ELECTRONIC SUPPLEMENARY INFORMATION

Stability, relaxometric and computational studies on Mn^{2+} complexes with ligands containing a cyclobutane scaffold

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Potentiometry studies

The protonation constants of the $\mathbf{L1}^{4-}$, $\mathbf{L2}^{4-}$ and $\mathbf{L3}^{4-}$ ligands determined at 25 °C in 0.1 M KCl were reported in a previous work.[1]

Once all ligands were studied, the stability constants of their manganese complexes were also determined from direct potentiometric titrations, as the complex formation was fast. The titrations of the metal complexes were performed at the same conditions that before but containing 1 equivalent of Mn^{2+} cation. The titrations curves of the three complexes in the absence and presence of this cation are presented in Figure S1. Figure S1 shows that in the presence of a metal, the equivalence point of the curves is shifted to higher equivalents of NaOH, indicating the formation of the metal ligand complexes. This shift was also used to calculate and to confirm the real concentration of the ligand stock solution and the resulting concentration was equal to that calculated before. Above pH 10, in some titrations a solid started to precipitate, possibly due to the formation of a hydroxo complex, which could be insoluble. For that reason, only experimental data below that point were used to fit the curves and to calculate the stability constants.

Stability and protonation constants are shown in Table 1, and species distribution plots in Figure 1, both in the main text.

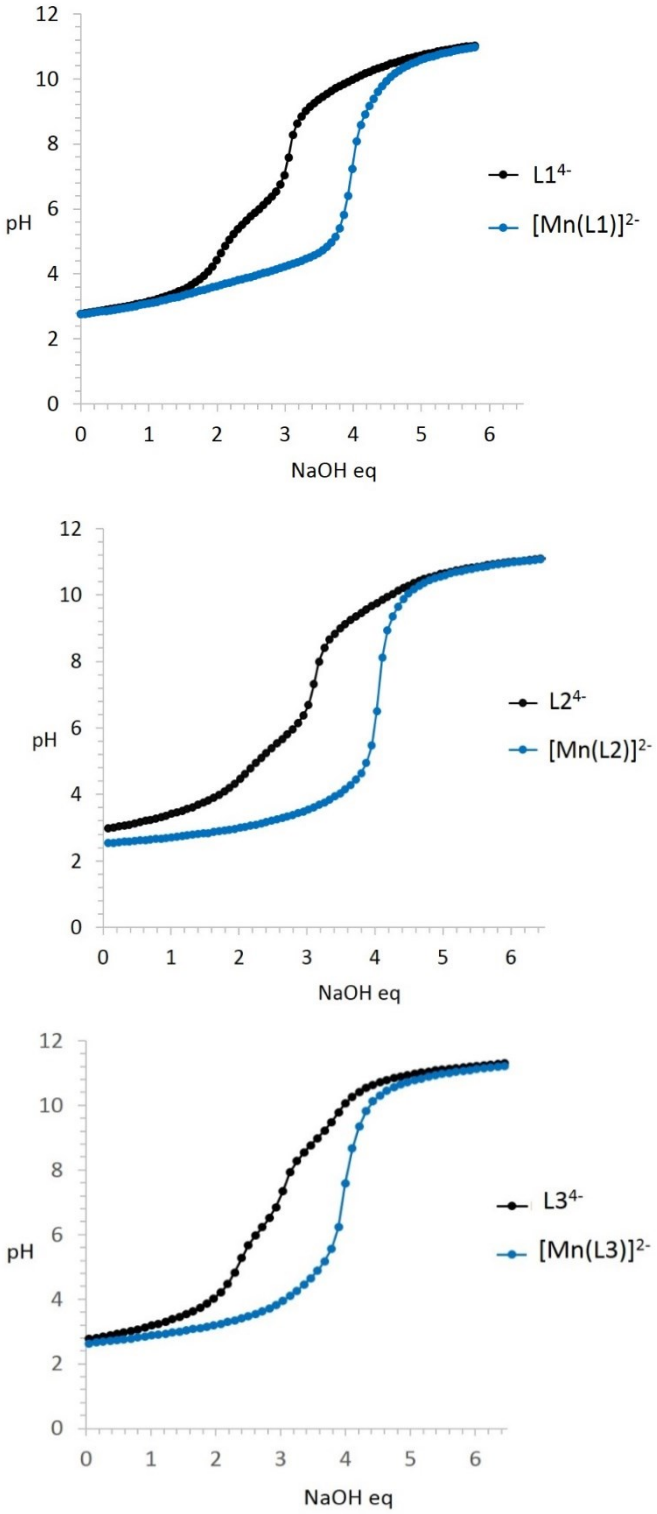

Figure S1. Potentiometric pH titrations curves for the ligands H_4(L1) (top), H_4(L2) (centre), and H_4(L3) (bottom) in the absence (black) and in the presence (blue) of 1 equivalent of Mn^{2+}. $[Mn^{2+}] = [L^{4-}] = 2$ mM + 0.1 M KCl, 25 ºC in N_2 (1atm).

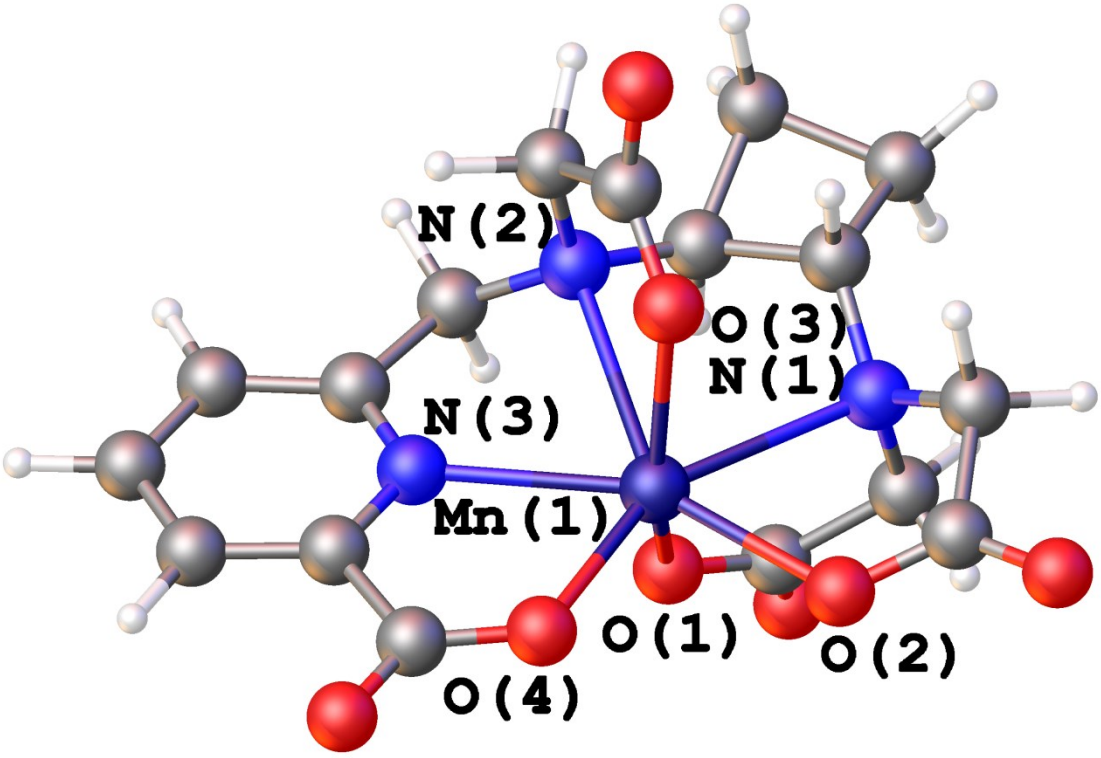

Figure S2. Structure of the [Mn(**L2**)]$^{2-}$ complex optimised at the M11/def2-TZVP level. Bond distances (Å): Mn(1)-N(1), 2.527; Mn(1)-N(2), 2.672; Mn(1)-N(3), 2.381; Mn(1)-O(1), 2.168; Mn(1)-O(2), 2.228; Mn(1)-O(3), 2.159; Mn(1)-O(4), 2.237.

