Hydrogen Peroxide Adducts

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Hydrogen Peroxide Coordination to Cobalt(II) Facilitated by Second-Sphere Hydrogen Bonding

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Abstract: *$M(H_2O_2)$ adducts have been postulated as intermediates in biological and industrial processes; however, only one observable $M(H_2O_2)$ adduct has been reported, where M is redox-inactive zinc. Herein, direct solution-phase detection of an $M(H_2O_2)$ adduct with a redox-active metal, cobalt(II), is described. This $Co^{II}(H_2O_2)$ compound is made observable by incorporating second-sphere hydrogen-bonding interactions between bound H_2O_2 and the supporting ligand, a trianionic trisulfonamido ligand. Thermodynamics of H_2O_2 binding and decay kinetics of the $Co^{II}(H_2O_2)$ species are described, as well as the reaction of this $Co^{II}(H_2O_2)$ species with Group 2 cations.*

Hydrogen peroxide is an attractive and green industrial oxidant that is readily prepared from H_2 and O_2.[1,2] Applications of H_2O_2 include bleaching of cotton and wood pulp[3,4] and oxygenation of propylene to propylene oxide.[5] Oxidations by H_2O_2 often employ metal catalysts, possibly involving $M(H_2O_2)$ intermediates, as such adducts have been computationally[6–9] and kinetically[10–13] implicated. An $Fe^{III}(H_2O_2)$ species has been proposed in cytochromes P450 as or en route to the ill-defined "second oxidant", the key intermediate in a minor oxidation pathway typically overshadowed by the canonical pathway proceeding through Compound I.[14–17] A computational study by Shaik et al.[18] predicted that longevity of $Fe^{III}(H_2O_2)$ adducts in cytochromes P450 is increased when hydrogen-bonding interactions are present between bound H_2O_2 and basic moieties in the active-site pocket (**A**, Figure 1). In 2015, we reported the first $M(H_2O_2)$ adduct, a Zn^{II} species (**B**, Figure 1), made observable by incorporating second-sphere hydrogen-bonding interactions between H_2O_2 and a trianionic trisulfonamido ancillary ligand.[19] Given the presence of a redox-active metal in the putative $Fe^{III}(H_2O_2)$ species in cytochromes P450, we became interested in studying the viability of coordination of H_2O_2 to redox-active metals. Herein, we detail the first observable $M(H_2O_2)$ adduct bearing a redox-active metal.

The disproportionation of H_2O_2 into O_2 and H_2O is accelerated by redox-active metals,[1] so we anticipated that analogues of **B** incorporating redox-active metals would be shorter-lived. We chose to explore a Co^{II} analogue of **B**, as a $Co^{II}(H_2O_2)$ species (**C**, Figure 1) had recently been computationally implicated as reactive for oxidation of hydroquinone to benzoquinone.[9] As described below, our observed $Co^{II}(H_2O_2)$ species is shorter-lived than **B**, but its accessibility corroborates the existence of $M(H_2O_2)$ adducts with redox-active metals and provides a platform for developing catalysts for oxidation reactions with H_2O_2.

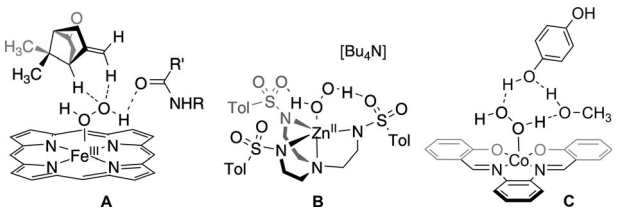
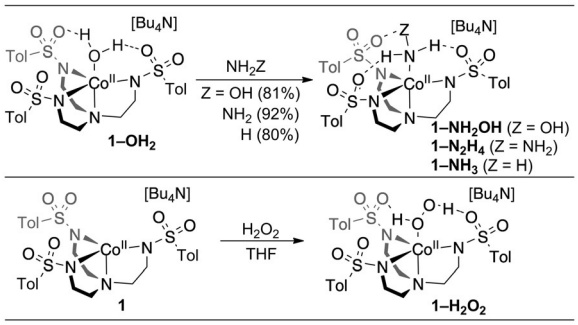


Figure 1. Computed structure[18] demonstrating the importance of hydrogen bonding in an $Fe^{III}(H_2O_2)$ species in cytochromes P450 (**A**); the first H_2O_2 coordination compound (**B**);[19] and a calculated $Co(H_2O_2)$ intermediate in aerobic hydroquinone oxidation (**C**).[9].

