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**Addition of HOTf to a mixture of  $\text{Co}^{\text{III}}(\text{BDPP})(\text{O}_2^{\bullet})$  (1,  $\text{H}_2\text{BDPP} = 2,6\text{-bis}((2\text{-}(S)\text{-diphenylhydroxymethyl-1-pyrrolidinyl)methyl)pyridine)$  and  $\text{Cp}^*\text{Fe}$  produced  $\text{H}_2\text{O}_2$  in high yield implying formation of  $\text{Co}^{\text{III}}(\text{BDPP})(\text{OOH})$  (3), and reaction of  $\text{Sc}(\text{OTf})_3$  with the same mixture gave a peroxy-bridged  $\text{Co}^{\text{III}}/\text{Sc}^{\text{III}}$  5. These findings demonstrate the ambiphilic property of  $\text{Co}^{\text{III}}\text{-superoxo}$  1.**

Metal-superoxo species are often believed to be the first intermediate following dioxygen ( $\text{O}_2$ ) association in the catalytic cycle of  $\text{O}_2$  activating metalloenzymes.<sup>1</sup> Despite intensive work in the past, the chemistry of metal-superoxo complexes remains largely unexplored, and hence attracts significant attention from chemists and biochemists.<sup>2</sup> *Inter alia*, metal-superoxo intermediates can react with  $\text{NO}^{\bullet}$  or organic radicals to furnish metal-peroxynitrite<sup>3</sup> and -alkylperoxo<sup>4</sup> complexes *via* radical coupling. Furthermore, they exhibit considerable electrophilicity as indicated by their capability of performing hydrogen atom abstraction (HAA)<sup>5</sup> from weak C–H and O–H bonds and oxygen atom transfer<sup>6</sup> to triphenylphosphine or thiol anisoles. On the other hand, they can initiate deformylation processes when treated with 2-phenylpropionaldehyde, thereby revealing their nucleophilic character.<sup>7,8</sup> Besides the aforementioned well known 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  $\text{O}_2$  activation catalyzed by  $\alpha$ -ketoglutarate dependent dioxygenases,<sup>9</sup> and by Cu, Fe and Co model complexes.<sup>10</sup> Only recently has such ambiphilic property been experimentally confirmed.<sup>8</sup> In our continuing efforts devoted to investigating reactivity of metal-superoxo intermediates, some of us succeeded in preparing a range of homologous  $\text{Fe}^{\text{III}}$ -,  $\text{Co}^{\text{III}}$ - and  $\text{Mn}^{\text{III}}$ -superoxo species by reacting  $\text{O}_2$  with the corresponding divalent precursors.<sup>11</sup> It has been shown that these trivalent metal-superoxo complexes can convert into the metal-hydroperoxo complexes *via* HAA. In particular, the reaction of  $\text{Mn}^{\text{III}}(\text{BDP}^{\text{Br}}\text{P})(\text{O}_2^{\bullet})$  ( $\text{H}_2\text{BDP}^{\text{Br}}\text{P} = 2,6\text{-bis}((2\text{-}(S)\text{-di(4-bromo)-phenylhydroxymethyl-1-pyrrolidinyl)methyl)pyridine)$  with trifluoroacetic acid (TFA) and  $\text{Sc}(\text{OTf})_3$  yields rare examples of  $\text{Mn}^{\text{IV}}$ -hydroperoxo complexes,  $\text{Mn}^{\text{IV}}(\text{BDP}^{\text{Br}}\text{P})(\text{OOH})$ , and  $[\text{Mn}^{\text{IV}}(\mu\text{-OO})\text{Sc}(\text{OTf})_n]^{(3-n)^+}$  as evidenced by the combined spectroscopic and computational studies (Scheme 1).<sup>8</sup> 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  $\text{Co}^{\text{III}}$ -superoxo complex,  $\text{Co}^{\text{III}}(\text{BDPP})(\text{O}_2^{\bullet})$  (1,  $\text{H}_2\text{BDPP} = 2,6\text{-bis}((2\text{-}(S)\text{-diphenylhydroxymethyl-1-pyrrolidinyl)methyl)pyridine)$  with TFA and  $\text{Sc}(\text{OTf})_3$  together with external electron donors.