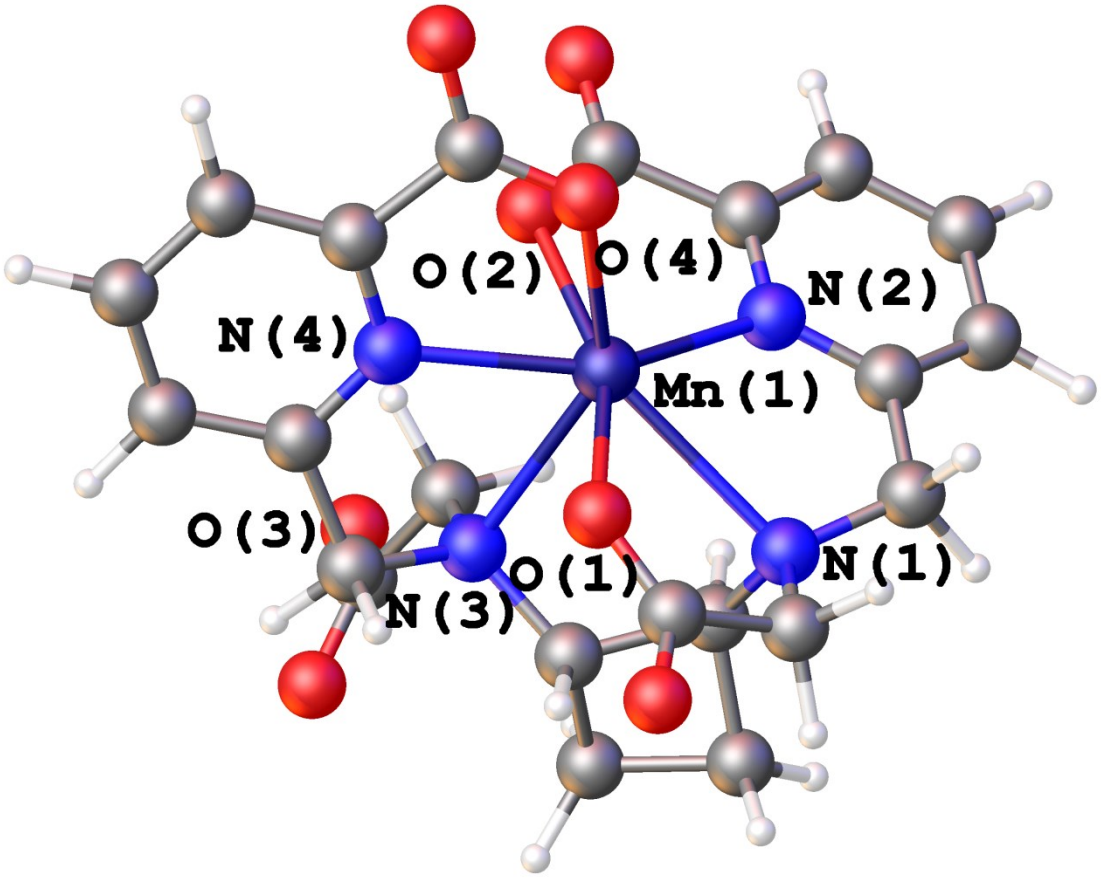

Figure S3. Structure of the [Mn(**L3**)]$^{2-}$ complex optimised at the M11/def2-TZVP level. Bond distances (Å): Mn(1)-N(1), 2.581; Mn(1)-N(2), 2.375; Mn(1)-N(3), 2.544; Mn(1)-N(4), 2.258; Mn(1)-O(1), 2.209; Mn(1)-O(2), 2.311; Mn(1)-O(4), 2.237.

