Supplementary Material

Switching on Oxygen Activation by Cobalt Complexes of Pentadentate Ligands

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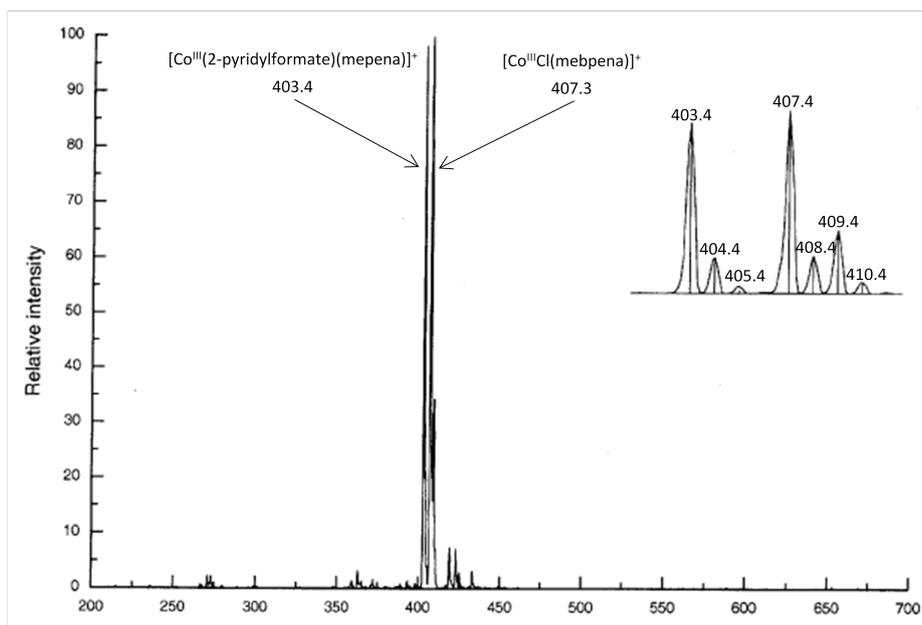
Figure S1. ESI mass spectrum of a solution of a red solid isolated from the reaction of mebpenaH and cobalt(II)perchlorate. Assignments: *m/z* 403.3 [Co(2-pyridylformate)(mepena)]$^+$ (**4**), 407.3 [Co(mebpena)(Cl)]$^+$ (**1**).
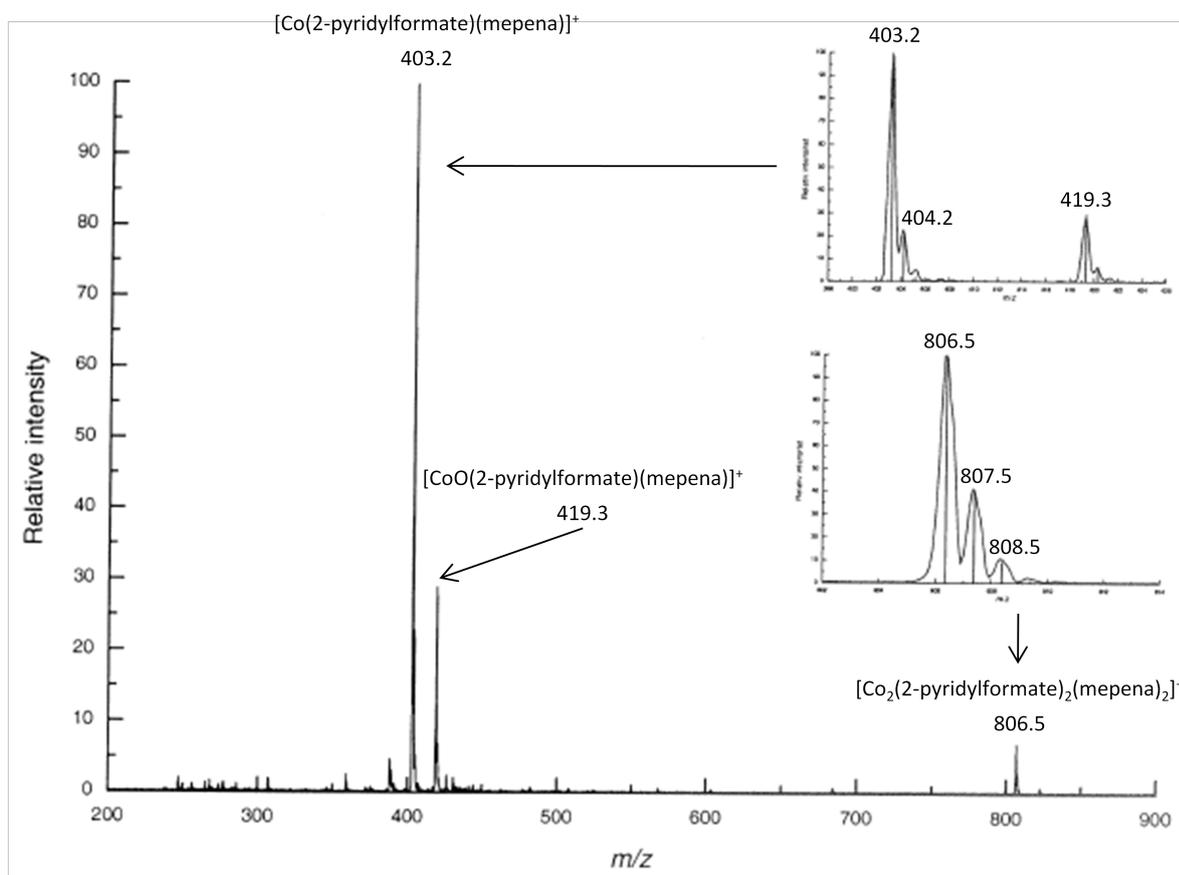
**Figure S2.** ESI mass spectrum of a crystal of the product of the reaction of $[Mn_2(mebpena)_2(H_2O)_2](ClO_4)_2$, cobalt(II)perchlorate and dioxygen in MeOH. Assignments: m/z 403.3 $[Co(2\text{-pyridylformate})(mepena)]^+$ (**4**), 419.3 $[CoO(2\text{-pyridylformate})(mepena)]^+$, 806.5 $[Co_2(2\text{-pyridylformate})_2(mepena)_2]^+$.
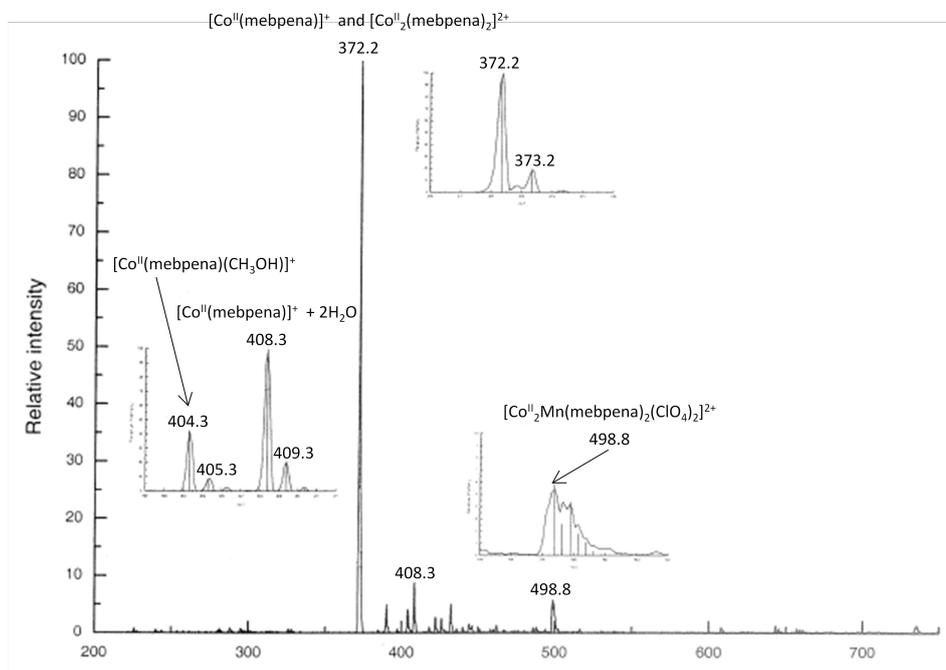
**Figure S3.** ESI mass spectrum of a sample of the reaction mixture of $[Mn_2(mebpena)_2(H_2O)_2](ClO_4)_2$ and cobalt(II)perchlorate directly after it was mixed and purged with dioxygen for 10 minutes. Assignments: m/z 372.2 $[Co(mebpena)]^+$, 404.3 $[Co^{II}(mebpena)(CH_3OH)]^+$, 408.3 $[Co^{II}(mebpena)]^+ + 2H_2O$, 498.2 $[Co_2Mn(mebpena)_2(ClO_4)_2]^{2+}$.

Observation of reactivity using benzylated ligand (Scheme 1(a) R= benzyl)

