Tuning the reactivity of mononuclear nonheme manganese(IV)-oxo complexes by triflic acid†

Junying Chen, a Hee jung Yoon, b Yong-Min Lee, a Mi Sook Seo, a Ritimukta Sarangi, c Shunichi Fukuzumi* a,b and Wonwoo Nam a

Triflic acid (HOTf)-bound nonheme Mn(IV)-oxo complexes, [[L]MnIV(O)]2+-(HOTf)2 (L = N4Py and Bn-TPEN; N4Py = N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methylamine and Bn-TPEN = N-benzyl-N,N,N′,N′-tris-(2-pyridylmethyl)ethane-1,2-diamine), were synthesized by adding HOTf to the solutions of the [[L]MnIV(O)]2+ complexes and were characterized by various spectroscopies. The one-electron reduction potentials of the MnIV(O) complexes exhibited a significant positive shift upon binding of HOTf. The driving force dependences of electron transfer (ET) from electron donors to the MnIV(O) and MnIV(O)-(HOTf)2 complexes were examined and evaluated in light of the Marcus theory of ET to determine the reorganization energies of ET. The smaller reorganization energies and much more positive reduction potentials of the [[L]MnIV(O)]2+-(HOTf)2 complexes resulted in greatly enhanced oxidation capacity towards one-electron reductants and para-X-substituted thioanisoles. The reactivities of the Mn(IV)-oxo complexes were markedly enhanced by binding of HOTf, such as a 6.4 × 105-fold increase in the oxygen atom transfer (OAT) reaction (i.e., sulfoxidation). Such a remarkable acceleration in the OAT reaction results from the enhancement of ET from para-X-substituted thioanisoles to the MnIV(O) complexes as revealed by the unified ET driving force dependence of the rate constants of OAT and ET reactions of [[L]MnIV(O)]2+-(HOTf)2. In contrast, deceleration was observed in the rate of H-atom transfer (HAT) reaction of [[L]MnIV(O)]2+-(HOTf)2 complexes with 1,4-cyclohexadiene as compared with those of the [[L]MnIV(O)]2+ complexes. Thus, the binding of two HOTf molecules to the MnIV(O) moiety resulted in remarkable acceleration of the ET rate when the ET is thermodynamically feasible. When the ET reaction is highly endergonic, the rate of the HAT reaction is decelerated due to the steric effect of the counter anion of HOTf.

Introduction

High-valent metal-oxo species have been invoked as key intermediates in biological and chemical oxidation reactions.1–5 In particular, high-valent manganese-oxo species have attracted much attention recently as an essential species in the oxygen-evolving complex (OEC) in photosystem II (PS II), which contains a redox-inactive Ca2+ ion in addition to redox-active evolving complex (OEC) in photosystem II (PS II), which much attention recently as an essential species in the oxygen-particularly, high-valent manganese-oxo species have attracted synthesis, characterization and kinetic details. See DOI: 10.1039/c5sc00535c† Electronic supplementary information (ESI) available: Experimental section; hydrogen atom transfer (HAT) reactions.1–5,9 It has been demonstrated that the reactivities of high-valent metal-oxo complexes are affected by various factors such as the structure and topology of supporting ligands, the identity of axial ligands, and the spin state of metal ions.5,9 The reactivity of metal-oxo complexes has been further enhanced by binding of a redox-inactive metal ions to the metal-oxo moiety, indicating that metal-oxo complexes act as very powerful oxidants by binding of redox-inactive metal ions.10–12 Binding of a redox-inactive metal ion acting as a Lewis acid to a high-valent metal-oxo complex has been confirmed by the crystal structure of a Sc3+ ion-bound nonheme iron(IV)-oxo complex, [[TMCFeIV(O)]2+ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane).14 In general, binding metal ions to oxygen and nitrogen atoms of C≡O and C≡N bonds of organic compounds as well as metal-oxo complexes results in enhancement of their reactivity towards electron donors, caused by a positive shift of the one-electron reduction potentials of metal ion-bound electron acceptors.9,14 Not only metal ions but also Brønsted acids, such as perchloric acid (HClO4) and trifluoromethanesulfonic acid (HOTf), accelerate electron transfer from electron donors to electron
acceptors including metal-oxo complexes when acids bind to the one-electron-reduced species of electron acceptors.\textsuperscript{15-18} The acceleration effects of Brønsted acids on the reactivity of electron acceptors towards electron donors are expected to be maximized when electron acceptors are protonated prior to electron transfer.\textsuperscript{19} In the catalytic cycles of metalloenzymes, Brønsted acids play a very important role in controlling the reactivity of high-valent metal-oxo intermediates via hydrogen bonding.\textsuperscript{20,21} However, evidence for the direct binding of Brønsted acids to high-valent metal-oxo complexes has yet to be obtained.

