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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 H_2O_2 in high yield implying formation of Co^{III}(BDPP)(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 O_2 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 $NO^{\bullet}$ or organic radicals to furnish metal-peroxynitrite[3] and -alkylperoxo[4] 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[6] 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 O_2 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 metal-superoxo 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 $[Mn^{IV}(\mu\text{-}OO)Sc(OTf)_n]^{(3-n)+}$ 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**, H_2BDPP = 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}(BDPP)(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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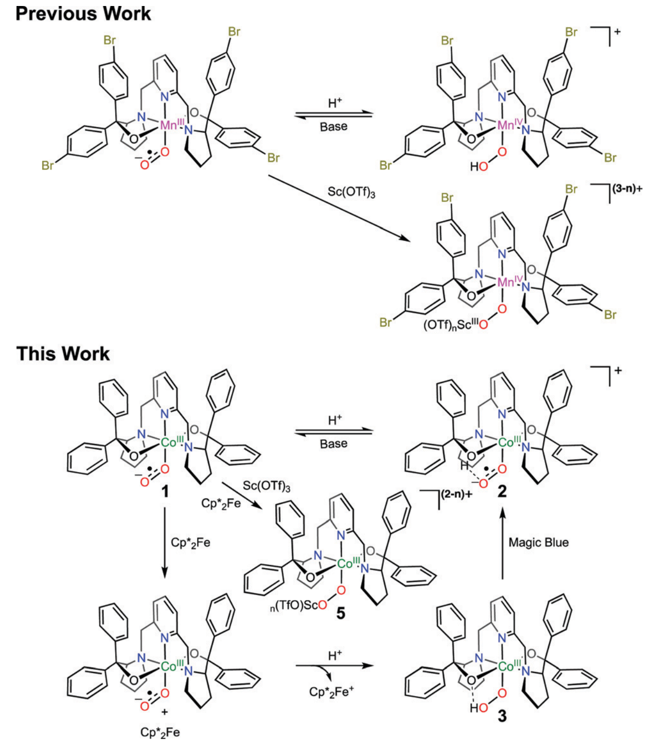

Scheme 1 Ambiphilicity of metal-superoxo complexes.

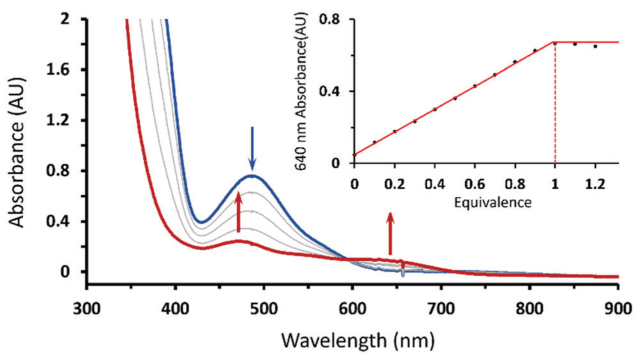

Fig. 1 UV-vis spectral changes of the reaction of **1** (1.0 mM, blue trace) with 1 equiv. of HOTf in THF at −90 °C. Inset: Titration curve of **1** with HOTf. *X*-axis: the equivalents of HOTf, *Y*-axis: the conversion ratio of the absorption peak at 640 nm.

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 ^{59}Co 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

