Supporting Information for

Effects of Non-covalent Interactions on High-spin Fe(IV)–oxido Complexes

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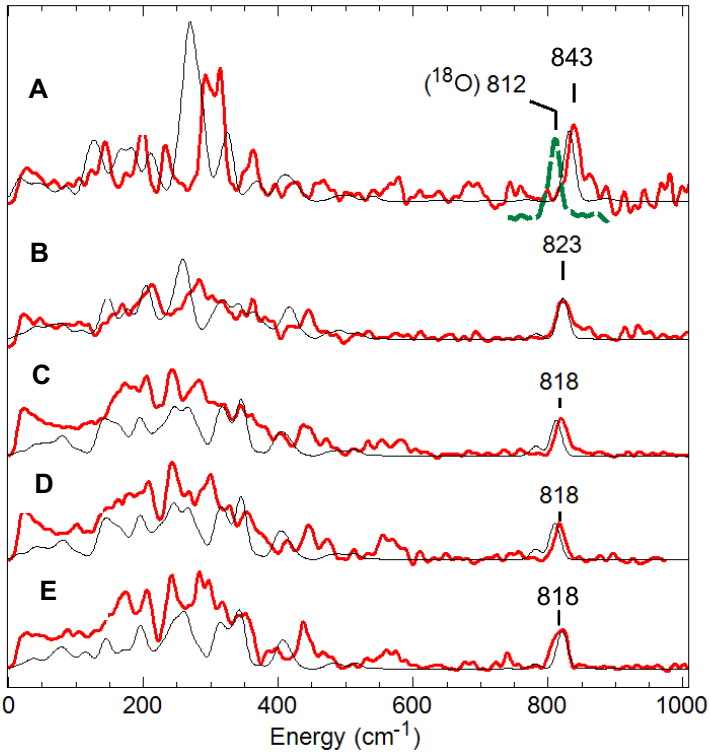

Figure S1. ^{57}Fe PVDOS spectra (red trace – experimental; grey trace – simulated) for [Fe^{IV}poat(O)]$^-$ (A), [Fe^{IV}poat(O)---Mg^{II}]$^+$ (B), [Fe^{IV}poat(O)---Ca]$^+$ (C), [Fe^{IV}poat(O)---Sr]$^+$ (D), and [Fe^{IV}poat(O)---Ba]$^+$ (E). The green spectrum is of [Fe^{IV}poat(^{18}O)]$^-$. Samples were ~20mM ^{57}Fe in a DMF:THF mixture.

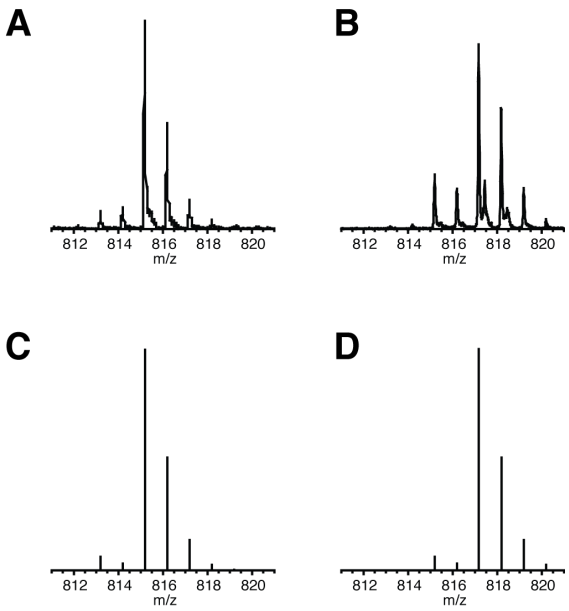

Figure S2. Negative-mode ESI mass spectra for [Fe^{IV}poat(^{16}O)]$^-$ (**A**) and [Fe^{IV}poat(^{18}O)]$^-$ (**B**) and their calculated spectra (**C**) and (**D**), respectively. The samples were prepared from [Fe^{II}poat]$^-$ and (^{16}O)IBX-iPr and (^{18}O)IBX-iPr, respectively, in EtCN at – 90 °C.

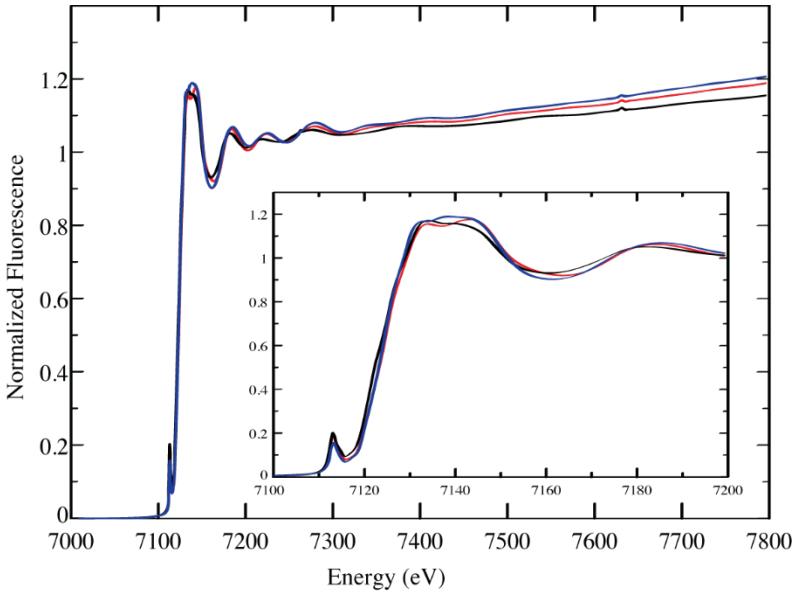

Figure S3. Normalized Fe K-edge fluorescence spectra of $[Fe^{IV}poat(O)]^-$ (black), $[Fe^{IV}poat(O)\text{---}Mg^{II}]^+$ (blue), and $[Fe^{IV}poat(O)\text{---}Ca]^+$ (red). Inset is the zoom on the XANES region.

