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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 Cp^*_2Fe produced H_2O_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 (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-peroxynitrite³ and -alkylperoxo⁴ 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 transfer⁶ 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 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 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 $\text{Mn}^{\text{III}}(\text{BDP}^{\text{Br}}\text{P})(\text{O}_2^{\bullet})$ ($\text{H}_2\text{BDP}^{\text{Br}}\text{P} = 2,6\text{-bis}((2\text{-}(S)\text{-di}(4\text{-bromo})\text{-phenylhydroxymethyl-1-pyrrolidinyl)methyl)pyridine)$ with trifluoroacetic acid (TFA) and $\text{Sc}(\text{OTf})_3$ yields rare examples of Mn^{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).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, $\text{Co}^{\text{III}}(\text{BDPP})(\text{O}_2^{\bullet})$ (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[†]). 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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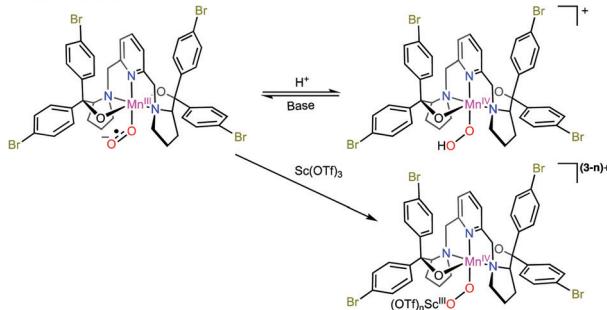
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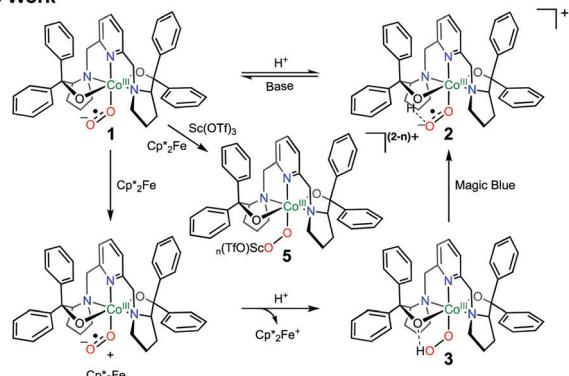
[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/d0cc05337f



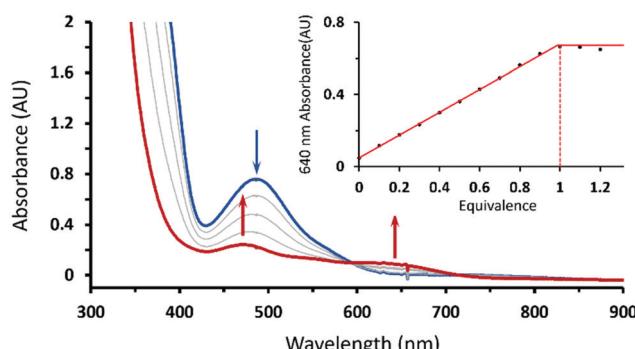
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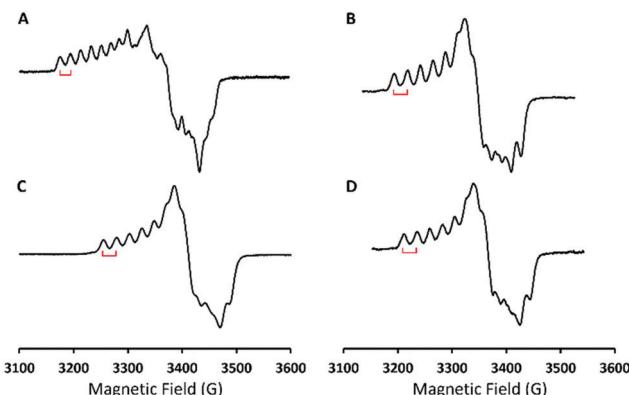


Scheme 1 Ambiphilicity of metal-superoxo complexes.

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

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}Co hyperfine coupling constant ($A_{\text{Co}} = 24\text{ G}$) 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 hydroperoxy radical or a superoxo having a strong hydrogen bonding interaction with the protonated BDPP²⁻ 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: $T = 77\text{ K}$, $f_{\text{mw}} = 9.6\text{ GHz}$.

