Redox Reactivity of a Mononuclear Manganese-Oxo Complex
Binding Calcium Ion and Other Redox-Inactive Metal Ions

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ABSTRACT: Mononuclear nonheme manganese(IV)-oxo complexes binding calcium ion and other redox-inactive metal ions, [(dpaq)MnIV(O)]+-Mn(III, IV; M = Ca2+, Mg2+, Zn2+, Y3+, Al3+, and Sc3+) (dpaq = 2-[bis(pyridin-2-ylmethyl)]amino-N-quinolin-8-yl-acetamidate), were synthesized by reacting a hydroxomanganese(III) complex, [(dpaq)MnIII(OH)]+, with iodo-sylbenzene (PhIO) in the presence of redox-inactive metal ions (MnIII). The Mn(IV)-oxo complexes were characterized using various spectroscopic techniques. In reactivity studies, we observed contrasting effects of MnIII on the reactivity of 1-MnIV in redox reactions such as electron-transfer (ET), oxygen atom transfer (OAT), and hydrogen atom transfer (HAT) reactions. In the OAT and ET reactions, the reactivity order of 1-MnIV, such as 1-Sc3+ > 1-Al3+ > 1-Y3+ > 1-Lu3+ > 1-Zn2+ > 1-Mg2+ > 1-Ca2+, follows the Lewis acidity of MnIII bound to the Mn–O moiety; that is, the stronger the Lewis acidity of MnIII, the higher the reactivity of 1-MnIV becomes. In sharp contrast, the reactivity of 1-MnIV in the HAT reaction was reversed, giving the reactivity order 1-Ca2+ > 1-Mg2+ > 1-Zn2+ > 1-Lu3+ > 1-Y3+ > 1-Al3+ ≈ 1-Sc3+. That is, the higher is Lewis acidity of MnIII, the lower the reactivity of 1-MnIV in the HAT reaction. The latter result implies that the Lewis acidity of MnIII bound to the Mn–O moiety can modulate the basicity of the metal-oxo moiety, thus influencing the HAT reactivity of 1-MnIV, cytochrome P450 utilizes the axial thiolate ligand to increase the basicity of the iron-oxo moiety, which enhances the reactivity of compound I in C–H bond activation reactions.

INTRODUCTION

High-valent manganese-oxo complexes play pivotal roles as reactive intermediates in enzymatic reactions; one example is the water oxidation by the oxygen-evolving complex (OEC) in photosystem II (PS II), where Ca2+ ion is an essential component for dioxygen evolution in the catalytic water oxidation reaction.1−5 The role of the Ca2+ ion, which is a redox-inactive metal ion, has been proposed to facilitate the O–O bond formation step occurring between a high-valent Mn(V)-oxo intermediate and an aqua (or hydroxide) ligand bound to the Ca2+ ion, although the exact role of the Ca2+ ion has yet to be clearly clarified.6−8

Recently, a large number of high-valent metal-oxo complexes bearing nonheme ligands have been successfully synthesized and characterized spectroscopically and/or structurally in biomimetic studies.9−20 Their reactivities have also been investigated intensively in various oxidation reactions.9−20 In addition, factors that modulate the reactivities and reaction mechanisms of the high-valent metal-oxo complexes have been the focus of current research.21−26 For example, it has been shown that binding of redox-inactive metal ions, such as scandium ion (Sc3+), to nonheme metal-oxo complexes enhanced their reactivities greatly in oxygen atom transfer (OAT) and electron-transfer (ET) reactions.22−24 Further, the oxidation of the hydride ion by nonheme iron(IV)-oxo complexes in the presence of redox-inactive metal ions was shown to be correlated with the Lewis acidity of the redox-inactive metal ions.25 In Mn-oxo complexes, binding of Sc3+ ion(s) to nonheme Mn(IV)-oxo complexes resulted in a large positive shift in the one-electron reduction potentials of the Mn(IV)-oxo complexes, thereby enhancing their reactivities in OAT and ET reactions but diminishing their reactivities in hydrogen atom transfer (HAT) reactions.26 Goldberg and co-

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workers reported the influence of a redox-inactive Zn
2+ on a valence tautomerization of a Mn(V)-oxo corollazine complex and the change of the reactivity of the Mn(V)-oxo complex in ET and HAT reactions.27 The redox-inactive metal ion effect has also been demonstrated in the catalytic oxidation of organic substrates by terminal oxidants, in which high-valent metal(IV)-oxo species binding a Sc
3+ ion was proposed as an active oxidant.28

As alluded to above, the effects of redox-inactive metal ions on the chemical properties of Mn-oxo complexes have merited significant interest due to the vital role of the Ca
2+ ion in OEC in PS II as well as the desire for the development of efficient catalytic oxidation systems. However, nonheme Mn(IV)-oxo complexes binding calcium ions and other redox-inactive metal ions other than Sc
3+ have yet to be reported. Herein, we report the synthesis and characterization of Mn(IV)-oxo complexes binding a series of redox-inactive metal ions, [(dpaq)-Mn
III
(III,IV) complex, [(dpaq)Mn
III
(OH)]
+ (1-M
III
, M
III
 = Ca
2+, Mg
2+, Zn
2+, Lu
3+, Y
3+, A1
3+, and Sc
3+ (dpaq = 2-[bis(pyridin-2-ylmethyl)amino-N-quinolin-8-yl-acetamidate], by reactivity a hydroxomanganese(III) complex, [(dpaq)Mn
II
(OH)]
+, with iodosylbenzene (PhIO) in the presence of redox-inactive metal ions (M
II
) (Scheme 1, reaction a). In the absence of M
II
, a bis(μ-

oxo)dimanganese(III,IV) complex, [(dpaq)Mn
III
(O)2Mn
IV
(dpaq)
+] (1-Sc
3+), was produced (Scheme 1, reaction b). We also report the contrasting effects of redox-inactive metal ions (M
II
) on the reactivity of 1-M
III
 in OAT, ET, and HAT reactions (Scheme 1). Interestingly, we found that the reactivities of 1-M
III
 differed markedly in the OAT, ET, and HAT reactions, depending on the Lewis acidity of M
II
 in 1-M
III
. For example, as the Lewis acidity of M
II
 increases, the reactivity of 1-M
III
 becomes greater in the OAT and ET reactions (Scheme 1). In sharp contrast, 1-M
III
 becomes a weaker oxidant in the HAT reaction as the Lewis acidity of M
II
 increases (Scheme 1). The latter result implies that the Lewis acidity of M
II
 modulates the reactivity of 1-M
III
 in abstracting a hydrogen atom (H atom) from substrate C–H bonds by controlling the basicity of the metal-oxo moiety; it has been discussed in the communities of bioinorganic/biomimetic and biological chemistry that cytochrome P450 enzymes utilize the axial thiolate ligand to modulate the basicity of the iron-oxo moiety that influences the reactivity of compound I in C–H bond activation reactions.47 To the best of our knowledge, the present study reports for the first time the synthesis of Mn(IV)-oxo complexes binding various redox-inactive metal ions, such as Ca
2+, Mg
2+, Zn
2+, Lu
3+, Y
3+, A1
3+, and Sc
3+, which provides us with an excellent opportunity to investigate the redox-inactive metal ion effect on the chemical properties of high-valent metal-oxo species systematically.

