Electronic Supplementary Information for:

The radical versus ionic mechanisms of reduced cobalamins inactivation by tert-butyl hydroperoxide and hydrogen peroxide in aqueous solution

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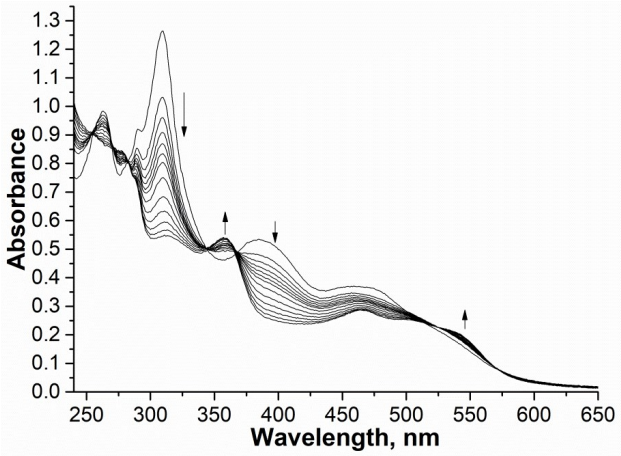


Fig. S1 UV-Vis spectra recorded during the reaction between SO_2^-Cbl(II) and hydrogen peroxide in aqueous solution (the *first step*): [SO_2^-Cbl(II)] = 5.0 ×10^{-5} M, [H_2O_2] = 0.14×10^{-3} M. pH 7.4, 25 ^{0}C, anaerobic conditions

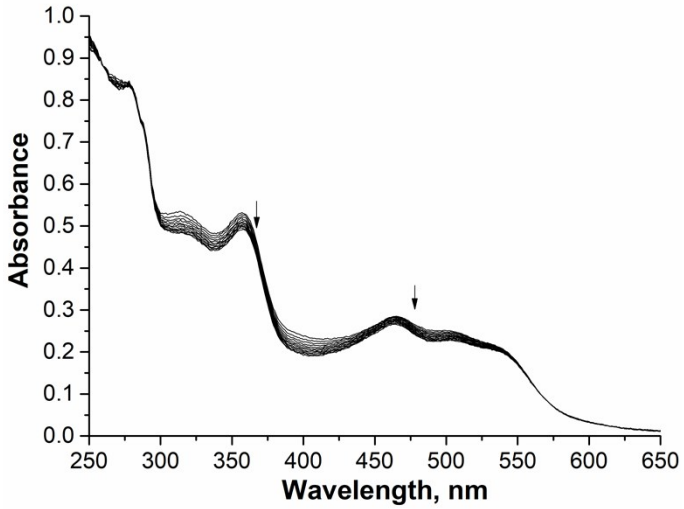


Fig. S2 UV-Vis spectra recorded during the reaction between SO_2^-Cbl(II) and hydrogen peroxide in aqueous solution (the *second step*): [SO_2^-Cbl(II)] = 5.0 ×10^{-5} M, [H_2O_2] = 0.14×10^{-3} M, pH 7.4, 25 ^{0}C, anaerobic conditions

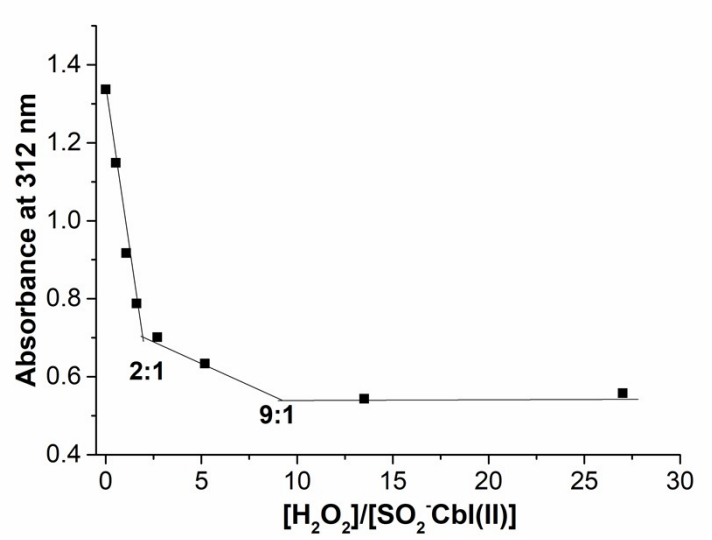


Fig. S3 Plots of absorbance at 312 nm *versus* $[H_2O_2]/[SO_2^-Cbl(II)]$ in aqueous media: $[SO_2^-Cbl(II)] = 5.0\times10^{-5}$ M, pH 7.4, 25 ^{0}C, anaerobic conditions

