3.317250
C	2.014719	1.455821	1.952521
H	0.014161	3.984556	0.843008
H	-0.020466	4.499252	3.269519

H	1.262466	3.071775	4.866515
H	2.574894	1.131342	4.009977
H	2.583756	0.602364	1.581361

IIIa7 (S = 1/2): E= -2520.645755

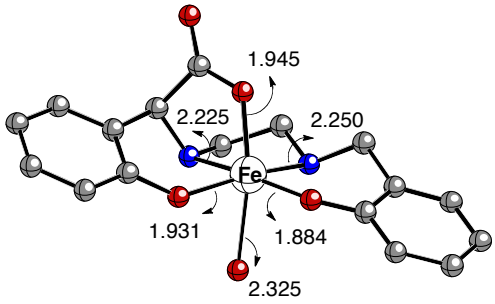
C	-3.741275	0.471517	-1.146918
C	-4.710849	-0.531244	-1.158417
C	-4.398159	-1.787373	-0.622264
C	-3.139805	-2.034359	-0.081277
C	-2.151306	-1.025659	-0.055451
C	-2.466980	0.245761	-0.608951
O	-0.970173	-1.295244	0.488384
Fe	0.540124	-0.227820	0.425029
O	0.975489	-1.260102	2.126581
C	-1.440146	1.351734	-0.566979
C	-1.171525	1.833670	0.891708
O	-1.824339	2.711731	1.402056
N	-0.129745	0.859278	-1.087261
C	0.846992	1.936233	-1.376190
C	2.250043	1.394631	-1.156464
N	2.326378	0.766794	0.185178
C	3.410144	-0.237258	0.280714
C	2.835093	-1.565506	-0.330860
O	1.558143	-1.506006	-0.578922
O	3.579087	-2.489493	-0.576906
O	-0.186350	1.172311	1.462796
H	-0.269643	0.265238	-1.908547
H	2.420399	1.493395	0.896724
H	0.304072	-1.956416	1.987724
H	0.610310	-0.708365	2.839017
C	4.002784	-0.391299	1.672738
H	4.237797	0.055977	-0.389771
H	0.725579	2.324582	-2.401101
H	0.646895	2.770727	-0.687020
H	3.009457	2.187032	-1.272203
H	2.466579	0.615219	-1.901076
H	-1.799064	2.212504	-1.152342
H	-3.973441	1.457978	-1.558688
H	-2.882765	-3.009282	0.338309
H	-5.698374	-0.337478	-1.582414
H	-5.145490	-2.585548	-0.628994
C	5.086278	-1.272998	1.830798
C	5.697846	-1.431935	3.074560
C	5.246832	-0.708393	4.183710
C	4.170975	0.168300	4.037219
C	3.550645	0.322853	2.792066
H	5.425247	-1.850560	0.968893
H	6.535703	-2.126277	3.177186

