Supporting Information for

Characterization of proton coupled electron transfer in a biomimetic oxomanganese complex: Evaluation of the DFT/B3LYP level of theory

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DFT Methods and Basis Sets

All ab initio computations were performed at the DFT/B3LYP level of theory by using the Jaguar 5.0 [1] suite of quantum chemistry software. Fully optimized molecular structures were obtained through minimum-energy geometry optimizations at the DFT/B3LYP (LACVP, 6-31G(2df), 6-31G(d), 6-31G, 3-21G) in a broken symmetry (BS) state. In this state the α and β electron densities are allowed to localize on different atomic centers, which provides a reasonable description of the multi-configurational character within the framework of DFT. Calculations of electronic and structural properties of the fully relaxed structures allow direct comparisons with experimental measurements, including the analysis of geometrical parameters such as bond lengths, bond angles and dihedral angles, and electronic properties such as spin populations, exchange coupling constants and electrostatic potential (ESP) atomic charges. Ionic spin states were characterized according to the analysis of Mulliken atomic spin density populations.

DFT Structural Models.

The X-ray atomic coordinates of complex **1** were obtained from the Cambridge Crystallographic Data Center (CCDC) with reference code SAWYEU [2]. Preparation of the models was subject to the constraints of total charge and total spin multiplicity, consistent with experimental data. Different arrangements of individual spin states were analyzed (subject to the constraints of total charge and spin multiplicity) by relaxing the molecular structures from appropriate initial-guess spin-electronic states, based on ligand field theory. Direct comparisons with both experimental magnetic and X-ray diffraction data allow one to evaluate the capabilities of the DFT/B3LYP methodology with regards to both electronic and structural properties, beyond the minimum energy criteria. Furthermore, the comparative analysis of both complete molecular structures and simplified models allows one to evaluate the capabilities and limitations of simplified model systems that might significantly reduce the computational cost of the calculations, and the effect of large and bulky substituents on the minimum energy geometries of the complexes.

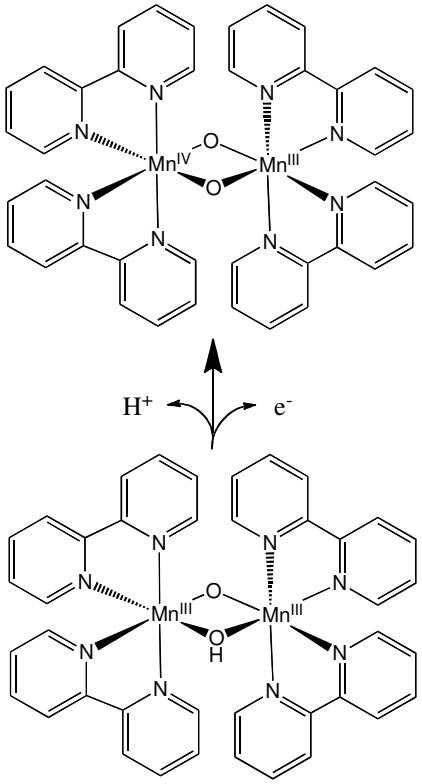

Figure S1. Schematic diagram of PCET in complex **1**.

Table S1.
Comparison between DFT/B3LYP and X-ray experimental inter-atomic distances (Å) in **1.**

Bond	Experimental	DFT/B3LYP
Mn(III)–Mn(IV)	2.71	2.72
Mn(III)–O	1.84	1.87
Mn(IV)–O	1.79	1.76

Cartesian Coordinates of Complex 1:

Complex 1
Number of atoms in complex **1**: 84

Mn1	0.4524353877	-0.8337746418	0.7354883506
Mn2	-0.3490546863	1.0732684572	-1.0330242090
O3	-0.9478269166	-0.4687817893	-0.4403202380
O4	1.0106144569	0.8082878162	0.0472466231
N5	0.0675364889	-2.9454752125	0.9013087940
N6	-0.9427733998	-0.5009190228	2.4592338387
N7	1.7025417047	-0.7871440513	2.4846772084
N8	0.3976479618	0.1944258584	-2.6920440505
N9	0.5740498756	2.7085898382	-1.9761868876
N10	-1.2396990185	2.2879717707	0.3144924862
C11	-1.0557800248	-3.4424106894	1.4559331086
C12	-2.2764267294	-0.3809051714	2.3219618865
C13	-3.1292676400	-0.3868306396	3.4236296629
C14	-2.5708477816	-0.5226314318	4.6981477116
C15	-1.1870119705	-0.6387737957	4.8312609591
C16	-0.3845431604	-0.6224532581	3.6842443408
C17	1.0878690055	-0.7242527431	3.6988131641
C18	1.0937317969	0.9915477003	-3.5477424071
C19	1.2183515258	2.3933107201	-3.1331668963
C20	1.9381964297	3.3583579607	-3.8377114272
C21	2.0034718881	4.6624648191	-3.3432193504
C22	1.3470988294	4.9689759349	-2.1517461182
C23	0.6403241778	3.9629263795	-1.4950141980
C24	-0.6358759480	2.6634202126	1.4610692619
C25	0.1861728672	-1.1067992908	-2.9784293164
C26	1.6117628541	0.4635629682	-4.7324690023
C27	0.6744544457	-1.6788300887	-4.1499664988
C28	1.4016586953	-0.8816721021	-5.0373218773
C29	-2.4757944328	2.7577511516	-0.0074763391
C30	-1.2546721310	3.5346023367	2.3534029524
C31	-3.1425531493	3.6272724000	0.8584882202
C32	-2.5289136715	4.0194259682	2.0485300581
C33	1.0141432141	-3.7990547466	0.4205008894
C34	-1.2850499346	-4.8106129584	1.5783932790
C35	-0.3121544139	-5.6951933068	1.1145785357
C36	0.8439063645	-5.1809618474	0.5267910486
C37	1.8394530706	-0.7221872579	4.8756128053
C38	3.0484414809	-0.8175066920	2.4210190746
C39	3.8493213801	-0.8061450821	3.5602619978
C40	3.2323904910	-0.7680266402	4.8101212977
H41	-4.1996389456	-0.2995428993	3.2876923222
H42	-0.7502562735	-0.7503539314	5.8139439293
H43	2.4482545409	3.1057362837	-4.7572013914
H44	1.3777205789	5.9666856607	-1.7332776721
H45	-3.2016220162	-0.5432147045	5.5786359881
H46	2.5602955760	5.4197017771	-3.8813124861
H47	0.4802766127	-2.7224038930	-4.3614062903
H48	1.7927530759	-1.2937939795	-5.9597692750
H49	2.1610643444	1.0931670846	-5.4188639824
H50	-0.3874196565	-1.6581268741	-2.2463959388
H51	-4.1225391322	4.0078842673	0.6054935114
H52	-3.0376514697	4.7015624018	2.7190222893
H53	-0.7430857870	3.8294639782	3.2604800204
H54	-0.4483348006	-6.7664469811	1.1978195941
H55	1.5972702557	-5.8569671256	0.1474096038
H56	4.9270471229	-0.8286630123	3.4637371605
H57	3.8188458012	-0.7651561588	5.7206939097