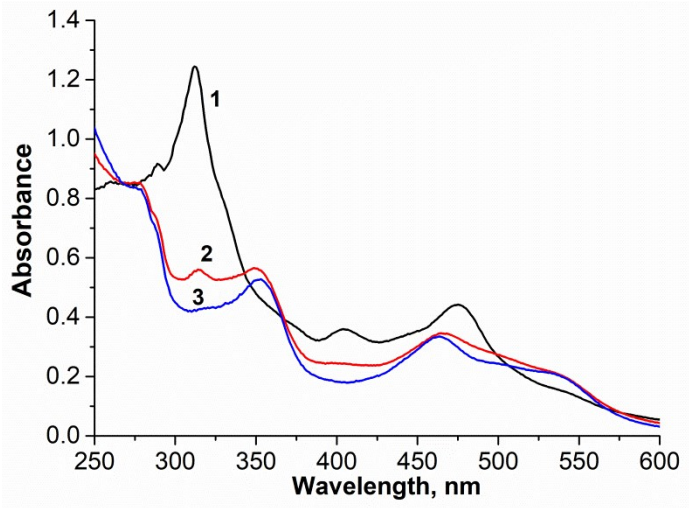


Fig. S4 UV-Vis spectra recorded during the reaction between Cbl(II) and hydrogen peroxide in aqueous solution: 1 – starting Cbl(II), 2 – product of the first step of the reaction, 3 – product of the second step of the reaction: $[Cbl(II)] = 5.0\times10^{-5}$ M, $[H_2O_2] = 0.14\times10^{-3}$ M, pH 7.4, 25 ^{0}C

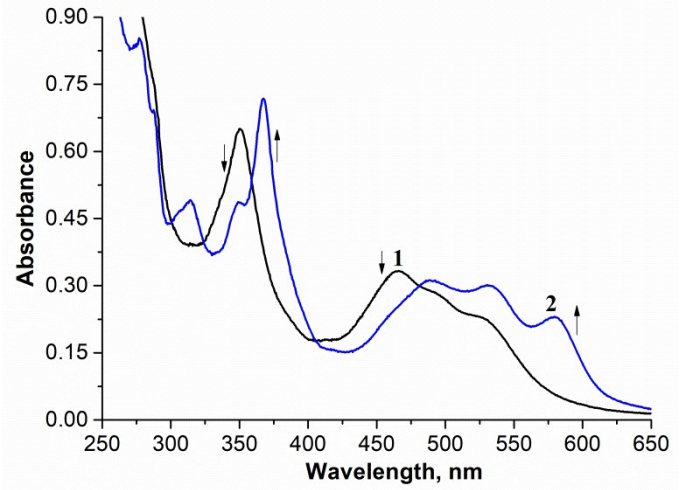


Fig. S5 UV-Vis spectra recorded before (1) and after (2) addition of an excess of sodium cyanide to product of the reaction of Cbl(II) with H_2O_2 in aqueous solution: $[Cbl(II)] = 5.0\times10^{-5}$ M, $[H_2O_2] = 0.26\times10^{-3}$ M, [NaCN] = 0 (1), 140×10^{-3} (2) M pH 7.4, 25 ^{0}C, anaerobic conditions.

