Electronic Supplementary Information For

Generation of reactive cobalt oxo oxamate radical species for biomimetic oxidation of contaminants

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Table S1. High-resolution parent and fragment ion data for complex **1**.

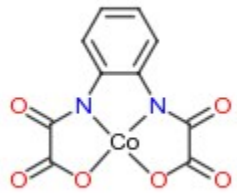
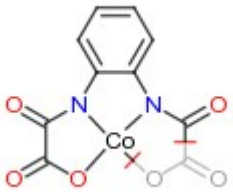
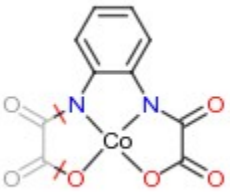
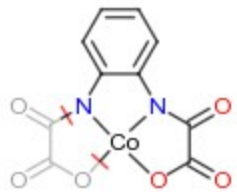
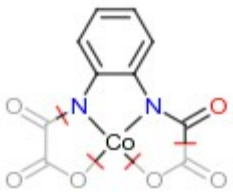
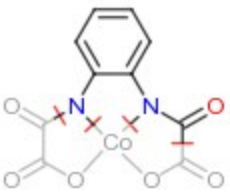
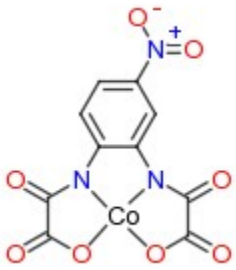
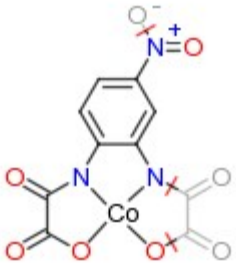
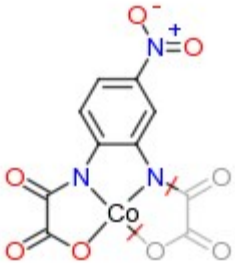
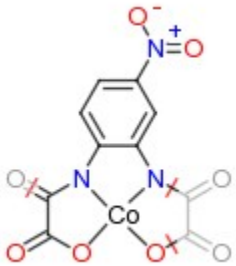
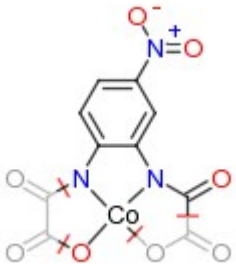
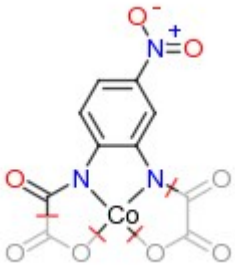
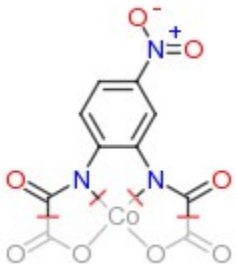
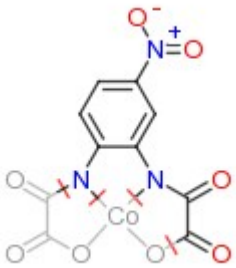
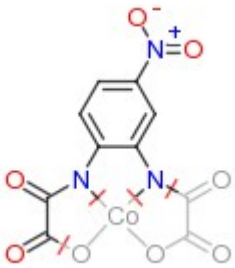
306.9402 ¬·- (+0H)  306.9401 (+0.1.mDa) $C_{10}H_4N_2O_6Co$ (-none)	**262.9504** ¬·- (+0H)  262.9503 (+0.1.mDa) (S:4.0, B:2) $C_9H_4N_2O_4Co$ (-CO_2)	**252.9663** ¬·- (+2H)  252.9660 (+0.3.mDa) (S:2.0, B:2) $C_8H_6N_2O_4Co$ (-C_2O_2)
234.9559 ¬·- (+0H)  234.9554 (+0.5.mDa) (S:3.0, B:2) $C_8H_4N_2O_3Co$ (-C_2O_3)	**190.9657** ¬·- (+0H)  190.9656 (+0.1.mDa) (S:9.5, B:4) $C_7H_4N_2OCo$ (-C_3O_5)	**132.0327** ¬·- (+0H)  132.0324 (+0.3.mDa) (S:12.0, B:4) $C_7H_4N_2O$ (-C_3O_5Co)

Table S2. High-resolution parent and fragment ion data for complex 2.

