Supplementary Information:

Figure S-1: related to Experimental Section.

The results are affected by the concentration of the PIPES buffer, Figure S-1. These effects are attributed to complex formation between the Co^{II} central ion and the sulfate or sulfonate anions, which affects the binding of the peroxide ligands.

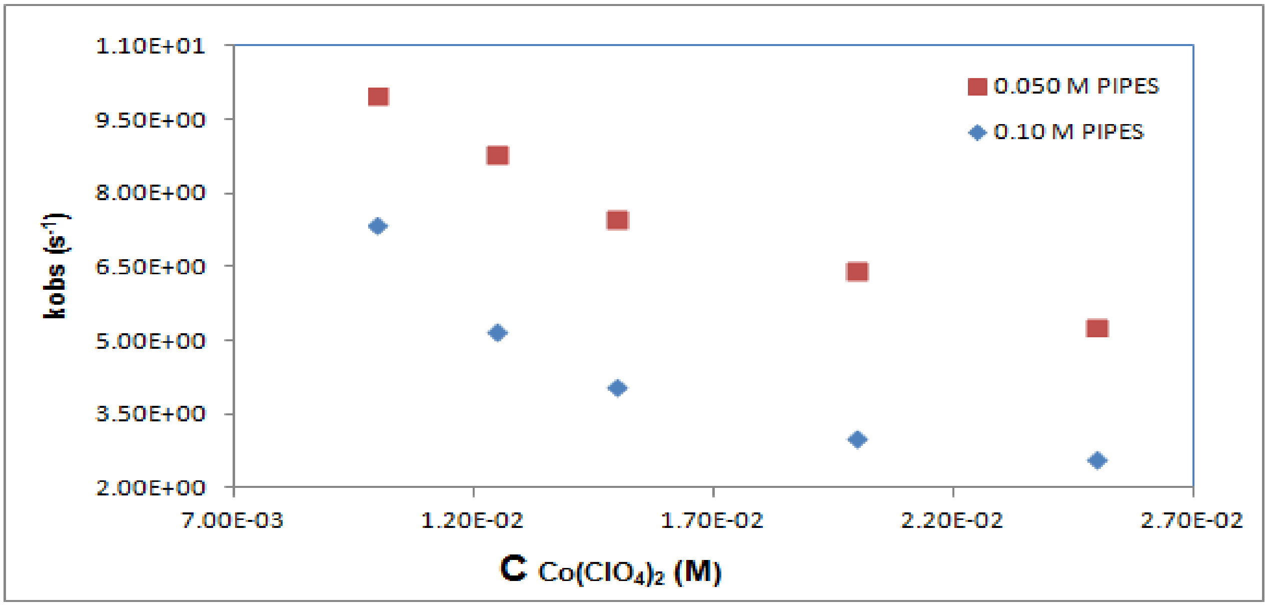

Figure S-1: Dependence of k_{obs}, of first reaction observed, on $[Co(ClO_4)_2]$.
Solutions composition: ■ 7.5×10^{-4} M H_2O_2. pH 6.5, PIPES 1.00×10^{-1} M. Ionic strength 5.5×10^{-1} M controlled by adding $NaClO_4$. ◆ 7.5×10^{-4} M H_2O_2. pH 6.5, PIPES 5.0×10^{-2} M. Ionic strength 4.75×10^{-1} M controlled by adding $NaClO_4$.

The data for Figure S-1 are summed up in table S-1

Table S-1: k_{obs} as a function of $[Co(ClO_4)_2]$ at two PIPES concentrations

$C_{(Co(ClO4)2)}$ M	k_{obs} s^{-1} 0.050M PIPES	k_{obs} s^{-1} 0.10M PIPES
0.010	9.99	7.34
0.013	8.81	5.19
0.015	7.49	4.07
0.020	6.44	3.04
0.025	5.29	2.58

Figure S-2 related to Experimental methods.

The results presented in Figure S-2, show that the kinetics of the reactions are affected by [SO_4^{2-}], therefore all the results presented are for $Co(ClO_4)_2$. Ionic strength doesn't affect the observed rate constants, Figure S-2.

