How Metal Ion Lewis Acidity and Steric Properties Influence the Barrier to Dioxygen Binding, Peroxo O–O Bond Cleavage, and Reactivity

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Supporting Information

ABSTRACT: Herein we quantitatively investigate how metal ion Lewis acidity and steric properties influence the kinetics and thermodynamics of dioxygen binding versus release from structurally analogous Mn–O2 complexes, as well as the barrier to Mn peroxy O–O bond cleavage, and the reactivity of Mn oxo intermediates. Previously we demonstrated that the steric and electronic properties of MnIII–OOR complexes containing N-heterocyclic (NAr) ligands can have a dramatic influence on alkylperoxo O–O bond lengths and the barrier to alkylperoxo O–O bond cleavage. Herein, we examine the dioxygen reactivity of a new MnII complex containing a more electron-rich, less sterically demanding NAr ligand scaffold, and compare it with previously reported MnIII complexes. Dioxygen binding is shown to be reversible with complexes containing the more electron-rich metal ions. The kinetic barrier to O2 binding and peroxy O–O bond cleavage is shown to correlate with redox potentials, as well as the steric properties of the supporting NAr ligands. The reaction landscape for the dioxygen chemistry of the more electron-rich complexes is shown to be relatively flat. A total of four intermediates, including a superoxo and peroxy species, are observed with the most electron-rich complex. Two new intermediates are shown to form following the peroxo, which are capable of cleaving strong X–H bonds. In the absence of a sacrificial H atom donor, a deuterium isotope effect is observed (kH/kD = 3.5), implicating a hydrogen atom transfer (HAT) mechanism. With 1,4-cyclohexadiene, 0.5 equiv of benzene is produced prior to the formation of an EPR detected MnIII–MnIV bimetallic species, and 0.5 equiv after its formation.

INTRODUCTION

Fundamental scientific research is needed in order to develop methods for efficiently capturing sunlight, and converting its energy into storable fuels. Nature accomplishes this via photosynthesis, which converts solar energy into energy that is stored in a chemical bond by extracting electrons from H2O to form O2.1–4 The sluggish kinetics of H2O oxidation has been a major concern for existing fuel cells.5 Nature had a few billion years to restructure H2O oxidation catalysts, therefore understanding the mechanism by which it facilitates this reaction, or its microscopic reverse, would be of value. However, despite its relevance to photosynthesis,6–9 the dioxygen chemistry of Mn remains relatively unexplored6,10–12 relative to that of Fe and Cu.13–19 Very little is known about the photosynthetic Mn-induced O–O bond forming step,20 because it occurs following the rate-determining step.21–25 An unobserved peroxy intermediate is proposed to form,22–24 which then readily evolves O2.

