

Activation of a High-Valent Manganese–Oxo Complex by a Nonmetallic Lewis Acid

Regina A. Baglia,[†] Maximilian Dürr,[‡] Ivana Ivanović-Burmazović,[‡] and David P. Goldberg^{*,†}

[†]Department of Chemistry, The Johns Hopkins University, 3400 North Charles Street, Baltimore, Maryland 21218, United States

[‡]Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, 91058 Erlangen, Germany

S Supporting Information

ABSTRACT: The reaction of a manganese(V)–oxo porphyrinoid complex with the Lewis acid B(C₆F₅)₃ leads to reversible stabilization of the valence tautomer Mn^{IV}(O)(π -radical cation). The latter complex, in combination with B(C₆F₅)₃, reacts with ArO–H substrates via formal hydrogen-atom transfer and exhibits dramatically increased reaction rates over the Mn^V(O) starting material.

High-valent metal–oxo species are invoked as key players in both biological and synthetic oxidations. Examples include an Fe^{IV}(O) porphyrin π -radical cation, the key intermediate in cytochrome P450,¹ and postulated Mn^{IV}/Mn^V(O) intermediates in photosynthetic water oxidation.² In heme systems such as P450, there are two possible valence tautomers, Fe^V(O)(p) or Fe^{IV}(O)(p^{•+}), and the redox-active nature of the porphyrin ligand plays a critical role in stabilizing the latter. The synthesis of analogous transition-metal complexes with redox-active ligands that enhance reactivity has been targeted for multielectron catalysis.³ The design of complexes that can undergo controlled valence tautomerism is also important for molecular device applications.⁴

Previously, we introduced a new method for controlling valence tautomerism in a Mn^V(O) porphyrinoid complex.⁵ The addition of the Lewis acidic Zn^{II} ion was shown to convert Mn^V(O)(TBP₈Cz) to the valence tautomer Mn^{IV}(O)-(TBP₈Cz^{•+}). The influence of Lewis acids on the reactivity of biologically relevant high-valent metal–oxo species is of intense current interest,⁶ especially because of the Ca²⁺ ion involved in manganese-mediated water oxidation.² Herein, we show for the first time that a nonmetal ion Lewis acid, B(C₆F₅)₃, can induce valence tautomerism in a high-valent metal–oxo complex. We find that the addition of B(C₆F₅)₃ also causes dramatically enhanced hydrogen-atom abstraction reactivity toward phenol substrates.

The reaction of Mn^V(O)(TBP₈Cz) with 1 equiv of B(C₆F₅)₃ in CH₂Cl₂ at room temperature (Scheme 1) was monitored by UV–vis spectroscopy. An immediate color change from the green solution for Mn^V(O)(TBP₈Cz) to a red-brown solution was observed together with the disappearance of the spectrum for Mn^V(O)(TBP₈Cz) (λ_{max} = 420 and 634 nm) and the appearance of new peaks at λ_{max} = 420 and 789 nm (Figure 1). The broadening and decrease in the intensity of the Soret band at 420 nm together with the formation of a relatively weak band in

Scheme 1. Formation of Mn^{IV}(O)(TBP₈Cz^{•+})

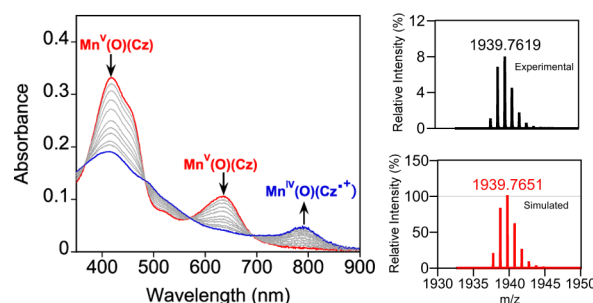
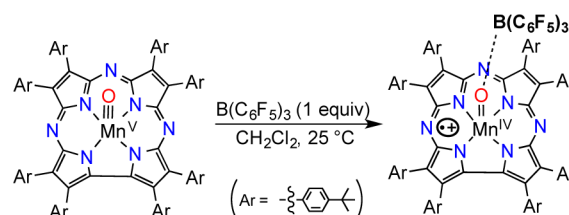


Figure 1. (a) Spectral titration of Mn^V(O)(TBP₈Cz) (5 μ M) + B(C₆F₅)₃ (0.1–1.0 equiv) in CH₂Cl₂. (b) CSIMS(+) of [Mn(O)-(TBP₈Cz):B(C₆F₅)₃ + H]⁺ at –50 °C.

the near-IR region at 789 nm is characteristic of the formation of a porphyrinoid π -radical cation.⁵