We initiated our studies with $[Bu_4N][(Ts_3tren)Co^{II}]$ (**1**) and $[Bu_4N][(Ts_3tren)Co^{II}(OH_2)]$ (**1-OH$_2$**)[20] (Scheme 1; $(Ts_3tren)^{3-}$ is the ancillary ligand on Zn^{II} in **B**, Figure 1). The H_2O ligand in **1-OH$_2$** is readily displaced by NH_2OH, N_2H_4, or NH_3 to afford **1-NH$_2$OH, 1-N$_2$H$_4$**, and **1-NH$_3$**, respectively. X-ray crystallographic characterization of these species[35] revealed the presence of hydrogen-bonding interactions between the sulfonyl oxygen atoms and the axial-ligand protons (Figure 2), including the protons of the distal heteroatom in N_2H_4 and NH_2OH. **1** and **1-OH$_2$** are differentiated by electronic absorption spectroscopy;[20] however, **1-OH$_2$** is not distinguishable from its 5-coordinate nitrogenous analogues **1-NH$_2$OH, 1-N$_2$H$_4$**, and **1-NH$_3$** by this technique



Scheme 1. Synthesis of **1** and **1-L**. Yields are of crystalline product.

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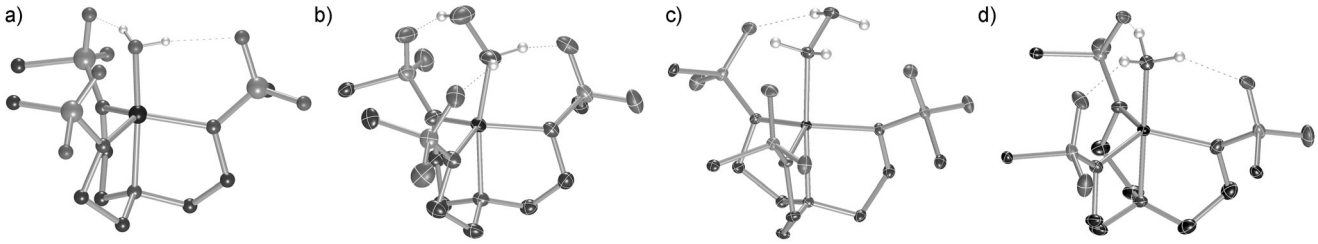


Figure 2. Structures of the anions in **1-OH$_2$** (a), **1-NH$_2$OH** (b), **1-N$_2$H$_4$** (c), and **1-NH$_3$** (d) in the crystalline state, demonstrating intramolecular hydrogen bonding with the axial ligand ([Bu$_4$N]$^+$ ions omitted).[35] Tolyl groups of the (Ts$_3$tren)$^{3-}$ ligand are truncated for clarity. Only hydrogen atoms of the axial ligands are shown. **1-OH$_2$**, which is very similar to a complex reported by Borovik et al.,[22] is an incommensurately modulated structure and is therefore represented as a ball-and-stick model.

except by band intensity, where complexes with axial nitrogen ligands show more intense d–d transitions than **1-OH$_2$** (Figure 3).