Previously we showed that coordinatively unsaturated [MnII(LMepy)]+ (LMepy = (6-Me-DPEN)N4Me2S) reacts with O2 at low temperatures (−40 °C) to form dioxygen-bound [Mn(MLmpy)(O2)]+ (MLmpy = (3Mepy)2), en route to the first example of a crystallographically characterized binuclear peroxy-bridged dimer.26 Dioxygen binding to 1MLmpy was shown to occur on the millisecond time-scale.6 A thiolate was incorporated into our ligand scaffold in order to (1) provide a chromophore that facilitates the spectroscopic
Rationale for the ligand design of the complexes studied herein stems in part from a previous study in which a correlation between peroxo $\mathrm{O-O}$ bond lengths and $\mathrm{Mn}^{III}$-$\mathrm{N}^{Au}$ distances ($\mathrm{N}^{Au} = \mathrm{N}$-heterocycle) was observed with a series of alkylperoxo $\mathrm{Quino,MePy,Mepy,MiPy,Lpy,MiPy}_{\text{LMn}^{III}-\text{OOR}}$ ($\text{R} = \text{Bu, Cm}$) compounds.\textsuperscript{49} We refer to the interaction between the Mn ion and the $\mathrm{N}^{Au}$ ligand as $\mathrm{Mn}^{III}$-$\mathrm{N}^{Au}$, because although not within bonding distance, the $\mathrm{N}^{Au}$ ligand was shown (by X-ray crystallography) to point directly toward the metal ion, and (by spectroscopic methods) to influence properties of the complex in a systematic way. A decrease in the mean $\mathrm{Mn}^{III}$-$\mathrm{N}^{Au}$ distance (from 2.510 to 2.411 Å) was found to elongate the peroxo $\mathrm{O-O}$ bond (from 1.431 to 1.468 Å).\textsuperscript{6,7} In addition, the kinetic barrier to alkylperoxo $\mathrm{O-O}$ bond cleavage ($\Delta H^\ddagger$) was shown to directly correlate with the $\mathrm{Mn}^{III}$-$\mathrm{N}^{Au}$ distance. At ambient temperatures, dioxygen was shown to react with the $\mathrm{Mn}^{II}$ precursors (1) to form fairly stable bimetallic mono-oxo-bridged $\mathrm{Mn}^{III}$ complexes, (e.g., $\text{MePy}_{6}$ of Figure 1) in high yields (96–98%).\textsuperscript{5,48} Comparison of the mean $\mathrm{Mn}^{III}$-$\mathrm{N}^{Au}$ distance (Table 1) in these mono oxo-bridged products provides us with a predictive metric that potentially reflects the $\mathrm{O-O}$ bond cleaving properties of the ligand. The $\mathrm{Mn}^{III}$-$\mathrm{N}^{Au}$ distance was shown to depend upon the steric properties of the $\mathrm{N}^{Au}$ ligand scaffold.\textsuperscript{11,49} Inspection of space filling models shows that the substituent in the 6-position of the pyridine ring clashes with one of the gem-dimethyis adjacent to the thiolate sulfur. This prevents the pyridine nitrogen from approaching the metal to the optimum $\mathrm{Mn}^{III}$-$\mathrm{N}^{Au}$ bond distance, if the substituent is larger than a hydrogen. With a hydrogen in the 6-position, the $\mathrm{Mn}^{III}$-$\mathrm{N}^{Au}$ distance is within the normal bonding range (Table 1), and thus the use of a single line to represent a bond. With larger substituents, the $\mathrm{Mn}^{III}$-$\mathrm{N}^{Au}$ separation is well outside the normal bonding range. For example, with a Me-group, the $\mathrm{Mn}^{III}$-$\mathrm{N}^{Au}_{\text{avg}}$ separation is 0.33 Å longer than that of the less sterically encumbered 6-H derivative, $\text{MePy}_{6}$ (Table 1), resulting in a more Lewis acidic metal ion. If this is extrapolated to the corresponding peroxo compounds, the more Lewis acidic metal ion associated with bulkier substituents would strengthen $\pi$-interaction metal, and therefore shift electron density out of the peroxo $\pi^*$ ($\mathrm{O-O}$) into the $\mathrm{Mn}-\mathrm{O}$ $\pi$-bonding region, thereby strengthen the peroxo $\mathrm{O-O}$ bond.