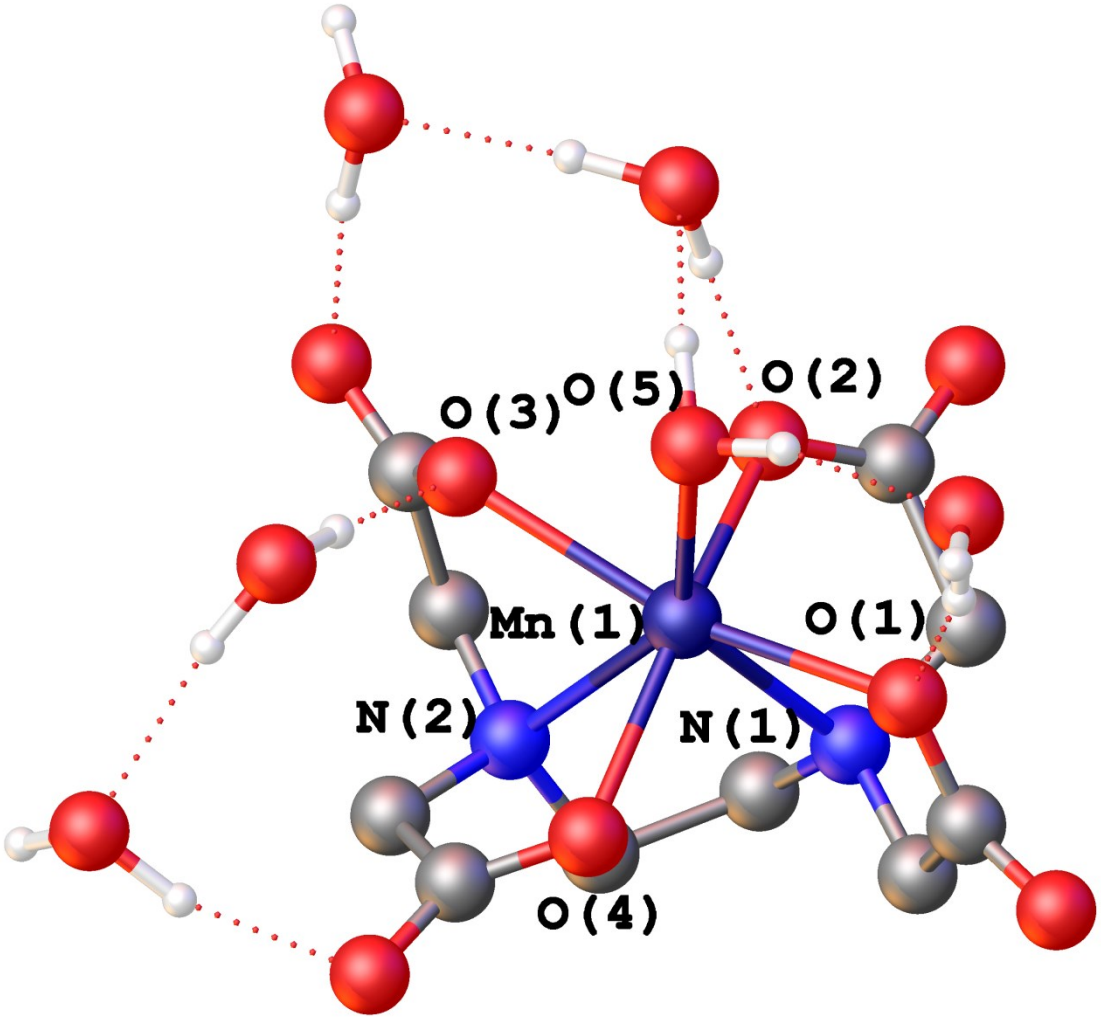

Figure S4. Structure of the $[Mn(edta)(H_2O)]^{2-}\cdot 5H_2O$ system optimised at the M11/def2-TZVP level.

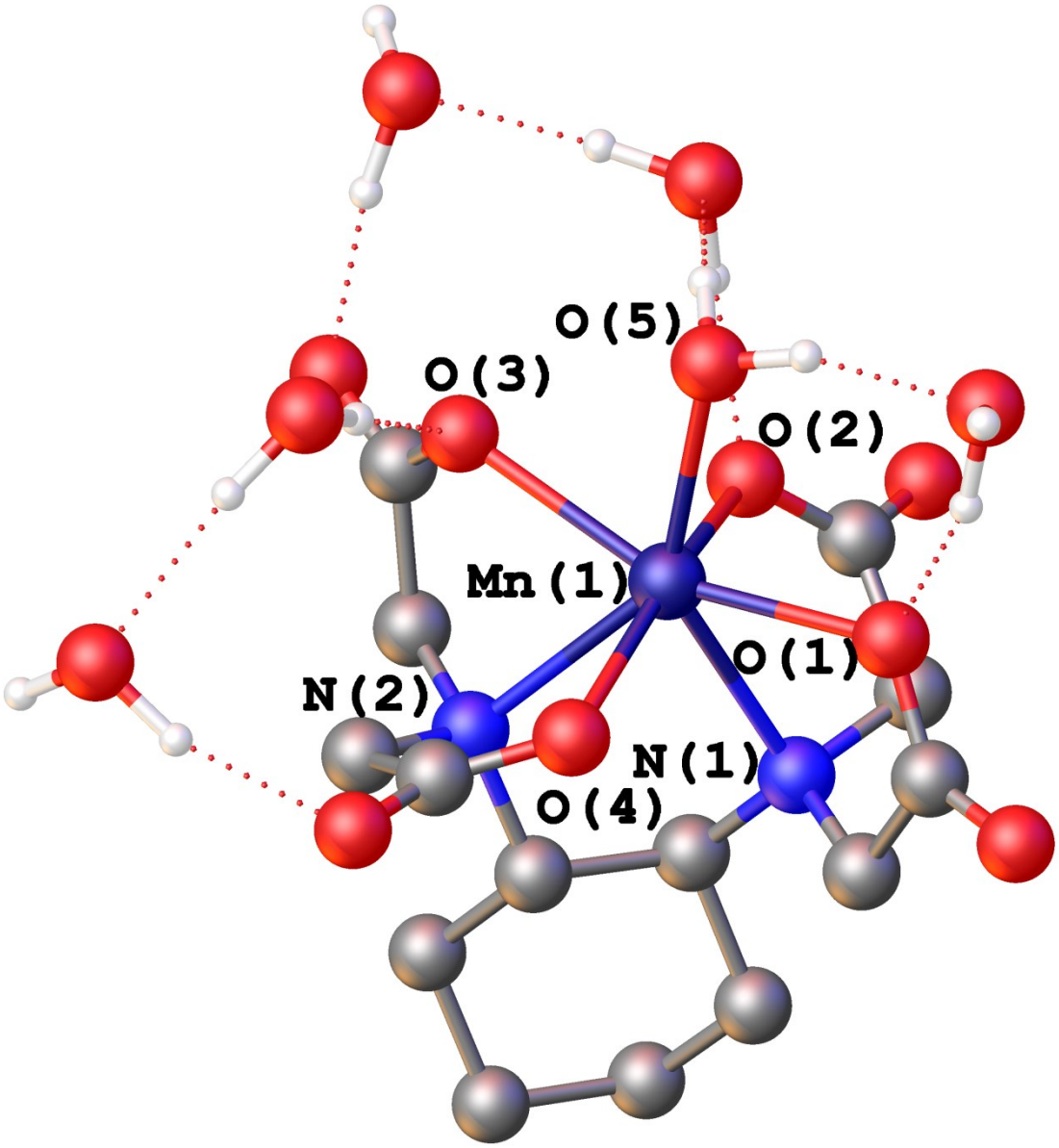

Figure S5. Structure of the $[Mn(cdta)(H_2O)]^{2-}\cdot 5H_2O$ system optimised at the M11/def2-TZVP level.