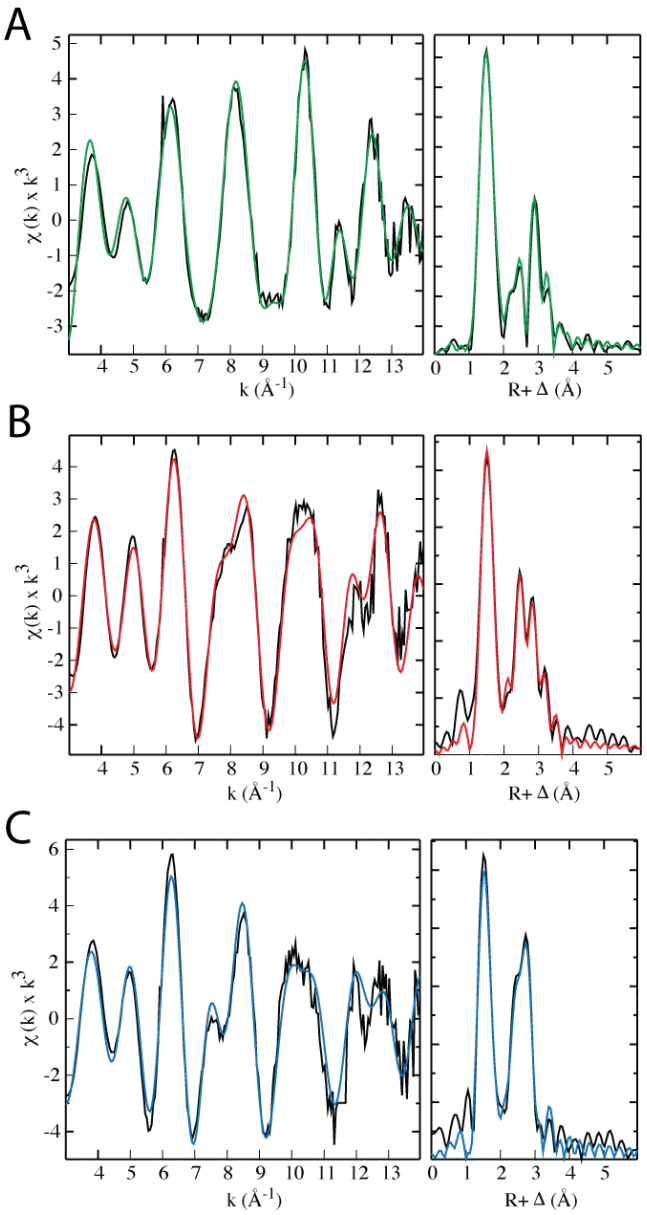

Figure S4. Unfiltered EXAFS data (left) and the Fourier transforms (right) for [Fe^{IV}poat(O)]$^{-}$ (**A**), [Fe^{IV}poat(O)---Ca^{II}]$^{+}$ (**B**), and [Fe^{IV}poat(O)---Mg]$^{+}$ (**C**). The black traces are experimental data and the colored traces are the corresponding simulated fits.

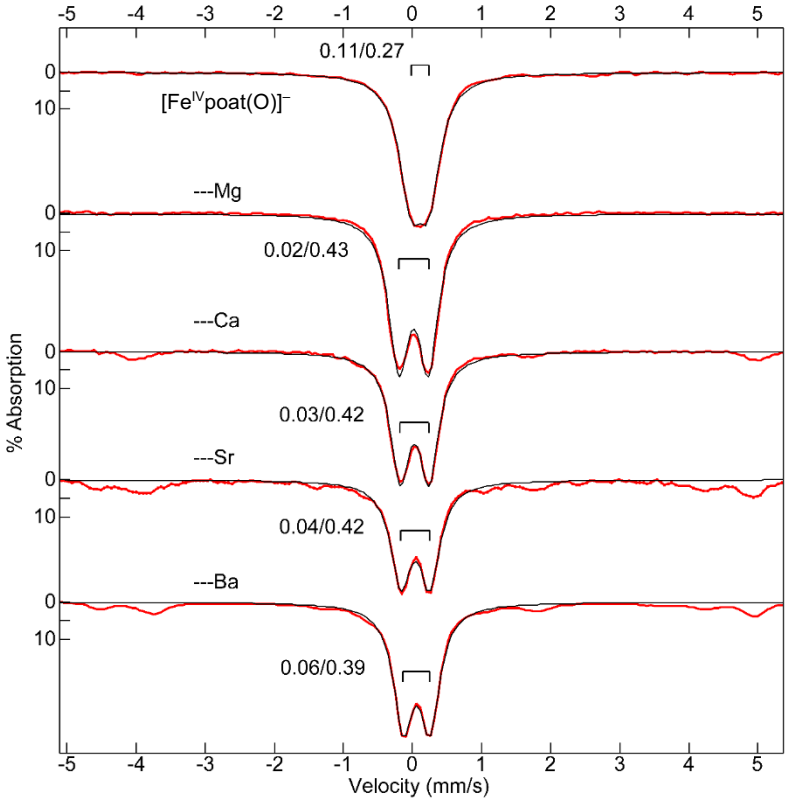

Figure S5. ^{57}Fe-enriched Mössbauer spectra of [Fe^{IV}poat(O)]$^-$ and with LA adducts as listed (red traces, 4.2 K, no applied magnetic field) generated at -80°C. The black traces are fits for $\delta/\Delta E_q$ in mm/s as listed.

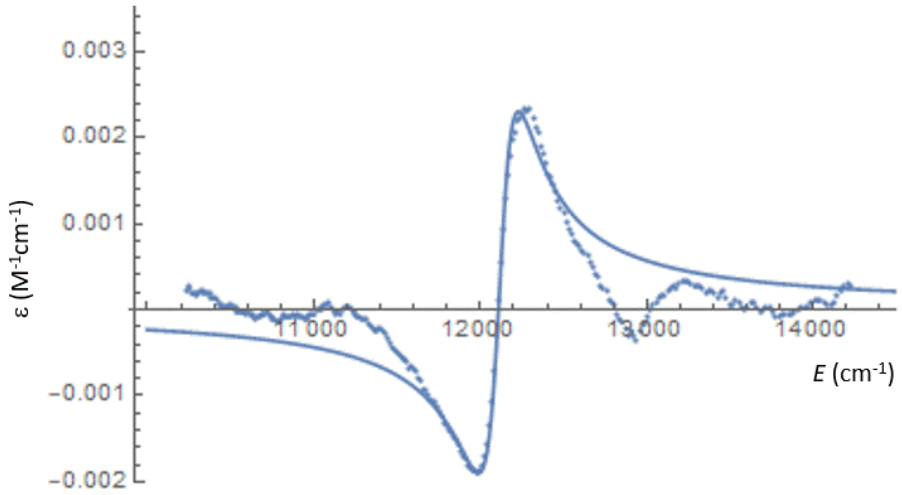

Figure S6. Fano interference observed for $[Fe^{IV}poat(O)]^-$ (see Figure 7A) from which the background was subtracted (dots). The solid curve is a simulation using eq S1,[1] from which the back ground was removed.

$$F(E) = f\left[\frac{\left(q+\left(\frac{E-E_0}{w}\right)\right)^2}{\left(1+\left(\frac{E-E_0}{w}\right)\right)^2} - 1\right]. \qquad \text{S1}$$

In eq S1, E is the energy of the incident radiation, E_0 and w are respectively energy at maximum and width parameter of the sharp $^5A \rightarrow {}^3E$ band, f is the back ground absorption, and q is a parameter which depends on the extent of the spin-orbit coupling between ^5E and ^3E. Parameters used in simulation: E_0 = 12120 cm^{-1}, w = 120 cm^{-1}, f = 0.0019, and q = 1.1.

