Lewis Acid Coupled Electron Transfer of Metal–Oxygen Intermediates

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Redox-inactive metal ions and Brønsted acids that function as Lewis acids play pivotal roles in modulating the redox reactivity of metal–oxygen intermediates, such as metal–oxo and metal–peroxo complexes. The mechanisms of the oxidative C–H bond cleavage of toluene derivatives, sulfoxidation of thioanisole derivatives, and epoxidation of styrene derivatives by mononuclear nonheme iron(IV)–oxo complexes in the presence of triflic acid (HOTf) and Sc(OTf)₃ have been unified as rate-determining electron transfer coupled with binding of Lewis acids (HOTf and Sc(OTf)₃) by iron(III)–oxo complexes. All logarithms of the observed second-order rate constants of Lewis acid-promoted oxidative C–H bond cleavage, sulfoxidation, and epoxidation reactions of iron(IV)–oxo complexes exhibit remarkably unified correlations with the driving forces of proton-coupled electron transfer (PCET) and metal ion-coupled electron transfer (MCET) in light of the Marcus theory of electron transfer when the differences in the formation constants of precursor complexes were taken into account. The binding of HOTf and Sc(OTf)₃ to the metal–oxo moiety has been confirmed for Mn(IV)–oxo complexes. The enhancement of the electron transfer reactivity of metal–oxo complexes by binding of Lewis acids increases with increasing the Lewis acidity of redox-inactive metal ions. Metal ions can also bind to mononuclear nonheme iron(III)–peroxo complexes, resulting in acceleration of the electron-transfer reduction but deceleration of the electron-transfer oxidation. Such a control on the reactivity of metal–oxygen intermediates by binding of Lewis acids provides valuable insight into the role of Ca²⁺ in the oxidation of water to dioxygen by the oxygen-evolving complex in photosystem II.

1. Introduction

Electron transfer accounts for the most important elementary reactions in both chemical and biological processes, such as respiration and photosynthesis, in which dioxygen is reduced to water and water is oxidized to dioxygen, respectively.[1–5] Redox-active metal–oxygen intermediates, such as metal–oxo and metal–peroxo complexes, act as key intermediates for the catalytic reduction of dioxygen and the oxidation of water and organic substrates.[6–18] For example, a Mn⁴⁺–oxo intermediate is proposed to be involved in water oxidation at the oxygen-evolving complex (OEC) in photosystem II (PS II), and Fe⁴⁺–oxo complexes are the key intermediates in cytochrome c oxidase, cytochrome P450 and nonheme iron enzymes.[19–22]

In the OEC, Ca²⁺ acts as an essential cofactor in the manganese–calcium–oxygen cluster (M₆CaO₆), which is responsible for water oxidation in PS II.[24–30] Among redox-inactive metal ions, Sr²⁺ is the only surrogate that can restore the activity of OEC after Ca²⁺ removal.[31–35] The similar size and Lewis acidity of the Ca²⁺ and Sr²⁺ ions may be responsible for their ability to function in OEC. However, the exact functional role of Ca²⁺ ion has yet to be clarified.

Redox-inactive metal ions, such as Ca²⁺ and Zn²⁺, play pivotal roles in controlling biological electron-transfer processes, not only in water oxidation to produce O₂ in OEC, but also in the dismutation of O₂⁻ in copper–zinc superoxide dismutase (CuZn-SOD).[36–38] Binding of metal ions to electron acceptors (A) results in enhancement of an electron-acceptor ability of A, because the one-electron reduction potential of A is shifted in a positive direction (ΔG_red) by the strong binding of metal ions to the radical anion (A⁻) to produce A⁻−−M⁺. Thus, electron transfer from electron donors (D) to A, which is thermodynamically infeasible in the absence of metal ions (ΔG_red > 0), would be made possible in the presence of M⁺, provided that the ΔG_red value is larger than ΔG_red (ΔG_red < ΔG_red; Scheme 1).[39–41]

This is defined as metal ion-coupled electron transfer (MCET).[40,41] Similarly, protonation of A⁻ by Brønsted acids enhances electron transfer from D to A by the positive shift of the reduction potential of A. This is well known as proton-coupled electron transfer (PCET).[42–46]

This Minireview focuses on the quantitative effects of redox-inactive metal ions and Brønsted acids on redox reactions of redox-active metal–oxygen intermediates. First, MCET reduction of O₂ is quantitatively analyzed based on the EPR spectra of O₂⁻−−M⁺ complexes. Then, the shifts of the one-electron reduction potentials (ΔG_red) of metal–oxo complexes by binding of redox-inactive metal ions and Brønsted acids, both of which act as Lewis acids, are quantitatively utilized to unify the dependence of the rate constants of various redox reactions of metal–oxo and metal–peroxo complexes. All logarithms of the observed second-order rate constants of Lewis acid-promoted oxidative C–H bond cleavage, sulfoxidation, and epoxidation reactions of iron(IV)–oxo complexes exhibit remarkably unified correlations with the driving forces of proton-coupled electron transfer (PCET) and metal ion-coupled electron transfer (MCET) in light of the Marcus theory of electron transfer when the differences in the formation constants of precursor complexes were taken into account. The binding of HOTf and Sc(OTf)₃ to the metal–oxo moiety has been confirmed for Mn(IV)–oxo complexes. The enhancement of the electron transfer reactivity of metal–oxo complexes by binding of Lewis acids increases with increasing the Lewis acidity of redox-inactive metal ions. Metal ions can also bind to mononuclear nonheme iron(III)–peroxo complexes, resulting in acceleration of the electron-transfer reduction but deceleration of the electron-transfer oxidation. Such a control on the reactivity of metal–oxygen intermediates by binding of Lewis acids provides valuable insight into the role of Ca²⁺ in the oxidation of water to dioxygen by the oxygen-evolving complex in photosystem II.

![Scheme 1. Metal ion-coupled electron transfer.](image-url)
metal–oxo complexes on the driving force of Lewis acid-coupled electron transfer in light of the Marcus theory of electron transfer.\textsuperscript{[47]} The effects of redox-inactive metal ions on the redox properties and the oxidation and reduction reactions of metal–peroxo complexes have been discussed as well. Thus, observation of the effects of redox-inactive metal ions on the redox reactions of both metal-oxo and metal–peroxo complexes may provide valuable insights into the actual role of Ca\textsuperscript{2+} in the OEC of PS II.