\textsuperscript{39} Conversely, the shorter $\mathrm{Mn}^{III}$-$\mathrm{N}^{Au}$ bond associated with 6-H-pyridine would create a more electron rich Mn ion, thereby weakening the peroxo $\mathrm{O-O}$ bond, and facilitating its cleavage. Consistent with this, no intermediates are observed in the reaction between $\mathrm{O}_2$ and $\text{Mn}^{III}(1\text{Py})^+$ ($1\text{Py}^*$) even at temperatures as low as $-78$ °C, whereas peroxo compound $3\text{MePy}$ (Figure 1) is stable enough to crystallize. In order to obtain more information regarding the $\mathrm{O-O}$ bond-cleaving step, we turned to ligand systems (Scheme 1) that support a $\mathrm{Mn}^{III}$-$\mathrm{O}$ bond cleaving step, we explore herein the low-temperature observation of metastable intermediates\textsuperscript{6,27–31} (2) lower the activation barrier to $\mathrm{O}_2$ binding, and (3) provide stability to $\mathrm{M}^{III}$-$\mathrm{O}_2$ species.\textsuperscript{32,33} The rate at which peroxo-bridged $3\text{MePy}$ forms is slow enough at $-40$ °C to monitor using a benchtop UV-vis spectrometer. However, with the $\text{LMePy}$ ligand system it was not possible to determine the mechanism by which the $\mathrm{O-O}$ bond of peroxo-bridged $3\text{MePy}$ cleaves to afford mono-oxo bridged $\text{Mn}^{III}$-$\mathrm{O}$-$\text{Mn}^{III}$ ($6\text{MePy}$, Figure 1), because this step was shown to be rate-determining.\textsuperscript{6} Mechanisms for $\mathrm{O-O}$ bond cleavage with Fe and Cu have been shown to involve either protonation of a $\mathrm{M}$-$\mathrm{OOH}$ at the distal oxygen,\textsuperscript{34} or the addition of a second metal ion to the distal oxygen to form a bridging peroxo. Ideally an $\eta^5$-$\eta^2$-side-on peroxo forms so as to maximize overlap with the empty $\eta^6$($\mathrm{O-O}$)\textsuperscript{14,19} In contrast, mechanistic details regarding Mn-promoted $\mathrm{O-O}$ bond cleavage versus formation remain relatively unexplored.\textsuperscript{35–41} An end-on peroxo complex is expected to be more stable than a side-on peroxo complex, perhaps explaining why we were able to crystallize $3\text{MePy}$. Prior to our work,\textsuperscript{6} there were no characterized examples of binuclear end-on or side-on $\text{Mn}^{III}$-peroxos, and there were only a handful of examples of mononuclear $\eta^5$-side-on $\text{Mn}^{III}$-peroxos,\textsuperscript{10,42–45} only one of which is derived from $\mathrm{O}_2$.\textsuperscript{10} An end-on $\text{Mn}^{III}$-OOH was shown to form upon protonation of the corresponding $\eta^7$-side-on $\text{Mn}^{III}$-peroxo compound; however, it was not crystallographically characterized.\textsuperscript{46} A series of structurally analogous five-coordinate, thiolate-ligated $\text{Mn}^{III}$ complexes (e.g., $1\text{MePy}$ of Figure 1) was previously reported by our group, which incorporate readily derivatized N-heterocycle amines ($\mathrm{N}^{Au} = 6$-H-pyridine (1Py), 6-Me-pyridine (1MePy), and quinoline (1Quino)), providing us with a method for tuning their steric and electronic properties.\textsuperscript{6,47} In order to obtain more information regarding the mechanism of the $\mathrm{O-O}$ bond cleaving step, we explore herein the low-temperature dioxygen chemistry of quinoline-ligated $[\text{Mn}^{III}(1\text{Quino})]^+$ (1Quino)\textsuperscript{48} in addition to that of a new $\text{Mn}^{III}$ complex, $[\text{Mn}^{III}(1\text{MePy})]^+$ (1MePy), containing a more electron donating substituent on the pyridine ring. We will show that the barrier to selected steps of the reaction, including $\mathrm{O}_2$ binding and release, and $\mathrm{O-O}$ bond cleavage, can be adjusted by changing the electron donor character of the ligand.\textsuperscript{37} Table 1. Mean Crystallography-Determined $\text{Mn}^{III}$-$\text{N}^{Au}$ Distance for Bimetallic Mono-Oxo-Bridged $\text{Mn}^{III}$ Complexes, 6

