International Edition: DOI: 10.1002/anie.201610828 German Edition: DOI: 10.1002/ange.201610828

Fine Control of the Redox Reactivity of a Nonheme Iron(III)–Peroxo Complex by Binding Redox-Inactive Metal Ions

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Abstract: Redox-inactive metal ions are one of the most important co-factors involved in dioxygen activation and formation reactions by metalloenzymes. In this study, we have shown that the logarithm of the rate constants of electrontransfer and C-H bond activation reactions by nonheme iron(III)-peroxo complexes binding redox-inactive metal ions, $[(TMC)Fe^{III}(O_2)]^+-M^{n+}$ $(M^{n+}=Sc^{3+}, Y^{3+}, Lu^{3+}, and La^{3+}),$ increases linearly with the increase of the Lewis acidity of the redox-inactive metal ions (ΔE), which is determined from the g_{zz} values of EPR spectra of $O_2^{-}-M^{n+}$ complexes. In contrast, the logarithm of the rate constants of the $[(TMC)Fe^{III}(O_2)]^+$ - M^{n+} complexes in nucleophilic reactions with aldehydes decreases linearly as the ΔE value increases. Thus, the Lewis acidity of the redox-inactive metal ions bound to the mononuclear nonheme iron(III)-peroxo complex modulates the reactivity of the $[(TMC)Fe^{III}(O_2)]^+$ - M^{n+} complexes in electrontransfer, electrophilic, and nucleophilic reactions.

 \mathbf{R} edox-inactive metal ions that function as Lewis acids are known to play pivotal roles in a variety of oxidation reactions by oxygen-containing metal intermediates, such as highvalent metal-oxo species, in biological and biomimetic systems.^[1-3] In particular, a redox-inactive Ca²⁺ ion is an essential component in the oxidation of water to evolve dioxygen in the oxygen-evolving complex (OEC, a heteronuclear Mn₄CaO₅ cubane complex) of Photosystem II (PS II),^[4-6] although the role of the Ca²⁺ ion in the O-O bond formation reaction has yet to be clarified. In biomimetic studies, it has been shown that reactivities of high-valent metal-oxo complexes in electron-transfer, oxygen atom transfer, and C-H bond activation reactions are enhanced markedly upon binding of redox-inactive metal ions, resulting from the positive shift of one-electron reduction potentials of the metal-oxo complexes.^[7-9] Redox-inactive metal ions are also reported to bind to various metal-(su)peroxo complexes

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	Supporting information for this article can be found under:

Supporting information for this article can be found under http://dx.doi.org/10.1002/anie.201610828.

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(for example, Fe–O₂, Ni–O₂, and Cu–O₂);^[10,11] metal–(su)peroxo complexes can be either electrophiles, which accept two electrons, or nucleophiles, which donate two electrons,^[12–16] and binding of redox-inactive metal ions by the metal– (su)peroxo complexes may affect the electrophilic and nucleophilic reactivities of the (su)peroxo ligand in oxidation reactions. However, effects of the redox-inactive metal ions on the redox reactivity of the metal–(su)peroxo complexes in electron-transfer and oxidation reactions have yet to be scrutinized quantitatively.

We report herein that the redox reactivity of a mononuclear nonheme iron(III)–peroxo complex bearing a macrocyclic *N*-tetramethylated cyclam ligand, $[(TMC)Fe^{III}(O_2)]^+$ (1, TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane),^[17] in electron-transfer, electrophilic, and nucleophilic reactions changes upon binding of redox-inactive metal ions (M^{*n*+}) at the iron–peroxo moiety (Scheme 1). The change in



Scheme 1. Molecular structure of $[(TMC)Fe^{III}(O_2)]^+ \cdot M^{n+}$; $M^{n+} = Sc^{3+}$, Y^{3+} , Lu^{3+} , and La^{3+}) and summary of the reactivities of 1- M^{n+} in electron-transfer, electrophilic, and nucleophilic reactions.

the redox reactivity of the iron(III)-peroxo complex (1) by binding of redox-inactive metal ions is then quantitatively evaluated as a function of the Lewis acidity of metal ions (ΔE) , which was determined from the g_{zz} values of EPR spectra of $O_2^{-}-M^{n+}$ complexes.^[18] To the best of our knowledge, the present study reports the first example showing the effects of the Lewis acidity of redox-inactive metal ions bound to a peroxo group in a mononuclear nonheme iron(III)– peroxo complex on the reactivity of the iron–peroxo complexes in electron-transfer and electrophilic and nucleophilic reactions.

