Oxygen-Atom Transfer Reactivity of Axially Ligated Mn(V)–Oxo Complexes: Evidence for Enhanced Electrophilic and Nucleophilic Pathways

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Supporting Information

ABSTRACT: Addition of anionic donors to the manganese(V)–oxo corrolazine complex Mn(V)(TBP8Cz) has a dramatic influence on oxygen-atom transfer (OAT) reactivity with thioether substrates. The six-coordinate anionic [Mn(V)(TBP8Cz)(X)]− complexes (X = F−, N3−, OCN−) exhibit a ~5 cm−1 downshift of the Mn–O vibrational mode relative to the parent Mn(V)(TBP8Cz) complex as seen by resonance Raman spectroscopy. Product analysis shows that the oxidation of thioether substrates gives sulfoxide product, consistent with single OAT. A wide range of OAT reactivity is seen for the different axial ligands, with the following trend determined from a comparison of their second-order rate constants for sulfoxidation: five-coordinate ≈ thiocyanate ≈ nitrate < cyanate < azide < fluoride ≪ cyanide. This trend correlates with DFT calculations on the binding of the axial donors to the parent Mn(V)(TBP8Cz) complex. A Hammett study was performed with p-X-C6H4SCH3 derivatives and [Mn(V)(TBP8Cz)(X)]− (X = CN− or F−) as the oxidant, and unusual “V-shaped” Hammett plots were obtained. These results are rationalized based upon a change in mechanism that hinges on the ability of the [Mn(V)(TBP8Cz)(X)]− complexes to function as either an electrophilic or weak nucleophilic oxidant depending upon the nature of the para-X substituents. For comparison, the one-electron-oxidized cationic Mn(V)(TBP8Cz(C6H4SCH3)+) complex yielded a linear Hammett relationship for all substrates (ρ = −1.40), consistent with a straightforward electrophilic mechanism. This study provides new, fundamental insights regarding the influence of axial donors on high-valent Mn(V) porphyrinoid complexes.

INTRODUCTION

A key structural factor that contributes to metal-oxo reactivity in heme enzymes is the nature of the axial ligands coordinated trans to the heme group. The concept of axial ligand tuning is exemplified in the powerful oxygenating enzyme Cytochrome P450, in which the anionic, deprotonated Cys ligand is believed to play a critical role. It has been suggested that the Cys in Cyt-P450, in which the anionic, deprotonated Cys ligand is believed to enhance the reactivity of Fe(O)(porph) in epoxidations.13−21 The preparation of synthetic analogs of heme enzymes has provided a means to test mechanistic hypotheses regarding the influence of axial donors. Synthetic models of heme active sites are particularly useful for examining complexes that are analogous to the highly unstable intermediates in enzyme systems, including high-valent metal-oxo species. Regarding the influence of axial donors on these species, a potential advantage of model systems is the ability to rationally tune the nature of the axial ligand by varying its structural and electronic properties in a systematic fashion. The influence of axial ligands on high-valent, iron-oxo porphyrin models has been investigated, including the examination of the effects of axial donors on oxygen-atom transfer (OAT) reactivity. For example, axial ligands were shown to enhance the reactivity of Fe(O)(porph) in epoxidations.13−21 A recent study on the effects of axial ligation on Cpd-I analogs, Fe(V)(O)(porph)(X), provided a detailed thermodynamic analysis which led to a possible explanation for the trend in OAT reactivity versus axial donor.15 The mechanisms of these reactions and especially the exact role played by the axial ligands are still not well understood.

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In contrast to Fe(O) species, the influence of axial donors on analogous Mn(O) porphyrinoid complexes has been much less studied, with very few systematic investigations for a wide range of axial ligands reported to date.\textsuperscript{22−30} One of the few examples comes from Chang and co-workers, who showed that the reactivity of an Mn(V) corrole toward styrene can be enhanced by 10-fold with an imidazole as an axial ligand.\textsuperscript{23} The effects of axial donors on nonheme Mn(O) complexes such as Mn(O)-salen)(X) have been reported.\textsuperscript{31−34} However, direct structural, spectroscopic, or reactivity information on these complexes is in general quite limited because of the transient nature of these species.\textsuperscript{35}

Previously, we took advantage of our ability to isolate and definitively characterize a relatively stable high-valent Mn(V) complex Mn(V)(O)(TBP8Cz) (TBP8Cz = octakis(p-tert-butylyphenyl)corrolazinato\textsuperscript{−}), which contains a ring-contracted porphyrinoid ligand, in order to examine the influence of cyanide and fluoride ions on C−H activation. Indirect evidence was obtained that suggested CN\textsuperscript{−} and F\textsuperscript{−} were weakly bound to the terminal oxo ligand and caused significant increases in H-atom abstraction rates.\textsuperscript{35} More recently, we used X-ray absorption spectroscopy to characterize one of these complexes, [Mn(V)(O)(TBP8Cz)(CN)]\textsuperscript{−}, and showed that CN\textsuperscript{−} was indeed coordinated to the metal while leaving the short Mn(V)−O bond intact.\textsuperscript{36} Addition of the CN\textsuperscript{−} donor caused a large rate enhancement in OAT to thioanisole, giving the predicted two-electron reduced Mn(III) complex and sulfoxide product.