We report herein the first spectroscopic evidence for binding of two HOTf molecules to mononuclear nonheme Mn(IV)-oxo complexes, [(N4Py)MnIV(O)]\textsuperscript{2+} and [(Bn-TPEN)MnIV(O)]\textsuperscript{2+} (N4Py = N,N-bis(2-pyridylmethyl)-N,N\textprime{}bis(2-pyridyl)ethylamine and Bn-TPEN = N-benzyl-N,N\textprime{}N\textprime{}tris(2-pyridylmethyl)ethane-1,2-diamine) to produce [(L)Mn\textsuperscript{III}(O)]\textsuperscript{2+} (L = N4Py and Bn-TPEN) (see Fig. 1). The binding of two HOTf molecules to [(L)MnIV(O)]\textsuperscript{2+} enhanced the reactivity of [(L)MnIV(O)]\textsuperscript{2+} dramatically in electron transfer (ET) reaction with one-electron reductants as well as in OAT reaction with thioanisoles. In contrast, the reactivity of [(L)MnIV(O)]\textsuperscript{2+} decreased significantly in the HAT reaction with 1,4-cyclohexadiene. A large positive shift of the one-electron reduction potentials of the Mn\textsuperscript{IV}(O) complexes was also observed upon binding of two HOTf molecules to the Mn\textsuperscript{IV}(O) complexes, resulting from the much larger binding constants of HOTf to the one-electron reduced species, [(L)Mn\textsuperscript{III}(O)]\textsuperscript{2+}, as compared with those of [(L)MnIV(O)]\textsuperscript{2+}. A unified ET driving force dependence of the rate constants of ET and OAT reactions of [(L)MnIV(O)]\textsuperscript{2+}–(HOTf)\textsubscript{2}, which were analyzed in light of the Marcus theory of electron transfer,\textsuperscript{22} provides valuable insights into the change in the mechanism depending on the ET driving force.

Results and discussion

Binding of HOTf to nonheme Mn\textsuperscript{IV}(O) complexes

Mononuclear high-valent Mn\textsuperscript{IV}(O) complexes, [(N4Py)Mn\textsuperscript{IV}(O)]\textsuperscript{2+} (1) and [(Bn-TPEN)Mn\textsuperscript{IV}(O)]\textsuperscript{2+} (2), were generated by reacting [(N4Py)Mn\textsuperscript{II}]+ and [(Bn-TPEN)Mn\textsuperscript{II}]+ with iodosylbenzene (PhIO), respectively, as reported previously.\textsuperscript{23-25} Addition of HOTf to an in situ generated solution of 1 in CF\textsubscript{3}CH\textsubscript{2}OH–CH\textsubscript{3}CN (v/v = 1 : 1) at 273 K afforded a reddish brown solution and resulted in the disappearance of the absorption band at 940 nm due to 1, accompanied by a new absorption band formation at 550 nm (shoulder, $\varepsilon = 540 \text{ M}^{-1} \text{ cm}^{-1}$) (Fig. 2). Similar spectral changes were also obtained for 2, indicating that the absorption band at 1020 nm due to 2 disappeared and concomitantly a new absorption band at 580 nm ($\varepsilon = 600 \text{ M}^{-1} \text{ cm}^{-1}$) was generated (see Fig. S1, ESI\textsuperscript{†}).

