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A mononuclear cobalt(III)-bis(tert-butylperoxo) adduct (CoIII-(OO^tBu)₂) 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^{III}-(OO^tBu)₂ 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^{III}-(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^{III}-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).^{8,9} 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

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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^tBu complexes, Fe-(OO^tBu)₂ 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^{III}-(OO^tBu)₂ 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^tBu 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^{III}- $(OO^tBu)(X)$ 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^{II}(Me₃-TPADP)(CH₃CN)₂]²⁺ (1), was synthesized by using a published method.³² When 10 equiv. of tert-butyl hydroperoxide (*BuOOH) was added to 1 in the presence of 2 equiv. of triethylamine (TEA) in CH₃CN 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 CH₃CN 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 (ε = 190 M⁻¹ cm⁻¹) (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 ¹H NMR spectral features (Fig. S1, ESI†) in the diamagnetic region confirm that complex 2 is a low-spin S = 0 cobalt(III) species.

[†] 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

[‡] These authors contributed equally to this work.

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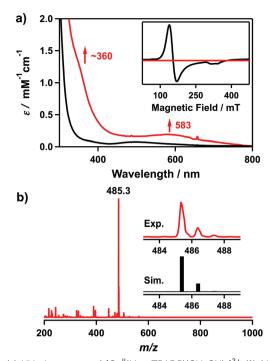


Fig. 1 (a) UV-vis spectra of $[Co^{II}(Me_3-TPADP)(CH_3CN)_2]^{2+}$ (1) (the black line) and $[Co^{III}(Me_3-TPADP)(OO^tBu)_2]^+$ (2) (the red line) in CH_3CN at 25 °C. 32 Inset shows the X-band EPR spectra of 1 (the black line) in frozen CH_3CN at 5 K and 2 (the red line) in frozen CH_3CN at 113 K. 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-BPh₄·Et₂O) 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†).^{1,33}

Thermal decomposition of 2 produced a Co^{III}-(OO^tBu)(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 H₂¹⁸O and D₂O into the solution of 3, mass peaks at 415.21 and 414.22 corresponding to [Co^{III}(Me₃-TPADP)(OO^tBu)(¹⁸OH)]⁺ (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^tBu)₂ species was also proposed as a precursor of the Fe-(OO^tBu) species.²⁹ Tajima et al. insisted that [Fe^{III}(TPP)(OO^tBu)₂]⁻, generated by adding an excess amount of sodium methoxide (NaOCH3) and ^tBuOOH to the [Fe^{III}(TPP)]⁺ solution, reacted with additional $NaOCH_3$, affording the formation of the $[Fe^{III}(TPP)(OO^tBu)]$ (OCH₃)] species. 29

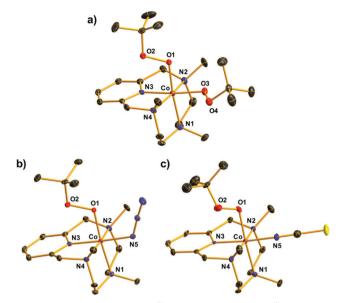
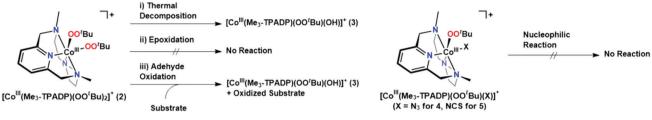


Fig. 2 ORTEP plots of the (a) $Co^{III}-(OO^tBu)_2$ complex, $[Co^{III}(Me_3-TPADP)(OO^tBu)_2]^+$ (2), and $Co^{III}-(OO^tBu)(X)$ complexes, $[Co^{III}(Me_3-TPADP)(OO^tBu)(X)]^+$ (X = (b) N_3 (4), (c) NCS (5)), with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for 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 CH₃CN 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 CH₃CN 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^{II}(Me₃-TPADP)(C₆H₅COO)]⁺, 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 CF₃) (Table S3, ESI†). The Hammett plot of the pseudofirst-order rate constants versus σ_p^+ gave a ρ value of 0.7(1) (Fig. 3b). The positive ρ 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 $\rm CH_3CN$ at 25 $^{\circ}C$ under ae robic conditions, the UV-vis absorption ChemComm Communication



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

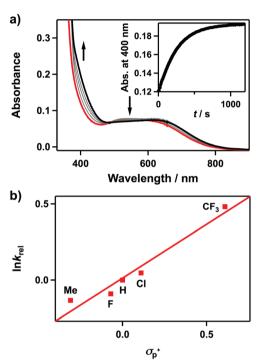


Fig. 3 Reactions of $[Co^{III}(Me_3-TPADP)(OO^rBu)_2]^+$ (2) with benzaldehyde in CH₃CN/MeOH (v/v = 3:1). (a) UV-vis spectral changes of 2 (0.5 mM) upon addition of 200 equiv. of benzaldehyde at 15 °C. Inset shows the time course of the absorbance at 400 nm. (b) Hammett plot of $\ln k_{\rm rel}$ against $\sigma_{\rm p}^+$ 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 CF₃) 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⁻¹ and $\Delta S^{\ddagger} =$ -22(3) cal mol⁻¹ K⁻¹ (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 N₂ atmosphere gives different products. The reaction of 2 with 2-PPA under N₂ in CH₃CN 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^{II}(Me₃-TPADP)(OCH=C(Me)Ph)]⁺, 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(Π)– 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 α -deprotonation of 2-PPA by one of the alkylperoxides of 2. The putative cobalt(III)-(OO^tBu) 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 = Me₃-TPADP, R = t Bu).

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of ^tBuOOH and 2 equiv. of TEA were added (Scheme S1, ESI†). Characterization of 4 and 5 was performed by UV-vis, ESI-MS, EPR, and ¹H 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^tBu 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^tBu 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^{III}–OO^tBu complexes and similar to those of 2 (Table S2, ESI†). ^{1,33}

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} – $(\text{OO}^t\text{Bu})_2$ intermediate, $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})$ $(\text{OO}^t\text{Bu})_2]^+$ (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} – $(\text{OO}^t\text{Bu})(\text{OH})$ 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, $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})(\text{OO}^t\text{Bu})(\text{X})]^+$ (X = N₃ 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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