Herein we describe a comprehensive study regarding the influence of a wide range of anionic axial ligands on the OAT reactivity of an Mn(V) porphyrinoid complex. Significant rate enhancements for OAT to thioether substrates are seen for different axial donors. The use of a series of p-X-C\textsubscript{6}H\textsubscript{4}SCH\textsubscript{3} substrates provides a range of OAT rates for the cyanide- and fluoride-ligated Mn(V) complexes, revealing unexpected "V-shaped" Hammett plots. These results point to a dramatic switch in mechanism for OAT, depending upon the nature of the substrate. This work provides new, fundamental insights regarding the influence of axial donors on the OAT reactivity of rarely observed Mn(V) porphyrinoid complexes.

**Experimental Section**

**Materials.** All reactions were performed under an argon atmosphere using dry solvents and standard Schlenk techniques. The Mn\textsubscript{III}(TBP8Cz) and Mn\textsubscript{VI}(O)(TBP8Cz) complexes were synthesized according to published methods.\textsuperscript{37} Solvents were purified via a Pure-Solv solvent purification system from Innovative Technologies, Inc. H\textsubscript{2}O\textsubscript{18} (97% \textsuperscript{18}O) was purchased from Cambridge Isotopes, Inc. All other reagents were purchased from Sigma-Aldrich at the highest level of purity and used as received.

**Instrumentation.** UV−vis spectroscopy was performed on a Hewlett-Packard 8542 diode-array equipped with HP ChemStation software. A filter was placed between the spectrometer light and the sample to prevent bleaching of [Mn\textsuperscript{VI}(O)(TBP8Cz)(X)]\textsuperscript{−} from UV light (<400 nm). The temperature-dependent kinetics were performed on an Agilent 6850 gas chromatograph fitted with a DB-5 5% phenylmethyl silicone capillary column (30 m × 0.32 mm × 0.25 \textmu m) and equipped with a flame-ionization detector. GC mass spectrometry (GC-MS) was performed on an Agilent 6890 gas chromatograph fitted with a DB-5 5% phenylmethyl silicone capillary column and equipped with a mass spectrometer. LDI-TOF was conducted on a Bruker Autoflex III TOF/TOF instrument equipped with a nitrogen laser at 335 nm using an MTP 384 ground steel target plate. \textsuperscript{31}P NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer at 298 K. All spectra were taken in 5 mm o.d. NMR tubes, and chemical shifts were reported as δ values from standard peaks.

**Resonance Raman Sample Preparation.** A solution of Mn\textsuperscript{VI}(O)(TBP8Cz) (1 mM) in CH\textsubscript{3}Cl\textsubscript{2} (250 \textmu L) at 25 °C was combined with Bu\textsubscript{4}N\textsubscript{F}−X (X = F, N\textsubscript{3}, OCN at 1 M). Samples were loaded into an EPR tube, immediately frozen in liquid nitrogen, and stored at 77 K until measurements were performed.

**Resonance Raman Spectroscopy.** Resonance Raman spectra were recorded on a triVista 555 triple monochromator (900/900/2400 gr/mm) equipped with a CCD camera (1340 × 100 pixels). A 413.2 nm line of a krypton-ion laser was used for excitation. The laser power was <15 mW at the sample to reduce the risk of photooxidation. 900/900/ 2400 gr/mm gratings provided a resolution of 0.69 cm\textsuperscript{−1} per CCD pixel at 413.2 nm. Samples were held in an EPR finger-dewar (77 K) in a 135° backscattering arrangement. Raw spectra were analyzed using the program Igor Pro for background subtraction. No smoothing procedures were performed on the raw data.