2. Binding of Redox-Inactive Metal Ions to O\textsuperscript{2--}

Binding of redox-inactive metal ions to superoxide anion (O\textsuperscript{2--}) has been confirmed by EPR spectroscopy. The EPR spectrum of O\textsuperscript{2--} in frozen media at 77 K shows anisotropic signals with \( g_{xx} = 2.072 \) and \( g_{yy} = g_{zz} = 2.009 \).\textsuperscript{[46,49]} In solution, the EPR spectrum of O\textsuperscript{2--} cannot be detected owing to fast relaxation caused by the orbital degeneracy. Binding of redox-inactive metal ions, such as Sc\textsuperscript{3+}, to O\textsuperscript{2--} results in the splitting of the degenerate \( \pi^* \) orbitals, enabling observation of the EPR spectrum of the O\textsuperscript{2--}–Sc(HMPA)\textsuperscript{3+} complex (HMPA = hexamethylphosphoronic triamide) in solution, as shown in Figure 1.\textsuperscript{[50,51]} O\textsuperscript{2--} was produced by photoinduced electron transfer from the dimeric 1-benzyl-1,4-dihydrionicotinamide (BNA\textsubscript{2}), which can act as a unique two-electron donor,\textsuperscript{[52]} to O\textsubscript{2} enriched in \textsuperscript{17}O in acetonitrile. The eight-line isotropic spectrum at the center due to the superhyperfine coupling of O\textsuperscript{2--} with the 7:2 nuclear spin of the scandium nucleus [coupling constant, \( \alpha(\text{Sc}) = 3.82 \text{ G} \)] clearly indicates the binding of Sc\textsuperscript{3+} to O\textsuperscript{2--}.\textsuperscript{[10]} The O\textsuperscript{2--} complex is relatively stable in the presence of HMPA and the EPR spectrum can be detected even at 60 °C under light irradiation, although it disappeared completely in 20 min after cutting off the light.\textsuperscript{[50]} The two inequivalent \( \alpha(\text{O}) \) values (21 and 14 G; Figure 1) indicate “end-on” coordination rather than “side-on” in the O\textsuperscript{2--}–Sc(HMPA)\textsuperscript{3+} complex in which the electron spin is more localized at the terminal oxygen.\textsuperscript{[50]} Without the HMPA ligand, the O\textsuperscript{2--}–Sc\textsuperscript{3+} complex becomes unstable due to the much faster disproportionation of the O\textsuperscript{2--}–Sc(HMPA)\textsuperscript{3+} complex.
The formation constants of 1:1 and 1:2 complexes are the binding strength of M\(^{n+}\) to O\(^{2-}\) [53], because the deviation of the \(g_{zz}\) value from the free spin value (\(g_{zz} = 2.0023\)) is caused by the spin–orbit coupling and the energy splitting of \(\pi_g\) levels due to the binding of M\(^{n+}\) to O\(^{2-}\) [53].

The \(g_{zz}\) value of the EPR spectrum of the O\(^{2-}\)–M\(^{n+}\) complex varies depending on the binding strength of M\(^{n+}\) to O\(^{2-}\) [53], because the deviation of the \(g_{zz}\) value from the free spin value (\(g_{zz} = 2.0023\)) is caused by the spin–orbit coupling and the energy splitting of \(\pi_g\) levels due to the binding of M\(^{n+}\) to O\(^{2-}\) [53].

\[ \Delta E = 2 \mu_{soc}/(g_{zz} - g_s) \]

where \(\mu_{soc}\) is the spin–orbit coupling constant (0.014 eV). [55] The \(\Delta E\) value, commonly in the range 0.3–1.0 eV, increases in the order of monovalent cations (M\(^+\)) < divalent cations (M\(^{2+}\)) < trivalent cations (M\(^{3+}\)). [56] The \(\Delta E\) value also increases with a decrease in the ionic radius when the oxidation state of the metal ion is the same. Scandium(III), with the smallest ionic radius among the trivalent metal cations, provides the largest \(\Delta E\) value, which indicates that Sc\(^{3+}\) ion is the strongest Lewis acid. The calculated O–O distance decreases in the order of O\(^{2-}\) (1.343 Å) > O\(^{-}\)–Li\(^+\) (1.309 Å) > O\(^{2-}\)–Mg\(^{2+}\) (1.297 Å) > O\(^{2-}\)–Sc\(^{3+}\) (1.211 Å) as the \(\Delta E\) value increases. [56] The \(\Delta E\) value can be used as a quantitative measure of the Lewis acidity of not only metal cations with different counter anions but also neutral Lewis acids, such as organotin compounds. [56,57] In the case of Sc\(^{3+}\), the Lewis acidity decreases in the order of Sc(OTf)\(_3\) > (TPP)ScCl > (TPP) = dianion of tetraphenylporphyrin > (HMPA)Sc(OTf)\(_3\). The fluorescence maxima (\(\lambda_{max}\)) of complexes with various Lewis acids can also be used as a quantitative measure of Lewis acidity and there is a linear correlation between the \(\Delta E\) values and the \(\Delta H_{max}\) values of 10-methylacridone–Lewis acid complexes. [56]

Binding of Lewis acids to O\(^{2-}\) makes electron transfer from (TPPCo to O\(_2\) possible, [55,56] and the second-order rate constant of Lewis acid–coupled electron transfer increased linearly with increasing concentrations of Lewis acids. [53] The rates of reduction of O\(_2\) by Mn\(^{n}\) and Fe\(^{n}\) complexes were also reported to be enhanced by the presence of redox-inactive metal ions, which act as Lewis acids. [56,61] There is a remarkable linear correlation between the logarithm of the rate constant of Lewis acid–coupled electron transfer (log \(k_{et}\)) from (TPPCo to O\(_2\) in MeCN and \(\Delta E\) of the O\(^{2-}\)–M\(^{n+}\) complexes (Figure 2). [56] The linear correlation spans a range of nearly 10\(^2\) in the rate constant. The slope of the linear correlation between log \(k_{et}\) and \(\Delta E\) is obtained as 14.0, which is close to the value of 1/(2(3.147) \(\times\) 16.9, where \(k_B\) is the Boltzmann constant and \(T = 298\) K). [56] This indicates that the variation of \(\Delta E\) is well reflected in the dependence on the activation free energy for the Lewis acid-coupled electron transfer from (TPPCo to O\(_2\). The stronger the binding of Lewis acids with O\(_2\) is, the larger the promoting effects of Lewis acids becomes. Thus, \(\Delta E\) can be regarded as the binding energy in O\(^{2-}\)–Lewis acid complexes.