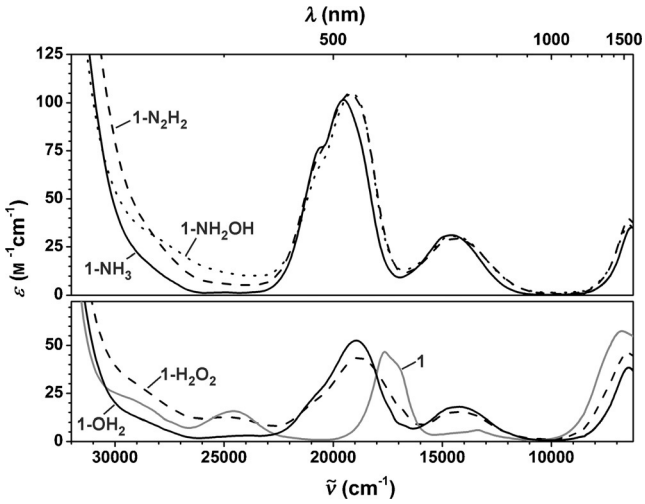


Figure 3. Electronic absorption spectra of **1-NH$_3$**, **1-N$_2$H$_4$**, **1-NH$_2$OH**, **1-OH$_2$**, **1**, and **1-H$_2$O$_2$**.

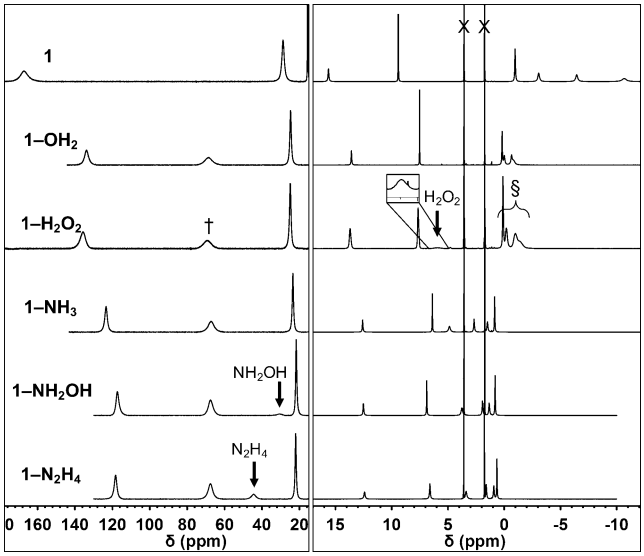


Figure 4. ^{1}H-NMR spectra (in [D$_8$]THF) of cobalt complexes scaled to show resonances for visible axial ligands (N$_2$H$_4$, NH$_2$OH, and H$_2$O$_2$), the presence of alkyl-bridge signals in the 5-coordinate complexes (†), and positions of [Bu$_4$N]$^+$ resonances (§), which are dependent on the number of second-sphere hydrogen bonds (0, 2, or 3). Residual [D$_8$]THF signals are indicated by X.

In 2015, we reported a method for accessing anhydrous H_2O_2 in THF.[19] Although we have not encountered problems with such solutions, they should be handled with care, as formation of radicals and/or organic peroxides is possible, particularly upon heating or irradiation. Addition of anhydrous H_2O_2 in THF to **1-OH$_2$** did not result in any notable changes in the electronic absorption spectrum, and addition of H_2O_2 to **1** provided an absorption spectrum of a five-coordinate Co^{II} species that was indistinguishable from that of **1-OH$_2$** (Figure 3). Despite the redox potential of **1-OH$_2$** (+78 mV vs. Fc/Fc$^+$ in CH_2Cl_2),[20] no cobalt oxidation products were spectroscopically observable on addition of H_2O_2 to **1** or **1-OH$_2$**.[21] Generation of 5-coordinate Co^{II} on addition of H_2O_2 to **1** is consistent with either formation of **1-H$_2$O$_2$** or formation of **1-OH$_2$** as a consequence of immediate H_2O_2 disproportionation by Co^{II}. Distinguishing between these possibilities required a method of directly detecting H_2O_2 in these **1**/H_2O_2 solutions. Despite the paramagnetic nature of the complexes studied, ^{1}H NMR spectroscopy proved a viable technique for studying coordination of H_2O_2 to **1** (Figure 4).