The spectral titration of 1 with HOTf (Fig. 2) exhibits a sigmoidal curvature (inset of Fig. 2), which suggests that more than one HOTf are attached to 1. In such a case, the absorption change ($\Delta A$) due to binding of $n$ molecules of HOTf to 1 is given by eqn (1),

$$\Delta A = \Delta A_0 [\text{HOTf}]^n/(1 + K[\text{HOTf}]^n)$$

(1)

where $\Delta A_0$ is the final absorption change due to binding of $n$ molecules of HOTf to 1 and $K$ is the binding constant. Eqn (1) is rewritten as eqn (2),

$$\log(\Delta A/(\Delta A_0 - \Delta A)) = \log K + n \log[\text{HOTf}]$$

(2)

which predicts a linear correlation between $\log(\Delta A/(\Delta A_0 - \Delta A))$ and $\log[\text{HOTf}]$ with a slope of $n$. From a linear correlation of $\log(\Delta A/(\Delta A_0 - \Delta A))$ vs. $\log[\text{HOTf}]$, the number of HOTf molecules bound to 1 and the binding constant were determined to be 2.0(1) and 1.3(3) $\times 10^5 \text{ M}^{-1}\text{M}^{-1}$, where $\log K = 5.1(1)$, respectively (inset of Fig. 2 for the fitting of spectral titration data; Fig. S2, ESI\textsuperscript{†} for linear plot using eqn (2)). Thus, 1 is bound to two HOTf molecules to afford the HOTf-bound species, [(N4Py)Mn\textsuperscript{IV}(O)]\textsuperscript{2+}–(HOTf)\textsubscript{2} (3) [eqn (3)], which is relatively stable at 273 K ($t_{1/2} \approx 6 \text{ h}$; see Fig. S3, ESI\textsuperscript{†}).

$$[(\text{N4Py})\text{MnIV(O)}]^{2+} + 2\text{HOTf} \rightarrow [(\text{N4Py})\text{MnIV(O)}]^{2+}-(\text{HOTf})_{2} \quad (3)$$

When 2 was bound to two HOTf molecules to form the HOTf-bound species, [(Bn-TPEN)Mn\textsuperscript{IV}(O)]\textsuperscript{2+}–(HOTf)\textsubscript{2} (4), the half-lifetime of 4 was 1.5 h, indicating 4 is somewhat less stable than 3 (Fig. S3, ESI\textsuperscript{†}). It is important to note that 3 and 4 reverted to 1 and 2, respectively, upon addition of base (i.e., triethylamine) as shown in Fig. S4, ESI\textsuperscript{†}.

![Fig. 1](https://example.com/f1.png)

**Fig. 1** Schematic drawing of the chemical structures of [(N4Py)Mn\textsuperscript{IV}(O)]\textsuperscript{2+} (a) and [(Bn-TPEN)Mn\textsuperscript{IV}(O)]\textsuperscript{2+} (b) species binding two HOTf molecules.

![Fig. 2](https://example.com/f2.png)

**Fig. 2** UV-vis spectral changes observed in the titration of 1 (black bold line) with HOTf. HOTf (0–20 mM) was added incrementally into the solution of 1 (0.50 mM) in CF\textsubscript{3}CH\textsubscript{2}OH–CH\textsubscript{3}CN (v/v = 1 : 1) at 273 K. Inset shows the spectral titration monitored at 550 nm (blue circles) due to the formation of 3.
The X-band EPR spectrum of 3 exhibits signals that are characteristic of $S = 3/2$ Mn$^{IV}$ ($g_1 = 5.8, g_2 = 3.2$ and $g_3 = 2.01$; see Fig. S3, ESf). The magnetic moment of 3 was also determined to be 4.3 $\mu_B$ by the modified $^1$H NMR technique of Evans, confirming the spin state of $S = 3/2$. The cold-spray ionization time-of-flight mass (CSI-TOF MS) spectrum of 3 exhibits ion peaks at $m/z$ 737.0 and 759.0, which shift to 739.0 and 761.0 upon introduction of $^{18}\text{O}$ during the generation of 3 using PhH$^{18}\text{O}$ (Fig. S6, ESf). This $^{18}\text{O}$-labeled experiment suggests that 3 contains one oxygen atom. It should be noted that a species containing one bound HOTf was detected in CSI-TOF MS spectra, but the species with two bound HOTf molecules was not detected, probably because the binding of HOTf is fragile and easily broken under the CSI-TOF MS conditions.