351.9253 ¬- (+0H)  351.9252 (+0.1.mDa) $C_{10}H_3N_3O_8Co$ (-none)	**279.9409** ¬- (+0H)  279.9405 (+0.4.mDa) (S:3.0, B:3) $C_8H_3N_3O_5Co$ ($-C_2O_3$)	**279.9409** ¬- (+0H)  279.9405 (+0.4.mDa) (S:3.0, B:2) $C_8H_3N_3O_5Co$ ($-C_2O_3$)
279.9409 ¬- (+0H)  279.9405 (+0.4.mDa) (S:4.0, B:3) $C_8H_3N_3O_5Co$ ($-C_2O_3$)	**252.9543** ¬- (+1H)  252.9534 (+0.9.mDa) (S:6.0, B:4) $C_7H_4N_3O_4Co$ ($-C_3O_4$)	**235.9515** ¬- (+0H)  235.9506 (+0.9.mDa) (S:9.5, B:4) $C_7H_3N_3O_3Co$ ($-C_3O_5$)
206.0203 ¬- (+1H)  206.0202 (+0.1.mDa) (S:10.5, B:4) $C_8H_4N_3O_4$ ($-C_2O_4Co$)	**206.0203** ¬- (+1H)  206.0202 (+0.1.mDa) (S:11.0, B:4) $C_8H_4N_3O_4$ ($-C_2O_4Co$)	**206.0203** ¬- (+1H)  206.0202 (+0.1.mDa) (S:11.0, B:4) $C_8H_4N_3O_4$ ($-C_2O_4Co$)
178.0256 ¬- (+1H)	**177.0179** ¬- (+0H)	**147.0197** ¬- (+0H)

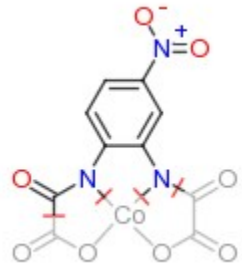
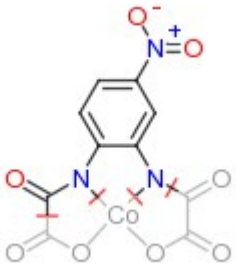
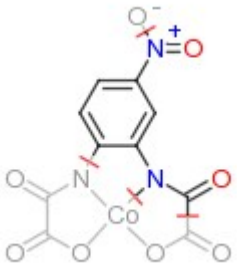
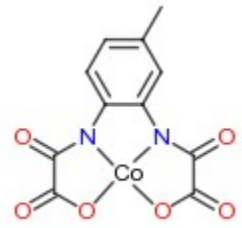
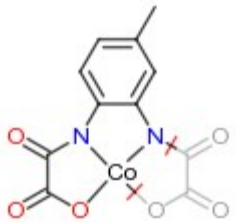
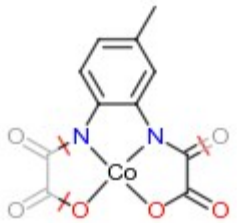
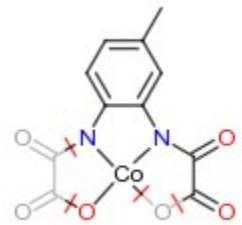
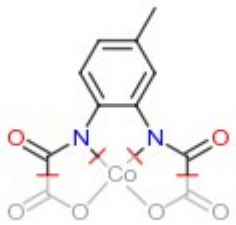
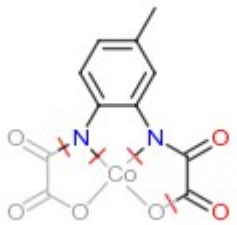
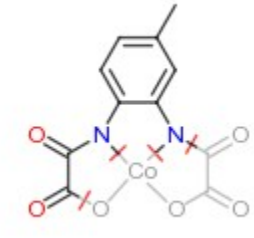
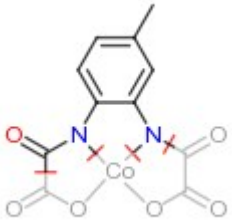
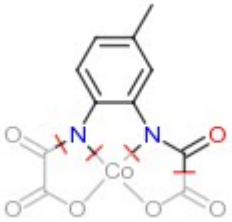
 178.0253 (+0.3.mDa) (S:12.0, B:4) $C_7H_4N_3O_3$ (-C_3O_5Co)	 177.0174 (+0.5.mDa) (S:12.0, B:4) $C_7H_3N_3O_3$ (-C_3O_5Co)	 147.0195 (+0.2.mDa) (S:6.0, B:4) $C_7H_3N_2O_2$ (-C_3NO_6Co)

Table S3. High-resolution parent and fragment ion data for complex **3**.