^{1}H NMR resonances associated with **1-L** were assigned by comparing spectra of related complexes (see the Supporting Information). All 5-coordinate Co^{II} species showed a CH_2 resonance near 65 ppm, and the presence of this signal in a solution containing H_2O_2 and **1** (†, Figure 4) corroborates the electronic absorption data (Figure 3) revealing a 5-coordinate Co^{II} ion. The positions of the Bu proton resonances of the [Bu$_4$N]$^+$ counterion are affected by the presence of axial ligands on cobalt. In the ^{1}H NMR spectrum of **1**, the Bu signals are spaced between 1 and −11 ppm, where the large paramagnetic shifting is consistent with interaction between the [Bu$_4$N]$^+$ cation and the cobalt complex in solution, likely through hydrogen bonding between the α-hydrogen atoms on Bu and the sulfonyl oxygen atoms as seen in the solid state. For derivatives **1-L** with three second-sphere hydrogen bonds (**1-NH$_2$OH**, **1-NH$_3$**, and **1-N$_2$H$_4$**) the Bu signals are less paramagnetically shifted (0 to 5 ppm), consistent with axial coordination disrupting hydrogen bond-

ing between the ions in solution. For **1-OH$_2$**, which only contains two second-sphere hydrogen bonds, the Bu proton resonances overlap between 1 and −1 ppm. When anhydrous H_2O_2 is combined with **1**, the Bu proton resonances appear between 1 and −2 ppm, similar to **1-OH$_2$** (§, Figure 4). These data suggest that the axial ligand in a solution of **1** and anhydrous H_2O_2 is diprotic, which could be explained by binding of H_2O or H_2O_2. For complexes **1-OH$_2$** and **1-NH$_3$**, the proton resonances corresponding to the axial ligand are not observable by ^{1}H NMR spectroscopy, even upon addition of excess ligand (see the Supporting Information). However, ^{1}H NMR spectra of **1-N$_2$H$_4$** and **1-NH$_2$OH** show signals at 44 ppm and 30 ppm, respectively, corresponding to the axial-ligand protons (Figure 4). The spectrum of a solution of **1** and anhydrous H_2O_2 contains a broad signal at 5.9 ppm (Figure 4). Over time, this signal shifts to 8.8 ppm (closer to that of free H_2O_2 at 9.4 ppm) and decreases in intensity following a first-order pathway with a half-life of (353 ± 33) s (Figure 5). This

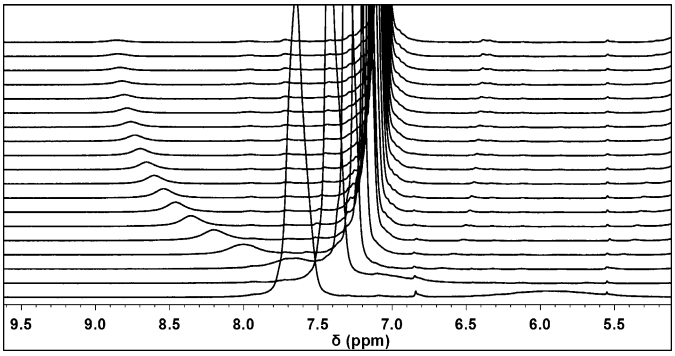


Figure 5. Room-temperature decay of **1-H$_2$O$_2$** measured by ^{1}H NMR spectroscopy (in [D$_8$]THF). The H_2O_2 resonance shifts from 5.9 ppm to 8.8 ppm. The decay product was confirmed by X-ray crystallography to be **1-OH$_2$**.[35] The tall signal at 7.7 ppm shifting to 7.1 ppm is a methyl group on the sulfonamidate ligand.

shifted H_2O_2 resonance is the first direct evidence that H_2O_2 is binding to Co^{II} in **1**, as the ^{1}H NMR and electronic spectra demonstrate that Co^{II} is five-coordinate under these conditions. The decay product of **1-H$_2$O$_2$** was identified as **1-OH$_2$** by crystallization of the bulk material. The shifting H_2O_2 resonance throughout decay of **1-H$_2$O$_2$** points to an equilibrium between free and bound H_2O_2 that is perturbed by H_2O formed upon H_2O_2 disproportionation, leading us to examine the equilibrium constants of binding H_2O_2 and H_2O to **1**.