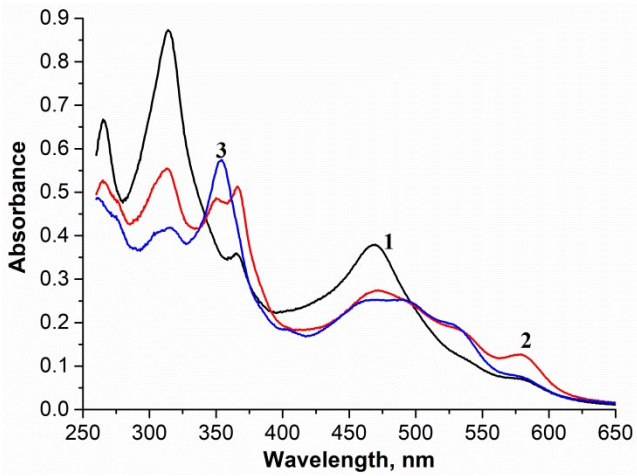


Fig. S6 UV-Vis spectral changes registered during the reaction between Cbi(II) and hydrogen peroxide: 1 – starting Cbi(II), 2 – product of the first step of the reaction, 3 – product of the second step of the reaction: [Cbi(II)] = 5.0×10^{-5} M, [H_2O_2] = 0.1×10^{-3} M, pH 7.4, 25 ^{0}C, anaerobic conditions

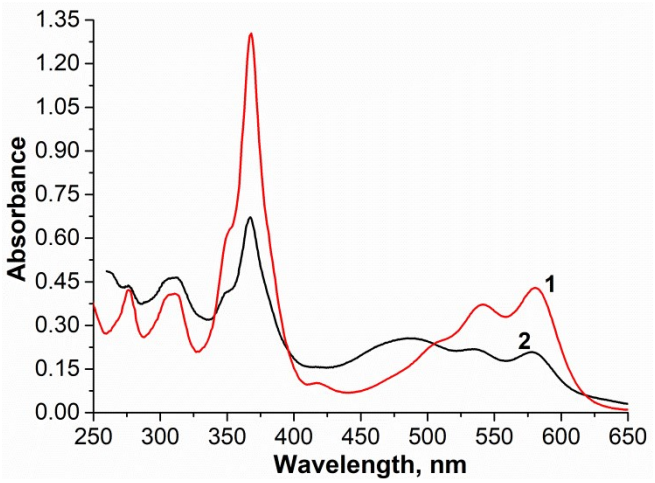


Fig. S7 UV-Vis spectra of dicyanocobinamide (1) and product of the reaction of Cbi(II) with H_2O_2, recorded after addition of an excess of sodium cyanide (2): [$(CN)_2$Cbi]=[Cbi(II)] = 4.3×10^{-5} M, [H_2O_2] = 0.26×10^{-3} M, [NaCN] = 140×10^{-3} M, pH 7.4, 25 ^{0}C

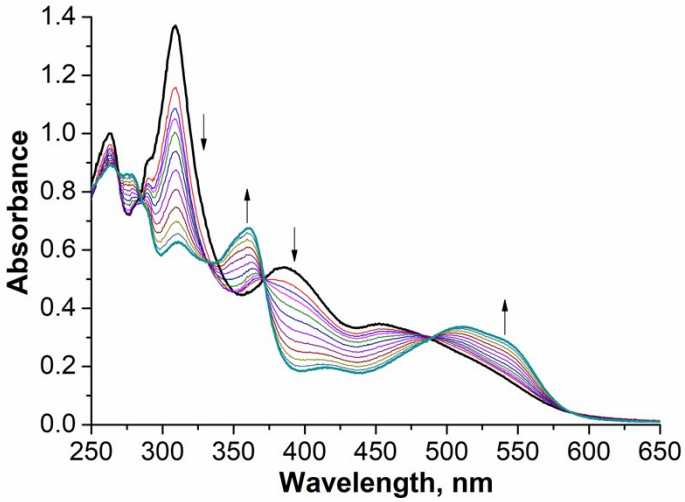


Fig. S8 UV-Vis spectral changes registered during the reaction between SO_2-Cbl(II) and tert-butyl hydroperoxide (the *first step*): [SO_2-Cbl(II)] = 4.5×10^{-5} M, [^{t}BuOOH] = 1.7×10^{-3} M, pH 7.4, 25 ^{0}C