3. Metal Ion-Coupled Electron Transfer of Metal–Oxo Complexes

3.1. Iron(IV)–oxo complexes

The electron-transfer reduction of an iron(IV)–oxo complex, [(N4Py)Fe\(^{n+}\)(O)]\(^{2+}\) [58], [(N4Py) = N,N-bis(2-pyridylmethyl)-N-bis(2-pyridylmethyl)amine], is accelerated by binding of redox-inactive metal ions (M\(^{n+}\)) to the corresponding iron(III)–oxo complex, as shown in the case of the electron-transfer reduction of O\(_2\) in Figure 3. [59] The one-electron reduction potential of [(N4Py)Fe\(^{n+}\)(O)]\(^{2+}\) in MeCN (\(E_{\text{red}} = \text{0.51 V vs. SCE}\)) [56] was shifted to a positive direction by binding of Sc(OTf)\(_3\) to [(N4Py)Fe\(^{n+}\)(O)]\(^{2+}\). [58] The \(E_{\text{red}}\) values in the presence of Sc(OTf)\(_3\) were determined from the equilibrium constants of electron transfer with various electron donors. [58] The \(E_{\text{red}}\) values increase linearly with increasing logarithm of concentration of Sc(OTf)\(_3\) (log [Sc\(^{3+}\)]) ; Figure 3), where the slope is 118 mV/log [Sc\(^{3+}\)]. [56] This indicates that the one-electron reduction of [(N4Py)Fe\(^{n+}\)(O)]\(^{2+}\) is accompanied by binding of one or two Sc\(^{3+}\) ions to [(N4Py)Fe\(^{n+}\)(O)]\(^{2+}\), in accordance with the Nernst equation [Equation (2)],

\[ E_{\text{red}} = E_{\text{red}}^{0} + (2.3 RT/F)\log(1 + K_s [Sc^{3+}] + K_s K_I [Sc^{3+}]^2) \]

where \(E_{\text{red}}^{0}\) is the one-electron reduction potential without Sc\(^{3+}\), and \(K_s\) and \(K_I\) are the formation constants of 1:1 and 1:2 complexes of [(N4Py)Fe\(^{n+}\)(O)]\(^{2+}\) with one Sc\(^{3+}\) and two Sc\(^{3+}\) ions, respectively (Scheme 2). [62]

The observed second-order rate constant (\(k_{obs}\)) of electron transfer from electron donors to [(N4Py)Fe\(^{n+}\)(O)]\(^{2+}\) in the presence of Sc(OTf)\(_3\) in MeCN increased with a first-order dependence on [Sc\(^{3+}\)] at low concentrations, changing to a second-
order dependence at high concentrations, as given by Equation (3).\[62]\n
\[
k_{\text{obs}} = k_1[\text{Sc}^{3+}] + k_2[\text{Sc}^{4+}]
\]

The \( k_1 \) and \( k_2 \) values were determined for MCET from ferrocene to \([\text{N4Py}]\text{Fe}^{2+}(O)\)]\(^{2+}\) in the presence of various metal ions.\[62]\n
Both log \( k_1 \) and log \( k_2 \) exhibit good linear correlations with the \( \Delta E \) values of metal ions [Equation (1)], as shown in Figure 4.\[62]\n
Thus, the stronger Lewis acidity of the metal ion is, the larger the rate constants \( (k_1 \) and \( k_2 \)) of MCET from ferrocene to \([\text{N4Py}]\text{Fe}^{2+}(O)\)]\(^{2+}\) become.

The binding of a redox-inactive metal ion to a high-valent metal-oxo complex was reported as the X-ray crystal structure of \( \text{Sc}^{3+}\)-bound \([\text{TMC}]\text{Fe}^{2+}(O)\)]\(^{2+}\) (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane),\[64]\n
which was initially formulated as the neutral \([\text{TMC}]\text{Fe}^{2+}\text{OSc}^{3+}(\text{OTf})_3(\text{OH})_2\]) (Figure 5).\[65]\n
However, density functional theory (DFT) calculations performed later suggested that the formula was \([\text{TMC}]\text{Fe}^{2+}\text{OSc}^{3+}(\text{OTf})_3(\text{OH})_2\])\[66]\n
which was supported by Mössbauer and X-ray absorption spectroscopies of the crystals as well as electrospray ionization mass spectrometry and EPR spectroscopy.\[67]\n
It may be suggested that the \( \text{Sc}^{3+}\) complex is reduced to the \( \text{Sc}^{3+}\)-bound \( \text{Fe}^{2+}\) species during the crystallization in the presence of ether. However, the source of one electron for the reduction of the \( \text{Fe}^{2+}\) complex to the \( \text{Fe}^{3+}\) complex has yet to be clarified. In any case, the strong binding of \( \text{Sc}^{3+}\) ion to the iron-oxo moiety of the \( \text{Fe}^{2+}\) complex results in enhancement of the two-electron reduction of the \( \text{Fe}^{2+}\) complex to the \( \text{Fe}^{3+}\) complex.\[65]\n
3.2. Manganese(IV)-oxo complexes

In contrast to the case of iron(IV)-oxo complexes, \( \text{Sc}^{3+}\) binds directly to manganese(IV)-oxo complexes, such as \([\text{N4Py}]\text{Mn}^{2+}(O)\)]\(^{2+}\) and \([\text{Bn-TPEN}]\text{Mn}^{2+}(O)\)]\(^{2+}\) (Bn-TPEN = N-benzyl-N,N,N-tris(2-pyridylmethyl)-1,2-diaminoethane).\[68,69]\n
Addition of up to two equivalents of \( \text{Sc}^{3+}\) to a solution of \([\text{Bn-TPEN}]\text{Mn}^{3+}(O)\)]\(^{2+}\) in a solvent mixture of \( \text{CF}_2\text{CH}_2\text{OH/CH}_3\text{CN} \) resulted in a blue shift of the absorption band at \( \lambda_{\text{max}} = 1020 \text{ nm} \) to that at \( \lambda_{\text{max}} = 740 \text{ nm} \) with an approximate isosbestic point at 900 nm (Figure 6a).\[69]\n
Further addition of \( \text{Sc}^{3+}\) resulted in an even larger blue-shift to give the absorption band at \( \lambda_{\text{max}} = 690 \text{ nm} \) (Figure 6b).\[69]\n
Such stepwise spectral changes indicate the binding of one and two \( \text{Sc}^{3+}\) ions to \([\text{Bn-TPEN}]\text{Mn}^{3+}(O)\)]\(^{2+}\) to produce \( \text{Mn}^{3+}(O)\)-( \( \text{Sc}^{3+}\) ) complexes, respectively.\[69]\n
The formation constants of the \([\text{Bn-TPEN}]\text{Mn}^{3+}(O)\)]\(^{2+}\)-( \( \text{Sc}^{3+}\) ) complexes were determined from the spectral titrations to be \( 4.0 \times 10^3 \text{ M}^{-1} \) and \( 1.2 \times 10^3 \text{ M}^{-1} \), respectively.\[69]\n
The formation constant of \([\text{N4Py}]\text{Mn}^{2+}(O)\)]\(^{2+}\)-( \( \text{Sc}^{3+}\) ) complex was also determined to be \( 6.1 \times 10^3 \text{ M}^{-1} \).\[69]\n
The extended X-ray absorption fine structure (EXAFS) spectroscopy results indicated that on going from no \( \text{Sc}^{3+}\) binding
Figure 6. a) UV/Vis spectral changes showing the conversion from [(Bn-TPEN)Mn\(^{\text{III}}\)(O)]\(^{2+}\) (red line) to [(Bn-TPEN)Mn\(^{\text{IV}}\)(O)]\(^{2+}\) (green line) upon addition of incremental amounts of Sc\(^{3+}\) (from 0.0 to 2.0 mM) in the titration experiment; b) UV/Vis spectral changes showing the conversion from [(Bn-TPEN)Mn\(^{\text{III}}\)(O)]\(^{2+}\)–(Sc\(^{3+}\)) \(_2\) (green line) to [(Bn-TPEN)Mn\(^{\text{IV}}\)(O)]\(^{2+}\)–(Sc\(^{3+}\)) \(_2\) (blue line) upon addition of Sc\(^{3+}\) ions (from 0 to 12 mM). Figure 6 was taken with permission from reference [69].