H	5.730185	-0.829771	5.156250
H	3.802989	0.736529	4.895386
H	2.695017	1.000645	2.727856

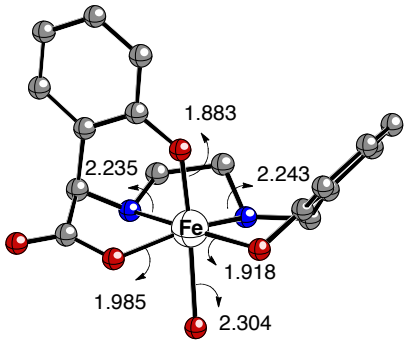
IIIa8 (S = 1/2): E = -2520.621706

C	-4.589862	-1.296824	-0.001585
C	-4.833445	-0.059780	0.608384
C	-3.762002	0.799405	0.851733
C	-2.451948	0.450648	0.498385
C	-2.200952	-0.801568	-0.142778
C	-3.297827	-1.662381	-0.368585
O	-0.987129	-1.200821	-0.537632
Fe	0.555888	-0.161812	-0.469283
O	2.265288	0.767517	-0.635893
C	3.361355	0.083521	-0.497689
O	4.466894	0.388922	-0.891733
C	-1.297810	1.405989	0.754705
C	-0.933306	2.083868	-0.593012
O	-1.366701	3.167410	-0.899955
N	-0.165383	0.550678	1.200349
C	0.988482	0.988005	1.992102
C	1.809215	-0.303263	2.183667
N	1.826431	-1.155540	0.944872
C	3.159027	-1.239873	0.306126
O	-0.196693	1.302137	-1.349427
O	1.029890	-0.907939	-2.296157
H	-3.096027	-2.620732	-0.852552
H	-3.937953	1.769235	1.325498
H	-5.418140	-1.983583	-0.196172
H	-5.846989	0.230694	0.892770
H	-1.566787	2.168608	1.500293
H	-0.589005	-0.243905	1.686374
H	1.510212	-2.094314	1.190122
H	0.693412	1.405404	2.971307
H	1.548065	1.745637	1.429457
H	2.836700	-0.065019	2.495597
H	1.357198	-0.898498	2.994003
H	0.165443	-1.192209	-2.638457
H	1.271812	-0.107783	-2.794767
H	3.942745	-1.242891	1.083799
C	3.355222	-2.491824	-0.533224
C	4.648011	-2.762077	-1.014604
C	4.899426	-3.908161	-1.768875
C	3.866960	-4.809991	-2.049987
C	2.578845	-4.545168	-1.582912
C	2.321217	-3.389876	-0.835894
H	5.448613	-2.048532	-0.809110
H	5.910294	-4.100114	-2.137570

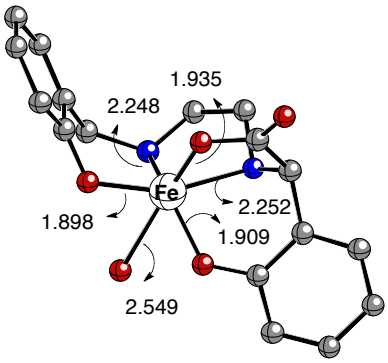
H	4.066245	-5.711396	-2.634883
H	1.760535	-5.234647	-1.806012
H	1.292982	-3.193321	-0.522518



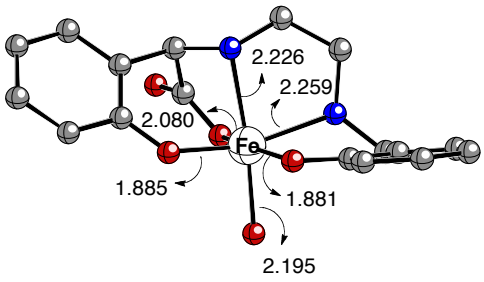
IV1 (*S* = 5/2), E_{rel} = **+1.0**



IV2 (*S* = 5/2), E_{rel} = **+7.5**



IV3 (*S* = 5/2), E_{rel} = **+8.9**



IV4 (*S* = 5/2), E_{rel} = **+0.0**

Figure S5. Minimum energy geometries calculated considering a high spin state (*S* = 5/2) for the Fe(III) in **IV.**

IV1 (S = 5/2) E = -2407.413070

C	-1.535173	-2.099609	-1.428824
C	-1.051955	-3.212970	-0.680823
C	-1.583711	-4.486704	-0.929401
C	-2.583627	-4.689854	-1.880729
C	-3.071025	-3.593624	-2.602416
C	-2.557973	-2.319367	-2.377235
C	0.060700	-3.055975	0.341443
C	1.437167	-2.929613	-0.381117
O	2.109638	-3.911920	-0.595799

O	-1.071190	-0.860527	-1.255629
Fe	0.488367	-0.270027	-0.281901
O	1.738063	-1.697643	-0.713461
O	1.100496	1.355952	-1.012794
C	2.743469	2.214282	0.509944
C	3.456357	3.328072	0.970685
C	2.976566	0.844473	1.095153
N	1.715867	0.203913	1.543507
C	1.904295	-1.052498	2.281373
C	0.558024	-1.758691	2.452891
N	-0.175865	-1.853639	1.180206
C	3.286760	4.592259	0.399416
C	2.381398	4.747723	-0.656543
C	1.653326	3.657357	-1.128690
C	1.814413	2.375781	-0.556904
H	-1.195461	-5.336728	-0.361382
H	-2.980234	-5.692365	-2.055443
H	-3.856197	-3.734413	-3.350309
H	-2.918942	-1.454928	-2.939075
H	0.107749	-3.964605	0.964023
H	4.168623	3.197245	1.791494
H	3.415585	0.165701	0.343485
H	3.691531	0.916375	1.934852
H	1.186067	0.868211	2.113790
H	2.362279	-0.883287	3.274268
H	2.602524	-1.676075	1.705886
H	0.713195	-2.752303	2.911235
H	-0.068358	-1.176169	3.148296
H	-1.176583	-1.763800	1.352185
H	3.857585	5.445460	0.772405
H	2.241870	5.729418	-1.117559
H	0.948177	3.760232	-1.956828
O	-1.245392	1.005939	0.598448
H	-1.050474	1.877999	0.219980
H	-1.767461	0.553453	-0.097219