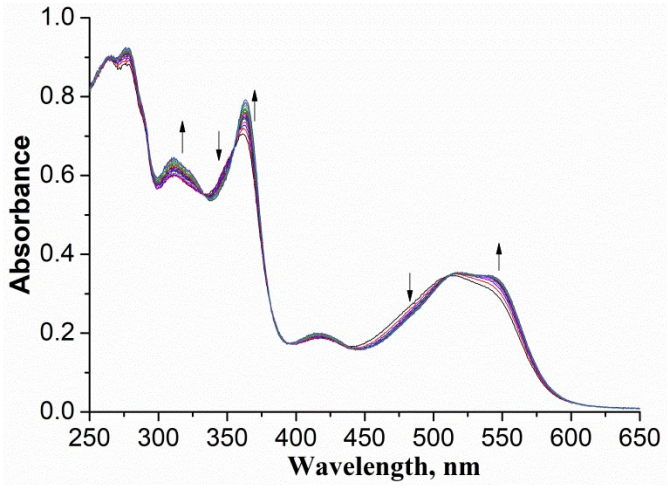


Fig. S9 UV-Vis spectral changes registered during the reaction between SO_2-Cbl(II) and tert-butyl hydroperoxide (the *second step*): [SO_2-Cbl(II)] = 4.5×10^{-5} M, [^{t}BuOOH] = 1.7×10^{-3} M, pH 7.4, 25 ^{0}C

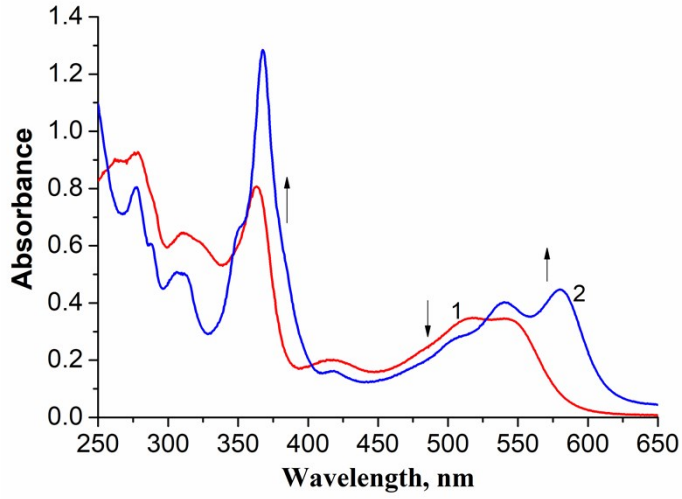


Fig. S10 UV-Vis spectral changes recorded during addition of sodium cyanide to the final product of the reaction between SO_2-Cbl(II) and ^{t}BuOOH: [SO_2-Cbl(II)] = 4.5×10^{-5} M, [^{t}BuOOH] = 1.7×10^{-3} M, [NaCN] = 0.01 M, pH 7.4, 25 ^{0}C

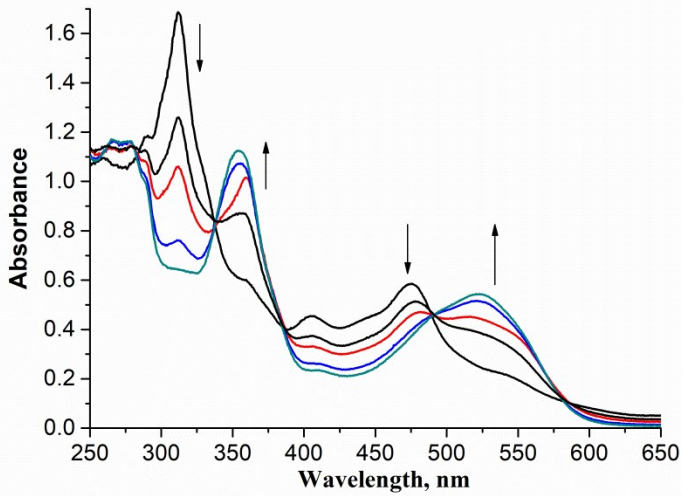


Fig. S11 UV-Vis spectral changes registered during the reaction between Cbl(II) and tert-butyl hydroperoxide: [Cbl(II)] = 6.0×10^{-5} M, [^{t}BuOOH] = 1.7×10^{-3} M, pH 7.4, 25 ^{0}C, anaerobic conditions