RESULTS AND DISCUSSION

Synthesis and Characterization of Mn
IV
(O)-M
II
. The starting [(dpaq)Mn
III
(OH)]
+ complex was synthesized according to the literature methods (see Scheme 2 for the structures of the dpaq ligand and the [(dpaq)Mn
III
(OH)]
+ complex; also see the X-ray crystal structure and 1H NMR spectrum of [(dpaq)Mn
III
(OH)]
+ (Supporting Information (SI), Figures S1 and S2)29,30 it has been reported very recently that the [(dpaq)Mn
II
(OH)]
+ complex is in equilibrium with a μ-oxodimanganese(III,III) complex, [(dpaq)Mn
III
(μ-O)]
2+.31 When the solution of [(dpaq)Mn
III
(OH)]
+ was reacted with PhIO in acetonitrile (MeCN) at 263 K, we observed the formation of a green-colored species with broad absorption bands at ∼520 nm within 2 min (Figure 1a). The manganese product was identified as a dinuclear bis(μ-oxo)dimanganese complex, [(dpaq)Mn
III
(OH)2Mn
IV
(dpaq)
+] (1-Sc
3+), by electron paramagnetic resonance (EPR) spectroscopy (SI, Figure S3); the yield of [(dpaq)Mn
III
(O)2Mn
IV
(dpaq)
+] was determined to be ∼90% by comparing the doubly integrated value of the EPR signal with that of the reference signal of 2,2-diphenyl-1-picrylhydrazyl radical (DPPH*) (SI, Figure S3).

Interestingly, when we reacted the solution of [(dpaq)-Mn
III
(OH)]
+ containing redox-inactive metal ions, such as Sc(OTf)
3, with PhIO in MeCN at 253 K, we observed the formation of a green-colored species with two electronic absorption bands at 510 and 700 nm (Figure 1b); this intermediate is denoted as 1-Sc
3+ (see Scheme 3 for the DFT-optimized schematic structure). 1-Sc
3+ was metastable (t1/2 ≈ 1 day at 253 K), allowing us to characterize it with cold-spray magnetic resonance (EPR) time-of-flight mass spectrometry (CSI-MS) and EPR. The CSI-MS of 1-Sc
3+ exhibits a prominent ion peak at a mass-to-charge (m/z) ratio of 945.0 (Figure 1c), whose mass and isotope distribution pattern correspond to [(dpaq)Mn
III
(O)Sc(OTf)
3]
+ (calcd m/z = 944.9). When the reaction was performed with isotopically labeled PhIO
18O, the mass peak at m/z = 945.0 shifted to m/z = 947.0 (Figure 1c, insets), indicating that this intermediate possesses one oxygen atom. The EPR spectrum exhibits signals at g∥ = 5.4, 4.0, and 1.81 (SI, Figures S4 and S5), suggesting a high-spin S = 3/2 Mn
IV
 species.26,31

1-Sc
3+ was further characterized using Mn K-edge X-ray absorption spectroscopy (XAS). Figure 2a shows the comparison of X-ray absorption near-edge structure (XANES) spectra for [(dpaq)Mn
III
(OH)]
+ (blue line) and 1-Sc
3+ (red line). A shift in the edge position of 1-Sc
3+ compared with [(dpaq)Mn
III
(OH)]
+ indicates that the Mn oxidation state in 1-Sc
3+ is higher than Mn
III
. Pre-edge structure characteristic for Mn
IV
 complexes at ∼6539 eV
decreased in intensity, which is consistent with the binding of a Sc$^{3+}$ ion at a Mn$^{IV}$−O fragment.\textsuperscript{26a,31b} Extended X-ray absorption fine structure (EXAFS) data for [(dpaq)-Mn$^{III}$(OH)]$^+$ and 1-Sc$^{3+}$ are shown in Figure 2b. Fit results for both curves are provided in the SI, Tables S1 and S2, and the comparison of best-fit curves with Fourier transformed (FT) EXAFS of 1-Sc$^{3+}$ is shown in the SI, Figure S6. EXAFS analysis of the 1-Sc$^{3+}$ spectrum indicates the presence of a 1.68 Å Mn−O interaction, which is close to the result obtained with Sc$^{3+}$ ion-bound [(N4Py)Mn$^{IV}$(O)]$^{2+}$ (N4Py = N$_2$N-bis-(pyridyl)methyl)-N-bis(2-pyridyl) methylamine) reported previously.\textsuperscript{26a} The EXAFS data also reveal a short Mn−Sc$^{3+}$ distance (3.99 Å), which clearly indicates that the Sc$^{3+}$ ion binds to the Mn−O moiety in 1-Sc$^{3+}$.\textsuperscript{6f} Very recently, we have shown the binding of Sc$^{3+}$ ion to the Mn(V)-oxo complex bearing a tetraamido macrocyclic ligand, [Mn$^{V}$(O)(TAML)]$^-$;\textsuperscript{32} the binding site of the Sc$^{3+}$ ion was proposed at the carbonyl group of the TAML ligand with the Mn−Sc$^{3+}$ bond length of ~6.0 Å, whereas in the present case, we observed a shorter bond length of Mn−Sc$^{3+}$ (3.99 Å). This result suggests the binding of the Sc$^{3+}$ ion to the Mn-oxo moiety, not to the carbonyl group in the dpaq ligand.

We have also observed the formation of 1-M$^{n+}$ binding a series of redox-inactive metal ions (M$^{n+}$), such as Ca$^{2+}$, Mg$^{2+}$, Zn$^{2+}$, Lu$^{3+}$, Y$^{3+}$, and Al$^{3+}$, in the reactions of [(dpaq)-Mn$^{III}$(OH)]$^+$ (0.50 mM) with PhIO (1.5 mM) in the presence of Ca(OTf)$_2$ (200 mM), Mg(OTf)$_2$ (25 mM), Zn(OTf)$_2$ (5.0

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Figure 1. (a) Visible−NIR absorption spectral changes showing the formation of a bis(μ-oxo)dimanganese(III,IV) complex ([[(dpaq)-Mn$^{III}$(O)$_2$Mn$^{IV}$(dpaq)]$^+$) in the reaction of [(dpaq)Mn$^{III}$(OH)]$^+$ (1.0 mM) and PhIO (0.50 mM) in the presence of H$_2$O (20 μL) in deaerated MeCN at 263 K. Inset shows the time course of the reaction monitored at 520 nm. (b) Visible−NIR absorption spectral changes showing the formation of [(dpaq)Mn$^{IV}$(O)]$^+$−Sc$^{3+}$ (1-Sc$^{3+}$) in the reaction of [(dpaq)Mn$^{IV}$(OH)]$^+$ (0.50 mM) and PhIO (1.5 mM) in the presence of Sc(OTf)$_3$ (1.0 mM) in deaerated MeCN at 253 K. Inset shows the time course of the reaction monitored at 700 nm. (c) CSI-MS spectrum of 1-Sc$^{3+}$. The peaks at 945.0 and 986.0 correspond to [(dpaq)Mn$^{IV}$(O)]$^+$−Sc(OTf)$_3$ (calcd m/z = 944.9) and [(dpaq)-Mn$^{IV}$(O)(CH$_3$CN)]$^+$−Sc(OTf)$_3$ (calcd m/z = 985.9), respectively. Insets show the observed isotope distribution patterns for 1-Sc$^{3+}$−$^{16}$O (left panel) and 1-Sc$^{3+}$−$^{18}$O (right panel); the 1-Sc$^{3+}$−$^{16}$O and 1-Sc$^{3+}$−$^{18}$O complexes were prepared by reacting [(dpaq)Mn$^{III}$(OH)]$^+$ (0.25 mM) with PhI$^{16}$O (0.75 mM) and PhI$^{18}$O (0.75 mM), respectively, in the presence of Sc(OTf)$_3$ (0.50 mM) in deaerated MeCN at 253 K. The percentage of $^{18}$O incorporation in 1-Sc$^{3+}$ was determined to be 85(5)%. 