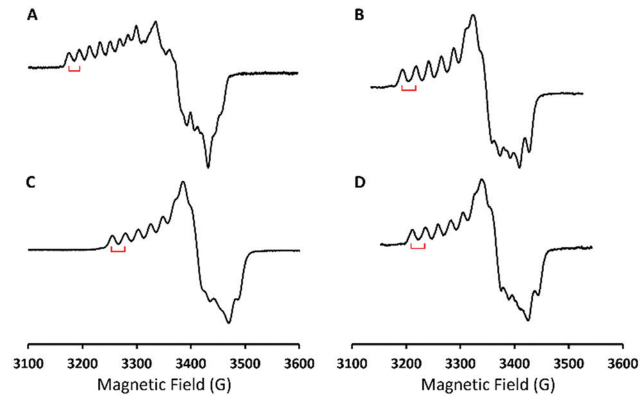

Fig. 2 X-band EPR spectra of (A) **1** (g_1 = 2.098, A_{Co} = 18 G); (B) **1** with 1 equiv. of HOTf (g_1 = 2.066, A_{Co} = 24 G); (C) **1** with 1 equiv. of DOTf (g_1 = 2.064, A_{Co} = 24 G) and (D) **1** with 1 equiv. of $Sc(OTf)_3$ (g_1 = 2.066, A_{Co} = 24 G). Measurement condition: T = 77 K, f_{mw} = 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 $BDPP^{2-}$ 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^*_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^*_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).

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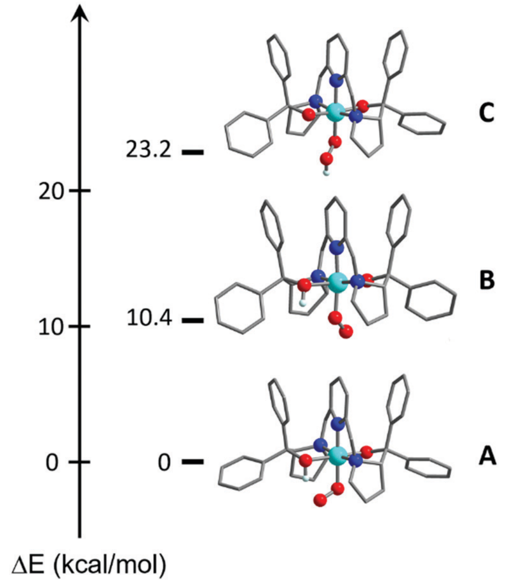

Fig. 3 Computed models for **2**.

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, 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**.

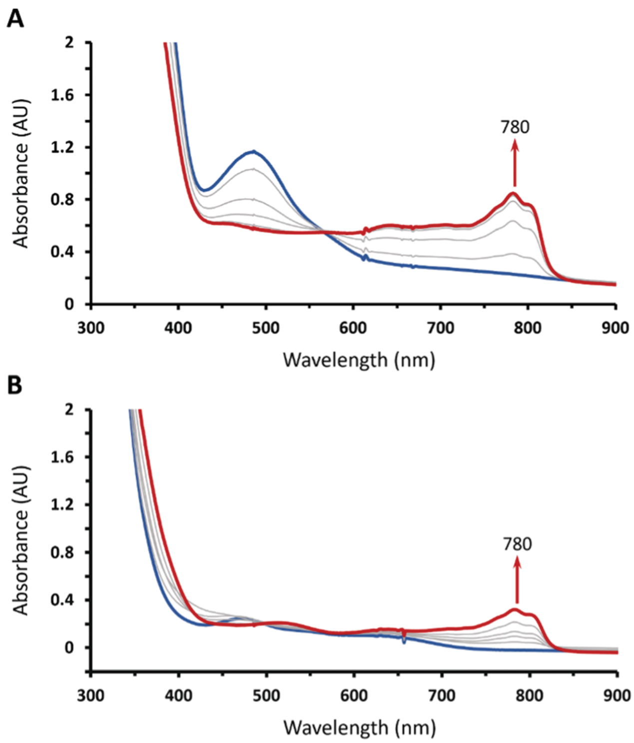

Fig. 4 UV-vis spectral changes of addition of (A) 1 equiv. of HOTf into a solution of **1** (1.0 mM) in the presence of 1 equiv. of $Cp^*{}_2Fe$ and (B) 1 equiv. of $Cp^*{}_2Fe$ into a solution of **2** (1.0 mM) in THF at −90 °C.

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, $[Co(BDPP)(O_2^{\bullet})\cdots Sc(OTf)_n]^{(3-n)+}$ (**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% H_2O_2 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)($O_2^{\bullet}$) (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 BDPP^{2-} 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 H_2O_2 suggesting the formation of Co^{III}-hydroperoxo **3**, and the reaction of $Sc(OTf)_3$ with **1** in the presence of $Cp^*{}_2Fe$ 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 one-electron 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 O_2 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

1 (*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.

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