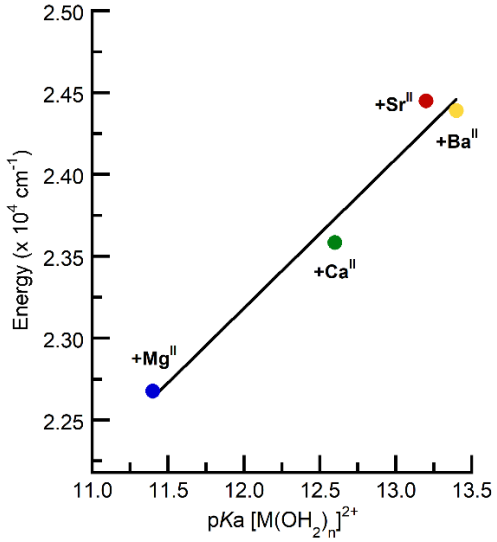

Figure S7. A plot of the energy of the LMCT absorbances versus the pK_a of $[LA(OH_2)_n]^{2+}$.

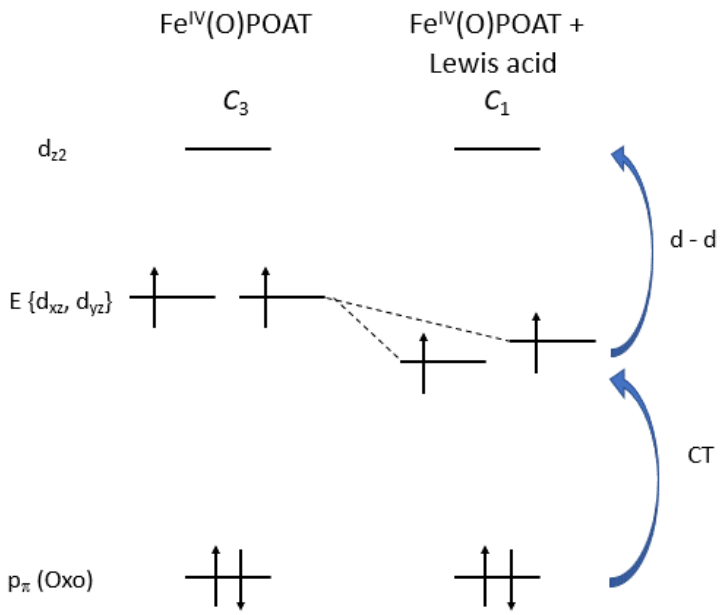

Figure S8. Schematic representation of the effects of H-bonds and electrostatic interactions on d-orbital energies.

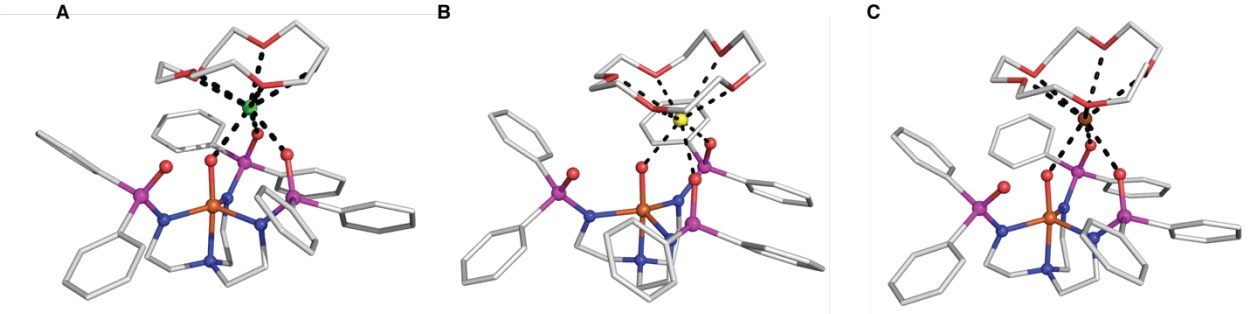

Figure S9. DFT-optimized structures for [Fe^{IV}poat(O)---Ca^{II}]$^+$ (**A**), [Fe^{IV}poat(O)---Sr^{II}]$^+$ (**B**), and [Fe^{IV}poat(O)---Ba^{II}]$^+$ (**C**). Key: Ca^{II} ion is the green sphere, Sr^{II} ion is the yellow sphere, and Ba^{II} ion is the brown sphere. The remaining colors of the atoms are the same as those listed in the legend of Figure 10 and hydrogen atoms are omitted for clarity.

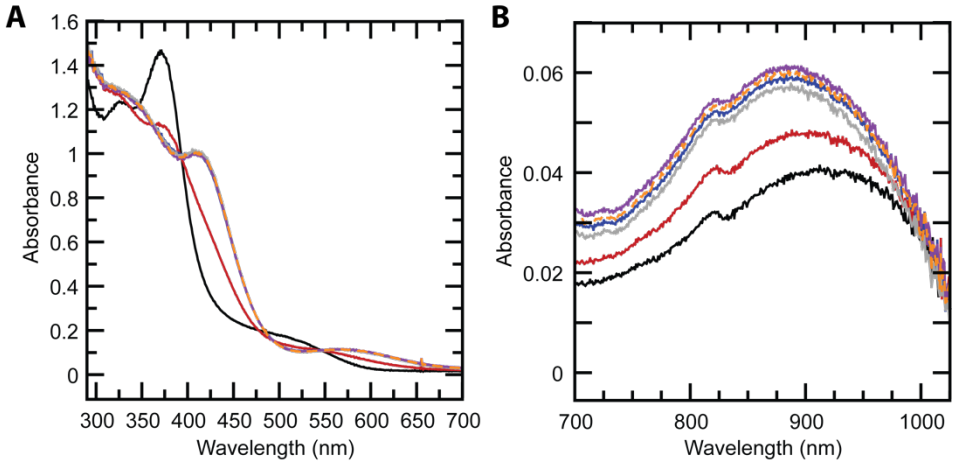

Figure S10. Optical spectra showing the titration of $[Fe^{IV}poat(O)]^-$ with $[15c5Sr^{II}](OTf)_2$ in THF:DMF at -60˚C. Higher energy region (**A**) and lower energy region (**B**). Key: $[Fe^{IV}poat(O)]^-$ (black solid-line), $[Fe^{IV}poat(O)]^-$ + 0.5 equiv of $[15c5Sr^{II}](OTf)_2$ (red solid-line); $[Fe^{IV}poat(O)]^-$ + 1.0 equiv of $[15c5Sr^{II}](OTf)_2$ (blue solid-line); $[Fe^{IV}poat(O)]^-$ + 2.0 equiv of $[15c5Sr^{II}](OTf)_2$ (gray solid-line); $[Fe^{IV}poat(O)]^-$ + 3.0 equiv of $[15c5Sr^{II}](OTf)_2$ (purple solid-line); $[Fe^{IV}poat(O)]^-$ + 4.0 equiv of $[15c5Sr^{II}](OTf)_2$ (orange dashed line) Initial $[[Fe^{IV}poat(O)]^-]$ = 0.20 mM.

