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

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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 MnIV(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 MnV(O) starting material.

High-valent metal–oxo species are invoked as key players in both biological and synthetic oxidations. Examples include an FeIV(O) porphyrin π-radical cation, the key intermediate in cytochrome P450,1 and postulated MnIV/MnV(O) intermediates in photosynthetic water oxidation.2 In heme systems such as FeIV(O)(p-cytochrome P450,1 and postulated MnIV/MnV(O) intermediates in photosynthetic 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 previously introduced a new method for controlling valence tautomerism in a MnV(O) porphyrinoid complex.3 The addition of the Lewis acid B(C6F5)3 causes a reorganization of the data, which was shown to convert the low-spin (S = 0) MnV 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 [B(C6F5)3] = 1.0 equiv. 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

The reaction of MnV(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 MnV(O)(TBP8Cz) to the red-brown solution for MnIV(O)(TBP8Cz) (λmax = 420 and 634 nm) and the appearance of new peaks at λmax = 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 the near-IR region at 789 nm is characteristic of the formation of a porphyrinoid π-radical cation.

The new spectrum matches that observed previously upon the addition of the Lewis acid ZnII(OTf)2 to the MnV(O) complex, which was shown to convert the low-spin (S = 0) MnV 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 The spectrum in Figure 1a was obtained with a model for MnIV(O)(TBP8Cz).Nano MOE model.

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The $^1$H NMR spectrum of Mn$^V$(O)(TBP$_8$Cz) + B(C$_6$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 Mn$^V$(O)(TBP$_8$Cz). The paramagnetic NMR spectrum is consistent with the formation of a Mn$^V$(O)-(TBP$_8$Cz$^*$) complex, in which a high-spin ($S = \frac{3}{2}$) Mn$^IV$ ion is either ferromagnetically ($S = 2$) or antiferromagnetically ($S = 1$) coupled to the corrolazine π-radical cation ($S = \frac{1}{2}$). An Evans method measurement in CDCl$_3$ gives $g_{eff} = 4.19$ $\mu_B$ which falls between the predicted spin-only values of 2.83 and 4.90 $\mu_B$ for the triplet and quintet spin states, respectively. The X-band electron paramagnetic resonance (EPR) spectrum of Mn$^V$(O)-(TBP$_8$Cz$^*$) in CH$_2$Cl$_2$ 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 B(C$_6$F$_5$)$_3$ stabilizes the open-shell valence tautomer Mn$^V$(O)(TBP$_8$Cz$^*$).

Attempts to isolate the 1:1 complex Mn$^V$(O)(TBP$_8$Cz$^*$)-B(C$_6$F$_5$)$_3$ in the solid state led to significant reduction, giving a Mn$^IV$(TBP$_8$Cz) product. However, it was possible to characterize the B(C$_6$F$_5$)$_3$ complex in solution by cryospray ionization mass spectrometry (CSIMS). The reaction of Mn$^V$(O)(TBP$_8$Cz) + B(C$_6$F$_5$)$_3$ (1 equiv) in CH$_2$Cl$_2$ at 20 °C was monitored by UV-vis to ensure good conversion to Mn$^V$(O)(TBP$_8$Cz$^*$) and then analyzed directly by CSIMS (Figure S4 in the SI). A cluster centered at $m/z$ 1939.7619 is observed, and the high-resolution, isotopic distribution pattern matches well for the complex of formula [Mn(O)(TBP$_8$Cz)-B(C$_6$F$_5$)$_3$ + H$^+$]. The cluster observed at $m/z$ 1426.7712 corresponds to [Mn(O)(TBP$_8$Cz)$^+$], which likely results from fragmentation of the B(C$_6$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 corrolazline and the Lewis acidic triarylboration.

