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Addition of HOTf to a mixture of  $Co^{III}(BDPP)(O_2^*)$  (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  $Co^{III}(BDP-P)(OOH)$  (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 (O2) association in the catalytic cycle of O<sub>2</sub> activating metalloenzymes. 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\* 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)5 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 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

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

of metal-superoxo species has been postulated in a series of theoretical and experimentally investigations including O2 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 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 O2 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<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)  $Sc(OTf)_n|^{(3-n)+}$  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<sup>III</sup>-superoxo complex, Co<sup>III</sup>(BDPP)(O<sub>2</sub>•) (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.

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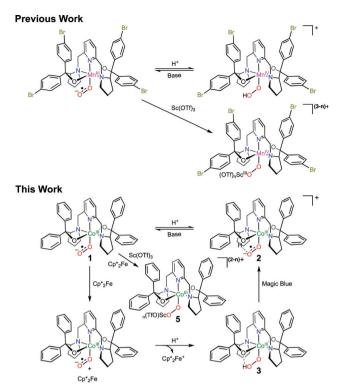
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Communication ChemComm



Scheme 1 Ambiphilicity of metal-superoxo complexes

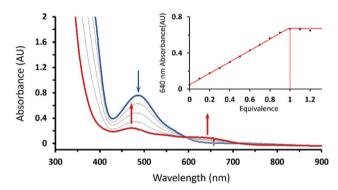


Fig. 1 UV-vis spectral changes of the reaction of 1 (1.0 mM, blue trace) with 1 equiv. of HOTf in THF at -90 °C. Inset: Titration curve of 1 with HOTf. X-axis: the equivalents of HOTf, Y-axis: the conversion ratio of the absorption peak at 640 nm

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 <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

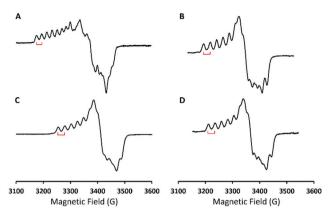


Fig. 2 X-band EPR spectra of (A) **1** ( $g_1 = 2.098$ ,  $A_{Co} = 18$  G); (B) **1** with 1 equiv. of HOTf ( $g_1$  = 2.066,  $A_{Co}$  = 24 G); (C) **1** with 1 equiv. of DOTf  $(g_1 = 2.064, A_{Co} = 24 \text{ G})$  and (D) **1** with 1 equiv. of  $Sc(OTf)_3$   $(g_1 = 2.066, B_1)$  $A_{Co}$  = 24 G). Measurement condition: T = 77 K,  $f_{mw}$  = 9.6 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 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<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 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<sup>III</sup> 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<sup>2-</sup> ligand stabilized A by 10.4 kcal  $\text{mol}^{-1}$  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  $(Cp*_2Fe)$  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\*<sub>2</sub>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\*2Fe+) emerged suggesting that CoIII-superoxo 1 was reduced in the presence of both HOTf and Cp\*2Fe (Fig. 4A).

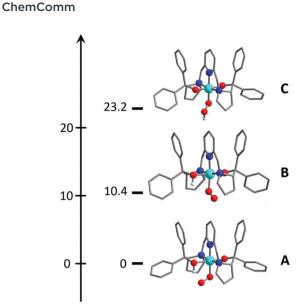


Fig. 3 Computed models for 2

ΔE (kcal/mol)

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†). When 2 equiv. of HOTf was added, 42% of  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$ . On the other hand,

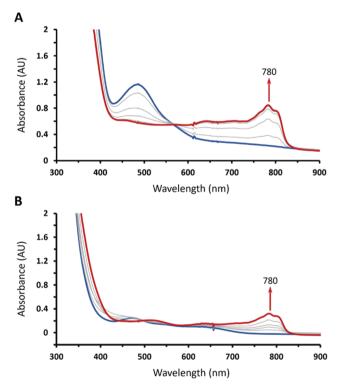


Fig. 4 UV-vis spectral changes of addition of (A) 1 equiv. of HOTf into a solution of  $\bf 1$  (1.0 mM) in the presence of 1 equiv. of Cp\*<sub>2</sub>Fe and (B) 1 equiv. of Cp\*<sub>2</sub>Fe into a solution of  $\bf 2$  (1.0 mM) in THF at  $-90\,^{\circ}$ C.

treating **2** with **1** equiv. of  $Cp_2^*Fe$  (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 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†) 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<sub>2</sub>•)···Sc(OTf)<sub>n</sub>]<sup>(3-n)+</sup> (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) ( $\mu$ -OO)Sc(OTf)<sub>n</sub>]<sup>(2-n)+</sup> (5), as depicted in Scheme 1 (Fig. S9, ESI†). 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†). 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  $Mn^{III}$  (BDPBrP)( $O_2^{\bullet}$ ) (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<sub>2</sub>• 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\*2Fe produced 42% of H2O2 suggesting the formation of CoIII-hydroperoxo 3, and the reaction of Sc(OTf)3 with 1 in the presence of Cp\*2Fe 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 CoIII-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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Communication ChemComm

## Conflicts of interest

There are no conflicts to declare.

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