<table>
<thead>
<tr>
<th>N^{Au} complex</th>
<th>Mn-$\text{N}^{Au}_{\text{avg}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-H-pyridine</td>
<td>6Py</td>
</tr>
<tr>
<td>6-MeO-pyridine</td>
<td>6MeOpy</td>
</tr>
<tr>
<td>Quinoline</td>
<td>6Quino</td>
</tr>
<tr>
<td>6-Me-pyridine</td>
<td>6MePy</td>
</tr>
</tbody>
</table>

Figure 1. Low temperature reaction between $1\text{MePy}$ and $\mathrm{O}_2$ affords $6\text{MePy}$ via observable superoxo $2\text{MePy}$ and peroxo $3\text{MePy}$ intermediates.
Scheme 1. Low Temperature Reaction between 1 and O2 Affords Mono Oxo Bridged 6 via Observable Superoxo, 2, and Peroxo, 3, Intermediates4

![Scheme 1](image)

footnotes:

1L = py, Mepy, MeOpy, and Quino.

than 6-Me-pyridine 6Mepy, but longer than pyridine 6py. Distances in 6 were used as a predictive parameter, since we do not have structures for all of the peroxo compounds. Quinoline \([\{\text{Mn}^\text{III}(\text{LQuino})\}_2(\mu-\text{O})\}^2\text{+}\) and 6-MeO-pyridine \([\{\text{Mn}^\text{III}(\text{LMepy})\}_2(\mu-\text{O})\}^2\text{+}\) both fit this criterion (Table 1). Below, we examine the temperature-dependent kinetics of the reaction between O2 and the MnII precursors to 6Quino and 6Mepy, \([\text{Mn}^\text{II}(\text{LQuino})\] \(\text{+}\) (1Quino) and \([\text{Mn}^\text{II}(\text{LMepy})\] \(\text{+}\) (1Mepy), respectively (Scheme 1). We will show that the relative stability and reactivity of metastable intermediates, and the barriers to O2 binding or release, and peroxo O–O bond cleavage, is highly dependent on the supporting ligands. By changing the solvents and corresponding solvent C–H bond strength, or by adding a sacrificial H atom donor, we are able to spectroscopically observe two new intermediates, each of which is capable of abstracting H atoms from strong X–H bonds (X = C, or O).

Reactivity of 1Quino with Dioxgen. The low-temperature (−73 °C) reaction between colorless \([\text{Mn}^\text{II}(\text{LQuino})\] \(\text{+}\) (1Quino) \(48\) and O2 affords a metastable green intermediate, 3Quino, which rapidly converts to mono oxo-bridged 6Quino \(\lambda_{\text{max}} = 580 \text{ nm}\). \(48\) The stability of 3Quino is temperature-dependent. In CH3CN \((\text{f.p.} = -40 ^\circ \text{C}, \text{C–H BDE} = 93 \text{ kcal/mol})\), metastable 3Quino decays in ~30 s at −40 °C, and is therefore best observed using a stopped-flow instrument. In CH3Cl \((\text{f.p.} = -90 ^\circ \text{C}, \text{C–H BDE} = 98 \text{ kcal/mol})\), on the other hand, intermediate 3Quino is more stable at −90 °C \((15048 \text{ ms}) = 7 \text{ min}\) making it possible to obtain a spectrum using a benchtop UV–vis spectrometer (Figure 2). Given the close similarity of its electronic absorption spectrum to that of peroxo-bridged 3Mepy \(\lambda_{\text{max}} = 640 \text{ nm}\), \(15057\) it was deemed likely that 3Quino is also a peroxo-bridged dimer, \([\{\text{Mn}^\text{III}(\text{LQuino})\}_2(\mu-\text{O}_2)\}^2\text{+}\) (3Quino). This is supported by a low-resolution crystal structure (Figure S1), the connectivity of which indicates that there are two bridging oxygens (Table S1). In addition, 0.48 equiv of H2O2 are released per Mn ion upon the addition of 1.34 equiv of H2SO4 to 3Quino (see assay conditions in SI) consistent with a peroxo-bridged dimer. Metrical parameters (Table S2) of the DFT optimized structure (Figure 3), calculated using the spin-unrestricted B3LYP hybrid functional and the 6-311G basis set, are consistent with a trans-\(\mu\)-1,2-peroxo-bridged \(\text{Mn}^\text{III}_2\) dimer \((\text{O–O} = 1.516 \text{ Å}, \text{Mn(1)–O(1)} = 1.856 \text{ Å}, \text{Mn(2)–O(2)} = 1.846 \text{ Å}, \text{Mn–S}\text{avg} = 2.35 \text{ Å}, \text{Mn(1)–S(Mn(2)} = 4.244 \text{ Å, Mn–O–O}\text{avg} = 101^\circ\) The time-dependent DFT (TD-DFT) calculated electronic absorption spectrum (Figure 3) is in good agreement with the experimental spectrum (Figure 2). Transition-difference density plots show that these bands correspond to charge transfer transitions, and involve a mixed peroxo/thiolate Mn(d) transition at higher energies and a thiolate \(\rightarrow\) Mn(d) transition at lower energies (Figure S2). The calculated exchange coupling constant, \(J_{\text{calc}} = 3.8 \text{ cm}^{-1}\), indicates that the two MnIII ions are essentially uncoupled. The calculated peroxo O–O bond length of 3Quino is 0.06 Å longer than the crystallographically determined O–O bond of peroxo-bridged 3Mepy \(1.452(5) \text{ Å}\), indicating that this bond should be more readily cleaved in 3Quino.