Comparison of X-ray absorption near edge structure (XANES) at the Mn K-edge for [[N4Py]Mn$^{IV}$O]^{2+} (1, red line in Fig. 3a) and [[N4Py]Mn$^{IV}$O]^{2+}−(HOTf)$_2$ (3, black line in Fig. 3a) clearly shows a decrease in pre-edge intensity and no change in the rising-edge energy position of 3 relative to 1, which is consistent with the elongation of the Mn−O bond and unchanged Mn$^{IV}$ oxidation state, also consistent with the EPR results (Fig. S6, ESf). Extended X-ray absorption fine structure (EXAFS) data as shown in Fig. 3b indicate a short Mn−O distance in 1.67 $\text{Å}$ observed in [[N4Py]Mn$^{IV}$O]^{2+} (1), indicating that the HOTf molecules interact with the oxo moiety of 1. This Mn−O bond distance in 3 is almost identical to that of the [[N4Py]Mn$^{IV}$O]^{2+} complex binding Se$^{3+}$ ions. A single Mn$^{IV}$−O unit by hydrogen bonding interaction. It is distinct from diprotonation, which would yield the putatively unstable [Mn$^{IV}$OH$_2$]$^{10+}$ species. This is evidenced by the small change in Mn−O distance upon binding of two HOTf molecules (less than 0.1 $\text{Å}$).

The Mn−O distance of 1.74 $\text{Å}$ indicates the double bond character of Mn−O, somewhat weakened by hydrogen bonding.

**Thermodynamic and kinetic evidence for binding of HOTf to [[N4Py]Mn$^{IV}$O]^2+ (1)**

Binding of two HOTf molecules to 1 was supported by the kinetic studies on the oxidation of para-CN-thioanisole by 3, which was prepared by adding different amounts of HOTf (0–50 mM) into a solution of 1 (0.50 mM). The observed second-order rate constants ($k_2$) were determined by monitoring a decrease in absorption bands at 550 nm due to 3 or 940 nm due to 1. The dependence of the second-order rate constant for the oxidation of para-CN-thioanisole on the concentration of HOTf shows a sigmoidal curvature as shown in Fig. 4. Such a sigmoidal curvature can be well explained by eqn (4),

$$k_2 = k_{ox}[\text{HOTf}]^2/(1 + K[\text{HOTf}]^2)$$

where $k_{ox}$ is the rate constant of OAT from 3 to para-CN-thioanisole. Eqn (4) is rewritten as eqn (5), which predicts a linear relation between $k_2^{-1}$ and [HOTf]$^{-2}$.

$$k_2^{-1} = (k_{ox}K)^{-1}[\text{HOTf}]^{-2} + k_{ox}^{-1}$$

A linear plot of $k_2^{-1}$ vs. [HOTf]$^{-2}$ (Fig. S7, ESf) afforded the $k_{ox}$ and $K$ values of 2.5 M$^{-1}$ s$^{-1}$ and 1.6(4) × 10$^5$ M$^{-2}$ [log $K = 5.2(1)$], respectively, determined from the slope and intercept. The $K$ value determined from the inset of Fig. 4 or S7, ESf is quite consistent with the value determined from the spectal titration under the same experimental conditions (Fig. S2, ESf). Furthermore, the fitting line in Fig. 4 obtained by using the $k_{ox}$ and $K$ values determined is well matched with...

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**Fig. 3**  (a) Normalized Mn K-edge XANES of 1 (red line) and 3 with 30 mM of HOTf (black line). Inset shows magnified pre-edge features. (b) Non-phase-shift corrected Fourier transforms (black line) and the corresponding Mn K-edge EXAFS data (inset; black line) for 3. Fits (red lines) were performed in the range of $k = 2–12$ $\text{Å}^{-1}$.

**Fig. 4** Dependence of the second-order rate constant, $k_2$, for the oxidation of para-CN-thioanisole by 3 (0.50 mM) on [HOTf] (0–50 mM) in CF$_3$CH$_2$OH–CH$_2$CN (v/v = 1 : 1) at 273 K. Inset shows a plot of log[$\Delta k_2$]/[$\Delta k_{2,0} - \Delta k_2$] vs. log[HOTf], where $\Delta k_{2,0}$ is the full change of second-order rate constant.
experimental data points, clearly indicating that two molecules of HOTf are involved in these reactions.