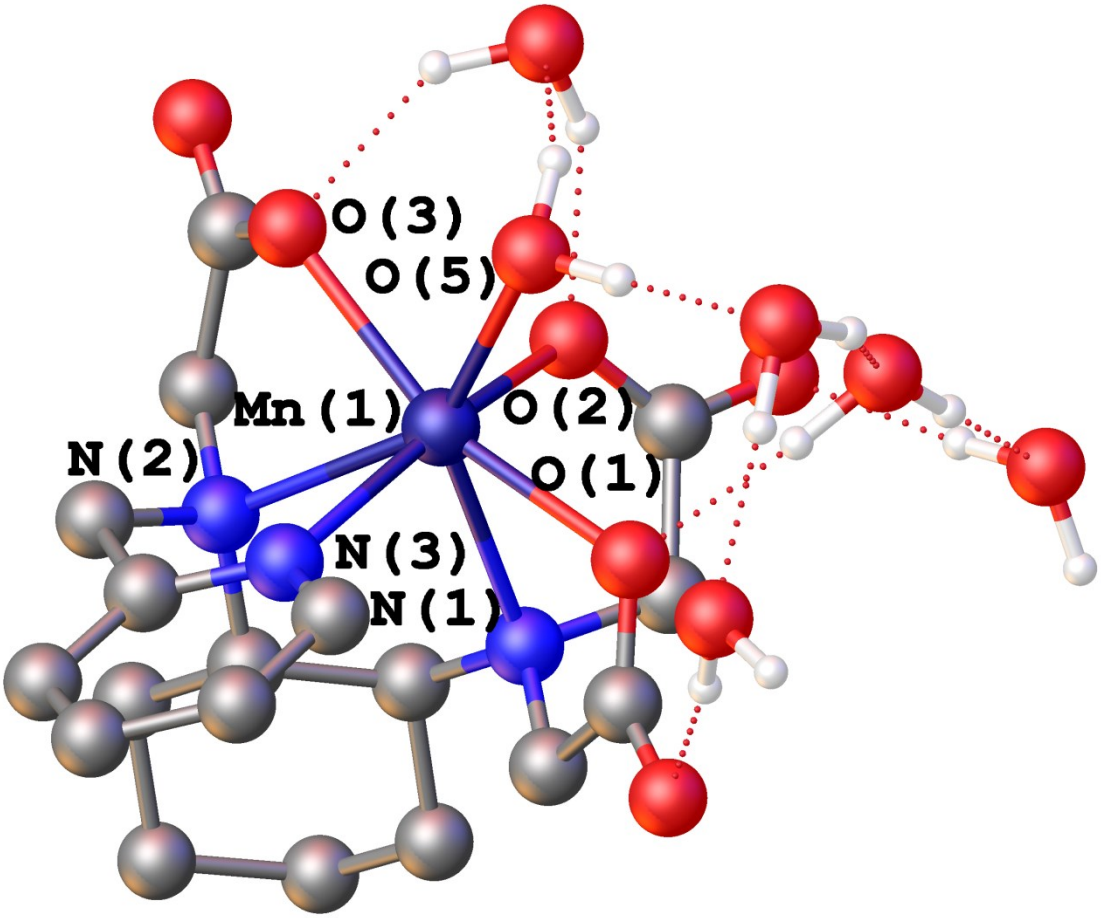

Figure S6. Structure of the $[Mn(Pyc3a)(H_2O)]^{-}\cdot 5H_2O$ system optimised at the M11/def2-TZVP level.

Table S1. Bond distances of the metal coordination environments calculated for the [Mn(**L1**)(H_2O)]$^{2-}$·5H_2O, [Mn(edta)(H_2O)]$^{2-}$·5H_2O, [Mn(cdta)(H_2O)]$^{2-}$·5H_2O and [Mn(pyc3a)(H_2O)]$^{-}$·5H_2O at the M11/Def2-TZVP level.[a]

	L1^{4-}	**Edta^{4-}**	**Edta^{4-}**	**cdta^{4-}**	**cdta^{4-}**	**Pyc3a^{4-}**
	DFT	DFT	X-ray	DFT	X-ray	DFT
Mn(1)-N(1)	2.491	2.414	2.363	2.418	2.350	2.453
Mn(1)-N(2)	2.502	2.424	2.368	2.425	2.385	2.422
Mn(1)-O(1)	2.271	2.271	2.302	2.258	2.240	2.269
Mn(1)-O(2)	2.206	2.230	2.250	2.220	2.182	2.213
Mn(1)-O(3)	2.306	2.302	2.237	2.294	2.264	2.236
Mn(1)-O(4)	2.187	2.211	2.181	2.203	2.179	-
Mn(1)-O(5)	2.253	2.260	2.241	2.271	2.272	2.253
Mn(1)-N(3)	-	-	-	-	-	2.313

[a] X-ray data taken from reference 2.

Table S2. Cartesian coordinates (Å) of the $[Mn(\mathbf{L1})(H_2O)]^{2-}\cdot 5H_2O$ system optimized at M11/Def2-TZVP level (0 imaginary frequency).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	2.019398	0.342337	1.882777
2	8	3.719789	-0.895014	2.632845
3	8	2.562715	2.741557	-2.108321
4	8	0.866000	1.739171	-1.061287
5	8	-0.341028	-1.492771	1.591843
6	8	-1.915422	-3.042996	1.880384
7	8	-1.847523	0.907464	-0.329509
8	8	-2.855345	1.239812	-2.290020
9	7	-0.720600	-1.376118	-1.092228
10	7	2.288190	-0.522313	-0.621254
11	6	0.490996	-2.097438	-1.409827
12	1	0.721387	-2.724856	-0.539728
13	6	1.707581	-1.247658	-1.729306
14	1	1.424013	-0.501081	-2.480864
15	6	2.958023	-1.290871	0.409012
16	1	2.436997	-2.244644	0.554360
17	1	4.006165	-1.519489	0.169217
18	6	2.913395	-0.559785	1.763371
19	6	3.013058	0.671331	-1.027396
20	1	3.586840	1.050135	-0.173735
21	1	3.724164	0.477492	-1.842591
22	6	2.079292	1.817891	-1.452241
23	6	-1.670803	-2.138086	-0.301311
24	1	-2.646436	-1.638055	-0.323233
25	1	-1.823142	-3.156137	-0.688142
26	6	-1.271732	-2.238161	1.180553
27	6	-1.333088	-0.581247	-2.136423
28	1	-0.561470	-0.167432	-2.794500
29	1	-2.032308	-1.150128	-2.766058
30	6	-2.079414	0.621099	-1.538671
31	8	-0.420415	1.976581	1.870382
32	1	0.211390	2.245435	2.563357
33	1	-0.620132	2.743344	1.290005
34	8	-0.713059	3.833806	-0.136481
35	8	1.638328	2.226358	3.726592
36	1	-0.195189	3.175898	-0.641288
37	1	-1.628919	3.789331	-0.473060
38	1	1.479262	1.912928	4.620181
39	1	1.921410	1.451656	3.183679
40	25	0.223116	0.313232	0.494353
41	6	0.811143	-2.925209	-2.684289
42	6	2.287577	-2.471775	-2.488638
43	1	0.378411	-2.463713	-3.577866
44	1	0.594378	-3.994209	-2.670615
45	1	2.815051	-3.149383	-1.809585
46	1	2.891530	-2.285465	-3.377725
47	8	-3.622692	0.203751	1.779512
48	1	-3.020595	0.457119	1.060234
49	1	-3.977639	-0.676216	1.575665
50	8	-4.536847	-2.499750	1.462996
51	8	-3.335366	3.627439	-1.110554
52	1	-3.234900	2.744459	-1.543792

53	1	-3.628640	4.244057	-1.785777
54	1	-4.920507	-2.910834	0.684653
55	1	-3.636593	-2.874489	1.584466

E(UM11) = -2787.2169128 Hartree
Zero-point correction = 0.421797
Thermal correction to Energy = 0.458872
Thermal correction to Enthalpy = 0.459816
Thermal correction to Gibbs Free Energy = 0.351597
Sum of electronic and zero-point Energies = -2786.795116
Sum of electronic and thermal Energies = -2786.758041
Sum of electronic and thermal Enthalpies = -2786.757097
Sum of electronic and thermal Free Energies = -2786.865316