The new spectrum matches that observed previously upon the addition of the Lewis acid Zn^{II}(OTf)₂ to the Mn^V(O) complex, which was shown to convert the low-spin ($S = 0$) Mn^V complex into a high-spin triplet ($S = 1$) (or possibly quintet $S = 2$) state with an electronic configuration best described as a manganese(IV) corrolazine π -radical cation.⁵ UV–vis spectral titrations were performed with B(C₆F₅)₃, and tight isosbestic behavior was seen throughout the titration (Figure 1a). A plot of the absorbance at 789 nm versus [B(C₆F₅)₃] (Figure S1 in the Supporting Information, SI) reaches a plateau at ~ 1 equiv of B(C₆F₅)₃, and no further spectral changes are seen with the addition of more B(C₆F₅)₃. Assuming that triarylborane reversibly binds to the Mn^V(O) complex under equilibrium conditions, a good fit of the data can be obtained with a model for a one-to-one binding isotherm. This fit gives an association constant (K_a) of $2.0 \times 10^7 \text{ M}^{-1}$, close to that measured for Zn²⁺ [$K_a(\text{Zn}^{2+}) = 4.0 \times 10^6 \text{ M}^{-1}$].⁵

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The ^1H NMR spectrum of $\text{Mn}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz}) + \text{B}(\text{C}_6\text{F}_5)_3$ (1:1 molar ratio) in CDCl_3 reveals paramagnetically shifted and broadened peaks, as opposed to the sharp, diamagnetic spectrum seen for low-spin $\text{Mn}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz})$. The paramagnetic NMR spectrum is consistent with the formation of a $\text{Mn}^{\text{IV}}(\text{O})-(\text{TBP}_8\text{Cz}^{\bullet+})$ complex, in which a high-spin ($S = 3/2$) Mn^{IV} ion is either ferromagnetically ($S = 2$) or antiferromagnetically ($S = 1$) coupled to the corrolazine π - radical cation ($S = 1/2$). An Evans method measurement in CDCl_3 gives $\mu_{\text{eff}} = 4.19 \mu_{\text{B}}$, which falls between the predicted spin-only values of 2.83 and $4.90 \mu_{\text{B}}$ for the triplet and quintet spin states, respectively. The X-band electron paramagnetic resonance (EPR) spectrum of $\text{Mn}^{\text{IV}}(\text{O})-(\text{TBP}_8\text{Cz}^{\bullet+})$ in CH_2Cl_2 at 12 K showed only relatively weak EPR-active impurities, consistent with the main product having an integer spin ($S = 1$ or 2). The UV–vis, NMR, and EPR data all support the conclusion that the nonmetallic Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ stabilizes the open-shell valence tautomer $\text{Mn}^{\text{IV}}(\text{O})(\text{TBP}_8\text{Cz}^{\bullet+})$.

Attempts to isolate the 1:1 complex $\text{Mn}^{\text{IV}}(\text{O})(\text{TBP}_8\text{Cz}^{\bullet+})\cdot\text{B}(\text{C}_6\text{F}_5)_3$ in the solid state led to significant reduction, giving a $\text{Mn}^{\text{III}}(\text{TBP}_8\text{Cz})$ product. However, it was possible to characterize the $\text{B}(\text{C}_6\text{F}_5)_3$ complex in solution by cryospray ionization mass spectrometry (CSIMS). The reaction of $\text{Mn}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz}) + \text{B}(\text{C}_6\text{F}_5)_3$ (1 equiv) in CH_2Cl_2 at 20°C was monitored by UV–vis to ensure good conversion to $\text{Mn}^{\text{IV}}(\text{O})(\text{TBP}_8\text{Cz}^{\bullet+})$ and then analyzed directly by CSIMS (Figure 1b). A cluster centered at m/z 1939.7619 is observed, and the high-resolution, isotopic distribution pattern matches well for the complex of formula $[\text{Mn}(\text{O})(\text{TBP}_8\text{Cz})\cdot\text{B}(\text{C}_6\text{F}_5)_3 + \text{H}]^+$. The cluster observed at m/z 1426.7712 corresponds to $[\text{Mn}(\text{O})(\text{TBP}_8\text{Cz})]^+$, which likely results from fragmentation of the $\text{B}(\text{C}_6\text{F}_5)_3$ complex (Figure S4 in the SI). These data provide strong evidence for the formation of a 1:1 complex between the manganese–oxo corrolazine and the Lewis acidic triarylborane.