**Product Analysis.** In a typical reaction, a stirring solution of Mn\textsuperscript{VI}(O)(TBP8Cz) (0.2 or 5 mM) in CH\textsubscript{3}Cl\textsubscript{2} (3 mL) was combined with an anionic donor Bu\textsubscript{4}N\textsubscript{F}− (1.3 or 12 mM) at 25 °C. To initiate the reaction, dimethyl sulfoxide (DMS): 11 M or triphenylphosphine (PPh\textsubscript{3}): 5 mM was added. Isosbestic conversion of [Mn\textsuperscript{VI}(O)(TBP8Cz)(F)]\textsuperscript{−} ([\textit{k}_{\text{obs}} = 419, 634 nm]) to [Mn\textsuperscript{III}(TBP8Cz)(F)]\textsuperscript{−} ([\textit{k}_{\text{obs}} = 428, 471, 680 nm]) was observed by UV−vis spectroscopy. Upon completion of the reaction, the solution was concentrated to ~50 \textmu L under vacuum. The phosphine reaction was dissolved in CDCl\textsubscript{3} and analyzed by \textsuperscript{31}P NMR. The yield was obtained by comparing the integration of the product peak, triphenylphosphine oxide, to that of the reactant peak (PPh\textsubscript{3}).

**Measurement of the Binding Constant for Fluoride to Mn\textsuperscript{VI}(O)(TBP8Cz).** A solution of Mn\textsuperscript{VI}(O)(TBP8Cz) (10 \muM) in CH\textsubscript{3}Cl\textsubscript{2} (2 mL) at 25 °C was combined with Bu\textsubscript{4}N\textsubscript{F}− (11 mM) X = N\textsubscript{3}, OCN, SCN, NO\textsubscript{3} or Bu\textsubscript{4}N\textsubscript{F}−·3H\textsubscript{2}O (0.03 M). Excess DMS or dibutyl sulfoxide (DBS) was added to begin the reaction. The changes in absorbance were monitored by UV−vis spectroscopy showing the isosbestic decay of [Mn\textsuperscript{VI}(O)(TBP8Cz)(X)]\textsuperscript{−} ([\textit{k}_{\text{obs}} = 419, 634 nm]) and formation the of [Mn\textsuperscript{III}(TBP8Cz)(X)]\textsuperscript{−}. A filter was placed between the spectrometer light and the sample to prevent bleaching of [Mn\textsuperscript{VI}(O)(TBP8Cz)(X)]\textsuperscript{−} from UV light (<400 nm). The pseudo-first-order rate constants, \textit{k}_{\text{obs}} were obtained by nonlinear least-squares fitting (eq 1) of the growth in absorbance of [Mn\textsuperscript{VI}(TBP8Cz)(X)]\textsuperscript{−} at 680−693 nm or decay of [Mn\textsuperscript{VI}(O)(TBP8Cz)(X)]\textsuperscript{−} at 634 nm versus time:

\[
\text{Abs}_t = \text{Abs}_0 + \text{Abs}_f \exp(-k_{\text{obs}}t) \\
\text{Abs}_0 = \text{final absorbance, } \text{Abs}_f = \text{initial absorbance, and } \text{Abs}_b = \text{absorbance at time } t.
\]

Second-order rate constants were obtained from the slope of the best-fit line of the linear plot of \textit{k}_{\text{obs}} versus substrate concentration.

**Measurement of the Binding Constant for Fluoride to Mn\textsuperscript{VI}(O)(TBP8Cz).** A solution of Mn\textsuperscript{VI}(O)(TBP8Cz) (10 \muM) in CH\textsubscript{3}Cl\textsubscript{2} (2 mL) at 25 °C was combined with DBS (2.7 mM). The reaction was initiated by the addition of Bu\textsubscript{4}N\textsubscript{F}−·3H\textsubscript{2}O (1.7−59 mM). The changes in absorbance were monitored by UV−vis spectroscopy showing the isosbestic decay of [Mn\textsuperscript{VI}(O)(TBP8Cz)(F)]\textsuperscript{−} ([\textit{k}_{\text{obs}} = 419, 634 nm]) and formation of [Mn\textsuperscript{III}(TBP8Cz)(F)]\textsuperscript{−} ([\textit{k}_{\text{obs}} = 469, 680 nm]). The pseudo-first-order rate constants, \textit{k}_{\text{obs}} were obtained by nonlinear least-squares fitting (eq 1) of the growth in absorbance of [Mn\textsuperscript{IV}(TBP8Cz)(F)]\textsuperscript{−} at 680 nm versus time. A plot of \textit{k}_{\text{obs}} versus [F] gave a straight line.

The data were modeled for a 1:1 binding event as shown in eq 2, where the association constant \textit{K} = \textit{k}_{\text{on}}/\textit{k}_{\text{off}}, \textit{k}_{\text{on}} is the pseudo-first-order rate constant for a given concentration of DMS, and [F] is total concentration of TBAF.\textsuperscript{38} A fit of 1/[\textit{k}_{\text{obs}}] and 1/[F] versus \textit{k}_{\text{obs}} plot is given in eq 3.
Investigations were initiated by examining the reactivity of the reactivity and the nature of the axial donor could be made. 

