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Ambiphilicity of a mononuclear cobalt(III) superoxo complex†

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Addition of HOTf to a mixture of $Co^{III}(BDPP)(O_2^{\bullet})$ (1, H_2BDPP = 2,6-bis((2-(*S*)-diphenylhydroxylmethyl-1-pyrrolidinyl)methyl)pyridine) and $Cp^*{}_2Fe$ produced H_2O_2 in high yield implying formation of $Co^{III}(BDPP)(OOH)$ (3), and reaction of $Sc(OTf)_3$ with the same mixture gave a peroxo-bridged Co^{III}/Sc^{III} 5. These findings demonstrate the ambiphilic property of Co^{III}-superoxo 1.

Metal-superoxo species are often believed to be the first intermediate following dioxygen (O_2) association in the catalytic cycle of O_2 activating metalloenzymes.[1] Despite intensive work in the past, the chemistry of metal-superoxo complexes remains largely unexplored, and hence attracts significant attention from chemists and biochemists.[2] *Inter alia*, metal-superoxo intermediates can react with $NO^{\bullet}$ or organic radicals to furnish metal-peroxynitrite[3] and -alkylperoxo[4] complexes *via* radical coupling. Furthermore, they exhibit considerable electrophilicity as indicated by their capability of performing hydrogen atom abstraction (HAA)[5] from weak C–H and O–H bonds and oxygen atom transfer[6] to triphenylphosphine or thiol anisoles. On the other hand, they can initiate deformylation processes when treated with 2-phenylpropionaldehyde, thereby revealing their nucleophilic character.[7,8] Besides the aforementioned well know activities, in a given elementary transformation metal-superoxo intermediates may function not only as an electrophile but also as a nucleophile. In fact, ambiphilicity of metal-superoxo species has been postulated in a series of theoretical and experimentally investigations including O_2 activation catalyzed by α-ketoglutarate dependent dioxygenases,[9] and by Cu, Fe and Co model complexes.[10] Only recently has such ambiphilic property been experimentally confirmed.[8] In our continuing efforts devoted to investigating reactivity of metal-superoxo intermediates, some of us succeeded in preparing a range of homologous Fe^{III}-, Co^{III}- and Mn^{III}-superoxo species by reacting O_2 with the corresponding divalent precursors.[11] It has been shown that these trivalent metal-superoxo complexes can convert into the metal-hydroperoxo complexes *via* HAA. In particular, the reaction of $Mn^{III}(BDP^{Br}P)(O_2^{\bullet})$ ($H_2BDP^{Br}P$ = 2,6-bis((2-(*S*)-di(4-bromo)-phenylhydroxylmethyl-1-pyrrolidinyl)methyl)pyridine) with trifluoroacetic acid (TFA) and $Sc(OTf)_3$ yields rare examples of Mn^{IV}-hydroperoxo complexes, $Mn^{IV}(BDP^{Br}P)(OOH)$, and $[Mn^{IV}(\mu\text{-}OO)Sc(OTf)_n]^{(3-n)+}$ as evidenced by the combined spectroscopic and computational studies (Scheme 1).[8] Obviously, these proton- and metal-coupled electron transfer processes provide the first experimental support for the proposed ambiphilicity of metal-superoxo species. In this regard, more examples are desired to fully understand how the ambiphilic property of metal-superoxo species affects their chemical reactivity. To this end, we examined the reaction of a Co^{III}-superoxo complex, $Co^{III}(BDPP)(O_2^{\bullet})$ (**1**, H_2BDPP = 2,6-bis((2-(*S*)-diphenylhydroxylmethyl-1-pyrrolidinyl)methyl)pyridine) with TFA and $Sc(OTf)_3$ together with external electron donors.

Treating **1** with HOTf in THF at −90 °C gave a gray-green solution attributed to intermediate **2** having two weak absorption bands at 470 and 640 nm, which reached maxima when 1 equiv. of HOTf was added (the inset of Fig. 1). The existence of an isosbestic point at 590 suggested that no intermediate was formed in the course of conversion of **1** to **2** (Fig. 1). Conversely, complex **1** can be retrieved from deprotonation of **2** by 1 equiv. of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with a yield of 80% with respect to **1** (Fig. S1, ESI†). Moreover, complex **2** can be obtained from one-electron oxidation of the hydroperoxo complex $Co^{III}(BDPP)(OOH)$ (**3**). Adding equimolar of tris(4-bromophenyl)ammoniumyl hexachloroantimonate, which is often referred to as magic blue, to a THF solution of **3** at −90 °C resulted in a gray-green solution, whose