Although we have yet to obtain direct structural information for the Zn^{II} - or borane-derived complexes, $\text{B}(\text{C}_6\text{F}_5)_3$ is anticipated to bind to the oxo ligand of $\text{Mn}^{\text{IV}}(\text{O})(\text{TBP}_8\text{Cz}^{\bullet+})$. Precedent for this conclusion can be seen in the X-ray structure of an isoelectronic $\text{Re}^{\text{V}}(\text{O})(\text{B}(\text{C}_6\text{F}_5)_3)$ complex, in which the boron atom is bound directly to the terminal oxo ligand.⁷ In addition, it was proposed that Sc^{3+} coordinates directly to the oxo group of nonheme $\text{Mn}^{\text{IV}}(\text{O})$ complexes based on X-ray absorption spectroscopy and other supporting data.^{6b,c}

The reversibility of the formation of $\text{Mn}^{\text{IV}}(\text{O})(\text{TBP}_8\text{Cz}^{\bullet+})$ was examined with the addition of fluoride anion. Triarylboranes are known to readily form fluoroborate products ($[\text{FB}(\text{Ar})_3]^-$) upon the addition of F^- .^{8a} The reagent $[(\text{CH}_3)_2\text{N}]_3\text{S}^+[\text{F}_2\text{Si}(\text{CH}_3)_3]^-$ (TASF) was employed as a soluble, anhydrous fluoride source. The addition of TASF to a freshly prepared solution of $\text{Mn}^{\text{IV}}(\text{O})(\text{TBP}_8\text{Cz}^{\bullet+})\cdot\text{B}(\text{C}_6\text{F}_5)_3$ led to rapid recovery of the starting low-spin $\text{Mn}^{\text{V}}(\text{O})$ complex, as seen by UV–vis ($\lambda_{\text{max}} = 634 \text{ nm}$; Figure S2 in the SI), together with a small amount of the reduced Mn^{III} complex $[\text{Mn}^{\text{III}}(\text{TBP}_8\text{Cz})(\text{F})]^-$.^{9a} The addition of excess chloride anion (Bu_4NCl), in contrast, produced no observable change by UV–vis. The difference in the reactivity of F^- versus Cl^- parallels their independent reactivity toward triarylboranes, in which Cl^- binds only weakly to $\text{B}(\text{Ar})_3$.^{8b}

The reactivity of $\text{Mn}^{\text{IV}}(\text{O})(\text{TBP}_8\text{Cz}^{\bullet+})\cdot\text{B}(\text{C}_6\text{F}_5)_3$ in hydrogen-atom-transfer (HAT) reactions was examined with phenol substrates. The reaction with 2,4-di-*tert*-butylphenol (2,4-DTBP) was monitored by UV–vis (Figure 2). Isosbestic conversion to a final spectrum with $\lambda_{\text{max}} = 443$ and 727 nm was observed and is similar to that seen for $[\text{Mn}^{\text{IV}}(\text{TBP}_8\text{Cz})]^+$.^{9b}

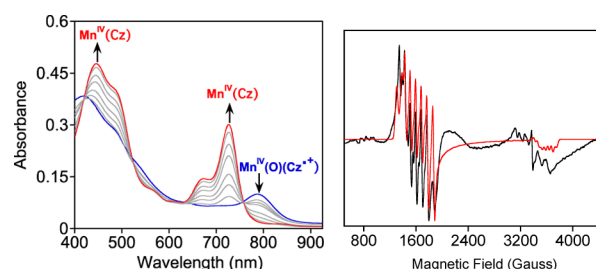
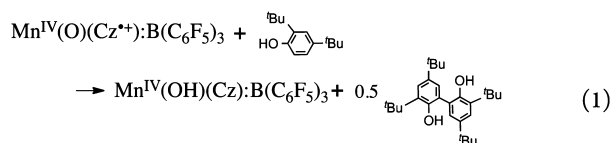


Figure 2. (a) UV–vis spectral changes (0–60 s) for $\text{Mn}^{\text{IV}}(\text{O})-(\text{TBP}_8\text{Cz}^{\bullet+})\cdot\text{B}(\text{C}_6\text{F}_5)_3 + 2,4\text{-DTBP}$ (300 equiv) at 25°C . (b) EPR spectrum (12 K) after reaction with 2,4-DTBP: exptl, black line; simulation, red line.

EPR spectroscopy gives a well-resolved spectrum with $g \sim 4$ and 2 and a hyperfine splitting consistent with ^{55}Mn ($I = 5/2$; Figure 2b). The spectrum was satisfactorily simulated with a fictitious spin of $S' = 1/2$, and $g = [4.61, 4.20, 1.92]$; $A_{\text{iso}}(^{55}\text{Mn}) = [82, 86, 50] \text{ G}$. These parameters are within the range of previously reported high-spin manganese(IV) corrolazines ($S = 3/2$) and other hs manganese(IV) porphyrinoid complexes.^{9b} These data indicate that the reaction with 2,4-DTBP results in a one-electron reduction of $\text{Mn}^{\text{IV}}(\text{O})(\text{TBP}_8\text{Cz}^{\bullet+})$, consistent with hydrogen-atom abstraction from the O–H bond.