Figure 7. DFT-optimized structure of [(Bn-TPEN)Mn\(^{\text{III}}\)(O)–Sc(OTf)\(_2\)]\(^{2+}\), calculated at the B3LYP/LACVP level. The Mn–O bond lengths of [Mn\(^{\text{III}}\)(O)]\(^{2+}\), [Mn\(^{\text{III}}\)(O)]\(^{2+}\)–Sc\(^{3+}\), and [Mn\(^{\text{III}}\)(O)]\(^{2+}\)–(Sc\(^{3+}\)) \(_2\) were calculated to be 1.68, 1.75, and 1.75 Å, respectively. Figure 7 was taken with permission from reference [69].

in [(Bn-TPEN)Mn\(^{\text{III}}\)(O)]\(^{2+}\) to binding one and two Sc\(^{3+}\) ions, the Mn–O bond elongates from 1.69 to 1.74(2) Å, which is consistent with a weakening of the Mn–O bond.[69] The EXAFS data also revealed a short Mn–Sc distance (3.45(10) Å), which clearly indicates that Sc\(^{3+}\) ions bind to the Mn\(^{\text{III}}\)(O) moiety in both [(Bn-TPEN)Mn\(^{\text{III}}\)(O)]\(^{2+}\)–(Sc\(^{3+}\)) \(_2\) and [(Bn-TPEN)Mn\(^{\text{III}}\)(O)]\(^{2+}\)–(Sc\(^{3+}\)) \(_3\).[69] DFT calculations of the Mn\(^{\text{III}}\)(O)–(Sc\(^{3+}\)) \(_2\) complex suggested that one Sc\(^{3+}\) ion binds directly to the Mn-O moiety of the Mn\(^{\text{III}}\)(O) complex but the second Sc\(^{3+}\) ion is located at the secondary coordination sphere (Figure 7).[69]

The \(E_{\text{red}}\) values of Mn\(^{\text{III}}\)(O) complexes, [(Bn-TPEN)Mn\(^{\text{III}}\)(O)]\(^{2+}\) and [(N4Py)Mn\(^{\text{III}}\)(O)]\(^{2+}\), in the presence of various concentrations of Sc(OTf)\(_3\) were determined from the \(K_a\) values obtained by the electron-transfer titrations with [Ru(II)(bpy)]\(^{2+}\). \(E_{\text{red}}\) values were shifted from 0.78 and 0.80 V vs. SCE[70] in the absence of Sc(OTf)\(_3\) to 1.28 and 1.31 V vs. SCE in the presence of two equivalents (for Bn-TREN) or one equivalent (for N4Py) of Sc(OTf)\(_3\) which correspondingly to the \(E_{\text{red}}\) values of [(Bn-TPEN)Mn\(^{\text{III}}\)(O)]\(^{2+}\)–(Sc\(^{3+}\)) \(_2\) and [(N4Py)Mn\(^{\text{III}}\)(O)]\(^{2+}\)–(Sc\(^{3+}\)) \(_2\), respectively.[69] The \(E_{\text{red}}\) values increase with increasing concentration of Sc(OTf)\(_3\) to reach constant values with more than six equivalents of Sc(OTf)\(_3\) (Figure 8).[69] This is consistent with the UV/Vis spectral change owing to the formation of the [Mn\(^{\text{III}}\)(O)]\(^{2+}\)–(Sc\(^{3+}\)) \(_2\) complex. The saturated \(E_{\text{red}}\) values of 1.36 and 1.42 V vs. SCE in the presence of large excess Sc(OTf)\(_3\) correspond to those of [(Bn-TPEN)Mn\(^{\text{III}}\)(O)]\(^{2+}\)–(Sc\(^{3+}\)) \(_2\) and [(N4Py)Mn\(^{\text{III}}\)(O)]\(^{2+}\)–(Sc\(^{3+}\)) \(_2\), respectively.[69] The large difference in the \(E_{\text{red}}\) values between [Mn\(^{\text{III}}\)(O)]\(^{2+}\) and [Mn\(^{\text{III}}\)(O)]\(^{2+}\)–Sc\(^{3+}\), indicating that the binding of Sc\(^{3+}\) to [Mn\(^{\text{III}}\)(O)]\(^{2+}\) is much stronger than that to [Mn\(^{\text{III}}\)(O)]\(^{2+}\), as expected from the increased basicity of the oxo moiety in [Mn\(^{\text{III}}\)(O)]\(^{2+}\). The smaller difference in \(E_{\text{red}}\) between [Mn\(^{\text{III}}\)(O)]\(^{2+}\)–(Sc\(^{3+}\)) \(_2\) and [Mn\(^{\text{III}}\)(O)]\(^{2+}\)–(Sc\(^{3+}\)) \(_3\) results from the binding of second Sc\(^{3+}\) ion at the secondary coordination sphere rather than the oxo moiety (see below).[69]

Figure 8. Dependence of \(E_{\text{red}}\) of [(N4Py)Mn\(^{\text{III}}\)(O)]\(^{2+}\) (blue circles) and [(Bn-TREN)Mn\(^{\text{III}}\)(O)]\(^{2+}\) (red circles) on Sc\(^{3+}\) in CF\(_3\)CH\(_2\)OH/CH\(_3\)CN (1:1 v/v) at 273 K. The \(E_{\text{red}}\) values were determined from the equilibrium constants \(K_a\) between one electron donors and [(N4Py)Mn\(^{\text{III}}\)(O)]\(^{2+}\). Figure 8 was taken with permission from reference [69].