IV2 (S = 5/2) E = -2407.402571

C	5.139272	1.429752	0.730777
C	4.342506	2.527893	1.074614
C	3.162837	2.762987	0.363435
C	2.764567	1.919557	-0.680665
C	3.569073	0.797300	-1.018138
C	4.758450	0.570908	-0.299979
C	1.562169	2.236348	-1.535197
N	0.568297	1.138126	-1.668782
C	-0.441157	1.009004	-0.606782

C	-1.419516	-0.130497	-0.972040
N	-0.735278	-1.205869	-1.720859
Fe	1.485442	-0.896787	-1.798744
O	1.522186	-0.550800	-4.077001
O	3.186363	-0.032076	-1.995736
O	1.243934	-2.719811	-2.545973
C	0.217454	-3.426807	-2.137162
C	-0.791151	-2.616391	-1.248700
C	-0.453206	-2.757872	0.219691
C	0.692580	-2.113307	0.768263
C	0.998464	-2.311350	2.133217
C	0.208354	-3.136808	2.928408
C	-0.912049	-3.780300	2.387454
C	-1.231747	-3.582423	1.042491
O	1.462806	-1.321368	0.036134
O	0.005723	-4.591328	-2.382517
H	-1.785337	-3.058113	-1.424061
H	1.067930	3.152952	-1.166201
H	1.904027	2.443184	-2.563775
H	0.099979	1.257894	-2.569138
H	-1.005233	1.949133	-0.458408
H	0.089917	0.784969	0.328421
H	-1.871445	-0.533631	-0.054297
H	-2.242919	0.268691	-1.588439
H	-1.035017	-1.195406	-2.694905
H	-2.102380	-4.085231	0.611983
H	-1.532136	-4.430615	3.008398
H	0.468110	-3.282340	3.980489
H	1.879234	-1.803912	2.532299
H	2.444070	-0.238000	-4.038200
H	1.580230	-1.509851	-4.245955
H	2.539901	3.627207	0.616207
H	4.638035	3.195784	1.886881
H	5.363908	-0.296816	-0.570515
H	6.065899	1.235285	1.278054

IV3 (S = 5/2) E = -2407.400411

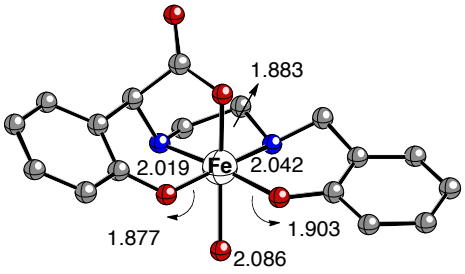
C	3.383705	1.187612	-1.735924
C	4.611109	1.650195	-1.261424
C	5.245047	1.018792	-0.184928
C	4.637694	-0.089973	0.411385
C	3.408236	-0.574167	-0.050045
C	2.766148	0.072159	-1.140699
C	2.771825	-1.819999	0.509263
N	1.375506	-1.626117	0.994154
C	1.196185	-1.277119	2.418819

