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

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A mononuclear cobalt(III)-bis(tert-butylperoxo) adduct $(Co^{III}-(OO^tBu)_2)$ 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 OO^tBu ligands bound to the equatorial position of the cobalt(III) center. Kinetic studies and product analyses indicate that the $Co^{III}-(OO^tBu)_2$ 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}

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 $[Fe^{III}(BPMCN)(OO^{t}Bu)(HOO^{t}Bu)]^{2+}$ (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, [Co^{III}(Me₃-TPADP)(OO^tBu)₂]⁺ (2, Me₃-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}- $(OO^{t}Bu)(X)$ complexes, $[CO^{III}(Me_{3}-TPADP)(OO^{t}Bu)(X)]^{+}$ $(X = N_{3})$ for 4, NCS for 5), were prepared as well.

The cobalt(II) starting complex, $[Co^{II}(Me_3-TPADP)(CH_3CN)_2]^{2+}$ (1), was synthesized by using a published method.³² When 10 equiv. of *tert*-butyl hydroperoxide (^tBuOOH) 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, $[Co^{III}(Me_3-TPADP)(OO^tBu)_2]^+$ (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 CH₃CN at 25 °C shows electronic absorption bands at $\lambda_{max} = \sim 360$ ($\varepsilon = 1100 \text{ M}^{-1} \text{ cm}^{-1}$) and 583 nm ($\varepsilon = 190 \text{ M}^{-1} \text{ cm}^{-1}$) (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}(Me₃-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(m) species.

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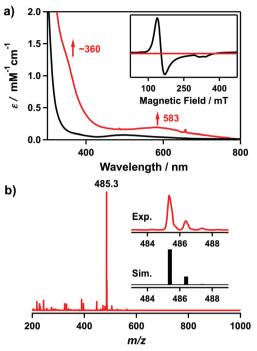


Fig. 1 (a) UV-vis spectra of $[Co^{II}(Me_3-TPADP)(CH_3CN)_2]^{2+}$ (1) (the black line) and $[Co^{III}(Me_3-TPADP)(OO^{T}Bu)_2]^{+}$ (2) (the red line) in CH₃CN at 25 °C.³² Inset shows the X-band EPR spectra of 1 (the black line) in frozen CH₃CN at 5 K and 2 (the red line) in frozen CH₃CN at 113 K.³² 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 CH₃CN at -40 °C. Insets show experimental (upper) and simulated (lower) isotope distribution patterns.

The X-ray crystal structure of $[Co^{III}(Me_3-TPADP)(OO'Bu)_2]$ (BPh₄)(Et₂O) (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'Bu)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'Bu 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^{\dagger}). 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 NaOCH₃, affording the formation of the $[Fe^{III}(TPP)(OO^tBu)]$ (OCH₃)]⁻ species.²⁹

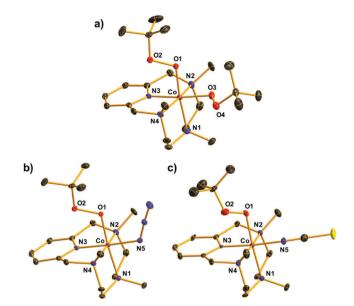
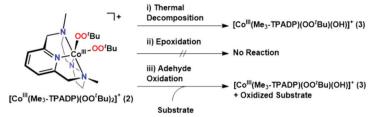


Fig. 2 ORTEP plots of the (a) Co^{III} -(OO^tBu)₂ complex, [Co^{III}(Me₃-TPADP) (OO^tBu)₂]⁺ (**2**), and Co^{III}-(OO^tBu)(X) complexes, [Co^{III}(Me₃-TPADP) (OO^tBu)(X)]⁺ (X = (b) N₃ (**4**), (c) NCS (**5**)), with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for 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, $[Co^{II}(Me_3-TPADP)(C_6H_5COO)]^+$, 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-phenyl propional dehyde (2-PPA) to 2 in CH₃CN at 25 $^\circ \rm C$ under a erobic conditions, the UV-vis absorption



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

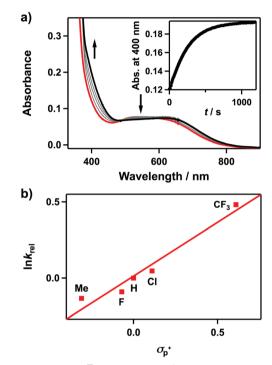
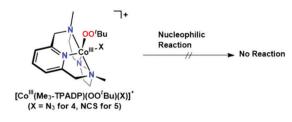


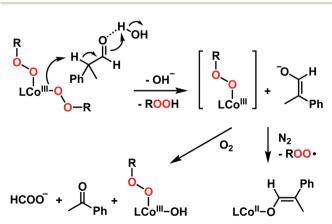
Fig. 3 Reactions of $[Co^{III}(Me_3-TPADP)(OO^{t}Bu)_2]^+$ (**2**) with benzaldehyde in CH₃CN/MeOH (v/v = 3 : 1). (a) UV-vis spectral changes of **2** (0.5 mM) upon addition of 200 equiv. of benzaldehyde at 15 °C. Inset shows the time course of the absorbance at 400 nm. (b) Hammett plot of ln k_{rel} against σ_p^+ of *para*-substituted benzaldehydes. The k_{rel} values were calculated by dividing k_{obs} of *para*-X-Ph-CHO (X = Me, F, H, Cl, and CF₃) by k_{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) × 10⁻¹ M⁻¹ 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 N_2 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 $cobalt(\pi)$ -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(II)enolate complex was exposed to O_2 , a cobalt(π)-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(μ)–(OO^tBu) species through α -deprotonation of 2-PPA by one of the alkylperoxides of 2. The putative cobalt(m)-(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, $[\text{Co}^{\text{III}}(\text{Me}_{3}-\text{TPADP})(\text{OO}^{t}\text{Bu})(\text{X})]^{+}$ (X = N₃ for 4, NCS for 5), were synthesized. 4 and 5 were prepared by adding 1.1 equiv. of NaX (X = N₃, NCS) to the reaction solution of **1** in CH₃CN at 25 °C and then 5 equiv.



Scheme 2 Proposed reaction pathways of 2 with 2-PPA under N_2 and O_2 (L = Me_3-TPADP, R = tBu).

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^{*t*}Bu ligand bound to the cobalt(m) 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^{*t*}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^{III}–OO^{*t*}Bu 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^tBu 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'Bu 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 O₂. Furthermore, Co^{III}– (OO^{t}Bu) 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'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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