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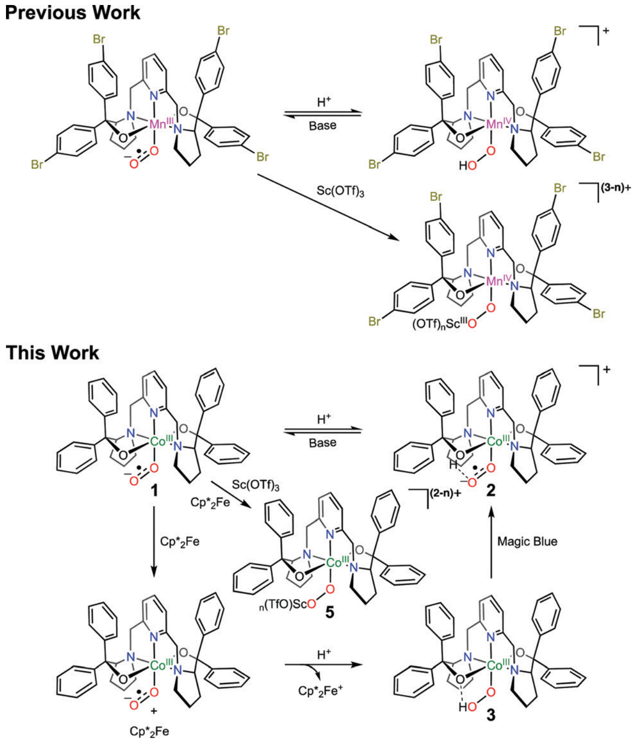

Scheme 1 Ambiphilicity of metal-superoxo complexes.

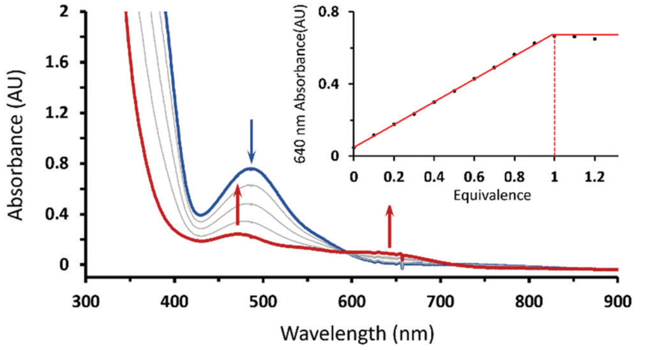

Fig. 1 UV-vis spectral changes of the reaction of **1** (1.0 mM, blue trace) with 1 equiv. of HOTf in THF at −90 °C. Inset: Titration curve of **1** with HOTf. *X*-axis: the equivalents of HOTf, *Y*-axis: the conversion ratio of the absorption peak at 640 nm.

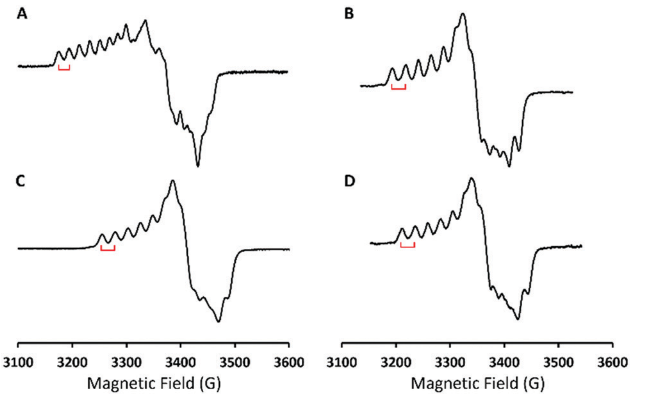

Fig. 2 X-band EPR spectra of (A) **1** (g_1 = 2.098, A_{Co} = 18 G); (B) **1** with 1 equiv. of HOTf (g_1 = 2.066, A_{Co} = 24 G); (C) **1** with 1 equiv. of DOTf (g_1 = 2.064, A_{Co} = 24 G) and (D) **1** with 1 equiv. of Sc(OTf)$_3$ (g_1 = 2.066, A_{Co} = 24 G). Measurement condition: T = 77 K, f_{mw} = 9.6 GHz.

absorption spectrum displayed the same signature features as those found for **2** (Fig. S2, ESI†).

To identify the exact nature of the resulting species **2**, we have undertaken detailed spectroscopic characterization and DFT calculations. The EPR measurement of **2** exhibited a spectrum similar to that of **1** (A_{Co} = 18 G) except for a slightly larger ^{59}Co hyperfine coupling constant (A_{Co} = 24 G) seen in Fig. 2, thus indicating that **2** still consists of a Co^{III} center coupled with a radical ligand yielding an overall doublet ground state. The radical ligand thus would be a hydroperoxyl radical or a superoxo having a strong hydrogen bonding interaction with the protonated BDPP^{2-} ligand (Scheme 1) as suggested by the crystal structure of **3**.[11b] However, the EPR spectrum of the product generated by reacting **1** with deuterated triflate acid (DOTf) is almost identical to that of **2** without discernable line broadening, which essentially rules out the possibility of the radical ligand being a hydroperoxyl radical (Fig. 2C). Repeated attempts to obtain the O–O vibrational frequencies of **2** from resonance Raman measurements did not accomplish, largely because **2** has only weak chromophores in the usual UV-vis region (Fig. 1). Consequently, the intensity of the O–O stretching signal is too low to be readily detected.

