Electronic Supplementary Information for Energy & Environmental Science

Activation of a water molecule using a mononuclear Mn complex :From Mn-aquo, to Mn-hydroxo to Mn-oxyl *via* charge compensation

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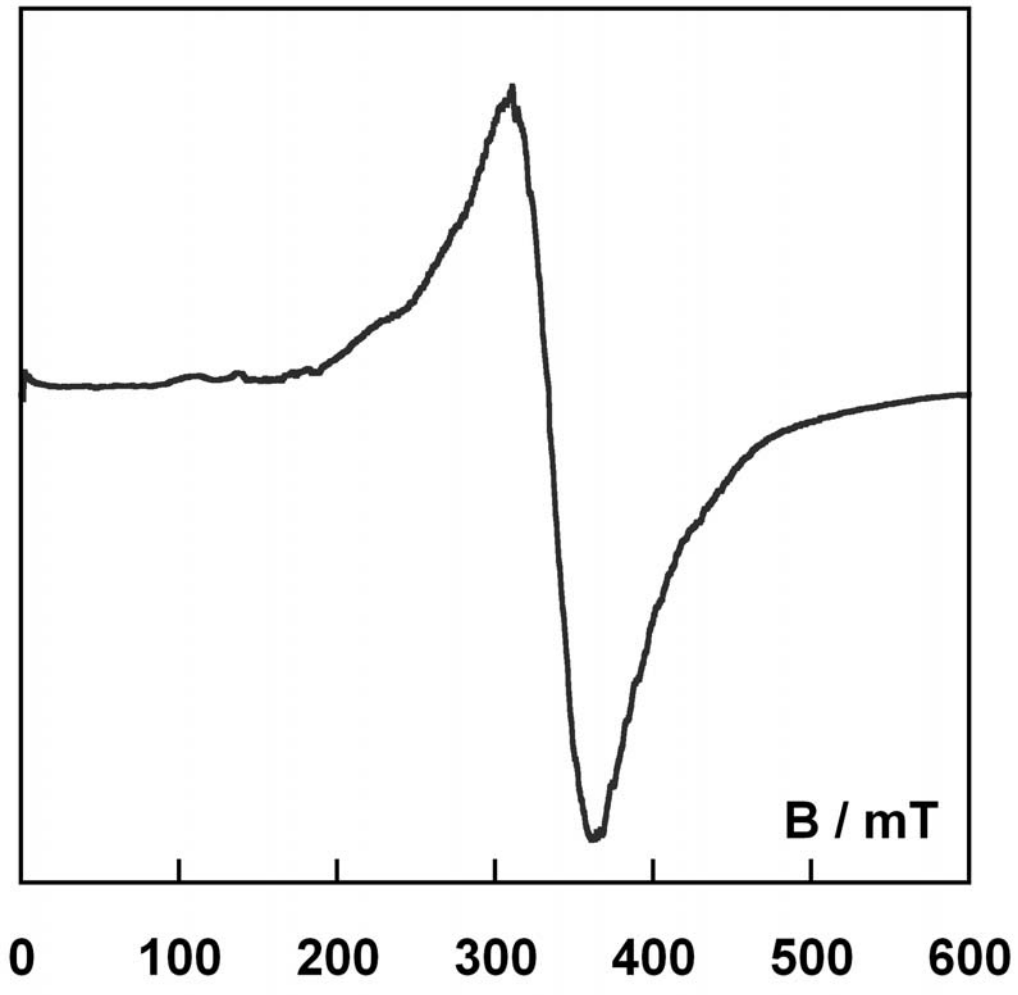
Supplementary Information

Figure S1: X-band EPR spectrum of a 2 mM solution of [**1**$(OH_2)]^+$ in a MeCN/H_2O (98:2) mixture (0.2 M NBu_4ClO_4). Recording conditions: ν = 9.38 GHz; Mod. Amp. = 0.5 mT Microwave power = 2.0 mW; T = 10 K.



X-band EPR spectrum of a 2 mM solution of [**1(**$OH_2)]^+$: spectral features consist of an intense transition at 330 mT (g = 2) and other transitions of lower intensity at 110 mT, and 220 mT. This signature is consistent with a mononuclear Mn(II) species, where the Zeeman effect dominates the zero-field splitting interaction.[1-5]

Direct electrochemical oxidation of $[\mathbf{1}(OH_2)]^+$ into $[\mathbf{3}(O)]^+$ (2 electrons / 2 protons reaction)

Quantitative preparation of $[\mathbf{3}(O)]^+$ was performed by exhaustive bulk electrolysis of $[\mathbf{1}(OH_2)]^+$ at +1.1 V in a MeCN/H_2O (98:2) mixture at –40°C. In order to assist the deprotonation of the coordinated water molecule, two equivalents of lutidine were added to the solution. Coulometry indicates a 2 electron *per* Mn process, with a conversion of ~95%. The voltammograms recorded on the electrolyzed solution show a cathodic process at $E_{pc3}' = 0.65$ V and an anodic process (2/2′) when scanning back to oxidative potentials (Figure S2). These processes correspond to the one observed after one electron/one proton oxidation of $[\mathbf{2}(OH)]^+$. The proton loss is further evidenced by the appearance of the reduction peak of protonated lutidine LH^+ (lutidinium) at –1.5 V (Figure S3) after electrolysis as already reported for similar electrochemical oxidations.[6] Moreover, as reported above for the one electron/one proton oxidation of $[\mathbf{2}(OH)]^+$ the addition of *tert*-butylamine to the medium does not lead to any modification. From all these observations we conclude that the water molecule of $[\mathbf{1}(OH_2)]^+$ has been fully deprotonated during the course of the electrolysis.

The UV-vis and EPR spectra of the $[\mathbf{3}(O)]^+$ solution prepared from direct 2 electron electrolysis of $[\mathbf{1}(OH_2)]^+$ are identical to those reported above for the $[\mathbf{3}(O)]^+$ solution prepared through the stepwise process.

Figure S2: Cyclic voltametry of [**1**(OH_2)]$^+$ 2mM in a MeCN/H_2O (98:2) mixture (A) and of [**3**(O)]$^+$ (B) T = –40°C, working electrode = glassy carbon, v = 100 mV/s, PE indicates the preparative electrolysis potential.