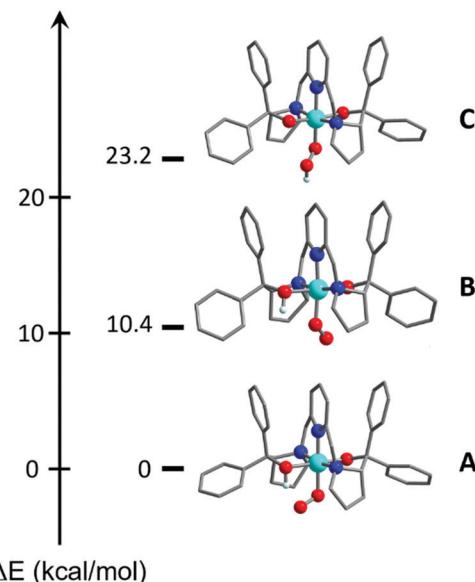
suggested by the crystal structure of **3**.^{11b} However, the EPR spectrum of the product generated by reacting **1** with deuterated triflate acid (DOTf) is almost identical to that of **2** without discernable line broadening, which essentially rules out the possibility of the radical ligand being a 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 BDPP²⁻ 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 BDPP²⁻ ligand, the geometry optimizations invariably shifted the H atom back to the O atom of BDPP²⁻ 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 hydroperoxy 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 BDPP²⁻ 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**.

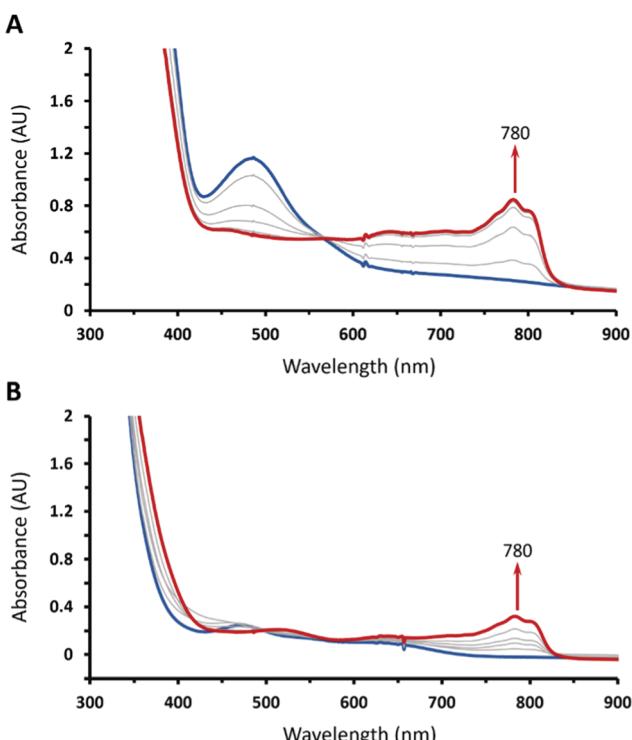
Alternatively, to transform **1** into the corresponding peroxy product, we then added 1 equiv. of decamethylferrocene ($\text{Cp}^*{}^2\text{Fe}$) or sodium naphthalenide ($\text{NaC}_{10}\text{H}_8$) to THF solutions of **1** at $-90\text{ }^\circ\text{C}$, but UV-vis measurements suggested that no reactions occurred (Fig. S3 and S4, ESI[†]). 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 Co^{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 Co^{III} -hydroperoxo **3**. Instead, the reaction produced 19% of H_2O_2 with respect to **1**, as determined by iodometric titration (Fig. S5, ESI[†]). When 2 equiv. of HOTf was added, 42% of H_2O_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_2O_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°C .

treating **2** with 1 equiv. of $\text{Cp}^*_{\text{2}}\text{Fe}$ (Fig. 4B) also generated 23% of H_2O_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**.

Reaction of **1** with $\text{Sc}(\text{OTf})_3$ 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} -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°C afforded a Co^{III} -peroxo- Sc^{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[†]). Addition of 2 equiv. of HOTf to the THF solution of **5** produced 76% H_2O_2 as quantified by iodometric titration experiments (Fig. S10, ESI[†]). Formation of H_2O_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 $\text{Mn}^{\text{III}}(\text{BDP}^{\text{Br}}\text{P})(\text{O}_2^{\bullet})$ (Scheme 1), the difference can be readily attributed to the much higher oxidation potential of 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 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 Co^{III} -superoxide **1** with HOTf and $\text{Sc}(\text{OTf})_3$ afforded the ligand-protonated Co^{III} -superoxide **2** with a hydrogen bond formed between the $\text{O}_2^{\bullet-}$ motif and the protonated BDPP^{2-} ligand and a superoxo-bridged binuclear $\text{Co}^{\text{III}}/\text{Sc}^{\text{III}}$ **4**, and Co^{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 H_2O_2 suggesting the formation of Co^{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 peroxo-bridged binuclear $\text{Co}^{\text{III}}/\text{Sc}^{\text{III}}$ **5**. These findings provided strong experimental support for the ambiphilic property of Co^{III} -superoxide **1**. Interestingly, the ligand-protonated Co^{III} -superoxide **2** can be prepared from one-electron oxidation of Co^{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 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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