C	0.137762	-0.173988	2.588312
N	-0.935637	-0.356622	1.604089
C	-1.835307	0.799270	1.389172
C	-1.010314	1.942905	0.718353
O	-1.320401	3.098988	0.881420
O	1.586286	-0.381653	-1.581424
Fe	0.105670	-0.394217	-0.392965
O	0.067612	-2.775392	-1.302596
O	-1.628027	-0.760037	-1.105612
C	-2.825222	-0.329296	-0.696138
C	-3.957351	-0.628235	-1.483742
C	-5.229481	-0.204551	-1.108425
C	-5.410521	0.526817	0.070732
C	-4.301482	0.820793	0.864776
C	-3.009832	0.404812	0.511797
O	-0.014474	1.499728	-0.010320
H	-3.798704	-1.191733	-2.406018
H	-4.432292	1.395923	1.785598
H	-6.086805	-0.445044	-1.742915
H	-6.405138	0.865033	0.369229
H	-2.216490	1.197445	2.343880
H	-1.491123	-1.191245	1.804525
H	0.867096	-2.484784	0.777723
H	-0.238992	-0.154825	3.627500
H	0.599506	0.803636	2.387902
H	2.150769	-0.922013	2.834674
H	0.913435	-2.178173	2.991731
H	-0.816849	-2.451575	-1.562652
H	0.662663	-2.441302	-1.994691
H	3.397378	-2.246565	1.312275
H	2.705114	-2.580381	-0.285603
H	5.131646	-0.597808	1.246183
H	6.203916	1.386987	0.186758
H	2.872774	1.677363	-2.567165
H	5.075948	2.520024	-1.733503

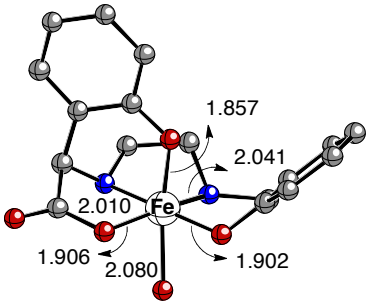
IV4 (S = 5/2) E = -2407.414597

Fe	0.098612	0.063978	0.694376
N	-0.811818	-0.631802	-1.214944
H	-0.821493	0.137595	-1.887181
N	1.521612	-1.580984	0.082451
H	1.087768	-2.376233	0.555546
C	-0.072942	-1.792317	-1.754881
H	-0.178610	-1.862472	-2.851250
H	-0.525594	-2.705116	-1.337002
C	1.403897	-1.738616	-1.370294
H	1.898407	-0.877636	-1.847231
H	1.918661	-2.647478	-1.738608

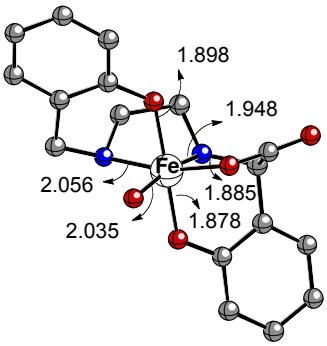
O	1.563541	1.196805	0.360504
O	-1.315964	1.306212	0.798266
O	-1.070647	-1.569768	1.236757
C	2.883175	-1.365444	0.612546
H	2.769728	-1.293708	1.708521
H	3.527941	-2.240687	0.407622
C	3.552253	-0.120754	0.078688
C	4.861387	2.211414	-0.795076
C	2.840427	1.111108	0.025390
C	4.895106	-0.152366	-0.317867
C	5.559076	0.998368	-0.750394
C	3.522459	2.268176	-0.416495
H	5.433897	-1.104638	-0.280528
H	6.608034	0.948330	-1.050927
H	2.960799	3.204398	-0.449249
H	5.365974	3.121205	-1.131979
C	-2.204323	-0.946366	-0.787901
H	-2.711085	-1.567034	-1.544665
C	-2.140120	-1.799606	0.523624
O	-3.037084	-2.569661	0.787130
C	-3.018525	0.312019	-0.573162
C	-4.595131	2.595055	-0.115052
C	-4.298171	0.427152	-1.131227
C	-2.516876	1.366325	0.244358
C	-3.325690	2.506636	0.449849
C	-5.091979	1.554358	-0.909483
H	-4.679948	-0.392491	-1.746690
H	-2.921748	3.308941	1.071184
H	-6.087790	1.620583	-1.353273
H	-5.204299	3.485389	0.063939
O	0.404428	-0.297748	2.837908
H	-0.335141	-0.947261	2.822590
H	0.109388	0.446280	3.383796



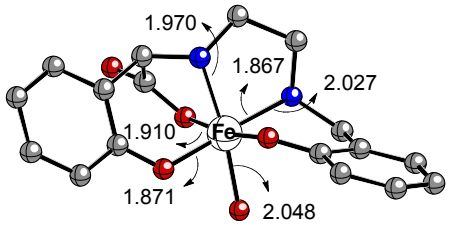
IV1 (*S* = 1/2), **E_{rel} = 14.4**



IV2 (*S* = 1/2), **E_{rel} = 21.0**



IV3 (*S* = 1/2), **E_{rel} = +27.4**



IV4 (*S* = 1/2), **E_{rel} = +8.6.0**

Figure S6. Minimum energy geometries calculated considering a low spin state (*S* = 1/2) for the Fe(III) in **IV.**