H58	-2.2028435456	-5.1669881997	2.0278490886
H59	1.3503752139	-0.6747721659	5.8384522957
H60	3.4849439046	-0.8522339058	1.4352107815
C61	4.3313958143	-3.2075126888	-1.3310863747
C62	3.2876760541	-3.8960452747	-0.7124124100
C63	2.1819590961	-3.1811736310	-0.2371480229
N64	2.1259693958	-1.8372131968	-0.3704494542
C65	3.1248484282	-1.1655962530	-0.9730037824
C66	4.2508039892	-1.8186913198	-1.4697813646
H67	5.1957109887	-3.7503411348	-1.6942114312
H68	3.3473580000	-4.9693716035	-0.5974357487
H69	2.9968102706	-0.0915503889	-1.0308709075
H70	5.0463033805	-1.2558412612	-1.9411661559
C71	-4.6718394373	2.1178954540	-3.0266132579
C72	-4.2681858687	2.6189509159	-1.7874037918
C73	-3.0003977868	2.3017928664	-1.2994995870
N74	-2.1516209292	1.5169841001	-2.0182215697
C75	-2.5400881322	1.0295407485	-3.2101236427
C76	-3.7954547488	1.3084211867	-3.7481520153
H77	-5.6544216255	2.3566936522	-3.4145102856
H78	-4.9408278969	3.2427877399	-1.2148676448
H79	-1.8375690232	0.4006297866	-3.7357363720
H80	-4.0724316936	0.8974307379	-4.7103895681
H81	-1.7799751640	-2.7240697316	1.8066370416
H82	-2.6347751802	-0.2942535191	1.3034371947
H83	0.1259971642	4.1599064919	-0.5666640777
H84	0.3493332211	2.2499790720	1.6263582302

Complex 1_{red}(Reduced form of Complex 1)

Number of atoms in complex $\mathbf{1}_{red}$: 85

Mn1	0.4275332270	-1.0685285056	0.7860964744
Mn2	-0.4905758357	1.0092539224	-1.0077308206
O3	-1.1952008167	-0.7792149650	-0.4261502767
O4	0.7841741815	0.5848032379	0.1879012240
N5	0.1726063928	-3.1198297469	1.0747504270
N6	-0.8948246950	-0.6287581513	2.5132846273
N7	1.7652660620	-0.9052296734	2.5492472073
N8	0.4019366569	0.1696071661	-2.9060692128
N9	0.6625036020	2.6449217882	-1.9113432713
N10	-1.4330594176	2.3885560875	0.3612139541
C11	-0.8528554375	-3.6544010848	1.7692238587
C12	-2.2315153706	-0.4938527397	2.3942458260
C13	-3.0576301271	-0.3452939212	3.5061698213
C14	-2.4724376952	-0.3352375806	4.7749778849
C15	-1.0881039273	-0.4611050692	4.8892042537
C16	-0.3094295393	-0.6043311193	3.7345625106
C17	1.1639271590	-0.7221569770	3.7517445359
C18	1.0626970688	1.0604144194	-3.6841010865
C19	1.2190294267	2.4216848426	-3.1291897433
C20	1.9246352573	3.4352814133	-3.7837737795
C21	2.0728452940	4.6808715615	-3.1715885689
C22	1.5172068192	4.8858577974	-1.9089723487
C23	0.8155227472	3.8402451545	-1.3124313502
C24	-0.9116122942	2.7293597754	1.5537363684
C25	0.2452891045	-1.1026924279	-3.3198642630
C26	1.5699735814	0.6724650188	-4.9308929093
C27	0.7237281930	-1.5496545519	-4.5486291727
C28	1.3945062803	-0.6391980038	-5.3696059554
C29	-2.5595747658	2.9826198214	-0.1001762471
C30	-1.5054272240	3.7041889490	2.3537933144
C31	-3.2038919094	3.9634008264	0.6591963739