Figure 2. (a) Normalized Mn K-edge XANES spectra of [(dpaq)-Mn$^{III}$(OH)]$^+$ (blue line) and 1-Sc$^{3+}$ (red line). (b) Fourier transformed EXAFS for [(dpaq)Mn$^{III}$(OH)]$^+$ (blue line) and 1-Sc$^{3+}$ (red line) ($k$ = 3.5−10.9 Å$^{-1}$).
mM), \( \text{Lu} \)(OTf)\(_3\) (1.5 mM), \( \text{Y} \)(OTf)\(_3\) (1.0 mM), and Al(OTf)\(_3\) (1.0 mM) in MeCN at 253 K; these are denoted as 1-Ca\(^{3+}\), 1-Mg\(^{2+}\), 1-Zn\(^{2+}\), 1-Lu\(^{3+}\), 1-Y\(^{3+}\), and 1-Al\(^{3+}\), respectively. In the case of weak Lewis acidic redox-inactive metal ions, a higher concentration of the redox-inactive metal ions is needed irrespective of the kind of M\(^{2+}\). In this section, we report the redox-inactive metal ion e\(^{-}\) production irrespective of the kind of M\(^{3+}\).

The EPR spectra of 1-M\(^{3+}\) exhibit signals at \( g_{eff} = 3.7 \) and 1.96 for 1-Ca\(^{3+}\), 1-Mg\(^{2+}\), and 1-Zn\(^{2+}\) and \( g_{eff} = 5.4, 4.0, \) and 1.81 for 1-Y\(^{3+}\), 1-Lu\(^{3+}\), and 1-Al\(^{3+}\) (SI, Figures S4, S5, and S7), indicating that all 1-M\(^{3+}\) are high-spin \( S = 3/2 \) Mn\(^{3+}\) species irrespective of the kind of M\(^{3+}\). The CSI-MS spectra of 1-Zn\(^{2+}\), 1-Lu\(^{3+}\), and 1-Y\(^{3+}\) exhibited prominent ion peaks at \( m/z = 815.1, 1075.1, \) and 989.0, respectively (SI, Figure S8); the mass and isotope distribution patterns of the ion peaks at \( m/z = 815.1, 1075.1, \) and 989.0 correspond to \( [(dpaq)\text{Mn}^{IV}(\text{O})]^{+} \) (calc. \( m/z = 815.1 \)), \( [(dpaq)\text{Mn}^{IV}(\text{O})\text{Lu}-(\text{OTf})]^{+} \) (calc. \( m/z = 1075.1 \)), and \( [(dpaq)\text{Mn}^{IV}(\text{O})\text{Y}-(\text{OTf})]^{+} \) (calc. \( m/z = 988.9 \)), respectively. We have also confirmed the oxidation state of 1-Zn\(^{2+}\) and 1-Lu\(^{3+}\) using Mn K-edge X-ray absorption spectroscopy (SI, Figure S9); in the XANES spectra of \( [(dpaq)\text{Mn}^{III}(\text{OH})]^{+} \), 1-Zn\(^{2+}\), and 1-Lu\(^{3+}\), the shift in the edge position of 1-M\(^{3+}\), compared to \( [(dpaq)\text{Mn}^{III}(\text{OH})]^{+} \), indicates that the oxidation state of the Mn ion in 1-M\(^{3+}\) is higher than Mn\(^{3+}\), as shown in the case of 1-Sc\(^{3+}\) (Figure 2; vide supra). EXAFS analysis of the 1-Lu\(^{3+}\) spectrum indicates the Mn–O and Mn–Lu–Lu distances are 1.73 and 4.25 Å, respectively (SI, Table S3 and Figure S10).

The EPR spectra of 1-M\(^{3+}\) exhibit signals at \( g_{eff} = 3.7 \) and 1.96 for 1-Ca\(^{3+}\), 1-Mg\(^{2+}\), and 1-Zn\(^{2+}\) and \( g_{eff} = 5.4, 4.0, \) and 1.81 for 1-Y\(^{3+}\), 1-Lu\(^{3+}\), and 1-Al\(^{3+}\) (SI, Figures S4, S5, and S7), indicating that all 1-M\(^{3+}\) are high-spin \( S = 3/2 \) Mn\(^{3+}\) species irrespective of the kind of M\(^{3+}\). The CSI-MS spectra of 1-Zn\(^{2+}\), 1-Lu\(^{3+}\), and 1-Y\(^{3+}\) exhibited prominent ion peaks at \( m/z = 815.1, 1075.1, \) and 989.0, respectively (SI, Figure S8); the mass and isotope distribution patterns of the ion peaks at \( m/z = 815.1, 1075.1, \) and 989.0 correspond to \( [(dpaq)\text{Mn}^{IV}(\text{O})]^{+} \) (calc. \( m/z = 815.1 \)), \( [(dpaq)\text{Mn}^{IV}(\text{O})\text{Lu}-(\text{OTf})]^{+} \) (calc. \( m/z = 1075.1 \)), and \( [(dpaq)\text{Mn}^{IV}(\text{O})\text{Y}-(\text{OTf})]^{+} \) (calc. \( m/z = 988.9 \)), respectively. We have also confirmed the oxidation state of 1-Zn\(^{2+}\) and 1-Lu\(^{3+}\) using Mn K-edge X-ray absorption spectroscopy (SI, Figure S9); in the XANES spectra of \( [(dpaq)\text{Mn}^{III}(\text{OH})]^{+} \), 1-Zn\(^{2+}\), and 1-Lu\(^{3+}\), the shift in the edge position of 1-M\(^{3+}\), compared to \( [(dpaq)\text{Mn}^{III}(\text{OH})]^{+} \), indicates that the oxidation state of the Mn ion in 1-M\(^{3+}\) is higher than Mn\(^{3+}\), as shown in the case of 1-Sc\(^{3+}\) (Figure 2; vide supra). EXAFS analysis of the 1-Lu\(^{3+}\) spectrum indicates the Mn–O and Mn–Lu–Lu distances are 1.73 and 4.25 Å, respectively (SI, Table S3 and Figure S10).

Based on the spectroscopic characterization discussed above, 1-M\(^{3+}\) is assigned as \( [(dpaq)\text{Mn}^{IV}(\text{O})]^{+} \) binding a redox-inactive metal ion (M\(^{3+}\)), \( [(dpaq)\text{Mn}^{IV}(\text{O})]^{+} \rightarrow M^{3+} (1-M^{3+}; M^{3+} = \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Zn}^{2+}, \text{Lu}^{3+}, \text{Y}^{3+}, \text{Al}^{3+}, \) and \( \text{Sc}^{3+} \)).