To probe whether H_2O_2 binding is perturbed by the presence of H_2O, H_2O_2 was added to **1-OH$_2$** and its decay monitored by ^{1}H NMR spectroscopy. Initially, the H_2O_2 resonance appeared at 8.8 ppm (c.f. 5.9 ppm in the absence of H_2O) and then shifted toward 9.1 ppm [$t_{1/2}$ = (1190 ± 10) s]. When H_2O_2 was added to **1-NH$_3$**, the H_2O_2 resonance remained at 9.5 ppm and decayed with a half-life of (13 700 ± 200) s. These data are consistent with H_2O_2 disproportionation occurring upon coordination to **1**, and with H_2O_2 being a weaker ligand for **1** than H_2O or NH_3, consistent with descriptions of H_2O_2 as a very poor ligand.[23–27] The first-order decay of **1-H$_2$O$_2$** contrasts the second-order decay mechanism of **B**, which bears the same ligand and counterion, and at the same starting concentration has a half-life of 10^4 s.[19] This comparison suggests that the redox-active nature of M has a dramatic effect on the stability of M(H_2O_2) species.

We sought to quantify binding affinities of **1** for H_2O and H_2O_2. H_2O_2 has been described as a poor ligand[23–27] such that its coordination to metals was not unambiguously detected until 2015.[19] Prikhodchenko et al. demonstrated that H_2O_2 is a more effective hydrogen-bond donor than H_2O, clarifying the importance of second-sphere hydrogen bonding in H_2O_2 coordination.[27–30] Because of the short lifetime of **1-H$_2$O$_2$**, we turned to photometric titrations using electronic absorption spectroscopy to determine the binding constants for H_2O and H_2O_2 to **1** at −70 °C, as decay of **1-H$_2$O$_2$** cannot be detected within one hour at temperatures below −40 °C by NMR spectroscopy. Titration of **1** with H_2O or anhydrous H_2O_2 in THF at −70 °C afforded the curves shown in Figure 6, from which K_{eq} values for the coordination of H_2O_2 and H_2O to **1** are derived: (31.3 ± 0.2) M^{-1} and (31 600 ± 12 600) M^{-1} at −70 °C, respectively. These data establish a preference for binding of **1** to H_2O over H_2O_2, where K_{eq} for displacing H_2O_2 in **1-H$_2$O$_2$** by H_2O at −70 °C is (1010 ± 400) ($\Delta G = -2.8$ kcal mol^{-1}). To our knowledge, this is the first H_2O_2/metal binding constant measured.

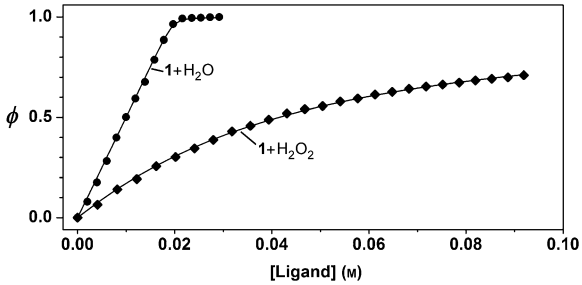
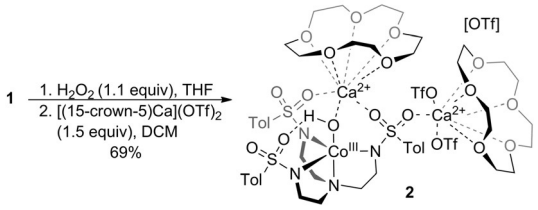


Figure 6. Photometric titrations of **1** with H_2O and H_2O_2 in THF at −70 °C. Data are plotted as fractional saturation vs. concentration of the ligand (H_2O or H_2O_2). The curves, which are nonlinear fits to the data, enable calculation of K_{eq} [(3.16 ± 1.26) × 10^4 M^{-1} for H_2O and (31.3 ± 0.2) M^{-1} for H_2O_2).

