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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, $H_2BDPP = 2,6-bis((2-(S)-diphenylhydroxylmethyl-1-pyrrolidinyl)methyl)pyridine) and Cp*₂Fe produced <math>H_2O_2$ 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 O₂ 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[•] 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 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 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^{III}-, Co^{III}- and Mn^{III}-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 $Mn^{III}(BDP^{Br}P)(O_2^{\bullet})$ (H₂BDP^{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}(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^{III}-superoxo complex, Co^{III}(BDPP)(O_2^{\bullet}) (1, H₂BDPP = 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}(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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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 \dagger).

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 ⁵⁹Co 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 BDPP²⁻ 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)₃ ($g_1 = 2.066$, $A_{Co} = 24$ G). Measurement condition: T = 77 K, $f_{mw} = 9.6$ GHz.

suggested by the crystal structure of 3.^{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 $Cp*_2Fe$ 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*₂Fe (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)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*₂Fe 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% H₂O₂ as quantified by iodometric titration experiments (Fig. S10, ESI[†]). Formation of H₂O₂ 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 BDPP²⁻ 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*₂Fe produced 42% of H₂O₂ suggesting the formation of Co^{III}-hydroperoxo 3, and the reaction of Sc(OTf)₃ with 1 in the presence of Cp*₂Fe 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 oneelectron 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 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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