Table S1. Best fits of EXAFS data collected for the Fe^{IV}–oxido complexes

		Complex		
		$[Fe^{IV}poat(O)]^-$	$[Fe^{IV}poat(O)\text{---}Ca^{II}]^+$	$[Fe^{IV}poat(O)\text{---}Mg^{II}]^+$
Fe–O	N	1	1	1
	R(Å)	1.65	1.67	1.67
	σ^2 (10^{-3})	2.34	1.36	3.18
Fe–N	N	4	4	4
	R(Å)	1.99	2.00	1.98
	σ^2 (10^{-3})	5.70	6.62	5.53
Fe–C	N	3	4	3
	R(Å)	2.85	2.95	2.94
	σ^2 (10^{-3})	5.75	2.41	1.63
Fe–P	N	3	3	3
	R(Å)	3.30	3.23	3.19
	σ^2 (10^{-3})	5.38	3.36	2.48
Fe–O_P	N	2	3	3
	R(Å)	3.72	3.59	3.46
	σ^2 (10^{-3})	3.32	4.05	4.71
GOF	E_0	-15.19	1.73	-4.63
	F	33	66	89
	F’	205	257	286

Table S2. Selected distances from DFT for $[Fe^{IV}poat(O)]^-$ and its LA bound derivatives[a]

	Bond distances (Å)			
Complex	Fe^{IV}–O	$Fe^{IV}O$---M^{II}	M^{II}–O(P)	M^{II}–O(15c5)
$[Fe^{IV}poat(O)]^-$	1.639	–	–	–
$[Fe^{IV}poat(O)---Mg^{2+}]^+$	1.665	2.05	2.02, 2.02	2.14, 2.18, 2.19, 4.63, 4.30
$[Fe^{IV}poat(O)---Ca^{2+}]^+$	1.662	2.33	2.32, 2.33	2.55, 2.62, 2.63, 2.63, 2.70
$[Fe^{IV}poat(O)---Sr^{2+}]^+$	1.659	2.45	2.45,2.50	2.67, 2.68, 2.73, 2.75, 2.80
$[Fe^{IV}poat(O)---Ba^{2+}]^+$	1.657	2.57	2.65,2.59	2.81, 2.84, 2.88, 2.91, 2.97

[a]M^{II} is LA bound species.

Table S3A. Coordinates (x,y,z) for DFT optimized structure of $[Fe^{IV}poat(O)]^-$.

	X	Y	Z
C	1.37687687	-0.39927127	-3.28214620
C	2.38957785	0.12491842	-2.27701413
C	-1.03207515	-0.99443656	-3.28204020
C	-1.08509016	-2.13292595	-2.27614813
C	-0.34286968	1.38934053	-3.28317220
C	-1.30301063	2.00531322	-2.27850213
Fe	0.00010203	-0.00008210	-0.64563201
N	0.00055401	-0.00128710	-2.84981417
N	1.97161070	-0.33989510	-0.92773703
N	-1.27990132	-1.53744934	-0.92759003
N	-0.69137029	1.87658315	-0.92925003
O	-0.00028595	0.00116091	0.99401611
P	3.21561597	-0.55374751	0.15707005
P	-2.08747815	-2.50628976	0.15834305
P	-1.12746171	3.06081398	0.15584205
H	1.57159470	-0.03383481	-4.29878627
H	1.42686754	-1.48656200	-3.29149320
H	2.44354227	1.21907979	-2.32190013
H	3.38171903	-0.24645868	-2.55293115
H	-1.99864463	-0.49395979	-3.29215920
H	-0.81244577	-1.34645948	-4.29833727
H	-1.90237510	-2.80688523	-2.55220115
H	-0.16426791	-2.72647112	-2.31973313
H	0.57388311	1.97608649	-3.29296220
H	-0.75676691	1.37452198	-4.29977627
H	-1.47709688	3.05007859	-2.55516715
H	-2.27773830	1.50523603	-2.32303013
O	3.99311205	0.66259533	0.63431708
O	-2.56903197	3.12565399	0.63472008
O	-1.42242396	-3.78604962	0.63959808
C	-2.66867669	-1.48156903	1.54423415
C	-3.04359900	-0.13736299	1.41445314

C	-2.80445201	-2.11214129	2.79237323
C	-3.54939375	0.56709872	2.50814822
H	-2.90698107	0.38793924	0.48289507
C	-3.31836479	-1.41030847	3.88448131
H	-2.49009354	-3.14112951	2.89721224
C	-3.69421817	-0.07087442	3.74295330
H	-3.78281597	1.61427487	2.37918521
H	-3.41062530	-1.90331929	4.84469039
H	-4.07992498	0.47689471	4.59443836
C	-3.65190477	-3.00032219	-0.70544102
C	-3.98662174	-4.36185587	-0.76730002
C	-4.52260848	-2.06303064	-1.28700506
C	-5.16280032	-4.77874840	-1.39921006
H	-3.31209409	-5.07481381	-0.31346399
C	-5.69918404	-2.47778817	-1.91544210
H	-4.28262658	-1.00939673	-1.23899705
C	-6.02142600	-3.83820302	-1.97433211
H	-5.40837421	-5.83302726	-1.43929807
H	-6.36371742	-1.74325336	-2.35344813
H	-6.93448531	-4.15941001	-2.46048514
C	0.04811924	3.05065749	1.54378815
C	1.40038078	2.70513664	1.41566514
C	-0.43289014	3.48008086	2.79199824
C	2.26127696	2.78961531	2.51108021
H	1.78925982	2.32669949	0.48399407
C	0.42984515	3.57308750	3.88581232
H	-1.48175305	3.72050570	2.89543825
C	1.77843174	3.23089670	3.74594430
H	3.28538881	2.46940079	2.38327521
H	0.04689939	3.89697757	4.84602938
H	2.44407656	3.29011094	4.59873737
C	-0.77064659	4.66236240	-0.70756402
C	-1.78184686	5.63347981	-0.77128702
C	0.47754126	4.94712097	-1.28704206
C	-1.55316667	6.86032085	-1.40300506
H	-2.73744392	5.40625136	-0.31911099
C	0.70827244	6.17324801	-1.91527510
H	1.26964763	4.21218548	-1.23749505
C	-0.30822299	7.13296847	-1.97606611
H	-2.34300698	7.60048535	-1.44455907
H	1.67750024	6.38096426	-2.35167414
H	-0.12861644	8.08412018	-2.46212414
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C	1.64280238	-2.56232093	1.42048414
C	3.23506729	-1.36412882	2.79336624
C	1.28620599	-3.34897128	2.51697422
H	1.11870940	-2.70975503	0.48987807
C	2.88497782	-2.15672227	3.88818732
H	3.96947471	-0.57741445	2.89512224
C	1.91232763	-3.15189952	3.75060231
H	0.49559237	-4.07471192	2.39083920
H	3.35910008	-1.98745251	4.84742039
H	1.63133964	-3.75710286	4.60419737
C	4.42340942	-1.66460151	-0.70617602