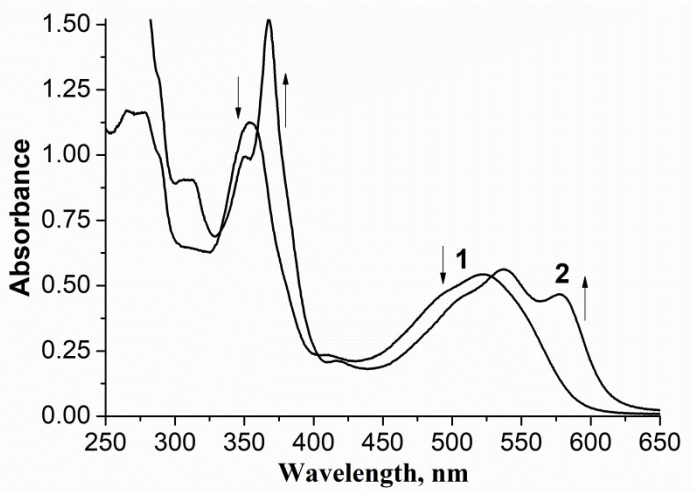


Fig. S12 UV-Vis spectra recorded before (1) and after (2) addition of sodium cyanide to the final product of the reaction between Cbl(II) and ^{t}BuOOH: [Cbl(II)] = 4.5×10^{-5} M, [tBuOOH] = 1.7×10^{-3} M, [NaCN] = 0 (1), 0.01 (2) M, pH 7.4, 25 ^{0}C, anaerobic conditions

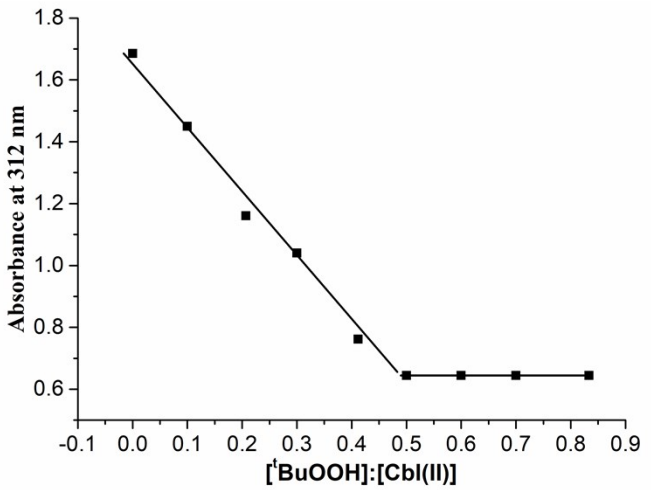
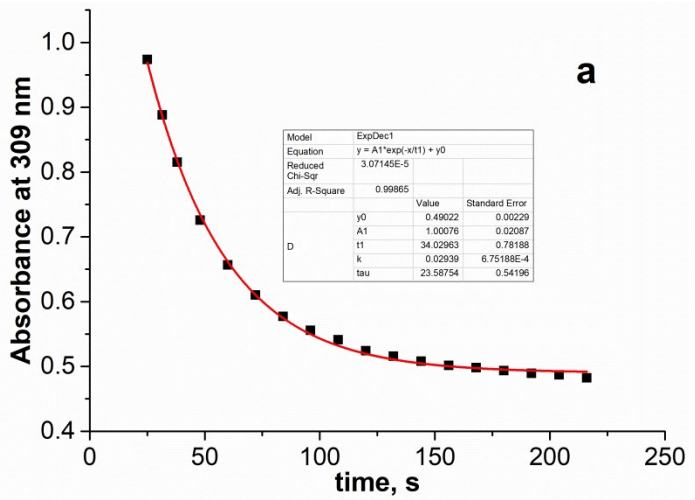


Fig. S13 Plots of absorbance at 312 nm *versus* [^{t}BuOOH]/[Cbl(II)] in aqueous media: [Cbl(II)] = 6×10^{-5} M, pH 7.4, 25 ^{0}C, anaerobic conditions