An alternate O-atom acceptor, PPh₃, showed similar reactivity, resulting in the rapid conversion of [Mn⁵(V)(TPB₈C₇)(F)]⁻ to [Mn⁴(III)(TPB₈C₇)(C)]⁻. The ³¹P NMR spectrum (Figure S1) of the reaction mixture identified OPPh₃ as the major product in 89% yield (Scheme 1). Thus, the Mn⁴(II) complex, in the presence of TBAF, reacts rapidly and quantitatively with both thioether and phosphine O-atom acceptors to give sulfoxide or phosphine oxide products via a formal OAT process.

Dependence of OAT Rates on Fluoride Concentration. In earlier work we showed that the rates of H-atom abstraction by Mn⁴(II)(TPB₈C₇) with C–H substrates depended on the concentration of added TBAF. A plot of pseudo-first-order rate

\[ k_{\text{obs}} = k_1 \left( \frac{K[F^{-}]_{\text{total}}}{1 + K[F^{-}]_{\text{total}}} \right) \]

\[ \frac{1}{k_{\text{obs}}} = \frac{1}{k_1 K[F^{-}]_{\text{total}}} + \frac{1}{k_2} \]

**RESULTS AND DISCUSSION**

**OAT Reactivity of [Mn⁴(V)(TPB₈C₇)(F)]⁻ with Thioether and Phosphine Substrates.** Kinetic analysis showed that the oxidation of thioether substrates by Mn⁴(II)(TPB₈C₇) was relatively slow, with second-order rate constants of 2.0 × 10⁻³ M⁻¹ s⁻¹ for DMS and 3.8 × 10⁻⁴ M⁻¹ s⁻¹ for DBS. The addition of CN⁻ to Mn⁴(II)(TPB₈C₇) dramatically increased the rates of sulfoxidation, giving a second-order rate constant of 9.2 M⁻¹ s⁻¹ for DBS. We next sought to extend our study on the influence of anionic donors and determine whether a correlation with the nature of the axial donor could be made. Investigations were initiated by examining the reactivity of the thioether anion. Addition of Bu₄N⁺F⁻ (TBAF) to Mn⁴(II)(TPB₈C₇) in the presence of excess DMS as substrate was monitored in CH₂Cl₂ at 25 °C (Scheme 1). The UV–vis spectra are shown in Figure 1a and reveal isosbestic conversion of the Mn⁴⁻‑oxo complex to the axially ligated complex [Mn⁴(II)(TPB₈C₇)(F)]⁻, with a split Soret band at 428 and 471 nm. As previously observed, there is little change in the UV–vis spectrum for Mn⁴(II)(TPB₈C₇) upon addition of F⁻, but splitting in the Soret region of the corresponding [Mn⁴(II)(TPB₈C₇)(F)]⁻ complex is clearly seen in Figure 1b. A related complex (Et₄N)³¹P[Mn⁴(II)(TPB₈C₇)(Cl)]⁻, has been characterized and exhibited a similar splitting in the Soret band. With the addition of excess TBAF, the OAT reaction was complete in 1.5 h, and analysis by GC-FID revealed DMSO as the major oxidation product (85%). In comparison, the oxidation of DMS by the five-coordinate Mn⁴(II)(TPB₈C₇) is much slower, taking over 17 h for completion.
constants \( k_{\text{obs}} \) versus [TBAF] for two different C–H substrates gave a saturation curve that was successfully modeled as a 1:1 binding equilibrium.\(^{35} \) In the present study, the rates of sulfoxidation of DBS under pseudo-first-order conditions were similarly monitored by UV–vis, and the concentration of TBAF was varied. Plots of the absorbance associated with the decay and growth of the Mn\(^{V} \) and Mn\(^{III} \) complexes, respectively, were well-fit to a single exponential kinetic model (Figure S2). The resulting \( k_{\text{obs}} \) values were plotted versus [F\(^{-}\)] (Figure 2a) and exhibit saturation behavior, indicative of a rapid pre-equilibrium for the binding of F\(^{-}\) prior to the rate-determining step. A double reciprocal plot \( (1/k_{\text{obs}} \) versus \( 1/[F^{-}] \)) (Figure 2b) reveals good linearity, with a best fit that gives a binding constant of \( K(F^{-}) = 115 \pm 4 \) M\(^{-1}\). This value is in good agreement with the binding constants found previously for fluoride anion and the Mn\(^{V} \)(O) complex in reactions with C–H substrates (163 ± 7 and 191 ± 10 M\(^{-1}\)).\(^{35} \) These results provide strong evidence that the anionic donors are coordinated trans to the terminal oxo ligand, thereby inducing a subtle weakening of the Mn–O vibrational mode. Similar effects on the metal-oxo stretch were seen upon variation of trans axial donors in both heme and nonheme Fe\(^{IV} \)(O) complexes.\(^{15,43,44} \)

