



## Nucleophilic reactivity of a mononuclear cobalt(III)–bis(*tert*-butylperoxy) complex†

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A mononuclear cobalt(III)–bis(*tert*-butylperoxy) adduct (Co<sup>III</sup>–(OO<sup>t</sup>Bu)<sub>2</sub>) bearing a tetraazamacrocyclic ligand was synthesized and characterized using various physicochemical methods, such as X-ray, UV-vis, ESI-MS, EPR, and NMR analyses. The crystal structure of the Co<sup>III</sup>–(OO<sup>t</sup>Bu)<sub>2</sub> complex clearly showed that two OO<sup>t</sup>Bu ligands bound to the equatorial position of the cobalt(III) center. Kinetic studies and product analyses indicate that the Co<sup>III</sup>–(OO<sup>t</sup>Bu)<sub>2</sub> intermediate exhibits nucleophilic oxidative reactivity toward external organic substrates.

Transition metal–alkylperoxy (M–OOR) species play an important role in oxidation reactions such as industrial and biological catalytic oxidation.<sup>1–6</sup> In industrial processes, M–OOR intermediates, such as Co<sup>III</sup>–OOR complexes, were proposed as key intermediates in hydrocarbon catalytic oxidation under harsh conditions.<sup>1,7</sup> Mononuclear nonheme M–OOR complexes have been suggested to play a significant role in the oxidation reaction of metalloenzyme systems (*e.g.*, lipoyxygenase and homoprotocatechuate 2,3-dioxygenase).<sup>8,9</sup> Biomimetic studies of M–OOR complexes enabled catalysts to be developed that produce high value-added organic products under mild conditions.

Mononuclear heme and nonheme first-row M–OOR intermediates (M = Mn, Fe, Co, Ni, and Cu) have been investigated as model complexes for the active sites of metalloenzymes.<sup>2,5,6,10–13</sup> A number of M–OOR complexes were mainly studied in the investigation of electrophilic reactions (*e.g.*, oxygen and hydrogen atom transfer reaction).<sup>14–25</sup> It has been reported that the reaction proceeds *via* the •OOR and •OR radicals from decomposition of the M–OOR species.<sup>1</sup> However, only a few examples of nucleophilic reactivity with M–OOR intermediates (M = Fe, Ni, and Cu) have been reported.<sup>19,20,23</sup>

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In the Sharpless–Katsuki epoxidation, Ti–(OOR)<sub>*n*</sub> (*n* = 1–4) species were proposed as reactive intermediates.<sup>26,27</sup> Furthermore, in the formation of Fe–OO<sup>t</sup>Bu complexes, Fe–(OO<sup>t</sup>Bu)<sub>2</sub> species, [Fe<sup>III</sup>(TPP)(OO<sup>t</sup>Bu)<sub>2</sub>]<sup>–</sup> (TPP = 5,10,15,20-tetraphenylporphyrinate) and [Fe<sup>III</sup>(BPMCN)(OO<sup>t</sup>Bu)(HOO<sup>t</sup>Bu)]<sup>2+</sup> (BPMCN = *N,N'*-bis(2-pyridylmethyl-*N,N'*-dimethyl-*trans*-1,2-diaminocyclohexane)) adducts, have been proposed as short-lived intermediates.<sup>28–31</sup> However, definitive evidence of bis(alkylperoxy) binding first-row transition metal compounds has not been reported yet. In this work, we report a fully characterized Co<sup>III</sup>–(OO<sup>t</sup>Bu)<sub>2</sub> complex bearing a tetraazamacrocyclic ligand, [Co<sup>III</sup>(Me<sub>3</sub>-TPADP)(OO<sup>t</sup>Bu)<sub>2</sub>]<sup>+</sup> (**2**, Me<sub>3</sub>-TPADP = 3,6,9-trimethyl-3,6,9-triaza-1(2,6)-pyridinacyclodecaphane). Intermediate **2** was investigated in nucleophilic reactions such as aldehyde oxidation. Only one of the two OO<sup>t</sup>Bu ligands in **2** is able to oxidize external substrates. In order to compare the structure and the reactivity of an alkylperoxy and bis(alkylperoxy) binding cobalt species, Co<sup>III</sup>–(OO<sup>t</sup>Bu)(X) complexes, [Co<sup>III</sup>(Me<sub>3</sub>-TPADP)(OO<sup>t</sup>Bu)(X)]<sup>+</sup> (X = N<sub>3</sub> for **4**, NCS for **5**), were prepared as well.