3.3. Cobalt(IV)–oxo complexes

Although high-valent cobalt–oxo complexes remain elusive, binding of redox-inactive metal ions has been shown to stabilize a cobalt(IV)–oxo complex (Scheme 3).[71] The cobalt(III) complex, [TAML-Co\(^{\text{IV}}\)]\(^{2+}\) (TAML = tetramido macrocyclic ligand), is readily oxidized by cerium ammonium nitrate (CAN) in acetone to afford the [TAML-Co\(^{\text{IV}}\)](O)–Ce\(^{3+}\) complex.[21] The reaction of [TAML-Co\(^{\text{IV}}\)] with iodosylbenzene (PhIO) in the presence of Sc(OTf)\(_3\) also generated the [TAML-Co\(^{\text{IV}}\)](O)–Sc\(^{3+}\) complex, which is stabilized by binding of Sc\(^{3+}\) ion to the metal–oxo moiety.[21] Theoretical calculations predict that the binding of Lewis acidic metal ions (M\(^{\text{III}}\)) to the cobalt–oxo core increases the electrophilicity of the oxygen atom, resulting in the redox tautomerism of a highly unstable [TAML-Co\(^{\text{IV}}\)] species to a more stable [TAML-Co\(^{\text{IV}}\)](O)(M\(^{\text{III}}\)) core.[21] The Co\(^{\text{IV}}\) oxidation state of [TAML-Co\(^{\text{IV}}\)](O)–Sc\(^{3+}\) was confirmed by EPR and XAS measurements. It should be noted that the Co–O distance of 1.67 Å for [TAML-Co\(^{\text{IV}}\)](O)–Sc\(^{3+}\) determined by EXAFS is significantly shorter than the Co–O distances of 1.79 Å and 1.85 Å determined for [(α-P3W\(_{10}\)O\(_{40}\))^\(_{4−}\)] by X-ray diffraction[72] and [(TMTG, tren)Co\(^{\text{IV}}\)](O)(Sc(OTf)\(_3\))\(^{2+}\) (TMTG, tren = tris[2-(N-tetramethylguanidyl)ethyl]amine) by EXAFS.[73] The latter species was later suggested to contain a Co\(^{\text{IV}}\)(OH) unit rather than a Co\(^{\text{IV}}\) unit,[21] and further investigation is needed to clarify the nature of the Co–O(H) moiety.
4. Proton-Coupled Electron Transfer of Metal-Oxo Complexes

As in the case of Sc(OTf)₃ (see above), the $E_{\text{red}}$ value of [(N4Py)Fe⁶⁺(O)]²⁺ was shifted in a positive direction by binding of triflic acid (HOTf) to [(N4Py)Fe⁶⁺(O)]²⁺. The dependence of $E_{\text{red}}$ of [(N4Py)Fe⁶⁺(O)]²⁺ on log [HOTf] and log [Sc(OTf)₃] is shown in Figure 9, where the slopes are determined to be 113 ± 6 mV for HOTf and 118 ± 8 mV for Sc(OTf)₃, in agreement with Equation (2). Either one or two HOTf molecules are bound to [(N4Py)Fe⁶⁺(O)]²⁺. The binding of HOTf molecules to [(N4Py)Fe⁶⁺(O)]²⁺ is stronger than that of Sc(OTf)₃ molecules, resulting in the more positive $E_{\text{red}}$ values of [(N4Py)Fe⁶⁺(O)]²⁺ in the presence of HOTf than those in the presence of the same concentration of Sc(OTf)₃.

When HOTf was replaced by the deuterated acid (DOTf), the $k_{\text{red}}$ value of PCET from [Ru⁶⁺(bpy)₃]²⁺ to [(N4Py)Fe⁶⁺(O)]²⁺ with DOTf in MeCN at 298 K was larger than that with the same concentration of HOTf (Figure 10). Both the $k_{\text{red}}$ values with DOTf and HOTf increased with increasing concentration of DOTf and HOTf, in accordance with Equation (3), where $[\text{Sc}^{3+}]$. The kinetic isotope effect (KIE) value ($k_{\text{red}}$(HOTf)/$k_{\text{red}}$(DOTf)) was determined to be 0.25 ± 0.05 at HOTf (DOTf) = 2.5 mM, which increases to a constant value of 0.40 ± 0.04 at higher concentrations of HOTf (DOTf). Such inverse KIEs indicate that binding of protons to the Fe-oxo group to produce an O–H (or O–D) bond is involved in the rate-determining step of PCET from [Ru⁶⁺(bpy)₃]²⁺ to [(N4Py)Fe⁶⁺(O)]²⁺ or [(N4Py)Fe⁶⁺(OH)]²⁺, because an inverse KIE results from a larger zero-point energy difference between the O–H and O–D bonds in the transition state relative to the ground state. Thus, the O–H bonds in the reduced species (e.g., [(N4Py)Fe⁶⁺(OH)]²⁺ and [(N4Py)Fe⁶⁺(OH)]²⁺) are much stronger than those in [(N4Py)Fe⁶⁺(O)]²⁺ and [(N4Py)Fe⁶⁺(OH)]²⁺, respectively. The inverse KIEs clearly indicate that electron transfer is coupled with the binding of one and two HOTf molecules to [(N4Py)Fe⁶⁺(O)]²⁺.

In contrast to [(N4Py)Fe⁶⁺(O)]²⁺, two HOTf molecules are directly bound to [(N4Py)Mn⁶⁺(O)]²⁺ to produce [(N4Py)Mn⁶⁺(O)]²⁺ or [(N4Py)Mn⁶⁺(OH)]²⁺ or [(N4Py)Mn⁶⁺(OH)]²⁺, as evidenced by UV/Vis spectra (Figure 11), where the absorption change at 550 nm, due to [(N4Py)Mn⁶⁺(O)]²⁺ or [(N4Py)Mn⁶⁺(OH)]²⁺, exhibits a sigmoidal curvature (inset of Figure 11). The EXAFS data of [(N4Py)Mn⁶⁺(O)]²⁺ or [(N4Py)Mn⁶⁺(OH)]²⁺ indicate an elongated Mn–O bond of 1.74 Å as compared with 1.67 Å for the Mn–O bond in [(N4Py)Mn⁶⁺(O)]²⁺. The Mn–O bond length in [(N4Py)Mn⁶⁺(O)]²⁺ or [(N4Py)Mn⁶⁺(OH)]²⁺ is nearly identical to that in the [(N4Py)Mn⁶⁺(O)]²⁺ complex binding two Sc(OTf)₃ molecules.

The $E_{\text{red}}$ value of [(N4Py)Mn⁶⁺(O)]²⁺ increased with increasing concentration of HOTf to reach a constant value of 1.65 V vs. SCE at more than 30 mM of HOTf at 273 K (Figure 12). The saturated $E_{\text{red}}$ value of 1.65 V vs. SCE in the presence of a large excess of HOTf corresponds to that of [(N4Py)Mn⁶⁺(O)]²⁺ or [(N4Py)Mn⁶⁺(OH)]²⁺. The large difference ($\Delta E_{\text{red}}$ = 0.85 V) in the $E_{\text{red}}$ values between [Mn⁶⁺(O)]²⁺ and [Mn⁶⁺(OH)]²⁺ or [(N4Py)Mn⁶⁺(OH)]²⁺ indicates that the binding of HOTf to [Mn⁶⁺(O)]²⁺ is much stronger than that to [Mn⁶⁺(OH)]²⁺, as expected from the increased basicity of the oxo moiety in [Mn⁶⁺(O)]²⁺. Thus, the HOTf-bound Mn⁶⁺(O) complex acts as the strongest oxidant among the nonheme Mn–oxo complexes bearing the same ligand system.