Reactivity Studies of \( [(dpaq)\text{Mn}^{IV}(\text{O})]^{+} \rightarrow M^{3+} \). In this section, we report the redox-inactive metal ions on the reactivities of the \( [(dpaq)\text{Mn}^{IV}(\text{O})]^{+} \rightarrow M^{3+} (1-M^{3+}) \) complexes in ET, OAT, and HAT reactions. It should be noted that the bis(μ-o xo) dimanganese(III,IV) complex, \( [(dpaq)-\text{Mn}^{III}(\text{O}),\text{Mn}^{IV}(\text{dpaq})]^{+} \), produced by the oxidation of \( [(dpaq)\text{Mn}^{III}(\text{OH})]^{+} \) by PhIO in the absence of M\(^{3+}\) exhibited no reactivity toward thiaoanisole, cyclohexadiene, and \( [\text{Fe}^{II}(\text{Me}_2\text{bpy})]^{2+} \) (SI, Figure S11).

(i) Redox Properties of 1-M\(^{3+}\). The one-electron reduction potential of 1-M\(^{3+}\), such as 1-Sc\(^{3+}\), was determined by performing the ET titration with tris(4-bromophenyl)amine (TBPA, \( E_{\text{ox}} = 1.08 \) V vs SCE). When 1-Sc\(^{3+}\) was employed as an electron acceptor, efficient ET occurred from TBPA to 1-Sc\(^{3+}\) (Figure 4a), where the absorbance band at 705 nm is assigned due to TBPA\(^{•+}\) (ε = 32 000 M\(^{-1}\) cm\(^{-1}\) at \( \lambda_{\text{max}} = 705 \) nm). The ET from TBPA to 1-Sc\(^{3+}\) was found to be in equilibrium, where the concentration of TBPA\(^{•+}\) produced increased with increasing the initial concentration of TBPA, as shown in Figure 4b. The equilibrium constant \( K_{eq} \) was determined to be 70 at 253 K by fitting the plot of [TBPA\(^{•+}\)]
vs [TBPA]₀ with the use of the ET equilibrium equations (eqs 7–9) in the Experimental Section (Figure 4c). The one-electron reduction potential (E_{red}) of 1-Sc³⁺ was determined to be 1.17 V vs SCE from the K_{st} value of 70 and the E_{ox} value of TBPA (1.08 V vs SCE) using the Nernst equation (eq 1).36

\[
E_{red} = E_{ox} + \frac{RT}{F} \ln K_{st}
\]

The rate of ET from a coordinatively saturated metal complex, such as \([\text{Fe}^{II}(\text{Me}_2\text{bpy})_3]^{2+}\) (Me-bpy = 4,4'-dimethyl-2,2'-bipyridine), to 1-Sc³⁺ obeyed the first-order kinetics, and the pseudo-first-order rate constant \((k_{et})\) was proportional to the concentration of \([\text{Fe}^{II}(\text{Me}_2\text{bpy})_3]^{2+}\), affording the second-order rate constant \((k_{ox})\) of \(8.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}\) in MeCN at 253 K for the ET from \([\text{Fe}^{II}(\text{Me}_2\text{bpy})_3]^{2+}\) to 1-Sc³⁺ (Figure 5a). Similarly, \(k_{ox}\) values of ET from various one-electron donors (i.e., coordinatively saturated metal complexes, such as \([\text{Fe}^{II}(\text{bpy})_3]^{2+}\) (bpy = 2,2'-bipyridine), \([\text{Fe}^{II}(\text{phen})_3]^{2+}\) (phen = 1,10-phenanthroline), and \([\text{Ru}^{II}(\text{Me}_2\text{bpy})_2]^{2+}\) to 1-Sc³⁺ (vide infra) were determined and listed in Table S4 (also see SI, Figure S12). The \(k_{et}\) values of ET from \([\text{Fe}^{II}(\text{Me}_2\text{bpy})_3]^{2+}\) to other 1-M⁺⁺ were also determined and are listed in Table 1 (also see the SI, Figure S13).

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<th>metal ion</th>
<th>([\text{Fe}^{II}(\text{Me}_2\text{bpy})_3]^{2+})</th>
<th>([\text{Fe}^{II}(\text{bpy})_3]^{2+})</th>
<th>([\text{Fe}^{II}(\text{phen})_3]^{2+})</th>
<th>([\text{Ru}^{II}(\text{Me}_2\text{bpy})_2]^{2+})</th>
<th>CHD</th>
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<tr>
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<td>1.5(1) \times 10^{-1}</td>
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<tr>
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<td>7.1(6) \times 10^{-2}</td>
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</tbody>
</table>

(ii) Sulfoxidation Reaction by 1-M⁺⁺. Oxygen atom transfer reactions by 1-M⁺⁺, such as 1-Sc³⁺, were performed using thioanisole derivatives as substrates in MeCN at 253 K. Upon addition of thioanisole to an MeCN solution of 1-Sc³⁺, the absorption band at 700 nm corresponding to 1-Sc³⁺ disappeared with the first-order decay kinetics profile (Figure 5a). Pseudo-first-order rate constants, determined by the first-order fitting of the kinetic data for the decay of 1-Sc³⁺, increased linearly with an increase in thioanisole concentration, giving the second-order rate constant \((k_{ox})\) of 2.2 M⁻¹ s⁻¹ at 253 K (Figure 5b). Similarly, the oxidation of other para-substituted thioanisoles (para-X-thioanisoles; X = OMe, Me, H, Cl, and Br) by 1-Sc³⁺ was also performed, and the second-order rate constants \((k_{ox})\), determined by the plots of pseudo-first-order rate constants vs concentrations of thioanisole derivatives (SI, Figure S14), were listed in the SI, Table S5. The logarithm of \(k_{ox}\) values is linearly correlated with the electron oxidation potentials of para-X-thioanisoles (SI, Figure S15a), where the \(k_{ox}\) value increases as the electron-donating ability of the para-substituent increases.21,22 The slope of −15 in the SI, Figure S15a, indicates that electron transfer is involved in the rate-determining step (vide infra).24a,24b In addition, a plot of the logarithm of rate constant as a function of \(\sigma_p^{ox}\) shows a good Hammett correlation with a largely negative \(\rho\) value of −4.5 (SI, Figure S15b).