The reactions of Co(II) salts with the benzylated ligand *N*-benzyl-*N*,*N'*-bis(2-pyridylmethyl)ethylenediamine-*N'*-acetate (bzbpena⁻) (Scheme 1(a) R= benzyl) were also investigated. The chloride complex analogous to **1** of the intact ligand can be made and so can the Mn(II) starting material $[Mn(bzbpena)]_n(ClO_4)_n \cdot nCH_3OH$ **(**R. K. Egdal et al., *Dalton Transactions,* **2011,** *40*, 3849 – 3858). However the reaction of bzbpenaH or $[Mn(bzbpena)]_n(ClO_4)_n \cdot nCH_3OH$ with cobalt perchlorate appears to give more products of more oxidised ligand derivatives compared the mebpena⁻ -derived system due to the involvement of the dangling benzyl group (although the reaction actually appears to be quite "clean").   Thus ESI mass spectra of reaction solution showed dominant ions consistent with the formation of several Co complexes of ligands derived, not only from an analogous C–N cleavage but also a second reaction, namely intramolecular oxygenation of the dangling benzyl group. Cations were observed corresponding to the formulation of Co complexes of all the ligands depicted in Scheme S1 (2-pyridylformate, *N*-benzyl-*N'*-2-pyridylmethylethylenediamine-*N'*-acetate, *N*-hydroxobenzyl-*N*,*N'*-bis(2-pyridylmethyl)ethylenediamine-*N'*-acetate (bzObpena²⁻) and *N*-hydroxybenzyl-*N'*-2-pyridylmethylethylenediamine-*N'*-acetate). Mass spectra and details of the assignments are shown in Figure S4. As described in the Introduction, we have previously observed aromatic oxygenation in the reaction of the Fe(II) complex of bzbpena⁻ to give $[Fe^{III}(bzObpena)]^+$ depicted in Scheme 2(c). In this case we were able to isolate $[Fe^{III}(bzObpena)]^+$ in yields greater than 50% suggesting that the Fe-dependent reaction is more specific than the Co-dependent reaction. On the basis of the current results it cannot be determined whether or not either of these ligand oxidations is favoured, or in the cases where both modifications occur whether the reactions are consecutive or concerted. Clearly, the mixture of products (for which several isomers may be possible!) has hampered the isolation of any of them from being obtained in a pure form.
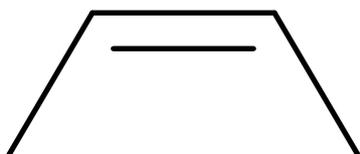
Scheme S1. C-N cleavage of bzbpena⁻ to give 2-pyridylformate (pfa⁻), *N*-benzyl-*N'*-(2-pyridylmethyl)ethylenediamine-*N'*-acetate (bzpena⁻), *N*-phenolato-*N*,*N'*-bis-2-pyridylmethyl-ethylenediamine-*N'*-acetate (bzObpena²⁻) and *N*-phenolato-*N'*-2-pyridylmethylethylenediamine-*N'*-acetate (bzOpena²⁻).
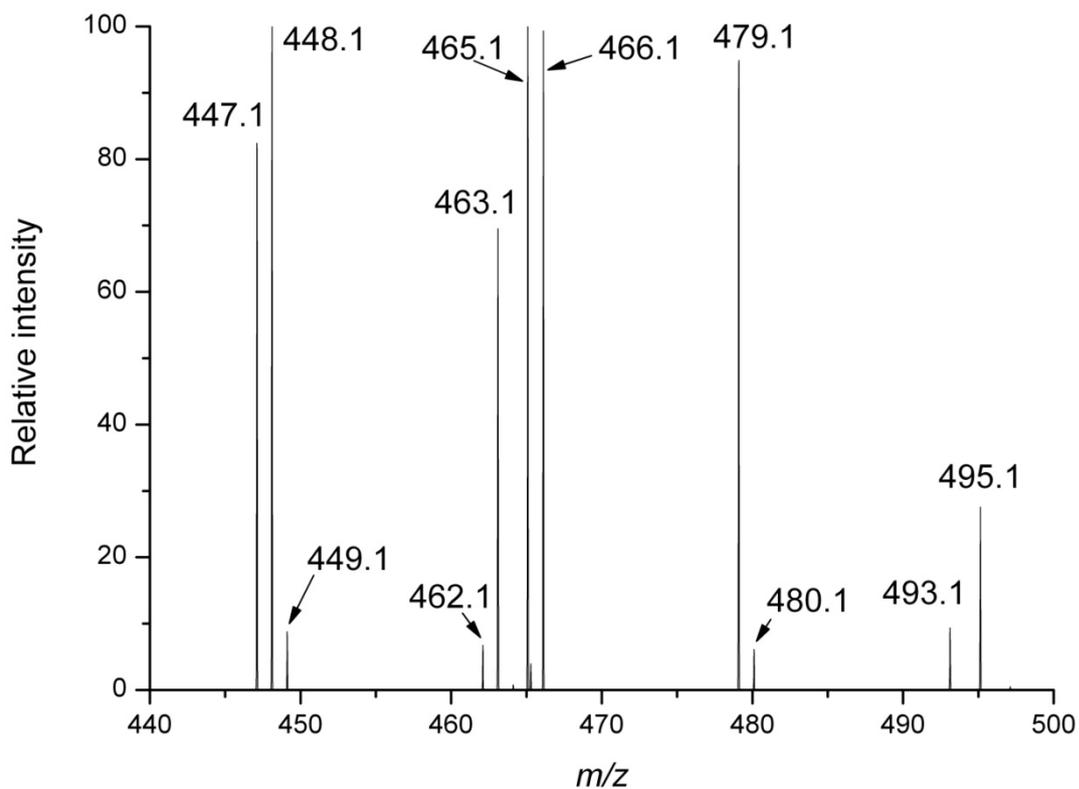
Figure S4. *In situ* oxidation of [Co(bzbpena)]$^+$: ESI mass spectrum (in methanol/water) of the reaction between [Mn(bzbpena)]$^+$ and Co^{2+}. A suspension of [Mn(bzbpena)]$_n$(ClO$_4$)$_n$·nCH$_3$OH (255 mg, 0.45 mmol) of Co(ClO$_4$)$_2$·6H$_2$O (165 mg, 0.45 mmol) in methanol (20 ml) and water (35 ml) was stirred vigorously for 4 hours, purged with oxygen for 10 minutes and filtered. Overnight a small amount of a fine brown powder, (MnO$_2$) was deposited. The ESI mass spectrum of the supernatant is shown. Possible assignments are depicted on next page.
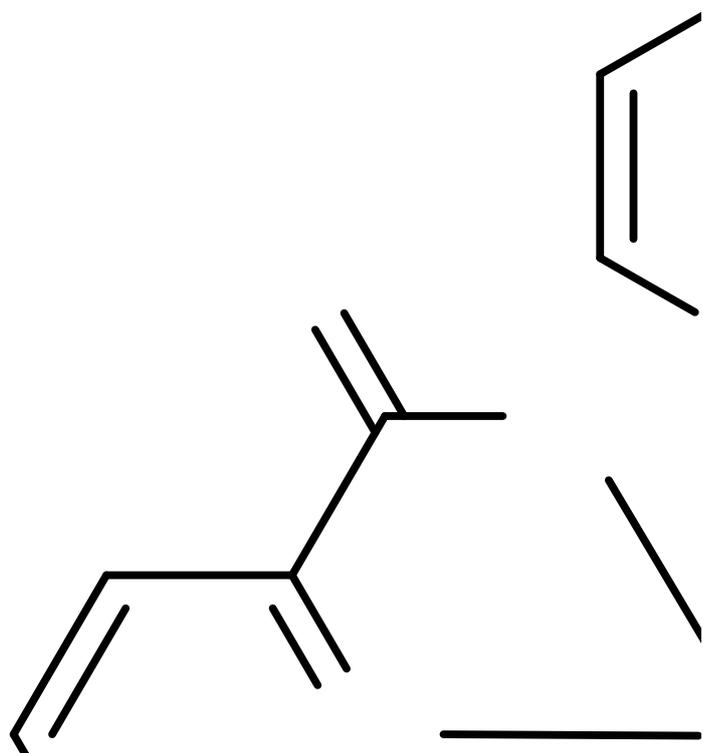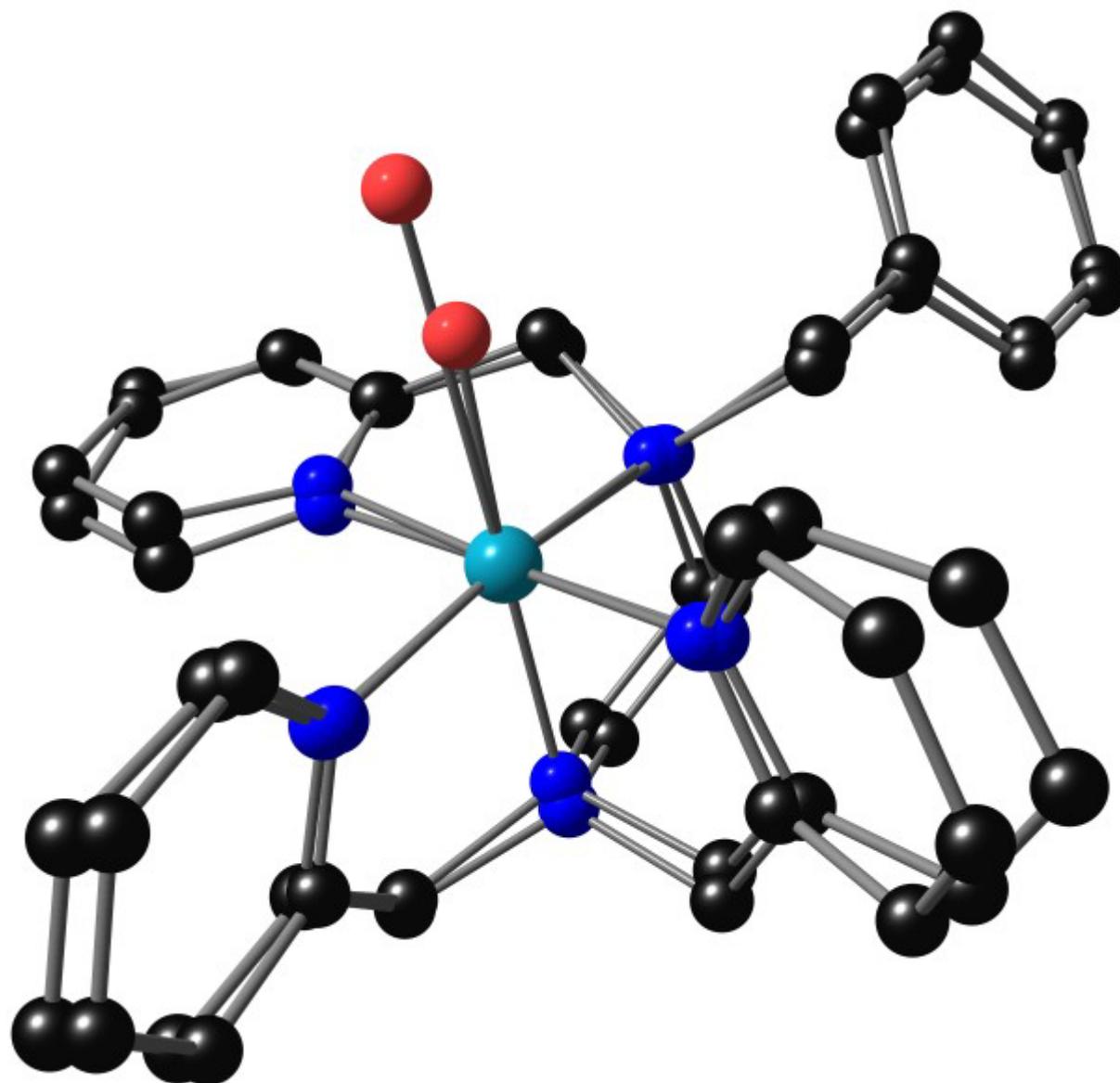
Figure S5. An overlay of the geometry of a minimum for $[Co^{II}(bztpen)(H_2O)]^{2+}$ optimised in a quartet electronic state and the crystal structure of the cation in **3**. The geometry is optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. The hydrogen atoms have been omitted for clarity.

Table S1 The Cartesian coordinates of **3** as acquired from the crystal structure.

C	2.398002	9.046745	10.905630
H	3.188289	9.260382	10.423743
C	1.479639	10.038563	11.162770
H	1.623263	10.921650	10.844377
C	0.341815	9.732059	11.891664
H	-0.297922	10.405376	12.089393
C	0.148307	8.434033	12.328417
H	-0.626830	8.205405	12.829340
C	1.091657	7.475515	12.028907

C	0.990878	6.024244	12.402105
H	0.475503	5.923361	13.240764
H	0.526192	5.521321	11.687181
C	5.142881	8.339112	12.541498
H	5.522658	8.510561	11.687181
C	5.441003	9.176595	13.593851
H	6.011979	9.925121	13.466432
C	4.899249	8.916685	14.838559
H	5.097001	9.482537	15.575743
C	4.064563	7.822914	15.003435
H	3.690877	7.623739	15.853608
C	3.787205	7.028185	13.909173
C	2.890265	5.824288	13.960140
H	2.127162	6.005028	14.564072
H	3.392906	5.051480	14.321517
C	1.447742	5.862407	9.136664
H	0.972550	6.608613	9.484225
C	0.927018	5.180503	8.060670
H	0.101621	5.448558	7.674270
C	1.621400	4.098175	7.548540
H	1.269800	3.605181	6.816115
C	2.833675	3.740570	8.114247
H	3.333197	3.012395	7.764844
C	3.304908	4.461683	9.195154
C	4.633426	4.216346	9.830250
H	5.337936	4.693751	9.324568
H	4.840454	3.248682	9.809679
C	3.937546	3.689891	12.153409
H	4.384907	3.689224	13.036587
H	4.025441	2.784115	11.763939
C	2.470719	4.025154	12.329799
H	1.964329	3.785694	11.513707
H	2.093488	3.520302	13.093388
C	6.033989	4.928154	11.716656
H	6.434669	5.646024	11.165226
H	6.006530	5.249874	12.652797
C	6.933718	3.716413	11.652947
C	7.151463	2.924561	12.784207
H	6.686560	3.115883	13.590780
C	8.041264	1.863966	12.738612
H	8.187443	1.337543	13.515557
C	8.719584	1.564532	11.567438
H	9.325368	0.833140	11.539805
C	8.507719	2.337958	10.438634
H	8.965016	2.133486	9.631600
C	7.631538	3.409013	10.482540
H	7.502666	3.942250	9.706823
Co	3.495444	6.352156	11.217560
N	2.204387	7.784525	11.319970
N	4.322908	7.280771	12.699159

N	4.613564	4.696943	11.245668
N	2.616075	5.500287	9.714806
N	2.378375	5.494994	12.584329
O	4.627871	7.216058	10.005258
H	4.278815	7.215056	9.240134

Table S2 The Cartesian coordinates for the structure of $[Co^{II}(bztpen)(H_2O)]^{2+}$ optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. $G = -1541.353885$ E_h, $<S^2> = 3.76$.

C	1.818302	9.291467	10.806278
H	2.698317	9.617176	10.254006
C	0.752409	10.160652	11.046644
H	0.793204	11.184606	10.681138
C	-0.351869	9.687416	11.764274
H	-1.198571	10.339260	11.973122
C	-0.349644	8.362238	12.217266
H	-1.192302	7.966886	12.782431
C	0.750815	7.546016	11.935696
C	0.812607	6.082118	12.341979
H	0.111212	5.874047	13.164293
H	0.503692	5.461904	11.490039
C	5.566633	8.177591	12.895150
H	6.000559	8.419898	11.927666
C	6.153078	8.641871	14.068957
H	7.045439	9.262387	14.023943
C	5.572709	8.284148	15.293032
H	6.005493	8.621932	16.233234
C	4.427426	7.485007	15.287260
H	3.952895	7.191704	16.222918
C	3.884235	7.062900	14.065282
C	2.596913	6.247013	14.047100
H	1.785746	6.899423	14.398158
H	2.667119	5.431449	14.781745
C	1.707379	6.116381	8.590568
H	1.421183	7.147386	8.784215
C	1.092285	5.378551	7.581838
H	0.322395	5.837497	6.965156
C	1.480142	4.045212	7.393589
H	1.011795	3.432635	6.624903
C	2.483064	3.515332	8.208527
H	2.813977	2.485357	8.082663
C	3.078167	4.323537	9.188833