Resonance Raman Spectroscopy of the Six-coordinate Mn\(^{V} \)(O) Complexes. The binding of X\(^{-}\) to Mn\(^{V} \)(O)(TBP\(_8\)C\(_z\)) can be described according to the simple equilibrium in eq 4:

\[
\text{Mn}^{V}(O)(\text{TBP}_{8}\text{C}_{z}) + X^{-} \rightleftharpoons \text{Mn}^{V}(O)(\text{TBP}_{8}\text{C}_{z})(X)^{-}
\]

\( \text{five-coordinate} \)

\( \text{six-coordinate} \)

The six-coordinate complexes were examined by resonance Raman spectroscopy for X = F\(^{-}\), N\(^{3-}\), and OCN\(^{-}\). Excess X\(^{-}\) was added to push the equilibrium in eq 4 to favor the six-coordinate complexes in CH\(_2\)Cl\(_2\). Frozen solution samples were excited with the 413.2 nm krypton-ion excitation line at 77 K. A Mn–O vibrational mode for the five-coordinate Mn\(^{V} \)(O)(TBP\(_8\)C\(_z\)) starting complex was identified at 981 cm\(^{-1}\), which downshifts to 939 cm\(^{-1}\) upon \(^{18}\)O substitution (Figure S3). This 42 cm\(^{-1}\) shift is in good agreement with diatomic harmonic oscillator predictions as well as previously published results.\(^{42} \) The spectra for the F\(^{-}\), N\(^{3-}\), and OCN\(^{-}\) complexes are shown in Figure 3, together with the five-coordinate starting material. The Mn–O mode clearly downshifts by 5 cm\(^{-1}\) to 976 cm\(^{-1}\) relative to the starting complex. The identity of the peak at 976 cm\(^{-1}\) was verified using \(^{18}\)O labeling for the F\(^{-}\) and N\(^{3-}\) complexes (Figures S4 and S5). These results provide strong evidence that the anionic donors are coordinated trans to the terminal oxo ligand, thereby inducing a subtle weakening of the Mn–O vibrational mode. Similar effects on the metal-oxo stretch were seen upon variation of trans axial donors in both heme and nonheme Fe\(^{IV} \)(O) complexes.\(^{3,43,44} \)

Kinetic Studies of OAT for a Series of Anionic Axial Donors. A broad series of anionic axial ligands (X\(^{-}\)), in conjunction with two thioether substrates (DMS and DBS), were employed for kinetic studies (Scheme 2). An example of the UV–vis spectral changes observed for these OAT reactions is shown in Figure 4, where X = N\(^{3-}\). Good isosbestic behavior is seen, and the final spectrum matches that for \([\text{Mn}^{III}(\text{TBP}_{8}\text{C}_{z})\text{-}(\text{N}^{3-})]^−\). Plots of absorbance versus time for the decay of the Mn\(^{V} \)(O) complex (634 nm) and the appearance of the Mn\(^{III} \)(N\(^{3-}\)) complex (685 nm) are shown in the inset, Figure 4. These plots, along with the plots for the other axial donors, were well fit by a single exponential model, consistent with the

![Figure 2](image-url)

**Figure 2.** (a) Dependence of the \( k_{\text{obs}} \) values on the concentration of Bu\(_4\)N\(^{+}\)F\(^−\) for the reaction of Mn\(^{V} \)(O)(TBP\(_8\)C\(_z\)) + DBS (270 equiv) in CH\(_2\)Cl\(_2\) at 25 °C. (b) Double-reciprocal plot \( (1/k_{\text{obs}} \) versus \( 1/[F^{-}] \)) (blue circles) and best fit line (black).

![Figure 3](image-url)

**Figure 3.** Low-frequency resonance Raman spectra of \(^{16}\)O \([\text{Mn}^{V}(O)-(\text{TBP}_{8}\text{C}_{z})(X)]^-\) where X = no ligand, F\(^−\), N\(^{3-}\), or OCN\(^−\). The resonances near 900 cm\(^{-1}\) were used to scale the spectra. Data were collected using a 413.2 nm krypton-ion laser line.

![Scheme 2](image-url)

**Scheme 2.** Kinetic Model for OAT to Thioether Substances
mechanism shown in Scheme 2. The resulting fits yielded pseudo-first-order rate constants (k_{obs}), which were found to be linearly dependent on substrate concentration (Figure 5). The best-fit lines of k_{obs} versus [substrate] yielded second-order rate constants (k) (Table 1) for the different axial donors.

