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# Nucleophilic reactivity of a mononuclear cobalt(III)-bis(tert-butylperoxo) complex†

Bongki Shin, 🕩 ± Younwoo Park, ± Donghyun Jeong and Jaeheung Cho 🕩 \*

A mononuclear cobalt(III)-bis(tert-butylperoxo) adduct (CoIII-(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 OOtBu ligands bound to the equatorial position of the cobalt(III) center. Kinetic studies and product analyses indicate that the Co<sup>III</sup>-(OOtBu)2 intermediate exhibits nucleophilic oxidative reactivity toward external organic substrates.

Transition metal-alkylperoxo (M-OOR) species play an important role in oxidation reactions such as industrial and biological catalytic oxidation. 1-6 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. 1,7 Mononuclear nonheme M-OOR complexes have been suggested to play a significant role in the oxidation reaction of metalloenzyme systems (e.g., lipoxygenase 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. 2,5,6,10-13 A number of M-OOR complexes were mainly studied in the investigation of electrophilic reactions (e.g., oxygen and hydrogen atom transfer reaction). 14-25 It has been reported that the reaction proceeds via the \*OOR and \*OR radicals from decomposition of the M-OOR species.1 However, only a few examples of nucleophilic reactivity with M-OOR intermediates (M = Fe, Ni, and Cu) have been reported. 19,20,23

Department of Emerging Materials Science, DGIST, Daegu 42988, Korea. E-mail: jaeheung@dgist.ar.kr

In the Sharpless-Katsuki epoxidation,  $Ti-(OOR)_n$  (n = 1-4) species were proposed as reactive intermediates. 26,27 Furthermore, in the formation of Fe-OO<sup>t</sup>Bu complexes, Fe-(OO<sup>t</sup>Bu)<sub>2</sub> species,  $[Fe^{III}(TPP)(OO^tBu)_2]^-$  (TPP = 5,10,15,20-tetraphenylporphyrinate) and  $[Fe^{III}(BPMCN)(OO^tBu)(HOO^tBu)]^{2+}$  (BPMCN = N,N'-bis (2-pyridylmethyl-*N*,*N*′-dimethyl-*trans*-1,2-diaminocyclohexane)) adducts, have been proposed as short-lived intermediates. 28-31 However, definitive evidence of bis(alkylperoxo) binding firstrow 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, [CoIII(Me3- $TPADP)(OO^{t}Bu)_{2}]^{+}$  (2,  $Me_{3}$ -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 alkylperoxo and bis(alkylperoxo) binding cobalt species, Co<sup>III</sup>- $(OO^tBu)(X)$  complexes,  $[Co^{III}(Me_3-TPADP)(OO^tBu)(X)]^+$   $(X = N_3)$ 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 (\*BuOOH) was added to 1 in the presence of 2 equiv. of triethylamine (TEA) in CH<sub>3</sub>CN at 25 °C, the  $Co^{III}$ – $(OO^tBu)_2$  adduct,  $[Co^{III}(Me_3-TPADP)(OO^tBu)_2]^{\dagger}$ (2), was generated and the solution color changed from purple to dark green (Scheme S1, ESI†). 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  $CH_3CN$  at 25  $^{\circ}C$  shows electronic absorption bands at  $\lambda_{\text{max}} = \sim 360 \ (\epsilon = 1100 \ \text{M}^{-1} \ \text{cm}^{-1})$  and 583 nm ( $\varepsilon$  = 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  $[Co^{III}(Me_3-TPADP)(OO^tBu)_2]^+$  (calcd m/z485.3) (Fig. 1b). The X-band electron paramagnetic resonance (EPR) silence (Fig. 1a, inset) and <sup>1</sup>H NMR spectral features (Fig. S1, ESI†) in the diamagnetic region confirm that complex 2 is a low-spin S = 0 cobalt(III) species.

<sup>†</sup> Electronic supplementary information (ESI) available: Synthesis and characterization data and kinetic details, CCDC 1906994-1906996. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ d0cc03385e

<sup>‡</sup> These authors contributed equally to this work.

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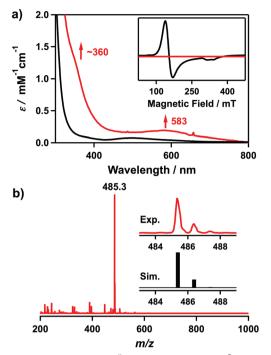


Fig. 1 (a) UV-vis spectra of  $[Co^{II}(Me_3-TPADP)(CH_3CN)_2]^{2+}$  (1) (the black line) and  $[Co^{III}(Me_3-TPADP)(OO^tBu)_2]^+$  (2) (the red line) in  $CH_3CN$  at 25 °C.  $^{32}$  Inset shows the X-band EPR spectra of 1 (the black line) in frozen  $CH_3CN$  at 5 K and 2 (the red line) in frozen  $CH_3CN$  at 113 K.  $^{32}$  The parameters for the measurement of 2: microwave power = 1.0 mW, frequency = 9.176 GHz, sweep width = 0.40 T, and modulation amplitude = 0.60 mT. (b) ESI-MS of 2 in  $CH_3CN$  at -40 °C. Insets show experimental (upper) and simulated (lower) isotope distribution patterns.