The product(s) formed in this reaction was analyzed using ESI-MS and EPR. Analysis of the Mn product by ESI-MS showed that a Mn³⁺ species was formed as a major product with an impurity scale of MnII in the sulfoxidation reaction by 1-Sc³⁺ (SI, Figure S16a). In the EPR analysis, an impurity scale (<1%) of Mn³⁺ was observed (SI, Figure S16b), confirming that a Mn³⁺ species was formed as the major product. It has been reported that (dpaq)Mn¹⁺ is not stable under certain circumstances and reacts with O₂ to form the [(dpaq)-Mn³⁺(OH)]⁺ complex.25a The organic product analysis of the reaction solution revealed that methyl phenyl sulfoxide was formed quantitatively. It was confirmed that oxygen in methyl phenyl sulfoxide derived from the oxo group of 1-Sc³⁺, not from water, by using ¹⁸O-labeled 1-Sc³⁺ as shown in SI Figure S17, like the case of anthracene oxidation by 1-Sc³⁺ to produce anthraquinone, in which two oxygen atoms originated from the oxo group of 1-Sc³⁺.37

The oxidation of thioanisole by other 1-M⁺⁺ was also performed in MeCN at 253 K (SI, Figure S18), and the second-order rate constants \((k_{ox})\) determined are listed in Table 1. The \(k_{ox}\) value increased with increasing the Lewis acidity of redox-inactive metal ions bound to the Mn³⁺(O) moiety.25,38 Thus, the reactivity order of 1-M⁺⁺ in the oxidation of thioanisole (i.e., OAT reaction) was determined to be 1-Al³⁺ > 1-Sc³⁺ > 1-Y³⁺ > 1-Lu³⁺ > 1-Zn²⁺ > 1-Mg²⁺ > 1-Ca²⁺.

The dependence of the logarithm of the second-order rate constants of ET \((k_{ox})\) from electron donors to 1-Sc³⁺ (vide supra) on the ET driving force \([−ΔG_{ox}(eV) = e(E_{red} − E_{ox})]\) is shown in Figure 6, where the logarithm of the second-order rate constants \((k_{ox})\) of sulfoxidation of thioanisole derivatives by 1-Sc³⁺ is also plotted.22a The driving force dependence of
the ET rate constants is well fitted by the Marcus theory of outer-sphere electron transfer (eq 2),

\[
k_{et} = Z \exp\left[-(\lambda/4) + \frac{1}{2} \frac{\Delta G_{et}}{\lambda^2} \right] k_B T
\]

where \(Z\) is the collision frequency taken as \(1 \times 10^{15}\) M\(^{-1}\) s\(^{-1}\), \(\lambda\) is the reorganization energy of ET, \(k_B\) is the Boltzmann constant, and \(T\) is the absolute temperature. The best fit \(\lambda\) value of ET from metal complexes to 1-Sc\(^{3+}\) is 1.85 eV (blue line in Figure 6), which is similar to the best fit \(\lambda\) value (1.79 eV) of sulfoxidation of thioanisole derivatives by 1-Sc\(^{3+}\) (black line in Figure 6). Such an agreement strongly indicates that sulfoxidation of thioanisole derivatives by 1-Sc\(^{3+}\) proceeds via the rate-determining ET (vide supra). It should be noted that the \(\lambda\) values (1.79 and 1.85 eV) are significantly smaller than those of ET reactions of (Bn-TPP)(Mn\(^{IV}(O)\))\(^{2+}\)(-Sc\(^{3+}\)), (Bn-TPEN = N-benzyl-N,N',N'-tris(2-pyridylmethyl)-1,2-diaminoethane; \(\lambda = 2.12\) eV) and [(N4Py)Mn\(^{IV}(O)\)]\(^{2+}\)(-Sc\(^{3+}\)) (\(\lambda = 2.21\) eV),\(^{2b}\) probably because of the more rigid structure of the dpaq ligand that contains a quinoline moiety. On the other hand, the reorganization energy of electron exchange between thioanisole and thioanisole radical cation was determined to be 0.80 eV from the rate constant of the electron exchange \((1 \times 10^7\) M\(^{-1}\) s\(^{-1}\))\(^{40}\) using eq 2 when \(\Delta G_{et} = 0\). The observed reorganization energy of electron transfer from thioanisole to 1-Sc\(^{3+}\) (\(\lambda = 1.79\) eV in Figure 6) is much larger than that of electron exchange between thioanisole and thioanisole radical cation (0.80 eV). It should be noted that the observed reorganization energy (1.79 eV) is the average of the reorganization energy of electron exchange between thioanisole and thioanisole radical cation (0.80 eV) and that of electron exchange between [(dpaq)Mn\(^{IV}(O)\)]\(^{2+}\)-Sc\(^{3+}\) and [(dpaq)Mn\(^{III}(O)\)]\(^{2+}\)-Sc\(^{3+}\) (2.78 eV).

(iii) C–H Bond Activation by 1-Mn\(^{II}\). The hydrogen atom (H atom) abstraction reactions of 1-Mn\(^{III}\), such as 1-Sc\(^{3+}\), with hydrocarbons having weak C–H bond dissociation energies (BDEs), such as xanthene (75.5 kcal mol\(^{-1}\)), dihydroanthracene (DHA; 77.0 kcal mol\(^{-1}\)), and 1,4-cyclohexadiene (CHD; 78.0 kcal mol\(^{-1}\)),\(^{11}\) were performed in MeCN at 253 K. Addition of DHA to an MeCN solution of 1-Sc\(^{3+}\) resulted in the disappearance of the absorption band at 700 nm due to 1-Sc\(^{3+}\)(SI, Figure S19a). Pseudo-first-order rate constants, determined by the first-order fitting of the kinetic data for the decay of 1-Sc\(^{3+}\), increased linearly with an increase in DHA concentration, giving the second-order rate constant \((k_{obs})\) of 2.5 × 10\(^{-1}\) M\(^{-1}\) s\(^{-1}\) at 253 K (Figure 7a). The C–H bond activation reactions were also investigated with other weak C–H bonds, such as xanthene and CHD. The second-order rate constants \((k_{obs})\) of 4.9 × 10\(^{-1}\) and 1.6 × 10\(^{-2}\) M\(^{-1}\) s\(^{-1}\) were determined in the oxidation of xanthene and CHD by 1-Sc\(^{3+}\), respectively (Figure 7a). As expected, the second-order rate constants decreased with an increase in the C–H BDEs of alkyl hydrocarbons, showing a correlation between the log \(k_{obs}\) values and the C–H BDEs of the substrates with a slope of −0.54 (SI, Figure S19b). The oxidation of DHA-h\(_i\) and DHA-d\(_i\) by 1-Sc\(^{3+}\) was also investigated, affording the kinetic isotope effect (KIE) value of 2.3(1) (Figure 7a). These results indicate that the C–H bond activation of alkyl hydrocarbons by 1-Sc\(^{3+}\) occurs via an H atom abstraction mechanism, and the H atom abstraction by 1-Sc\(^{3+}\) is the rate-determining step.

The product(s) formed in the oxidation reactions was analyzed using ESI-MS and EPR spectroscopic techniques. Analysis of the Mn product by ESI-MS shows that a Mn\(^{III}\) species was formed as a major product with an impurity scale of Mn\(^{II}\) in the C–H bond activation reaction by 1-Sc\(^{3+}\) (SI, Figure S20a), as observed in the oxidation of thioanisole derivatives by 1-Sc\(^{3+}\) (vide supra). In the EPR analysis, a trace amount of Mn\(^{III}\) active signal was observed (SI, Figure S20b), confirming that a Mn\(^{III}\) species was the major product. The product analysis of the reaction solution of xanthene revealed that xanthene was formed as the sole product. In addition, by carrying out the oxidation of xanthene with the 18O-labeled 1-...
Sc⁴⁺, the oxygen atom in the xanthone was found to derive from the ¹⁸O-labeled 1-Sc⁴⁺ (SI, Figure S21).