Temperature-Dependent Kinetics for the Formation of Peroxo 3Quino. Kinetics data for the formation of peroxo 3Quino and its subsequent conversion to mono-oxo bridged 6Quino (Scheme 1), were collected at low temperatures using a
stopped-flow instrument. The build-up and decay of $3^{\text{Quino}}$ was followed at 749 nm, where interference from $6^{\text{Quino}}$ is minimal. As illustrated in the time-resolved electronic absorption spectra of Figure S3, intermediate $3^{\text{Quino}}$ forms in less than 10 s at $-20$ °C (blue trace, $\lambda_{\text{max}} = 652$ nm) en route to the purple mono oxo bridged product, $6^{\text{Quino}}$ (pink trace, $\lambda_{\text{max}} = 565$ nm). No additional intermediates, prior to $3^{\text{Quino}}$, or in between $3^{\text{Quino}}$ and $6^{\text{Quino}}$, were detected with this particular ligand system (vide infra). The general kinetic scheme reflecting the two spectrophotometrically observed processes is shown in eqs 1 and 2 below. Under pseudo-first-order conditions, in the presence of excess $O_2$, kinetic traces could be fit to the biexponential eq 3, affirming the pseudo-first-order rate constants ($k_{\text{obs,Quino}}$ and $k_{\text{obs,Quino}}$) of eqs 1 and 2, respectively. Residuals were slightly larger for fits to a single exponential relative to fits to a biexponential. The observed rate constant for eq 1, $k_{\text{obs,Quino}}$, was found to increase linearly (Table S3) with increasing $O_2$ concentration (Figure S4), indicating that the reaction is first order with respect to $[O_2]$. The second-order rate constant ($k_{\text{Quino}}$) was obtained from the slope of $k_{\text{obs,Quino}}$ vs $[O_2]$ plots (Table 2) at four different temperatures. The nonzero, and increasing value of the $y$-intercept with temperature in Figure S4, indicates that either peroxo $3^{\text{Quino}}$ formation (eq 1), or a step prior to peroxo formation, is reversible. The final absorbance values associated with the maximum accumulation of $6^{\text{Quino}}$ were found to be independent of $[O_2]$, providing support for irreversible formation of peroxo $3^{\text{Quino}}$. Together these suggest that a step prior to peroxo $3^{\text{Quino}}$ formation, i.e., $O_2$ binding, is reversible (vide infra). The observed pseudo-first-order rate constants, $k_{\text{obs,Quino}}$, for eq 2 were found to be independent of $[O_2]$ over the temperature range examined (Figure S5) indicating that the rate of $3^{\text{Quino}}$ to $6^{\text{Quino}}$ conversion is zero-order with respect to $[O_2]$.

Table 2. Experimentally Obtained Rate Constants and Activation Parameters for the Formation of Peroxo-Bridged $3^{\text{Quino}}$ ($k_{\text{1,obs,Quino}}$) from $1^{\text{Quino}}$ (0.30 mM) + $O_2$ (4.1 mM) in CH$_3$CN, and Its Conversion to Mono Oxo-Bridged $6^{\text{Quino}}$ ($k_{\text{2,obs,Quino}}$)

<table>
<thead>
<tr>
<th>temperature (K)</th>
<th>$k_{\text{1,obs,Quino}}$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_{\text{2,obs,Quino}}$ (M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>243.15</td>
<td>3.7 ± 0.3 × 10$^1$</td>
<td>1.49 ± 0.78 × 10$^{-2}$</td>
</tr>
<tr>
<td>253.15</td>
<td>4.78 ± 0.08 × 10$^1$</td>
<td>2.07 ± 0.26 × 10$^{-2}$</td>
</tr>
<tr>
<td>263.15</td>
<td>5.42 ± 0.06 × 10$^1$</td>
<td>3.01 ± 0.13 × 10$^{-2}$</td>
</tr>
<tr>
<td>273.15</td>
<td>6.3 ± 0.2 × 10$^1$</td>
<td>3.33 ± 0.11 × 10$^{-2}$</td>
</tr>
<tr>
<td>$\Delta H^{\ddagger}$ (kJ mol$^{-1}$)</td>
<td>7.8(9)</td>
<td>15(1)</td>
</tr>
<tr>
<td>$\Delta S^{\ddagger}$ (J mol$^{-1}$ K$^{-1}$)</td>
<td>$-182(3)$</td>
<td>$-220(4)$</td>
</tr>
<tr>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>10(1)</td>
<td>15(1)</td>
</tr>
</tbody>
</table>