320.9558 ¬- (+0H)  320.9558 (+0.0.mDa) $C_{11}H_6N_2O_6Co$ (-none)	**248.9711** ¬- (+0H)  248.9710 (+0.1.mDa) (S:3.0, B:2) $C_9H_6N_2O_3Co$ (-C_2O_3)	**248.9711** ¬- (+0H)  248.9710 (+0.1.mDa) (S:4.0, B:3) $C_9H_6N_2O_3Co$ (-C_2O_3)
248.9711 ¬- (+0H)  248.9710 (+0.1.mDa) (S:7.5, B:4) $C_9H_6N_2O_3Co$ (-C_2O_3)	**175.0507** ¬- (+1H)  175.0508 (-0.1.mDa) (S:10.5, B:4) $C_9H_7N_2O_2$ (-C_2O_4Co)	**175.0507** ¬- (+1H)  175.0508 (-0.1.mDa) (S:11.0, B:4) $C_9H_7N_2O_2$ (-C_2O_4Co)
175.0507 ¬- (+1H)	**147.0550** ¬- (+1H)	**147.0550** ¬- (+1H)

 175.0508 (-0.1.mDa) (S:11.0, B:4) $C_9H_7N_2O_2$ (-C_2O_4Co)	 147.0558 (-0.8.mDa) (S:12.0, B:4) $C_8H_7N_2O$ (-C_3O_5Co)	 147.0558 (-0.8.mDa) (S:12.0, B:4) $C_8H_7N_2O$ (-C_3O_5Co)

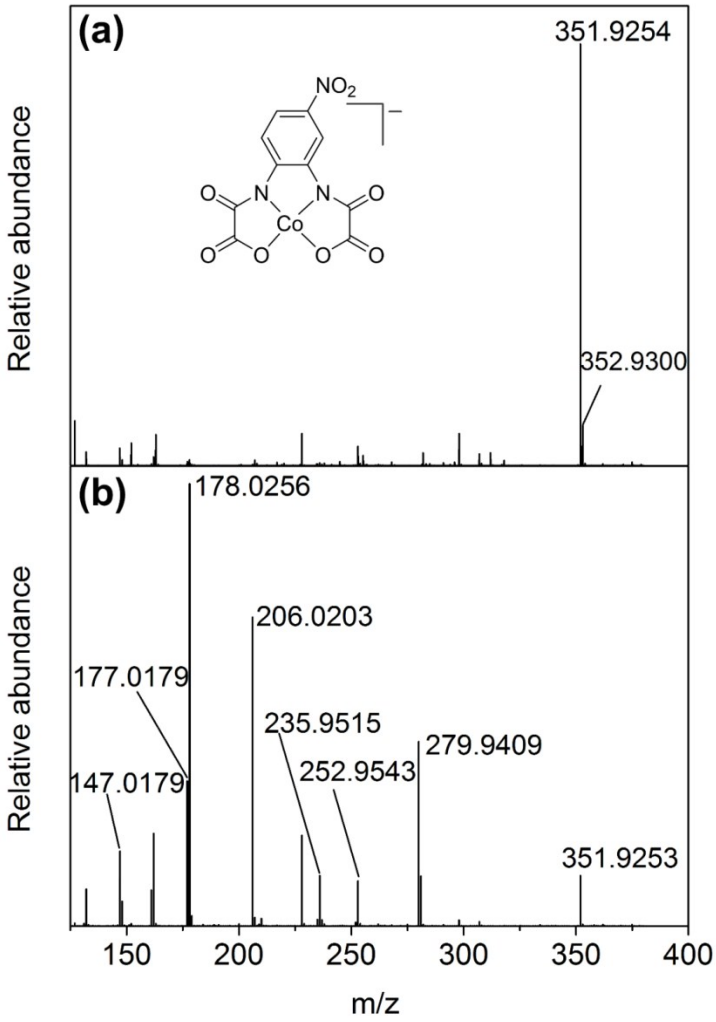


Fig. S1. Synapt G2-S HDMS (ESI) in negative mode of complex **2** in MeCN aqueous solution for (a) QTOF-MS and (b) MS/MS.