![Scheme 3. Oxidation of a cobalt(III) complex to a cobalt(IV)-oxo-metal ion complexes by CAN/H₂O or PhIO/M⁺.](image)

![Figure 9. Dependence of $E_{\text{red}}$ of [(N4Py)Fe⁶⁺(O)]²⁺ on log[HOTf] (red circles) and log[Sc(OTf)₃] (black circles) in deaerated MeCN at 298 K. Black and red lines are fitted by Equation (2), where Sc³⁺ is replaced by HOTf. Figure 9 was taken with permission from reference [75].](image)

![Figure 10. Plots of $k_{\text{red}}$ vs. [HOTf] (black circles) and [DOTf] (red circles) for oxidation of toluene by [(N4Py)Fe⁶⁺(O)]²⁺ in the presence of HOTf and DOTf in MeCN at 298 K, respectively. Figure 10 was taken with permission from reference [75].](image)
5. Unified Mechanism of Lewis Acid-Promoted Oxidation of Substrates by Metal–Oxo Complexes

Not only the rates of electron-transfer reactions of [(N4Py)FeIV(O)]2+ but also the rates of the oxidative C–H bond cleavage of toluene derivatives, benzyl alcohol derivatives, sulfoxidation of thioanisole derivatives, and epoxidation of styrene derivatives with [(N4Py)FeIV(O)]2+ were remarkably enhanced by the presence of perchloric acid (HClO4), HOTf, or Sc(OTf3) in acetonitrile at 298 K.75,79-85 The enhancement of electron-transfer reactions is ascribed to the positive shifts of $E_{1/2}$ values of [(N4Py)FeIV(O)]2+ in the presence of Sc(OTf3) and HOTf (Figure 9).75 The driving-force dependence of log $k_{\text{obs}}$ of electron transfer from coordinatively saturated metal complexes (electron donors) to [(N4Py)FeIV(O)]2+ in the absence and presence of 10 mM of HOTf (black line in Figure 13) is well fitted by the Marcus equation of outer-sphere electron transfer [Equation (4)],235

$$k_{\text{obs}} = Z \exp[-(\lambda/4)(1 + \Delta G_{\text{et}}/\lambda)^2/k_BT]$$

where $Z$ is the frequency factor, which is $k_BT/\hbar$ (k$_B$ is the Boltzmann constant, T is absolute temperature, $\hbar$ is the Planck constant), using the same value of reorganization energy of electron transfer ($\lambda = 2.74$ eV). The Z value of outer-sphere electron-transfer reactions is taken as $1.0 \times 10^{11}$ M$^{-1}$ s$^{-1}$.86,87 The log $k_{\text{obs}}$ values of oxidation of toluene and thioanisole derivatives by [(N4Py)FeIV(O)]2+ in the absence of an acid (Figure 13; nos. 1–12, black) are much larger than those predicted by Equation (4) with $\lambda = 2.74$ eV (black line in Figure 13), because the oxidation of toluene and thioanisole derivatives by [(N4Py)FeIV(O)]2+ in the presence of an acid proceeds by hydrogen atom transfer (HAT) and oxygen atom transfer (OAT), which require significant interactions in the transition state as compared with outer-sphere electron-transfer processes.75 In contrast to the results without acid, log $k_{\text{obs}}$ values of oxidation of toluene and thioanisole derivatives by [(N4Py)FeIV(O)]2+ in the presence of HOTf and Sc(OTf3) are parallel with those of outer-sphere electron-transfer reactions of [(N4Py)FeIV(O)]2+.235 Such parallel relations suggest that the oxidation of toluene and thioanisole derivatives by [(N4Py)-FeIV(O)]2+ in the presence of HOTf and Sc(OTf3) proceeds by the rate-determining electron-transfer steps.75 The larger log $k_{\text{obs}}$ for oxidation of toluene and thioanisole derivatives (1. hexamethylbenzene; 2. 1,2,3,4,5-pentamethylbenzene; 3. 1,2,4,5-tetramethylbenzene; 4. 1,2,4-trimethylbenzene; 5. 1,4-dimethylbenzene; 6. 1,3,5-trimethylbenzene; 7. toluene; 8. p-Me-thioanisole; 9. thioanisole; 10. p-Cl-thioanisole; 11. p-Br-thioanisole; 12. p-CN-thioanisole) by [(N4Py)-

![Figure 11. UV/Vis spectral changes observed in the titration of [(N4Py)MnIV–(O)]2+ (black bold line) with HOTf. HOTf (0–20 mM) was added incrementally into the solution of [(N4Py)MnIV–(O)]2+ (0.50 mM) in CF$_3$CH$_2$OH/CH$_2$CN (1:1 v/v) at 273 K. Inset shows the spectral titration monitored at 550 nm (blue circles) due to the formation of [(N4Py)MnIV–(O)]2+–HOTf. Figure 11 was taken with permission from reference [78].](Image 344x297 to 509x454)

![Figure 12. Dependence of $E_{1/2}$ of [(N4Py)MnIV–(O)]2+ on the concentration of HOTf (0–80 mM) in CF$_3$CH$_2$OH/CH$_2$CN (1:1 v/v) at 273 K. Figure 12 was taken with permission from reference [78].](Image 56x253 to 278x400)

![Figure 13. Plots of log $k_{\text{obs}}$ for oxidation of toluene and thioanisole derivatives (1. hexamethylbenzene; 2. 1,2,3,4,5-pentamethylbenzene; 3. 1,2,4,5-tetramethylbenzene; 4. 1,2,4-trimethylbenzene; 5. 1,4-dimethylbenzene; 6. 1,3,5-trimethylbenzene; 7. toluene; 8. p-Me-thioanisole; 9. thioanisole; 10. p-Cl-thioanisole; 11. p-Br-thioanisole; 12. p-CN-thioanisole) by [(N4Py)-FeIV(O)]2+ in the absence (black) and presence of 10 mM HOTf (red) and Sc(OTf3) (blue) in MeCN at 298 K vs. the driving-force electron transfer $-\Delta G_{\text{et}} = -(E_{1/2} - E_{1/2})$ from toluene derivatives (squares) and thioanisole derivatives (triangles) to [(N4Py)FeIV(O)]2+ in the presence of HOTf (red) and Sc(OTf3) (blue). The red and blue circles show the driving-force dependence of the rate constants (log $k_{\text{et}}$) of electron transfer from electron donors (13. [Fe(phen)2(bpy)],2+; 14. [Fe(phen)3]2+; 15. [Ru(4,4’-Me-phen)$_2$(bpy)]2+; 16. [Ru(5,5’-Me-phen)$_2$(bpy)]2+; 17. [Fe(phen)$_2$(NCS)$_2$]2+; 18. [Ru(phen)$_2$(NCS)$_2$]2+ to [(N4Py)-FeIV(O)]2+ in the presence of HOTf (10 mM) and Sc(OTf3) (10 mM) in MeCN at 298 K. The black line is drawn using Equation (4) with $\lambda = 2.74$ eV. The black circles show the driving-force dependence of the rate constants (log $k_{\text{et}}$) of electron transfer from electron donors (19. decamethylferrocene; 20. octamethylferrocene; 21. 1,1-dimethylferrocene; 22. n-amyferrocene and 23. ferrocene) to [(N4Py)FeIV(O)]2+ in the absence of acids in MeCN at 298 K. Figure 13 was taken with permission from reference [75].](Image 59x626 to 278x775)
$k_{obs}$ values than the log $k_{eq}$ values of outer-sphere electron transfer reactions result from the larger $K$ values of precursor complexes formed prior to electron transfer, because the stronger interaction with toluene and thioanisole derivatives is expected as compared with that with coordinately saturated metal complexes. This was confirmed by the driving-force dependence of logarithm of the first-order rate constants ($\log k_{\text{eq}}$) of electron transfer in the precursor complexes, which were determined from the dependence of the pseudo-first-order rate constants on concentrations of substrates (Figure 14).\[75\]