In the next set of stopped-flow experiments, the concentration of $1^{\text{Quino}}$ was varied (0.2–0.8 mM after mixing) while maintaining a fixed excess concentration of $O_2$ (4.1 mM after mixing) at $-10$ °C, allowing us to verify the proposed mechanism, and determine the reaction order with respect to $Mn^{\text{II}}$ $1^{\text{Quino}}$. The observed rate constants ($k_{\text{1,obs,Quino}}$ and $k_{\text{2,obs,Quino}}$) were obtained by fitting kinetic traces to eq 3. The observed pseudo-first-order rate constant for the formation of $3^{\text{Quino}}$ ($k_{\text{1,obs,Quino}}$) displays a linear dependence on the concentration of $1^{\text{Quino}}$ in the presence of excess $[O_2]$ (Figure S6), confirming second-order dependence on $Mn^{\text{II}}$ overall. This would be consistent with $3^{\text{Quino}}$ being a binuclear peroxy (Figures 3 and S1). A large nonzero intercept (Figure S6) indicates that a process that is first order in $Mn^{\text{II}}$ (eq 4) contributes to the rate-determining step. Observed rate constants, $k_{\text{3,obs,Quino}}$, for the conversion of peroxo $3^{\text{Quino}}$ to oxo-bridged $6^{\text{Quino}}$ in the presence of excess $[O_2]$ are independent of $[1^{\text{Quino}}]$, indicating that this step (eq 6) is zero-order with respect to Mn (Figure S7). Collectively, the $O_2$ and $Mn^{\text{II}}$ concentration-dependence experiments described above are consistent with the proposed stepwise mechanism, outlined in eqs 4–6 above. This reaction sequence is analogous to that previously established for the reaction between $Mn^{\text{II}}$ 2Me-pyridine and $O_2$. Although not directly observed spectrophotometrically, superoxo $[Mn^{\text{II}}(L^{\text{Quino}})(O_2)]^+$ ($2^{\text{Quino}}$) is proposed to form as a transient intermediate (eq 4), prior to the formation of the observable peroxy intermediate 3Quino (eq 5). The analogous 6-Me-pyridine superoxo 2Me-pyridine (Figure 1) is, in contrast, observed by transient absorption spectroscopy using a stopped-flow instrument. The rate laws for each step in the mechanism are provided in eqs 7–9 below. The first two rate laws, eqs 7 and 8, are analogous to that previously established for $[Mn^{\text{II}}(L^{\text{Me-py}})]^+$ (1Me-py, Figure 1). Information regarding the rate of peroxy $O-O$ bond cleavage was not available for the 6-Me-pyridine system, however, because this step was too slow.6

$$2Mn^{\text{II}}(1^{\text{Quino}}) + O_2 \rightarrow Mn^{\text{III}}-O_2-Mn^{\text{II}}(3^{\text{Quino}})$$

(1)

$$Mn^{\text{III}}-O_2-Mn^{\text{III}}(3^{\text{Quino}})$$

$$\rightarrow Mn^{\text{III}}-O-Mn^{\text{III}}(6^{\text{Quino}}) + H_2O$$

(2)

rate = $ae^{-k_{\text{1,obs,Quino}}^{\text{Quino}} t} + be^{-k_{\text{2,obs,Quino}}^{\text{Quino}} t}$

(3)

Table 3. Calculated Rate Constants, Obtained from Global Fits to Time-Resolved Spectra, and Activation Parameters for the Formation of Putative Superoxo 2Quino ($k_{\text{1,cac,Quino}}$), Peroxo-Bridged 3Quino ($k_{\text{2,cac,Quino}}$), and Oxo-Bridged 6Quino ($k_{\text{3,cac,Quino}}$) in the Reaction between 1Quino and $O_2$ in CH$_3$CN