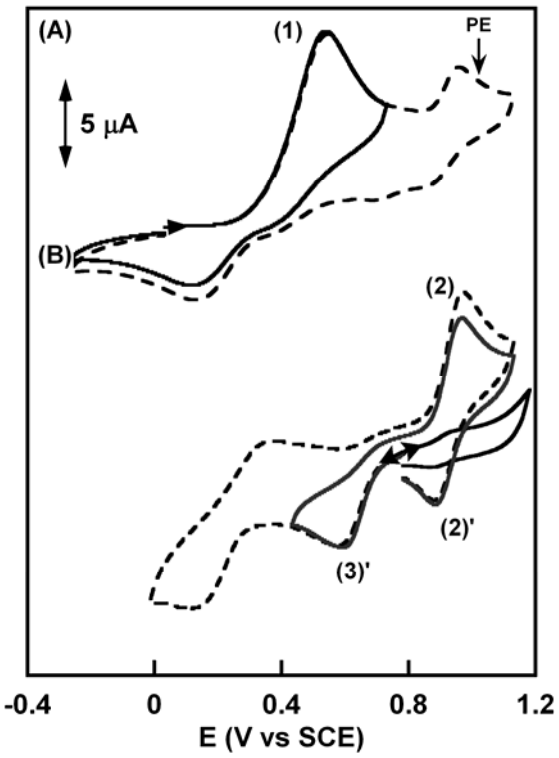


Figure S3: Cyclic voltametry of [**1**(OH_2)]$^+$ 2mM in a MeCN/H_2O (98:2) mixture before electrolysis (A) and after electrolysis at E = + 1 V vs SCE (B); Lutidine 4mM in a MeCN solution (C); Lutidinium 4mM 4mM in a MeCN solution; T = –40°C, working electrode = glassy carbon, v = 100 mV/s, PE indicates the preparative electrolysis potential

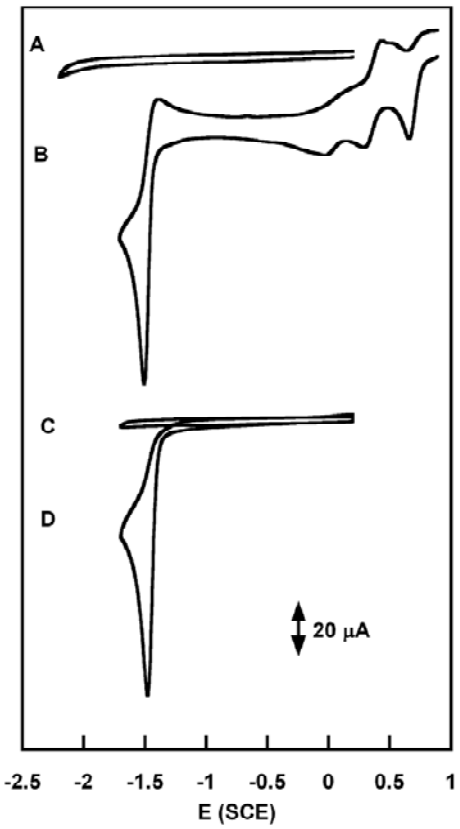


Figure S4: ^{31}P NMR spectra of 10mM $CDCl_3$ solutions of PMe_2Ph without (a) and with (b) addition of one equivalent of $[\mathbf{3}(O)]^+$. PMe_2Ph and $OPMe_2Ph$ show chemical shifts of -45.4 ppm and 34.0 ppm, respectively. Trace $OPMe_2Ph$ is observed in the initial phosphine solution due to air oxidation. Peak integration indicates 5:0 and 4:1 PMe_2Ph/ $OPMe_2Ph$ ratios before and after reaction with $[\mathbf{3}(O)]^+$, respectively. This indicates a yield close to 100% for the oxygen atom transfer reaction between $[\mathbf{3}(O)]^+$ and $OPMe_2Ph$.