As can be seen from Table 1, there is a remarkable enhancement in OAT reactivity for the MnV(O) complex in the presence of anionic donors. The second-order rate constant for F\(^-\) reveals a dramatic rate enhancement of 1100-fold in the oxidation of DMS compared to the MnV(O) complex. Addition of CN\(^-\) as the axial donor has an even more dramatic effect, revealing a rate enhancement of 24,000 for DMS oxidation by the [MnV(O)(TBP8Cz)(CN)]\(^-\) complex.

Further examination of the other anionic axial donors in Table 1 reveals some important trends. The addition of azide (N3\(^-\)) leads to a 70-fold rate enhancement over the reaction rate with DBS as substrate. Taken together, the kinetic data indicate the following trend regarding the influence of X\(^-\) on the reactivity of MnV(O)-(TBP8Cz) (vide infra).

**Influence of para-Substituents on the Reactivity of Thioanisole Derivatives.** The reactive cyanide-ligated [MnV(O)(TBP8Cz)(CN)]\(^-\) complex was chosen for further study with a series of p-X-C6H4SCH3 derivatives (Scheme 3). The oxidation of C6H4SC6H4 proceeds in good yield (84%) to give the mono-oxygenated sulfoxide product, with 71% of the \(^{18}\)O label in [MnV(O)(TBP8Cz)(CN)]\(^-\) transferring to the sulfur atom.\(^{16}\) The reactions between the p-X-substituted thioanisole derivatives and [MnV(O)(TBP8Cz)(CN)]\(^-\) were monitored by UV–vis spectroscopy, and good isosbestic behavior for the conversion of the MnV starting material to the [Mn\(^{18}\)O(CN)]\(^-\) product was seen for all substrates. The resulting pseudo-first-order rate constants (k) for the different para-substituted derivatives were used to construct the Hammett plot shown in Figure 6. For the electron-donating substituents, there is a good linear correlation with a clear negative slope of rho (\(\rho\)) = −1.29. This trend is easily explained by a mechanism involving electrophilic attack of the oxo group of the MnV(O) complex on the sulfur atom.\(^{36}\)

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**Figure 4.** UV–vis spectral changes for the reaction of [MnV(O)-(TBP8Cz)(N3)]\(^-\) (9 \(\mu\)M) (419, 634 nm) with DMS (4.0 mM) in CH2Cl2 at 25 °C. Inset: changes in absorbance versus time for the growth of [MnIII(TBP8Cz)(N3)]\(^-\) (685 nm) (open blue square) together with best fits (solid black line).

**Figure 5.** (a) Plots of k_{obs} versus concentration of DBS for X\(^-\) = CN\(^-\) (solid blue triangle), F\(^-\) (solid red circle), and SCN\(^-\) (solid green diamond). Inset: expanded region from 0 to 0.05 M. (b) Plots of k_{obs} versus concentration of DMS for X\(^-\) = F\(^-\) (solid red circle), N3\(^-\) (solid purple diamond), OCN\(^-\) (solid blue square) and NO3\(^-\) (solid green triangle). Inset: expanded region from 0 to 0.045 M.

**Table 1. Second-Order Rate Constants for OAT to Thioether Substrates**

| axial ligand | substrate | k (M\(^{-1}\)s\(^{-1}\)) | \(k/[MnV(O)(X)]^-/[MnV(O)]\) |
|-------------|-----------|----------------|-----------------------------|
| none\(^a\)  | DBS       | 3.8 \times 10^{-4} | 1500                        |
| CN\(^-\)\(^c\) | DBS       | 9.2 ± 0.3          | 24,000                      |
| F           | DBS       | 0.63 ± 0.02        | 1700                        |
| SCN         | DBS       | (1.5 ± 0.1) \times 10^{-4} | 0.4                      |
| none\(^b\)  | DMS       | (2.0 ± 0.2) \times 10^{-3} | 1100                      |
| F           | DMS       | 2.3 ± 0.3          | 1100                        |
| N3\(^-\)    | DMS       | 0.14 ± 0.01        | 70                          |
| OCN         | DMS       | (2.9 ± 0.3) \times 10^{-3} | 1.5                      |
| NO3\(^-\)   | DMS       | (1.5 ± 0.1) \times 10^{-3} | 0.75                      |