The X-ray crystal structure of  $[Co^{III}(Me_3\text{-TPADP})(OO^fBu)_2]$   $(BPh_4)(Et_2O)$  (2-BPh<sub>4</sub>·Et<sub>2</sub>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  $Co^{III}$ – $(OO^fBu)_2$  complex. The average Co–O (1.8590 Å) and O–O (1.4757 Å) bond distances of 2 are comparable to those of the  $Co^{III}$ – $OO^fBu$  complexes (Table S2, ESI†).<sup>1,33</sup>

Thermal decomposition of 2 produced a Co<sup>III</sup>-(OO<sup>t</sup>Bu)(OH) complex,  $[Co^{III}(Me_3-TPADP)(OO^tBu)(OH)]^+$  (3), in  $CH_3CN$ at 25 °C (Fig. S2, ESI†).34 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/z413.20) (Fig. S3, ESI†). Upon adding isotopically labeled H<sub>2</sub><sup>18</sup>O and D<sub>2</sub>O into the solution of 3, mass peaks at 415.21 and 414.22 corresponding to [Co<sup>III</sup>(Me<sub>3</sub>-TPADP)(OO<sup>t</sup>Bu)(<sup>18</sup>OH)]<sup>+</sup> (calcd m/z 415.20) and  $[Co^{III}(Me_3-TPADP)(OO^tBu)(OD)]^+$ (calcd m/z 414.20), respectively, were observed (Fig. S3, ESI,† the inset). These mass shifts demonstrate that 3 contains a hydroxide ligand. In a previous study, the Fe-(OO<sup>t</sup>Bu)<sub>2</sub> species was also proposed as a precursor of the Fe-(OO<sup>t</sup>Bu) species.<sup>29</sup> Tajima et al. insisted that [Fe<sup>III</sup>(TPP)(OO<sup>t</sup>Bu)<sub>2</sub>]<sup>-</sup>, generated by adding an excess amount of sodium methoxide (NaOCH3) and <sup>t</sup>BuOOH to the [Fe<sup>III</sup>(TPP)]<sup>+</sup> solution, reacted with additional  $NaOCH_3$ , affording the formation of the  $[Fe^{III}(TPP)(OO^tBu)]$ (OCH<sub>3</sub>)]<sup>-</sup> species.<sup>29</sup>

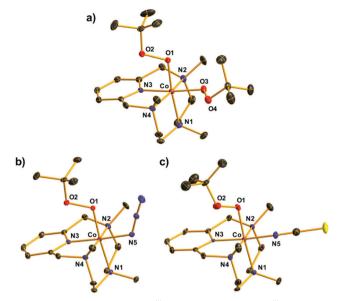
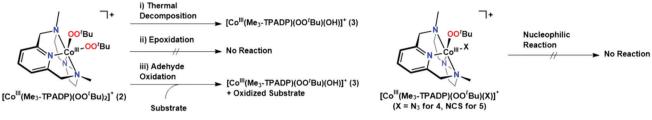


Fig. 2 ORTEP plots of the (a)  $Co^{III}-(OO^tBu)_2$  complex,  $[Co^{III}(Me_3-TPADP)(OO^tBu)_2]^+$  (2), and  $Co^{III}-(OO^tBu)(X)$  complexes,  $[Co^{III}(Me_3-TPADP)(OO^tBu)(X)]^+$  (X = (b)  $N_3$  (4), (c) NCS (5)), with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are 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 CH<sub>3</sub>CN at 10 °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 CH<sub>3</sub>CN at 15 °C, the characteristic absorption band of 2 disappeared with a pseudo-first-order decay (Fig. 3a, the inset and Table S3, ESI†). The product analysis of the reaction solution revealed that benzoic acid (95(1)%) was produced in the oxidation of benzaldehyde (Scheme S2, ESI†). In addition, the cobalt(II)-benzoato complex, [Co<sup>II</sup>(Me<sub>3</sub>-TPADP)(C<sub>6</sub>H<sub>5</sub>COO)]<sup>+</sup>, was generated after the reaction was completed (Fig. S7, ESI† for CSI-MS analysis). The reactivity of 2 was further investigated with para-substituted benzaldehydes, para-X-Ph-CHO (X = Me, F,Cl, and CF<sub>3</sub>) (Table S3, ESI†). The Hammett plot of the pseudofirst-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°-CHO), secondary (2-methylbutanal for 2°-CHO), and tertiary (pivalaldehyde for 3°-CHO) aldehydes, and the observed reactivity order of 1°-CHO > 2°-CHO > 3°-CHO supports the nucleophilic character of 2 as well (Fig. S8, ESI†). Product analyses of the resulting solutions revealed that pentanoic acid (94(3)%), 2-methylbutanoic acid (94(4)%), and 2,2dimethylpropanoic acid (94(1)%) were produced in the oxidation of 1-pentanal, 2-methylbutanal, and pivalaldehyde, respectively (Table S4, ESI†).