The cobalt(II) starting complex, [Co<sup>II</sup>(Me<sub>3</sub>-TPADP)(CH<sub>3</sub>CN)<sub>2</sub>]<sup>2+</sup> (**1**), was synthesized by using a published method.<sup>32</sup> When 10 equiv. of *tert*-butyl hydroperoxide (<sup>t</sup>BuOOH) was added to **1** in the presence of 2 equiv. of triethylamine (TEA) in CH<sub>3</sub>CN at 25 °C, the Co<sup>III</sup>–(OO<sup>t</sup>Bu)<sub>2</sub> adduct, [Co<sup>III</sup>(Me<sub>3</sub>-TPADP)(OO<sup>t</sup>Bu)<sub>2</sub>]<sup>+</sup> (**2**), was generated and the solution color changed from purple to dark green (Scheme S1, ESI<sup>†</sup>). Intermediate **2** is thermally metastable in CH<sub>3</sub>CN at 25 °C, which allowed us to use it for characterization and reactivity studies.

The UV-vis spectrum of **2** in CH<sub>3</sub>CN at 25 °C shows electronic absorption bands at λ<sub>max</sub> = ~360 (ε = 1100 M<sup>–1</sup> cm<sup>–1</sup>) and 583 nm (ε = 190 M<sup>–1</sup> cm<sup>–1</sup>) (Fig. 1a). Electrospray ionization mass spectrometry (ESI-MS) analysis of **2** exhibits a prominent ion peak at *m/z* 485.3, whose mass and isotope distribution pattern correspond to [Co<sup>III</sup>(Me<sub>3</sub>-TPADP)(OO<sup>t</sup>Bu)<sub>2</sub>]<sup>+</sup> (calcd *m/z* 485.3) (Fig. 1b). The X-band electron paramagnetic resonance (EPR) silence (Fig. 1a, inset) and <sup>1</sup>H NMR spectral features (Fig. S1, ESI<sup>†</sup>) in the diamagnetic region confirm that complex **2** is a low-spin *S* = 0 cobalt(III) species.



**Fig. 1** (a) UV-vis spectra of  $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})(\text{CH}_3\text{CN})_2]^{2+}$  (**1**) (the black line) and  $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})(\text{OO}^t\text{Bu})_2]^+$  (**2**) (the red line) in  $\text{CH}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .<sup>32</sup> Inset shows the X-band EPR spectra of **1** (the black line) in frozen  $\text{CH}_3\text{CN}$  at  $5\text{ K}$  and **2** (the red line) in frozen  $\text{CH}_3\text{CN}$  at  $113\text{ K}$ .<sup>32</sup> The parameters for the measurement of **2**: microwave power =  $1.0\text{ mW}$ , frequency =  $9.176\text{ GHz}$ , sweep width =  $0.40\text{ T}$ , and modulation amplitude =  $0.60\text{ mT}$ . (b) ESI-MS of **2** in  $\text{CH}_3\text{CN}$  at  $-40\text{ }^\circ\text{C}$ . Insets show experimental (upper) and simulated (lower) isotope distribution patterns.

The X-ray crystal structure of  $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})(\text{OO}^t\text{Bu})_2]$  ( $\text{BPh}_4$ )( $\text{Et}_2\text{O}$ ) ( $2\text{-BPh}_4\cdot\text{Et}_2\text{O}$ ) revealed a distorted octahedral geometry where two *tert*-butyl peroxide ligands coordinate to the cobalt(III) center in the *cis* positions (Fig. 2a). To the best of our knowledge, this is the first crystal structure of a mononuclear  $\text{Co}^{\text{III}}\text{-(OO}^t\text{Bu)}_2$  complex. The average Co–O ( $1.8590\text{ \AA}$ ) and O–O ( $1.4757\text{ \AA}$ ) bond distances of **2** are comparable to those of the  $\text{Co}^{\text{III}}\text{-OO}^t\text{Bu}$  complexes (Table S2, ESI<sup>†</sup>).<sup>1,33</sup>