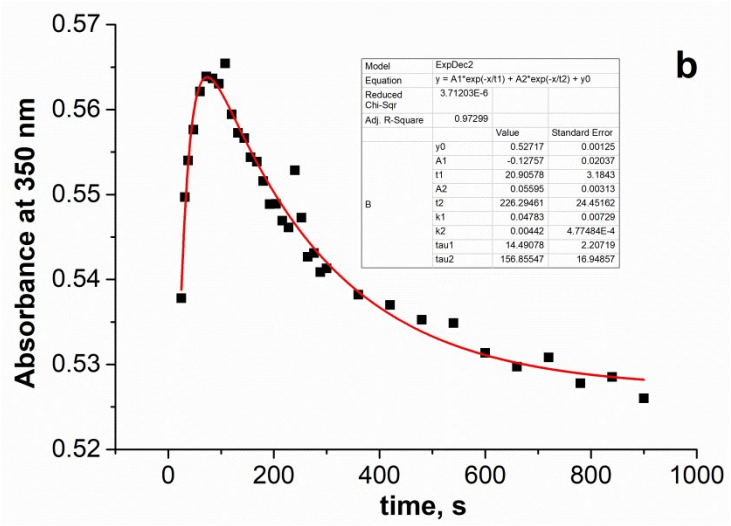


Fig. S14 Typical kinetic traces recorded at different wavelengths for the reaction of Cbl(II) with H_2O_2: [Cbl(II)] = 5.0×10^{-5} M, [H_2O_2] = 0.14×10^{-3} M, pH 7.4, 25 ^{0}C

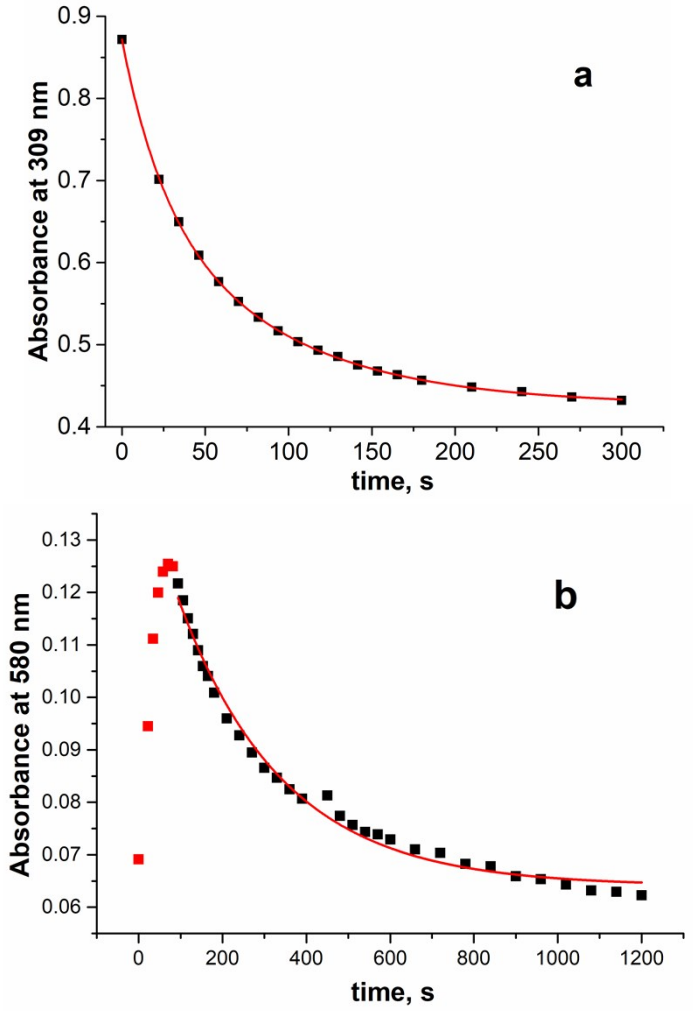


Fig. S15 Typical kinetic traces recorded at different wavelengths for the reaction of Cbi(II) with H_2O_2: [Cbi(II)] = 3.8×10^{-5} M, [H_2O_2] = 0.1×10^{-3} M, pH 7.4, 25 ^{0}C