The iron(III)-peroxo complex, $[(TMC)Fe^{III}(O_2)]^+$ (1), was synthesized by reacting $[Fe^{II}(TMC)(CF_3SO_3)_2]$ with 5 equiv H₂O₂ in the presence of 2 equiv triethylamine in acetonitrile (MeCN) at -40 °C and isolated as crystals for further studies.^[17] Redox-inactive metal ion-bound iron(III)peroxo complexes, $[(TMC)Fe^{III}(O_2)]^+$ -Mⁿ⁺ (1-Mⁿ⁺; Mⁿ⁺ =

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Sc³⁺, Y³⁺, Lu³⁺, and La³⁺), were generated by adding metal triflates (M^{*n*+}(CF₃SO₃)_{*n*}) to the solution of **1** in MeCN at 0°C according to previously reported methods (see Figure 1 for UV/Vis spectra of **1**-M^{*n*+}).^[19] We then investigated the electron-transfer (ET) reactions of **1**-M^{*n*+} complexes with ferrocene (Fc) derivatives. Upon addition of bromoferrocene (BrFc, $E_{ox} = 0.54$ V vs. SCE) to the solution of **1**-M^{*n*+} (M^{*n*+} = Sc³⁺, Y³⁺, Lu³⁺, and La³⁺) in MeCN at 0°C, the absorption band of **1**-M^{*n*+} decreased with the concurrent appearance of absorption bands at 820 nm owing to an iron(IV)–oxo complex, [(TMC)Fe^{IV}(O)]^{2+,[20]} and at 675 nm owing to the bromoferrocene (Fc) derivatives to **1**-M^{*n*+} afforded the formation of



Figure 1. UV/Vis spectra of 1 and 1-M $^{n+}$ (M $^{n+}\!=\!Sc^{3+},\,Y^{3+},\,Lu^{3+},$ and La $^{3+})$ in MeCN at 0°C.



Figure 2. Stopped-flow absorption spectral changes observed in ET from BrFc (0.50 mM) to $1-Sc^{3+}$ (0.50 mM, red line) in MeCN at 0 °C. The reaction was completed within 10 s. Inset shows UV/Vis spectra of $1-Sc^{3+}$ (0.50 mM, red line) and the final reaction solution (black line); the absorption bands at 675 and 820 nm correspond to BrFc⁺ and [(TMC)Fe^{IV}(O)]²⁺, respectively.



Scheme 2. Proposed mechanism of ET from BrFc to $1-M^{n+}$.

a putative $[(TMC)Fe^{II}(O_2)]-M^{n+}$ species (Scheme 2, reaction a), followed by a heterolytic O–O bond cleavage of the peroxide ligand in [(TMC)Fe^{II}(O₂)]-Mⁿ⁺ to form [(TMC)Fe^{IV}-(O)]²⁺ (Scheme 2, reaction *b*), as reported previously in ET reactions between $1-M^{n+}$ and Fc.^[19,21] The rate of ET was determined by following the decrease in the absorption band due to $1-M^{n+}$. The second-order rate constant of ET from BrFc to $1-Sc^{3+}$ was then determined to be $6.4(4) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ in MeCN at 0°C under second-order kinetic conditions owing to a fast reaction between 1-Sc³⁺ and BrFc (Supporting Information, Figure S1 a). In the cases of other 1- M^{n+} ($M^{n+} = Y^{3+}$, Lu³⁺, and La³⁺) complexes, the rates obeyed first-order kinetics under the pseudo first-order reaction conditions $([BrFc]/[1-M^{n+}] > 10)$. The first-order rate constants increased linearly with the increase in the BrFc concentration, and second-order rate constants (k_2) were determined at 0 °C (Supporting Information, Figure S1b and Table S1). The $\log k_2$ values increased linearly with the Lewis acidity of the metal ions (ΔE), which was determined from the $g_{\tau\tau}$ values of EPR spectra of $O_2^{-}-M^{n+}$ complexes, as shown in Figure 3.^[18] The ΔE is the energy splitting value of the π_{g} levels due to the binding of M^{n+} to a superoxo species.^[18] Thus, the ΔE value has been regarded as the binding energy of M^{n+} to $O_2^{-,[18]}$ which may be comparable to the binding energy of M^{n+} to the peroxo moiety of $[(TMC)Fe^{III}(O_2)]^+$. The stronger the Lewis acidity of M^{n+} is, the larger the splitting value is and the larger the $k_{\rm et}$ value becomes. The slope (18.4) of the linear plot with



Figure 3. Plots of $\log k_2$ values of ET from BrFc to $1-M^{n+}$ (blue circles), C⁻H bond activation reaction of CHD (black circles), and aldehyde deformylation reactions of 2-PPA (red circles) and CCA (green circles) by $1-M^{n+}$ in MeCN at 0°C against the quantitative measure of the Lewis acidity of metal ions (ΔE).

