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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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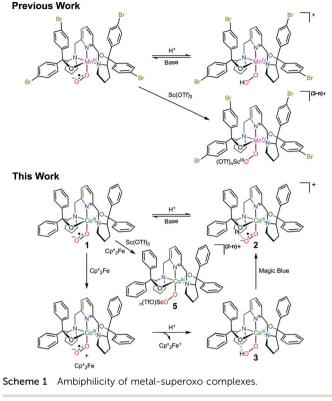
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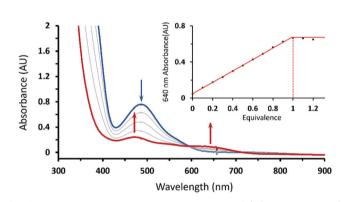


Fig. 1 UV-vis spectral changes of the reaction of 1 (1.0 mM, blue trace) with 1 equiv. of HOTf in THF at -90 °C. Inset: Titration curve of 1 with HOTf. *X*-axis: the equivalents of HOTf, *Y*-axis: the conversion ratio of the absorption peak at 640 nm.

absorption spectrum displayed the same signature features as those found for 2 (Fig. S2, ESI[†]).

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



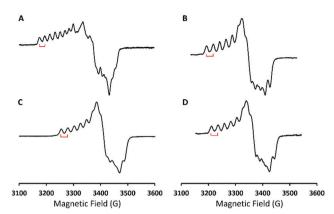


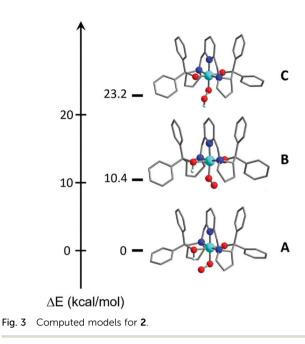
Fig. 2 X-band EPR spectra of (A) **1** ($g_1 = 2.098$, $A_{Co} = 18$ G); (B) **1** with 1 equiv. of HOTf ($g_1 = 2.066$, $A_{Co} = 24$ G); (C) **1** with 1 equiv. of DOTf ($g_1 = 2.064$, $A_{Co} = 24$ G) and (D) **1** with 1 equiv. of Sc(OTf)₃ ($g_1 = 2.066$, $A_{Co} = 24$ G). Measurement condition: 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 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 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 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 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 $Cp*_2Fe$ 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,

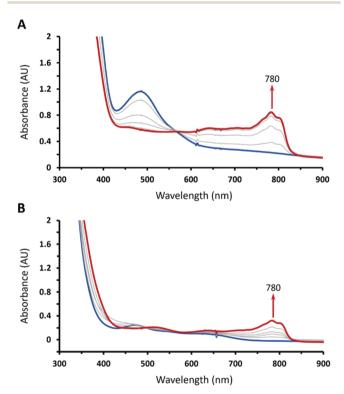


Fig. 4 UV-vis spectral changes of addition of (A) 1 equiv. of HOTf into a solution of **1** (1.0 mM) in the presence of 1 equiv. of $Cp*_2Fe$ and (B) 1 equiv. of $Cp*_2Fe$ into a solution of **2** (1.0 mM) in THF at -90 °C.

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, $[Co(BDPP)(\mu\text{-OO})Sc(OTf)_n]^{(2-n)+}$ (**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.