C	4.265636	3.812605	9.986427
H	5.146576	3.896449	9.337141
H	4.150972	2.738023	10.188503
C	3.945049	3.909305	12.456087
H	4.480029	4.281068	13.337386
H	4.095087	2.820115	12.429902
C	2.450612	4.215128	12.595618
H	1.899409	3.851529	11.721183
H	2.048184	3.686755	13.475134
C	6.074154	4.745246	11.427810
H	6.394195	5.396121	10.605125
H	6.200651	5.301308	12.362417
Co	3.502093	6.597437	11.147977
N	1.822754	8.006959	11.236559
N	4.450364	7.401316	12.879564
N	4.554741	4.570168	11.248642
N	2.684561	5.607384	9.389605
N	2.216657	5.695115	12.701127
O	4.749290	7.710201	9.596098
H	4.615228	7.458662	8.663710
H	5.438271	8.400204	9.595607
C	6.918774	3.480612	11.444947
C	7.099268	2.739673	12.630674
C	7.579010	3.048953	10.276931
C	7.887802	1.583146	12.638995
C	8.369675	1.893260	10.283468
C	8.518467	1.153455	11.463469
H	6.647538	3.077451	13.563927
H	7.503383	3.634439	9.358909
H	8.024174	1.026697	13.565111
H	8.880411	1.580034	9.374162
H	9.138562	0.258531	11.472518
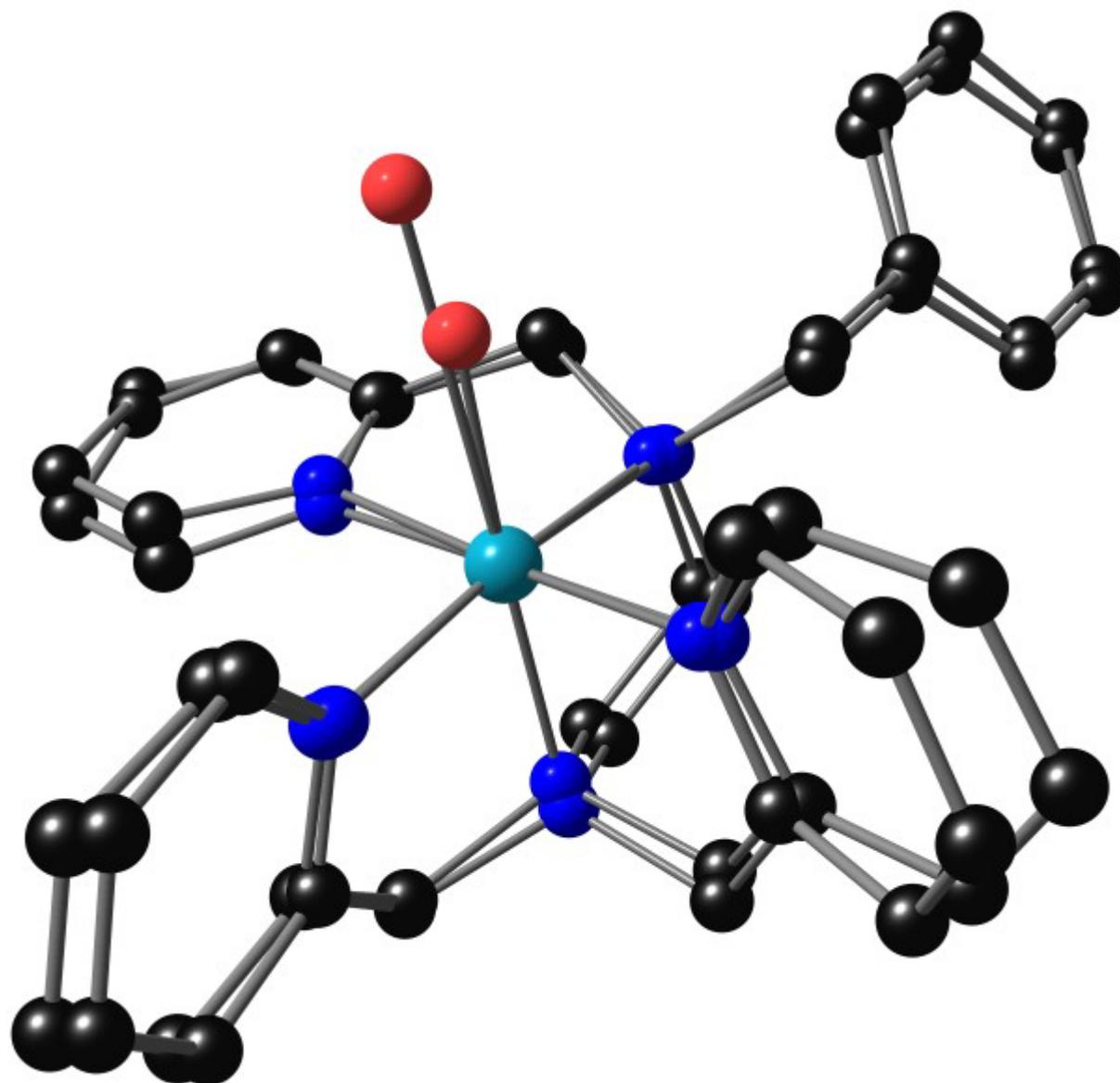
Figure S6. An overlay of the geometry of a minimum for $[Co^{II}(bztpen)(H_2O)]^{2+}$ optimised in a doublet electronic state and the crystal structure of the cation in **3**. The geometry is optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. The hydrogen atoms have been omitted for clarity.

Table S3 The Cartesian coordinates for the structure of $[Co^{II}(bztpen)(H_2O)]^{2+}$ optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. $G = -1541.358727$ E_h, $<S^2> = 0.76$.

C	2.129585	9.081062	10.860420
H	3.056311	9.305748	10.335529
C	1.120215	10.031357	11.021436
H	1.252715	11.032380	10.616487
C	-0.043241	9.673578	11.711999
H	-0.844623	10.395427	11.860162

C	-0.159952	8.373201	12.218996
H	-1.050336	8.068447	12.766848
C	0.878800	7.459711	12.018910
C	0.807783	6.008897	12.485443
H	0.105694	5.910210	13.327691
H	0.416365	5.387614	11.668495
C	5.289357	8.191038	12.696943
H	5.622838	8.393745	11.682499
C	5.860217	8.825786	13.796348
H	6.664256	9.543555	13.649086
C	5.379762	8.520901	15.077007
H	5.805432	8.997548	15.958332
C	4.337315	7.599960	15.204356
H	3.934573	7.349807	16.185110
C	3.801792	6.997492	14.058326
C	2.646542	6.006554	14.156750
H	1.813767	6.486582	14.689621
H	2.947242	5.154109	14.782661
C	1.545455	5.974050	8.921404
H	1.096266	6.912892	9.228355
C	1.029769	5.255796	7.845182
H	0.169813	5.644834	7.304156
C	1.626369	4.040219	7.488170
H	1.237091	3.449363	6.660946
C	2.738642	3.603685	8.213024
H	3.238554	2.670692	7.958203
C	3.223639	4.382366	9.269323
C	4.501378	4.048774	9.988848
H	5.329524	4.450447	9.390723
H	4.660472	2.964818	10.056550
C	3.940595	3.824134	12.425308
H	4.449139	4.062206	13.364872
H	4.132098	2.762352	12.221838
C	2.430202	4.060735	12.595803
H	1.876005	3.755580	11.702094
H	2.068620	3.440082	13.432911
C	6.076767	4.939298	11.686961
H	6.402805	5.708512	10.978407
H	6.087741	5.374930	12.689489
C	7.004457	3.737889	11.619475
C	7.169457	2.879339	12.725501
H	6.632040	3.070922	13.654832
C	8.051114	1.793752	12.664249

H	8.173467	1.145312	13.530458
C	8.792247	1.555240	11.498906
H	9.485025	0.716472	11.454683
C	8.658459	2.414634	10.400672
H	9.253699	2.251131	9.503582
C	7.774247	3.498208	10.463025
H	7.708694	4.179378	9.613030
Co	3.397933	6.403947	11.273260
N	2.011661	7.818269	11.342432
N	4.284039	7.282959	12.820992
N	4.583870	4.694703	11.350248
N	2.624417	5.552053	9.640677
N	2.172974	5.515006	12.824152
O	5.058903	7.838251	9.216759
H	4.665348	7.766612	8.327578
H	5.914767	8.279301	9.057680
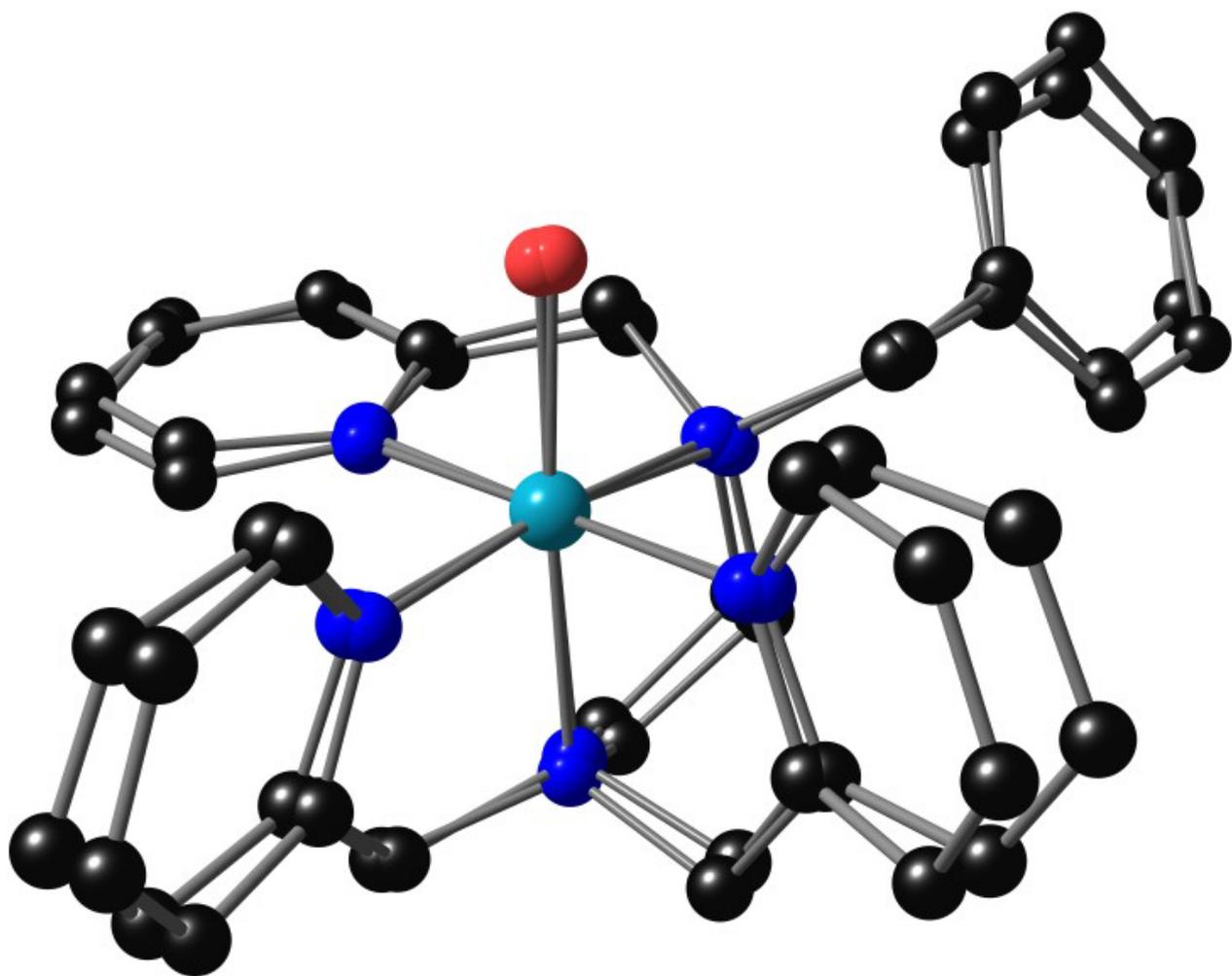
**Figure S7.** An overlay of the geometry of a minimum for [Co^{III}(bztpen)(OH)]$^{2+}$ optimised in a singlet electronic state and the crystal structure of the cation in **3**. The geometry is optimised at

BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. The hydrogen atoms have been omitted for clarity.

Table S4 The Cartesian coordinates for the structure of **3** optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. G = -1540.760065 E_h, $\langle S^2 \rangle = 0$.

C	2.228465	9.113309	10.794782
H	3.185789	9.297745	10.311496
C	1.230320	10.083044	10.915015
H	1.397700	11.078580	10.509364
C	0.035286	9.754036	11.564655
H	-0.754680	10.494573	11.678629
C	-0.132274	8.459982	12.077864
H	-1.048525	8.179772	12.595117
C	0.894338	7.527341	11.918271
C	0.815701	6.080882	12.372814
H	0.134874	5.959664	13.226562
H	0.429851	5.455200	11.558028
C	5.334113	8.189330	12.651395
H	5.660396	8.359538	11.627516
C	5.915767	8.806012	13.757739
H	6.742213	9.498056	13.611320
C	5.424478	8.518212	15.037283
H	5.863045	8.983723	15.918378
C	4.354157	7.627896	15.169344
H	3.943145	7.391146	16.149735
C	3.808107	7.043224	14.021554
C	2.626389	6.098120	14.079148
H	1.775050	6.607899	14.548059
H	2.854590	5.235672	14.718908
C	1.494175	5.880050	8.975826
H	1.019134	6.807162	9.279454
C	1.008542	5.148559	7.894201
H	0.139396	5.510954	7.349515
C	1.653258	3.959309	7.532516
H	1.290570	3.361447	6.698120
C	2.780856	3.560299	8.254435
H	3.320773	2.652810	7.989683
C	3.233914	4.349143	9.318105
C	4.529210	4.073653	10.028705
H	5.331306	4.533946	9.438450
H	4.746838	2.999863	10.084836
C	3.905545	3.830832	12.449380