DFT calculations also suggested the O donor of the BDPP^{2-} ligand to be the favored protonation site of **1**, consistent with experiment. Even when the starting geometry contained a OOH ligand in which the distal H atom forms a hydrogen bond with the BDPP^{2-} ligand, the geometry optimizations invariably shifted the H atom back to the O atom of BDPP^{2-} and eventually converged to **A** (Fig. 3). We also tested the initial geometry without the hydrogen bond by tilting the H atom upward. The computations indeed yielded a Co^{III} center bound to a hydroperoxyl radical ligand (**C**), but **C** lies 23.2 kcal mol^{-1} higher in energy above **A** (Fig. 3). Moreover, formation of a hydrogen bond between the superoxo motif and the proton of the OH group of the protonated BDPP^{2-} ligand stabilized **A** by 10.4 kcal mol^{-1} relative to **B** (Fig. 3). Thus, **A** is best deemed as the most appropriate model for **2**.

Alternatively, to transform **1** into the corresponding peroxo product, we then added 1 equiv. of decamethylferrocene (Cp*$_2$Fe) or sodium naphthalenide (NaC$_{10}$H$_8$) to THF solutions of **1** at −90 °C, but UV-vis measurements suggested that no reactions occurred (Fig. S3 and S4, ESI†). Taken together, neither proton nor electron donors alone can realize the superoxo-to-peroxo conversion for **1**.

Interestingly, upon treating a mixture containing equimolar **1** and Cp*$_2$Fe with 1 equiv. of HOTf, the color of the reaction solution gradually changed from gray-green to dark green then orange; meanwhile, characteristic features of decamethylferrocenium (Cp*$_2$Fe$^+$) emerged suggesting that Co^{III}-superoxo **1** was reduced in the presence of both HOTf and Cp*$_2$Fe (Fig. 4A).

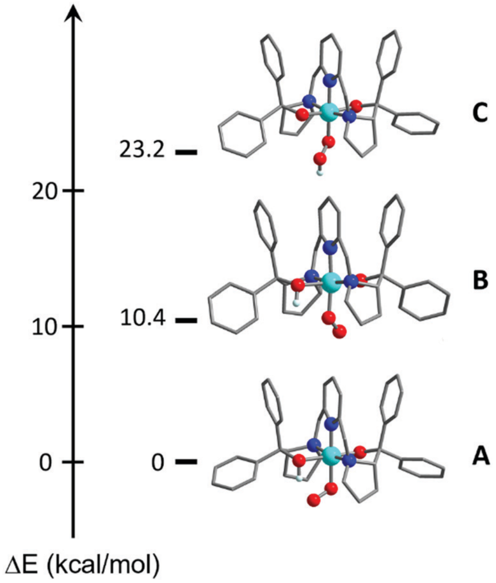

Fig. 3 Computed models for **2**.

During this process, we did not observe the formation of Co^{III}-hydroperoxo **3**. Instead, the reaction produced 19% of H$_2$O$_2$ with respect to **1**, as determined by iodometric titration (Fig. S5, ESI†). When 2 equiv. of HOTf was added, 42% of H$_2$O$_2$ was furnished (Fig. S6, ESI†). Thus, we reasoned that the aforementioned reaction indeed generates **3**; however, once formed, **3** further reacted with HOTf to produce H$_2$O$_2$. On the other hand, treating **2** with 1 equiv. of Cp*$_2$Fe (Fig. 4B) also generated 23% of H$_2$O$_2$ (Fig. S7, ESI†). Therefore, all experimental findings revealed that transformation of **1** to **3** proceeds *via* concerted proton coupled electron transfer, which clearly demonstrated the ambiphilicity of **1**.