Treating 1 with HOTf in THF at  $-90\text{ }^{\circ}\text{C}$  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<sup>†</sup>). Moreover, complex 2 can be obtained from one-electron oxidation of the hydroperoxo complex  $\text{Co}^{\text{III}}(\text{BDPP})(\text{OOH})$  (3). Adding equimolar of tris(4-bromophenyl)ammonium hexachloroantimonate, which is often referred to as magic blue, to a THF solution of 3 at  $-90\text{ }^{\circ}\text{C}$  resulted in a gray-green solution, whose

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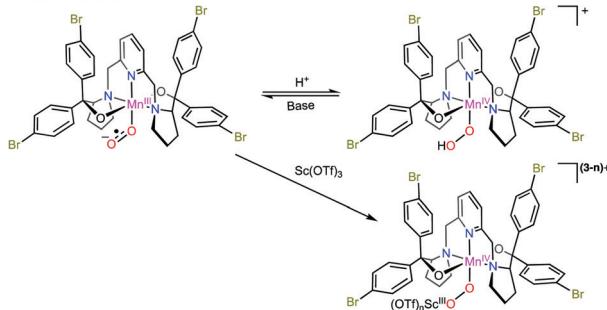
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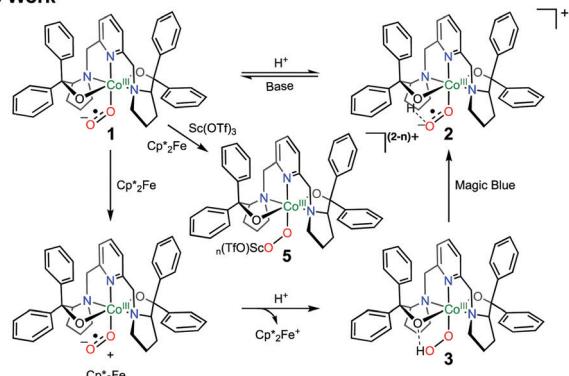
<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/d0cc05337f



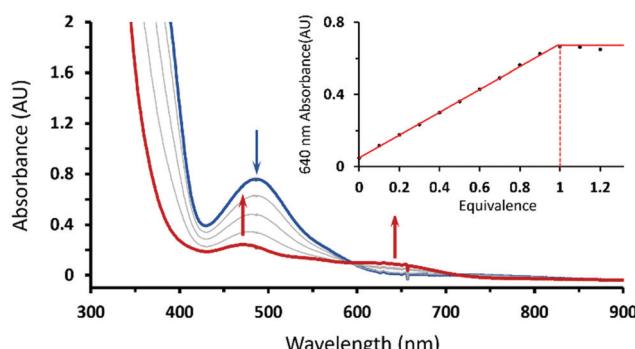
## Previous Work



## This Work

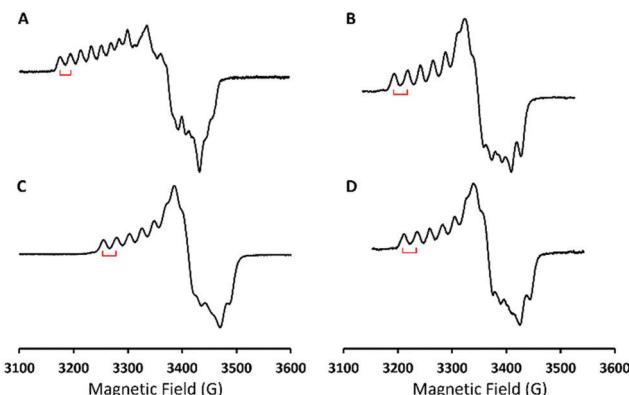


Scheme 1 Ambiphilicity of metal-superoxo complexes.

Fig. 1 UV-vis spectral changes of the reaction of **1** (1.0 mM, blue trace) with 1 equiv. of HOTf in THF at  $-90\text{ }^\circ\text{C}$ . 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.

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

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** ( $A_{\text{Co}} = 18\text{ G}$ ) except for a slightly larger  $^{59}\text{Co}$  hyperfine coupling constant ( $A_{\text{Co}} = 24\text{ G}$ ) seen in Fig. 2, thus indicating that **2** still consists of a  $\text{Co}^{\text{III}}$  center coupled with a radical ligand yielding an overall doublet ground state. The radical ligand thus would be a hydroperoxy radical or a superoxo having a strong hydrogen bonding interaction with the protonated BDPP<sup>2-</sup> ligand (Scheme 1) as