\(^a\)In toluene. \(^b\)Ref 40. \(^c\)Ref 36.
the sulfur center of the thioanisole derivatives. A negative \( \rho \) value was also seen for H-atom abstraction by the five-coordinate Mn\(^{V}\)(O) complex with a series of \( \sigma \)-substituted phenols.\(^{45}\) These data indicate that the anionic, six-coordinate Mn\(^{V}\)(O) complex maintains significant electrophilic character. However, the electron-withdrawing \( p\)-COOME, \( p\)-CN, and \( p\)-NO\(_2\) substituents lead to a substantial increase in reaction rate and a positive \( \rho \) value of \( \rho = +1.22 \). Such a “V-shaped” Hammett plot suggests a distinct change in mechanism for the electron-poor substrates. For comparison, a V-shaped Hammett plot was observed for a related Mn\(^{V}\)(imido)(corrole) complex, also implicating a mechanistic switch.\(^{46}\) The generalizability of this change in mechanism for the six-coordinate anionic Mn\(^{V}\)(O) complexes was confirmed by examining the fluoride-ligated \([\text{Mn}^{V}(\text{O})(\text{TBP8Cz})(\text{F})]^{-}\). Reaction of this complex with \( p\)-X-C\(_6\)H\(_4\)SCH\(_3\) derivatives also revealed a clear V-shaped Hammett plot (Figure S14).

A possible explanation for the V-shaped Hammett plots comes from consideration of the contributing resonance structures shown in Figure 7. The quinoid-type resonance forms may be partly stabilized by the electron-withdrawing \( p\)-COOME, \( p\)-CN, and \( p\)-NO\(_2\) substituents. Evidence for the contribution of a similar quinoid-type resonance form in a \( p\)-nitrophenylthiolate–Ni\(^{II}\) complex was observed by X-ray crystallography.\(^{47}\) The quinoid-type resonance form shown in Figure 7 generates partial positive charge on the sulfur center, making these relatively electron-poor substrates potentially electrophilic in nature. A different mechanism for sulfoxidation could then result for the \( p\)-COOME, \( p\)-CN, and \( p\)-NO\(_2\) substrates.

The two possible mechanistic scenarios are shown in Scheme 4. Pathway A corresponds to the electron-donating \( para-X\) substituents and shows the sulfoxidation reaction formally broken into electron-transfer and O–S bond formation steps. The redox potentials of the thioether substrates (\( E_{\text{oxygen}}^{0} = 1.2–1.6 \) V vs SCE)\(^{37}\) indicate that pure outer-sphere ET between Mn\(^{V}\)(O) complexes is highly disfavored. Thus, a more reasonable mechanism, which we favor, involves a single transition state with contributions from both the ET and S–O bond formation steps formally depicted in Pathway A. The rates for the electron-donating substituents correlate with the trend expected from a significant contribution of the ET process, which should get slower as the redox potential of the thioether increases. In contrast, the electron-withdrawing substituents may exhibit negligible contribution from electron-transfer because of their very high redox potentials. For these substrates, the quinoid-type resonance structure can enhance the rate of S–O bond formation, taking advantage of the ability of the anionic \([\text{Mn}^{V}(\text{O})(\text{TBP8Cz})(\text{X})]^{-}\) (\( X = \text{CN}^{-} \) or \( F^{-} \)) complex to serve as a potential weak nucleophile.\(^{48,49}\) Thus, for pathway B, the transition state is dominated by S–O bond formation. This barrier would be lower for more electron-withdrawing substrates, providing an explanation for the positive \( \rho \) value and the V-shaped Hammett plot seen in Figure 6.

The cationic complex \([\text{Mn}^{V}(\text{O})(\text{TBP8Cz})]^{2+}\) was previously prepared by some of us and, to our knowledge, is the only example of an Mn\(^{V}\)(O)(\( \pi \)-radical cation) complex. This cationic complex functioned as an electrophilic oxidant toward phosphine and thioether substrates and was an ideal candidate for comparison of its OAT reactivity with the anionic axially ligated Mn\(^{V}\)(O) complexes. The Mn\(^{V}\)(O)(\( \pi \)-radical cation) complex...
was generated by chemical oxidation of the neutral Mn\(^{V}(O)\) starting material with the one-electron oxidant [(4-BrC\(_6\)H\(_4\))\(_2\)N\(^+\)](SbCl\(_6\)-) (Scheme 5). Isosbestic behavior was observed for the reactions with the \(p\)-X-substituted thioanisole derivatives, and in this case the two-electron reduced product of Mn\(^{V}(O)(TBP\(_8\)C\(_2\))\(^+\)) is the Mn\(^{IV}\) complex [Mn\(^{IV}(TBP\(_8\)C\(_2\))\(^+\)], as expected following OAT. The resulting Hammett plot of log\(k_{\text{rel}}\) versus \(\sigma\) values for the \(para\)-X derivatives is shown in Figure 8. A strong linear correlation with a slope \(\rho = -1.40\) is found throughout the range of \(para\)-X derivatives, in stark contrast to the V-shaped Hammett plot seen for the anionic [Mn\(^{V}(O)-(TBP\(_8\)C\(_2\))(X)\(^-\) (X = CN\(^-\) or F\(^-\)). A single mechanism involving electrophilic attack of Mn\(^{V}(O)(TBP\(_8\)C\(_2\))\(^+\) (Pathway A) is inferred. These findings provide strong support for the conclusion that there is a mechanistic switch for the CN\(^-\) and F\(^-\) complexes and the electron-poor substrates (Pathway B), and it is the anionic nature of the CN\(^-\) and F\(^-\) species that likely facilitates the opening of this unique reaction channel.

