Supplementary Information:

Experimental

All experiments were carried out at pH 6.5, at which Co^{II}_{aq} does not precipitate. At this pH nearly all the cobalt is present as $Co(H_2O)_6^{2+}$, as the pKa of $Co(H_2O)_6^{2+}$ is 9.82[1], and as in the pH range 3.9-9.6 at $[Co^{II}_{aq}] < 0.1$ M no other cobalt containing specie is experimentally observable[1-2]. All solutions contained 0.10 M PIPES (1,4-piperazinediethane-sulfonic acid) buffer. The results are affected by the concentration of the buffer. Ionic strength doesn't affect the observed rate constants.

H_2O_2 concentration was determined by the iodide procedure[3].

Materials: A.R. grade $Co(ClO_4)_2$, $NaClO_4$, H_2O_2, $NaHCO_3$ and PIPES were purchased from Aldrich. All solutions were prepared in de-ionized water that was further purified by passing through a Milli Q Millipore setup, final resistivity >10 MΩ/cm.

Kinetic measurements: Stopped-flow experiments were carried out using a PBP Spectra Kinetic Monochromator 05-109 by Photophysics, which enables measurements in the range of 200-700 nm. The optical path was 10 mm. The stopped-flow enables kinetic measurements of reactions with halve-lifetimes ≥ 2 msec. Some experiments were carried out using a UV-VIS Agilent 8453 Diode Array spectrophotometer. Kinetics were measured at 352 nm, at this wavelength the largest absorbance changes are observed.

The reaction order and the observed rate constant for each kinetic run were fitted by Pro-data SX software that is connected to the Stopped-flow.

DFT calculations: A package of quantum chemical programs, Gaussian 09, was used as the major computational tool in this study[4]. The DFT approach used the B3LYP hybrid functional developed by Becke. The basis set 6-311+G**, that is large enough to yield a good approximation of the molecular orbitals and enables calculations in a reasonable time, was used for all the systems in this study. Hydration was considered using Truhlar's SMD model for solvation[5]. This model is based on solute electron density and a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions.

Figure S-1 - After mixing H_2O_2, with a solution containing HCO_3^- and $Co(ClO_4)_2$, two kinetic processes are observed, the first being a fast decrease in absorbance, followed by an increase in absorbance. The absorbance changes are followed at 352 nm.

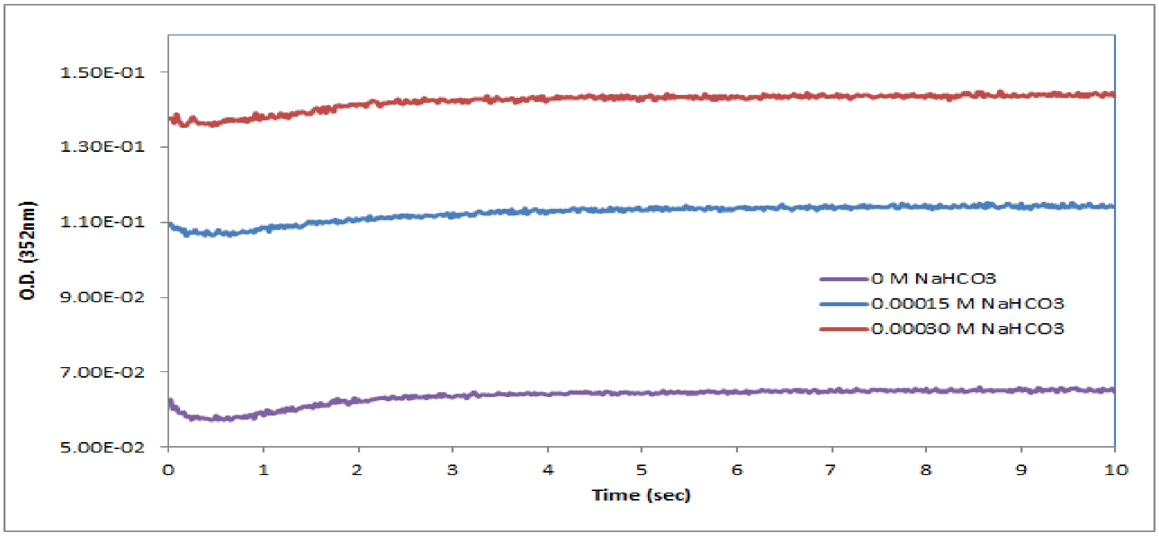


Figure S-1- Dependence of O.D. (at 352 nm) on time.