Finally, we probed the reactivity of **1-H$_2$O$_2$**. Borovik et al. reported that a species closely related to **1** is inert to PhIO, but upon addition of Group 2 ions, oxidation of the Co^{II} center by PhIO afforded an isolable Co^{III}(μ-OH)Ca^{2+} species.[22] This transformation may involve a transient Co^{IV} intermediate, as redox-inert cations are known to facilitate two-electron oxidation of Co^{II} to Co^{IV}.[31,32] We probed whether Group 2 ions could similarly promote cobalt oxidation and cleavage of the O–O bond of H_2O_2 in **1-H$_2$O$_2$**. We have shown that **1** and related species react readily with Group 2 ions to afford heterotrimetallic sandwich compounds.[20] Addition of M(OTf)$_2$ (M = Ca^{2+}, Sr^{2+}, or Ba^{2+}) to **1-H$_2$O$_2$** resulted in rapid conversion into intensely green products, each with nearly identical electronic absorption spectra. The spectroscopic properties of these green species did not satisfactorily agree with Borovik's report of a red-brown Co^{III}(μ-OH)Ca^{2+} species;[22] however, combination of [(15-crown-5)Ca](OTf)$_2$

and **1-H_2O_2** afforded X-ray-quality crystals of a Co^{III}(μ-OH)Ca^{2+} complex (**2**, Scheme 2),[35] demonstrating Group 2 ion induced oxidation of Co^{II} to Co^{III} by H_2O_2. The oxidation potential of **1-OH_2** is +78 mV vs. Fc/Fc^+ in CH_2Cl_2,[20] so the oxidative stability of the Co^{II} ion in **1-H_2O_2** suggests that one-electron redox processes involving **1-H_2O_2** are not preferred.



Scheme 2. Reaction of **1-H_2O_2** with Ca^{2+} to form **2**. The crystal structure analysis of **2** is included in the Supporting Information. DCM: dichloromethane.

We expect that the Group 2 ions are brought into close proximity with coordinated H_2O_2 in **1-H_2O_2**, as we[20] and Borovik et al.[22,33] have shown that such sulfonyl oxygen atoms bind Group 2 metal ions without significantly impacting the electronic properties of Co^{II}. We hypothesize that the Group 2 ion induced oxidative conversion of **1-H_2O_2** into **2** may involve a transient Co^{IV}(oxo)/Ca^{2+}(OH_2) or Co^{IV}(OH)/Ca^{2+}(OH) species that rapidly reacts with a hydrogen-atom donor, likely THF, to afford the observed Co^{III} species **2**. Rapid decomposition of Co^{IV} has been demonstrated in the instability of related Co^{IV}(oxo)[22,31,32] and Co^{IV}(nitrido)[34] species. Regardless of mechanism, the Group 2 ion induced conversion of **1-H_2O_2** into **2** provides a new approach to H_2O_2 activation involving coordination to one metal center and activation by a second metal center. We are currently exploring this dual activation of H_2O_2 for use in oxidation catalysis.

In summary, we have obtained the first direct evidence for formation of an M(H_2O_2) complex with a redox-active metal. Mixing **1** and anhydrous H_2O_2 resulted in coordination of an axial ligand to cobalt(II) at temperatures where H_2O_2 is not disproportionated by **1**, and low-temperature photometric titration of **1** with H_2O_2 or H_2O, as well as decay kinetics of **1-H_2O_2** in the presence of H_2O, revealed that H_2O_2 is a weaker ligand for the Co^{II} center in **1** than H_2O. **1-H_2O_2** is stable to oxidation of the Co^{II} center, but addition of [(15-crown-5)Ca]$(OTf)_2$ induced oxidation to afford the Co^{III}(μ-OH)Ca^{2+} complex **2**. Activation of coordinated H_2O_2 by a secondary metal is a novel approach to developing oxidation reactions with H_2O_2, and our efforts on expanding the coordination chemistry of H_2O_2 and exploiting the reactivity of M(H_2O_2) adducts are on-going.

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Keywords: cobalt · hydrogen bonds · peroxides · peroxido ligands · second-sphere interactions

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[35] CCDC 144760 (**1-OH$_2$**), 144761 (**1-N$_2$H$_4$**), 144762 (**1-NH$_2$OH**), 144763 (**2**), and 1489712 (**1-NH$_3$**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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