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blue line in Figure 3 indicates that about 100% of the change in the spitting energy of the π_g levels is reflected as the change in the transition state energy of ET from BrFc to **1**- M^{n+} at 0°C, because F/(2.3RT) at 0°C = 18.5. Virtually the same slopes were also obtained in ET from Fc ($E_{ox} = 0.37$ V vs. SCE) and dibromoferrocene (Br₂Fc; $E_{ox} = 0.71$ V vs. SCE) to **1**- M^{n+} complexes (Supporting Information, Figure S2 and Table S1).

The reactivity of iron(III)-peroxo complexes binding different redox-inactive metal ions, $1-M^{n+}$, was investigated in hydrogen atom transfer (HAT) reactions. While 1 was not able to activate the C-H bonds of 1,4-cyclohexadiene (CHD), 1-Mⁿ⁺ showed a reactivity with CHD. Upon addition of CHD to a solution of 1-Sc³⁺ in MeCN at 0°C, the UV/Vis absorption band of 1-Sc3+ disappeared with a pseudo firstorder decay profile (Figure 4a), and product analysis of the reaction solution revealed the formation of benzene (92 \pm 6%) as a product. Furthermore, $[(TMC)Fe^{III}(OH)]^+$ was formed as a decay product of $1-Sc^{3+}$ in the reaction solution (Supporting Information, Figure S3 for EPR and CSI-MS spectra). We have shown recently that a high-spin nonheme iron(III)-hydroperoxo complex, [(TMC)Fe^{III}(O₂H)]²⁺, is capable of activating C-H bonds of hydrocarbons with weak C-H bonds.^[17] The first-order rate constant was proportional to the substrate concentration, from which a second-order rate constant (k_2) was determined (Figure 4b). The second-order rate constants (k_2) of C-H bond activation of 1,4-cyclohexadiene by other $1-M^{n+}$ ($M^{n+} = Y^{3+}$, Lu^{3+} , and La³⁺) complexes were also determined (Supporting Information, Figure S4 and Table S1). The $\log k_2$ values increase linearly with increasing the Lewis acidity of metal ions (ΔE ; Figure 3, black line), and the slope (8.9) indicates that 48 % of



Figure 4. a) UV/Vis spectral changes observed in the electrophilic oxidation of CHD (200 mM) by $1-Sc^{3+}$ (0.50 mM) in MeCN at 0°C. Inset: time course monitored at 530 nm due to $1-Sc^{3+}$. b) Plot of the pseudo first-order rate constant (k_{obs}) versus the concentration of CHD to determine the second-order rate constant. c) UV/Vis spectral changes observed in the nucleophilic oxidation of 2-PPA (200 mM) by $1-Sc^{3+}$ (0.50 mM) in MeCN at 0°C. Inset: time course monitored at 530 nm due to $1-Sc^{3+}$. d) Plot of the pseudo first-order rate constant (k_{obs}) versus the concentration of 2-PPA to determine the second-order rate constant.

the change in the spitting energy of the π_g levels is reflected as the change in the transition state energy of the C–H bond activation of CHD by 1-M^{*n*+} at 0 °C. This percent is smaller than the case of electron-transfer from BrFc to 1-M^{*n*+} (ca. 100%, see above) because of a partial charge transfer in the electrophilic reaction instead of a full electron transfer. The k_2 values of C–H bond activation by 1-Sc³⁺ with alkylaromatic compounds bearing weak C–H bonds, such as xanthene (75.5 kcal mol⁻¹) and 9,10-dihydroanthracene (DAH, 77 kcal mol⁻¹), were determined as well (Supporting Information, Figure S5). The log k_2 values increase linearly with decreasing the C–H bond dissociation energies (BDEs) of the substrates.

The effect of the Lewis acidity of metal ions (ΔE) on the reactivity of $1-M^{n+}$ was also investigated in aldehyde deformylation reactions. The nucleophilic character of $1-M^{n+}$ was demonstrated by the reactions with 2-phenylpropionaldehyde (2-PPA) in MeCN at 0°C. Addition of 2-PPA to a solution of **1**-Sc³⁺ caused the decay of the **1**-Sc³⁺ intermediate with the concomitant formation of the corresponding iron(IV)-oxo complex, [(TMC)Fe^{IV}(O)]²⁺, as detected by UV/Vis and CSI-MS (Figure 4c; Supporting Information, Figure S6); we have shown the formation of $[(TMC)Fe^{IV}(O)]^{2+}$ in the reaction of [(TMC)Fe^{III}(O₂H)]²⁺ and aldehydes.^[17a] The pseudo firstorder rate constant increased proportionally with the increase of the concentration of 2-PPA, giving k_2 value of $2.1 \times$ $10^{-2} \text{ m}^{-1} \text{s}^{-1}$ (Figure 4 d). The product analysis of the reaction solutions of $1-Sc^{3+}$ with 2-PPA revealed the formation of acetophenone $(90\pm5\%)$ based on the intermediate). The second-order rate constants (k_2) of the nucleophilic reactions of other $1-M^{n+}$ ($M^{n+} = Y^{3+}$, Lu^{3+} , and La^{3+}) with 2-PPA were also determined (Supporting Information, Figure S7 and Table S1).