Table S3. Cartesian coordinates (Å) of the $[Mn(\mathbf{L1})]^{2-}\cdot 6H_2O$ system optimized at M11/Def2-TZVP level (1 imaginary frequency).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	1.841840	0.665706	1.814773
2	8	3.466400	-0.399200	2.911977
3	8	2.647262	2.392967	-2.371966
4	8	0.904209	1.509517	-1.295284
5	8	-0.338521	-1.336763	1.726415
6	8	-1.912258	-2.842486	2.201414
7	8	-1.790166	0.782117	-0.498340
8	8	-2.765689	0.846160	-2.500465
9	7	-0.658923	-1.588534	-0.939226
10	7	2.310689	-0.632828	-0.458088
11	6	0.570066	-2.334071	-1.102419
12	1	0.760099	-2.833138	-0.144236
13	6	1.799184	-1.525440	-1.474261
14	1	1.554941	-0.901453	-2.343014
15	6	2.891458	-1.204020	0.740850
16	1	2.354643	-2.120945	1.011196
17	1	3.955171	-1.458388	0.633887
18	6	2.738115	-0.240207	1.933919
19	6	3.055352	0.493261	-0.998850
20	1	3.592004	0.995828	-0.186338
21	1	3.801039	0.187480	-1.745332
22	6	2.139077	1.557612	-1.625227
23	6	-1.631502	-2.241794	-0.080361
24	1	-2.606528	-1.752608	-0.192284
25	1	-1.772772	-3.302704	-0.331042
26	6	-1.261115	-2.138224	1.408854
27	6	-1.235730	-0.930189	-2.093000
28	1	-0.441531	-0.598330	-2.770800
29	1	-1.917369	-1.570984	-2.669739
30	6	-1.999277	0.336124	-1.669001
31	8	-0.920197	3.102036	1.931006
32	1	-0.066104	3.124866	2.392852
33	1	-0.770772	3.367207	1.004290
34	8	-0.597687	3.795212	-0.795061

35	8	1.563744	2.876441	3.327443
36	1	-0.096281	3.011525	-1.093551
37	1	-1.507957	3.688229	-1.129214
38	1	1.480410	2.699481	4.267458
39	1	1.745484	2.016409	2.882182
40	25	0.193753	0.305450	0.388804
41	6	0.960390	-3.328926	-2.228398
42	6	2.423523	-2.840276	-2.014209
43	1	0.579978	-3.001202	-3.201233
44	1	0.743153	-4.386814	-2.075611
45	1	2.909912	-3.408480	-1.214751
46	1	3.078577	-2.777598	-2.884046
47	8	-3.624492	0.365903	1.637878
48	1	-3.037822	0.519949	0.879938
49	1	-3.982262	-0.533143	1.558347
50	8	-4.529729	-2.352960	1.682479
51	8	-3.226541	3.412022	-1.734133
52	1	-3.136801	2.468932	-2.009330
53	1	-3.520532	3.905148	-2.503950
54	1	-4.912378	-2.867845	0.967990
55	1	-3.635163	-2.714614	1.864965

E(UM11) = -2787.205095 Hartree
Zero-point correction = 0.420666
Thermal correction to Energy = 0.457715
Thermal correction to Enthalpy = 0.458659
Thermal correction to Gibbs Free Energy = 0.349750
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Sum of electronic and thermal Energies = -2786.747380
Sum of electronic and thermal Enthalpies = -2786.746436
Sum of electronic and thermal Free Energies = -2786.855345

Table S4. Cartesian coordinates (Å) of the $[Mn(edta)(H_2O)]^{2-}\cdot 5H_2O$ system optimized at M11/Def2-TZVP level (0 imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	2.261552	-0.721128	1.366625
2	8	3.750417	-2.382156	1.260291
3	8	2.701827	3.027558	-1.478846
4	8	1.004032	1.892436	-0.575313
5	8	-0.271492	-2.128191	0.636871
6	8	-1.986805	-3.529899	0.378332
7	8	-1.692816	1.014165	0.145010
8	8	-2.735047	2.265054	-1.378289
9	7	-0.825286	-0.766197	-1.630219
10	7	2.059633	-0.496606	-1.281584
11	6	0.130306	-1.424389	-2.523239
12	1	0.307937	-2.429204	-2.122554
13	6	1.447073	-0.666505	-2.601325
14	1	1.272186	0.334416	-3.012327
15	6	2.714200	-1.691634	-0.769513
16	1	2.066552	-2.560406	-0.932371

17	1	3.676891	-1.891989	-1.263209
18	6	2.944708	-1.603146	0.748077
19	6	2.937936	0.667941	-1.258319
20	1	3.592876	0.605968	-0.382152
21	1	3.577375	0.724281	-2.150713
22	6	2.158356	1.984288	-1.111716
23	6	-1.823014	-1.706192	-1.137159
24	1	-2.700047	-1.155887	-0.778487
25	1	-2.171675	-2.393118	-1.922380
26	6	-1.313942	-2.531843	0.054628
27	6	-1.424692	0.445541	-2.165613
28	1	-0.658609	1.053647	-2.657477
29	1	-2.215883	0.242340	-2.902996
30	6	-2.005078	1.314762	-1.042782
31	8	0.078029	0.976752	2.364094
32	1	0.814200	0.891704	2.998369
33	1	-0.080157	1.926290	2.169650
34	8	-0.176083	3.518449	1.339225
35	8	2.350885	0.298522	3.823724
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37	1	-1.116903	3.699795	1.151311
38	1	2.259978	-0.327676	4.545952
39	1	2.464222	-0.219287	2.991011
40	25	0.349857	-0.025432	0.356829
41	8	-3.320702	-0.446996	1.958325
42	1	-2.778018	0.074732	1.344189
43	1	-3.787519	-1.123495	1.441748
44	8	-4.544749	-2.659550	0.602988
45	8	-2.886507	3.942854	0.741727
46	1	-2.912637	3.324878	-0.029374
47	1	-3.163619	4.805744	0.424201
48	1	-5.038675	-2.637864	-0.220202
49	1	-3.690788	-3.112296	0.425163
50	1	-0.286421	-1.549908	-3.535185
51	1	2.130157	-1.180626	-3.295716

E(UM11) = -2709.8497385 Hartree
Zero-point correction = 0.387377
Thermal correction to Energy = 0.422871
Thermal correction to Enthalpy = 0.423815
Thermal correction to Gibbs Free Energy = 0.318406
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Sum of electronic and thermal Energies = -2709.426867
Sum of electronic and thermal Enthalpies = -2709.425923
Sum of electronic and thermal Free Energies = -2709.531333

Table S5. Cartesian coordinates (Å) of the $[Mn(edta)]^{2-}\cdot 6H_2O$ system optimized at M11/Def2-TZVP level (1 imaginary frequency).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	1.931879	-1.056320	1.543547
2	8	3.005665	-3.005607	1.719882
3	8	3.234802	2.061220	-1.670049
4	8	1.306628	1.433152	-0.736180
5	8	-0.778247	-2.045495	0.922456

