ChemComm

COMMUNICATION

Cite this: *Chem. Commun.*, 2020, 56, 14821

Received 5th August 2020, Accepted 15th October 2020

DOI: 10.1039/d0cc05337f

rsc.li/chemcomm

Ambiphilicity of a mononuclear cobalt(III) superoxo complex†

Ting-Yi Chen,^{ab} Po-Hsun Ho,^a Can-Jerome Spyra,^b Franc Meyer, D^{*b} Eckhard Bill, \mathbf{D}^c Shengfa Ye $\mathbf{D}^{\star \text{de}}$ and Way-Zen Lee $\mathbf{D}^{\star \text{ad}}$

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 H₂O₂ 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 (O_2) 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 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 $Mn^{III}(BDP^{Br}P)(O_2^{\bullet})$ $(H_2BDP^{Br}P = 2,6$ -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 $[Mn^{IV}(\mu-OO)]$ $\text{Sc}(\text{OTf})_{n}$]⁽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, $Co^{III}(BDPP)(O_2^{\bullet})$ (1, H₂BDPP = 2,6-bis((2-(S)-diphenylhydroxylmethyl-1-pyrrolidinyl)methyl)pyridine) with TFA and $\text{Sc}(\text{OTf})_3$ together with external electron donors. COMMUNICATION

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> 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

 a^a Department of Chemistry, National Taiwan Normal University, Taipei 11677, Taiwan. E-mail: wzlee@ntnu.edu.tw

 b Universität Göttingen, Institut für Anorganische Chemie, D-37077 Göttingen, Germany. E-mail: franc.meyer@chemie.uni-goettingen.de

 ϵ Max-Planck-Institut für Chemische Energiekonversion, Mülheim an der Ruhr D-45470, Germany. E-mail: eckhard.bill@cec.mpg.de

^d State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. E-mail: shengfa.ye@dicp.ac.cn

 e^e Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, D-45470, Germany. E-mail: shengfa.ye@kofo.mpg.de

 f Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 807, Taiwan

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/ d0cc05337f

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 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 $BDPP^{2-}$ ligand (Scheme 1) as

Fig. 2 X-band EPR spectra of (A) $\mathbf{1}$ ($g_1 = 2.098$, $A_{Co} = 18$ G); (B) $\mathbf{1}$ 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 $(g_1 = 2.066, A_{Co} = 24 \text{ G})$ 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 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 $BDPP^{2-}$ 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 $(Cp^*{}_2Fe)$ or sodium naphthalenide (NaC₁₀H₈) 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^*_{2} 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 $(\rm{Cp^{*}}_{2}\rm{Fe}^{+})$ emerged suggesting that $\rm{Co}^{\rm{III}}$ -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 $Cp^*{}_{2}Fe$ 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 $Cp_{2}^{*}Fe$ (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)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 $\cdots Sc^{III}$ species, $[Co(BDPP)(O_2 \bullet) \cdots Sc(OTf)_n]^{(3-n)+}$ (4). Furthermore, addition of Sc(OTf)₃ to the mixture of 1 and $\text{Cp*}_2\text{Fe}$ in THF at -90 °C afforded a Co^{III}-peroxo-Sc^{III} complex, [Co(BDPP) $(\mu$ -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 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 Mn ^{III} $(BDP^{Br}P)(O₂[*])$ (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 ^{•-} 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^*_{2} Fe produced 42% of H_2O_2 suggesting the formation of Co^{III}-hydroperoxo 3, and the reaction of Sc(OTf)₃ with 1 in the presence of $Cp^*{}_{2}Fe$ 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.

We are grateful for the financial supports from the Ministry of Science and Technology of Taiwan (MOST 108-2113-M-003- 009-MY3 to W.-Z. L.) and the Max-Planck Society. W.-Z. L. and S. Y. also acknowledge the MOST-DAAD Project-Based Personnel Exchange Program (MOST 107-2911-I-003-502 and DAAD 57320810). Open Access funding provided by the Max Planck Society.

Conflicts of interest

There are no conflicts to declare.

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