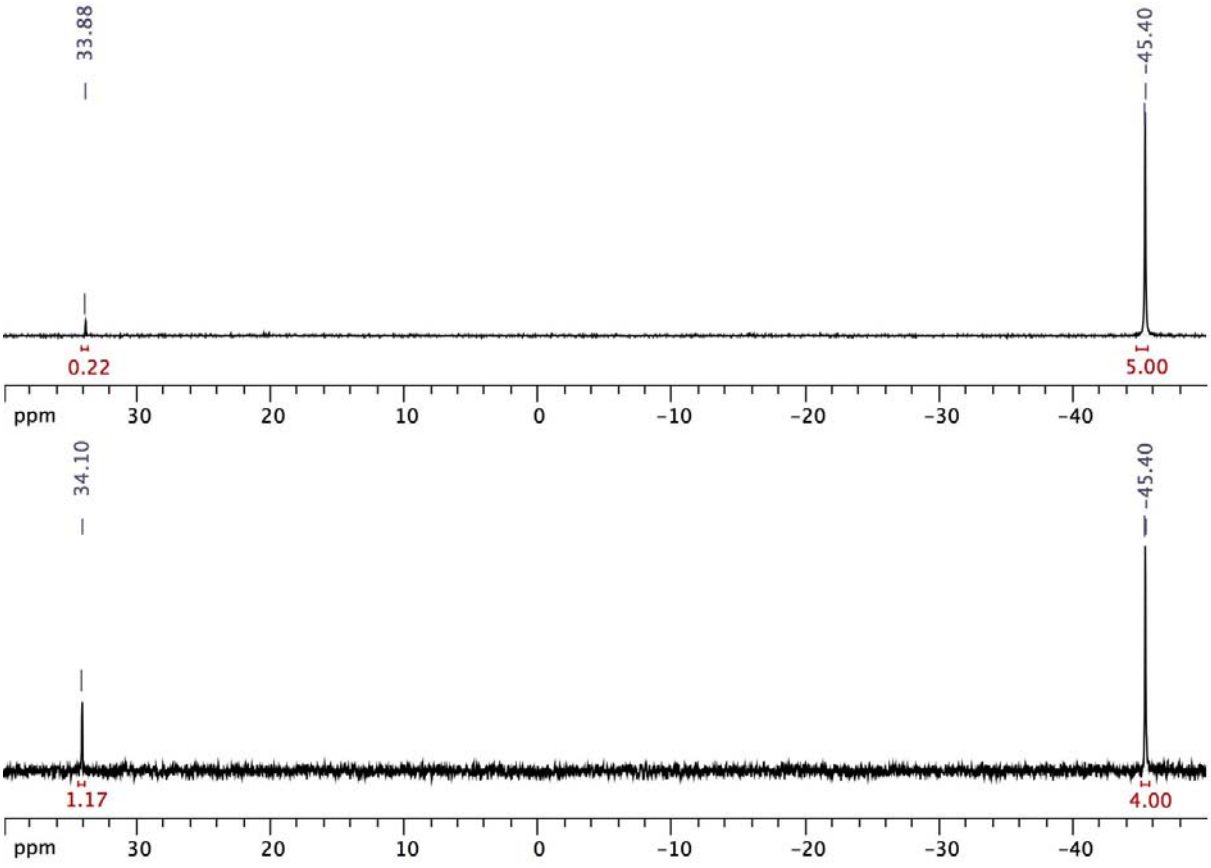
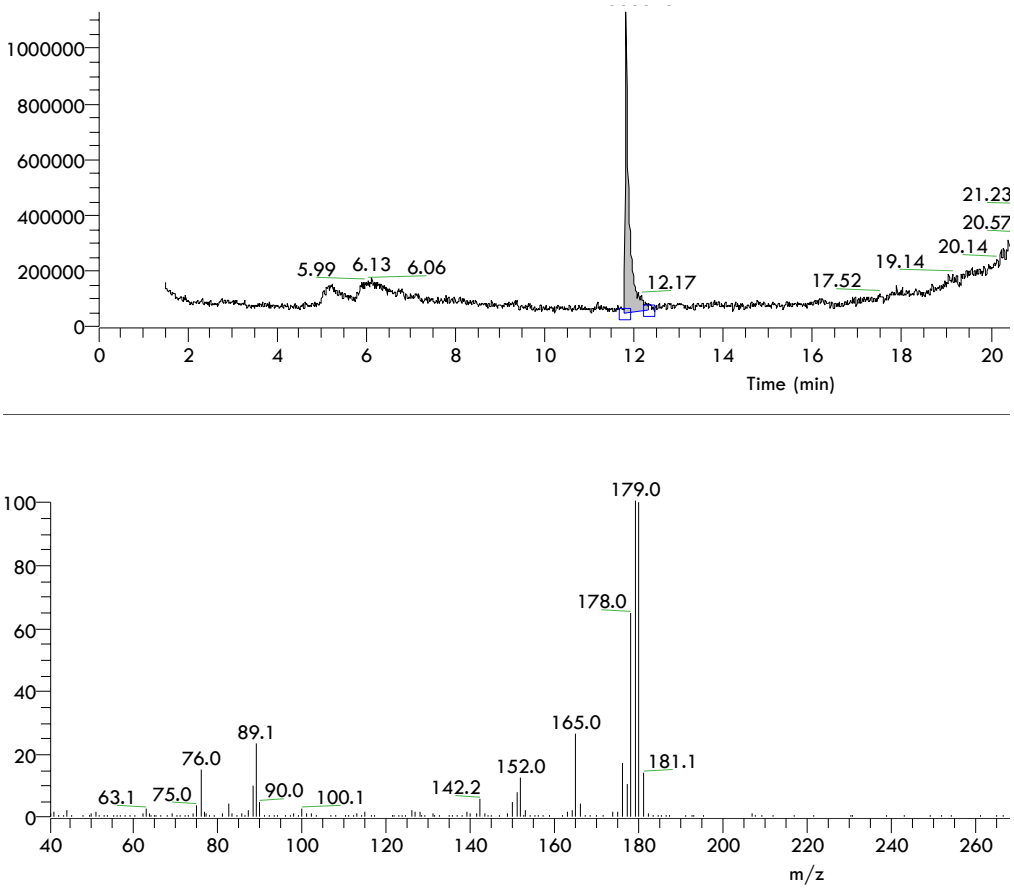


Figure S5: GC-MS (Electronic Impact) recorded on an equimolar mixture of $[\mathbf{3}(O)]^+$ and DHA after 20 minutes stirring at room temperature. The mass spectrograph presented corresponds to the fraction eluted after 11.82 minutes, which contains both dihydroanthracene (M/z = 180) and anthracene (M/z = 178). Although no precise yield can be obtained from these data, the reactant and product are present in an approximate1:1 ratio.



Scheme S1: HAT and OAT reactivity's scheme of complex [**3**(O)]$^{+}$

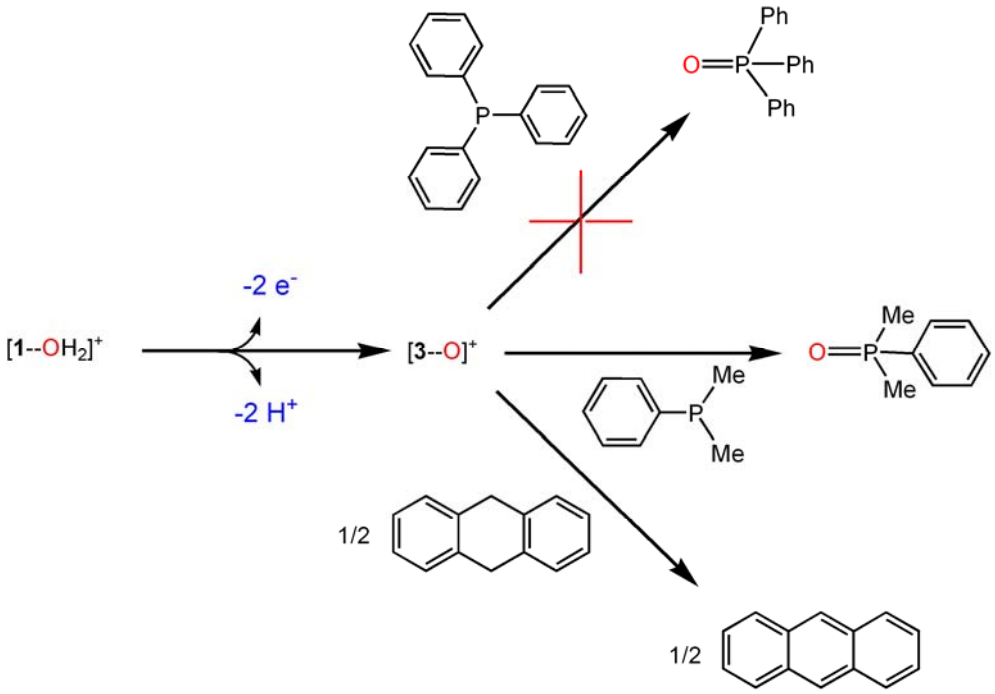


Table S1. EXAFS curve fitting of Complex [**1**$(OH_2)]^+$.

Fit No.	Shell	R (Å)	N	σ^2(Å^2)*10^3	ΔE	R factor
1	Mn-O	2.15	**2.0**	0.002	-8.0	0.051
	Mn-N	2.31	**4.0**	0.004		
	Mn-C	3.10	**6.0**	0.005		
	Mn-C	3.30	**5.0**	0.007		
	Mn-C	3.39	**2.0**	0.002		
2	Mn-O	2.13	**2.0**	0.002	-8.5	0.079
	Mn-N	2.27	**4.0**	0.004		
	Mn-C	3.08	**6.0**	0.008		
	Mn-C	3.25	**5.0**	0.006		
	Mn-C	3.54	**2.0**	0.002		
	Mn-Mn	3.41	**1.0**	0.002		

k-range of 2.4 to 11.7 Å^{-1} was used for the fitting. Bold number shows the fixed parameters.