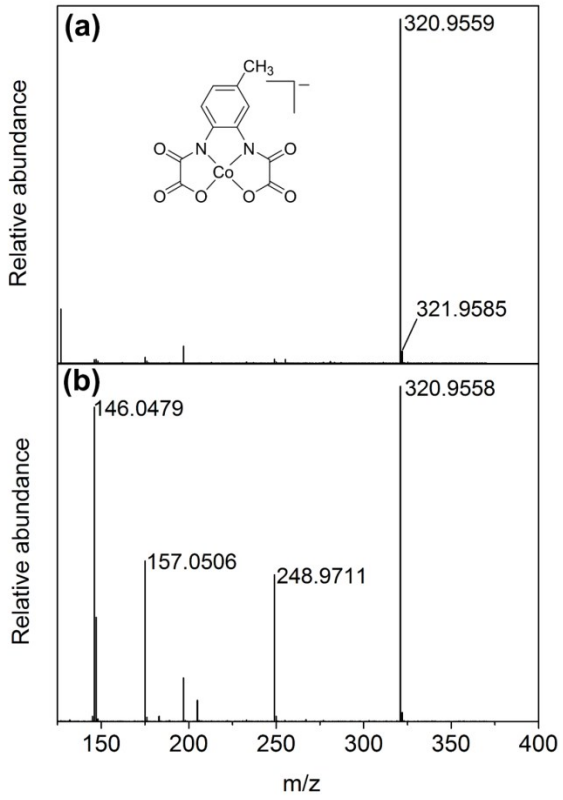


Fig. S2. Synapt G2-S HDMS (ESI) in negative mode of complex **3** in MeCN aqueous solution for (a) QTOF-MS and (b) MS/MS.

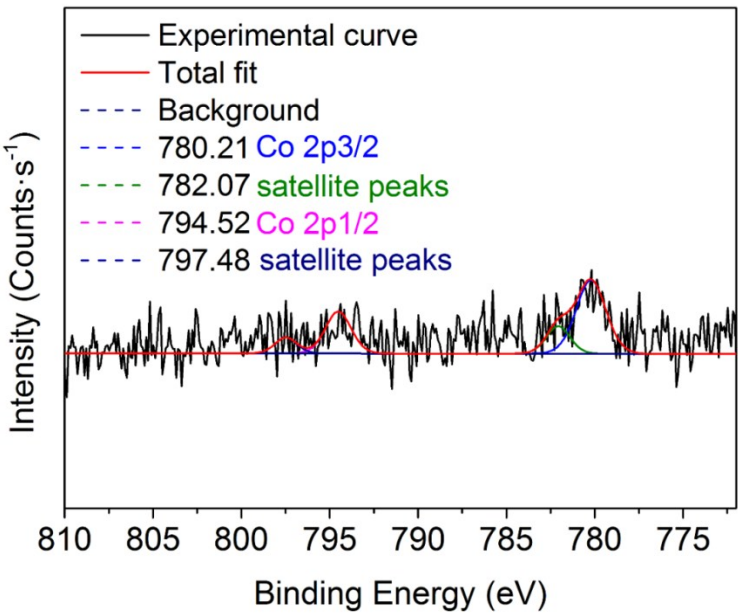


Fig. S3. The Co 2p spectra of the cobalt complex **1**.

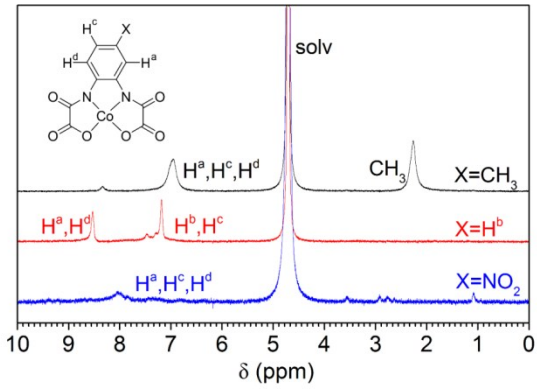


Fig. S4. ^{1}H NMR spectrum of the complex **1** in D_2O at room temperature (solv=solvent, internal standard).