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



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

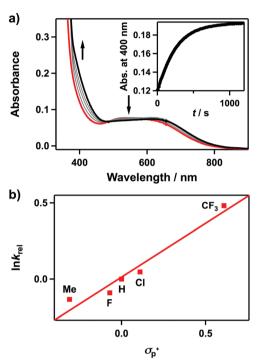


Fig. 3 Reactions of  $[Co^{III}(Me_3-TPADP)(OO^tBu)_2]^+$  (2) with benzaldehyde in CH<sub>3</sub>CN/MeOH (v/v = 3:1). (a) UV-vis spectral changes of 2 (0.5 mM) upon addition of 200 equiv. of benzaldehyde at 15 °C. Inset shows the time course of the absorbance at 400 nm. (b) Hammett plot of  $\ln k_{\rm rel}$  against  $\sigma_{\rm p}^+$  of para-substituted benzaldehydes. The  $k_{\rm rel}$  values were calculated by dividing  $k_{\rm obs}$  of para-X-Ph-CHO (X = Me, F, H, Cl, and CF<sub>3</sub>) by  $k_{\rm obs}$  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†). 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†). 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)-formato species was also detected under an inert atmosphere (Fig. S11, ESI†). 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  $\Delta H^{\ddagger} = 11(1)$  kcal mol<sup>-1</sup> and  $\Delta S^{\ddagger} =$ -22(3) cal mol<sup>-1</sup> K<sup>-1</sup> (Fig. S10b, ESI†). 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 N<sub>2</sub> atmosphere gives different products. The reaction of 2 with 2-PPA under N<sub>2</sub> in CH<sub>3</sub>CN at 25 °C gave a new absorption band at 480 nm (Fig. S12, ESI†). By analysing the resulting solution with CSI-MS, we found that a cobalt(II)-enolate complex, [Co<sup>II</sup>(Me<sub>3</sub>-TPADP)(OCH=C(Me)Ph)]<sup>+</sup>, was formed as a decomposed product (Fig. S13, ESI†). The product analysis of the reaction solution indicated that trace amounts of acetophenone were produced (<1%) after the reaction. When the cobalt( $\Pi$ )– enolate complex was exposed to O2, a cobalt(II)-formato complex was obtained as a major product, as observed by CSI-MS (Fig. S14, ESI†). These results are very similar to Tolman's recent mechanism of the aldehyde deformylation pathway via a copper(II)enolate species.35 Based on the kinetic studies and product analyses under N2 and O2, 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 $^t$ 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  $N_2$ . In the presence of  $O_2$ , the enolate is oxidized to acetophenone, and complex 3 is produced as a final product.

In the aldehyde oxidation, only one  $OO^tBu$  ligand in 2 was able to participate in the oxidation of 2-PPA (Scheme 1). To compare the reactivity properties of  $CO^{III}$ – $(OO^tBu)$  and  $CO^{III}$ – $(OO^tBu)_2$  complexes,  $CO^{III}$ – $(OO^tBu)(X)$  complexes,  $[CO^{III}(Me_3-TPADP)(OO^tBu)(X)]^+$  ( $X = N_3$  for 4, NCS for 5), were synthesized. 4 and 5 were prepared by adding 1.1 equiv. of NaX ( $X = N_3$ , NCS) to the reaction solution of 1 in  $CH_3CN$  at 25 °C and then 5 equiv.

Scheme 2 Proposed reaction pathways of  ${\bf 2}$  with 2-PPA under  $N_2$  and  $O_2$  (L = Me<sub>3</sub>-TPADP, R =  $^t$ Bu).

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of <sup>t</sup>BuOOH and 2 equiv. of TEA were added (Scheme S1, ESI†). 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†).

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>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'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  $Co^{III}$ – $(OO^tBu)_2$  intermediate,  $[Co^{III}(Me_3\text{-TPADP})(OO^tBu)_2]^+$  (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  $OO^tBu$  ligands in 2 is capable of performing a nucleophilic reaction (*i.e.*, aldehyde oxidation). A  $Co^{III}$ – $(OO^tBu)(OH)$  complex, 3, was generated by thermal decomposition of 2 and/or deformylation reaction of 2-PPA by 2 in the presence of  $O_2$ . Furthermore,  $Co^{III}$ – $(OO^tBu)$  complexes,  $[Co^{III}(Me_3\text{-TPADP})(OO^tBu)(X)]^+$  ( $X = N_3$  for 4, NCS for 5), which have a  $OO^tBu$  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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