Table S2. EXAFS curve fitting of Complex [**2**(OH)]$^{+}$.

Fit No.	Shell	R (Å)	N	σ^2(Å^2)*10^3	ΔE	R factor
1	Mn-O	1.88	**2.0**	0.003	-6.8	0.089
	Mn-N	2.20	**4.0**	0.005		
	Mn-C	2.94	**6.0**	0.012		
	Mn-C	3.11	**5.0**	0.006		
	Mn-C	3.58	**2.0**	0.004		

k-range of 2.4 to 11.7 Å^{-1} was used for the fitting. Bold number shows the fixed parameters.

Table S3. EXAFS curve fitting of $[\mathbf{3}(O)]^+$ obtained by the two electron oxidation of complex $[\mathbf{1}(OH)_2]^+$

Fit No.	Shell	R (Å)	N	$\sigma^2(Å^2)*10^3$	ΔE	R factor
1	Mn-O	1.82	**2.0**	0.003	-4.3	0.071
	Mn-N	2.07	**4.0**	0.005		
	Mn-C	2.94	**10.0**	0.013		
	Mn-C	3.34	**2.0**	0.007		
2	Mn-O	1.79	**1.0**	0.001	-5.5	0.056
	Mn-O	1.84	**1.0**	0.001		
	Mn-N	2.06	**4.0**	0.005		
	Mn-C	2.93	**10.0**	0.013		
	Mn-C	3.34	**2.0**	0.004		
3	Mn-O	1.79	**1.0**	0.001	-5.5	0.053
	Mn-O	1.84	**1.0**	0.001		
	Mn-N	2.06	**4.0**	0.005		
	Mn-C	2.93	**10.0**	0.013		
	Mn-C	3.34	**2.0**	0.004		
	Mn-N	4.05	**1.0**	0.006		

k-range of 2.5 to 11.7 $Å^{-1}$ was used for the fitting. Bold number shows the fixed parameters.

EXAFS curve fitting:

As a goodness-of-fit index, we used the R-factor (the absolute difference between theory and data), which is defined as the sum of the squares of the differences between each experimental point and the fit normalized to the sum of the squares of the experimental points.[7]

For complex $[\mathbf{1}(OH)_2]^+$, the curve fitting was carried out using the distances and coordination numbers obtained from X-ray crystallography. The EXAFS data of the solution sample is consistent with the XRD structure of $[\mathbf{1}(OH)_2]^+$ (Fit N1 in Table S1). The data was also fit by considering a possible formation of a dimeric form of Complex $[\mathbf{1}(OH_2)]^+$ in solution (Fit N2 in Table S1). Fit N2 is less preferable than Fit N1, supporting the EPR result (Figure S1) which shows the presence of the monomeric Mn(II) form.

For complex $[\mathbf{2}(OH)]^+$, the fitting parameters used for the $[\mathbf{1}(OH)_2]^+$ complex were used as initial parameters. The fitting result indicates a shortening of Mn─O distances, from ~ 2.2Å in $[\mathbf{1}(OH)_2]^+$ to ~ 1.9Å in $[\mathbf{2}(OH)]^+$.

For the two-electron oxidation product, $[\mathbf{3}(O)]^+$, the structural parameters obtained from the DFT calculations were taken as initial curve fitting parameters. However, the fitting quality was not satisfactory (R factor > 0.20, data not shown). In Fit N1 in Table S3, Mn─O distance was fit as one shell. This fit gives a Mn─O distance of 1.82 Å. Such a distance is close to the 1.82 Å[8] or 1.83 Å[9]

distances reported for Mn─OH bond in non porphyrinic mononuclear Mn(IV) complexes. In the present case, however, we can exclude the presence of two Mn─OH interactions, since we use a [N_4O] pentadentate ligand and therefore one Mn─O distance comes from the Mn─O_{ph} (O_{ph}: oxygen from phenolate ligand) bond. Then, the other Mn─O interaction must come from either a Mn─OH or Mn─O bond. The Mn─O_{ph} distances reported in the CS database is typically ~ 1.86 Å, but range from 1.84 to 1.92 Å in Mn(IV) mononuclear complexes.[10-12] In Fit N2 we set two shells for the Mn─O distances in which one Mn─O_{ph} distance is fixed to be longer than 1.84 Å. In this case, the second Mn─O distance comes to 1.79 Å. However, the current EXAFS resolution is not sufficient to distinguish two sub-shells which differ by 0.05 Å. Therefore, this distance remains ambiguous, although the fitting procedure is reasonable with two Mn─O shells on the basis of the chemical structure of the starting complex ([**1**(OH_2)]$^+$) as described above. Additionally, the electrochemical experiments show the deprotonation of the coordinated water molecule upon two electron oxidation of the [**1**(OH_2)]$^+$ complex, which suggests the presence of Mn-oxo species and therefore excludes a Mn─OH bond in the [**3**(O)]$^+$ complex. The Mn─O distance of ~1.79 Å obtained from the EXAFS experiment compares better with a distance of 1.72 Å obtained from DFT calculations of an Mn-oxyl trans species, while it is longer than the distance obtained from the DFT models of the oxo compounds (1.66 – 1.68 Å, Table 3). We also tested a possible hydrogen bond between lutidinium and Mn-oxo by adding an additional Mn-N shell (Fit N3 in Table S3). The fitting quality improved slightly, which could indicate the presence of an O···H bond between the Mn-oxo and the N-H group of lutidinium.

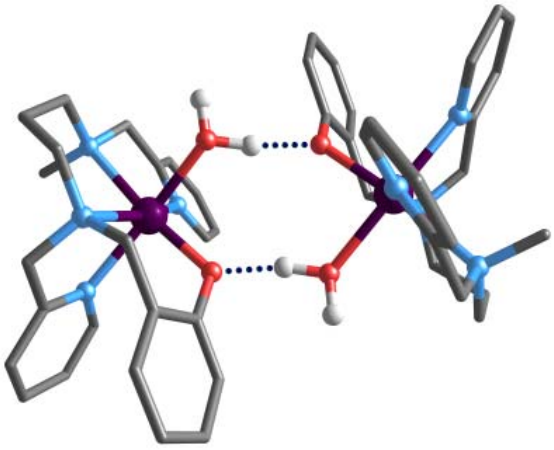
In summary, the distance from EXAFS is closer to the Mn─O distance obtained from DFT calculations for the Mn-oxyl species which is 1.72 Å, or the Mn(IV)-hydroxy species which is 1.81-1.82 Å, but not the oxo species (1.66 – 1.68 Å). However, the Mn─O_{ph} distance from DFT is 1.98-2.15 Å for the OH species while it is shorter for the oxyl species (1.87-2.0 Å). The EXAFS fit (Mn─O_{ph} = 1.84 Å) seems to support the shorter Mn─O_{ph} distance. Therefore, the overall evidence (including DFT and EXAFS Mn─O and Mn─O_{ph} distances for all the species) seems to prefer the oxyl species.

