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Reaction of hydrogen peroxide with superoxide in $[(NH_3)_5Co^{III}(\mu\text{–}O_2)Co^{III}(NH_3)_5]^{5+}$: A mechanistic study

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Contents	Page

Table S1. Stoichiometric results for the oxidation of H_2O_2 by **1**.

[**1**], mM	[H_2O_2], mM	[H_2O_2] left, mM	Δ[**1**]/Δ[H_2O_2]
5.0	7.0	4.4	1.92[a]
7.0	10.0	6.2	1.84[b]
5.5	7.0	4.2	1.96[c]
4.5	7.0	4.8	2.04[d]

Average: 1.94 ± 0.10

[a] at I = 0.1 M ($NaClO_4$), pH = 5.07, T_{OAc} = 0.20 M, T = 25.0 ^oC.

[b] at I = 0.2 M ($NaClO_4$), pH = 5.23, T_{OAc} = 0.30 M, T = 25.0 ^oC.

[c,d] at I = 0.5 M ($NaClO_4$), pH = 5.34, T_{OAc} = 0.40 M, T = 25.0 ^oC.

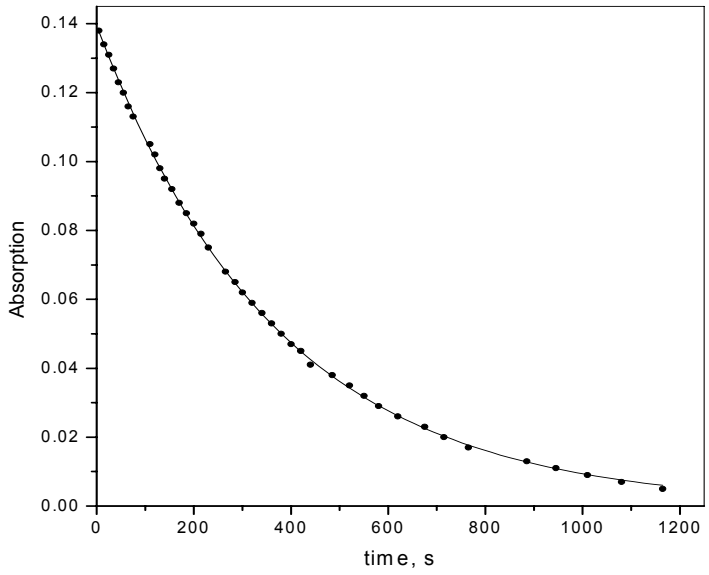

Figure S1. Kinetic profile at 670 nm for the reduction of **1** (0.20 mM) with H_2O_2 (0.50 M) at pH 5.01 (T_{OAc} = 0.20 M), I = 0.50 M ($NaClO_4$); T = 25.0 ^oC. The solid line is the first-order fit of the experimental values (shown in solid circles).

Table S2. Some representative first-order rate constants (k_{obs}) for the oxidation of hydrogen peroxide by the title complex **1** (0.2 mM) at T = 25.0 ^{o}C, T_{OAc} = 0.20 M.[a] Calculated k_{obs} values on the basis of eqn. (6) are shown in parenthesis.

pH	$[H_2O_2]$, M	I, M	$10^3 k_{obs}$, s^{-1}
4.76	0.50	0.50	1.71 (1.54)
5.01	0.50	0.50	2.70 (2.74)
5.30	0.50	0.50	5.30 (5.34)
5.46	0.50	0.50	8.10 (7.71)
5.60	0.50	0.50	10.5 (10.7)
5.85	0.50	0.50	19.1 (18.9)
6.02	0.50	0.50	28.1 (28.0)
5.01	0.20	0.50	1.20 (1.09)
5.01	0.30	0.50	1.70 (1.64)
5.01	0.40	0.50	2.20 (2.19)
5.01	0.60	0.50	3.20 (3.28)
5.01	0.70	0.50	3.70 (3.83)
5.01	0.50	1.0	2.71 (2.74)
5.01	0.50	1.5	2.80[b] (2.74)

[a] Under the experimental conditions, the superoxo complex, **1**, suffered practically no self-decomposition. We verified that in blank runs without H_2O_2, absorbance of **1** decreased by less than 1% of its initial value.