C	5.76976264	-1.27407422	-0.77305702
C	4.04531925	-2.88909661	-1.28281806
C	6.71704500	-2.08635476	-1.40502907
H	6.05131610	-0.33202786	-0.32301799
C	4.99095759	-3.70279913	-1.91127010
H	3.01298597	-3.20785903	-1.23091206
C	6.33011096	-3.30203075	-1.97515111
H	7.75278622	-1.77214239	-1.44898307
H	4.68575913	-4.64692318	-2.34540913
H	7.06339870	-3.93382146	-2.46129014

Table S3B. Coordinates (x,y,z) for DFT optimized structure of $[Fe^{IV}poat(O)---Mg^{II}]^{+}$

	X	Y	Z
C	2.34352826	0.00827297	-3.70735198
C	3.34214637	-0.42564874	-2.63811451
C	3.18913144	-2.87138751	0.02198368
C	2.38774376	-3.51533997	-0.93249753
C	2.20969931	-4.90237622	-0.89413529
C	2.83318584	-5.66043044	0.09987299
C	3.63165619	-5.02825394	1.06040128
C	3.80802532	-3.64413091	1.02302815
C	5.20927069	-0.79829328	-0.26633133
C	6.02363976	-1.71549089	-0.95090715
C	7.38145117	-1.44847139	-1.14706560
C	7.93939084	-0.26242643	-0.66295063
C	7.13834259	0.65385322	0.02561538
C	5.78262016	0.38760875	0.22710249
C	0.21393225	1.29116946	-3.96307307
C	-0.75857393	0.13712024	-3.73315870
C	-2.33285406	-2.53432875	-1.78883208
C	-1.54768064	-3.21617562	-2.73380238
C	-1.71013753	-4.58969433	-2.93082509
C	-2.65033102	-5.29678798	-2.17536857
C	-3.41921206	-4.63077565	-1.21669894
C	-3.26766063	-3.25657033	-1.02461992
C	-3.62571984	0.00565730	-2.37542177
C	-4.35114746	-0.65430759	-3.38061547
C	-5.44229336	-0.02853475	-3.99098864
C	-5.82058619	1.25818407	-3.60171554
C	-5.10690569	1.92127834	-2.59759549
C	-4.01567306	1.30117720	-1.98735868
C	2.20594529	2.35172290	-2.87716689
C	1.40136925	3.24332983	-1.93190190
C	1.44170036	3.74409981	1.39316902
C	2.20596431	2.82703381	2.14364387
C	3.32893876	3.26297680	2.84799798
C	3.71101363	4.60831372	2.80966183
C	2.97346601	5.51860887	2.05023853
C	1.84757095	5.08963909	1.34018600
C	-1.04983704	4.44298105	-0.02740148
C	-1.69559747	4.44898637	-1.27539406
C	-2.63911897	5.43155773	-1.58565858

C	-2.95743922	6.41733234	-0.64836021
C	-2.33854090	6.40962456	0.60512375
C	-1.39525997	5.42827387	0.91578127
Fe	0.85971980	0.38650528	-1.28904569
N	1.45479227	1.07770249	-3.14337997
N	2.63281161	-0.44468288	-1.33006131
N	-0.80493104	-0.15816586	-2.27674356
N	0.69488280	2.37939741	-0.94961573
O	0.42076985	-0.24538453	0.18749265
P	3.41940297	-1.05485964	0.02845926
P	-2.17702450	-0.73735334	-1.55102002
P	0.06376879	3.06423223	0.41209778
H	2.84310586	0.36806161	-4.61250339
H	1.70482379	-0.82943381	-3.97965129
H	4.20576027	0.24459566	-2.61280830
H	3.73162884	-1.41155682	-2.91113761
H	1.89006369	-2.92436627	-1.68824482
H	1.58604321	-5.38564726	-1.63421033
H	2.70281104	-6.73400053	0.12582714
H	4.11794985	-5.61276913	1.82993956
H	4.42758322	-3.16171838	1.76723114
H	5.60737724	-2.64492028	-1.31602913
H	8.00081858	-2.16583324	-1.66853000
H	8.99095218	-0.05808556	-0.81263482
H	7.57057128	1.56675890	0.41306379
H	5.16725027	1.08189274	0.78282103
H	-0.24013986	2.21664783	-3.62214411
H	0.47641779	1.39844298	-5.02058276
H	-1.73801658	0.42671132	-4.12332928
H	-0.44564596	-0.74122629	-4.30898704
H	-0.80488687	-2.67774427	-3.30465014
H	-1.10741075	-5.10419299	-3.66741804
H	-2.77582730	-6.36049934	-2.32626993
H	-4.12220539	-5.17784745	-0.60561365
H	-3.84412053	-2.76084432	-0.25669562
H	-4.07842860	-1.65776877	-3.67680071
H	-5.99698743	-0.54765325	-4.76061487
H	-6.66808880	1.73848635	-4.07157042
H	-5.40270820	2.91426024	-2.28666532
H	-3.47357880	1.81176919	-1.20299297
H	3.14291267	2.07495384	-2.40337752
H	2.42843251	2.85931966	-3.82117370
H	2.09768730	3.93697130	-1.44706781
H	0.69622621	3.86251262	-2.49555695
H	1.94843064	1.77717587	2.15417812
H	3.90787929	2.54808698	3.41674322
H	4.58079586	4.94177603	3.35968369
H	3.27074179	6.55772116	2.00704612
H	1.29141289	5.80705444	0.75333919
H	-1.47137036	3.67342516	-1.99400191
H	-3.12192423	5.42689801	-2.55365459
H	-3.68326134	7.18182005	-0.88975550
H	-2.58955930	7.16438313	1.33797623
H	-0.93079552	5.43107486	1.89226191