**Density Functional Theory (DFT) Calculations.** Computational studies were undertaken to help explain the trend in reactivity for the different anionic axial ligands. Calculations were performed at RIJCOSX-B3LYP/LANLDZ/6-31G level of theory, and the optimized geometries revealed a variation in Mn\(^{V}-X\) bond distances that were used for a qualitative comparison of the binding interactions for the various axial (X\(^-\)) donors. The TBP groups were replaced with H-atoms on the C\(_2\) ligand to facilitate the computations. The calculations were performed on the singlet state only for the Mn\(^{V}\) ion, which has been shown to be the ground state in previous calculations\(^{35,40}\) and which is consistent with XAS measurements for the CN\(^-\) complex.\(^{36}\) The optimized geometries for the six-coordinate F\(^-\) and CN\(^-\) structures were calculated previously\(^{35}\) but were repeated here for comparative purposes. The calculated structures for [Mn\(^{V}(O)(H\(_8\)C\(_2\))(X)\(^-\)] with \(X = F\(^-\), CN\(^-\)) revealed Mn–X distances (Table 2) indicating a binding interaction. The

| none   | CN\(^-\) | F\(^-\) | N\(^+_2\) | OCN\(^-\) | NO\(^+_3\) |
|--------|----------|--------|-----------|----------|-----------|
| Mn\(^{V}-O\) | 1.549    | 1.568  | 1.568     | 1.568    | 1.561     | 1.557     |
| Mn\(^{V}-X\) | -       | 2.146  | 1.931     | 2.354    | 2.420     | 2.518     |

**CONCLUSIONS**

Addition of anionic axial donors (X\(^-\)) to an Mn\(^{V}(O)\) corrolazine results in binding to the Mn\(^{V}\) center. Resonance Raman spectroscopy confirms a subtle weakening of the Mn\(^{V}-O\) triple bond upon addition of the X\(^-\) ligand, providing strong evidence for coordination of X\(^-\) in a position trans to the terminal oxo group. The axial donors CN\(^-\) and F\(^-\) lead to dramatic increases in OAT reactivity to thioether substrates, and N\(^+_2\) also shows a strong effect. The OCN\(^-\), NO\(^+_3\), and SCN\(^-\) anions, however, exhibit little or no influence on OAT. These trends in reactivity correlate well with the trend in the DFT-derived Mn\(^{V}-X\) distances. A Hammett analysis with a range of \(p\)-X-C\(_6\)H\(_5\)SHCH\(_3\) derivatives revealed an unusual V-shaped Hammett plot for [Mn\(^{V}(O)(TBP\(_8\)C\(_2\))(X)\(^-\)] (X = CN\(^-\) or F\(^-\)) complexes, indicating a distinct change in mechanism for OAT to the thioether substrates. This Hammett behavior strongly contrasts the linear plot seen for the cationic complex Mn\(^{V}(O)-(TBP\(_8\)C\(_2\))\(^+\)]. These findings suggest a novel bifurcated mechanistic scenario in which the axially ligated anionic complexes can function in either a purely electrophilic capacity or in an initial nucleophilic manner when strong electron-withdrawing substituents are present on the thioanisole derivatives. Our results suggest that axial ligation is a key factor in the OAT reactivity of Mn\(^{V}\) complexes, and the addition of the appropriate axial donor can be a good strategy for dramatically increasing OAT reactivity. Even though the axially ligated complexes bear an overall negative charge, they function as more powerful, electrophilic oxidizing agents as compared to the nonligated, neutral Mn\(^{V}\) precursor complex. With the strong electron-withdrawing \(p\)-X substituents on the thioanisole derivatives, the nucleophilic properties of the anionic Mn\(^{V}\) complexes provide a further boost to their reactivity. These new mechanistic insights should help in our understanding of axial ligand effects in heme enzymes as well as in the potential design of new synthetic oxidation catalysts.
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