<table>
<thead>
<tr>
<th>temperature (K)</th>
<th>$k_{\text{1,cac,Quino}}$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_{\text{2,cac,Quino}}$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_{\text{3,cac,Quino}}$ (s$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>243.15</td>
<td>1.79 ± 0.05 × 10$^1$</td>
<td>8.80 ± 0.05 × 10$^1$</td>
<td>1.54 ± 0.16 × 10$^{-2}$</td>
</tr>
<tr>
<td>253.15</td>
<td>2.24 ± 0.01 × 10$^1$</td>
<td>1.30 ± 0.20 × 10$^1$</td>
<td>2.31 ± 0.12 × 10$^{-2}$</td>
</tr>
<tr>
<td>263.15</td>
<td>3.00 ± 0.08 × 10$^1$</td>
<td>1.59 ± 0.06 × 10$^1$</td>
<td>3.07 ± 0.30 × 10$^{-2}$</td>
</tr>
<tr>
<td>273.15</td>
<td>4.98 ± 0.09 × 10$^1$</td>
<td>2.30 ± 0.30 × 10$^1$</td>
<td>3.12 ± 0.25 × 10$^{-2}$</td>
</tr>
<tr>
<td>$\Delta H^{\ddagger}$ (kJ mol$^{-1}$)</td>
<td>16(3)</td>
<td>15(6)</td>
<td>16(2)</td>
</tr>
<tr>
<td>$\Delta S^{\ddagger}$ (J mol$^{-1}$ K$^{-1}$)</td>
<td>$-150(12)$</td>
<td>$-106(5)$</td>
<td>$-211(6)$</td>
</tr>
<tr>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>18(3)</td>
<td>17(5)</td>
<td>18(3)</td>
</tr>
</tbody>
</table>
The proposed mechanism for the formation of quinino peroxo 3^{Quino} and its conversion to mono oxo-bridged 6^{Quino} (Scheme 1), summarized in eqs 4–6, was verified using global fits to the time-resolved spectra using ReactLab. The rate constants \( k_{\text{calc}}^{\text{Quino}} \) obtained from these global fits (Table 3) show that the rate at which O\(_2\) binds to 1^{Quino} \( (k_{\text{calc}}^{\text{Quino}}, \text{Table 3}) \) is roughly equivalent to the rate at which peroxo 3^{Quino} is observed to form \( (k_{\text{eq}}^{\text{Quino}}, \text{Table 2, Figure 4}) \). In other words, the rate-determining step in peroxo 3^{Quino} formation involves O\(_2\) binding. Consistent with this, the rate at which superoxo 2^{Quino} converts to peroxo 3^{Quino} \( (k_{\text{calc}}^{\text{Quino}}) \) is 2 orders of magnitude faster (Table 3) than the rate at which it forms \( (k_{\text{eq}}^{\text{Quino}}) \), making it impossible to observe (Figure 4). Calculated spectra (Figure S8) are in good agreement with the experimentally measured spectrum (Figure 2). A comparison with our previously reported system,\(^6\) shows that the rate at which O\(_2\) binds to 1^{Quino} \( (30.0(8) \text{ M}^{-1} \text{s}^{-1}, \text{Table 3}) \) is 2 orders of magnitude slower than the rate at which O\(_2\) binds to 1^{Meppy} \( (3.8(2) \times 10^3 \text{ M}^{-1} \text{s}^{-1}) \), at 263 K. The rate at which superoxo 2^{Quino} converts to peroxo 3^{Quino} \( (1.6(6) \times 10^3 \text{ M}^{-1} \text{s}^{-1}, \text{Table 3}) \), on the other hand, is 2 orders of magnitude faster (at 263 K) than the conversion (Figure 1) of superoxo 2^{Meppy} to peroxo 3^{Meppy} \( (k_2 = 4.17(3) \times 10^7 \text{ M}^{-1} \text{s}^{-1}) \). It is worth noting that the rate constant \( k_{\text{eq}}^{\text{Quino}} \) is less reliable than \( k_{\text{calc}}^{\text{Quino}} \) since it was calculated using global fits. The nonzero, and increasing value of the y-intercept with temperature in the \( k_{\text{obs}}^{\text{Quino}} \) versus [O\(_2\)] plots of Figure S4 indicates that the rate-determining step, i.e., O\(_2\) binding to 1^{Quino} is reversible. One can obtain the rate constant associated with the release of O\(_2\) from the intercept of these plots, and then calculate the temperature-dependent equilibrium constants, \( K_{\text{eq}}^{\text{Quino}} = k_{1}^{\text{Quino}} / k_{-1}^{\text{Quino}} \), summarized in Table 4. Previously reported superoxo 2^{Meppy} on the other hand, does not release O\(_2\) once it binds.