IV1 (S=1/2) E = -2407.391531

C	-1.494007	-1.962107	-1.317180
C	-0.944046	-3.125150	-0.705240
C	-1.345620	-4.396616	-1.140939
C	-2.284515	-4.552083	-2.159102
C	-2.833452	-3.410236	-2.758648
C	-2.447066	-2.139230	-2.346536
C	0.126008	-2.990439	0.354863
C	1.474798	-2.622773	-0.318397
O	2.293390	-3.466094	-0.605897
O	-1.181073	-0.722614	-0.947595
Fe	0.228077	-0.250226	0.199320
O	1.584170	-1.335652	-0.529584
O	0.579696	1.400081	-0.681268
C	2.614698	2.092802	0.449389
C	3.548982	3.121835	0.647522
C	2.808896	0.772874	1.144504
N	1.545984	0.199991	1.692954
C	1.776419	-1.051615	2.450298

C	0.463313	-1.815120	2.592144
N	-0.240034	-1.884435	1.289109
C	3.478993	4.325178	-0.052843
C	2.442968	4.506311	-0.978399
C	1.496643	3.507826	-1.183012
C	1.550515	2.283012	-0.474373
H	-0.901715	-5.278605	-0.670429
H	-2.584432	-5.550613	-2.484056
H	-3.569494	-3.514192	-3.560668
H	-2.860186	-1.241019	-2.810643
H	0.249257	-3.940451	0.898023
H	4.359830	2.962356	1.365828
H	3.190531	0.013685	0.443431
H	3.542356	0.885266	1.962222
H	1.103641	0.898084	2.297987
H	2.211872	-0.847215	3.444108
H	2.511005	-1.646067	1.890963
H	0.642954	-2.822295	3.006315
H	-0.204188	-1.284734	3.290196
H	-1.246803	-1.931015	1.453454
H	4.220795	5.108407	0.117411
H	2.371170	5.438931	-1.545156
H	0.682862	3.637104	-1.900257
O	-1.278464	0.974916	0.962826
H	-0.905463	1.688434	0.391467
H	-1.948797	0.576011	0.370773

IV2 (S=1/2) E = -2407.380980

C	0.387516	-3.369182	-2.125454
O	0.270226	-4.533018	-2.427190
C	-0.711267	-2.634808	-1.291733
C	0.677387	-1.913756	0.692785
C	-0.387101	-2.701613	0.175803
O	1.399654	-2.587763	-2.427583
Fe	1.238817	-0.771378	-1.870745
O	1.340935	-1.029147	-0.033931
O	3.032746	-0.149745	-1.993466
C	1.534502	2.195534	-1.469554
N	0.512032	1.127677	-1.685577
C	-0.560830	1.007767	-0.676731
C	-1.479674	-0.170946	-1.066379
N	-0.719317	-1.223830	-1.802740
C	-1.063933	-3.598956	1.015445
C	-0.717619	-3.734102	2.358831
C	0.328856	-2.954616	2.873515
C	1.014502	-2.058983	2.060051
H	-1.674970	-3.129802	-1.486823

H	1.048100	3.092190	-1.048720
H	1.886623	2.461736	-2.481493
H	0.086319	1.308800	-2.598138
H	-1.148349	1.940689	-0.602212
H	-0.075515	0.824816	0.288956
H	-1.934186	-0.603069	-0.164010
H	-2.299848	0.179481	-1.713796
H	-1.052463	-1.258193	-2.767000
H	-1.870634	-4.207272	0.595842
H	-1.253487	-4.438872	2.998198
H	0.613393	-3.050020	3.925205
H	1.834851	-1.449166	2.444239
O	1.438224	-0.456300	-3.917554
H	2.352876	-0.133752	-3.739909
H	1.564929	-1.399974	-4.139401
C	2.717967	1.793094	-0.628970
C	3.165576	2.593671	0.427944
C	3.455799	0.637785	-1.002392
C	4.341633	2.285022	1.116760
C	4.641210	0.339276	-0.304349
C	5.079332	1.157495	0.736638
H	2.588719	3.481186	0.708597
H	4.679320	2.918130	1.940468
H	5.195593	-0.554160	-0.599117
H	6.001783	0.905826	1.267548