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

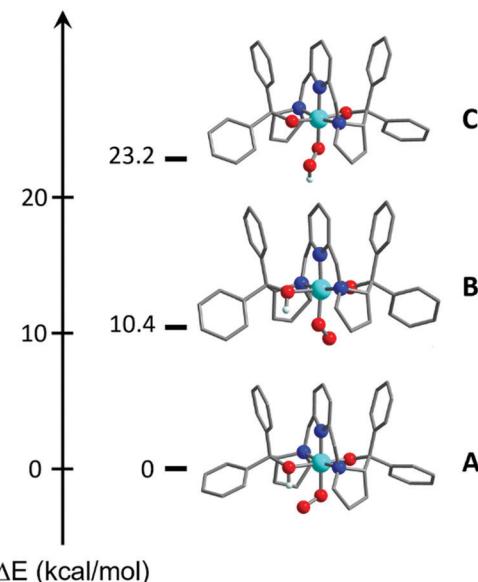
suggested by the crystal structure of **3**.<sup>11b</sup> However, the EPR spectrum of the product generated by reacting **1** with deuterated triflate acid (DOTf) is almost identical to that of **2** without discernable line broadening, which essentially rules out the possibility of the radical ligand being a hydroperoxy 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<sup>2-</sup> 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<sup>2-</sup> ligand, the geometry optimizations invariably shifted the H atom back to the O atom of BDPP<sup>2-</sup> 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  $\text{Co}^{\text{III}}$  center bound to a hydroperoxy radical ligand (**C**), but **C** lies 23.2 kcal mol<sup>-1</sup> 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<sup>2-</sup> ligand stabilized **A** by 10.4 kcal mol<sup>-1</sup> relative to **B** (Fig. 3). Thus, **A** is best deemed as the most appropriate model for **2**.

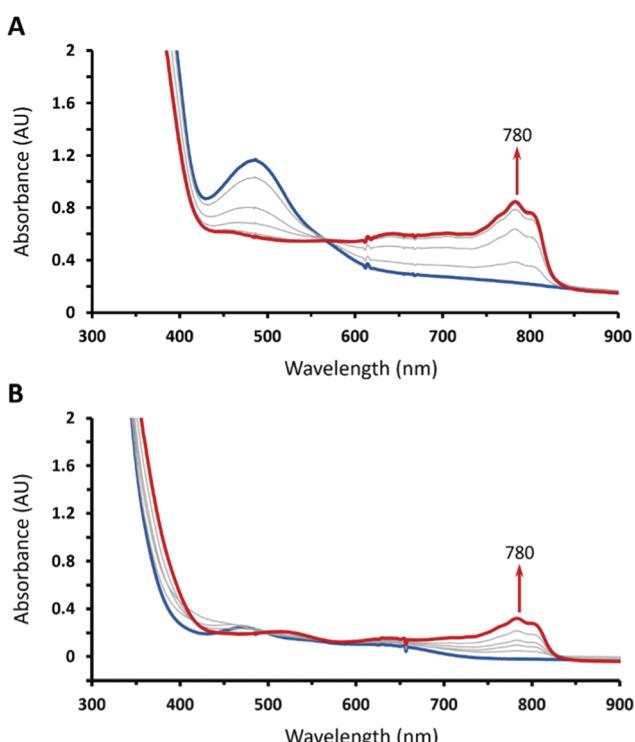
Alternatively, to transform **1** into the corresponding peroxy product, we then added 1 equiv. of decamethylferrocene ( $\text{Cp}^*{}^2\text{Fe}$ ) or sodium naphthalenide ( $\text{NaC}_{10}\text{H}_8$ ) to THF solutions of **1** at  $-90\text{ }^\circ\text{C}$ , but UV-vis measurements suggested that no reactions occurred (Fig. S3 and S4, ESI<sup>†</sup>). Taken together, neither proton nor electron donors alone can realize the superoxo-to-peroxy conversion for **1**.

Interestingly, upon treating a mixture containing equimolar **1** and  $\text{Cp}^*{}^2\text{Fe}$  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 ( $\text{Cp}^*{}^2\text{Fe}^+$ ) emerged suggesting that  $\text{Co}^{\text{III}}$ -superoxo **1** was reduced in the presence of both HOTf and  $\text{Cp}^*{}^2\text{Fe}$  (Fig. 4A).



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

During this process, we did not observe the formation of  $\text{Co}^{\text{III}}$ -hydroperoxo **3**. Instead, the reaction produced 19% of  $\text{H}_2\text{O}_2$  with respect to **1**, as determined by iodometric titration (Fig. S5, ESI<sup>†</sup>). When 2 equiv. of HOTf was added, 42% of  $\text{H}_2\text{O}_2$  was furnished (Fig. S6, ESI<sup>†</sup>). Thus, we reasoned that the aforementioned reaction indeed generates **3**; however, once formed, **3** further reacted with HOTf to produce  $\text{H}_2\text{O}_2$ . On the other hand,

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  $\text{Cp}^*_{\text{2}}\text{Fe}$  and (B) 1 equiv. of  $\text{Cp}^*_{\text{2}}\text{Fe}$  into a solution of **2** (1.0 mM) in THF at  $-90^{\circ}\text{C}$ .

treating **2** with 1 equiv. of  $\text{Cp}^*_{\text{2}}\text{Fe}$  (Fig. 4B) also generated 23% of  $\text{H}_2\text{O}_2$  (Fig. S7, ESI<sup>†</sup>). 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**.

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

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

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