O	3.02538751	-0.45362176	1.36112874
O	-0.74499907	2.06315967	1.24101291
O	-2.26538061	-0.42004791	-0.04965406
C	-1.16854400	1.45832892	4.17189135
O	-0.29585179	0.49504842	3.50145557
C	-2.60649461	0.95247633	4.11405141
O	-2.80926252	0.42095578	2.76607475
C	-4.20175276	0.31042725	2.29373866
O	-4.58702901	-2.09356193	2.76333356
C	-5.02677726	-0.73561662	3.02379075
O	-2.58999115	-4.24505215	2.12423941
C	-3.61987413	-2.63733014	3.71034449
O	-0.55668632	-1.84978113	2.37489888
C	-3.36155750	-4.08415966	3.34486673
C	-1.13640795	-4.27025339	2.22468049
C	-0.49943570	-3.07221612	1.54582468
C	0.62361907	-1.66122508	3.24874322
C	0.20654210	-0.63896246	4.27798628
H	-0.84039876	1.62113503	5.19955746
H	-3.30264017	1.77469761	4.29778356
H	-4.67070428	1.29526443	2.38711170
H	-5.06690504	-0.54762925	4.10320183
H	-2.68928619	-2.07033128	3.67643876
H	-4.04375274	-2.59313210	4.72298018
H	-2.85576535	-4.58540292	4.17891090
H	-4.31032294	-4.58406126	3.16068998
H	-0.82160063	-4.34877761	3.27101907
H	-0.80703110	-5.17179227	1.70319944
H	0.54443209	-3.27052499	1.30201685
H	-1.03386417	-2.83781232	0.63313446
H	0.88198809	-2.60581607	3.73046487
H	1.45737504	-1.30578943	2.63748868
H	-0.58317203	-1.02787282	4.92521152
H	1.05511643	-0.31830959	4.88408142
Mg	-1.09916164	0.09594664	1.51377545
H	-1.05353845	2.36567842	3.59067656
H	-2.79318220	0.16244164	4.84388547
H	-6.04651054	-0.67613580	2.63979705
H	-4.09337069	0.05013954	1.24600710

Table S3C. Coordinates (x,y,z) for DFT optimized structure of $[Fe^{IV}poat(O)\text{---}Ca^{II}]^{+}$

	X	Y	Z
C	1.89000	-0.69900	-3.88900
C	3.03000	-0.74800	-2.88200
C	3.82900	-2.51200	0.06100
C	3.09600	-3.50800	-0.60200
C	3.33300	-4.86200	-0.33900
C	4.30700	-5.23500	0.59000
C	5.04200	-4.25000	1.26000
C	4.80400	-2.90000	0.99900
C	5.10200	-0.03100	-0.77200
C	6.09700	-0.77900	-1.42400

C	7.28800	-0.17100	-1.83200
C	7.49700	1.19000	-1.59500
C	6.51600	1.94100	-0.94200
C	5.32700	1.33600	-0.52900
C	-0.41900	0.16400	-4.17400
C	-1.18300	-1.02000	-3.59400
C	-2.62600	-3.17600	-1.27200
C	-1.47800	-3.96000	-1.47000
C	-1.55600	-5.35500	-1.44300
C	-2.78400	-5.98400	-1.22100
C	-3.93400	-5.21400	-1.02000
C	-3.85600	-3.82000	-1.04200
C	-4.00100	-0.73400	-2.03500
C	-4.60100	-1.35500	-3.14600
C	-5.75200	-0.81500	-3.72700
C	-6.32100	0.34800	-3.20300
C	-5.73900	0.96900	-2.09400
C	-4.58700	0.43300	-1.51300
C	1.42400	1.71500	-3.49900
C	0.56900	2.64000	-2.63700
C	1.03800	3.87600	0.44500
C	1.96500	3.32400	1.35100
C	3.09100	4.05200	1.73800
C	3.31400	5.33500	1.22600
C	2.40900	5.88500	0.31600
C	1.27900	5.16000	-0.07600
C	-1.69500	3.91800	-0.62500
C	-2.53900	3.53600	-1.68200
C	-3.64200	4.31900	-2.03200
C	-3.92200	5.49000	-1.32500
C	-3.10300	5.87100	-0.25800
C	-1.99900	5.08900	0.09100
C	-0.70200	2.47000	4.09300
C	-2.06100	2.03900	4.60300
C	-3.98900	0.70100	3.80500
C	-3.84400	-0.70100	4.35800
C	-2.96400	-2.86800	3.58300
C	-2.29400	-3.42800	2.34600
C	0.12700	-3.44800	2.81400
C	1.26300	-2.45900	2.82100
C	1.78200	-0.32100	3.93700
C	1.04700	0.78100	4.65900
Ca	-1.09900	-0.17300	1.97400
Fe	0.54400	-0.07300	-1.41400
H	2.24700	-0.45900	-4.89700
H	1.38400	-1.66100	-3.92900
H	3.76000	0.04100	-3.08400
H	3.56400	-1.69500	-3.01000
H	2.33500	-3.21500	-1.31200
H	2.76500	-5.62000	-0.86200
H	4.49700	-6.28100	0.78800
H	5.79900	-4.53500	1.97900
H	5.37800	-2.14500	1.52100
H	5.95300	-1.83600	-1.60300

H	8.04900	-0.75900	-2.32700
H	8.42000	1.65900	-1.90900
H	6.67800	2.99300	-0.74700
H	4.57800	1.91100	-0.00200
H	-0.99600	1.07000	-4.01600
H	-0.23300	0.05000	-5.24700
H	-2.19900	-0.99200	-3.99400
H	-0.74700	-1.97000	-3.92500
H	-0.52800	-3.47000	-1.63400
H	-0.66600	-5.94800	-1.60100
H	-2.84700	-7.06400	-1.21100
H	-4.88800	-5.69700	-0.85300
H	-4.75200	-3.23400	-0.89000
H	-4.19000	-2.27300	-3.54600
H	-6.20400	-1.30600	-4.57800
H	-7.21500	0.76200	-3.64900
H	-6.18100	1.86400	-1.67800
H	-4.14200	0.90500	-0.64800
H	2.43300	1.68400	-3.10100
H	1.46800	2.05700	-4.53800
H	1.15900	3.54100	-2.43200
H	-0.31400	2.97300	-3.19200
H	1.81100	2.32400	1.72900
H	3.79700	3.61600	2.43200
H	4.18600	5.89800	1.53100
H	2.57800	6.87500	-0.08800
H	0.58500	5.60400	-0.77600
H	-2.34200	2.61500	-2.21300
H	-4.27900	4.01200	-2.85100
H	-4.77200	6.10100	-1.59900
H	-3.32100	6.77200	0.29800
H	-1.37500	5.39500	0.92000
H	-0.16600	3.05200	4.84600
H	-2.68100	2.91300	4.82500
H	-4.54300	1.34400	4.49300
H	-3.35800	-0.71000	5.33800
H	-2.40600	-3.09400	4.49700
H	-3.97600	-3.27700	3.67700
H	-2.18500	-4.51300	2.41500
H	-2.87200	-3.18200	1.46300
H	-0.14900	-3.71200	3.83900
H	0.40500	-4.35400	2.26900
H	2.11100	-2.86200	3.38000
H	1.58200	-2.19500	1.81600
H	2.46600	-0.83100	4.62300
H	2.33000	0.04000	3.06700
H	0.54300	0.39800	5.55100
H	1.74100	1.57500	4.94800
H	-0.81100	3.04600	3.18000
H	-1.97200	1.42500	5.50500
H	-4.82900	-1.17200	4.44900
H	-4.50400	0.67400	2.84800
N	0.88100	0.31600	-3.44100
N	2.44800	-0.61100	-1.51800