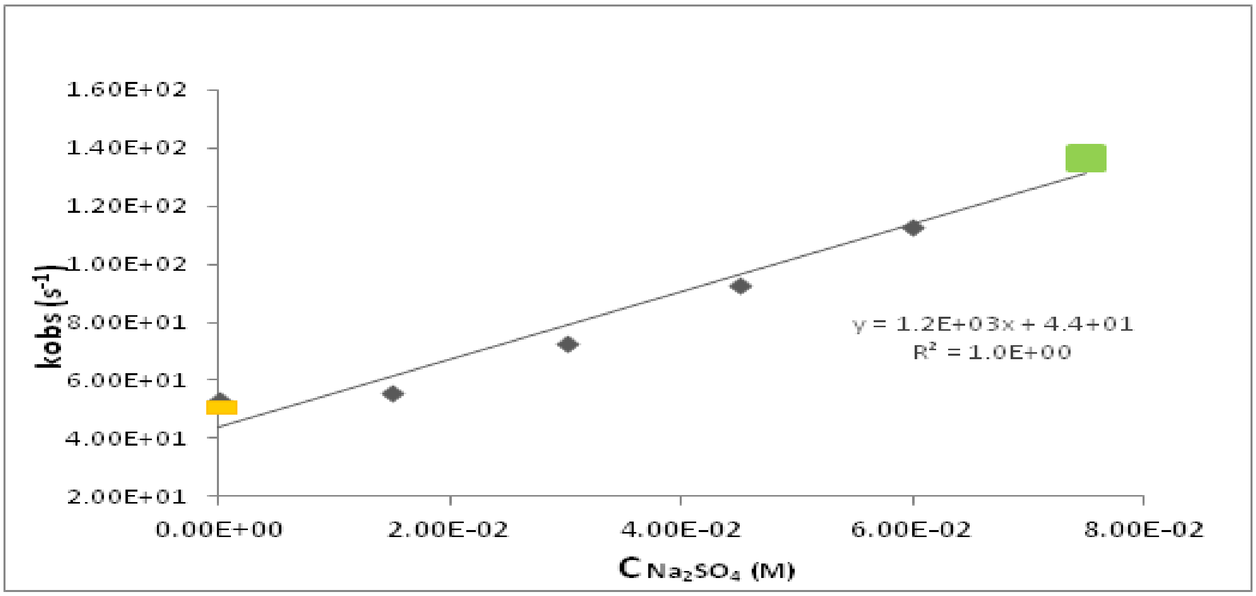

Figure S-2: Dependence of k_{obs} on C_{Na2SO4}.

Solutions composition: 1.5×10^{-2} M $Co(ClO_4)_2$, 1.5×10^{-1} M H_2O_2. In pH 6.5, HEPES buffer (4-(2-Hydroxyethyl)piperazine-1-ethaesulfonic acid sodium salt) 1.0×10^{-1}M, ionic strength for and 3.7×10^{-1}M, controlled by adding $NaClO_4$.

The data for Figure S-2 are summed up in table S-2

Table S-2: k_{obs} as a function of C_{Na2SO4}:

C_{Na2SO4} M	k_{obs} s^{-1}
0.000	53.5
0.015	55.6
0.030	72.9
0.045	93.0
0.060	112
0.075	137

Table S-3: k_{obs} as a function of C_{H2O2} (data for figure 1):

C_{H2O2} M	k_{obs} s^{-1}
0.0750	7.84
0.105	10.2
0.150	11.9
0.200	14.4
0.240	15.7

Table S-4: k_{obs} as a function of $C_{Co(ClO4)2}$ (data for figure 2):

$C_{Co(ClO4)2}$ M	k_{obs} s^{-1}
0.0100	7.34
0.0125	5.19
0.0150	4.07
0.0200	3.04
0.0250	2.58

Table S-5: k_{obs} as a function of C_{H2O2} (data for figure 3):

C_{H2O2} M	k_{obs} s^{-1}
0.075	0.37
0.105	0.45
0.150	0.53
0.200	0.62
0.240	0.78

Table S-6: k_{obs} as a function of $C_{Co(ClO4)2}$ (data for figure 4):

$C_{Co(ClO4)2}$ M	k_{obs} s^{-1}
0.0125	0.46
0.0150	0.37
0.0200	0.31
0.0250	0.28

Figure S-3 related to DFT calculations, reaction (10).

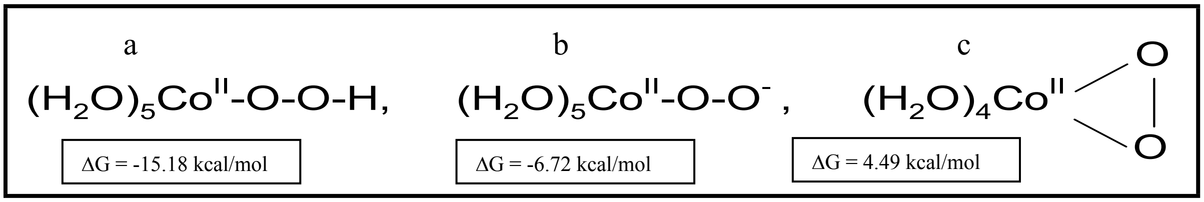

Figure S-3: The three plausible species a, b, c that can be formed in reactions S(1), S(2), S(3) respectively.

Reactions S(1) – S(3) related to DFT calculations, reaction (10).

S(1) $Co(H_2O)_6^{2+} + OOH^- \rightarrow Co(H_2O)_5OOH^+ + H_2O$ ΔG = -15.18 kcal/mol

S(2) $Co(H_2O)_6^{2+} + OOH^- \rightarrow Co(H_2O)_5(OO^{2-}) + H_3O^+$ ΔG = -6.72 kcal/mol

S(3) $Co(H_2O)_6^{2+} + OOH^- \rightarrow Co(H_2O)_4OO$(triangle) $+ H_3O^+ + H_2O$ ΔG = 4.49 kcal/mol