Table S4: DFT optimized Cartesian coordinates of $[\mathbf{1}(OH_2)]^+$.

Mn	9.078530	11.925531	8.180379	O	9.507440	9.732294	11.853283
N	9.201124	14.220154	8.515232	C	8.934920	12.409687	14.370719
N	11.177731	12.006667	6.980373	C	10.109241	8.927113	15.494200
N	7.809176	12.845685	6.470969	H	10.065100	10.002101	15.620584
N	9.389581	9.852893	7.312367	C	5.535416	11.022664	14.614717
C	8.423016	8.931275	7.187692	H	5.082682	11.316862	13.663897
C	7.015342	12.138813	5.650263	H	4.775263	11.191537	15.387711
H	7.173491	11.067252	5.636369	C	6.724601	11.926890	14.860282
C	11.687957	10.622298	7.076253	C	10.288264	8.666380	11.620288
H	12.075296	10.465779	8.086572	C	8.232254	7.215516	11.308834
H	12.527298	10.459535	6.388520	H	8.003855	6.219789	10.908331
C	10.614322	9.584598	6.829039	H	7.782658	7.954727	10.643216
C	8.373383	14.423207	9.759352	C	6.077950	7.079440	12.406922
H	8.470737	15.470429	10.071695	H	5.772635	7.677760	11.546945
H	8.834247	13.799307	10.527498	H	5.966596	6.025200	12.117498
C	10.587584	14.681129	8.812163	C	9.206403	7.060271	14.479447
H	10.571148	15.764242	8.996705	C	4.806510	8.821317	13.897469
C	7.650483	14.176465	6.530138	H	3.922372	8.848735	14.549792
C	12.142832	12.947589	7.605956	H	4.531172	9.335494	12.974428
H	13.075047	12.951211	7.023588	C	12.509772	7.701724	11.364842
H	12.395356	12.555113	8.593591	H	13.586483	7.824395	11.387662
C	4.181376	13.487992	9.455876	C	9.726896	7.394634	11.355166
H	3.126757	13.250914	9.375960	C	6.175980	9.094656	15.898869
C	6.911909	14.086229	9.621712	H	5.270163	9.134583	16.517024
C	10.974474	12.340561	5.553189	H	6.535638	8.070101	15.870543
H	11.926964	12.332808	5.008190	H	6.946919	9.702527	16.369115
H	10.519007	13.321158	5.448245	C	11.065128	8.178021	16.157068
H	10.304477	11.614516	5.096239	H	11.777685	8.660382	16.812611
C	6.045200	12.718598	4.852094	C	11.085654	6.802190	15.948890
H	5.435759	12.105211	4.202108	H	11.823386	6.180360	16.440499
C	5.874602	14.098072	4.918636	C	5.119320	7.358951	13.570573
H	5.119850	14.590591	4.318310	H	5.413063	6.817843	14.472085
C	11.663364	14.393456	7.757885	H	4.165131	6.908280	13.281553
H	11.393988	14.811554	6.786145	C	10.573433	6.316935	11.086442
H	12.541718	14.967845	8.067233	H	10.136556	5.347784	10.867432
C	5.945409	15.089043	9.722434	C	11.687963	8.789853	11.631486
H	6.266309	16.114584	9.875130	H	12.119655	9.751677	11.888277
C	8.622876	14.968735	7.377985	C	8.101721	6.455089	13.639317
H	9.436003	15.282896	6.720977	H	7.309061	6.150932	14.325400
C	10.896896	8.383262	6.187428	H	8.463517	5.534735	13.169206
H	11.889120	8.198055	5.796050	C	6.612471	13.083184	15.625529
C	9.892618	7.432561	6.055215	H	5.676804	13.319931	16.116022
H	10.091840	6.492651	5.555655	C	7.712468	13.922634	15.751165
C	6.685871	14.833441	5.768573	H	7.646073	14.825904	16.344786
H	6.574310	15.907427	5.847828	C	10.146472	6.239054	15.099201
C	8.630729	7.707884	6.569826	H	10.139172	5.172744	14.911739
C	4.586188	14.806335	9.645069	C	8.896945	13.583974	15.106540
H	3.856244	15.601139	9.727266	C	11.956826	6.455242	11.084104

H	8.140686	15.889139	7.723349	H	12.592005	5.604508	10.873972
H	7.457947	9.197216	7.603557	O	7.396288	11.746880	9.381290
H	7.820855	6.995432	6.486859	C	6.499897	12.743777	9.446479
H	7.047313	10.764792	10.637044	C	5.124128	12.471406	9.356032
H	5.750651	10.695979	11.478532	H	4.812135	11.448226	9.175122
Mn	7.904605	9.596374	13.174494	H	9.878372	10.877683	10.777766
O	6.627149	10.298270	11.428673	O	10.266459	11.516224	10.094089
N	7.523635	7.368891	12.630403	H	11.213848	11.348880	10.133738
N	5.906846	9.594216	14.532142	H	10.876362	14.206954	9.751925
N	9.192203	8.387390	14.674800	H	9.833296	12.098801	13.850032
N	7.875938	11.594950	14.251863	H	9.776155	14.210236	15.178157

Figure S6: Representation of the DFT optimized geometry of $[\mathbf{1}(OH_2)]^+$



The aqua complex in the crystal adopts the form of hydrogen-bonded dimers, therefore its structure can only be satisfactorily reproduced if these interactions are taken explicitly into account. As anticipated due to the lack of external (packing) constraints, the freely optimized structure from DFT calculations expands slightly, resulting in elongation of the Mn–OH_2 bond by approximately 0.1 Å compared to the crystallographic value. All other bond lengths involving Mn are reproduced with an average accuracy better than 0.03 Å, which is typically expected from the current level of theory.[13-16]

Table S5: DFT optimized Cartesian coordinates of *cis* and *trans* [**3**(O)]$^{+}$.