IV3 (S = ½) E = -2407.370736

C	3.802818	1.477641	-0.485694
C	5.152385	1.152613	-0.558336
C	5.582043	-0.159143	-0.312184
C	4.632159	-1.127748	0.008251
C	3.262815	-0.827975	0.074984
C	2.821439	0.502977	-0.170365
C	2.286292	-1.941277	0.368041
N	1.001796	-1.470020	0.937858
C	1.097396	-0.787151	2.276802
C	0.208461	0.489929	2.347680
N	-0.868620	0.250590	1.379850
C	-1.954379	1.181431	0.965342
C	-1.489337	2.048299	-0.243789
O	-1.858014	3.191651	-0.376625
O	1.560634	0.890127	-0.065501
Fe	0.006609	-0.173022	-0.309257
O	0.653309	-0.730969	-2.157060
O	-1.501927	-1.239640	-0.648704
C	-2.751040	-0.867926	-0.339757
C	-3.820669	-1.663036	-0.807439

C	-5.144972	-1.336939	-0.527014
C	-5.451161	-0.204210	0.236626
C	-4.410131	0.590072	0.717985
C	-3.069712	0.279956	0.454625
O	-0.777345	1.351624	-1.093613
H	-3.570028	-2.541215	-1.407304
H	-4.634933	1.480117	1.312492
H	-5.947941	-1.972377	-0.910739
H	-6.488863	0.056596	0.455472
H	-2.297911	1.825818	1.787625
H	-1.345400	-0.607890	1.665967
H	0.381201	-2.277020	1.014152
H	-0.179582	0.636284	3.371238
H	0.773009	1.376477	2.039965
H	2.146506	-0.518000	2.456485
H	0.802504	-1.505352	3.059835
H	-0.197106	-1.062936	-2.498370
H	0.790248	0.125801	-2.597758
H	2.754584	-2.679397	1.045437
H	2.019601	-2.476174	-0.559748
H	4.957247	-2.153987	0.211043
H	6.641603	-0.419270	-0.362656
H	3.452212	2.496414	-0.666130
H	5.880789	1.929926	-0.806251

IV4 (S= ½) E = -2407.400802

C	-4.861487	1.754779	-0.795035
C	-4.271191	2.687347	0.068205
C	-3.024763	2.440114	0.636034
C	-2.324363	1.242545	0.363105
C	-2.925083	0.298795	-0.518613
C	-4.180565	0.570645	-1.078644
C	-2.223824	-1.009587	-0.798914
C	-2.135114	-1.899181	0.481851
O	-3.017031	-2.669507	0.778532
O	-1.151160	1.029908	0.937856
Fe	0.075604	-0.300720	0.462371
O	0.730441	0.040974	2.372591
N	-0.817271	-0.759104	-1.232768
C	-0.133913	-1.934784	-1.829827
C	1.343133	-1.927179	-1.445420
N	1.442338	-1.730245	0.017278
C	2.795498	-1.441609	0.536060
C	3.363798	-0.116842	0.076991
C	2.532446	0.974743	-0.302109
C	3.159102	2.197393	-0.649936

C	4.541877	2.338614	-0.625575
C	5.357778	1.259641	-0.259447
C	4.757471	0.048371	0.080508
O	1.213451	0.893453	-0.412882
O	-1.022500	-1.700427	1.157413
H	-0.759785	0.052746	-1.851995
H	1.064197	-2.551009	0.496480
H	-0.256353	-1.953902	-2.925139
H	-0.619186	-2.841203	-1.435854
H	1.867075	-1.092396	-1.930637
H	1.833580	-2.864892	-1.762824
H	2.705899	-1.454988	1.635089
H	3.485518	-2.258816	0.255809
H	5.386771	-0.802382	0.363196
H	6.445203	1.360636	-0.244414
H	2.508746	3.024591	-0.943185
H	4.990829	3.297757	-0.898675
H	-2.782094	-1.569552	-1.565468
H	-4.632348	-0.170195	-1.744972
H	-2.555197	3.160456	1.309592
H	-5.839231	1.949299	-1.240937
H	-4.789992	3.622060	0.299071
H	0.124176	-0.562491	2.839916
H	0.295263	0.911089	2.465662