C32	-2.6692984838	4.3280382725	1.8964646186
C33	1.1148928925	-3.9369508988	0.5197084004
C34	-0.9852357381	-5.0285279059	1.9525386308
C35	-0.0221272356	-5.8745201668	1.4026667041
C36	1.0342264520	-5.3205705038	0.6776997976
C37	1.9257467270	-0.6189576855	4.9191174962
C38	3.1071222939	-0.9606887190	2.4718019564
C39	3.9217356337	-0.8532613195	3.5970103617
C40	3.3176999113	-0.6882233085	4.8432416744
H41	-4.1283774839	-0.2482522486	3.3806811746
H42	-0.6291685744	-0.4543029648	5.8678791485
H43	2.3629438693	3.2644733215	-4.7568083499
H44	1.6211492678	5.8323094477	-1.3943743190
H45	-3.0807097386	-0.2330944725	5.6655568757
H46	2.6188562863	5.4701626924	-3.6735991787
H47	0.5704628000	-2.5763882862	-4.8551406539
H48	1.7759980564	-0.9417052684	-6.3372789021
H49	2.0911867433	1.3804211698	-5.5596770436
H50	-0.2704106561	-1.7654195795	-2.6383643369
H51	-4.0999232145	4.4484497311	0.2973022510
H52	-3.1550183848	5.0940551374	2.4888321623
H53	-1.0630356663	3.9723596527	3.3045159309
H54	-0.0884874686	-6.9482132143	1.5290152079
H55	1.7815406376	-5.9670489088	0.2386307967
H56	4.9982306075	-0.8986898134	3.4942268237
H57	3.9143706463	-0.6071248788	5.7435083442
H58	-1.8230815382	-5.4190410854	2.5154693355
H59	1.4500122229	-0.4773357399	5.8792671704
H60	3.5319043467	-1.0870141595	1.4867800419
C61	4.2283406680	-3.1468653584	-1.5037690815
C62	3.2756964420	-3.9053794644	-0.8202627667
C63	2.1767230762	-3.2620649073	-0.2446835493
N64	2.0332165472	-1.9184828736	-0.3545285626
C65	2.9449436183	-1.1783148549	-1.0117672216
C66	4.0646619106	-1.7624083798	-1.6020083060
H67	5.0893502927	-3.6343260007	-1.9452533802
H68	3.4030291403	-4.9755577649	-0.7317933236
H69	2.7513824020	-0.1137790238	-1.0355895012
H70	4.7920398441	-1.1478215167	-2.1164951192
C71	-4.5359916150	2.4780438532	-3.2951838759
C72	-4.1771722104	2.9719323548	-2.0406406740
C73	-3.0064842230	2.5246054627	-1.4264720575
N74	-2.2060699286	1.6087634052	-2.0460780494
C75	-2.5548054069	1.1279732801	-3.2574075292
C76	-3.7124981459	1.5371376715	-3.9135350852
H77	-5.4435852539	2.8232287291	-3.7750479089
H78	-4.8103500770	3.6970199047	-1.5484970207
H79	-1.8877372647	0.4051125125	-3.7021466573
H80	-3.9563506118	1.1259624877	-4.8845514976
H81	-1.5717670516	-2.9624684845	2.1807253714
H82	-2.6098042618	-0.5111211848	1.3809953018
H83	0.3692524965	3.9532006870	-0.3357592781
H84	-0.0073840696	2.2050466760	1.8350606911
H85	-1.6605282376	-1.4265378990	-0.9783130382

Spin Population Analysis:

Complex 1

Atom	Mn1	Mn2	O3	O4	N5
Spin	3.85841	-2.58253	-0.22845	-0.22945	-0.01347

Atom	N6	N7	N8	N9	N10
Spin	0.04564	-0.01392	0.03196	0.02401	0.03179

Atom	C11	C12	C13	C14	C15
Spin	0.00900	-0.00042	0.00087	0.00328	0.00135

Atom	C16	C17	C18	C19	C20
Spin	0.00042	0.00752	-0.00363	-0.00221	0.00158

Atom	C21	C22	C23	C24	C25
Spin	-0.00553	0.00284	-0.00705	-0.01092	-0.01098

Atom	C26	C27	C28	C29	C30
Spin	0.00340	0.00602	-0.00826	-0.00363	0.00599

Atom	C31	C32	C33	C34	C35
Spin	0.00339	-0.00824	0.00742	-0.00515	0.00936

Atom	C36	C37	C38	C39	C40
Spin	-0.00452	-0.00460	0.00915	-0.00524	0.00950

Atom	H41	H42	H43	H44	H45
Spin	0.00079	0.00069	0.00021	-0.00011	-0.00026

Atom	H46	H47	H48	H49	H50
Spin	0.00031	-0.00046	0.00050	0.00034	0.00059

Atom	H51	H52	H53	H54	H55
Spin	0.00034	0.00050	-0.00046	-0.00056	0.00019

Atom	H56	H57	H58	H59	H60
Spin	0.00042	-0.00056	0.00041	0.00018	-0.00025

Atom	C61	C62	C63	N64	C65
Spin	0.00324	0.00136	0.00042	0.04586	-0.00048

Atom	C66	H67	H68	H69	H70
Spin	0.00089	-0.00026	0.00070	0.00188	0.00079

Atom	C71	C72	C73	N74	C75
Spin	-0.00549	0.00155	-0.00218	0.02399	-0.00702

Atom	C76	H77	H78	H79	H80
Spin	0.00282	0.00030	0.00021	0.00089	-0.00011

Atom	H81	H82	H83	H84
Spin	-0.00022	0.00188	0.00089	0.00059

Sum of atomic spins: 1.0

Complex 1_{red}(Reduced form of Complex 1)

Atom	Mn1	Mn2	O3	O4	N5
Spin	3.79731	-3.80027	-0.00196	0.00446	-0.04618
Atom	N6	N7	N8	N9	N10
Spin	0.03582	0.02502	-0.04043	-0.01442	-0.02923
Atom	C11	C12	C13	C14	C15
Spin	0.01441	0.00012	0.00070	0.00243	0.00022
Atom	C16	C17	C18	C19	C20
Spin	0.00173	0.00298	-0.00031	-0.00426	0.00174
Atom	C21	C22	C23	C24	C25
Spin	-0.00520	0.00194	-0.00309	-0.00574	0.00122
Atom	C26	C27	C28	C29	C30
Spin	-0.00128	-0.00155	-0.00116	-0.00201	0.00200
Atom	C31	C32	C33	C34	C35
Spin	0.00026	-0.00703	0.00981	-0.00825	0.01332
Atom	C36	C37	C38	C39	C40
Spin	-0.00657	-0.00081	0.00171	-0.00084	0.00420
Atom	H41	H42	H43	H44	H45
Spin	0.00060	0.00068	-0.00053	-0.00052	-0.00021
Atom	H46	H47	H48	H49	H50
Spin	0.00037	-0.00065	0.00014	-0.00068	-0.00204
Atom	H51	H52	H53	H54	H55
Spin	-0.00045	0.00045	-0.00085	-0.00075	-0.00017
Atom	H56	H57	H58	H59	H60
Spin	0.00057	-0.00032	0.00019	0.00062	0.00143
Atom	C61	C62	C63	N64	C65
Spin	0.00898	-0.00135	0.00351	0.01832	0.00837
Atom	C66	H67	H68	H69	H70
Spin	-0.00353	-0.00056	0.00036	0.00112	0.00083
Atom	C71	C72	C73	N74	C75
Spin	-0.01238	0.00664	-0.00971	0.04573	-0.01301
Atom	C76	H77	H78	H79	H80
Spin	0.00777	0.00070	0.00016	0.00143	-0.00016
Atom	H81	H82	H83	H84	H85
Spin	-0.00154	0.00108	-0.00107	-0.00144	0.00100

Sum of atomic spins: 0.000000

ESP atomic charges:

Complex 1

Atom	Mn1	Mn2	O3	O4	N5
Charge	-0.06023	-0.38035	-0.35021	-0.35813	-0.14245
Atom	N6	N7	N8	N9	N10
Charge	0.28630	-0.11787	0.83277	-0.16626	0.83670
Atom	C11	C12	C13	C14	C15
Charge	0.09191	-0.07593	-0.17210	-0.06302	-0.12533
Atom	C16	C17	C18	C19	C20
Charge	-0.17077	0.29329	-0.47944	0.46946	-0.31306
Atom	C21	C22	C23	C24	C25
Charge	0.02068	-0.17804	0.01237	-0.29637	-0.29874
Atom	C26	C27	C28	C29	C30
Charge	-0.01827	-0.09730	-0.13238	-0.48177	-0.09700
Atom	C31	C32	C33	C34	C35
Charge	-0.01976	-0.13210	0.31931	-0.22935	0.02494
Atom	C36	C37	C38	C39	C40
Charge	-0.27463	-0.26787	0.07629	-0.22237	0.02182
Atom	H41	H42	H43	H44	H45
Charge	0.19214	0.18205	0.22389	0.20281	0.19425
Atom	H46	H47	H48	H49	H50
Charge	0.18685	0.19743	0.21267	0.17374	0.19998
Atom	H51	H52	H53	H54	H55
Charge	0.17416	0.21268	0.19670	0.18270	0.20737
Atom	H56	H57	H58	H59	H60
Charge	0.20605	0.18289	0.20692	0.20575	0.11464
Atom	C61	C62	C63	N64	C65
Charge	-0.08229	-0.09788	-0.22444	0.34853	-0.11250
Atom	C66	H67	H68	H69	H70
Charge	-0.15402	0.19741	0.17729	0.14326	0.19015
Atom	C71	C72	C73	N74	C75
Charge	0.02207	-0.31439	0.47400	-0.17419	0.01673
Atom	C76	H77	H78	H79	H80
Charge	-0.17974	0.18652	0.22388	0.14319	0.20280
Atom	H81	H82	H83	H84	
Charge	0.11203	0.13684	0.14323	0.20110	

Sum of atomic charges: 3.0

Complex 1_{red}(Reduced form of Complex 1)

Atom	Mn1	Mn2	O3	O4	N5
Charge	0.30958	0.10378	-0.53254	-0.51051	-0.31080
Atom	N6	N7	N8	N9	N10
Charge	0.26991	-0.20520	0.43484	-0.14847	0.31080
Atom	C11	C12	C13	C14	C15
Charge	0.12914	-0.02577	-0.18086	-0.07623	-0.10643
Atom	C16	C17	C18	C19	C20
Charge	-0.20523	0.34514	-0.26856	0.32146	-0.27528
Atom	C21	C22	C23	C24	C25
Charge	0.01928	-0.20721	0.04520	-0.05267	-0.16529
Atom	C26	C27	C28	C29	C30
Charge	-0.07819	-0.13471	-0.10418	-0.25245	-0.17396
Atom	C31	C32	C33	C34	C35
Charge	-0.08107	-0.06971	0.43032	-0.22786	0.04963
Atom	C36	C37	C38	C39	C40
Charge	-0.30886	-0.29663	0.07045	-0.22273	0.03654
Atom	H41	H42	H43	H44	H45
Charge	0.19836	0.17581	0.20637	0.20284	0.19641
Atom	H46	H47	H48	H49	H50
Charge	0.18174	0.19344	0.20316	0.17522	0.12001
Atom	H51	H52	H53	H54	H55
Charge	0.17203	0.19702	0.19659	0.18128	0.21790
Atom	H56	H57	H58	H59	H60
Charge	0.20250	0.17750	0.20920	0.20918	0.12276
Atom	C61	C62	C63	N64	C65
Charge	-0.08646	-0.05007	-0.27486	0.25951	-0.07331
Atom	C66	H67	H68	H69	H70
Charge	-0.14246	0.19868	0.16625	0.13409	0.19005
Atom	C71	C72	C73	N74	C75
Charge	0.04455	-0.30393	0.40905	-0.23992	0.07826
Atom	C76	H77	H78	H79	H80
Charge	-0.21709	0.18136	0.21756	0.11343	0.20688
Atom	H81	H82	H83	H84	H85
Charge	0.09947	0.08168	0.12750	0.12929	0.35652