**Enhancement of the oxidation capacity of the nonheme MnIV(O) complexes by binding of two HOTf molecules**

Electron transfer from coordinatively saturated metal complexes to [MnIV(O)]2+–(HOTf)2 complexes, 3 and 4, were investigated, and these 3 and 4 species were found to perform electron transfer (ET) reaction with the one-electron reductant, [RuII(5-NO2-phen)]3+PF6, (5-NO2-phen: 5-nitro-1,10-phenanthroline), which has a one-electron oxidation potential as high as 1.50 V vs. SCE, whereas no ET was observed for 1 (E_red = 0.80 V vs. SCE) and 2 (E_red = 0.78 V vs. SCE). The redox titration for formation of [RuIII(5-NO2-phen)]3+, as shown in Fig. 5, indicates only one-electron reduction of 3 occurred without further reduction by [RuII(5-NO2-phen)]3+. Upon addition of [RuII(5-NO2-phen)]3+ to a solution of 3, the absorption band at 450 nm due to [RuII(5-NO2-phen)]3+ disappeared (data not shown) and concomitantly the absorption band at 650 nm due to [RuIII(5-NO2-phen)]3+ appeared with an isosbestic point at 550 nm (Fig. 5a). By analyzing the resulting solution by EPR, we found that a MnIII species was formed as a major product in the ET reaction by 3 (Fig. 5c, ESI†). It should be noted that the second ET could be observed to form the MnII product when a large excess of [RuII(5-NO2-phen)]3+ upon addition of [RuII(5-NO2-phen)]3+ to a solution of HOTf at 273 K. The redox titration for formation of [RuIII(5-NO2-phen)]3+ upon addition of HOTf to reach the constant value of 1.65 V vs. SCE at more than 30 mM of HOTf at 273 K. The saturated E_red value of 1.65 V vs. SCE in the presence of a large excess of HOTf corresponds to that of the [MnIV(O)]2+–(HOTf)2 complex of 3. There is a large difference (AE_red = 0.85 V in the case of N4Py in the E_red values between [MnIV(O)]2+ and [MnIV(O)]3–(HOTf)2, which indicates that the binding of HOTf to [MnIII(O)]0 (the species derived from one-electron reduction of [MnIV(O)]2+) is much stronger than that to [MnIV(O)]3+, as expected from the increased basicity of the oxo moiety in [MnIII(O)]0. Thus, the HOTf-bound MnIV(O) complex
acts as the strongest oxidant among the nonheme Mn-oxo complexes bearing the same ligand system.

As compared with the \( E_{\text{red}} \) values of \([\text{N4Py}]\text{Mn}^{IV}(\text{O})^{2+} (0.80 \text{ V vs. SCE})\) and \([\text{N4Py}]\text{Mn}^{IV}(\text{O})^{2+}-(\text{Sc}^{3+}) \) \( (1.42 \text{ V vs. SCE}) \), a remarkable positive shift of \( E_{\text{red}} \) of 3 \( (1.65 \text{ V vs. SCE}) \) was observed under the same conditions in \( \text{CF}_2\text{CH}_2\text{OH}-\text{CH}_3\text{CN} (v/v = 1:1) \) at 273 K, resulting in significant enhancement of the ET reactivity. Rates of ET from various one-electron donors, coordinatively saturated iron(n) and ruthenium(n) complexes, to 3 and 4 were investigated and the rate constants were determined by monitoring the absorbance changes due to the decay of iron(n) or the formation of corresponding ruthenium(n) species. Rates of ET obeyed pseudo-first-order or second-order kinetics, and the pseudo-first-order rate constant \( k_{\text{obs}} \) increased linearly with increasing concentrations of electron donors. The second-order rate constants \( k_{\text{et}} \) of ET thus determined are listed in Table 1 together with the one-electron oxidation potentials \( (E_{\text{ox}})\) of one-electron reductants in \( \text{CF}_2\text{CH}_2\text{OH}-\text{CH}_3\text{CN} (v/v = 1:1) \) and the driving force of ET \( (-\Delta G_{\text{et}}) \) (see also Fig. S12 and S13, ESI, for 3 and 4, respectively).