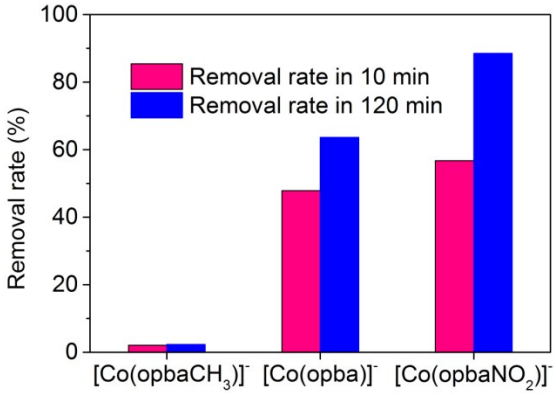


Fig. S5. Substitute effect of oxamate anionic cobalt(III) complexes on the removal efficiency of p-chlorophenol (0.05mM) by H_2O_2 catalyzed by various cobalt(III) complexes containing a series of electron-rich and electron–poor substrates on the ligands, where the temperature is 25 ºC, the concentration of $[Co^{III}(opbaX)]^-$ (X=CH_3, H, NO_2) is 0.02mM, and that of H_2O_2 is 40mM.

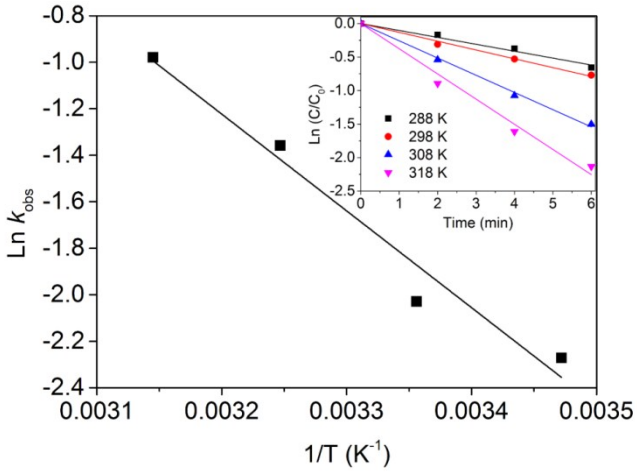


Fig. S6. The effect of temperature on the degradation kinetics of AR1 by complex **1** and H_2O_2, T=25 ºC, pH 9.0.

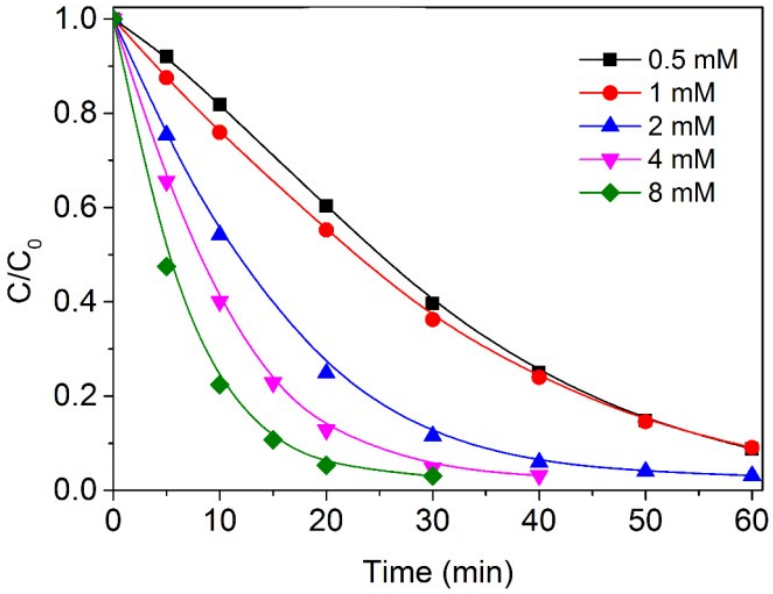


Fig. S7. Effect of initial H_2O_2 concentration on catalyst oxidation of AR1 (0.05 mM) by complex **1**(0.02 mM) and H_2O_2, T=25 ºC, pH 9.0.