In contrast to the cases of electrophilic reactions of $1-M^{n+}$, the $\log k_2$ values decrease linearly with increasing the ΔE values (Figure 3, red and green lines). The slope (-5.7) of the linear plot with the red line in Figure 3 indicates that 31 % of the change in the spitting energy of the π_{α} levels is reflected as the change in the transition state energy of the nucleophilic reaction of 2-PPA with $1-M^{n+}$ at 0 °C. It should be noted that the sign of the slopes of the nucleophilic reactions is negative, which is different from the positive slopes determined in electron-transfer and electrophilic reactions (Figure 3), since the direction of the charge transfer in the transition state is opposite. The slope (-5.2) of the linear plot with the green line in Figure 3 for the nucleophilic reaction of CCA with 1- M^{n+} is slightly less negative as compared to the nucleophilic reaction of 2-PPA with $1-M^{n+}$, indicating that the degree of the charge transfer is less in this reaction. The nucleophilic character of 1-Sc³⁺ was also demonstrated by the reactions with para-substituted benzaldehydes bearing a series of electron-donating and -withdrawing substituents at the paraposition of the phenyl group (para-Y-C₆H₄CHO; Y = OMe, Me, H, and F); a positive ρ value of 2.0 was obtained in the Hammett plot (Figure 5; Supporting Information, Table S2).

In conclusion, we have shown that redox-inactive metal ion-bound iron(III)-peroxo complexes, $[(TMC)Fe^{III}(O_2)]^+$ - M^{n+} (1- M^{n+} ; $M^{n+} = Sc^{3+}$, Y^{3+} , Lu^{3+} , and La^{3+}), act as both electrophiles and nucleophiles as well as electron acceptors. The electron-transfer and electrophilic reactivities of the 1-

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Figure 5. Hammett plot for the reactions of $1-Sc^{3+}$ with *para*-substituted benzaldehydes, *para*-Y-C₆H₄CHO (Y=OMe, Me, H, and F), in deaerated MeCN at 0°C.

 M^{n+} complexes are enhanced with the increase in the Lewis acidity of the binding M^{n+} (ΔE), whereas the nucleophilic reactivity of the 1- M^{n+} complexes diminishes with the increase in the Lewis acidity of the M^{n+} (ΔE). Thus, the reactivity of a mononuclear nonheme iron(III)–peroxo complex in electron-transfer, electrophilic, and nucleophilic reactions can be finely tuned by binding of redox-inactive metal ions, and the Lewis acidity of the redox-inactive metal ions is a determining factor that controls the reactivities of the mononuclear nonheme iron(III)–peroxo complex in electrontransfer, electrophilic, and nucleophilic reactions.

Acknowledgements

The authors acknowledge financial support from the NRF of Korea through CRI (NRF-2012R1A3A2048842 to W.N.), GRL (NRF-2010-00353 to W.N.), and from a Grant-in-Aid (no. 16H02268 to S.F.) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) and a SENTAN project (to S.F.) from the Japan Science and Technology Agency, Japan.

Keywords: iron-peroxo intermediates · Lewis acidity · nonheme iron enzymes · reactive species · redox-inactive metal ions

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Manuscript received: November 6, 2016 Final Article published:



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Redox Reactivity

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Fine Control of the Redox Reactivity of a Nonheme Iron(III)-Peroxo Complex by Binding Redox-Inactive Metal Ions



 $[(TMC)Fe^{III}(O_2)]^{+}-Mn^{+} \\ (M^{n+} = Sc^{3+}, Y^{3+}, Lu^{3+} and La^{3+}) \\ \cdot Lewis Acidity: \\ Sc^{3+} > Y^{3+} > Lu^{3+} > La^{3+} \\ \cdot Electron Transfer \\ Sc^{3+} > Y^{3+} > Lu^{3+} > La^{3+} \\ \cdot Electrophilic Reactivity: \\ Sc^{3+} > Y^{3+} > Lu^{3+} > La^{3+} \\ \cdot Nucleophilic Reactivity: \\ Sc^{3+} < Y^{3+} < Lu^{3+} < La^{3+} \\ \end{bmatrix}$

Inactive but influential: The Lewis acidity of the redox-inactive metal ions bound to a mononuclear nonheme iron(III)–peroxo complex, [(TMC)Fe^{III}(O₂)]⁺-Mⁿ⁺ (1-Mⁿ⁺; $M^{n+} = Sc^{3+}, Y^{3+}, Lu^{3+}, and La^{3+}$), determines the reactivities of 1-Mⁿ⁺ in electron-transfer, electrophilic, and nucleophilic reactions.

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Angew. Chem. Int. Ed. 2016, 55, 1-6