Solution composition after mixing, 1.00×10^{-2} M $Co(ClO_4)_2$, 2.50×10^{-3} M H_2O_2, pH 6.5, PIPES 1.00×10^{-1} M, ionic strength 2.31×10^{-1} M controlled by adding $NaClO_4$.

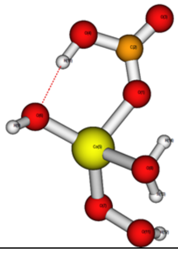
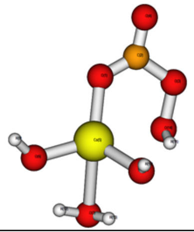
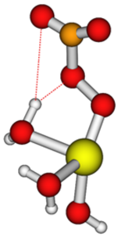
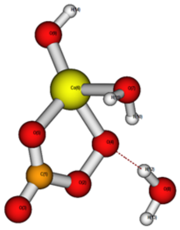
DFT calculations regarding the nature of reaction (11) products.

(S-11a) $Co(H_2O)_6^{2+} + OOH^- + CO_3^{2-} \rightarrow$ cyclic-$Co^{II}(CO_4)(H_2O)_3 + OH^- + 3H_2O$ $\Delta G^o = -37.8$ kcal/mol

(S-11b) $Co(H_2O)_6^{2+} + OOH^- + CO_3^{2-} \rightarrow Co^{II}(OOH)(CO_3)(H_2O)_2^- + 4H_2O$ $\Delta G^o = -56.3$ kcal/mol

$Co^{II}(OOH)(CO_3)(H_2O)_2^-$, the product of reaction (11) might rearrange into one of three plausible percarbonate complexes, S-11c, S-11d and S-11e. Table S-1 sums up the energy and the structure of these species.

Table S-1: Energy and structure of species S-11c, S-11d and S-11e, calculated by DFT[4-5]:

Species	formula	structure	Energy (Hartree/Particle)
Product of S-11b	$Co^{II}(OOH)(CO_3)(H_2O)_2^-$		-1950.756107
S- 11c	$Co^{II}(OH)(H_2O)_2OCO_3^-$ (Due to a shift of a proton from H_2O to the carbonate, the structure is: $Co^{II}(OH)(H_2O)OC(OOH)O^-$)		-1950.740875
S- 11d	$Co^{II}(OH)(H_2O)_2(OOCO_2)^-$		-1950.740597
S- 11e	cyclic-(CO_4)-$Co^{II}(OH)(H_2O)^- \cdot H_2O$		-1950.765967

DFT calculations regarding the nature of reactions (12) and (13) products.

$(CO_3)Co^{II}(OOH)(H_2O_2)(H_2O)^-$, the product of reaction (13), could rearrange into six plausible products, S-13a – S-13f. Table S-2 sums up the energy and the structure of these species.

(13) $(CO_3)Co^{II}(OOH)(H_2O)_2^- + H_2O_2 \rightarrow (CO_3)Co^{\mathbf{II}}(OOH)(H_2O_2)(H_2O)^-$

Table S-2: Energy and structure of species S-13a – S-13f, calculated by DFT[4-5]:

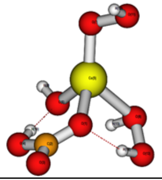
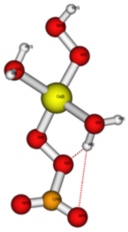
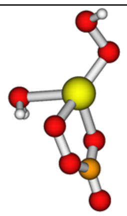
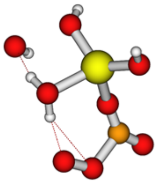
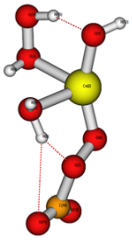
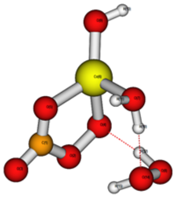
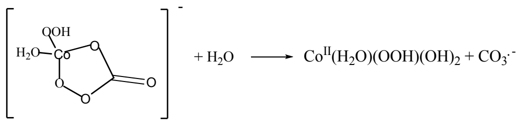
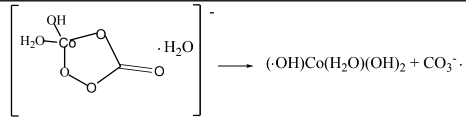
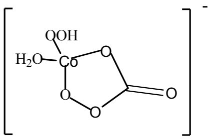
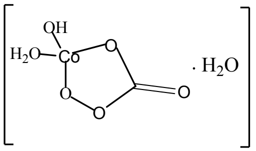
Species	formula	structure	Energy (Hartree/Particle)
Product of S-13	$(CO_3)Co^{II}(OOH)(H_2O_2)(H_2O)^-$ (Due to a shift of a proton from H_2O to the carbonate, the structure is: $(HCO_3)Co^{\mathbf{II}}(OOH)(H_2O_2)(OH)^-$)		-2025.895956
S- 13a	$Co^{II}(OOH)(H_2O)_2(OCO_3)^-$		Failed to converge
S- 13b	$Co^{II}(OOH)(H_2O)_2(OOCO_2)^-$		-2025.901514
S- 13c	cyclic-(CO_4)-$Co^{II}(OOH)(H_2O)^-$		-2025.918017
S-13d	$Co^{II}(OH)(H_2O)(\cdot OH)(OCO_3)^- \cdot (\cdot OH)$		-2025.889889
S-13e	$Co^{II}(OH)(H_2O)(H_2O_2)(OOCO_2)^-$		- 2025.887682
S-13f	cyclic-$(CO_4)Co^{II}(OH)(H_2O)^- \cdot H_2O_2$		-2025.908396

Table S-3: Spin density calculations for the reactants and products of reactions (16) and (19) by the Mulliken method[6]:

(16) 		(19) 	
Mulliken atomic spin densities for 	Mulliken atomic spin densities for $Co(H_2O)(OOH)(OH)_2$	Mulliken atomic spin densities for 	Mulliken atomic spin densities for $(\cdot OH)Co(H_2O)(OH)_2$
1 C 0.006852	1 O 0.048305 (O of H_2O)	1 C 0.009604	1 O 0.045833 (O of H2O)
2 O 0.002713	2 Co 3.055103	2 O 0.000552	2 Co 2.962027
3 O 0.002096	3 O 0.235558 (O of OH)	3 O 0.003426	3 O 0.278445 (O of OH)
4 O 0.073075	4 O 0.312338 (O of OOH, Co-O-)	4 O 0.066747	4 O 0.352179 (O of OH)
5 O 0.039601	5 O 0.293122 (O of OH)	5 O 0.039833	5 O 0.350728(O of OH)
6 Co 2.748663	6 H -0.003066	6 Co 2.782122	6 H -0.003735
7 O 0.013659	7 O 0.049478 (O of OOH, -O-H)	7 O 0.007844	7 H 0.007058
8 O 0.100880	8 H 0.001602	8 O 0.083711	8 H -0.001094
9 H 0.004941	9 H 0.005452	9 H 0.004262	9 H 0.003086
10 H 0.002130	10 H -0.000249	10 H 0.001878	10 H 0.005474
11 O 0.003717		11 H 0.000020	
Sum of Mulliken atomic spin densities = 3.00000	Sum of Mulliken atomic spin densities = 4.00000	Sum of Mulliken atomic spin densities = 3.00000	Sum of Mulliken atomic spin densities = 4.00000

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