H	4.394371	4.051185	13.403651
H	4.078729	2.767225	12.240166
C	2.403970	4.115447	12.560373
H	1.863245	3.788411	11.667817
H	1.980739	3.575360	13.420988
C	6.065730	4.959719	11.763210
H	6.360274	5.791146	11.115698
H	6.060632	5.307769	12.800075
C	7.013300	3.785978	11.593766
C	7.141425	2.788097	12.581975
H	6.560278	2.845093	13.503165
C	8.046637	1.732843	12.417838
H	8.142583	0.975220	13.194151
C	8.845946	1.664183	11.268249
H	9.556564	0.848294	11.146396
C	8.746334	2.661480	10.289424
H	9.385378	2.628520	9.408341
C	7.837985	3.714078	10.452669
H	7.795035	4.502729	9.699972
Co	3.416350	6.422994	11.260043
N	2.054443	7.861532	11.278758
N	4.304190	7.316493	12.789111
N	4.580644	4.701534	11.397780
N	2.580787	5.484830	9.693619
N	2.207924	5.603988	12.701771
O	4.630685	7.279474	10.092672
H	4.345670	7.225123	9.162183
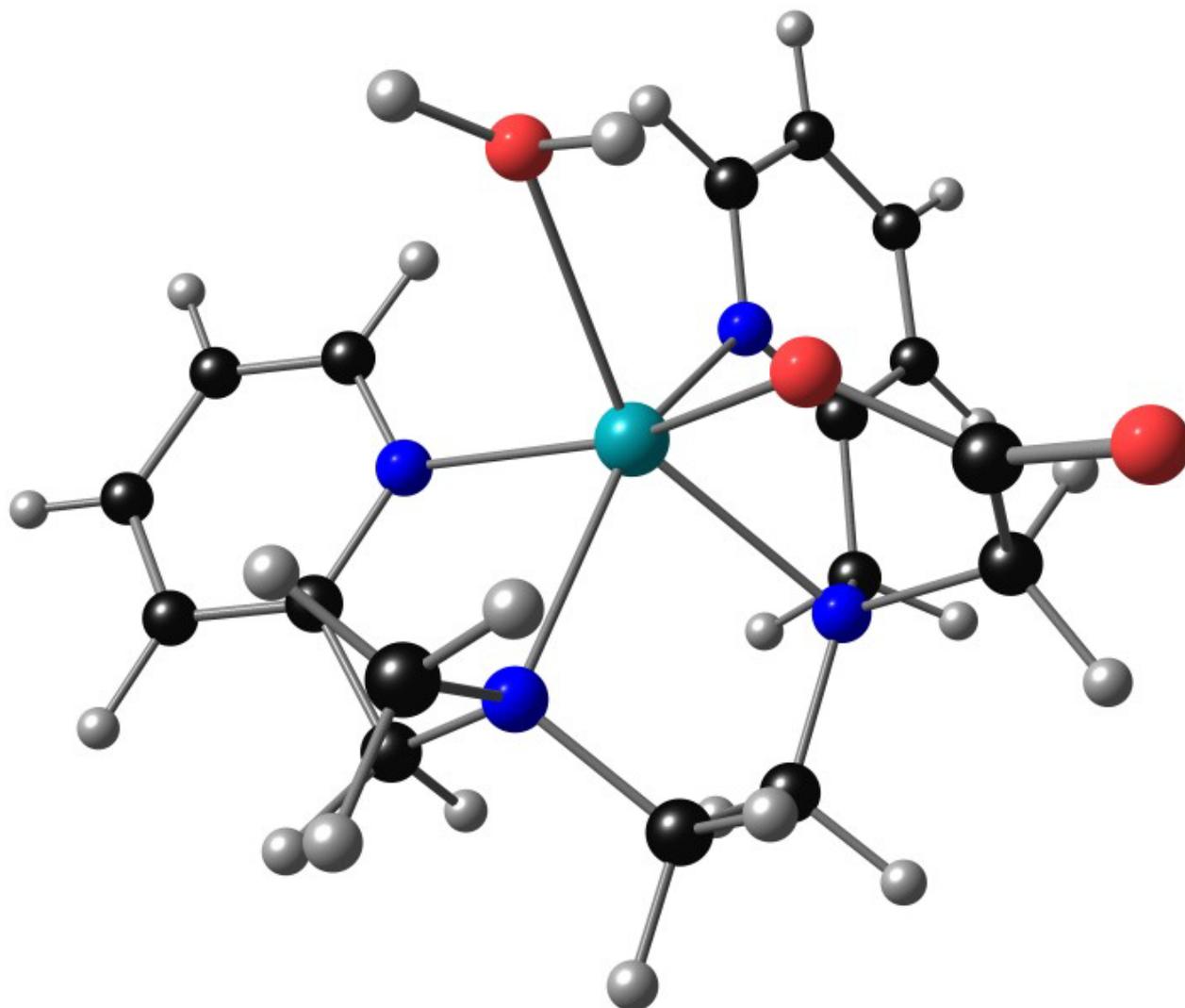
**Figure S8.** The geometry of a minimum for the coordination isomer of $[Co^{II}(mebpena)(H_2O)]^+$ with the lowest free energy. The geometry is optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co.

Table S5 The Cartesian coordinates for the structure of $[Co^{II}(mebpena)(H_2O)]^+$ for the coordination isomer with the lowest free energy optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. $G = -1251.697585\ E_h$, $<S^2> = 3.76$.

Co	0.033736	-0.287099	0.418511
N	-1.659038	1.064912	0.303452
N	-1.620499	-1.625967	-0.341120
N	1.013058	-1.012793	-1.458790
N	1.535703	1.233778	0.048709
O	1.073231	-1.774902	1.207371
O	2.458597	-3.523317	0.790706
C	-1.699642	2.287682	0.885726
H	-0.763525	2.650557	1.302863
C	-2.863713	3.052942	0.959918

H	-2.841103	4.030682	1.436555
C	-4.045449	2.532255	0.420525
H	-4.975398	3.096347	0.469159
C	-4.012285	1.269867	-0.180041
H	-4.913447	0.832177	-0.606962
C	-2.803214	0.565621	-0.230602
C	-2.679649	-0.768408	-0.946620
H	-3.650638	-1.289053	-0.964372
H	-2.412435	-0.564782	-1.992669
C	-2.179405	-2.419798	0.797023
H	-2.935901	-3.140909	0.446003
H	-2.651753	-1.741015	1.516332
H	-1.366992	-2.955562	1.296852
C	-0.974651	-2.527877	-1.350348
H	-1.731375	-3.041204	-1.967808
H	-0.435431	-3.303178	-0.795101
C	-0.008645	-1.753867	-2.258661
H	0.467043	-2.457706	-2.961550
H	-0.557414	-1.022078	-2.864987
C	2.115686	-1.917234	-0.973969
H	3.043414	-1.334709	-0.910013
H	2.292758	-2.737856	-1.682389
C	1.879719	-2.501984	0.449517
C	1.539020	0.192029	-2.162375
H	0.695168	0.680785	-2.670987
H	2.279617	-0.069012	-2.935777
C	2.140977	1.171932	-1.166217
C	3.242192	1.975838	-1.479187
H	3.711410	1.897231	-2.458635
C	3.736136	2.865313	-0.518050
H	4.594015	3.497211	-0.742137
C	3.123824	2.912456	0.738771
H	3.489349	3.572370	1.522652
C	2.031186	2.078433	0.983972
H	1.539912	2.051264	1.955323
O	0.076619	0.063065	2.779886
H	-0.604477	0.037047	3.475404
H	0.592449	-0.773051	2.853464
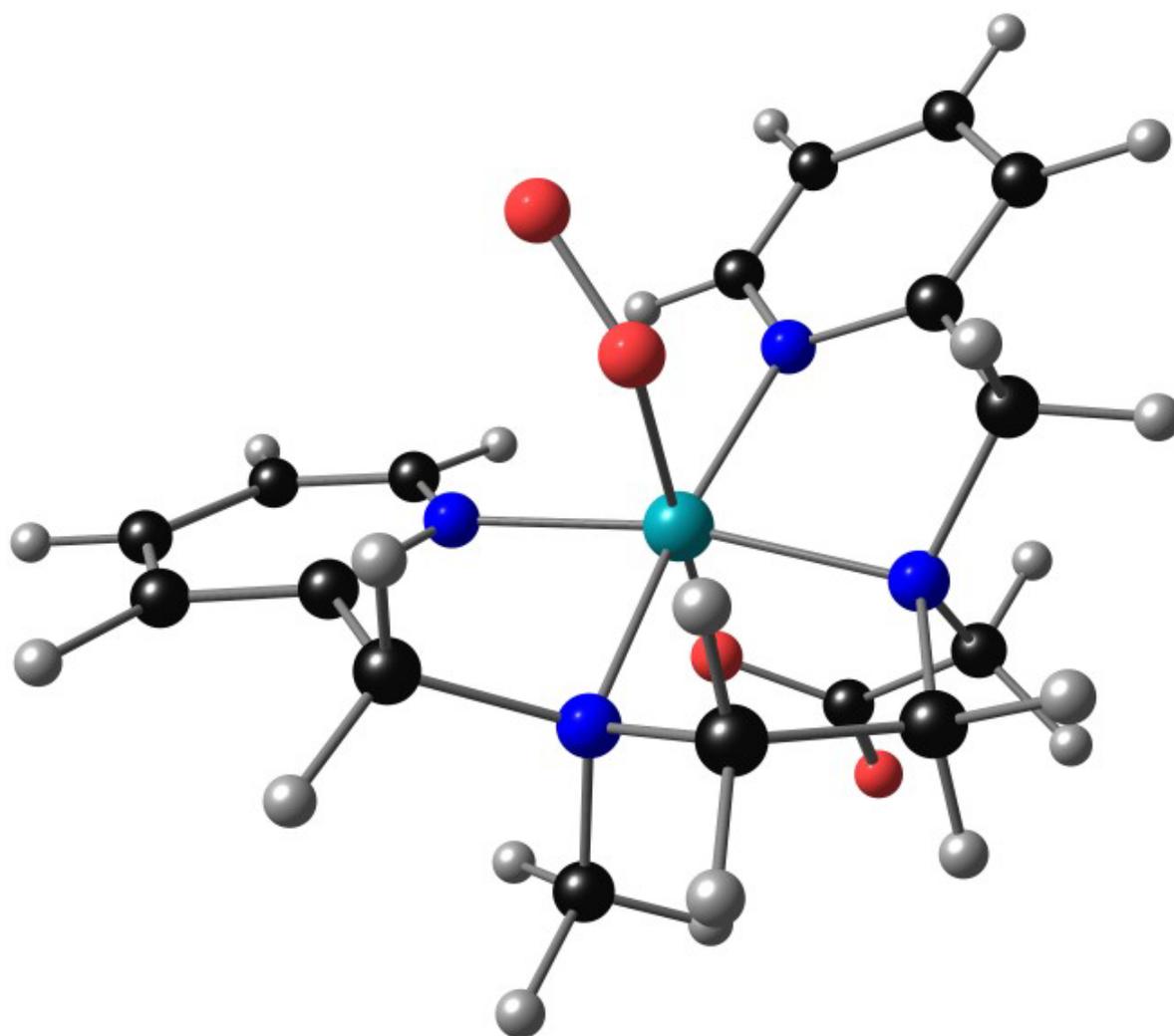
**Figure S9**. The geometry of a minimum of $[Co^{III}(O_2)(mebpena)]^+$. The geometry is optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co.

Table S6 The Cartesian coordinates for the structure of $[Co^{III}(O_2)(mebpena)]^+$ optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. $G = 1325.652644\ E_h$, $<S^2> = 0.77$.

```
Co   -1.137809   -2.390818   2.765145
O    -0.389449   -1.356254   1.278297
N    -0.821794   -0.875299   4.029188
N     0.784336   -2.83785 0   3.241204
N    -1.186052   -4.095936   1.709999
N    -2.913233   -2.106842   1.819728
O    -1.904451   -3.429832   4.234981
O    -2.707234   -5.482073   4.748538
C    -1.731526   -0.195215   4.759430
H    -2.766952   -0.502488   4.654178
C    -1.369298    0.826633   5.637240
H    -2.139283    1.349810   6.199647
```

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C	-0.015856	1.143782	5.784695
H	0.298436	1.937044	6.460644
C	0.933178	0.401975	5.073645
H	1.997878	0.592936	5.195395
C	0.503844	-0.606482	4.208408
C	1.446842	-1.491604	3.422756
H	1.627687	-1.060850	2.431799
H	2.412813	-1.600229	3.935312
C	0.977262	-3.659235	4.486319
H	2.053454	-3.797437	4.665296
H	0.496810	-4.633076	4.385390
H	0.515161	-3.149577	5.334436
C	1.264854	-3.570960	2.009008
H	1.374017	-2.832958	1.209784
H	2.246420	-4.034920	2.189332
C	0.234480	-4.642110	1.625523
H	0.434318	-5.019966	0.613978
H	0.296756	-5.495925	2.306480
C	-2.103177	-5.052332	2.455082
H	-1.744622	-6.082895	2.357154
H	-3.102270	-5.007464	2.008119
C	-2.257599	-4.667512	3.954026
C	-1.777441	-3.709609	0.382358
H	-2.062269	-4.602137	-0.193795
H	-1.020337	-3.152681	-0.183926
C	-2.971369	-2.816312	0.654101
C	-4.056323	-2.705547	-0.217211
H	-4.076422	-3.291681	-1.134324
C	-5.107816	-1.840472	0.105137
H	-5.961347	-1.737607	-0.562576
C	-5.046484	-1.12106 0	1.300991
H	-5.843266	-0.442674	1.597316
C	-3.934652	-1.281314	2.129647
H	-3.856309	-0.735059	3.063094
O	-0.830545	-0.125061	1.127439
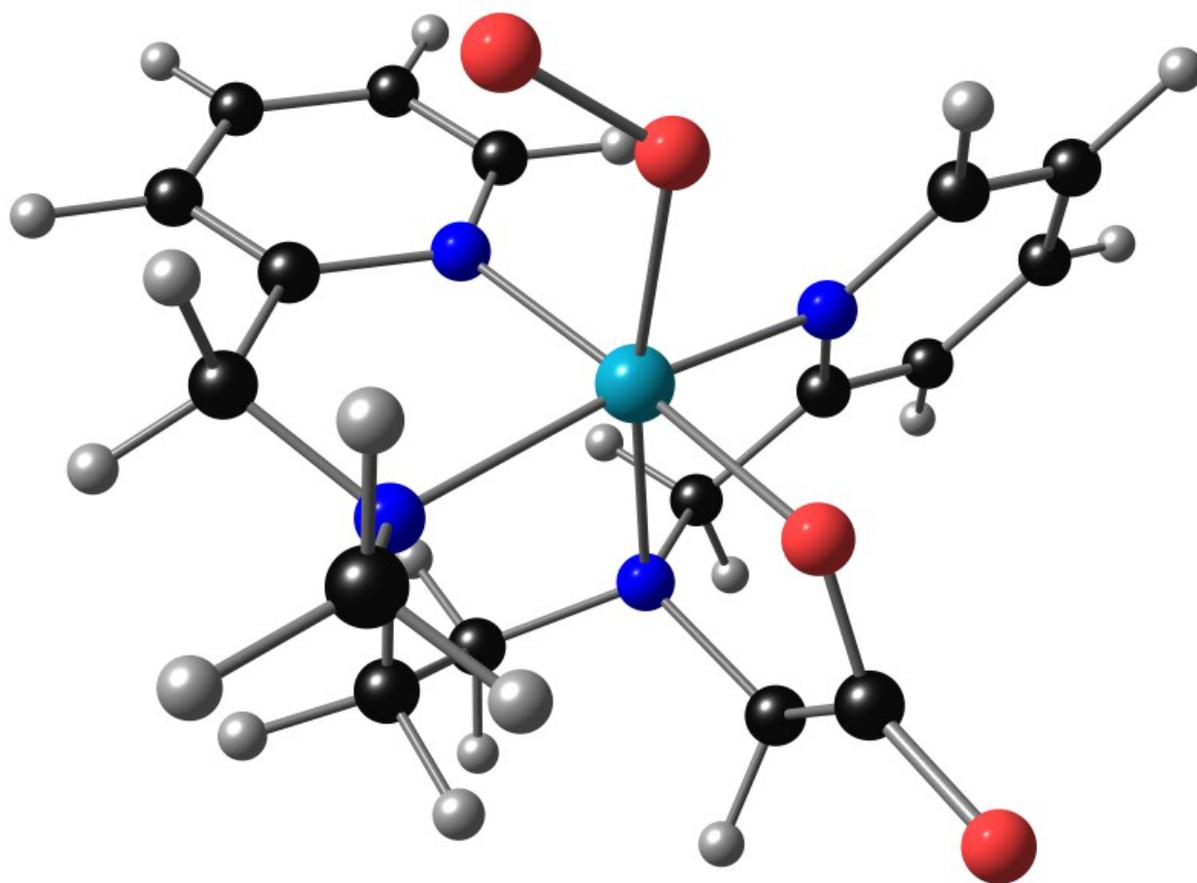
Figure S10. The geometry of a minimum for the coordination isomer of $[Co^{III}(O_2)(mebpena)]^+$ with the lowest free energy. The geometry is optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co.