6	8	-2.771836	-3.043581	0.838730
7	8	-1.449346	1.247259	0.109300
8	8	-2.334398	2.488226	-1.518138
9	7	-1.070713	-0.860131	-1.474888
10	7	1.801911	-1.185415	-1.119160
11	6	-0.295771	-1.806757	-2.280846
12	1	-0.345603	-2.777022	-1.773417
13	6	1.157705	-1.378238	-2.421021
14	1	1.209389	-0.421604	-2.953844
15	6	2.156615	-2.413900	-0.423407
16	1	1.324688	-3.123992	-0.485928
17	1	3.049411	-2.899103	-0.844279
18	6	2.396326	-2.155470	1.074597
19	6	2.923958	-0.256913	-1.218809
20	1	3.567369	-0.365345	-0.338394
21	1	3.542095	-0.446617	-2.107236
22	6	2.464575	1.208976	-1.227946
23	6	-2.242733	-1.497088	-0.887124
24	1	-2.975189	-0.732824	-0.602958
25	1	-2.744002	-2.177033	-1.590973
26	6	-1.901805	-2.269831	0.396197
27	6	-1.395696	0.394539	-2.133400
28	1	-0.518755	0.771112	-2.670537
29	1	-2.220431	0.301053	-2.854921
30	6	-1.761815	1.469633	-1.101305
31	8	0.927706	2.163678	2.695311
32	1	1.847542	1.867916	2.596956
33	1	0.776353	2.796152	1.968651
34	8	0.632424	3.843742	0.445289
35	8	3.500321	1.060173	2.166945
36	1	0.800153	3.053675	-0.106934
37	1	-0.311663	4.072373	0.369697
38	1	4.156363	0.912779	2.852770
39	1	3.036457	0.209583	2.016375
40	25	0.265365	-0.158186	0.388875
41	8	-3.352997	0.437703	2.064807
42	1	-2.738071	0.757490	1.385541
43	1	-3.971592	-0.177836	1.638852
44	8	-5.059189	-1.590546	0.987085
45	8	-2.120736	4.466683	0.306986
46	1	-2.305152	3.751971	-0.348318
47	1	-2.374891	5.298583	-0.099895
48	1	-5.570803	-1.549878	0.175497
49	1	-4.338069	-2.243934	0.852475
50	1	-0.739998	-1.942069	-3.279224
51	1	1.702344	-2.113977	-3.032860

E(UM11) = -2709.8378983 Hartree
Zero-point correction = 0.386169
Thermal correction to Energy = 0.421678
Thermal correction to Enthalpy = 0.422622
Thermal correction to Gibbs Free Energy = 0.316371
Sum of electronic and zero-point Energies = -2709.451729
Sum of electronic and thermal Energies = -2709.416220
Sum of electronic and thermal Enthalpies = -2709.415276
Sum of electronic and thermal Free Energies = -2709.521527