The unified correlations of driving-force dependence of log $k_{eq}$ of oxidation of all kinds of substrates by [(N4Py)Fe III] + (Figure 14) indicate that oxidations of toluene and thioanisole derivatives by [(N4Py)Fe III] \(^{1+}\) in the presence of HOTf and Sc(OTf) \(_3\) proceeds via rate-determining PCET and MCET of toluene derivatives, with formation of the precursor complexes as shown in Scheme 4, provided that the free energy change of electron transfer is smaller than 0.5 eV.\[72\] When the free energy change of electron transfer is larger than 0.5 eV, HAT and OAT processes become predominant.\[76\]

The rate-determining PCET and MCET of toluene derivatives are followed by rapid proton transfer and oxygen rebound to produce the corresponding benzyl alcohol derivatives and [(N4Py)Fe \(^2\) II] + , which is oxidized by [(N4Py)Fe \(^2\) II] + to [(N4Py)Fe IV] + in the presence of HOTf and Sc(OTf) \(_3\). In the case of oxidation of thioanisole derivatives and styrene derivatives by [(N4Py)Fe \(^2\) II] + in the presence of HOTf and Sc(OTf) \(_3\), the PCET and MCET are followed by rapid O− transfer to produce the corresponding sulfoxide and epoxide derivatives and [(N4Py)Fe IV] \(^{2+}\) (Scheme 4), which is also oxidized by [(N4Py)Fe \(^2\) II] + to [(N4Py)Fe IV] \(^{2+}\) in the presence of HOTf and Sc(OTf) \(_3\). In the case of [(N4Py)Fe \(^3\) III] + , H\(_2\)O is likely coordinated to Fe \(^{2+}\).

In the case of oxidation of N,N-dimethylaniline (DMA) by [(N4Py)Fe \(^2\) II] + , competition between DMA and [(N4Py)Fe \(^2\) II] + for the binding of Sc \(^{2+}\) ion results in overall enhancement of electron transfer from DMA to [(N4Py)Fe \(^2\) II] + , leading to the formation of DMA dimer radical cation (TMB \(^{2+}\), tetramethylbenzidine radical cation),\[88\] in contrast to demethylation in the absence of an acid.\[89–91\]

6. Lewis Acid-Coupled Electron Transfer of Metal–Peroxo Complexes

The reaction of [(TMC)Fe \(^{2+}\) II] + with situs-form O\(_2\) \(^{−}\)–M \(^{2+}\) species affords the iron(II)—peroxo-metal ion complex ([(TMC)Fe \(^{2+}\) II] \(^{−}\)–M \(^{2+}\)).\[92,93\] The [(TMC)Fe \(^{2+}\) II] \(^{−}\)–M \(^{2+}\) complexes were also synthesized by the reaction of [(TMC)Fe \(^{2+}\) II] \(^{−}\) with reoxidative metal ions.\[92,93\] The absorption maxima due to the ligand to metal charge transfer (LMCT) transition of [(TMC)Fe \(^{2+}\) II] \(^{−}\)–M \(^{2+}\) vary depending on the Lewis acidity of metal ions (Figure 15) and the \(h\nu_{\text{max}}\) value increased linearly with increasing Lewis acidity of M \(^{2+}\) (Δ$\lambda$), which was determined from the $g_{\lambda\nu}$ value of O\(_2\) \(^{−}\)–M \(^{2+}\) complexes [Equation (1)] as shown in Figure 16.\[93\] It is of interest to note that the \(h\nu_{\text{max}}\) value of [(TMC)Fe \(^{2+}\) II] \(^{−}\)–Ca \(^{2+}\) is similar to that of [(TMC)Fe \(^{2+}\) II] \(^{−}\)–Sr \(^{2+}\).\[93\] The EXAFS data, together with DFT calculations, indicate that the optimized Fe–M \(^{2+}\) distances and the Fe–O–M \(^{2+}\) angles in [(TMC)Fe \(^{2+}\) II] \(^{−}\)–Ca \(^{2+}\) and [(TMC)Fe \(^{2+}\) II] \(^{−}\)–Sr \(^{2+}\) are 4.11 Å and 4.34 Å and 140° and 142°, respectively.\[93\]

The electron-transfer reduction of [(TMC)Fe \(^{2+}\) II] \(^{−}\)–M \(^{2+}\) to undergo the O–O bond cleavage was found to be accelerated by increasing the Lewis acidity of M \(^{2+}\), but this led to deceleration of the electron-transfer oxidation of [(TMC)Fe \(^{2+}\) II] \(^{−}\)–M \(^{2+}\) to release O\(_2\).\[93\] Thus, it was proposed that, in addition to the role(s) of the Ca \(^{2+}\) (or Sr \(^{2+}\)) ion in facilitating the O–O bond