Notes and references

- (a) E. G. Kovaleva and J. D. Lipscomb, Nat. Chem. Biol., 2008, 4, 186–193; (b) M. Costas, M. P. Mehn, M. P. Jensen and L. Que, Chem. Rev., 2004, 104, 939–986; (c) A. J. Jasniewski and L. Que, Jr., Chem. Rev., 2018, 118, 2554–2592; (d) C. E. Elwell, N. L. Gagnon, B. D. Neisen, D. Dhar, A. D. Spaeth, G. M. Yee and W. B. Tolman, Chem. Rev., 2017, 117, 2059–2107; (e) K. Ray, F. F. Pfaff, B. Wang and W. Nam, J. Am. Chem. Soc., 2014, 136, 13942–13958; (f) S. Sahu and D. P. Goldberg, J. Am. Chem. Soc., 2016, 138, 11410–11428.
- 2 (a) M. H. Dickman and M. T. Pope, Chem. Rev., 1994, 94, 569-584;
 (b) S. Fukuzumi, Y. M. Lee and W. Nam, Dalton Trans., 2019, 48, 9469-9489;
 (c) H. Noh and J. Cho, Coord. Chem. Rev., 2019, 382, 126-144;
 (d) X. Cai, S. Majumdar, G. C. Fortman, C. S. J. Cazin, A. M. Z. Slawin, C. Lhermitte, R. Prabhakar, M. E. Germain, T. Palluccio, S. P. Nolan, E. V. Rybak-Akimova, M. Temprado, B. Captain and C. D. Hoff, J. Am. Chem. Soc., 2011, 133, 1290-1293;
 (e) R. Huacuja, D. J. Graham, C. M. Fafard and C.-H. Chen, J. Am. Chem. Soc., 2011, 133, 3820-3823;
 (f) X. Zhang, G. R. Loppnow, R. McDonald and J. Takats, J. Am. Chem. Soc., 1995, 117, 7828-7829.
- 3 (a) S. Herold and W. H. Koppenol, Coord. Chem. Rev., 2005, 249, 499–506; (b) R. D. Harcourt, Coord. Chem. Rev., 2018, 358, 178–180; (c) P. R. Gardner, A. M. Gardner, L. A. Martin and A. L. Salzman, Proc. Natl. Acad. Sci. U. S. A., 1998, 95, 10378–10383; (d) A. K. Das and M. Meuwly, Angew. Chem., Int. Ed., 2018, 57, 3509–3513; (e) S. K. Sharma, A. W. Schaefer, H. Lim, H. Matsumura, P. Moënne-Loccoz, B. Hedman, K. O. Hodgson, E. I. Solomon and K. D. Karlin, J. Am. Chem. Soc., 2017, 139, 17421–17430; (f) R. Cao, L. T. Elrod, R. L. Lehane, E. Kim and K. D. Karlin, J. Am. Chem. Soc., 2016, 138, 16148–16158; (g) J. J. Liu, M. A. Siegler, K. D. Karlin and P. Moenne-Loccoz, Angew. Chem., Int. Ed., 2019, 58, 10936–10940.
- 4 (a) E. G. Kovaleva and J. D. Lipscomb, *Science*, 2007, **316**, 453; (b) P. Kumar, S. V. Lindeman and A. T. Fiedler, *J. Am. Chem. Soc.*, 2019, **141**, 10984–10987.
- 5 (a) M. N. Blakely, M. A. Dedushko, P. C. Yan Poon, G. Villar-Acevedo and J. A. Kovacs, J. Am. Chem. Soc., 2019, 141, 1867–1870;
 (b) A. Kunishita, M. Kubo, H. Sugimoto, T. Ogura, K. Sato, T. Takui and S. Itoh, J. Am. Chem. Soc., 2009, 131, 2788–2789;
 (c) R. L. Peterson, R. A. Himes, H. Kotani, T. Suenobu, L. Tian, M. A. Siegler, E. I. Solomon, S. Fukuzumi and K. D. Karlin, J. Am.

Chem. Soc., 2011, **133**, 1702–1705; (d) J. Cho, J. Woo and W. Nam, J. Am. Chem. Soc., 2010, **132**, 5958–5959; (e) H. Kelm and H.-J. Krüger, Angew. Chem., Int. Ed., 2001, **40**, 2344–2348; (f) E. Tamanaha, B. Zhang, Y. Guo, W.-C. Chang, E. W. Barr, G. Xing, J. St Clair, S. Ye, F. Neese, J. M. Bollinger, Jr. and C. Krebs, J. Am. Chem. Soc., 2016, **138**, 8862–8874; (g) N. Kindermann, C.-J. Günes, S. Dechert and F. Meyer, J. Am. Chem. Soc., 2017, **139**, 9831–9834.