N	-1.15300	-0.90600	-2.11200
N	0.18700	1.92300	-1.39400
O	0.33900	-0.51800	0.17400
O	3.06800	-0.04800	1.06600
O	-0.82700	1.94000	1.05500
O	-2.47000	-0.84100	0.21500
O	0.07100	1.29500	3.70700
O	-2.67200	1.26500	3.52400
O	-3.02900	-1.42300	3.39300
O	-0.99500	-2.79600	2.14500
O	0.74700	-1.26000	3.48800
P	3.50000	-0.72900	-0.21500
P	-2.47900	-1.35100	-1.22500
P	-0.34000	2.80500	-0.10100

Table S3D. Coordinates (x,y,z) for DFT optimized structure of $[Fe^{IV}poat(O)\text{---}Sr^{II}]^{+}$

	X	Y	Z
C	1.89400	-0.68300	-4.01000
C	3.00700	-0.85300	-2.98500
C	3.57600	-2.73300	-0.01500
C	2.76800	-3.66200	-0.68800
C	2.87700	-5.03000	-0.41700
C	3.79700	-5.48400	0.53100
C	4.60600	-4.56700	1.21100
C	4.49600	-3.20200	0.94100
C	5.08300	-0.37600	-0.81900
C	6.03000	-1.21000	-1.43700
C	7.27800	-0.70700	-1.81500
C	7.59300	0.63400	-1.58300
C	6.65900	1.47100	-0.96500
C	5.41400	0.97100	-0.58100
C	-0.33900	0.36100	-4.30300
C	-1.20100	-0.78000	-3.77700
C	-2.68000	-3.00200	-1.49200
C	-1.54800	-3.79500	-1.73900
C	-1.64100	-5.19000	-1.73200
C	-2.86700	-5.81000	-1.48000
C	-4.00200	-5.03100	-1.23100
C	-3.90900	-3.63700	-1.23500
C	-4.02500	-0.54800	-2.27700
C	-4.61100	-1.17200	-3.39400
C	-5.74200	-0.62200	-4.00200
C	-6.30500	0.55500	-3.50100
C	-5.73700	1.17800	-2.38600
C	-4.60500	0.63100	-1.77700
C	1.60100	1.74600	-3.54800
C	0.80000	2.70300	-2.67100
C	1.36800	3.90700	0.37800
C	2.26000	3.32100	1.29700
C	3.42600	3.99300	1.67100
C	3.72100	5.25000	1.13300
C	2.84800	5.83400	0.21200

C	1.67900	5.16500	-0.16600
C	-1.38200	4.08000	-0.65500
C	-2.26800	3.71100	-1.68100
C	-3.34500	4.53400	-2.02200
C	-3.55400	5.73400	-1.33800
C	-2.69000	6.10200	-0.30200
C	-1.61400	5.28000	0.04000
C	-0.19100	2.37300	4.24900
C	-1.53400	2.07300	4.88600
C	-3.71100	1.06200	4.22500
C	-3.77000	-0.40200	4.60800
C	-3.36100	-2.60400	3.59100
C	-2.75200	-3.19900	2.33700
C	-0.36200	-3.59500	2.87500
C	0.93000	-2.81500	2.85300
C	1.84800	-0.75000	3.86200
C	1.34700	0.44300	4.63800
Fe	0.55400	-0.03500	-1.54100
H	2.28900	-0.44100	-5.00300
H	1.31700	-1.60200	-4.09100
H	3.80000	-0.11800	-3.14900
H	3.46900	-1.83500	-3.13400
H	2.05100	-3.30300	-1.41400
H	2.25200	-5.73700	-0.94700
H	3.88900	-6.54300	0.73500
H	5.32400	-4.91600	1.94200
H	5.12700	-2.49900	1.46900
H	5.80300	-2.25300	-1.61200
H	8.00100	-1.36100	-2.28400
H	8.56000	1.02200	-1.87500
H	6.90300	2.50800	-0.77500
H	4.69900	1.61200	-0.08300
H	-0.84800	1.30400	-4.12400
H	-0.14400	0.26900	-5.37700
H	-2.20700	-0.65700	-4.18500
H	-0.83500	-1.74700	-4.14300
H	-0.59900	-3.31300	-1.92900
H	-0.76200	-5.79000	-1.92900
H	-2.94100	-6.88900	-1.48500
H	-4.95500	-5.50600	-1.04200
H	-4.79500	-3.04400	-1.05000
H	-4.20200	-2.09700	-3.77800
H	-6.18500	-1.11400	-4.85800
H	-7.18400	0.97700	-3.96900
H	-6.17600	2.08200	-1.98600
H	-4.17400	1.10300	-0.90600
H	2.59800	1.63000	-3.13300
H	1.69000	2.11900	-4.57400
H	1.44200	3.56500	-2.45200
H	-0.06200	3.09700	-3.22000
H	2.04800	2.34000	1.69800
H	4.10500	3.53200	2.37600
H	4.62400	5.76900	1.42800
H	3.07200	6.80400	-0.20900

H	1.00900	5.63500	-0.87300
H	-2.12400	2.77100	-2.19500
H	-4.01600	4.23700	-2.81700
H	-4.38300	6.37500	-1.60600
H	-2.85300	7.02600	0.23700
H	-0.95700	5.57500	0.84700
H	0.47100	2.87700	4.95800
H	-2.01200	3.00200	5.21100
H	-4.07200	1.69300	5.04100
H	-3.16700	-0.61300	5.49700
H	-2.84300	-2.93600	4.49600
H	-4.41600	-2.88800	3.66500
H	-2.82500	-4.28900	2.35000
H	-3.25400	-2.81600	1.45400
H	-0.67100	-3.78000	3.90700
H	-0.24400	-4.54800	2.35400
H	1.70600	-3.36400	3.39500
H	1.27000	-2.62800	1.83400
H	2.51500	-1.35000	4.48800
H	2.35800	-0.45500	2.94200
H	0.83500	0.12800	5.55200
H	2.18300	1.09900	4.89900
H	-0.32600	2.99100	3.36600
H	-1.43100	1.40500	5.74700
H	-4.80700	-0.69400	4.80700
H	-4.32200	1.24400	3.34300
N	0.95600	0.39100	-3.54700
N	2.41000	-0.71500	-1.62900
N	-1.18300	-0.72500	-2.29200
N	0.37500	1.99000	-1.43700
O	0.29200	-0.55200	0.01400
O	3.01500	-0.21200	0.97200
O	-0.58500	2.09100	1.04500
O	-2.55500	-0.68700	0.01400
O	0.42400	1.14700	3.75400
O	-2.35000	1.43800	3.85000
O	-3.24800	-1.15200	3.47200
O	-1.36200	-2.78100	2.18800
O	0.65500	-1.54300	3.52100
P	3.41300	-0.93000	-0.30100
P	-2.52700	-1.17900	-1.43100
P	-0.07500	2.90800	-0.13800
Sr	-1.11500	-0.11200	1.97000