### Outer-sphere electron transfer of \([\text{Mn}^{IV}(\text{O})^{2+}-(\text{HOTf})_2\] \)

The driving force dependence of the rate constants of electron transfer from one-electron reductants to 3 (Fig. 7 and Table 1) is well fitted in the light of the Marcus theory of adiabatic outer-sphere electron transfer [eqn (8)].

### Table 1: One-electron oxidation potentials \( (E_{\text{ox}})\) of one-electron reductants and para-X-substituted thioanisoles and second-order rate constants of ET and sulfoxidation reactions by \([\text{N4Py}]\text{Mn}^{IV}(\text{O})^{2+}-(\text{HOTf})_2\) (3) and \([\text{Bn-TPEN}]/\text{Mn}^{IV}(\text{O})^{2+}-(\text{HOTf})_2\) (4) with driving force of ET \( (-\Delta G_{\text{et}}) \) in the presence of HOTf (30 mM) in \( \text{CF}_2\text{CH}_2\text{OH}-\text{CH}_3\text{CN} (v/v = 1:1) \) at 273 K.

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<th>Electron donor</th>
<th>( E_{\text{ox}} ) (V vs. SCE)</th>
<th>( k_{\text{et}} ) M(^{-1}) s(^{-1})</th>
<th>( -\Delta G_{\text{et}} ) eV</th>
<th>( k_{\text{et}} ) M(^{-1}) s(^{-1})</th>
<th>( -\Delta G_{\text{et}} ) eV</th>
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<tr>
<td>([\text{N4Py}]/\text{Mn}^{IV}(\text{O})^{2+}-(\text{HOTf})_2]</td>
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* The one-electron oxidation potentials of coordinatively saturated metal complexes were determined by cyclic voltammetry in \( \text{CF}_2\text{CH}_2\text{OH}-\text{CH}_3\text{CN} (v/v = 1:1) \) containing 0.10 M \( n\)-BuNPf\(_6\) as a supporting electrolyte at 298 K. The one-electron oxidation potentials of coordinatively saturated metal complexes in the presence of HOTf (30 mM) were identical to those in the absence of HOTf. "The one-electron oxidation potentials of para-X-thioanisoles were determined by second harmonic A.C. voltammetry (SHACV) in \( \text{CF}_2\text{CH}_2\text{OH}-\text{CH}_3\text{CN} (v/v = 1:1) \) containing 0.10 M \( n\)-BuNPf\(_6\) as a supporting electrolyte at 298 K. " Not measured.
\[ k_{\text{et}} = Z \exp\left(-\frac{\Delta E}{RT}\right) \]

where \( Z \) is the collision frequency, taken as \( 1 \times 10^{11} \) M\(^{-1}\) s\(^{-1}\), \( \lambda \) is the reorganization energy of electron transfer, \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature. From the fitting of the ET rate constants (red circles in Fig. 7), the \( \lambda \) value of ET from one-electron reductants to 3 was determined to be 2.20 \( \pm \) 0.02 eV. Similarly, the \( \lambda \) values of the ET reaction of 4 with one-electron reductants was determined to be 2.15 \( \pm \) 0.03 eV (Table 1; see also Fig. S11 and S14, ESIf). Both \( \lambda \) values of the ET reduction of \([L]_{\text{MnIV(O)}}\)\(^2+\)–(HOTf)\(_2\) (L = N4Py and Bn-TPEN) are smaller than those of \([L]_{\text{MnIV(O)}}\)\(^2+\) in the absence of HOTF, since the elongation of the Mn–O bond distance by binding of two HOTF molecules occurs prior to the ET, resulting in slower change in the Mn–O bond distance after ET reduction. However, the \( \lambda \) values for \([\text{MnIV(O)}]\)\(^2+\)–(HOTf)\(_2\) are quite similar to those for \([\text{MnIV(O)}]\)\(^2+\)–(Sc\(^{3+}\))\(_2\). This result is quite reasonable because, according to the XANES/EXAFS analyses, the elongation of the Mn–O bond due to binding of HOTF is almost identical to the case of the Mn–O species binding Sc\(^{3+}\) ions (vide supra).

