**Ambiphilicity of a mononuclear cobalt(iii) superoxo complex†**

Ting-Yi Chen, Po-Hsun Ho, Can-Jerome Spyra, Franc Meyer, Eckhard Bill, Shengfa Ye and Way-Zen Lee

Metal-superoxo species are often believed to be the first intermediate following dioxygen (O₂) association in the catalytic cycle of O₂ 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. Inter alia, metal-superoxo intermediates can react with NO* or organic radicals to furnish metal-peroxynitrite and -alkylperoxo complexes via radical coupling. Furthermore, they exhibit considerable electrophilicity as indicated by their capability of performing hydrogen atom abstraction (HAA) from weak C–H and O–H bonds and oxygen atom transfer to triphenylphosphine or thiol anisoles. On the other hand, they can initiate deformylation processes and Sc(OTf)₃ together with external electron donors. 

The ambiphilic property of metal-superoxo species has been postulated in a series of theoretical and experimentally investigations including O₂ activation catalyzed by α-ketoglutarate dependent dioxygenases, and by Cu, Fe and Co model complexes. Only recently has such ambiphilic property been experimentally confirmed. In our continuing efforts devoted to investigating reactivity of metal-superoxo intermediates, some of us succeeded in preparing a peroxo-bridged Co(III)/Sc(III) complex. These findings demonstrate the ambiphilic property of Co(III)-peroxo 1.

Addition of HOTf to a mixture of Co(III)(BDPP)(O₂) (1, H₂BDPP = 2,6-bis[(2-S)-diphenylhydroxymethyl-1-pyrrolidinyl]methyl)pyridine) and Cp₃Fe produced H₂O₂ in high yield implying formation of Co(III)(BDPP)(O₂) (3), and reaction of Sc(OTf)₃ with the same mixture gave a peroxo-bridged Co(III)/Sc(III) complex. These findings demonstrate the ambiphilic property of Co(III)-peroxo 1.

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**† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0cc05337f**
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\textsubscript{Co} = 18 G) except for a slightly larger \(^{59}\)Co hyperfine coupling constant (A\textsubscript{Co} = 24 G) seen in Fig. 2, thus indicating that 2 still consists of a Co\textsuperscript{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 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 an 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\textsuperscript{III} center bound to a hydroperoxyl radical (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 peroxy product, we then added 1 equiv. of decamethylferrocene (Cp\(^{*}\)\textsubscript{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\(^{*}\)\textsubscript{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 (Cp\(^{*}\)\textsubscript{2}Fe\(^{+}\)) emerged suggesting that Co\textsuperscript{III}-superoxo 1 was reduced in the presence of both HOTf and Cp\(^{*}\)\textsubscript{2}Fe (Fig. 4A).
During this process, we did not observe the formation of Co\textsuperscript{III}-hydroperoxo \textit{3}. Instead, the reaction produced 19\% of H\textsubscript{2}O\textsubscript{2} with respect to \textit{1}, as determined by iodometric titration (Fig. S5, ESI\textsuperscript{[†]}). When 2 equiv. of HOTf was added, 42\% of H\textsubscript{2}O\textsubscript{2} was furnished (Fig. S6, ESI\textsuperscript{[†]}). Thus, we reasoned that the aforementioned reaction indeed generates \textit{3}; however, once formed, \textit{3} further reacted with HOTf to produce H\textsubscript{2}O\textsubscript{2}. On the other hand, treating 2 with 1 equiv. of Cp\textsuperscript{∗}\textsubscript{2}Fe (Fig. 4B) also generated 23\% of H\textsubscript{2}O\textsubscript{2} (Fig. S7, ESI\textsuperscript{[†]}). Therefore, all experimental findings revealed that transformation of \textit{1} to \textit{3} proceeds \textit{via} concerted proton coupled electron transfer, which clearly demonstrated the ambiphilicity of \textit{1}.

Reaction of \textit{1} with Sc(OTf)\textsubscript{3} in THF at −90 °C generated a product, which showed nearly identical absorption and EPR spectra to those of \textit{2} (Fig. S8 (ESI\textsuperscript{[†]})) and Fig. 2D). On the basis of these observations, we tentatively suggest that the reaction furnished a Co\textsuperscript{III}-superoxo-Sc\textsuperscript{III} species, [Co(BDPP)(O\textsubscript{2}–)\textsuperscript{–}·Sc(OTf)\textsubscript{3}]	extsuperscript{3–} (\textit{4}). Furthermore, addition of Sc(OTf)\textsubscript{3} to the mixture of \textit{1} and Cp\textsuperscript{∗}\textsubscript{2}Fe in THF at −90 °C afforded a Co\textsuperscript{III}-peroxo-Sc\textsuperscript{III} complex, [Co(BDPP)(μ-O)	extsubscript{2}Sc(OTf)\textsubscript{3}]	extsuperscript{2–} (\textit{5}), as depicted in Scheme 1 (Fig. S9, ESI\textsuperscript{[†]}).

Addition of 2 equiv. of HOTf to the THF solution of \textit{5} produced 76\% H\textsubscript{2}O\textsubscript{2} as quantified by iodometric titration experiments (Fig. S10, ESI\textsuperscript{[†]}). Formation of H\textsubscript{2}O\textsubscript{2} thus strongly supports the identity of peroxo-bridged binuclear \textit{5}. These findings further reinforce the ambiphilic property of \textit{1}.

In conclusion, treatment of Co\textsuperscript{III}-superoxo \textit{1} with HOTf and Sc(OTf)\textsubscript{3} afforded the ligand-protonated Co\textsuperscript{III}-superoxo \textit{2} with a hydrogen bond formed between the O\textsubscript{2}–\textsuperscript{–} motif and the protonated BDPP\textsuperscript{2+} ligand and a superoxo-bridged binuclear Co\textsuperscript{III}/Sc\textsuperscript{III} \textit{4}, and Co\textsuperscript{III}-superoxo \textit{1} can be regenerated from deprotonation of \textit{2} by DBU. However, addition of 2 equiv. of HOTf into the reaction mixture of \textit{1} and Cp\textsuperscript{∗}\textsubscript{2}Fe produced 42\% of H\textsubscript{2}O\textsubscript{2} suggesting the formation of Co\textsuperscript{III}-hydroperoxo \textit{3}, and the reaction of Sc(OTf)\textsubscript{3} with \textit{1} in the presence of Cp\textsuperscript{∗}\textsubscript{2}Fe gave a peroxo-bridged binuclear Co\textsuperscript{III}/Sc\textsuperscript{III} \textit{5}. These findings provided strong experimental support for the ambiphilic property of Co\textsuperscript{III}-superoxo \textit{1}. Interestingly, the ligand-protonated Co\textsuperscript{III}-superoxo \textit{2} can be prepared from one-electron oxidation of Co\textsuperscript{III}-hydroperoxo \textit{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 O\textsubscript{2} 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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