Table S4. The total electron spin energy of $[•O=Co^{IV}(opbaCH_3)]^-$, $[•O=Co^{IV}(opba)]^-$ and $[•O=Co^{IV}(opbaNO_2)]^-$.

Total energy	$[•O=Co^{IV}(opbaCH_3)]^-$ (a.u.)	$[•O=Co^{IV}(opba)]^-$ (a.u.)	$[•O=Co^{IV}(opbaNO_2)]^-$ (a.u.)
S=0	-2441.28342893	-2401.97477567	-2606.40178006
S=1	-2441.31674986	-2402.00879031	-2606.43523960
S=2	-2441.30774637	-2401.99902687	-2606.42342433

Table S5. The structure of $[Co^{III}(opba)]^{-}$ calculated by DFT (S=1).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-0.700275	3.940718	0.000233
2	6	0.700664	3.940668	0.000275
3	6	1.419699	2.737082	0.000182
4	6	0.71118	1.529754	0.00004
5	6	-0.710961	1.529786	0.000004
6	6	-1.419395	2.737183	0.000099
7	1	-1.241891	4.882087	0.000303
8	1	1.242367	4.881989	0.000379
9	1	2.500907	2.716495	0.000213
10	1	-2.500603	2.716651	0.00006
11	7	1.247588	0.222483	-0.000038
12	7	-1.247494	0.222645	-0.000082
13	6	2.56823	-0.160101	0.000043
14	8	3.568136	0.58632	-0.000115
15	6	2.647221	-1.703994	-0.000832
16	8	3.720973	-2.311404	0.000675
17	6	-2.568185	-0.159865	-0.000052
18	8	-3.568019	0.586684	0.00027
19	6	-2.647415	-1.703779	-0.000218
20	8	-3.721284	-2.310943	0.000516
21	27	-0.000069	-1.114212	-0.000209
22	8	-1.428641	-2.297395	-0.00008
23	8	1.428317	-2.297525	-0.000405

Table S6. Mulliken spin densities of $[Co^{III}(opba)]^{-}$ (S=1).

Center Number	Atomic Number	density
1	C	0.006637
2	C	0.006657
3	C	0.008147
4	C	0.000867
5	C	0.000846
6	C	0.008166
7	H	-0.000587
8	H	-0.000588
9	H	-0.000529
10	H	-0.00053
11	N	0.005209
12	N	0.00523

13	C	0.000107
14	O	0.049417
15	C	-0.006278
16	O	0.014033
17	C	0.000103
18	O	0.04942
19	C	-0.006274
20	O	0.01403
21	Co	1.816417
22	O	0.014742
23	O	0.014758

Table S7. The structure of $[\bullet O=Co^{IV}(opba)]^{-}$ calculated by DFT (S=1).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	C	0.701462	3.995124	0.002592
2	C	-0.70514	3.994514	0.002841
3	C	-1.42511	2.797443	0.000404
4	C	-0.71323	1.586533	-0.00217
5	C	0.711659	1.587163	-0.00252
6	C	1.42247	2.798674	-0.00016
7	H	1.238953	4.9385	0.004479
8	H	-1.24344	4.93743	0.004888
9	H	-2.50587	2.777856	-0.01237
10	H	2.503239	2.780088	-0.01346
11	N	-1.23389	0.289901	-0.03895
12	N	1.233341	0.290887	-0.03984
13	C	-2.54238	-0.10609	-0.22321
14	O	-3.5264	0.64641	-0.35761
15	C	-2.6062	-1.64218	-0.30658
16	O	-3.66662	-2.24644	-0.50558
17	C	2.54234	-0.10382	-0.22362
18	O	3.525459	0.649698	-0.35885
19	C	2.607932	-1.63989	-0.30581
20	O	3.66911	-2.24297	-0.5044
21	Co	0.000501	-1.04842	0.305524
22	O	1.404347	-2.2245	-0.18733
23	O	-1.40182	-2.22541	-0.18901
24	O	0.000255	-1.20639	1.936327