The product of oxidation of 2,4-DTBP was identified by gas chromatography with flame ionization detection as the expected bisphenol dimer (eq 1). A maximal yield of 0.5 equiv of dimer per



manganese complex is predicted if the manganese complex serves as a one-electron oxidant, and a yield of 0.39 equiv based on manganese was obtained. This result further supports the $\text{Mn}^{\text{IV}}(\text{O})(\text{TBP}_8\text{Cz}^{\bullet+})$ complex functioning as a one-electron oxidant, in stark contrast to the reactivity seen for the low-spin $\text{Mn}^{\text{V}}(\text{O})$ complex, which acts as a two-electron oxidant toward phenol and C–H substrates.⁹

The kinetics for phenol substrates were measured to gain insight into the reactivity of $\text{Mn}^{\text{IV}}(\text{O})(\text{TBP}_8\text{Cz}^{\bullet+})\cdot\text{B}(\text{C}_6\text{F}_5)_3$. Reactions with excess 2,4-DTBP were monitored by UV–vis and found to be first-order over 5 half-lives (Figure S10 in the SI). A plot of $[2,4\text{-DTBP}]$ versus k_{obs} was linear, consistent with the rate law $\text{rate} = k_2[\text{Mn}(\text{O})][\text{ArOH}]$. These methods yielded second-order rate constants, k_2 , for both $\text{B}(\text{C}_6\text{F}_5)_3$ and Zn^{II} , as well as the more sterically hindered 2,4,6-tri-*tert*-butylphenol (2,4,6-TTBP), and are compared in Table 1. The generation of $\text{Mn}^{\text{IV}}(\text{O})-(\text{TBP}_8\text{Cz}^{\bullet+})$ by either Zn^{II} or $\text{B}(\text{C}_6\text{F}_5)_3$ leads to a significant increase (up to 130-fold) in reactivity compared to the starting low-spin $\text{Mn}^{\text{V}}(\text{O})$ complex for both phenol substrates. The

Table 1. Rate Constants for Oxidation of Phenol Substrates

substrate	Lewis acid	k_2 ($\text{M}^{-1} \text{s}^{-1}$)	$k_{\text{acid}}/k_{\text{none}}$
2,4-DTBP	Zn^{2+}	17 ± 1	5.9
	$\text{B}(\text{C}_6\text{F}_5)_3$	107 ± 8	37
	none	2.9 ± 0.1	
2,4,6-TTBP	Zn^{2+}	0.157 ± 0.008	2.1
	$\text{B}(\text{C}_6\text{F}_5)_3$	9.5 ± 0.7	130
	none	0.074 ± 0.007	

identity of the Lewis acid further influences the reaction rates, with triarylborane being more reactive in both cases. In addition, the much slower rate constants for the more sterically hindered 2,4,6-TTBP indicate a mechanism involving HAT. Support for this mechanism was obtained by measuring a kinetic isotope effect of 3.2 ± 0.3 for 2,4,6-TTBP-OD (Figure S11 in the SI).¹⁰ It was reported that the addition of Sc^{3+} to a nonheme $\text{Mn}^{\text{IV}}(\text{O})$ complex caused a decrease in HAT rates, attributed to steric hindrance from the Sc^{3+} ion.^{6b} Our results appear to contrast these findings, with Lewis acids strongly increasing the HAT reactivity of a $\text{Mn}^{\text{IV}}(\text{O})(\text{Cz}^{\bullet+})$ complex. However, this comparison is complicated by the fact that the inherent HAT reactivity of the valence tautomer with the electronic structure $\text{Mn}^{\text{IV}}(\text{O})(\text{Cz}^{\bullet+})$ is not known. The influence of the electronic structure on the reactivity of high-valent metal–oxo complexes remains an area of intense debate.¹¹

In summary, we have demonstrated for the first time that a nonmetal ion Lewis acid can induce reversible valence tautomerism in a metalloporphyrinoid compound. We have also shown that the HAT reactivity of a $\text{Mn}^{\text{IV}}(\text{O})$ -(porphyrinoid $^{\bullet+}$) complex in the presence of Lewis acids is strongly enhanced compared to its closed-shell $\text{Mn}^{\text{V}}(\text{O})$ valence tautomer. This work provides new insight regarding how to control valence tautomerism in porphyrinoid compounds, as well as on how Lewis acids influence the reactivity of high-valent metal–oxo species.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures, kinetic studies, and EPR and MS data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dpg@jhu.edu.

Notes

The authors declare no competing financial interest.

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