### Contrasting effects of binding of HOTF on the reactivity of nonheme MnIV(O) complexes in OAT and HAT reactions

The reactivity of the HOTF-bound MnIV(O) complexes, 3 and 4, was investigated in OAT and HAT reactions. The OAT reaction (e.g., the oxidation of thioanisoles) was markedly influenced by binding of two HOTF molecules to the Mn-oxo moiety (Table 1; Fig. S15 and S16, ESIf for 3 and 4, respectively). Upon addition of thioanisole to a solution of 3 (Fig. 8a), the MnIV(O) complex reverted to the starting MnIV complex, which was confirmed by EPR (Fig. S17, ESIf). Product analysis of the reaction solutions revealed the formation of methyl phenyl sulfide in a quantitative yield. These results indicate that the oxidation of thioanisole by the HOTF-bound MnIV(O) complexes, MnIV(O)–(HOTf)\(_2\), occurs via a two-electron oxidation process as reported previously for MnIV(O) and MnIV(O)–(Sc\(^{3+}\))\(_2\). The second-order rate constant (5.9 \( \times \) 10\(^3\) M\(^{-1}\) s\(^{-1}\)) determined in the reaction of thioanisole with 3 at 273 K is 6.4 \( \times \) 10\(^3\)-fold and 3.0 \( \times \) 10\(^2\)-fold greater than those of 1 (9.2 \( \times \) 10\(^3\) M\(^{-1}\) s\(^{-1}\)) and \([\text{N4PyMnIV(O)}]\)\(^2+\)–(Sc\(^{3+}\))\(_2\) (2.0 \( \times \) 10 M\(^{-1}\) s\(^{-1}\)), respectively, demonstrating that the reactivity of the Mn(oxo) complex in the OAT reaction is markedly enhanced by binding of two HOTF molecules. Much accelerated reactivity of the HOTF-bound MnIV(O) species was also observed in the reactions of other para-X-substituted thioanisoles (Table 1; Fig. S15, ESIf). In addition, a good linear correlation was obtained by plotting the log \( k_2 \) values against one-electron oxidation potentials of thioanisoles (Fig. 8b). The slope of –11.4(5) in Fig. 8b is in between those reported for outer-sphere electron transfer reductions of \([\text{TMCFeIII}+\text{OOH}]^{2+}\) [slope = –9.7(6)] and \([\text{TMCFeIII}–\text{OOO(CH}_3)_2\text{OH}]^{2+}\) [slope = –12(1)].

As shown in Fig. 7, the electron-transfer driving force dependence of log \( k_2 \) for the oxidation of thioanisoles by 3 (blue circles) exhibits virtually the same relationship with the driving force dependence of log \( k_{\text{et}} \) of electron-transfer reactions of 3 (red circles), whereas a huge deviation from the ET line for those of 1 (black circles) was shown. This result together with the slope in the plot of the log \( k_2 \) values against one-electron oxidation potentials of thioanisoles and the activation parameters (vide supra) strongly indicates that the oxidation of thioanisoles by MnIV(O)–(HOTf)\(_2\) intermediates proceeds via an outer-sphere electron-transfer pathway.
The reactivities of the HOTf-bound Mn-oxo species, 3 and 4, were also investigated kinetically in HAT, such as the C–H bond activation of 1,4-cyclohexadiene (CHD). Outer-sphere electron transfer from CHD to 3 is highly endergonic and thereby unlikely to occur judging from the more positive one-electron oxidation potential of CHD \( (E_{ox} = 1.89 \text{ V vs. SCE}) \) than the one-electron reduction potential of 3 \( (E_{red} = 1.65 \text{ V vs. SCE}) \). As shown in Fig. 9a, addition of CHD to a solution of 3 in CF\textsubscript{3}CH\textsubscript{2}OH–CH\textsubscript{3}CN \( (v/v = 1:1) \) at 298 K afforded the decay of absorption band at 550 nm due to 3. Analysis of the resulting solution with EPR, GC and GC-MS showed that the major product was a Mn\textsuperscript{III} species, which is EPR silent (Fig. S17, ESI\textsuperscript{†} for EPR),\textsuperscript{23} and that benzene was obtained as the sole organic product with a yield of 48% based on the concentration of 3, similar to that observed in the oxidation of CHD by nonheme Mn\textsuperscript{IV}(O)\textsubscript{2} complexes and other nonheme metal-oxo species.\textsuperscript{21,25} The second-order rate constant \( (9.2 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}) \) determined in the oxidation of CHD by 3 was smaller, by a factor of \( \sim 4 \), than that for 1 \( (3.5 \text{ M}^{-1} \text{ s}^{-1}) \) at 298 K (Fig. 9b), indicating that the reactivity of the Mn\textsuperscript{IV}(O) complex is diminished by binding of two HOTf molecules to the Mn\textsuperscript{IV}(O) moiety. As reported previously, the reactivity of the Mn\textsuperscript{IV}(O) complex in the oxidation of CHD was diminished by a factor of \( \sim 180 \) upon binding of two Sc\textsuperscript{3+} ions and the reason for the significant deceleration of the rate was proposed to be owing to the steric effect of the Sc\textsuperscript{3+} ions.\textsuperscript{23} The smaller deceleration \( (\sim 4\text{-fold}) \) due to HOTf binding, as compared to the Sc(OTf)\textsubscript{3}, binding, may be explained by the smaller molecular size of HOTf than that of Sc(OTf)\textsubscript{3}. The Mn\textsuperscript{III}(O) moiety in [Mn\textsuperscript{IV}(O)\textsubscript{2}–(HOTf)\textsubscript{2}] can provide suitable interaction with the substrate, but the interaction was slightly hindered by binding of HOTf. However, the interaction between substrate and intermediate was more hindered by binding of Sc\textsuperscript{3+} ions, which has a relatively larger size, to the Mn\textsuperscript{IV}(O) moiety, leading to the more diminished reactivity in HAT reactions. Similarly, in the reaction of 4 with CHD, a deceleration of \( \sim 9\text{-fold} \) was detected by comparison of the reactivity of 2 (Fig. S21, ESI\textsuperscript{†}).