Table S6. Cartesian coordinates (Å) of the $[Mn(edta)(H_2O)_2]^{2-}\cdot 4H_2O$ system optimized at M11/Def2-TZVP level (1 imaginary frequency).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	-2.260044	-0.074219	1.290224
2	8	-4.296296	0.813005	1.065548
3	8	-1.010007	-3.894607	-1.251130
4	8	0.049912	-2.050829	-0.565432
5	8	-0.918040	2.257320	0.122902
6	8	0.268688	4.151914	0.053049
7	8	2.059743	-0.162687	0.218849
8	8	3.600449	-0.895468	-1.218995
9	7	0.578002	1.003708	-1.687481
10	7	-1.933623	-0.430947	-1.331013
11	6	-0.517312	1.112319	-2.656364
12	1	-1.119341	1.981827	-2.375538
13	6	-1.394134	-0.131982	-2.658848
14	1	-0.797147	-0.997288	-2.969160
15	6	-3.053290	0.400570	-0.922478
16	1	-2.857101	1.440697	-1.198832
17	1	-4.001267	0.093185	-1.390265
18	6	-3.235896	0.385591	0.604900
19	6	-2.233807	-1.849876	-1.199484
20	1	-2.843991	-2.005746	-0.302589
21	1	-2.797856	-2.239724	-2.060003
22	6	-0.961823	-2.685019	-1.005314
23	6	1.033187	2.315460	-1.246067
24	1	1.972970	2.200854	-0.693558
25	1	1.219578	3.000381	-2.087760
26	6	0.033732	2.968655	-0.279110
27	6	1.677353	0.158452	-2.124113
28	1	1.279089	-0.738628	-2.608919
29	1	2.339954	0.663851	-2.843272
30	6	2.517100	-0.336821	-0.938280
31	8	0.357590	-1.091387	2.291073
32	1	-0.369486	-1.297485	2.906778
33	1	0.856362	-1.904915	2.060953
34	8	1.715560	-3.233882	1.235994
35	8	-2.040560	-1.211748	3.693894
36	1	1.237513	-2.905177	0.444195
37	1	2.651686	-2.978015	1.133198
38	1	-2.154151	-0.630412	4.449599
39	1	-2.293678	-0.704591	2.886418
40	25	-0.220962	0.046661	0.349690
41	8	1.025801	1.575361	2.279944
42	1	1.405460	0.691426	2.358872
43	1	1.715099	2.175702	1.950884
44	8	2.606431	3.782635	1.410510
45	8	4.375570	-2.395005	0.867756
46	1	4.154665	-1.797436	0.107258
47	1	5.010206	-3.040175	0.546755
48	1	3.408559	3.861923	0.888795
49	1	1.857468	4.088275	0.855272
50	1	-0.131312	1.293748	-3.672010
51	1	-2.198913	-0.015430	-3.402410

```
E(UM11) = -2709.8429018 Hartree
Zero-point correction = 0.387468
Thermal correction to Energy = 0.421961
Thermal correction to Enthalpy = 0.422905
Thermal correction to Gibbs Free Energy = 0.321123
Sum of electronic and zero-point Energies = -2709.455434
Sum of electronic and thermal Energies = -2709.420941
Sum of electronic and thermal Enthalpies = -2709.419997
Sum of electronic and thermal Free Energies = -2709.521779
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Table S7. Cartesian coordinates (Å) of the $[Mn(cdta)(H_2O)]^{2-}\cdot 5H_2O$ system optimized at M11/Def2-TZVP level (0 imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	-0.283590	-2.319731	1.688466
2	8	-1.929959	-2.683748	3.151585
3	8	-0.947398	-2.918136	-2.919534
4	8	0.260780	-1.547071	-1.637187
5	8	0.219340	0.587396	2.181952
6	8	0.535331	2.640772	2.990589
7	8	2.075410	0.564867	-0.751164
8	8	2.235247	1.513504	-2.761939
9	7	-0.398245	1.495581	-0.308311
10	7	-1.864740	-0.997447	-0.024983
11	6	-1.873001	1.490742	-0.234717
12	1	-2.120537	1.596808	0.832894
13	6	-2.464181	0.160767	-0.718389
14	1	-2.196278	0.046439	-1.780192
15	6	-2.391631	-1.251518	1.311411
16	1	-2.457499	-0.306386	1.863442
17	1	-3.392863	-1.705046	1.300374
18	6	-1.469873	-2.168319	2.131000
19	6	-1.910658	-2.189353	-0.868577
20	1	-1.763258	-3.076932	-0.243732
21	1	-2.874342	-2.305245	-1.382903
22	6	-0.785784	-2.222334	-1.915245
23	6	0.176931	2.432043	0.651467
24	1	1.189813	2.704685	0.334960
25	1	-0.394838	3.367973	0.723691
26	6	0.312957	1.838572	2.062772
27	6	0.149046	1.676657	-1.646849
28	1	-0.407217	1.059530	-2.361010
29	1	0.102349	2.718153	-1.996461
30	6	1.608869	1.216698	-1.728052
31	8	2.428728	-1.776633	0.764041
32	1	2.360890	-2.602405	1.277848
33	1	2.786740	-1.976770	-0.127957
34	8	2.937786	-2.238425	-1.903474
35	8	1.716512	-3.932819	2.388096
36	1	2.002528	-1.972618	-2.005708
37	1	3.480081	-1.505753	-2.253685
38	1	1.975609	-3.906393	3.312306
39	1	0.875926	-3.423093	2.298511

40	25	0.493914	-0.651395	0.381140
41	8	3.681846	1.653446	1.327268
42	1	3.151930	1.280008	0.603785
43	1	3.343097	2.543383	1.516232
44	8	2.610887	4.178065	2.173017
45	8	4.425382	-0.062580	-2.864160
46	1	3.673564	0.579119	-2.830761
47	1	4.741881	-0.083182	-3.770569
48	1	2.369029	4.919994	1.613445
49	1	1.779593	3.780407	2.515281
50	6	-2.506867	2.659675	-1.002370
51	1	-2.251156	2.560186	-2.066056
52	1	-2.075463	3.605717	-0.655581
53	6	-3.995392	0.191289	-0.611740
54	1	-4.273041	0.303972	0.444896
55	1	-4.406112	-0.766375	-0.951995
56	6	-4.598827	1.355189	-1.393026
57	6	-4.027686	2.672650	-0.873952
58	1	-5.689985	1.340625	-1.303722
59	1	-4.358966	1.249596	-2.460172
60	1	-4.309655	2.801249	0.180246
61	1	-4.442600	3.522494	-1.425720

E(UM11) = -2865.8601876 Hartree
Zero-point correction = 0.481081
Thermal correction to Energy = 0.519799
Thermal correction to Enthalpy = 0.520743
Thermal correction to Gibbs Free Energy = 0.409560
Sum of electronic and zero-point Energies = -2865.379107
Sum of electronic and thermal Energies = -2865.340388
Sum of electronic and thermal Enthalpies = -2865.339444
Sum of electronic and thermal Free Energies = -2865.450628

Table S8. Cartesian coordinates (Å) of the $[Mn(cdta)]^{2-}\cdot 6H_2O$ system optimized at M11/Def2-TZVP level (1 imaginary frequency).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	-0.204379	-2.278787	-1.563816
2	8	1.211758	-2.933082	-3.157503
3	8	0.730509	-3.003278	2.922607
4	8	-0.321701	-1.447097	1.716215
5	8	-0.203524	0.628088	-2.129943
6	8	-0.277016	2.696365	-2.959705
7	8	-1.868977	0.839883	0.835424
8	8	-1.849218	1.834209	2.827228
9	7	0.675134	1.454939	0.296776
10	7	1.732760	-1.231471	-0.038619
11	6	2.126036	1.232138	0.138198
12	1	2.321436	1.305604	-0.942984
13	6	2.548226	-0.172144	0.589119
14	1	2.350150	-0.245554	1.669918
15	6	2.083865	-1.566780	-1.414549
16	1	2.240218	-0.645287	-1.987829
17	1	2.996875	-2.173445	-1.491780

18	6	0.948264	-2.330785	-2.118294
19	6	1.669333	-2.415248	0.816170
20	1	1.362194	-3.278281	0.215670
21	1	2.639149	-2.659899	1.269385
22	6	0.620203	-2.283118	1.930263
23	6	0.188462	2.462514	-0.640910
24	1	-0.752588	2.885509	-0.271902
25	1	0.888080	3.301504	-0.758843
26	6	-0.114615	1.882197	-2.031446
27	6	0.217213	1.702286	1.658815
28	1	0.711881	1.008907	2.348203
29	1	0.418957	2.725370	2.006525
30	6	-1.290289	1.442637	1.791662
31	8	-3.600240	-1.651110	-0.820422
32	1	-3.257780	-2.417269	-1.309165
33	1	-3.416910	-1.794485	0.127005
34	8	-3.067843	-1.902833	1.956268
35	8	-2.340349	-3.721912	-2.338875
36	1	-2.106531	-1.740090	1.998996
37	1	-3.494721	-1.095593	2.300299
38	1	-2.494925	-3.704547	-3.286345
39	1	-1.492946	-3.246688	-2.171704
40	25	-0.528754	-0.523131	-0.282217
41	8	-3.443514	2.175356	-1.122236
42	1	-2.929152	1.740553	-0.423261
43	1	-2.997366	3.008410	-1.345327
44	8	-2.076319	4.514015	-2.058986
45	8	-4.217494	0.478551	2.936991
46	1	-3.404565	1.034903	2.901099