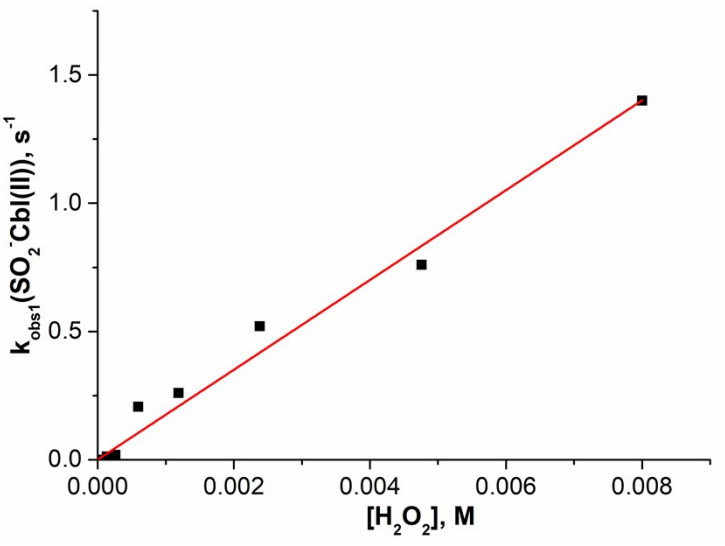


Fig. S16. Plot of $kobs_1(SO_2^-Cbl(II))$ vs $[H_2O_2]$ measured for the first step of the reaction of SO_2^-Cbl(II) with H_2O_2: $[SO_2^-Cbl(II)] = 5 \times 10^{-5}$ M, pH 7.4, 25 ^{0}C

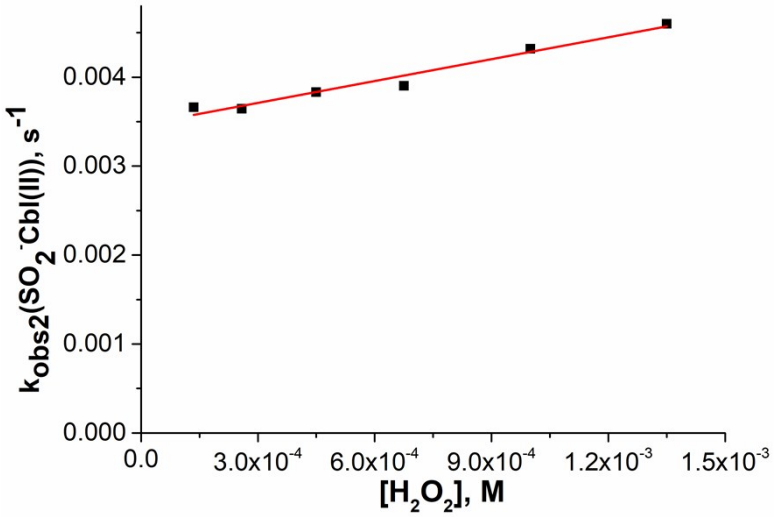


Fig. S17. Plot $k_{obs2}(SO_2^-Cbl(II))$ vs $[H_2O_2]$, measured for the second step of the reaction of SO_2^-Cbl(II) with H_2O_2: $[SO_2^-Cbl(II)] = 5 \times 10^{-5}$ M, pH 7.4, 25 ^{0}C, anaerobic conditions

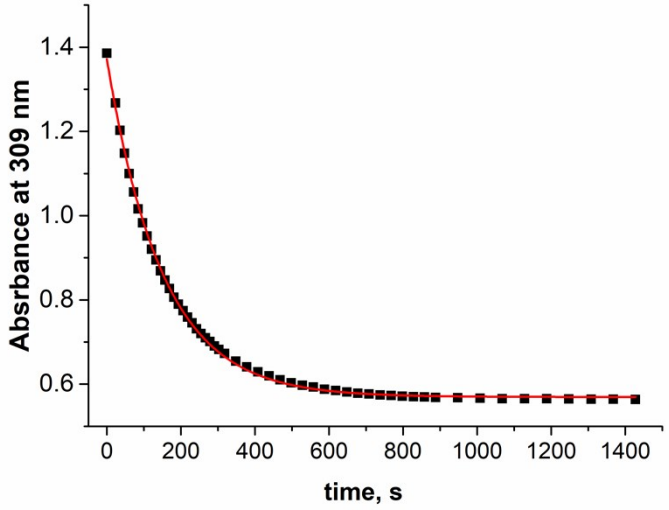


Fig. S18. Typical kinetic traces recorded for the reaction of SO_2^-Cbl(II) with ^{t}BuOOH: $[SO_2^-Cbl(II)] = 5\times10^{-5}$ M, $[^t$BuOOH$] = 0.6\times10^{-3}$ M, pH 7.4, 25 ^{0}C