Thermal decomposition of **2** produced a  $\text{Co}^{\text{III}}\text{-(OO}^t\text{Bu)(OH)}$  complex,  $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})(\text{OO}^t\text{Bu)(OH)}]^+$  (**3**), in  $\text{CH}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$  (Fig. S2, ESI<sup>†</sup>).<sup>34</sup> Formation of **3** was confirmed by cold spray ionization spectrometry (CSI-MS). The CSI-MS spectrum of **3** shows a prominent signal at  $m/z$  413.17 (calcd  $m/z$  413.20) (Fig. S3, ESI<sup>†</sup>). Upon adding isotopically labeled  $\text{H}_2^{18}\text{O}$  and  $\text{D}_2\text{O}$  into the solution of **3**, mass peaks at 415.21 and 414.22 corresponding to  $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})(\text{OO}^t\text{Bu})(^{18}\text{OH})]^+$  (calcd  $m/z$  415.20) and  $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})(\text{OO}^t\text{Bu)(OD)}]^+$  (calcd  $m/z$  414.20), respectively, were observed (Fig. S3, ESI<sup>†</sup>, the inset). These mass shifts demonstrate that **3** contains a hydroxide ligand. In a previous study, the  $\text{Fe}\text{-(OO}^t\text{Bu)}_2$  species was also proposed as a precursor of the  $\text{Fe}\text{-(OO}^t\text{Bu)}$  species.<sup>29</sup> Tajima *et al.* insisted that  $[\text{Fe}^{\text{III}}(\text{TPP})(\text{OO}^t\text{Bu})_2]^-$ , generated by adding an excess amount of sodium methoxide ( $\text{NaOCH}_3$ ) and  $^t\text{BuOOH}$  to the  $[\text{Fe}^{\text{III}}(\text{TPP})]^+$  solution, reacted with additional  $\text{NaOCH}_3$ , affording the formation of the  $[\text{Fe}^{\text{III}}(\text{TPP})(\text{OO}^t\text{Bu)(OCH}_3)]^-$  species.<sup>29</sup>



**Fig. 2** ORTEP plots of the (a)  $\text{Co}^{\text{III}}\text{-(OO}^t\text{Bu)}_2$  complex,  $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})(\text{OO}^t\text{Bu})_2]^+$  (**2**), and  $\text{Co}^{\text{III}}\text{-(OO}^t\text{Bu)(X)}$  complexes,  $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})(\text{OO}^t\text{Bu)(X)}]^+$  ( $X =$  (b)  $\text{N}_3$  (**4**), (c)  $\text{NCS}$  (**5**)), with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

We then investigated the electrophilic and nucleophilic reactivities of **2**. The electrophilic reaction of **2** was performed by using styrene and 2,3-dimethyl-2-butene. Upon addition of substrates to the solution of **2** in  $\text{CH}_3\text{CN}$  at  $10\text{ }^\circ\text{C}$ , the intermediate remained intact without showing specific UV-vis spectral changes, and product analysis of these reaction solutions did not show oxidized products (Scheme 1). In contrast, the nucleophilic reactivity of **2** was observed in the oxidation of aldehydes (Scheme 1). Upon the addition of benzaldehyde to **2** in  $\text{CH}_3\text{CN}$  at  $15\text{ }^\circ\text{C}$ , the characteristic absorption band of **2** disappeared with a pseudo-first-order decay (Fig. 3a, the inset and Table S3, ESI<sup>†</sup>). The product analysis of the reaction solution revealed that benzoic acid (95(1)%) was produced in the oxidation of benzaldehyde (Scheme S2, ESI<sup>†</sup>). In addition, the cobalt(II)-benzoato complex,  $[\text{Co}^{\text{II}}(\text{Me}_3\text{-TPADP})(\text{C}_6\text{H}_5\text{COO})]^+$ , was generated after the reaction was completed (Fig. S7, ESI<sup>†</sup> for CSI-MS analysis). The reactivity of **2** was further investigated with *para*-substituted benzaldehydes, *para*- $X\text{-Ph-CHO}$  ( $X = \text{Me, F, Cl, and CF}_3$ ) (Table S3, ESI<sup>†</sup>). The Hammett plot of the pseudo-first-order rate constants *versus*  $\sigma_p^+$  gave a  $\rho$  value of  $0.7(1)$  (Fig. 3b). The positive  $\rho$  value indicates that **2** has nucleophilic character. The reactivity of **2** was further examined by using primary (1-pentanal for  $1^\circ\text{-CHO}$ ), secondary (2-methylbutanal for  $2^\circ\text{-CHO}$ ), and tertiary (pivalaldehyde for  $3^\circ\text{-CHO}$ ) aldehydes, and the observed reactivity order of  $1^\circ\text{-CHO} > 2^\circ\text{-CHO} > 3^\circ\text{-CHO}$  supports the nucleophilic character of **2** as well (Fig. S8, ESI<sup>†</sup>). Product analyses of the resulting solutions revealed that pentanoic acid (94(3)%), 2-methylbutanoic acid (94(4)%), and 2,2-dimethylpropanoic acid (94(1)%) were produced in the oxidation of 1-pentanal, 2-methylbutanal, and pivalaldehyde, respectively (Table S4, ESI<sup>†</sup>).