Table S8. The structure of $[\bullet O=Co^{IV}(opbaCH_3)]^-$ calculated by DFT (S=1).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	C	-3.73973542	-0.68786101	-0.00110193
2	C	-3.23564573	-2.00907665	-0.00349168
3	C	-1.86751676	-2.27646976	-0.00464854
4	C	-0.96975391	-1.19539593	-0.00452562
5	C	-1.46330828	0.14020774	-0.00358425
6	C	-2.84570212	0.38950046	-0.00250968
7	H	-3.93528595	-2.84085698	-0.00512715
8	H	-1.48245576	-3.286553	-0.0201308
9	H	-3.19697002	1.41255332	-0.01547311
10	N	0.42507853	-1.23805507	-0.04132501
11	N	-0.42841352	1.07730724	-0.03865215
12	C	1.24731216	-2.3309564	-0.22537856
13	O	0.87733856	-3.51289668	-0.36294158
14	C	2.71221241	-1.8626524	-0.30454382
15	O	3.64337573	-2.65210727	-0.5042123
16	C	-0.50894704	2.44204259	-0.22473652
17	O	-1.55522276	3.10522437	-0.36026169
18	C	0.91092754	3.03271129	-0.31001981
19	O	1.10926443	4.23692721	-0.51159441
20	Co	1.25566233	0.38117757	0.30870277
21	O	1.87430819	2.10543209	-0.19080587
22	O	2.84624852	-0.5325271	-0.18180823
23	O	1.40250331	0.43924824	1.94287797
24	C	-5.23361	-0.44461065	0.01193209
25	H	-5.73489319	-0.981673	-0.80367615
26	H	-5.46208078	0.62013643	-0.09623464
27	H	-5.68777699	-0.78920883	0.95112597

Table S9. The structure of $[\bullet O=Co^{IV}(opbaNO_2)]^-$ calculated by DFT (S=1).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	C	-3.29653114	-0.49054248	-0.00275171
2	C	-2.90704272	-1.83976583	-0.00624603
3	C	-1.5551274	-2.16852088	-0.00700361
4	C	-0.60365043	-1.13207088	-0.00163718
5	C	-1.01950591	0.23389776	-0.00127994
6	C	-2.37708009	0.56438477	-0.00245955
7	H	-3.66923583	-2.60686401	-0.00747386

8	H	-1.22189673	-3.19623819	-0.02117705
9	H	-2.70280987	1.59369925	-0.01680289
10	N	0.78108698	-1.2550603	-0.03156334
11	N	0.0699159	1.10996637	-0.03911146
12	C	1.54267919	-2.3944824	-0.21085645
13	O	1.1094984	-3.55409686	-0.33111465
14	C	3.02824523	-2.00365375	-0.30615031
15	O	3.91803364	-2.83661151	-0.50254928
16	C	0.06575035	2.47896492	-0.22016018
17	O	-0.94119526	3.19653244	-0.35272199
18	C	1.51633076	2.98539062	-0.29810832
19	O	1.7951201	4.17166266	-0.49298266
20	Co	1.70774455	0.32101237	0.29622914
21	O	2.42506626	1.99649535	-0.18061879
22	O	3.23084555	-0.67610923	-0.2034469
23	O	1.85625635	0.35201193	1.91917227
24	N	-4.71819923	-0.17742536	0.00038882
25	O	-5.07150174	1.03973091	0.01180856
26	O	-5.54827243	-1.13985407	-0.00764798

Table S10. Mulliken spin densities of $[\bullet O=Co^{IV}(opba)]^{-}$ (S=1).

Center Number	Atomic Number	density
1	C	-0.017188
2	C	-0.017268
3	C	0.001146
4	C	-0.018543
5	C	-0.018463
6	C	0.00108
7	H	0.000914
8	H	0.000917
9	H	0.000199
10	H	0.000201
11	N	-0.048369
12	N	-0.048377
13	C	0.011299
14	O	-0.037603
15	C	0.000093
16	O	-0.003415
17	C	0.011327
18	O	-0.037606
19	C	0.000084
20	O	-0.003426

21	Co	1.244726
22	O	0.026031
23	O	0.026217
24	O	0.926025

Table S11. Mulliken spin densities of $[\bullet O=Co^{IV}(opbaCH_3)]^-$ (S=1).