- 6 (a) M. T. Kieber-Emmons, J. Annaraj, M. S. Seo, K. M. Van Heuvelen, T. Tosha, T. Kitagawa, T. C. Brunold, W. Nam and C. G. Riordan, J. Am. Chem. Soc., 2006, 128, 14230–14231; (b) S. Yao, E. Bill, C. Milsmann, K. Wieghardt and M. Driess, Angew. Chem., Int. Ed., 2008, 47, 7110–7113; (c) J. Cho, J. Woo and W. Nam, J. Am. Chem. Soc., 2012, 134, 11112–11115; (d) K. Fujita, R. Schenker, W. Gu, T. C. Brunold, S. P. Cramer and C. G. Riordan, Inorg. Chem., 2004, 43, 3324–3326; (e) T. Tano, Y. Okubo, A. Kunishita, M. Kubo, H. Sugimoto, N. Fujieda, T. Ogura and S. Itoh, Inorg. Chem., 2013, 52, 10431–10437; (f) L.-L. Liu, H.-X. Li, L.-M. Wan, Z.-G. Ren, H.-F. Wang and J.-P. Lang, Chem. Commun., 2011, 47, 11146–11148.
- 7 (a) P. Pirovano, A. M. Magherusan, C. McGlynn, A. Ure, A. Lynes and
 A. R. McDonald, Angew. Chem., Int. Ed., 2014, 126, 6056–6060;
 (b) W. D. Bailey, N. L. Gagnon, C. E. Elwell, A. C. Cramblitt,
 C. J. Bouchey and W. B. Tolman, Inorg. Chem., 2019, 58, 4706–4711.
- 8 Y.-H. Lin, Y. Kutin, M. van Gastel, E. Bill, A. Schnegg, S. Ye and W.-Z. Lee, *J. Am. Chem. Soc.*, 2020, **142**, 10255–10260.
- 9 (a) S. Ye, C. Riplinger, A. Hansen, C. Krebs, J. M. Bollinger, Jr. and F. Neese, *Chem. – Eur. J.*, 2012, 18, 6555–6567; (b) T. Borowski, A. Bassan and P. E. M. Siegbahn, *Chem. – Eur. J.*, 2004, 10, 1031–1041.
- 10 (a) W. D. Bailey, D. Dhar, A. C. Cramblitt and W. B. Tolman, J. Am. Chem. Soc., 2019, 141, 5470-5480; (b) S. Hong, K. D. Sutherlin, J. Park, E. Kwon, M. A. Siegler, E. I. Solomon and W. Nam, Nat. Commun., 2014, 5, 5440-5547; (c) M. Sankaralingam, Y.-M. Lee, W. Nam and S. Fukuzumi, Coord. Chem. Rev., 2018, 365, 41-59; (d) A. R. Corcos, O. Villanueva, R. C. Walroth, S. K. Sharma, J. Bacsa, K. M. Lancaster, C. E. MacBeth and J. F. Berry, J. Am. Chem. Soc., 2016, 138, 1796-1799.
- 11 (a) C. W. Chiang, S. T. Kleespies, H. D. Stout, K. K. Meier, P. Y. Li, E. L. Bominaar, L. Que, Jr., E. Munck and W. Z. Lee, *J. Am. Chem. Soc.*, 2014, **136**, 10846–10849; (b) C. C. Wang, H. C. Chang, Y. C. Lai, H. Fang, C. C. Li, H. K. Hsu, Z. Y. Li, T. S. Lin, T. S. Kuo, F. Neese, S. Ye, Y. W. Chiang, M. L. Tsai, W. F. Liaw and W. Z. Lee, *J. Am. Chem. Soc.*, 2016, **138**, 14186–14189; (c) Y. H. Lin, H. H. Cramer, M. van Gastel, Y. H. Tsai, C. Y. Chu, T. S. Kuo, I. R. Lee, S. Ye, E. Bill and W. Z. Lee, *Inorg. Chem.*, 2019, **58**, 9756–9765.