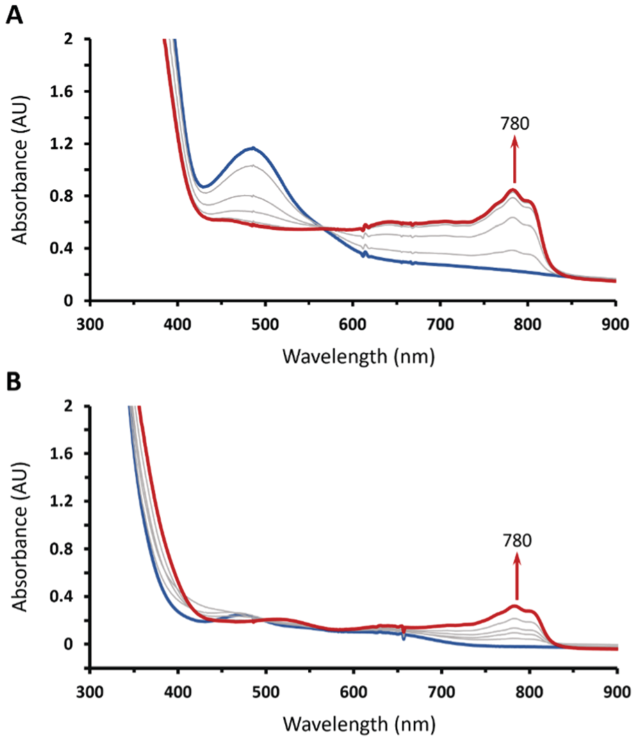

Fig. 4 UV-vis spectral changes of addition of (A) 1 equiv. of HOTf into a solution of **1** (1.0 mM) in the presence of 1 equiv. of Cp*$_2$Fe and (B) 1 equiv. of Cp*$_2$Fe into a solution of **2** (1.0 mM) in THF at −90 °C.

Reaction of **1** with Sc(OTf)$_3$ in THF at −90 °C generated a product, which showed nearly identical absorption and EPR spectra to those of **2** (Fig. S8 (ESI†) and Fig. 2D). On the basis of these observations, we tentatively suggest that the reaction furnished a Co^{III}-superoxo···Sc^{III} species, [Co(BDPP)(O$_2^{\bullet}$)···Sc(OTf)$_n$]$^{(3-n)+}$ (**4**). Furthermore, addition of Sc(OTf)$_3$ to the mixture of **1** and Cp*$_2$Fe in THF at −90 °C afforded a Co^{III}-peroxo-Sc^{III} complex, [Co(BDPP)(μ-OO)Sc(OTf)$_n$]$^{(2-n)+}$ (**5**), as depicted in Scheme 1 (Fig. S9, ESI†). Addition of 2 equiv. of HOTf to the THF solution of **5** produced 76% H$_2$O$_2$ as quantified by iodometric titration experiments (Fig. S10, ESI†). Formation of H$_2$O$_2$ thus strongly supports the identity of peroxo-bridged binuclear **5**. These findings further reinforce the ambiphilic property of **1**.

In comparison with the similar reaction found for Mn^{III}(BDP^{Br}P)(O$_2^{\bullet}$) (Scheme 1), the difference can be readily attributed to the much higher oxidation potential of Co^{III} to Co^{IV} than that of Mn^{III} to Mn^{IV}, which can ultimately be rooted back to the distinct effective nuclear charge of low spin Co^{III} compared to high spin Mn^{III} centers. Therefore, formation of an otherwise hydroperoxo O–H bond does not provide a sufficient driving force to trigger an electron transfer from the Co^{III} center to the superoxo ligand. Consequently, the superoxo motif is not electron rich enough to accommodate the incoming proton from HOTf and protonation of the supporting BDPP^{2-} ligand is preferred. Therefore, to effect surperoxo-to-peroxo conversion for **1**, an external electron source has to be provided in addition to Brønsted or Lewis acids.

In conclusion, treatment of Co^{III}-superoxo **1** with HOTf and Sc(OTf)$_3$ afforded the ligand-protonated Co^{III}-superoxo **2** with a hydrogen bond formed between the O$_2^{\bullet-}$ motif and the protonated BDPP^{2-} ligand and a superoxo-bridged binuclear Co^{III}/Sc^{III} **4**, and Co^{III}-superoxo **1** can be regenerated from deprotonation of **2** by DBU. However, addition of 2 equiv. of HOTf into the reaction mixture of **1** and Cp*$_2$Fe produced 42% of H$_2$O$_2$ suggesting the formation of Co^{III}-hydroperoxo **3**, and the reaction of Sc(OTf)$_3$ with **1** in the presence of Cp*$_2$Fe gave a peroxo-bridged binuclear Co^{III}/Sc^{III} **5**. These findings provided strong experimental support for the ambiphilic property of Co^{III}-superoxo **1**. Interestingly, the ligand-protonated Co^{III}-superoxo **2** can be prepared from one-electron oxidation of Co^{III}-hydroperoxo **3**. The unveiled results underline the critical property of ambiphilicity for metal-superoxo species and direct us to design further investigation strategies towards better understanding O$_2$ activation processes carried out by metalloenzymes and related catalysts.

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Conflicts of interest

There are no conflicts to declare.

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