Although we have yet to obtain direct structural information for the Zn$^{II}$- or borane-derived complexes, B(C$_6$F$_5$)$_3$ is anticipated to bind to the oxo ligand of Mn$^V$(O)(TBP$_8$Cz$^*$). Precedent for this conclusion can be seen in the X-ray structure of an iso electronic Re$^{V}$O(B(C$_6$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$^{III}$ coordinates directly to the oxo ligand of Mn$^IV$(O)(TBP$_8$Cz$^*$). Precedent for electron/atom-transfer (HAT) reactions was examined with phenol substrates. The reactivity of Mn$^V$(O)(TBP$_8$Cz$^*$)-B(C$_6$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 $\lambda_{max} = 443$ and 727 nm was observed and is similar to that seen for [Mn$^V$(TBP$_8$Cz)]$^+$.8b

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\[\text{Mn}^V(O)(\text{Cz})_8 + \text{Bu}_4\text{N}^+\text{F}^- \rightarrow \text{Mn}^V(O)(\text{Cz})_8^+ + \text{Bu}_4\text{NF} \]

As seen in the X-ray structure of an Mn$^IV$(O)(TBP$_8$Cz$^*$)-B(C$_6$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 corrolazline and the Lewis acidic triarylboration.

The kinetics for phenol substrates were measured to gain insight into the reactivity of Mn$^IV$(O)(TBP$_8$Cz$^*$)-B(C$_6$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 $k_2$ versus [Mn(O)(ArOH)] showed linear, consistent with the rate law rate = $k_2$[Mn(O)][ArOH]. These methods yielded second-order rate constants, $k_2$, for both B(C$_6$F$_5$)$_3$ and Zn$^{II}$, as well as the more sterically hindered 2,4,6-tri-tert-butylphenol (2,4,6-TTBP), and compared in Table 1. The generation of Mn$^IV$(O)(TBP$_8$Cz$^*$) by either Zn$^{II}$ or B(C$_6$F$_5$)$_3$ leads to a significant increase (up to 130-fold) in reactivity compared to the starting low-spin Mn$^V$(O) complex for both phenol substrates.

### Table 1. Rate Constants for Oxidation of Phenol Substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Lewis Acid</th>
<th>$k_2$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_{max}$/inactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-DTBP</td>
<td>Zn$^{II}$</td>
<td>17 ± 1</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>B(C$_6$F$_5$)$_3$</td>
<td>107 ± 8</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>none</td>
<td>2.9 ± 0.1</td>
<td>1.1</td>
</tr>
<tr>
<td>2,4,6-TTBP</td>
<td>Zn$^{II}$</td>
<td>0.157 ± 0.008</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>B(C$_6$F$_5$)$_3$</td>
<td>9.5 ± 0.7</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>none</td>
<td>0.074 ± 0.007</td>
<td>0.1</td>
</tr>
</tbody>
</table>

EPR spectroscopy gives a well-resolved spectrum with $g \approx 4$ and 2 and a hyperfine splitting consistent with $^{55}$Mn ($I = \frac{7}{2}$; Figure 2b). The spectrum was satisfactorily simulated with a fictitious spin of $S = \frac{1}{2}$, and $g = [4.61, 4.20, 1.92]$; $A_{57^{10}}$($^{55}$Mn) = [82, 86, 50] G. These parameters are within the range of previously reported high-spin manganese(IV) corrolazines ($S = \frac{3}{2}$) and other hs manganese(IV) porphyrin complexes.9b These data indicate that the reaction with 2,4-DTBP results in a one-electron reduction of Mn$^IV$(O)(TBP$_8$Cz$^*$), 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 biphenol dimer (eq 1). A maximal yield of 0.5 equiv of dimer per
identification 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 $3.2 \pm 0.3$ for 2,4,6-TTBP-OD (Figure S11 in the SI). It was reported that the addition of Sc$^{3+}$ to a nonheme Mn$^{IV}(O)$ complex caused a decrease in HAT rates, attributed to steric hindrance from the Sc$^{3+}$ ion. Our results appear to contrast with Lewis acids strongly increasing the HAT reactivity of a Mn$^{IV}(O)($porphyrin$)^+$ complex. However, this comparison is complicated by the fact that the inherent HAT reactivity of the valence tautomer with the electronic structure Mn$^{IV}(O)($porphyrin$)^+$ is not known. The influence of the electronic structure on the reactivity of high-valent metal–oxo complexes remains an intense area of debate.

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 Mn$^{IV}(O)$–(porphyrinoid$)^+$ complex in the presence of Lewis acids is strongly enhanced compared to its closed-shell Mn$^{IV}(O)$ 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.

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Notes
The authors declare no competing financial interest.

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**REFERENCES**


(10) An electron transfer/proton transfer or proton transfer/electron transfer mechanism cannot be definitely ruled out.