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.

![Graph](image)

**Figure S-1: Dependence of** \(k_{\text{obs}}\) **of first reaction observed, on** \([\text{Co(ClO}_4]\text{)}_2\]**.

Solutions composition: 7.5\(\times10^{-4}\) M \(\text{H}_2\text{O}_2\). pH 6.5, PIPES 1.00\(\times10^{-1}\) M. Ionic strength 5.5\(\times10^{-1}\) M controlled by adding \(\text{NaClO}_4\). 7.5\(\times10^{-4}\) M \(\text{H}_2\text{O}_2\). pH 6.5, PIPES 5.0\(\times10^{-2}\) M. Ionic strength 4.75\(\times10^{-1}\) M controlled by adding \(\text{NaClO}_4\).

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

**Table S-1:** \(k_{\text{obs}}\) as a function of \([\text{Co(ClO}_4]\text{)}_2\] at two PIPES concentrations

<table>
<thead>
<tr>
<th>(C_{(\text{Co(ClO}_4)}\text{)}_2) M</th>
<th>(k_{\text{obs}}) (s^{-1}) 0.050M PIPES</th>
<th>(k_{\text{obs}}) (s^{-1}) 0.10M PIPES</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>9.99</td>
<td>7.34</td>
</tr>
<tr>
<td>0.013</td>
<td>8.81</td>
<td>5.19</td>
</tr>
<tr>
<td>0.015</td>
<td>7.49</td>
<td>4.07</td>
</tr>
<tr>
<td>0.020</td>
<td>6.44</td>
<td>3.04</td>
</tr>
<tr>
<td>0.025</td>
<td>5.29</td>
<td>2.58</td>
</tr>
</tbody>
</table>
**Figure S-2** related to Experimental methods.

The results presented in Figure S-2, show that the kinetics of the reactions are affected by \([\text{SO}_4^{2-}]\), therefore all the results presented are for \(\text{Co(ClO}_4\text{)}_2\). Ionic strength doesn’t affect the observed rate constants, Figure S-2.

**Figure S-2: Dependence of \(k_{\text{obs}}\) on \(C_{\text{Na}_2\text{SO}_4}\).**

Solutions composition: \(1.5\times10^{-2} \text{ M Co(ClO}_4\text{)}_2, 1.5\times10^{-1} \text{ M H}_2\text{O}_2\). In pH 6.5, HEPES buffer (4-(2-Hydroxyethyl)piperazine-1-ethaesulfonic acid sodium salt) \(1.0\times10^{-1}\text{M},\) ionic strength for \(3.7\times10^{-1}\text{M},\) controlled by adding \(\text{NaClO}_4\).

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

**Table S-2: \(k_{\text{obs}}\) as a function of \(C_{\text{Na}_2\text{SO}_4}\):**

<table>
<thead>
<tr>
<th>(C_{\text{Na}_2\text{SO}_4} \text{ M})</th>
<th>(k_{\text{obs}} \text{ s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>53.5</td>
</tr>
<tr>
<td>0.015</td>
<td>55.6</td>
</tr>
<tr>
<td>0.030</td>
<td>72.9</td>
</tr>
<tr>
<td>0.045</td>
<td>93.0</td>
</tr>
<tr>
<td>0.060</td>
<td>112</td>
</tr>
<tr>
<td>0.075</td>
<td>137</td>
</tr>
</tbody>
</table>
### Table S-3: $k_{\text{obs}}$ as a function of $C_{\text{H}_2\text{O}_2}$ (data for figure 1):

<table>
<thead>
<tr>
<th>$C_{\text{H}_2\text{O}_2}$ M</th>
<th>$k_{\text{obs}}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0750</td>
<td>7.84</td>
</tr>
<tr>
<td>0.105</td>
<td>10.2</td>
</tr>
<tr>
<td>0.150</td>
<td>11.9</td>
</tr>
<tr>
<td>0.200</td>
<td>14.4</td>
</tr>
<tr>
<td>0.240</td>
<td>15.7</td>
</tr>
</tbody>
</table>

### Table S-4: $k_{\text{obs}}$ as a function of $C_{\text{Co(ClO}_4)_2}$ (data for figure 2):

<table>
<thead>
<tr>
<th>$C_{\text{Co(ClO}_4)_2}$ M</th>
<th>$k_{\text{obs}}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0100</td>
<td>7.34</td>
</tr>
<tr>
<td>0.0125</td>
<td>5.19</td>
</tr>
<tr>
<td>0.0150</td>
<td>4.07</td>
</tr>
<tr>
<td>0.0200</td>
<td>3.04</td>
</tr>
<tr>
<td>0.0250</td>
<td>2.58</td>
</tr>
</tbody>
</table>

### Table S-5: $k_{\text{obs}}$ as a function of $C_{\text{H}_2\text{O}_2}$ (data for figure 3):

<table>
<thead>
<tr>
<th>$C_{\text{H}_2\text{O}_2}$ M</th>
<th>$k_{\text{obs}}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.075</td>
<td>0.37</td>
</tr>
<tr>
<td>0.105</td>
<td>0.45</td>
</tr>
<tr>
<td>0.150</td>
<td>0.53</td>
</tr>
<tr>
<td>0.200</td>
<td>0.62</td>
</tr>
<tr>
<td>0.240</td>
<td>0.78</td>
</tr>
</tbody>
</table>

### Table S-6: $k_{\text{obs}}$ as a function of $C_{\text{Co(ClO}_4)_2}$ (data for figure 4):

<table>
<thead>
<tr>
<th>$C_{\text{Co(ClO}_4)_2}$ M</th>
<th>$k_{\text{obs}}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0125</td>
<td>0.46</td>
</tr>
<tr>
<td>0.0150</td>
<td>0.37</td>
</tr>
<tr>
<td>0.0200</td>
<td>0.31</td>
</tr>
<tr>
<td>0.0250</td>
<td>0.28</td>
</tr>
</tbody>
</table>
Figure S-3 related to DFT calculations, reaction (10).

\[ (H_2O)_5Co^{II}-O-O-H, \quad (H_2O)_5Co^{II}-O-O^{-}, \quad (H_2O)_4Co^{II} \]

\[ \Delta G = -15.18 \text{ kcal/mol} \quad \Delta G = -6.72 \text{ kcal/mol} \quad \Delta G = 4.49 \text{ kcal/mol} \]

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) \( Co(H_2O)_6^{2+} + OOH^{-} \rightarrow Co(H_2O)_5OOH^{+} + H_2O \quad \Delta G = -15.18 \text{ kcal/mol} \)
S(2) \( Co(H_2O)_6^{2+} + OOH^{-} \rightarrow Co(H_2O)_4OO^{2-} + H_3O^{+} \quad \Delta G = -6.72 \text{ kcal/mol} \)
S(3) \( Co(H_2O)_6^{2+} + OOH^{-} \rightarrow Co(H_2O)_4OO(\text{triangle}) + H_3O^{+} + H_2O \quad \Delta G = 4.49 \text{ kcal/mol} \)