**Figure 14.** Plots of log $k_{eq}$ for C–H bond cleavage of toluene derivatives and sulfoxidation of thioanisole derivatives (1. hexamethylbenzene; 2. 1,2,3,4,5-pentamethylbenzene; 3. 1,4,5,6-tetramethylbenzene; 4. 1,2,4-trimethylbenzene; 5. 1,4-dimethylbenzene; 6. 1,3,5-trimethylbenzene; 7. toluene; 8. p-Mthaioanisole; 9. thioanisole; 10. p-Cl-thioanisole; 11. p-CN-thioanisole; 12. p-CN-thioanisole) by [(N4Py)Fe \(^{2+}\) II] + in the absence (black) and presence of acids (10 mM) of HOTf (red) and Sc(OTf) (blue), in MeCN at 298 K vs. the driving force of electron transfer ($-\Delta G_m = nF\Delta \mu_m$) from toluene derivatives (squares) and thioanisole derivatives (triangles) to [(N4Py)Fe \(^{2+}\) II] + in the presence of HOTf (red) and Sc(OTf) (blue). The red and blue circles show the driving-force dependence of the rate constants ($k_{eq}$) of electron transfer from electron donors (13. Fe \(^{2+}\) /phenyl; 14. Fe \(^{2+}\) /bpy); \(15\). [Ru \(^{2+}\)/4,4,4-phenyl]; \(16\). [Ru \(^{2+}\)/5,5-Me-phenyl]; \(17\). [Fe \(^{2+}\)/Cl/phenyl]; \(18\). [Ru \(^{2+}\)/bpy] \(^{2+}\) to [(N4Py)Fe \(^{2+}\) II] + in the presence of acids (10 mM) of HOTf and Sc(OTf) in MeCN at 298 K, respectively. The black circles show the driving-force dependence of the rate constants ($k_{eq}$) of electron transfer from electron donors (19. decamethylenecroccene; 20. octamethylenecroccene; 21. 1,1-dimethylferrocene; 22. n-amylerrocene; 23. ferrocene) to [(N4Py)Fe \(^{2+}\) II] + in the absence of acids in MeCN at 298 K. Figure 14 was taken with permission from reference [75].
making process in the water oxidation reaction, another possible role of the Ca$^{2+}$ (or Sr$^{2+}$) ion is to release O$_2$ by controlling the redox potential of the manganese–peroxo (or –hydroperoxo) species in the OEC.\[93\] The stronger Lewis acid that binds to the Mn$^{n+}$ complex in OEC may facilitate the O–O bond formation with water but decelerate the oxidation of the resulting Mn$^{n+}$–peroxo (or –hydroperoxo) complex.\[93\] This hypothesis, derived from the study on [(TMC)Fe$^{n+}$](O)$_2$ complexes, provides valuable mechanistic insights into the actual role of Ca$^{2+}$ and Sr$^{2+}$ in the reaction of the isolated [(TMC)Fe$^{n+}$](O)$_2$ (pink), V$^{3+}$ (cyan), Lu$^{3+}$ (green), Zn$^{2+}$ (blue), Ca$^{2+}$ (red), Sr$^{2+}$ (black) complexes vs. Lewisa cidity.\[93\]

![Figure 15. UV/Vis spectra of [(TMC)Fe$^{n+}$(O)$_2$]–M$^{n+}$ complexes (M$^{n+}$ = Sc$^{3+}$, Lu$^{3+}$, Ca$^{2+}$, Sr$^{2+}$).](image)

In another reaction, [(TMC)Fe$^{n+}$(O)$_2$]–Sc$^{3+}$ was suggested as an intermediate for Sc$^{3+}$–ion-promoted O$_2$ activation by [(TMC)Fe$^{n+}$(O)$_2$]–O$_2$ followed by Sc$^{3+}$–ion-promoted electron transfer from BPh$_3^-$ to the superoxo complex [(TMC)Fe$^{n+}$(O)$_2$]–Sc$^{3+}$, which was further reduced to yield [(TMC)Fe$^{n+}$(O)$_2$]–Sc$^{3+}$, via O–O bond cleavage.\[93\] Sc$^{3+}$ could be replaced by Brønsted acids for the formation of [(TMC)Fe$^{n+}$(O)$_2$]–Sc$^{3+}$ from [(TMC)Fe$^{n+}$] with O$_2$ and BPh$_3^-$.\[93\] However, the actual mechanism was later clarified to be an autocatalytic radical chain reaction (Scheme 5) rather than direct O$_2$ activation by [(TMC)Fe$^{2+}$(O)$_2$]–. The initiation is started by Sc$^{3+}$–ion-promoted electron transfer from BPh$_3^-$ to [(TMC)Fe$^{2+}$(O)$_2$]– to produce phenyl radical (Ph$^·$). The chain propagation step is composed of the addition of O$_2$ to Ph$^·$ and Sc$^{3+}$–ion-promoted electron transfer from BPh$_3^-$ to the resulting phenylperoxyl radical (PhOO$^·$) to produce the PhOO$^·$–Sc$^{3+}$ complex, accompanied by regeneration of Ph$^·$ (propagation step). The PhOO$^·$–Sc$^{3+}$ complex reacts with [(TMC)Fe$^{2+}$(O)$_2$]– to produce [(TMC)Fe$^{2+}$(O)$_2$] and PhOH after the reaction with residual water.\[97\] Such radical chain autoxidation reactions of iron(II) complexes by O$_2$ have also been reported for formation of iron(IV)–oxo complexes from the reactions of iron(II) complexes with hydrogen sources and O$_2$.\[96,99\] Sc$^{3+}$ ion has also been reported to bind to copper(II)–peroxo complexes in the Sc$^{3+}$–ion-promoted catalytic two-electron oxidation of O$_2$ by decamethylferrocene (Fc$^+$).\[100\] The Sc$^{3+}$–bound peroxo complex, [(tmpa)Cu$^+$(O)$_2$–Sc(O Tf)]$^-$, (tmpa = tris(2-pyridylmethyl)amine) was formed by addition of one equivalent of Sc(O Tf), to an acetone solution of a trans-$\mu$-1,2-peroxodicopper complex, [(tmpa)Cu$^+$(O)$_2$Cu$^+$tmpa)]$^+$. When Sc(O Tf) was replaced by HOTf, [(tmpa)Cu$^+$(OOH)]$^-$ was further reduced by the PCET reduction, acting as an intermediate for the catalytic four-electron reduction of O$_2$ by Fe$^+$\[101,102\].

![Figure 16. Plot of $h_n$ vs. Lewis acidity of metal ions (ΔE).](image)

7. Conclusion

Redox-inactive metal ions and Brønsted acids, which act as Lewis acids, bind to O$_2$–, metal–oxygen and metal–peroxo complexes, thereby tuning the redox reactivity of the metal–oxygen intermediates. The quantitative measure of the Lewis acidity of metal ions with different counter anions and ligands is obtained from the $g_n$ values of EPR spectra of O$_2$–metal ion complexes. The driving-force dependence of rate constants of proton-coupled electron transfer (PCET) and metal ion-coupled electron transfer (MCET) of metal–oxo complexes has been evaluated quantitatively in light of the Marcus theory of electron transfer, enabling the unification of the mechanisms of Lewis acid-promoted oxidation of substrates by metal–oxo complexes. Metal ions can also bind to iron(III)–peroxo complexes to accelerate the electron-transfer reduction but decelerate the electron-transfer oxidation. Such reactivity control of metal–oxygen intermediates by binding of Lewis acids provides valuable mechanistic insights into the actual role of Ca$^{2+}$ ion on water oxidation at the OEC in PS II.
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