Upon the addition of 2-phenylpropionaldehyde (2-PPA) to **2** in  $\text{CH}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$  under aerobic conditions, the UV-vis absorption

Scheme 1 Overall electrophilic and nucleophilic reactivities of **2**, **4** and **5**.

Fig. 3 Reactions of  $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})(\text{OO}^t\text{Bu})_2]^+$  (**2**) with benzaldehyde in  $\text{CH}_3\text{CN}/\text{MeOH}$  ( $v/v = 3:1$ ). (a) UV-vis spectral changes of **2** (0.5 mM) upon addition of 200 equiv. of benzaldehyde at 15 °C. Inset shows the time course of the absorbance at 400 nm. (b) Hammett plot of  $\ln k_{\text{rel}}$  against  $\sigma_p^+$  of *para*-substituted benzaldehydes. The  $k_{\text{rel}}$  values were calculated by dividing  $k_{\text{obs}}$  of *para*-X-Ph-CHO ( $X = \text{Me}, \text{F}, \text{H}, \text{Cl}, \text{and CF}_3$ ) by  $k_{\text{obs}}$  of benzaldehyde at 15 °C.

band of **2** slightly changed with isosbestic points at 390 and 452 nm, which follows a pseudo-first-order decay profile (Fig. S9, ESI<sup>†</sup>). The pseudo-first-order rate constants increased proportionally with the 2-PPA concentration, giving a second-order rate constant ( $k_2$ ) of  $4.1(3) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C (Fig. S10a, ESI<sup>†</sup>). After the reaction of **2** with 2-PPA, product analysis revealed that acetophenone (95(1)%) was produced as a final product. The CSI-MS spectrum of the reaction solution revealed the formation of **3** and a small amount of cobalt(II)-formate species was also detected under an inert atmosphere (Fig. S11, ESI<sup>†</sup>). The temperature dependence of the  $k_2$  values was examined in the range of 273–298 K, where a linear Eyring plot was obtained with the activation parameters of  $\Delta H^\ddagger = 11(1) \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -22(3) \text{ cal mol}^{-1} \text{ K}^{-1}$  (Fig. S10b, ESI<sup>†</sup>). The observed negative entropy value and the second-order kinetics suggest that the oxidation of 2-PPA by **2** is performed through a bimolecular mechanism.

Interestingly, the same reaction performed under a  $\text{N}_2$  atmosphere gives different products. The reaction of **2** with 2-PPA under  $\text{N}_2$  in  $\text{CH}_3\text{CN}$  at 25 °C gave a new absorption band at 480 nm (Fig. S12, ESI<sup>†</sup>). By analysing the resulting solution with CSI-MS, we found that a cobalt(II)-enolate complex,  $[\text{Co}^{\text{II}}(\text{Me}_3\text{-TPADP})(\text{OCH}=\text{C}(\text{Me})\text{Ph})]^+$ , was formed as a decomposed product (Fig. S13, ESI<sup>†</sup>). The product analysis of the reaction solution indicated that trace amounts of acetophenone were produced (<1%) after the reaction. When the cobalt(II)-enolate complex was exposed to  $\text{O}_2$ , a cobalt(II)-formate complex was obtained as a major product, as observed by CSI-MS (Fig. S14, ESI<sup>†</sup>). These results are very similar to Tolman's recent mechanism of the aldehyde deformylation pathway *via* a copper(II)-enolate species.<sup>35</sup> Based on the kinetic studies and product analyses under  $\text{N}_2$  and  $\text{O}_2$ , the possible reaction mechanisms for 2-PPA oxidation by **2** are summarized in Scheme 2. The reaction of **2** and 2-PPA in the presence of water afforded enolate and a putative cobalt(III)-(OO<sup>t</sup>Bu) species through  $\alpha$ -deprotonation of 2-PPA by one of the alkylperoxides of **2**. The putative cobalt(III)-(OO<sup>t</sup>Bu) species decomposed to the cobalt(II)-enolate complex under  $\text{N}_2$ . In the presence of  $\text{O}_2$ , the enolate is oxidized to acetophenone, and complex **3** is produced as a final product.