The CHD was chosen as the C–H bond substrate to compare the oxidizing ability of 1-M⁴⁺ complexes in MeCN at 253 K. The second-order rate constants of 1-M⁴⁺ were determined and listed in Table 1 (see also Figure 7b). Interestingly, the $k_{ox}$ values decreased with increasing the Lewis acidity of redox-inactive metal ions bound to the Mn-oxo moiety. Thus, the reactivity order of 1-M⁴⁺ in the oxidation of CHD (i.e., HAT reaction) is opposite that obtained in the ET and OAT reactions by 1-M⁴⁺; that is, the reactivity order is 1-Ca⁴⁺ > 1-Mg⁴⁺ > 1-Zn⁴⁺ > 1-Lu⁴⁺ > 1-Y⁴⁺ > 1-AI⁴⁺ ≥ 1-Sc⁴⁺ in the HAT reaction (vide infra). The reason that the reactivity order of 1-M⁴⁺ in HAT is opposite that in ET and OAT is discussed as follows.

There are two extreme mechanisms for hydrogen atom transfer reactions. The first one is electron transfer, followed by proton transfer, referred to as ET-PT. In this case, the HAT reactivity is in parallel with the ET reactivity. The other one is proton transfer followed by electron transfer (PT-ET), when the HAT reactivity is in parallel with the PT reactivity, which is opposite the ET reactivity, because the stronger base for the PT reaction acts as the weaker electron acceptor for the ET reaction. A change of the mechanism between ET-PT and PT-ET was reported as a V-shaped Hammett plot for the HAT from para-substituted 2,6-di-tert-butylphenols to an imido manganese(V) corrole (tpfc)Mn⁴⁺(NTs), where tpfc = S,10,15-tetrakis(pentfluorophenyl)corrole. As the more withdrawing substituents are employed, the acidity of the phenolic proton increases to enhance the initial rate-determining proton transfer from the phenolic proton to (tpfc)Mn⁴⁺NTs, followed by fast electron transfer. When electron-donating substituents are employed, the rate-determining step is changed from PT-ET to ET-PT, exhibiting a V-shaped Hammett plot. In most cases, however, ET and PT may occur in a concerted manner. In such a case, the HAT reactivity may be determined by the compensation between the ET and PT reactivity depending on the ET and PT driving force. In the case of 1-M⁴⁺, the HAT reactivity seems to be determined by the PT reactivity rather than the ET reactivity, because the stronger the Lewis acidity of M⁴⁺ binding to the MnIV(O) moiety, the weaker the basicity of the oxo group in the PT reaction. The decreased reactivity of a trivalent metal ion-bound MnIV(O) complex such as 1-Sc(OTf)₃, as compared with a divalent metal ion-bound MnIV(O) complex such as 1-Ca(OTf)₂ may also result from the steric effects of Sc(OTf)₃ that binds with the oxo moiety stronger than Ca(OTf)₂.

■ CONCLUSION

Redox-inactive metal ion-bound MnIV(O) complexes, [[(dpaq)-MnIV(O)(OH)]₃⁻ (1-M⁴⁺; M⁴⁺ = Ca⁴⁺, Mg⁴⁺, Zn⁴⁺, Lu⁴⁺, Y⁴⁺, Al⁴⁺, and Sc⁴⁺)], were synthesized in the oxidation of a mononuclear hydroxamagnetane(III) complex, [(dpaq)-MnIV(OH)]⁺, by PhIO in the presence of various metal triflates, M⁺⁺(OTf)₆⁻ whereas a bis-µ-o xo dimer, [(dpaq)-MnIV(O)(O)₂MnIV(dpaq)⁺], was formed in the absence of M⁺⁺(OTf)₆. Although the bis(µ-o xo)dimanganese(III,IV) complex exhibited no reactivity in OAT and HAT reactions, 1-M⁴⁺ oxidized thioanisoles and CHD efficiently via ET and HAT reactions, respectively. Interestingly, when the log $k_{ox}$ values obtained in the OAT (e.g., thioanisole) and HAT (e.g., CHD) reactions as well as the log $k_{et}$ values of ET (e.g., [FeIII(Me₂bpy)]²⁺) were plotted against a quantitative measure of Lewis acidity of metal ions ($ΔE$), the reactivity trends differed markedly (Figure 8). For example, the log $k_{ox}$ values of the oxidation of thioanisole (red line in Figure 8), which proceeds via ET, and the log $k_{et}$ values of ET of [FeIII(Me₂bpy)]²⁺ (blue line in Figure 8) increase with an increase in the Lewis acidity ($ΔE$), since the stronger the Lewis acidity of the redox-inactive metal ions bound to the Mn-oxo moiety, the faster the ET to 1-M⁴⁺ due to the more positive shift in the one-electron reduction potentials of 1-M⁴⁺. The binding of metal ions to the one-electron-reduced species of electron acceptors generally results in the large positive shift in the one-electron reduction potentials of electron acceptors.

In the case of the HAT reaction, however, the log $k_{ox}$ values decrease as the Lewis acidity of the redox-inactive metal ions increases (green line in Figure 8). It has been reported previously that the basicity of the metal-oxo group determines the capability of high-valent metal-oxo intermediates in abstracting an H atom from substrate C–H bonds. One notable example is the role of the thiolate ligand in cytochrome P450 enzymes. It has also been demonstrated in synthetic metal-oxo complexes that the HAT reactivity of high-valent metal-oxo complexes increases as the axial ligand becomes a better electron donor (Scheme 4A). In the present study, we have shown for the first time that the basicity of the metal-oxo group can be tuned by binding redox-inactive metal ions (Scheme 4B). For example, the Mn(IV)-oxo group of 1-M⁴⁺ binding Ca⁴⁺ ($ΔE = 0.58$ eV) is more basic than that binding Sc⁴⁺ ($ΔE = 1.00$ eV), which resulted in showing a higher reactivity than Sc⁴⁺.

Scheme 4. Influence of Axial Ligand and Lewis Acid Metal Ion on the Basicity of the Oxo Ligand

![Scheme 4](image-url)
reactivity in the HAT reaction by 1-Ca2+ (green circles in Figure 8). In addition, on the basis of the reactivity of 1-MnIV in the HAT reaction, we can predict that the basicity of the metal-oxo moiety for 1-Ca2+ is the highest and decreases in the order 1-Ca2+ > 1-Mg2+ > 1-Zn2+ > 1-Lu3+ > 1-Y3+ > 1-Al3+ > 1-Sc3+. Further investigation is underway to fully understand the redox-inactive metal ion effect on the basicity of the metal-oxo moiety and the reactivity of metal-oxo species in HAT reactions.