[**3**(O)]$^{+}$, oxo *cis*				[**3**(O)]$^{+}$, oxo *trans*			
Mn	3.361175	1.452717	7.244774	Mn	-0.132586	6.407855	3.181072
O	2.258554	1.262826	6.023973	O	0.920276	7.704951	2.088260
N	3.281526	3.562285	7.074204	O	-0.943100	5.245441	4.085675
N	1.613215	1.268207	8.627456	N	1.617403	5.972366	4.217708
N	4.725096	2.082978	8.925977	N	-0.341683	7.865145	4.700736
N	3.420320	-0.572865	7.698436	N	-2.018149	6.817773	2.228369
O	4.974747	1.279495	6.324046	C	1.526301	9.306663	3.731499
C	4.452578	-1.379816	7.413667	N	0.011357	5.272212	1.420900
H	5.297908	-0.899300	6.939893	C	1.819853	8.550347	2.576287
C	5.525101	1.277512	9.642405	C	1.724984	6.642236	5.377196
H	5.298637	0.219814	9.606599	C	0.130806	9.237814	4.262936
C	1.149538	-0.119418	8.350788	H	-0.563236	9.563150	3.489830
H	0.655846	-0.107925	7.377423	H	0.014694	9.908777	5.120035
H	0.426617	-0.445625	9.104993	C	-1.751289	7.969910	5.201917
C	2.299080	-1.079091	8.241022	H	-1.766643	8.732665	5.988145
C	5.833610	2.238802	5.962821	H	-1.995073	7.007913	5.650028
C	3.932618	3.857379	5.733502	C	3.077554	8.718658	1.972008
H	3.768455	4.915950	5.510865	H	3.297331	8.160540	1.069596
H	3.379881	3.257729	5.009489	C	-1.275327	4.219677	-0.289930
C	1.866367	4.052856	6.989972	H	-2.248869	3.980363	-0.697411
H	1.458509	3.646704	6.066020	C	3.719913	10.326270	3.664469
H	1.900945	5.144133	6.896784	H	4.449100	11.010671	4.078095
C	4.979346	3.399264	8.917920	C	3.883085	5.688747	5.789089
C	0.533529	2.213753	8.214442	H	4.773005	5.590205	6.397629
H	-0.309960	2.100461	8.905827	C	-2.356837	5.484584	1.637002
H	0.210027	1.903412	7.222945	H	-3.235356	5.570437	0.991003
C	8.104660	2.908089	5.457659	H	-2.579470	4.813675	2.467442
H	9.152603	2.650875	5.359677	C	3.741277	4.957977	4.615209
C	5.397615	3.548930	5.687994	H	4.503259	4.265776	4.284247
C	1.905126	1.401954	10.074410	C	2.597659	5.133352	3.856869
H	0.995625	1.243730	10.663913	H	2.450541	4.572546	2.947530
H	2.300744	2.389055	10.295942	C	0.499096	7.373819	5.830824
H	2.648639	0.665463	10.371830	H	-0.101837	6.656850	6.393773
C	6.590704	1.748249	10.388290	H	0.754984	8.201496	6.496858
H	7.203436	1.058968	10.953513	C	4.008031	9.596282	2.510977
C	6.857849	3.114428	10.376384	H	4.969721	9.716054	2.025664
H	7.692569	3.518454	10.935304	C	2.856073	6.534240	6.177799
C	0.948886	3.679632	8.153596	H	2.919861	7.104519	7.095156
H	1.344037	4.022289	9.113057	C	2.474655	10.179948	4.263397
H	0.030037	4.254896	8.008029	H	2.227428	10.766216	5.142995
C	6.330354	4.517983	5.315928	C	-3.105828	7.154082	3.197455
H	5.988443	5.523860	5.095244	H	-3.291283	6.255268	3.783080
C	7.197438	1.933000	5.846216	H	-4.009031	7.380910	2.620349
H	7.522763	0.919794	6.046648	C	-2.804846	8.301591	4.150915
C	4.006640	4.272233	8.170095	H	-3.731502	8.498496	4.697519
H	3.270762	4.640538	8.886653	H	-2.584183	9.228448	3.620114
H	4.518928	5.148645	7.768958	C	-1.926506	7.847260	1.158132

C	2.201085	-2.426243	8.563141	H	-1.702843	8.816170	1.593714
H	1.293016	-2.810044	9.009776	H	-2.874460	7.904259	0.614381
C	3.272809	-3.266400	8.285049	H	-1.115675	7.605668	0.477629
H	3.214125	-4.321797	8.520049	C	-0.110795	3.825408	-0.935724
C	6.042923	3.949816	9.629499	H	-0.159970	3.248631	-1.850691
H	6.228796	5.015371	9.587023	C	1.132444	4.961598	0.757444
C	4.412439	-2.737019	7.690700	H	2.054297	5.352998	1.159604
H	5.259982	-3.360894	7.441402	C	-1.178737	4.951214	0.886067
C	7.679748	4.209340	5.195714	C	1.114694	4.221215	-0.413077
H	8.388927	4.968747	4.893214	H	2.044255	3.981311	-0.911038

Table S6: DFT optimized Cartesian coordinates of the oxyl form of *trans* [**3**(O)]$^{+}$.

Mn	-0.011408	6.322145	3.130321	C	2.842168	5.198672	4.063332
O	1.003090	7.583757	2.161060	H	2.782229	4.635279	3.141451
O	-0.853776	5.105277	4.005023	C	0.499750	7.344523	5.911431
N	1.772275	5.937494	4.386026	H	-0.106851	6.605747	6.439895
N	-0.309004	7.844895	4.770092	H	0.713086	8.156203	6.614441
N	-2.077345	6.832371	2.152747	C	4.013352	9.602568	2.501317
C	1.543106	9.275899	3.764678	H	4.966334	9.733311	2.002769
N	-0.046070	5.164520	1.234198	C	2.888779	6.651765	6.364815
C	1.865232	8.492279	2.637906	H	2.876125	7.246790	7.268914
C	1.782076	6.649101	5.521110	C	2.470638	10.200291	4.243401
C	0.157979	9.204854	4.342031	H	2.215249	10.811154	5.103065
H	-0.550106	9.551264	3.589888	C	-3.118948	7.135395	3.170979
H	0.079303	9.884468	5.199041	H	-3.291183	6.218124	3.736974
C	-1.736558	7.923331	5.217898	H	-4.057223	7.381248	2.655906
H	-1.801947	8.669651	6.020014	C	-2.781854	8.257420	4.151274
H	-1.983089	6.953655	5.651427	H	-3.705170	8.465797	4.699982
C	3.106071	8.672787	2.011875	H	-2.552318	9.187688	3.630161
H	3.333969	8.077956	1.135941	C	-1.973592	7.914767	1.149600
C	-1.441587	4.319401	-0.503203	H	-1.694072	8.849218	1.628562
H	-2.435329	4.207756	-0.917773	H	-2.928778	8.052827	0.628423
C	3.705038	10.366588	3.625028	H	-1.196030	7.676284	0.427556
H	4.411956	11.092019	4.006395	C	-0.332469	3.803118	-1.160134
C	3.997292	5.888187	6.030712	H	-0.448767	3.269754	-2.095267
H	4.868342	5.876724	6.673778	C	1.026339	4.697404	0.583457
C	-2.423422	5.555526	1.483348	H	1.989953	4.909652	1.027513
H	-3.292896	5.682659	0.827807	C	-1.263865	4.995142	0.699275
H	-2.687895	4.834325	2.259420	C	0.928730	3.999637	-0.609611
C	3.972058	5.137308	4.860405	H	1.821519	3.633459	-1.098162
H	4.811374	4.522852	4.564422				