Table S7 The Cartesian coordinates for the structure of $[Co^{III}(O_2)(mebpena)]^+$ for the coordination isomer with the lowest free energy optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. G = -1325.660224 E_h, $<S^2>$ = 0.78.

Co	0.011947	-0.329335	0.440902
O	-0.312724	0.016335	2.299598
N	-1.444863	0.980611	-0.043618
N	-1.448296	-1.751688	0.085658
N	0.703836	-0.696800	-1.505080
N	1.482589	0.998406	0.398300
O	1.249208	-1.687759	0.968084
O	2.789162	-3.170363	0.253503
C	-1.324672	2.327564	-0.167108
H	-0.333947	2.740751	-0.003127
C	-2.405578	3.150853	-0.473381
H	-2.257519	4.225584	-0.552259

|			
C	-3.664635	2.571077	-0.669803
H	-4.527834	3.186103	-0.918139
C	-3.797166	1.188325	-0.526980
H	-4.764607	0.704583	-0.650792
C	-2.675058	0.419378	-0.195631
C	-2.780220	-1.047845	0.135006
H	-3.137647	-1.113602	1.170052
H	-3.512488	-1.559434	-0.506818
C	-1.473523	-2.894965	1.069539
H	-2.258032	-3.613343	0.788918
H	-1.677751	-2.493360	2.065184
H	-0.498199	-3.384067	1.079934
C	-1.149505	-2.297012	-1.303691
H	-2.071304	-2.680037	-1.764985
H	-0.477605	-3.150813	-1.170273
C	-0.487520	-1.253412	-2.214262
H	-0.206900	-1.725003	-3.169784
H	-1.171718	-0.428039	-2.438865
C	1.835393	-1.693560	-1.390402
H	2.779319	-1.210196	-1.667080
H	1.687227	-2.524028	-2.091424
C	2.001632	-2.259135	0.043522
C	1.189264	0.631320	-1.989086
H	0.316560	1.235824	-2.269764
H	1.826303	0.534947	-2.880918
C	1.944866	1.299189	-0.850038
C	3.034809	2.153505	-1.026602
H	3.396630	2.372285	-2.029835
C	3.660356	2.705221	0.099529
H	4.514851	3.369404	-0.018479
C	3.187806	2.373722	1.373214
H	3.658709	2.765360	2.272069
C	2.097334	1.509036	1.488741
H	1.691401	1.201910	2.450594
O	-1.517631	-0.116644	2.779693
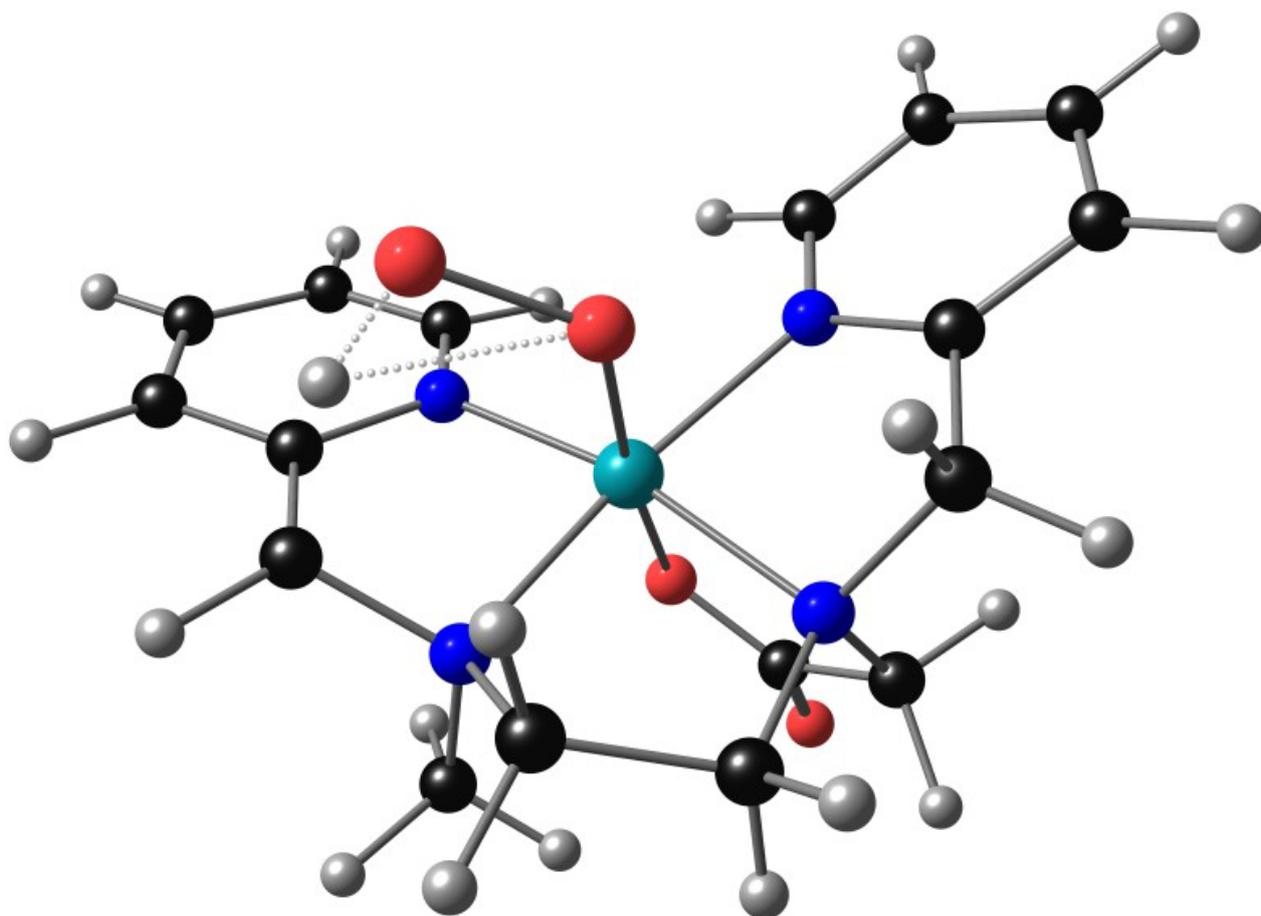
Figure S11. The geometry of the transition state of the hydrogen abstraction for mebpena⁻. The geometry is optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co.

Table S8 The Cartesian coordinates for the structure of the transition state of the hydrogen abstraction for mebpena⁻ optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. $G = -1325.64059\ E_h$, $<S^2> = 0.76$

Co	-1.142364	-2.390174	2.750996
O	-0.508496	-1.480574	1.169749
N	-0.822337	-0.884855	4.014781
N	0.763991	-2.868133	3.248767
N	-1.202489	-4.114740	1.704979
N	-2.943416	-2.116928	1.825103
O	-1.919603	-3.385900	4.208317
O	-2.755308	-5.405065	4.775953
C	-1.714094	-0.164129	4.722820
H	-2.758623	-0.438745	4.613549
C	-1.333499	0.871875	5.575417

|			
H	-2.093812	1.429773	6.116252
C	0.033568	1.168388	5.713933
H	0.357828	1.978718	6.364659
C	0.970117	0.393329	5.041386
H	2.037544	0.564867	5.165451
C	0.532967	-0.668959	4.213490
C	1.390338	-1.552247	3.478724
H	2.469922	-1.547518	3.637138
C	0.914711	-3.733371	4.482204
H	1.985185	-3.841637	4.702690
H	0.474873	-4.720013	4.319217
H	0.398699	-3.262781	5.320166
C	1.267786	-3.591985	2.016046
H	1.433000	-2.847709	1.235198
H	2.226517	-4.085807	2.234382
C	0.227699	-4.639593	1.580430
H	0.419454	-4.952600	0.546212
H	0.300912	-5.533017	2.207148
C	-2.090664	-5.070970	2.481946
H	-1.693943	-6.090862	2.436430
H	-3.085953	-5.086766	2.024264
C	-2.279309	-4.632336	3.957912
C	-1.839193	-3.752668	0.390024
H	-2.143987	-4.658370	-0.153859
H	1.043781	-0.756035	2.118875
C	-3.025459	-2.852685	0.677723
C	-4.132828	-2.763516	-0.168188
H	-4.174666	-3.372008	-1.069882
C	-5.177559	-1.892335	0.158425
H	-6.046826	-1.806043	-0.491104
C	-5.089817	-1.145886	1.336180
H	-5.880653	-0.462228	1.636320
C	-3.959473	-1.288069	2.142790
H	-3.861613	-0.724712	3.064260
O	0.451905	-0.464426	1.265338
H	-1.102766	-3.207864	-0.211404
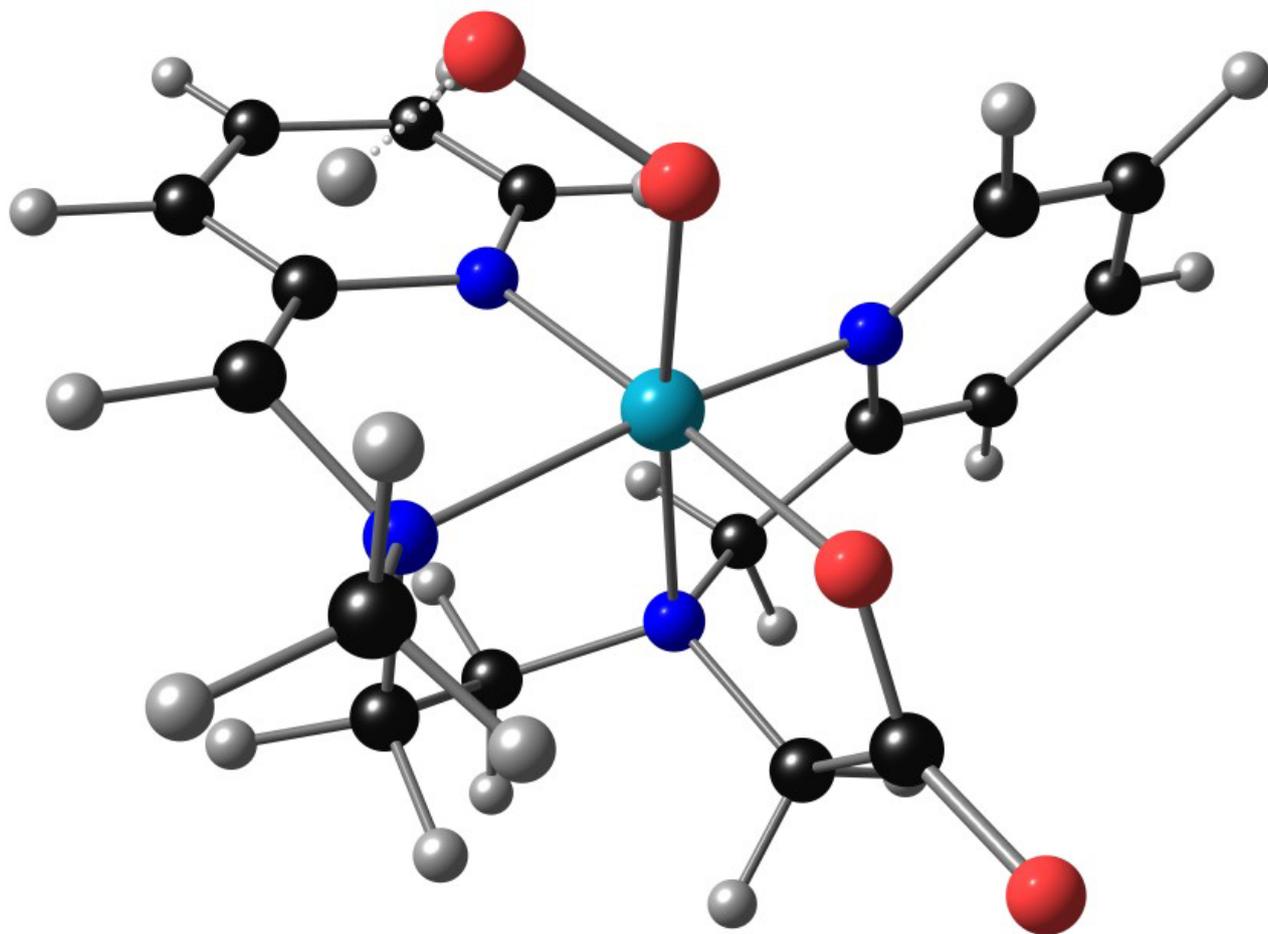
Figure S12. The geometry of the transition state of the hydrogen abstraction for mebpena⁻ for the coordination isomer with the lowest free energy. The geometry is optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co.