[b] $10^3 k_{obs}$ = 2.82 and 2.73 s^{-1} at T_{OAc} = 0.30 and 0.50 M respectively.

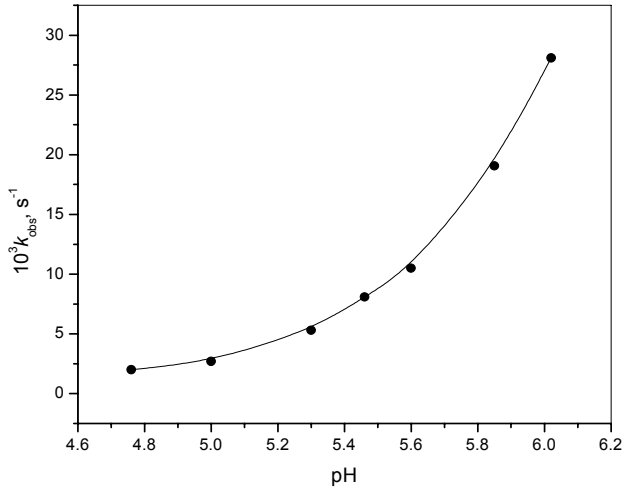

Fig. S2 Effect of acidity on k_{obs} for the oxidation of H_2O_2 (0.50 M) by **1** (0.2 mM), T_{OAc} = 0.20 M, I = 0.50 M ($NaClO_4$), T = 25.0 ^oC. The solid line is the fit of the experimental values (shown in solid circles) drawn on the basis of eqn. 6.

pH	[phenol], mM	*I*, M	$10^3 k_{obs}$, s^{-1}
4.34	2.0	0.50	0.61
4.78	2.0	0.50	1.96
5.04	2.0	0.50	2.93
5.42	2.0	0.50	6.76
5.61	2.0	0.50	9.58
5.84	2.0	0.50	18.3
5.04	4.0	0.50	5.13

Table S3. Some representative first-order rate constants (k_{obs}) for the oxidation of phenol by the title complex **1** (0.2 mM) at T = 25.0 ^{o}C, T_{OAc} = 0.20 M

5.04	6.0	0.50	7.86
5.04	8.0	0.50	9.72
5.04	10.0	0.50	12.9
5.04	2.0	0.50	2.47[a]
5.04	2.0	0.50	2.20[b]
5.04	2.0	0.50	1.99[c]
5.04	2.0	0.50	1.72[d]

[a] at 30% D_2O content

[b] at 58% D_2O content

[c] at 67% D_2O content

[d] at 90% D_2O content

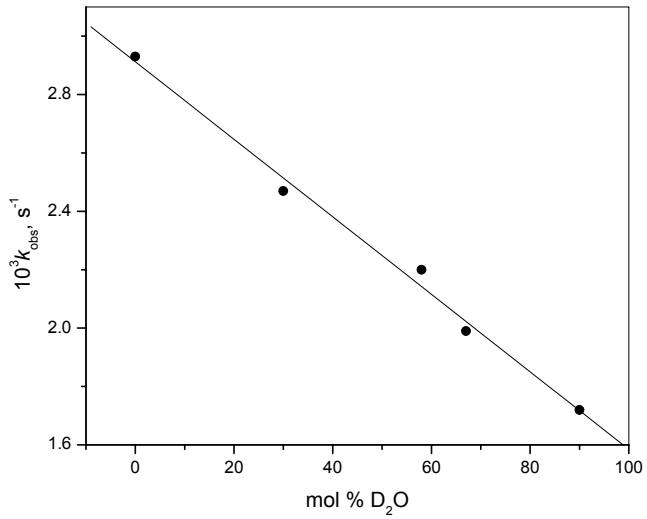

Fig. S3 Effect of mol % D_2O on k_{obs}, [**1**] = 0.20 mM, [phenol] = 2.0 mM, pH/pD = 5.01, T_{OAc} = 0.20 M, I = 0.50 M ($NaClO_4$), T = 25.0 ^oC.