The contrasting effects by binding of two HOTf molecules observed in OAT and HAT reactions were brought to light for the first time experimentally in the study of the effect of Bronsted acid. This contrasting effect in OAT and HAT reactions might give rise to the different reaction mechanisms; OAT reactions proceed \( \text{via} \) an outer-sphere electron-transfer pathway, which should not be influenced by steric hindrance, whereas HAT reactions should require the direct interaction between Mn\textsuperscript{IV}(O) moiety and substrates, which should be sensitive to the steric hindrance. In agreement with the results reported for the promotion effect of Lewis acid in the reaction of \([\text{N4PyFeIV(O)}]^{2+}\), our results also have shown that Bronsted acid has the ability to promote the ET reaction intensely efficiently, but relatively, the possibility of steric hindrance caused by binding of two HOTf molecules to the metal-oxo group should also be taken into consideration when a Bronsted acid is involved in a reaction system.

**Conclusion**

Mononuclear nonheme Mn\textsuperscript{IV}(O) complexes binding two HOTf molecules were generated for the first time and characterized by various spectroscopic techniques. Their reactivities in electron transfer (ET), oxygen atom transfer (OAT) and hydrogen atom transfer (HAT) reactions were investigated. Binding of two HOTf molecules to the Mn-oxo moiety leads to a more positive shift of the one-electron reduction potential and a contrasting effect on the reactivities in OAT and HAT reactions. The reactivity of the nonheme Mn\textsuperscript{IV}(O) complexes was markedly enhanced by binding of two HOTf molecules: \( 6.4 \times 10^{5}\text{-fold} \) increase in OAT reaction \( \text{i.e.,} \), oxygenation of thioanisole, whereas deceleration was observed in the rate of HAT reaction of Mn\textsuperscript{IV}(O)–(HOTf)\textsubscript{2} complexes with CHD relative to that of the corresponding Mn\textsuperscript{IV}(O) complexes. However, HAT was faster compared to that of the Sc\textsuperscript{3+} ion-bound complex, which may be explained by the relatively smaller molecular size of HOTf compared with that of Sc(OTf)\textsubscript{3}, when the interaction between Mn\textsuperscript{IV}(O) and substrate required for HAT reactions would be less hindered. Thus, the binding of two HOTf molecules to the Mn\textsuperscript{IV}(O) moiety resulted in remarkable acceleration of the ET rate, when thermodynamically feasible. When the ET reaction is highly endergonic as with CHD, the rate of HAT is decelerated due to steric effects of the counter anion of HOTf.

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Notes and references