In the aldehyde oxidation, only one OO<sup>t</sup>Bu ligand in **2** was able to participate in the oxidation of 2-PPA (Scheme 1). To compare the reactivity properties of  $\text{Co}^{\text{III}}\text{-(OO}^t\text{Bu)}$  and  $\text{Co}^{\text{III}}\text{-(OO}^t\text{Bu)}_2$  complexes,  $\text{Co}^{\text{III}}\text{-(OO}^t\text{Bu)(X)}$  complexes,  $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})(\text{OO}^t\text{Bu)(X})]^+$  ( $X = \text{N}_3$  for **4**, NCS for **5**), were synthesized. **4** and **5** were prepared by adding 1.1 equiv. of NaX ( $X = \text{N}_3$ , NCS) to the reaction solution of **1** in  $\text{CH}_3\text{CN}$  at 25 °C and then 5 equiv.



Scheme 2 Proposed reaction pathways of **2** with 2-PPA under  $\text{N}_2$  and  $\text{O}_2$  ( $L = \text{Me}_3\text{-TPADP}$ ,  $R = ^t\text{Bu}$ ).

of <sup>t</sup>BuOOH and 2 equiv. of TEA were added (Scheme S1, ESI<sup>†</sup>). Characterization of **4** and **5** was performed by UV-vis, ESI-MS, EPR, and <sup>1</sup>H NMR analyses (Experimental section and Fig. S15–S19, ESI<sup>†</sup>).

The single crystals of **4** and **5** revealed a similar distorted octahedral geometry to that of **2** in which one OO<sup>t</sup>Bu ligand bound to the cobalt(III) center was located in the *trans* position of the amine group and the other anionic monodentate ligand, X, was located in the *trans* position of the pyridine ring (Fig. 2b and c). These data clearly indicate that the OO<sup>t</sup>Bu ligand in the *trans* position of the pyridine ring in **2** was substituted with an anionic ligand in **3** and **4**. The Co–O1 bond distances (1.862(3) Å for **4**, 1.880(4) Å for **5**) and O1–O2 bond distances (1.479(4) Å for **4**, 1.430(6) Å for **5**) were within the range of those of the reported Co<sup>III</sup>–OO<sup>t</sup>Bu complexes and similar to those of **2** (Table S2, ESI<sup>†</sup>).<sup>1,33</sup>

In the reactions of **4** and **5** with 2-PPA, we could not observe any change in the UV-vis spectra. Based on the reactivity and structural comparison of **2**, **4**, and **5**, the reaction site of **2** is presumed to be the OO<sup>t</sup>Bu ligand in the *trans* position of the pyridine ring. Further theoretical calculations on the detailed reaction mechanism of **2** with substrates are underway and will clarify the reaction site of **2**.

In conclusion, we have synthesized and characterized a mononuclear Co<sup>III</sup>–(OO<sup>t</sup>Bu)<sub>2</sub> intermediate, [Co<sup>III</sup>(Me<sub>3</sub>-TPADP)(OO<sup>t</sup>Bu)<sub>2</sub>]<sup>+</sup> (**2**), with various physicochemical methods including UV-vis, ESI-MS, EPR, X-ray, and NMR analyses. In the kinetic studies, under mild conditions, one of the two OO<sup>t</sup>Bu ligands in **2** is capable of performing a nucleophilic reaction (*i.e.*, aldehyde oxidation). A Co<sup>III</sup>–(OO<sup>t</sup>Bu)(OH) complex, **3**, was generated by thermal decomposition of **2** and/or deformylation reaction of 2-PPA by **2** in the presence of O<sub>2</sub>. Furthermore, Co<sup>III</sup>–(OO<sup>t</sup>Bu) complexes, [Co<sup>III</sup>(Me<sub>3</sub>-TPADP)(OO<sup>t</sup>Bu)(X)]<sup>+</sup> (X = N<sub>3</sub> for **4**, NCS for **5**), which have a OO<sup>t</sup>Bu ligand in the *trans* position of the amine group were prepared, and **4** and **5** did not undergo aldehyde oxidation.

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## Conflicts of interest

The authors declare no competing financial interest.

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- Interestingly, the decay of **2** was facilitated by adding excess water in **2**, and a cobalt(II)–hydroxo complex was observed as a major peak in CSI-MS (Fig. S4–S6, ESI<sup>†</sup>).
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