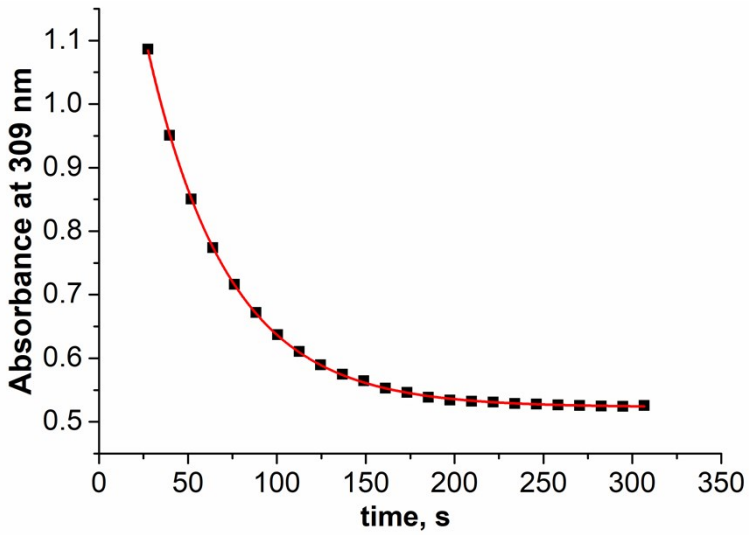


Fig. S19. Typical kinetic traces recorded for the reaction of Cbl(II) with ^{t}BuOOH: [Cbl(II)] = 5×10^{-5} M, [^{t}BuOOH] = 0.34×10^{-3} M, pH 7.4, 25 ^{0}C

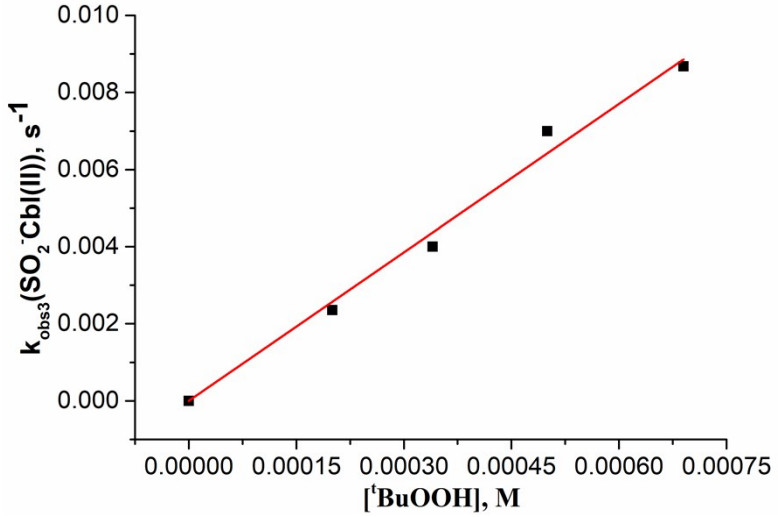


Fig. S20. Plot of $k_{obs3}(SO_2^-Cbl(II))$ versus [^{t}BuOOH] for the reaction of $SO_2^-Cbl(II)$ with ^{t}BuOOH: [$SO_2^-Cbl(II)$] = 5.0×10^{-5} M, pH 7.4, 25 ^{0}C

Table S1. Extinction coefficients of corrinoids in aqueous solution at 25 ^{0}C

Corrinoids	Wavelength, nm			
	580	367	348	313
	Extinction coefficients, L/(mol × cm)			
$(CN)_2$Cbl	10000	30400	13000	9200
$(CN)_2$Cbi	10000	30400	13372	9535
$(CN)_2$SYC1	1230	3077	9615	5000
$(CN)_2$SYC2	600	2160	2400	9200