Table S7: DFT optimized Cartesian coordinates of *cis* and *trans* [**3**(O···HLut)]$^{2+}$

[**3**(O···HLut)]$^{2+}$, ***cis***				[**3**(O···HLut)]$^{2+}$, ***trans***			
Mn	3.541640	1.213166	7.028876	Mn	-3.324969	-0.639098	-1.823802
C	7.471994	4.611009	5.266894	O	-2.537989	0.707827	-2.971093
C	8.065179	3.381096	5.542611	O	-3.909551	-1.944205	-0.859203
C	7.284161	2.269612	5.833485	N	-1.422378	-0.878718	-1.002939
C	5.889030	2.373031	5.825294	N	-3.494144	0.797688	-0.270064
C	5.282943	3.610586	5.546858	N	-5.331878	-0.338406	-2.542534
C	6.085701	4.718738	5.276328	C	-1.907721	2.415517	-1.447115
O	5.133332	1.279632	6.052810	N	-3.308436	-1.720748	-3.644588
N	3.934260	-0.743984	7.583438	C	-1.670873	1.661686	-2.610023
C	5.100744	-1.377090	7.380073	C	-1.239107	-0.180522	0.131039
C	5.295711	-2.689386	7.779058	C	-3.212499	2.214583	-0.748493
C	4.255774	-3.359213	8.415087	H	-4.027669	2.474076	-1.420662
C	3.046908	-2.701580	8.611725	H	-3.283655	2.866764	0.126740
C	2.910408	-1.392189	8.170420	C	-4.835423	0.776916	0.403309
C	1.613345	-0.638864	8.211617	H	-4.814788	1.530543	1.196474
N	1.835338	0.826086	8.387066	H	-4.936009	-0.202602	0.866862
C	2.070802	1.099309	9.830657	C	-0.528336	1.929645	-3.374418
C	3.787723	3.693319	5.509104	H	-0.361696	1.367070	-4.284926
N	3.119381	3.280150	6.811485	C	-4.721529	-2.715286	-5.292910
C	3.664419	4.098641	7.940379	H	-5.721129	-2.970831	-5.619652
C	4.741052	3.398985	8.721438	C	0.129188	3.661777	-1.818667
N	4.746668	2.056966	8.674468	H	0.820268	4.439021	-1.520324
C	5.643876	1.392939	9.425327	C	1.072273	-0.806283	0.206190
C	6.548563	2.032013	10.252604	H	2.048848	-0.764615	0.671506
C	6.545903	3.423377	10.295808	C	-5.651131	-1.657750	-3.174912
C	5.630226	4.114417	9.518132	H	-6.596938	-1.590666	-3.718893
O	2.527182	0.767962	5.746720	H	-5.753368	-2.383758	-2.369328
C	1.648300	3.542262	6.658653	C	0.866884	-1.555875	-0.947267
C	0.750002	3.054291	7.793294	H	1.669211	-2.118575	-1.404676
C	0.609220	1.542415	7.915264	C	-0.390323	-1.559599	-1.523160
H	5.865590	-0.796519	6.882723	H	-0.582230	-2.129157	-2.418916
H	5.629503	0.314463	9.355151	C	-2.473705	0.402534	0.746400
H	1.124049	-0.781620	7.247210	H	-2.921064	-0.370179	1.374008
H	0.952356	-1.023989	8.992990	H	-2.233318	1.256106	1.384110
H	3.475020	4.717362	5.287759	C	0.356245	2.924814	-2.980153
H	3.369830	3.032899	4.749195	H	1.229433	3.132950	-3.586618
H	1.349201	3.066249	5.726785	C	0.001621	-0.117690	0.754782
H	1.518858	4.623234	6.541290	H	0.120419	0.469770	1.655751
H	-0.211219	1.307004	8.601973	C	-1.006167	3.406140	-1.060036
H	0.365812	1.130272	6.938713	H	-1.206061	3.998811	-0.173339
H	9.144165	3.287168	5.535056	C	-6.335108	-0.122486	-1.453030
H	1.181448	0.836982	10.411381	H	-6.383924	-1.050289	-0.885624
H	2.298169	2.148457	9.992135	H	-7.308523	0.038023	-1.927605
H	2.910770	0.508701	10.188160	C	-6.036668	1.023524	-0.499780
H	7.245409	1.451559	10.842041	H	-6.904392	1.110914	0.159771
H	7.247974	3.958049	10.923142	H	-5.978167	1.981966	-1.016205
H	1.016766	3.507036	8.750445	C	-5.428897	0.744854	-3.565254