Table S9 The Cartesian coordinates for the structure of the coordination isomer for the transition state of the hydrogen abstraction for mebpena⁻ with the lowest free energy, optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. $G = -1325.622524\ E_h$, $\langle S^2 \rangle = 0.76$

Co	3.936184	2.855750	3.590145
O	5.786478	3.065205	3.889347
N	4.195259	2.373766	1.646566
N	3.744785	4.766944	2.870246
N	1.883548	2.698414	3.554314
N	3.818340	0.979005	4.205113
O	3.713808	3.441332	5.398214
O	2.221739	3.880428	7.026723
C	4.285363	1.150308	1.071298
H	4.156256	0.294452	1.728211

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C    4.549969    0.975164   -0.283257
H    4.618159   -0.029156   -0.693960
C    4.738974    2.113722   -1.090193
H    4.941517    2.005818   -2.154530
C    4.672045    3.374982   -0.515681
H    4.825579    4.273772   -1.109627
C    4.403538    3.500377    0.870961
C    4.511576    4.718182    1.618299
H    4.650332    5.672121    1.106563
C    4.289990    5.866096    3.750327
H    3.795610    5.839468    4.722633
H    5.360395    5.711195    3.896867
H    4.119422    6.837511    3.264577
C    2.233669    4.983512    2.688667
H    1.882862    5.488005    3.595514
H    2.062309    5.662284    1.842832
C    1.469308    3.670596    2.487707
H    1.695107    3.224941    1.514903
H    0.386229    3.865417    2.529626
C    1.363411    3.073096    4.927794
H    0.631678    3.885608    4.846257
H    0.840561    2.218647    5.371837
C    2.490717    3.504914    5.895756
C    1.603544    1.256448    3.245891
H    0.567874    0.987051    3.497268
H    1.732554    1.104218    2.166788
C    2.597645    0.401034    4.014970
C    2.329015   -0.882415    4.493689
H    1.345603   -1.324727    4.343853
C    3.335381   -1.579565    5.175822
H    3.143942   -2.580264    5.559405
C    4.578012   -0.968753    5.373330
H    5.377645   -1.472745    5.911460
C    4.786692    0.320878    4.880127
H    5.723153    0.857656    5.016126
O    6.548122    3.541748    2.842278
H    5.856799    4.186670    2.226529
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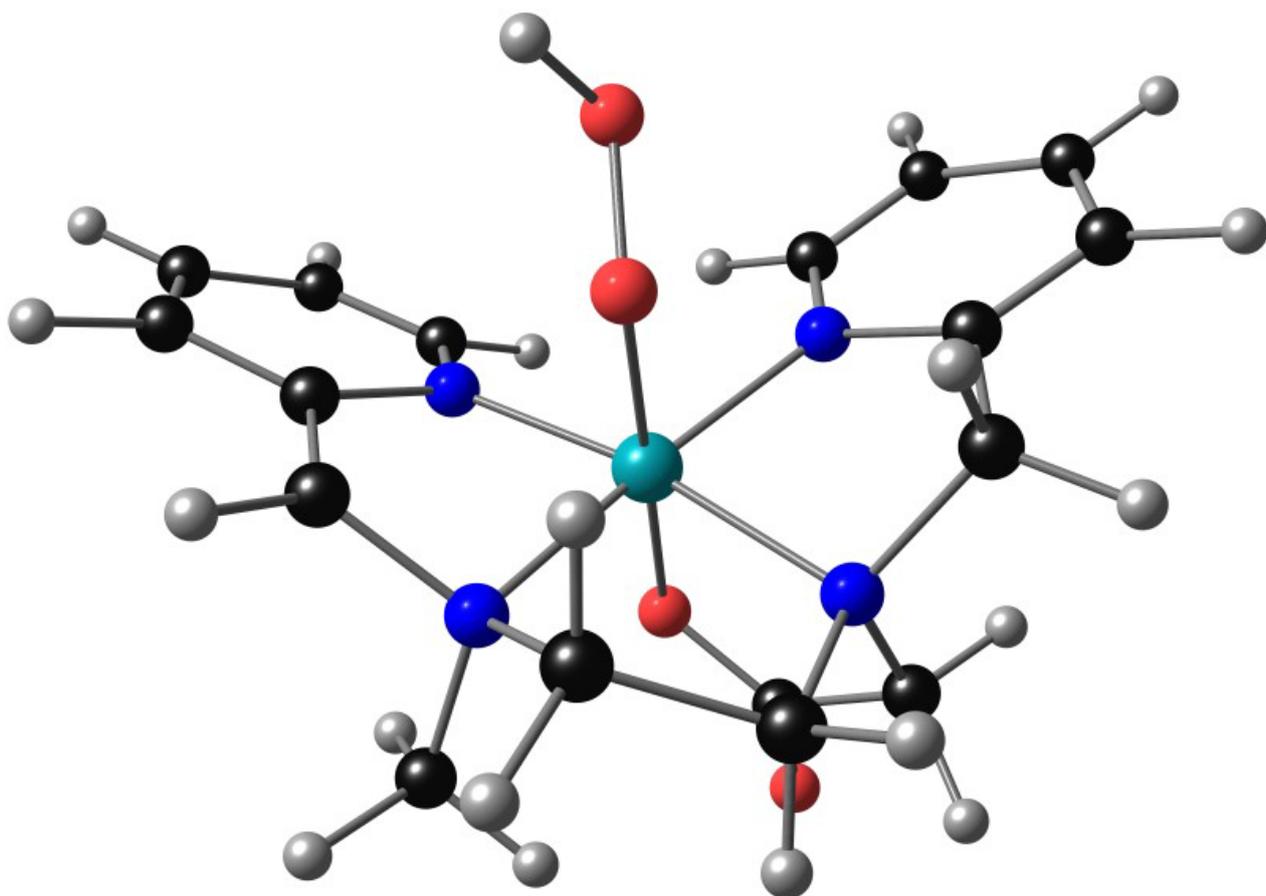
Figure S13. The geometry of a minimum of [Co^{III}(OOH)(mebpena-H$^•$)]$^+$. The geometry is optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co.

Table S10 The Cartesian coordinates for the structure of [Co^{III}(OOH)(mebpena-H$^•$)]$^+$ optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. G = -1325.631713 E_h, $<S^2> = 0.76$.

Co	0.062002	-0.221301	-0.023772
O	0.228879	0.294416	-1.880250
N	1.740315	0.736677	0.391975
N	1.323909	-1.688707	-0.584138
N	-1.456797	-1.475789	-0.426613
N	-1.454719	1.106730	0.116577
O	-0.096797	-0.804211	1.803047
O	-1.334375	-2.094488	3.184981
C	1.996149	1.729726	1.258310
H	1.190635	2.003704	1.934633
C	3.231837	2.381826	1.306806

H	3.388749	3.184451	2.023017
C	4.243435	1.989150	0.410408
H	5.204572	2.500424	0.409358
C	4.020777	0.918328	-0.444791
H	4.803501	0.551003	-1.105855
C	2.766528	0.249815	-0.413062
C	2.461487	-0.938434	-1.099177
H	3.115087	-1.408991	-1.830875
C	1.788716	-2.631838	0.508257
H	2.558370	-3.300328	0.099529
H	0.949179	-3.223823	0.880467
H	2.190769	-2.047467	1.337289
C	0.537472	-2.417578	-1.657302
H	0.516330	-1.763497	-2.532085
H	1.037477	-3.359769	-1.926403
C	-0.880393	-2.694065	-1.136519
H	-1.538009	-2.995708	-1.962835
H	-0.870659	-3.515962	-0.414456
C	-2.083752	-1.848090	0.903787
H	-2.421279	-2.890335	0.896496
H	-2.964323	-1.218377	1.072132
C	-1.112804	-1.599582	2.089780
C	-2.402166	-0.659307	-1.264216
H	-1.960469	-0.543446	-2.260624
C	-2.534401	0.702901	-0.613325
C	-3.669336	1.505882	-0.740887
H	-4.519450	1.152372	-1.321671
C	-3.698180	2.755793	-0.112686
H	-4.572899	3.397495	-0.202739
C	-2.592624	3.158374	0.641025
H	-2.574720	4.115910	1.156475
C	-1.491193	2.306140	0.732342
H	-0.615806	2.587020	1.307746
O	0.315076	1.770601	-2.003817
H	0.911156	1.835562	-2.779022
H	-3.376681	-1.161593	-1.353110
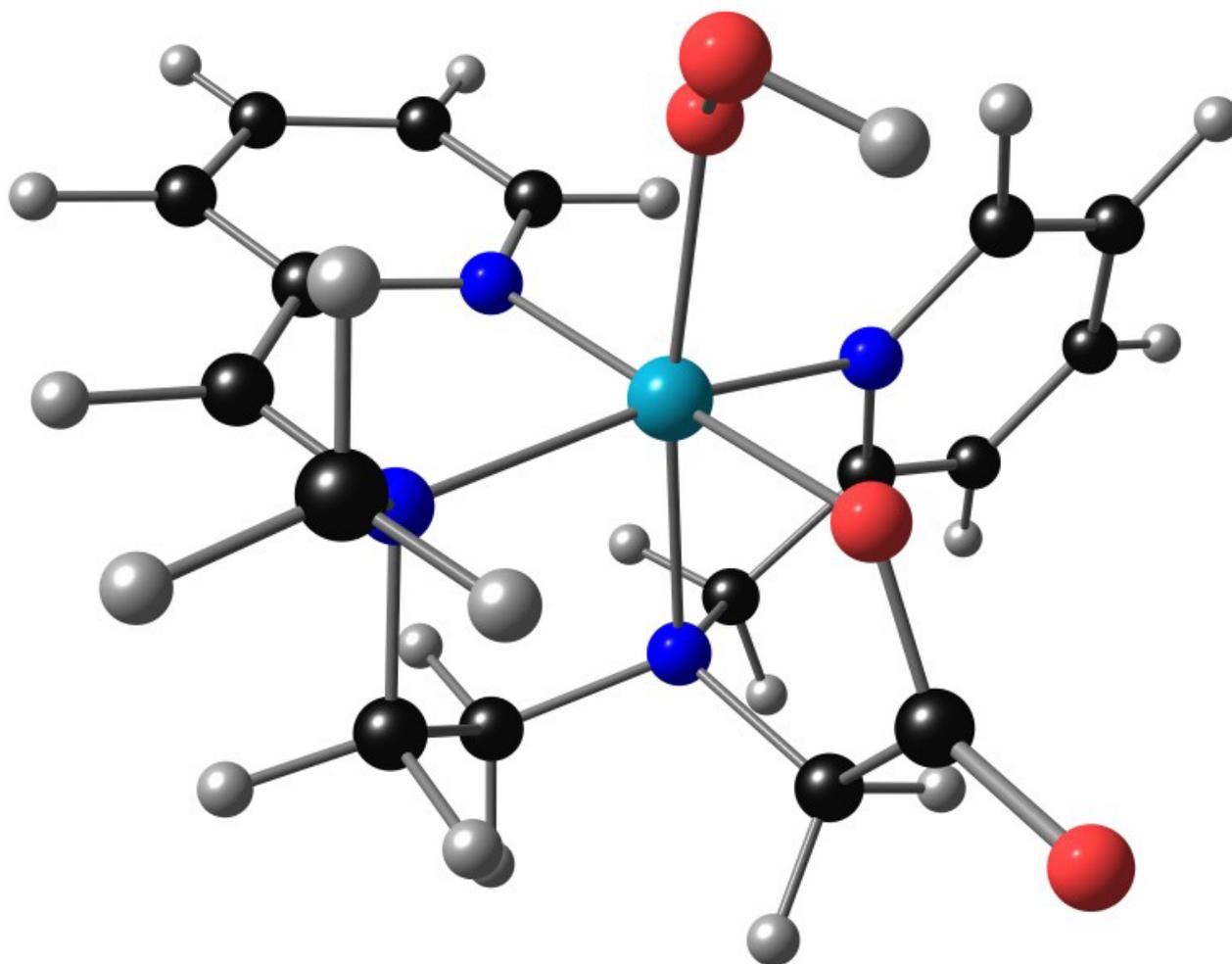
Figure S14. The geometry of the minimum for the coordination isomer of [Co^{III}(OOH)(mebpena-H$^{\bullet}$)]$^{+}$ with the lowest free energy. The geometry is optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co.

Table S11 The Cartesian coordinates for the structure of [Co^{III}(OOH)(mebpena-H$^{\bullet}$)]$^{+}$ for the coordination isomer with the lowest free energy optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. G = -1325. 639534 E_h, $<S^2>$ = 0.76.