**EXPERIMENTAL SECTION**

**Materials.** Commercially available chemicals were used without further purification unless otherwise indicated. 8-Aminoquinoline, bromoacetyl bromide, dipicolylamine, sodium carbonate, trifluoromethanesulfonic acid, manganese powder, (diacetoxyiodo)benzene, sodium hydrosulphide, calcium trifluoride (Ca[OTf]2) (OTf = SO3CF3), magnesium triflate (Mg[OTf]2), magnesium perchlorate (Mg(ClO4)2), zinc triflate (Zn[OTf]2), scandium triflate (Sc[OTf]3), aluminium triflate (Al[OTf]3), yttrium triflate (Y[OTf]3), lutetium triflate (Lu[OTf]3), and acetonic were purchased from Aldrich Chemical Co. 2,2-Diphenyl-1-picrylhydrazyl radical was purchased from Wako Pure Chemicals (Osaka, Japan). H2O2 (95% (O)-enriched) was purchased from ICON Services Inc. (Summit, NJ, USA). Iodosylbenzene and Mn(OTf)2·2CH3CN were prepared by the literature method. The dpaq ligand was synthesized according to the previously reported methods.30 PhlO was prepared by the addition of H2O2 (140 mM, 5 μL) to PhlO (50 μL) in trifluoroethanol at 298 K and waiting for 20 min for the exchange. Then PhlO was used to synthesize the 15O-labeled 1-Sc3+. The ([dpaq]MnIV(OH))(OTf) complex was synthesized by mixing stoichiometric amounts of the dpaq ligand and Mn(OTf)2 in an oxygen-saturated MeCN solution, followed by the addition of triethylamine.31 The deuterated DHA-d4 was synthesized by a literature method.31 DHA (0.50 g, 2.7 mmol) was reacted with NaH (0.20 g, 8.1 mmol) in DMSO-δ6 (3.0 mL) under an Ar atmosphere. The deep red solution was stirred at room temperature for 8 h and then quenched with D2O (5.0 mL). The crude product was filtered and washed with copious amounts of distilled H2O. A purity of >99% deuterium was confirmed by 1H NMR.

**Instrumentation.** UV–vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer equipped with a UNISOKU Scientific Instruments Cryostat USP-203A for low-temperature experiments or on a Hi-Tech Scientific (U.K.) SF-61 DX2 cryogenic stopped-flow spectrophotometer equipped with a Xe arc lamp and a KinetaScan diode array rapid scanning unit. The CSI-MS data were collected on a JMS-T100CS (JEOL) mass spectrometer arc lamp and a KinetaScan diode array rapid scanning unit. The CSI-voltage, 0 to 20 V; ring lens voltage, 10 V; ion source temperature, 5 °C; spray temperature, 40 °C; ESI+ mode unless otherwise indicated. 8-Aminoquinoline, yttrium triflate (Y[OTf]3), lutetium triflate (Lu[OTf]3), and acetonic were purchased from Aldrich Chemical Co. The deep red solution was stirred at room temperature for 8 h and then quenched with D2O (5.0 mL). The crude product was filtered and washed with copious amounts of distilled H2O. A purity of >99% deuterium was confirmed by 1H NMR.

**EPR Measurements.** EPR measurements were performed with a JEOL JES-FA100 spectrometer equipped with an Oxford Instruments ESR900 liquid He quartz cryostat with an Oxford Instruments ITC503 temperature and gas flow controller. The experimental parameters for EPR measurements were as follows: microwave frequency = 9.467 GHz, microwave power = 1.0 mW, modulation amplitude = 3.0 G, modulation frequency = 100 kHz, and time constant = 0.03 s. The product analyses were performed with an Agilent 6890N gas chromatograph (GC) and a FOCUS DSQ (dual-stage quadrupole) mass spectrometer (Thermo Finnigan, Austin, TX, USA) interfaced with a Finnigan FOCUS gas chromatograph (GC-MS). Product analysis of thiourea oxidation was performed on a high-performance liquid chromatograph (HPLC, DIOMEX pump series P580) equipped with a variable-wavelength UV-200 detector and a Diacel OD-H column (4.6 mm × 25 cm). The fluorescence spectra were recorded using a four-facet quartz cuvette (10 mm i.d., containing 10-methylacridone (AcrCO) with Al[OTf]3 in deaerated MeCN at 298 K, which was irradiated with monochromatic light of 430 nm from a Shimadzu RF-5300PC fluorescence spectrophotometer with excitation and emission slit widths of 2 nm.

Generation of [([dpaq]MnIV(O)(OH))](OTf)4+. ([dpaq]MnIV(O)(OH))2+ species were generated in the solvent mixture (i.e., MeCN/tetrafluoroethanol) in the solution of [([dpaq]MnIV(O)(OH))](OTf)4+ (0.50 mM) in the presence of Ca(OTf)2 (200 mM), Mg(OTf)2 (25 mM), Zn(OTf)2 (5.0 mM), Lu(OTf)3 (1.5 mM), Y(OTf)3 (1.0 mM), Al(OTf)3 (1.0 mM), and Sc(OTf)3 (1.0 mM) in MeCN at 253 K, respectively. 1-MnIV species were also generated in the solvent mixture (i.e., MeCN/tetrafluoroethanol) (v/v 1:1). The characteristic peaks of 1-MnIV species were red-shifted as compared with those in MeCN (data are not shown).

XAS and EXAFS Measurements. X-ray absorption spectra were collected at the Advanced Photon Source (APS) at Argonne National Laboratory on bending magnet beamline 20 at an electron energy of 6 keV and average current of 100 mA. The radiation was monochromatized by a Si(110) crystal monochromator. The intensity of the X-rays was monitored by three ion chambers (I1, I2, and I3) filled with 20% nitrogen and 80% helium and placed before the sample (I0) and after the sample (I1 and I2). KMnO4 powder was placed between I1 and I2 and its absorption was recorded with each scan for energy calibration. Plastic (Lexan) EXAFS sample holders (inner dimensions of 12 mm × 2 mm × 3 mm) filled with frozen solutions were inserted into a cryostat precooled to 20 K. The samples were kept at 20 K in a He atmosphere at ambient pressure. Data were recorded as fluorescence excitation spectra using a 13-element energy-resolving detector. In order to reduce the risk of sample damage by X-ray, defocused mode (beam size 1 × 2 mm) was used and no damage was observed. Shutter was synchronized with the scan software, preventing exposure to X-rays in between scans and during spectrometer movements. Mn XAS energy was calibrated by the maximum of the pre-edge feature of the potassium permanganate powder XANES spectrum (6543.3 eV), which was placed between I1 and I2 ionization chambers. EXAFS scans with 5 eV steps in the pre-edge region (6537.67–6529.67 eV), 0.5 eV steps (6529.67–6537.67 eV) through the edge, and 0.05 Å−1 steps at k = 2.0–12 Å−1 were used.

EXAFS Data Analysis. Athena software was used for data processing.52 The energy scale for each scan was normalized using potassium permanganate powder standard, and scans for same samples were added. Data in energy space were pre-edge corrected, normalized, and background corrected. The processed data were converted to the photoelectron wave vector (k) space and weighted by k4. The electron wavenumber is defined as in eq 3:

\[
k = \left(\frac{2m(E - E_0)}{\hbar^2}\right)^{1/2}
\]
where $E_0$ is the threshold energy. k-Space data were truncated near zero crossings and Fourier-transformed into R-space. Artemis software was used for curve fitting. In order to fit the data, the Fourier peaks were isolated separately, or the entire experimental spectrum was fitted. The individual Fourier peaks were isolated by applying a Hanning window. Curve fitting was performed using ab initio-calculated phases and amplitudes from the FEFF8 program from the University of Washington. Ab initio-calculated phases and amplitudes were used in the EXAFS equation (eq 4):\(^{3,5}\)

$$\chi(k) = \sum_{j} \frac{N_j}{kR_j^2} e^{-2kR_j^2} e^{-2ikR_j} \sin(2kR_j + \phi_j(k))$$

(4)

where $N_j$ is the number of atoms in the j\textsuperscript{th} shell, $R_j$ is the distance between the absorbing atoms and the atoms in the j\textsuperscript{th} shell; $f_{\text{ab initio}}$ is the ab initio amplitude function for j, and $e^{-2ikR_j}$ is the Debye–Waller factor for shell j accounting for damping due to thermal and static disorder in the shell. The mean free path term ($e^{-2kR_j^2}$) accounts for losses due to inelastic scattering. The oscillations in the EXAFS spectrum are reflected in the $\sin(2kR_j + \phi_j(k))$ term, where $\phi_j(k)$ is the phase function for the shell j. $S_0$ is an amplitude reduction factor. The EXAFS equation was used to fit experimental data using $N_j$, $R_j$, and $\sigma_j$ as variable parameters, while $S_0$ was kept fixed. The quality of fit was evaluated by the R-factor: if the R-factor is less than 2%, then the fit is good enough. Reduced $\chi^2$ was used to justify the addition of new absorber-backscatter shells.