Center Number	Atomic Number	density
1	C	-0.022771
2	C	-0.024299
3	C	0.001909
4	C	-0.025985
5	C	-0.022891
6	C	0.005978
7	H	0.001215
8	H	0.000248
9	H	0.000071
10	N	-0.060499
11	N	-0.057163
12	C	0.013261
13	O	-0.046033
14	C	0.000186
15	O	-0.00345
16	C	0.01266
17	O	-0.042948
18	C	0.00012
19	O	-0.002937
20	Co	1.284437
21	O	0.024963
22	O	0.023876
23	O	0.940231
24	C	0.001978
25	H	-0.000783
26	H	-0.00005
27	H	-0.001324

Table S12. Mulliken spin densities of $[\bullet O=Co^{IV}(opbaNO_2)]^-$ (S=1).

Center Number	Atomic Number	density
1	C	-0.005699
2	C	-0.003526

3	C	-0.000164
4	C	-0.004122
5	C	-0.00545
6	C	-0.005774
7	H	0.000223
8	H	0.000066
9	H	0.000244
10	N	-0.014642
11	N	-0.021156
12	C	0.005355
13	O	-0.016278
14	C	0.000073
15	O	-0.003468
16	C	0.007312
17	O	-0.020575
18	C	0.000325
19	O	-0.004811
20	Co	1.130697
21	O	0.027168
22	O	0.030516
23	O	0.906423
24	N	0.000726
25	O	0.000058
26	O	-0.003522

Table S13. The total electron spin energy of HO−Co^{III}(opbaCH_3)•, HO−Co^{III}(opba)• and HO−Co^{III}(opbaNO_2)•.

Total energy	HO−Co^{III}(opbaCH_3)• (a.u.)	HO−Co^{III}(opba)• (a.u.)	HO−Co^{III}(opbaNO_2)• (a.u.)
S=0	-2441.78671069	-2402.47353885	-2606.87669333
S=1	-2441.80261400	-2402.49020651	-2606.88366260
S=2	-2441.79370375	-2402.48109935	-2606.88609619

Table S14. Mulliken spin densities of HO−Co^{III}(opbaNO_2)• (S=2).

Center Number	Atomic Number	density
1	C	0.092813
2	C	0.116385
3	C	-0.047266
4	C	0.138211

5	C	0.155262
6	C	0.017176
7	H	-0.005066
8	H	0.000526
9	H	-0.001488
10	N	0.142102
11	N	0.207607
12	C	-0.031422
13	O	0.10779
14	C	-0.006757
15	O	0.00377
16	C	-0.046056
17	O	0.141434
18	C	-0.006579
19	O	0.004353
20	Co	2.273277
21	O	0.100559
22	O	0.086938
23	O	0.534305
24	N	-0.013619
25	O	-0.021493
26	O	0.05066
27	H	0.006577

Table S15. Mulliken spin densities of HO−Co^{III}(opba)• (S=1).

Center Number	Atomic Number	density
1	C	-0.120116
2	C	-0.120118
3	C	0.049756
4	C	-0.158409
5	C	-0.158366
6	C	0.049744
7	H	0.005726
8	H	0.005726
9	H	-0.000683
10	H	-0.000683
11	N	-0.12719
12	N	-0.127107
13	C	0.031807
14	O	-0.0741
15	C	-0.013013
16	O	0.022934

17	C	0.031836
18	O	-0.074141
19	C	-0.013015
20	O	0.022881
21	Co	2.152981
22	O	0.062174
23	O	0.062503
24	O	0.486382
25	H	0.002489

Table S16. Mulliken spin densities of HO−Co^{III}(opbaCH_3)• (S=1).

Center Number	Atomic Number	density
1	C	-0.141564
2	C	-0.128656
3	C	0.048066
4	C	-0.177364
5	C	-0.149817
6	C	0.076466
7	H	0.005969
8	H	-0.000517
9	H	-0.001616
10	N	-0.127819
11	N	-0.099952
12	C	0.030782
13	O	-0.07712
14	C	-0.012522
15	O	0.022774
16	C	0.025969
17	O	-0.060269
18	C	-0.01247
19	O	0.022413
20	Co	2.154454
21	O	0.061888
22	O	0.0603
23	O	0.48371
24	C	0.009941
25	H	-0.007635
26	H	0.000062
27	H	-0.007882
28	H	0.002409