Co	3.950454	2.869375	3.623599
O	5.837720	2.807989	3.866409
N	4.366278	2.436273	1.715652
N	3.725082	4.809901	2.898147
N	1.870043	2.729401	3.581453
N	3.770414	0.970160	4.166971
O	3.721896	3.455787	5.428430
O	2.225020	3.913898	7.053952
C	4.708179	1.245035	1.193902

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H   4.609002   0.383053    1.847487
C   5.186049   1.090847   -0.113935
H   5.447627   0.098383   -0.473150
C   5.334530   2.227380   -0.928624
H   5.710024   2.134092   -1.945968
C   5.005580   3.470696   -0.410915
H   5.120547   4.377158   -1.002108
C   4.527052   3.573749    0.928689
C   4.218568   4.792499    1.536804
H   4.353744   5.748610    1.031173
C   4.414070   5.920385    3.659285
H   4.068599   5.899072    4.695592
H   5.489397   5.737450    3.644821
H   4.171518   6.888862    3.197800
C   2.211569   5.065929    2.913894
H   1.973014   5.443377    3.913912
H   1.959296   5.854370    2.190872
C   1.432500   3.783817    2.615831
H   1.642562   3.428491    1.600477
H   0.350604   3.978357    2.689842
C   1.383037   2.995567    4.991194
H   0.552629   3.712171    4.982328
H   0.995808   2.065594    5.422809
C   2.499854   3.509986    5.934087
C   1.587503   1.321280    3.162338
H   0.543060   1.035570    3.357438
H   1.756956   1.245757    2.079629
C   2.554616   0.411427    3.902397
C   2.264783  -0.897304    4.292589
H   1.285095  -1.323078    4.082393
C   3.245181  -1.641643    4.963138
H   3.036597  -2.662279    5.279595
C   4.484612  -1.052242    5.233222
H   5.265977  -1.594942    5.760729
C   4.715655   0.263120    4.824008
H   5.652747   0.792153    4.989019
O   6.378849   3.884873    4.680277
H   5.987253   3.696760    5.564109
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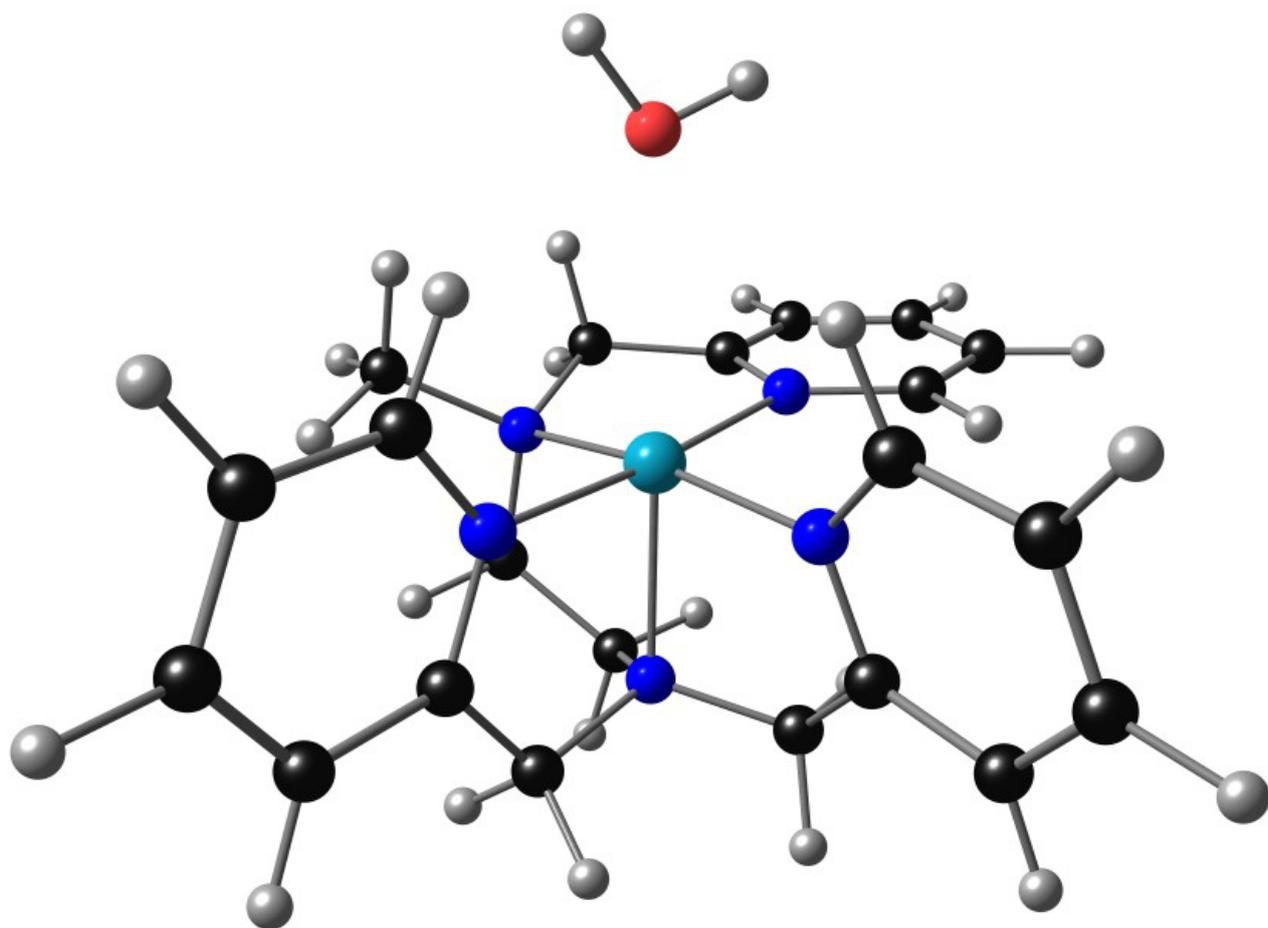
Figure S15. The geometry of a minimum of $[\text{Co}^{\text{II}}(\text{metpen})(\text{H}_2\text{O})]^{2+}$. The geometry is optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co.

Table S12 The Cartesian coordinates for the structure of $[\text{Co}^{\text{II}}(\text{metpen})(\text{H}_2\text{O})]^{2+}$ optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. $G = -1310.405623$ E_h, $<S^2> = 0.76$.

C	2.088657	9.080435	-10.873250
H	3.010192	9.312500	-10.342499
C	1.075598	10.025017	-11.043263
H	1.198871	11.026822	-10.637345
C	-0.079128	9.660740	-11.745089
H	-0.882970	10.378215	-11.900985
C	-0.183812	8.359854	-12.253525
H	-1.067076	8.050629	-12.810320
C	0.857860	7.451924	-12.043700
C	0.798462	6.000676	-12.510518
H	0.105989	5.898340	-13.360068

|			
H	0.400768	5.378150	-11.697496
C	5.268459	8.207225	-12.689370
H	5.579677	8.427283	-11.671226
C	5.856437	8.828881	-13.787418
H	6.654375	9.552615	-13.635968
C	5.400070	8.504301	-15.072127
H	5.840029	8.970189	-15.952202
C	4.362730	7.578241	-15.205807
H	3.978453	7.314009	-16.190265
C	3.808443	6.989701	-14.061521
C	2.654818	5.996988	-14.166060
H	1.826306	6.474695	-14.707508
H	2.960751	5.142262	-14.786281
C	1.521539	5.958587	-8.930722
H	1.045981	6.878956	-9.253835
C	1.026076	5.243634	-7.842433
H	0.154499	5.616353	-7.308531
C	1.658001	4.053039	-7.463646
H	1.286196	3.466044	-6.625715
C	2.782684	3.635496	-8.181373
H	3.308480	2.721630	-7.909663
C	3.243244	4.409363	-9.250991
C	4.525606	4.100321	-9.974680
H	5.349377	4.538794	-9.394833
H	4.712784	3.018447	-10.034718
C	3.935149	3.826322	-12.408021
H	4.456255	4.035498	-13.348430
H	4.125498	2.770777	-12.167124
C	2.426707	4.058499	-12.596124
H	1.865719	3.758195	-11.705064
H	2.075060	3.430655	-13.431897
C	6.028990	4.918079	-11.700226
H	6.481562	5.607819	-10.982219
H	6.118058	5.334200	-12.705577
H	6.561715	3.956777	-11.663101
Co	3.376159	6.416952	-11.278392
N	1.982148	7.816828	-11.356058
N	4.268946	7.293335	-12.819975
N	4.574194	4.726865	-11.349506
N	2.612801	5.556307	-9.641830
N	2.169493	5.510908	-12.834878
O	5.096604	7.797163	-9.225438
H	4.681170	7.837914	-8.344142
H	5.986913	8.169200	-9.079103
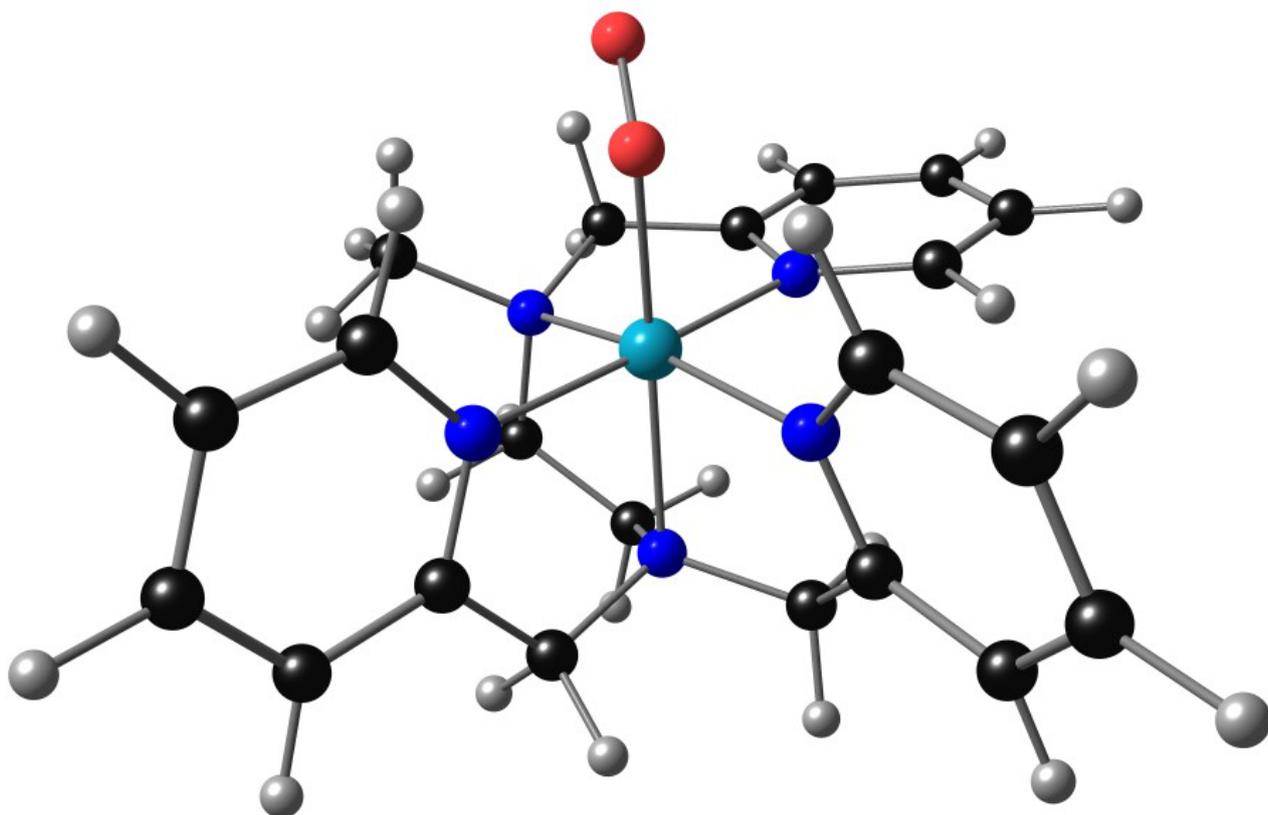
Figure S16. The geometry of a minimum of $[Co^{III}(metpen)OO^{\bullet}]^{2+}$. The geometry is optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co.

Table S13 The Cartesian coordinates for the structure of $[Co^{III}(metpen)OO^{\bullet}]^{2+}$ optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. E = -1384.364869 E_h, $\langle S^2 \rangle = 0.79$.

Co	-0.094054	-0.298763	0.481813
O	-0.488701	0.075022	2.322372
N	-1.488721	1.046089	-0.066141
N	-1.601951	-1.683958	0.081983
N	0.628153	-0.703495	-1.450636
N	1.382115	1.042316	0.451081
N	1.223761	-1.695627	1.027563
C	2.890214	-3.268300	0.294854
C	-1.315902	2.389792	-0.192042
H	-0.319182	2.773988	-0.005394
C	-2.358846	3.248759	-0.528512
H	-2.168603	4.316984	-0.606341
C	-3.633198	2.715827	-0.756447
H	-4.466569	3.361389	-1.028287

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C	-3.819858	1.339331	-0.612563
H	-4.801265	0.891215	-0.758934
C	-2.736572	0.531302	-0.249082
C	-2.910782	-0.923079	0.090658
H	-3.303622	-0.971139	1.113658
H	-3.639094	-1.416159	-0.568530
C	-1.750058	-2.840803	1.040207
H	-2.603487	-3.466765	0.742774
H	-1.924992	-2.450673	2.046434
H	-0.844359	-3.450453	1.030962
C	-1.289063	-2.236391	-1.305679
H	-2.212994	-2.584820	-1.787745
H	-0.653900	-3.116986	-1.160735
C	-0.574640	-1.213430	-2.191993
H	-0.291734	-1.679687	-3.148282
H	-1.220347	-0.359918	-2.418686
C	1.730895	-1.737630	-1.373308
H	2.665641	-1.287064	-1.732064
H	1.510925	-2.565004	-2.061877
C	1.950947	-2.264360	0.030628
C	1.165175	0.610631	-1.939806
H	0.317077	1.224677	-2.268792
H	1.826935	0.481324	-2.808014
C	1.886516	1.298989	-0.793297
C	2.960867	2.174254	-0.967177
H	3.353056	2.361067	-1.965652
C	3.521313	2.804280	0.152286
H	4.358861	3.489834	0.034160
C	2.994120	2.535989	1.420109
H	3.400623	3.004208	2.314039
C	1.925840	1.644425	1.535726
H	1.475173	1.403586	2.496392
O	-1.713877	0.015744	2.755263
C	3.098582	-3.684747	1.612264
C	2.361099	-3.078851	2.637207
C	1.434451	-2.091423	2.311855
H	0.838088	-1.594275	3.071903
H	2.495226	-3.364625	3.678264
H	3.826003	-4.463393	1.835622
H	3.454635	-3.710812	-0.524770
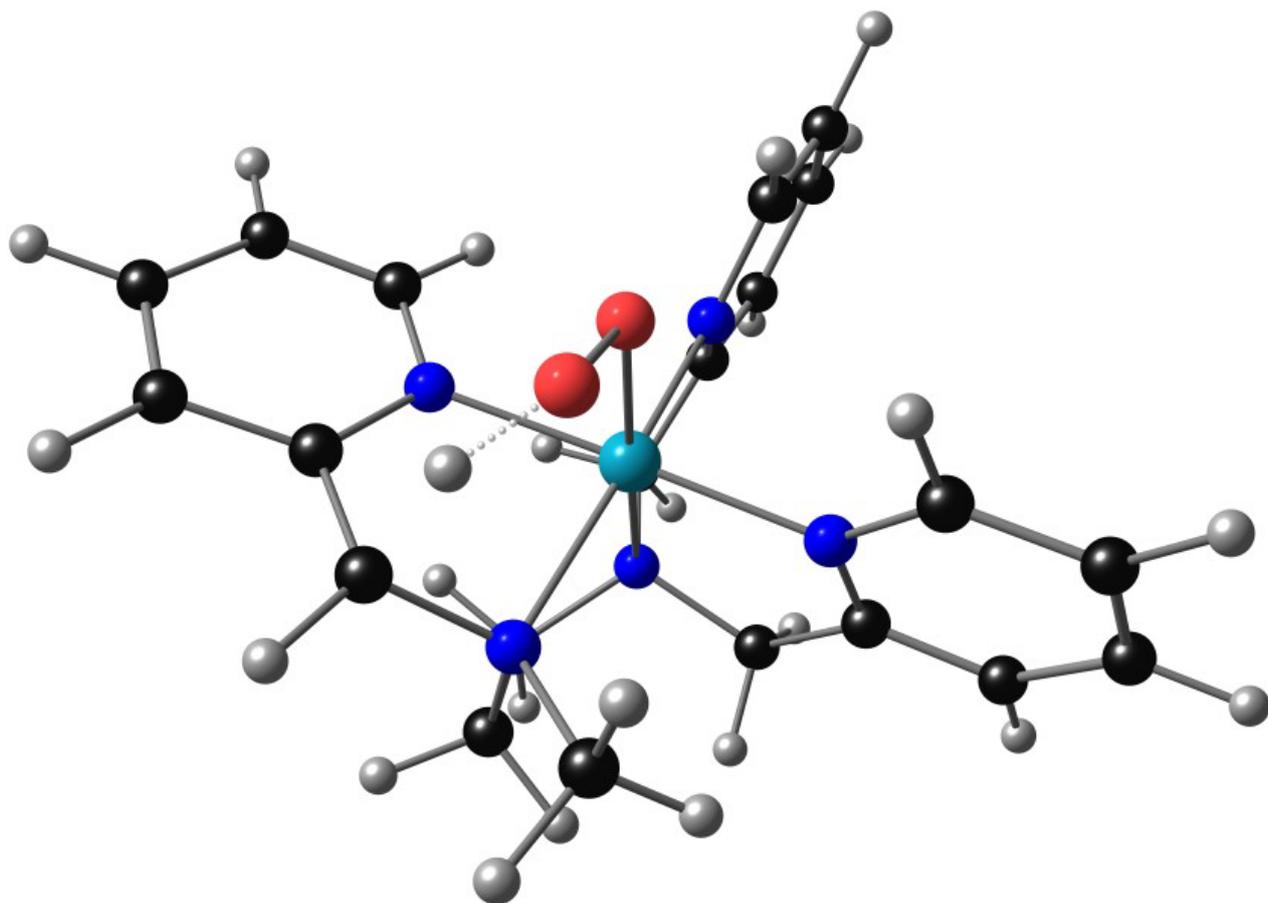
Figure S17. The geometry of the transition state of the hydrogen abstraction for metpen. The geometry is optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co.

