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# Ambiphilicity of a mononuclear cobalt(III) superoxo complex<sup>†</sup>

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

Metal-superoxo species are often believed to be the first intermediate following dioxygen (O<sub>2</sub>) association in the catalytic cycle of O<sub>2</sub> 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 NO<sup>•</sup> 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.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 O2 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 metalsuperoxo intermediates, some of us succeeded in preparing a range of homologous Fe<sup>III</sup>-, Co<sup>III</sup>- and Mn<sup>III</sup>-superoxo species by reacting O<sub>2</sub> 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  $Mn^{III}(BDP^{Br}P)(O_2^{\bullet})$  (H<sub>2</sub>BDP<sup>Br</sup>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<sup>IV</sup>-hydroperoxo complexes, Mn<sup>IV</sup>(BDP<sup>Br</sup>P)(OOH), and [Mn<sup>IV</sup>(µ-OO)  $Sc(OTf)_n$ <sup>(3-n)+</sup> 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<sup>III</sup>-superoxo complex, Co<sup>III</sup>(BDPP)( $O_2^{\bullet}$ ) (1, H<sub>2</sub>BDPP = 2,6-bis((2-(S)-diphenylhydroxylmethyl-1-pyrrolidinyl)methyl)pyridine) with TFA and Sc(OTf)<sub>3</sub> 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<sup>III</sup>(BDP-P)(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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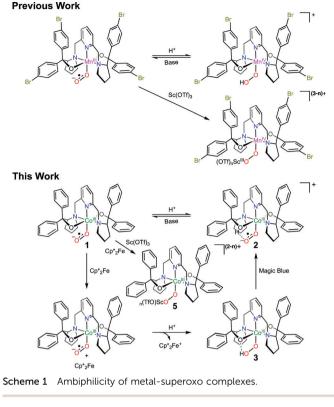
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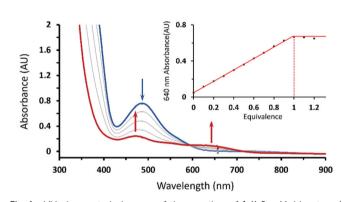
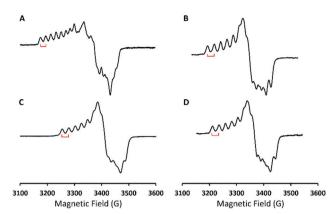


Fig. 1 UV-vis spectral changes of the reaction of 1 (1.0 mM, blue trace) with 1 equiv. of HOTf in THF at -90 °C. Inset: Titration curve of 1 with HOTf. *X*-axis: the equivalents of HOTf, *Y*-axis: the conversion ratio of the absorption peak at 640 nm.

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 ( $A_{Co}$  = 18 G) except for a slightly larger <sup>59</sup>Co hyperfine coupling constant ( $A_{Co}$  = 24 G) seen in Fig. 2, thus indicating that 2 still consists of a Co<sup>III</sup> 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<sup>2-</sup> ligand (Scheme 1) as





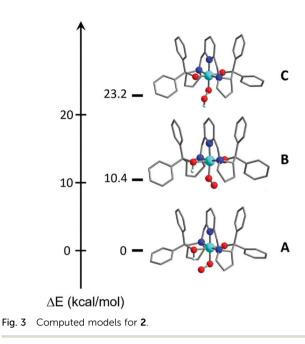
**Fig. 2** X-band EPR spectra of (A) **1** ( $g_1 = 2.098$ ,  $A_{Co} = 18$  G); (B) **1** with 1 equiv. of HOTf ( $g_1 = 2.066$ ,  $A_{Co} = 24$  G); (C) **1** with 1 equiv. of DOTf ( $g_1 = 2.064$ ,  $A_{Co} = 24$  G) and (D) **1** with 1 equiv. of Sc(OTf)<sub>3</sub> ( $g_1 = 2.066$ ,  $A_{Co} = 24$  G). Measurement condition: T = 77 K,  $f_{mw} = 9.6$  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 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.

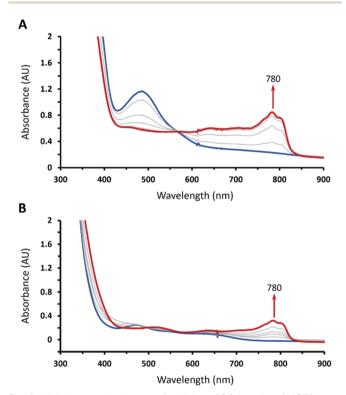
DFT calculations also suggested the O donor of the  $BDPP^{2-}$  ligand to be the favored protonation site of **1**, consistent with experiment. Even when the starting geometry contained a OOH ligand in which the distal H atom forms a hydrogen bond with the  $BDPP^{2-}$  ligand, the geometry optimizations 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<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  $BDPP^{2-}$  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 peroxo product, we then added 1 equiv. of decamethylferrocene (Cp\*<sub>2</sub>Fe) or sodium naphthalenide (NaC<sub>10</sub>H<sub>8</sub>) 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  $Cp*_2Fe$  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 ( $Cp*_2Fe^+$ ) emerged suggesting that  $Co^{III}$ -superoxo **1** was reduced in the presence of both HOTf and  $Cp*_2Fe$  (Fig. 4A).



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  $Cp*_2Fe$  and (B) 1 equiv. of  $Cp*_2Fe$  into a solution of **2** (1.0 mM) in THF at -90 °C.

treating 2 with 1 equiv. of Cp\*<sub>2</sub>Fe (Fig. 4B) also generated 23% of  $H_2O_2$  (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 Sc(OTf)<sub>3</sub> in THF at -90 °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 Co<sup>III</sup>-superoxo···Sc<sup>III</sup> species,  $[Co(BDPP)(O_2^{\bullet})···Sc(OTf)_n]^{(3-n)+}$  (**4**). Furthermore, addition of Sc(OTf)<sub>3</sub> to the mixture of **1** and Cp\*<sub>2</sub>Fe in THF at -90 °C afforded a Co<sup>III</sup>-peroxo-Sc<sup>III</sup> complex,  $[Co(BDPP)(\mu\text{-OO})Sc(OTf)_n]^{(2-n)+}$  (**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% H<sub>2</sub>O<sub>2</sub> as quantified by iodometric titration experiments (Fig. S10, ESI<sup>†</sup>). Formation of H<sub>2</sub>O<sub>2</sub> 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<sup>Br</sup>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<sup>2–</sup> 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<sup>III</sup>-superoxo 1 with HOTf and Sc(OTf)<sub>3</sub> afforded the ligand-protonated Co<sup>III</sup>-superoxo 2 with a hydrogen bond formed between the  $O_2^{\bullet-}$  motif and the protonated BDPP<sup>2-</sup> ligand and a superoxo-bridged binuclear Co<sup>III</sup>/Sc<sup>III</sup> 4, and Co<sup>III</sup>-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\*<sub>2</sub>Fe produced 42% of H<sub>2</sub>O<sub>2</sub> suggesting the formation of Co<sup>III</sup>-hydroperoxo 3, and the reaction of Sc(OTf)<sub>3</sub> with 1 in the presence of Cp\*<sub>2</sub>Fe gave a peroxo-bridged binuclear Co<sup>III</sup>/Sc<sup>III</sup> 5. These findings provided strong experimental support for the ambiphilic property of Co<sup>III</sup>-superoxo 1. Interestingly, the ligand-protonated Co<sup>III</sup>-superoxo 2 can be prepared from oneelectron oxidation of Co<sup>III</sup>-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 O2 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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