Sum of atomic charges: 3.000000

Thermodynamic Cycle and Thermodynamic Energy Data

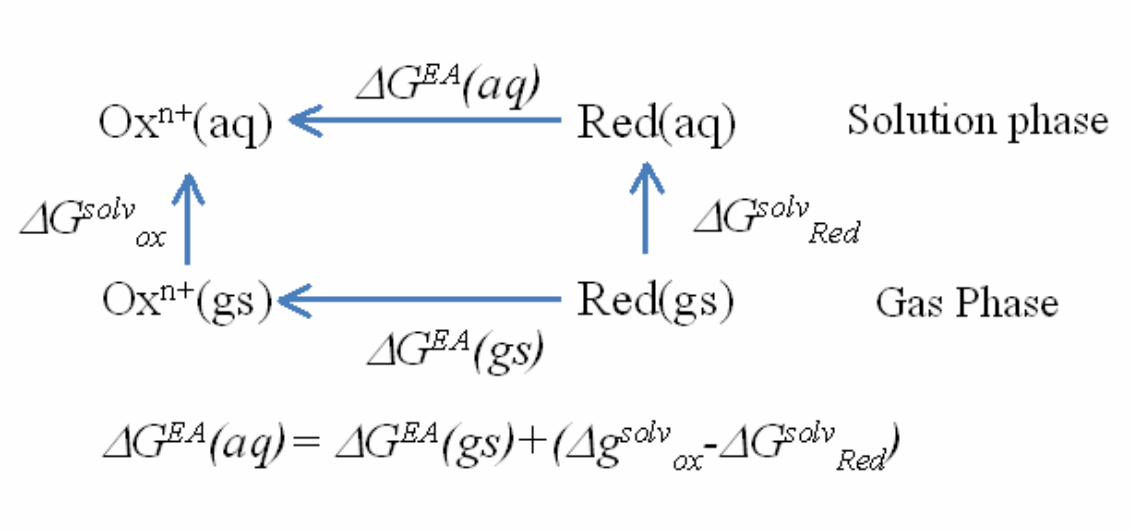

Table S2. Thermodynamic energy data for complex **1** in various oxidation and protonation states, including the zero point energy (ZPE), entropy (S) and enthalpy in the gas phase (H_g), solvation free energies (G_{solv}) and free energies in the gas phase (G_g), computed at room temperature, T=298.15K. The solvation free energy of a proton in aqueous solutions was defined as $G_{solv}(H^+)$=-260 kcal mol^{-1}, as in Refs. [3,4,5].

	H_g eV	G_g eV
$[(bpy)_4Mn^{III}(\mu\text{-}O)_2Mn^{III}]^{2+}$	-63650.07246	-63633.06647
$[(bpy)_4Mn^{III}(\mu\text{-}O)(\mu\text{-}OH)Mn^{III}]^{3+}$	-63656.68789	-63639.44604
$[(bpy)_4Mn^{III}(\mu\text{-}O)_2Mn^{IV}]^{3+}$	-63639.42202	-63622.14780
$[(bpy)_4Mn^{III}(\mu\text{-}O)(\mu\text{-}OH)Mn^{IV}]^{4+}$	-63642.65612	-63625.65647

	ZPE kcal mol^{-1}	S Cal mol^{-1} K^{-1}	G_{solv} eV
$[(bpy)_4Mn^{III}(\mu\text{-}O)_2Mn^{III}]^{2+}$	455.496	210.458	-4.91218
$[(bpy)_4Mn^{III}(\mu\text{-}O)(\mu\text{-}OH)Mn^{III}]^{3+}$	462.951	217.192	-10.65361
$[(bpy)_4Mn^{III}(\mu\text{-}O)_2Mn^{IV}]^{3+}$	456.325	211.688	-10.64256
$[(bpy)_4Mn^{III}(\mu\text{-}O)(\mu\text{-}OH)Mn^{IV}]^{4+}$	452.221	219.191	-18.69101

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