47	1	-4.533979	0.497374	3.843506
48	1	-1.706313	5.225026	-1.530187
49	1	-1.326867	4.005656	-2.439990
50	6	2.969948	2.290018	0.861228
51	1	2.773566	2.217499	1.939898
52	1	2.656702	3.291298	0.543960
53	6	4.053074	-0.365578	0.361378
54	1	4.258577	-0.286875	-0.715021
55	1	4.345026	-1.375391	0.672024
56	6	4.877275	0.691410	1.092036
57	6	4.464107	2.085054	0.624271
58	1	5.944505	0.522188	0.916031
59	1	4.709693	0.606274	2.174643
60	1	4.685144	2.189450	-0.446971
61	1	5.035947	2.857332	1.148851

E(UM11) = -2865.8497055 Hartree
Zero-point correction = 0.480513
Thermal correction to Energy = 0.518942
Thermal correction to Enthalpy = 0.519886
Thermal correction to Gibbs Free Energy = 0.408680
Sum of electronic and zero-point Energies = -2865.369193
Sum of electronic and thermal Energies = -2865.330764
Sum of electronic and thermal Enthalpies = -2865.329820
Sum of electronic and thermal Free Energies = -2865.441026

Table S9. Cartesian coordinates (Å) of the $[Mn(pyc3a)(H_2O)]^{-}\cdot 5H_2O$ system optimized at M11/Def2-TZVP level (0 imaginary frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	0.351645	-0.179302	2.918080
2	8	1.572484	-1.710627	3.986698
3	8	-0.709241	-2.067518	0.910144
4	8	-1.536530	-3.789314	-0.236126
5	8	-1.820812	0.666819	-0.833247
6	8	-1.736657	1.709013	-2.797433
7	7	0.304529	-0.864908	-1.322352
8	7	2.049332	-0.018691	0.830533
9	6	1.715127	-1.302545	-1.279961
10	1	1.716611	-2.252027	-0.723338
11	6	2.599331	-0.311905	-0.510937
12	1	2.588855	0.642770	-1.059476
13	6	2.293249	-1.065271	1.821306
14	1	2.119362	-2.045843	1.365091
15	1	3.323299	-1.054305	2.204911
16	6	1.336143	-0.981018	3.020710
17	6	2.502421	1.284878	1.318939
18	1	2.297438	1.333814	2.394329
19	1	3.584930	1.423235	1.185357
20	6	-0.598222	-2.002108	-1.486065
21	1	-1.542734	-1.664669	-1.928958
22	1	-0.192714	-2.766466	-2.162904
23	6	-0.971599	-2.686242	-0.162863
24	6	0.024255	0.195358	-2.283836
25	1	0.811390	0.958328	-2.237097
26	1	-0.026206	-0.159713	-3.322891
27	6	-1.289772	0.911679	-1.958928
28	8	-2.210148	0.707333	1.978918
29	1	-2.411130	-0.024316	2.588841
30	1	-3.031711	0.970953	1.507936
31	8	-4.538773	1.416063	0.660251
32	8	-1.916469	-1.687002	3.431362
33	1	-4.246669	2.000126	-0.068808
34	1	-4.665152	0.536895	0.268578
35	1	-1.685877	-2.107050	2.584034
36	1	-1.100363	-1.199460	3.644853
37	25	-0.368690	0.117640	0.822107
38	8	-3.910365	-1.112420	-0.310940
39	1	-3.132389	-0.576730	-0.545799
40	1	-3.939685	-1.879312	-0.909482
41	8	-3.721658	-3.482938	-1.827189
42	8	-3.626525	3.086102	-1.371501
43	1	-2.996588	2.587953	-1.942300
44	1	-4.196512	3.602706	-1.946154
45	1	-3.571506	-3.554017	-2.773021
46	1	-2.897116	-3.755823	-1.371588
47	6	4.047013	-0.821552	-0.467640
48	6	2.299918	-1.558120	-2.676040
49	1	2.295032	-0.614810	-3.238751
50	1	1.659135	-2.260812	-3.220947
51	6	3.736540	-2.068956	-2.607729
52	1	4.118164	-2.247397	-3.618158

53	1	3.763197	-3.030144	-2.076132
54	6	4.607761	-1.056971	-1.867755
55	1	4.672342	-0.114881	0.089564
56	1	4.070970	-1.773830	0.078536
57	1	5.642510	-1.408040	-1.801064
58	1	4.621407	-0.110634	-2.425924
59	6	1.757889	2.428295	0.667107
60	6	2.381742	3.633450	0.383388
61	6	1.629096	4.671753	-0.138440
62	1	3.445096	3.748083	0.572538
63	6	-0.271132	3.243804	-0.066131
64	6	0.274904	4.479280	-0.361760
65	1	2.097010	5.624800	-0.370254
66	1	-1.327898	3.035843	-0.231694
67	1	-0.351256	5.268230	-0.765201
68	7	0.457911	2.242599	0.430442

E(UM11) = -2924.761062 Hartree
Zero-point correction = 0.549712
Thermal correction to Energy = 0.589952
Thermal correction to Enthalpy = 0.590897
Thermal correction to Gibbs Free Energy = 0.477657
Sum of electronic and zero-point Energies = -2924.211350
Sum of electronic and thermal Energies = -2924.171110
Sum of electronic and thermal Enthalpies = -2924.170165
Sum of electronic and thermal Free Energies = -2924.283405

Table S10. Cartesian coordinates (Å) of the $[Mn(pyc3a)]^{-}\cdot 6H_2O$ system optimized at M11/Def2-TZVP level (1 imaginary frequency).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	0.194929	0.001851	2.863912
2	8	1.385361	-1.387977	4.140552
3	8	-0.612886	-2.067975	0.944791
4	8	-1.342451	-3.868906	-0.145534
5	8	-1.737096	0.540642	-0.881388
6	8	-1.685922	1.451614	-2.910540
7	7	0.446382	-0.935558	-1.282346
8	7	2.049371	0.071982	0.910857
9	6	1.867893	-1.319091	-1.156319
10	1	1.872706	-2.249041	-0.567332
11	6	2.682912	-0.275054	-0.380615
12	1	2.687499	0.653464	-0.972870
13	6	2.233683	-0.915358	1.974232
14	1	2.089853	-1.921798	1.565931
15	1	3.235570	-0.873993	2.422999
16	6	1.195790	-0.759032	3.100995
17	6	2.451529	1.407595	1.358511
18	1	2.190482	1.505182	2.418306
19	1	3.536392	1.561238	1.274396
20	6	-0.408913	-2.110613	-1.441290
21	1	-1.344831	-1.825091	-1.936676
22	1	0.053174	-2.884516	-2.068432
23	6	-0.814407	-2.747736	-0.105560
24	6	0.158114	0.084847	-2.283649

25	1	0.906811	0.885410	-2.227299
26	1	0.161706	-0.298179	-3.313317
27	6	-1.202538	0.742484	-2.020710
28	8	-3.073110	1.058187	2.330366
29	1	-2.951642	0.123666	2.563213
30	1	-3.728687	1.107363	1.611153
31	8	-4.964473	1.228307	0.213240
32	8	-2.124728	-1.509495	3.238035
33	1	-4.546316	1.795615	-0.463044
34	1	-4.810993	0.310404	-0.067355
35	1	-1.805908	-1.985399	2.452157
36	1	-1.355276	-0.957625	3.465349
37	25	-0.314399	0.112390	0.743876
38	8	-3.806208	-1.250038	-0.304564
39	1	-3.048930	-0.688628	-0.545269
40	1	-3.793013	-2.034418	-0.881602
41	8	-3.530158	-3.648984	-1.755236
42	8	-3.690313	2.860603	-1.669079
43	1	-3.014048	2.345452	-2.163947
44	1	-4.174109	3.390272	-2.307527
45	1	-3.384534	-3.749917	-2.699084
46	1	-2.703473	-3.903102	-1.295025
47	6	4.132597	-0.754112	-0.228839
48	6	2.531145	-1.598111	-2.511172
49	1	2.530825	-0.671140	-3.100987
50	1	1.938943	-2.333931	-3.067150
51	6	3.973786	-2.070410	-2.348131
52	1	4.416969	-2.263247	-3.330291
53	1	3.990505	-3.018277	-1.792917
54	6	4.780629	-1.022525	-1.585040
55	1	4.710111	-0.016468	0.339464
56	1	4.137770	-1.686110	0.352298
57	1	5.814657	-1.353456	-1.445537
58	1	4.813767	-0.092005	-2.168294
59	6	1.719217	2.499452	0.612855
60	6	2.324251	3.712756	0.324242
61	6	1.577619	4.705444	-0.286680
62	1	3.368243	3.869198	0.579498
63	6	-0.278783	3.219141	-0.285394
64	6	0.248314	4.459773	-0.592081
65	1	2.030617	5.664390	-0.523472
66	1	-1.315931	2.973373	-0.510118
67	1	-0.373204	5.212280	-1.065960
68	7	0.444775	2.260714	0.297671

E(UM11) = -2924.7492649 Hartree
Zero-point correction = 0.549025
Thermal correction to Energy = 0.589030
Thermal correction to Enthalpy = 0.589974
Thermal correction to Gibbs Free Energy = 0.476397
Sum of electronic and zero-point Energies = -2924.200240
Sum of electronic and thermal Energies = -2924.160235
Sum of electronic and thermal Enthalpies = -2924.159291
Sum of electronic and thermal Free Energies = -2924.272868

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