Table S14 The Cartesian coordinates of the transition state of the hydrogen abstraction for metpen optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. $G = -1384.323730\ E_h$, $<S^2> = 0.76$

Co	-0.078651	-0.317222	0.399668
O	-0.675757	0.200716	2.132212
N	-1.482055	1.025439	-0.202175
N	-1.596864	-1.680853	-0.012982
N	0.658575	-0.739722	-1.470009
N	1.377498	1.033709	0.446063
N	1.203479	-1.668268	1.027659
C	2.934158	-3.207676	0.387378
C	-1.342474	2.343479	-0.471083
H	-0.328845	2.730392	-0.522173
C	-2.436773	3.186549	-0.667170
H	-2.270329	4.237488	-0.892165
C	-3.734264	2.658143	-0.560030

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H	-4.604021	3.297061	-0.703007
C	-3.894309	1.308436	-0.264982
H	-4.884285	0.868347	-0.160842
C	-2.751275	0.493776	-0.091773
C	-2.796302	-0.883962	0.317093
H	-2.422902	-0.700402	1.790700
H	-3.746237	-1.424040	0.305918
C	-1.652022	-2.980486	0.760799
H	-2.534130	-3.555273	0.446212
H	-1.717911	-2.769886	1.829920
H	-0.753540	-3.567831	0.558663
C	-1.466452	-2.032840	-1.513057
H	-2.463674	-2.072190	-1.968664
H	-1.054497	-3.046397	-1.552722
C	-0.568297	-1.061288	-2.286902
H	-0.295589	-1.505883	-3.256570
H	-1.085154	-0.119755	-2.484954
C	1.613274	-1.916323	-1.373815
H	2.532544	-1.692489	-1.930393
H	1.158725	-2.782285	-1.872620
C	1.943327	-2.275656	0.061854
C	1.367870	0.509881	-1.930989
H	0.615632	1.174923	-2.375072
H	2.100851	0.284985	-2.717365
C	2.012769	1.209329	-0.748697
C	3.122878	2.049858	-0.856861
H	3.621324	2.173417	-1.817045
C	3.576568	2.732494	0.279836
H	4.440434	3.391960	0.214572
C	2.905792	2.556650	1.495278
H	3.223351	3.074463	2.397801
C	1.810440	1.692433	1.547528
H	1.250882	1.516974	2.464233
O	-1.700426	-0.572250	2.659946
C	3.165500	-3.520253	1.730737
C	2.400274	-2.886616	2.717646
C	1.431537	-1.960855	2.335208
H	0.817000	-1.435203	3.060650
H	2.549806	-3.098379	3.774178
H	3.932917	-4.243133	2.002388
H	3.515614	-3.680625	-0.402756
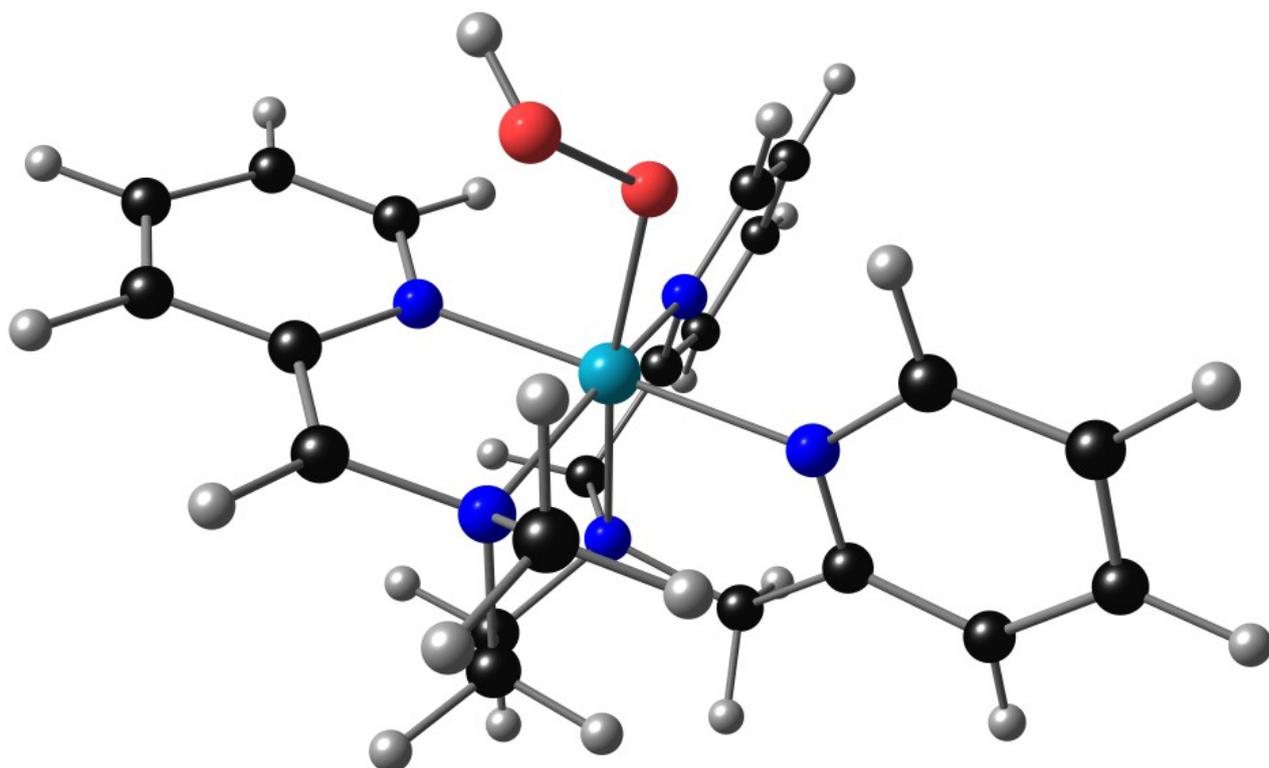
Figure S18. The geometry of a minimum of $[Co^{III}(OOH)(metpen-H^{\bullet})]^{2+}$. The geometry is optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co.

Table S15 The Cartesian coordinates for the structure of $[Co^{III}(OOH)(metpen-H^{\bullet})]^{2+}$ optimised at BLYP/TZVP level of theory with the SDD Stuttgart/Dresden effective core potential basis set on Co. G = -1384.346585 E_h. $<S^2> = 0.76$.

Co	-0.066593	-0.312719	0.440484
O	-0.422129	0.034170	2.272899
N	-1.454245	1.027015	-0.073712
N	-1.582781	-1.696171	0.013492
N	0.674042	-0.725188	-1.463799
N	1.394057	1.025954	0.412272
N	1.229427	-1.729368	1.001719
C	2.901288	-3.307862	0.299568
C	-1.340251	2.370271	-0.083731
H	-0.352833	2.779277	0.106549
C	-2.426069	3.225934	-0.310432
H	-2.265727	4.301663	-0.305483
C	-3.702686	2.677413	-0.527484
H	-4.560450	3.323752	-0.704604
C	-3.852153	1.298421	-0.501446
H	-4.824465	0.832451	-0.650386

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C   -2.717004    0.469311   -0.261901
C   -2.796108   -0.921238   -0.168145
H   -2.060964    0.782192    2.940430
H   -3.740889   -1.461173   -0.220619
C   -1.851530   -2.794271    1.021796
H   -2.664993   -3.438937    0.660309
H   -2.134163   -2.333959    1.970069
H   -0.948436   -3.395523    1.147878
C   -1.180065   -2.331420   -1.329190
H   -2.068705   -2.746443   -1.823958
H   -0.513594   -3.168757   -1.094281
C   -0.486986   -1.305210   -2.222817
H   -0.158557   -1.777308   -3.161071
H   -1.168014   -0.487886   -2.482349
C    1.828778   -1.706612   -1.367714
H    2.755142   -1.183581   -1.638378
H    1.697987   -2.504145   -2.111672
C    1.986385   -2.286290    0.021762
C    1.160350    0.603611   -1.972922
H    0.285741    1.187183   -2.286987
H    1.811480    0.489164   -2.851073
C    1.877713    1.308477   -0.834632
C    2.932388    2.206809   -1.008375
H    3.309645    2.416016   -2.008127
C    3.494369    2.828529    0.115457
H    4.317715    3.531263   -0.001641
C    2.989682    2.528859    1.385627
H    3.401755    2.988635    2.281382
C    1.937460    1.617741    1.501631
H    1.492337    1.350823    2.458234
O   -1.811172   -0.135903    2.700487
C    3.051149   -3.751433    1.617119
C    2.280009   -3.157685    2.623898
C    1.376702   -2.152127    2.284303
H    0.742663   -1.650534    3.011509
H    2.368715   -3.467898    3.662844
H    3.759477   -4.543807    1.853374
H    3.492232   -3.741978   -0.505705
```

19.9 kcal/mol

9.3 kcal/mol
$[Co(OOH)(mebpena-H')]^+$ (↑)
$+ H_2O$

0.0
$[Co(H_2O)(mebpena)]^+$ (↑↑↑)
$+ O_2$ (↓↓)

-3.7 kcal/mol
$[Co(O_2)(mebpena)]^+$ (↑) $+ H_2O$
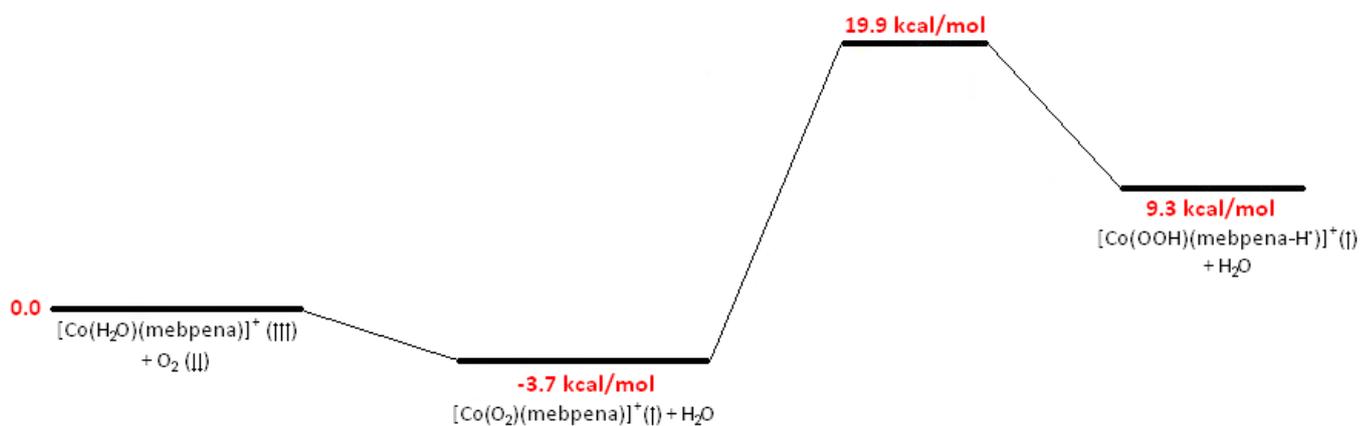
Figure S19. Free energy diagram for the first steps in the proposed reaction mechanism of the oxidative *N*-dealkylation of mebpena⁻ in the presence of Co(II) and dioxygen.