Table S3E. Coordinates (x,y,z) for DFT optimized structure of $[Fe^{IV}poat(O)\text{---}Ba^{II}]^{+}$

	X	Y	Z
Ba	-1.14700	-0.14300	1.92900
C	2.02200	-0.45600	-4.12500
C	3.09600	-0.70800	-3.07100
C	3.27800	-2.72900	-0.04000
C	2.24500	-3.50900	-0.58100
C	2.14500	-4.87000	-0.27600

C	3.08300	-5.47000	0.56800
C	4.11700	-4.70300	1.11500
C	4.21200	-3.34200	0.81700
C	5.12600	-0.62500	-0.82500
C	5.92800	-1.55800	-1.50400
C	7.24900	-1.24800	-1.83800
C	7.78400	-0.00200	-1.50000
C	6.99600	0.93200	-0.82100
C	5.67700	0.62200	-0.48100
C	-0.18000	0.65600	-4.43200
C	-1.07200	-0.50600	-4.01000
C	-2.50500	-2.96500	-1.90300
C	-1.41800	-3.69300	-2.40900
C	-1.47900	-5.08600	-2.51200
C	-2.62800	-5.76800	-2.10500
C	-3.71700	-5.05300	-1.59300
C	-3.65700	-3.66200	-1.49300
C	-3.91200	-0.52000	-2.59300
C	-4.49200	-1.16000	-3.70300
C	-5.62100	-0.61800	-4.32400
C	-6.18400	0.56700	-3.84400
C	-5.61900	1.20800	-2.73700
C	-4.49100	0.66900	-2.11400
C	1.77100	1.95600	-3.56000
C	0.95500	2.89200	-2.67400
C	1.46000	3.98600	0.36900
C	2.42200	3.29600	1.13400
C	3.59100	3.94300	1.53900
C	3.82200	5.27700	1.18600
C	2.88300	5.96200	0.41300
C	1.71000	5.31900	0.00200
C	-1.30000	4.20700	-0.66800
C	-2.13500	3.90300	-1.75700
C	-3.21400	4.72800	-2.08200
C	-3.47900	5.86700	-1.31800
C	-2.66900	6.17100	-0.22000
C	-1.59100	5.34500	0.10700
C	-0.17100	2.31000	4.40300
C	-1.47800	1.95400	5.08800
C	-3.68200	0.94900	4.48400
C	-3.72500	-0.52800	4.82200
C	-3.38200	-2.72000	3.77200
C	-2.74600	-3.34100	2.54100
C	-0.37000	-3.67800	3.18800
C	0.94000	-2.93000	3.10200
C	1.90600	-0.77600	3.86900
C	1.45800	0.43000	4.66100
Fe	0.62100	0.11100	-1.68000
H	2.45900	-0.17700	-5.09000
H	1.42600	-1.35400	-4.27100
H	3.92100	0.00100	-3.18200
H	3.52100	-1.70200	-3.24700
H	1.51400	-3.03800	-1.22200
H	1.33900	-5.45700	-0.69800

H	3.01500	-6.52700	0.79200
H	4.85000	-5.16400	1.76500
H	5.01600	-2.75700	1.24400
H	5.53200	-2.53100	-1.76100
H	7.85800	-1.97700	-2.35500
H	8.80700	0.23600	-1.75900
H	7.40900	1.89400	-0.55000
H	5.07200	1.33400	0.06300
H	-0.68100	1.59200	-4.20200
H	0.03900	0.63500	-5.50500
H	-2.07100	-0.33000	-4.41500
H	-0.72100	-1.44400	-4.45800
H	-0.52800	-3.16400	-2.71800
H	-0.63800	-5.63500	-2.91400
H	-2.68000	-6.84500	-2.19100
H	-4.61200	-5.57800	-1.28400
H	-4.50900	-3.11600	-1.11000
H	-4.07700	-2.08800	-4.07300
H	-6.06000	-1.12200	-5.17400
H	-7.06000	0.98300	-4.32300
H	-6.05900	2.11900	-2.35400
H	-4.06500	1.15400	-1.24800
H	2.74500	1.79500	-3.10800
H	1.91300	2.37100	-4.56400
H	1.60500	3.72600	-2.38400
H	0.12900	3.33500	-3.24000
H	2.27200	2.25400	1.38300
H	4.32200	3.40200	2.12500
H	4.72800	5.77500	1.50500
H	3.06000	6.99000	0.12700
H	0.99500	5.86400	-0.59800
H	-1.94900	3.00600	-2.33200
H	-3.84500	4.48100	-2.92500
H	-4.31100	6.51100	-1.57200
H	-2.87700	7.04600	0.38100
H	-0.98000	5.58600	0.96600
H	0.50200	2.81600	5.10200
H	-1.94700	2.85800	5.48900
H	-4.01700	1.54400	5.33900
H	-3.05900	-0.76900	5.65700
H	-2.86700	-3.02600	4.68800
H	-4.43000	-3.02900	3.84300
H	-2.82800	-4.43100	2.58200
H	-3.23700	-2.98700	1.63800
H	-0.69600	-3.73900	4.22900
H	-0.25600	-4.68700	2.78400
H	1.69800	-3.44900	3.69800
H	1.29000	-2.85900	2.07200
H	2.63500	-1.34900	4.45000
H	2.34100	-0.49200	2.90600
H	1.01800	0.12200	5.61500
H	2.30900	1.09000	4.85000
H	-0.35800	2.95500	3.54900
H	-1.32200	1.24200	5.90400

H	-4.74700	-0.81100	5.09500
H	-4.33500	1.15800	3.63900
N	1.09500	0.61900	-3.64400
N	2.46200	-0.59900	-1.73100
N	-1.07300	-0.58500	-2.52400
N	0.45700	2.13300	-1.49300
O	0.32300	-0.47300	-0.15800
O	3.03700	-0.13100	0.88400
O	-0.52700	2.18700	0.98900
O	-2.52400	-0.75300	-0.25700
O	0.46700	1.12300	3.84600
O	-2.34600	1.36600	4.06500
O	-3.30400	-1.26700	3.63500
O	-1.35100	-2.94100	2.39300
O	0.70300	-1.59600	3.64900
P	3.37600	-0.92700	-0.36200
P	-2.42100	-1.14500	-1.73100
P	0.00400	3.02200	-0.17300

References

(1) Fano, U. *Effects of Configuration Interaction on Intensities and Phase Shifts*, *Phys. Rev.* **1961**, *124*, 1866-1878.