Spectral Redox Titration for the ET Equilibrium Constant ($K_{\text{eq}}$). Redox titration of ET from TBPA to 1-Sc\textsuperscript{3+} was examined with various concentrations of TBPA in MeCN at 253 K using a Hewlett-Packard 8453 photodiode-array spectrometer with a quartz cuvette (path length = 1.0 cm). Typically, a deaerated MeCN solution of TBPA (0.00–0.12 mM) was added to a deaerated MeCN solution containing 1-Sc\textsuperscript{3+} (0.050 mM). The concentration of TBPA\textsuperscript{−} was determined from the absorption band at $\lambda = 705$ nm ($\varepsilon_1 = 3.2 \times 10^4$ M\textsuperscript{−1} cm\textsuperscript{−1}) and 1-Sc\textsuperscript{3+} ($\varepsilon_2 = 1.2 \times 10^4$ M\textsuperscript{−1} cm\textsuperscript{−1}) using eq 5 derived from eq 6, where 1-Sc\textsuperscript{3+}\textsubscript{0} is the initial concentration of 1-Sc\textsuperscript{3+} and [1-Sc\textsuperscript{3+}−1] = [1-Sc\textsuperscript{3+}]\textsubscript{0} − [TBPA\textsuperscript{−}].

$$[\text{TBPA}^\text{−}] = ([\text{Abs}_{705} − \varepsilon_1][\text{Sc}/\text{TBPA}]^\text{−1})/\varepsilon_1$$

(5)

$$[\text{Abs}_{705}] = \varepsilon_1[\text{TBPA}^\text{−}] + \varepsilon_2[1-\text{Sc}^\text{3+}]$$

(6)

The $\varepsilon_1$ value of TBPA\textsuperscript{−} (3.2 × 10\textsuperscript{4} M\textsuperscript{−1} cm\textsuperscript{−1}) was confirmed by the standard authentic sample of tris(4-bromophenyl)ammoniumyl hexachloroantimonate, [(4-BrC\textsubscript{6}H\textsubscript{4})\textsubscript{3}N\textsubscript{−}]-SbCl\textsubscript{6}, in MeCN at 253 K. The expression used for determination of $K_{\text{eq}}$ was derived according to our previous work.\(^{34}\) The equilibrium constant ($K_{\text{eq}}$) in eq 1 is expressed by eq 7, from which eq 8 is derived.

$$K_{\text{eq}} = ([\text{TBPA}^\text{−}]\gamma[\text{Mn}^\text{III}(O)\text{Sc}^\text{3+}])/[\text{TBPA}][1-\text{Sc}^\text{3+}]$$

(7)

$$K_{\text{eq}}^{−1} = ([\text{TBPA}^\text{−}] - [\text{TBPA}^\text{−}])/(1-[1-\text{Sc}^\text{3+}]^\text{−1} - [\text{TBPA}^\text{−}])$$

(8)

where [Mn\textsuperscript{III}(O)Sc\textsuperscript{3+}] = [TBPA\textsuperscript{−}]), [TBPA\textsuperscript{−}] = [TBPA] + [TBPA\textsuperscript{−}], and 1-Sc\textsuperscript{3+}\textsubscript{0} = [1-Sc\textsuperscript{3+}] + [Mn\textsuperscript{III}(O)Sc\textsuperscript{3+}). 1-Sc\textsuperscript{3+}\textsubscript{0} and [TBPA\textsuperscript{−}] are the initial concentrations of 1-Sc\textsuperscript{3+} and [TBPA\textsuperscript{−}], respectively.

Equation 9 is derived from eq 8, where $\alpha = [\text{TBPA}^\text{−}]/[\text{TBPA}^\text{−}]$, and $\chi = 1/\alpha$ (see eq 4).

$$\alpha^{−1} = \chi_\text{AT}$$

(9)

The $K_{\text{eq}}$ value of 70 was determined from the slope of the linear plot between $\alpha^{−1}$ and $1-[1-\text{Sc}^\text{3+}]^\text{−1} - [\text{TBPA}^\text{−}]$ as shown in Figure 4c.

Kinetic Measurements. All the reactions were run in a 1 cm UV cuvette by monitoring UV–vis spectral changes of reaction solutions. First-order rate constants for the oxidation of substrates by

\begin{align*}
([\text{dpq}]\text{Mn}^\text{III}(O)^{\text{−}}\text{M}^\text{−}\text{−}\text{O}^{\text{−}}\text{OTf}_\text{2}^{\text{−}}; \text{M}^\text{−} = \text{Ca}^\text{2+}, \text{Mg}^\text{2+}, \text{Zn}^\text{2+}, \text{Lu}^\text{3+}, \text{Y}^\text{3+}, \text{Al}^\text{3+}, \text{and} \text{Sc}^\text{3+}) \text{ were determined under pseudo-first-order conditions (e.g., [substrate]/[1-M\text{−}]) > 10} \text{ by fitting the decay of absorbance due to 1-M\text{−} in the ET, OAT, and HAT reactions in MeCN at 253 K. The first-order plots were linear for three or more half-lives with the correlation coefficient of } \rho > 0.99. \text{ In each case, it was confirmed that the rate constants derived from at least three independent measurements agreed within an experimental error of } \pm 10\%. \text{ The pseudo-first-order rate constants increased proportionally with the concentrations of substrates, from which second-order rate constants were determined.}

Product Analysis. Products formed in the oxidation of thioanisole by 1-Sc\textsuperscript{3+} in MeCN at 253 K were analyzed by HPLC and GC-MS. Phenyl methyl sulfoxide was formed as a sole product in the oxidation of thioanisole by 1-Sc\textsuperscript{3+}. Products formed in the oxidation of xanthene by 1-Sc\textsuperscript{3+} were analyzed by GC and GC-MS. Quantitative analysis was performed by comparison against standard curves prepared with known authentic samples and using decane as an internal standard. In the reaction of 1-Sc\textsuperscript{3+} and xanthene, xanthone was obtained as the sole product. The manganese products formed in the reaction of 1-Sc\textsuperscript{3+} with xanthioline and xanthene were analyzed by ESI-MS and EPR techniques. In both the reactions, Mn\textsuperscript{III} species were produced as a major product.
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**REFERENCES**