H	-0.249079	3.441836	7.574461	H	-5.219294	1.707259	-3.111247
H	5.620555	5.672599	5.051712	H	-6.436894	0.757391	-3.988813
H	7.741383	1.311238	6.045870	H	-4.693628	0.586460	-4.347527
H	2.847438	4.331059	8.624183	C	-3.616026	-2.996299	-6.086545
H	4.031218	5.052933	7.558700	H	-3.737196	-3.498232	-7.038158
H	2.215770	-3.198142	9.095686	C	-2.251287	-1.924515	-4.444368
H	4.382430	-4.380984	8.750557	H	-1.308491	-1.514595	-4.117109
H	5.603026	5.196608	9.522171	C	-4.533739	-2.069953	-4.078004
H	6.248446	-3.169309	7.600127	C	-2.360683	-2.576930	-5.661393
H	8.083243	5.475365	5.043071	H	-1.479814	-2.726950	-6.270763
H	2.538924	0.157450	4.163727	H	-3.825094	-3.398493	-0.138048
N	2.431103	-0.141504	3.157264	N	-3.845464	-4.356835	0.333777
C	3.540685	-0.522530	2.477367	C	-4.545773	-4.491722	1.485991
C	3.405577	-0.867197	1.141218	C	-4.599483	-5.738889	2.088398
C	2.154315	-0.820505	0.539268	C	-3.940310	-6.813642	1.504836
C	1.042743	-0.431225	1.276624	C	-3.235062	-6.633671	0.321554
C	1.191582	-0.087709	2.610718	C	-3.191563	-5.379701	-0.266872
C	4.840330	-0.578161	3.214277	C	-5.207546	-3.277850	2.058650
H	4.280848	-1.167609	0.581598	H	-5.158633	-5.861256	3.006020
H	2.045212	-1.086325	-0.504969	H	-3.980188	-7.791098	1.969385
H	0.061145	-0.389154	0.824386	H	-2.721176	-7.459883	-0.150597
C	0.046531	0.318891	3.484911	C	-2.436728	-5.094748	-1.527454
H	5.027674	-1.602347	3.551594	H	-6.133198	-3.549541	2.564615
H	5.661387	-0.298410	2.554605	H	-4.554506	-2.807904	2.799878
H	4.843592	0.073783	4.087698	H	-5.421078	-2.547650	1.280009
H	0.400209	0.811342	4.388894	H	-2.834484	-4.217014	-2.033344
H	-0.627413	0.985753	2.946706	H	-1.383164	-4.910909	-1.298009
H	-0.531509	-0.562402	3.777249	H	-2.481000	-5.951555	-2.199184

Table S8: DFT optimized Cartesian coordinates of *cis* and *trans* [**3**(OH)]$^{2+}$

[**3**(OH)]$^{2+}$, ***cis***				[**3**(OH)]$^{2+}$, ***trans***			
H	2.634592	0.661512	5.210564	H	-0.560563	4.284337	4.404740
Mn	3.447170	1.453557	7.335695	Mn	-0.031916	6.294564	3.175355
O	2.335039	1.251079	5.915176	O	1.108973	7.611594	2.235900
N	3.379606	3.611460	7.069896	O	-1.008028	5.081352	4.092542
N	1.576788	1.266763	8.692642	N	1.690802	5.885181	4.422499
N	4.723449	2.051619	8.897830	N	-0.285581	7.890108	4.845513
N	3.431205	-0.624995	7.770028	N	-1.960085	6.840870	2.181138
O	5.238840	1.361232	6.142760	C	1.537882	9.367132	3.801529
C	4.444862	-1.479025	7.528529	N	0.024156	5.115670	1.259505
H	5.338516	-1.049447	7.094106	C	1.836453	8.592299	2.612059
C	5.410350	1.202415	9.690947	C	1.727830	6.563529	5.583830
H	5.203790	0.149834	9.563192	C	0.203942	9.249932	4.490063
C	1.123592	-0.109651	8.375515	H	-0.535024	9.691297	3.818428
H	0.633895	-0.084481	7.400348	H	0.215369	9.878140	5.388204
H	0.389495	-0.461733	9.107404	C	-1.732301	7.988728	5.251226
C	2.270085	-1.088842	8.275354	H	-1.817697	8.743862	6.041152
C	5.982715	2.306409	5.732216	H	-1.997783	7.025499	5.684181
C	3.985148	3.926369	5.721755	C	2.990415	8.926068	1.818191
H	3.800824	4.982564	5.505723	H	3.165092	8.343470	0.922818
H	3.418961	3.335218	5.000169	C	-1.391781	4.300923	-0.482862
C	1.943236	4.076801	7.007388	H	-2.385724	4.220894	-0.904079
H	1.526059	3.657843	6.093048	C	3.567285	10.637551	3.397018
H	1.959662	5.166732	6.897260	H	4.236506	11.428647	3.712457
C	4.945612	3.377432	9.013307	C	3.877837	5.630930	6.104836
C	0.554175	2.258411	8.242965	H	4.730066	5.534712	6.765900
H	-0.314009	2.198675	8.908833	C	-2.346427	5.583227	1.480774
H	0.230537	1.960377	7.246748	H	-3.193132	5.769453	0.813224
C	8.182332	3.051660	4.974002	H	-2.665540	4.870141	2.242087
H	9.219698	2.853402	4.736307	C	3.822231	4.916060	4.912660
C	5.456897	3.650327	5.552313	H	4.619672	4.247964	4.616751
C	1.812214	1.378187	10.151979	C	2.716442	5.077656	4.097397
H	0.877783	1.238539	10.705870	H	2.635270	4.540287	3.161945
H	2.221072	2.353615	10.404347	C	0.487631	7.328022	5.983899
H	2.521044	0.616828	10.474569	H	-0.162708	6.620399	6.502122
C	6.331879	1.636933	10.622892	H	0.745100	8.109047	6.706429
H	6.854079	0.917821	11.239504	C	3.839539	9.922187	2.214190
C	6.568845	3.003705	10.741386	H	4.715509	10.165630	1.626742
H	7.287799	3.379116	11.458631	C	2.818863	6.463769	6.441270
C	1.045955	3.706206	8.190660	H	2.826718	7.021906	7.368832
H	1.480619	4.013130	9.145186	C	2.422791	10.355721	4.166535
H	0.154012	4.329525	8.083015	H	2.223996	10.958402	5.045190
C	6.311268	4.629967	5.103042	C	-3.035650	7.169031	3.169998
H	5.943967	5.636984	4.942436	H	-3.227286	6.261010	3.740174
C	7.369815	2.048584	5.433397	H	-3.946718	7.409300	2.610268
H	7.730907	1.037672	5.572185	C	-2.729887	8.309350	4.138002
C	4.109319	4.306804	8.170505	H	-3.673163	8.532625	4.644489
H	3.382784	4.791708	8.824041	H	-2.482867	9.232324	3.609207
H	4.732664	5.108206	7.768128	C	-1.805247	7.931622	1.183391

C	2.116877	-2.433215	8.593037	H	-1.493377	8.852284	1.669797
H	1.181806	-2.783502	9.011091	H	-2.753007	8.113308	0.667640
C	3.164897	-3.314317	8.357492	H	-1.048207	7.659829	0.450882
H	3.058159	-4.365210	8.595554	C	-0.300009	3.730279	-1.123946
C	5.868149	3.879415	9.925461	H	-0.430699	3.189249	-2.052639
H	6.027335	4.948085	9.995698	C	1.080927	4.587090	0.621326
C	4.347411	-2.830832	7.804952	H	2.052398	4.749560	1.069930
H	5.180863	-3.486924	7.593349	C	-1.196894	4.984065	0.712098
C	7.662218	4.348372	4.810467	C	0.963911	3.879957	-0.563070
H	8.302615	5.142593	4.447495	H	1.843688	3.465957	-1.036738

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