\(^6\) Thermodynamic parameters for O\(_2\) binding to 1^{Quino} \( (\Delta H = -20 \text{ kJ mol}^{-1} \text{ and } \Delta S = -23 \text{ J mol}^{-1} \text{ K}^{-1}) \) were obtained from a van’t Hoff plot (Figure S9). The negative entropy value is consistent with an associative process. The activation parameters for O\(_2\) release from 2^{Quino}, \( E_a = 30(5) \text{ kJ mol}^{-1}, \Delta H^\ddagger = 28(3), \Delta S^\ddagger = -160(9) \), were obtained from Arrhenius (Figure S10) and Eyring (Figure S11) plots, respectively. Although the negative entropy of activation is not what one would expect for a dissociative process, it indicates that the barrier associated with the bond rearrangement required for electron transfer (\( \text{Mn}^{III} \rightarrow \text{Mn}^{II} \)) is large enough to offset the entropy gained via O\(_2\) release. The \( K_{\text{eq}}^{\text{Quino}} \) for O\(_2\) binding to 1^{Quino} is 4 orders of magnitude larger than \( K_{\text{eq}}^{\text{Meppy}} \) for O\(_2\) binding to \( [\text{ppy}^{\text{II}}(\text{TPP})] \) \( (K_{\text{eq}}^{\text{298 K}} = 2.3 \times 10^{-2} \text{ M}^{-1} \) \( \) \( \text{E} = 26(2) \text{ kJ mol}^{-1} \)), but comparable to \( K_{\text{eq}}^{\text{Meppy}} \) for O\(_2\) binding to \( [\text{Co}^{\text{III}}(\text{SalMeDPT})] \) \( (7, K_{\text{eq}}^{233 K}) = 1.63 \times 10^{10} \text{ M}^{-1} \) \( \) \( \text{E} = 7.50 \text{ kJ mol}^{-1} \), but \( 7 \text{ kJ mol}^{-1} \) lower than O\(_2\) binding to MbFe(II) \( (\text{Mb} = \text{myoglobin}) \).\(^5\) The barrier to O\(_2\) release is \( 13 \text{ kJ mol}^{-1} \), lower than that of O\(_2\) binding to MbFe-O\(_2\).\(^5\) Activation parameters (Tables 2 and 3) for peroxo 3^{Quino} formation (Figure S12 and S13), O\(_2\) binding to 1^{Quino} (Figure S14 and S15), as well as superoxo 2^{Quino} \rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\right
The barrier to cleavage of the peroxo O–O bond of 3Quino is comparable to the barrier to homolytic O–O bond cleavage for Fe hydroperoxo [(TMC)FeIII−OOH]2+.52 If Mn peroxo 3Quino follows a pathway (Figure 4) analogous to that of Cu- and Fe-peroxo compounds,15–19 then homolytic O–O bond cleavage would afford a high-valent bis-oxo-bridged compound, L3QuinoMnIV(μ-O)2MnIVL3Quino (4Quino). Two electrons, and two protons, or, two H atoms, would then be required to convert this high-valent bis-oxo intermediate to mono-oxo bridged L3QuinoMnIII(μ-O) (6Quino). We were unable to observe intermediates following quinoline peroxo 3Quino, however, even at temperatures as low as −120 °C (in Me-THF). This implies that O–O bond cleavage is the rate-determining step in this case. In order to increase the stability of high-valent intermediates and increase the likelihood of observing intermediates beyond the peroxo, we synthesized a more electron-rich ligand system, containing a 6-MeO-pyridine substituent, LMeOpy.

**Synthesis of a New MnII Complex Containing a Less Sterically Encumbered, More Electron-Donating Pyridine Substituent.** The pentadentate ligand LMeOpy, which is a derivative of previously reported LMePy, was synthesized according to the procedure outlined in the Supporting Information. This ligand features a 6-methoxy-pyridine substituent, which is simultaneously more electron-donating and less sterically encumbering than LMePy (A-value = 0.6 versus 1.7 for MeO and Me, respectively).53 The corresponding MnII complex, [MnII(LMeOpy)]2(μ-O)2 (1MeOpy), was synthesized via a metal-templated Schiff-base condensation between N,N-bis(6-methoxy-2-pyridylimethyl)ethane-1,2-diamine and 3-methyl-3-mercaptopro-2-butanone, as previously described for 1Mepy and 1Quino.54 Crystallographic characterization showed that the MnII complex derived from this ligand, 1MeOpy, is dimeric in the solid state (Figure S21). However, its magnetic moment (μeff = 5.88 μμ, CH3CN, 298 K), EPR spectrum (hyperfine splitting 90 G, Figure S22), and solution-state ESI-MS (Figure S23), and cyclic voltammogram (Figure S24) all indicate that it is monomeric in solution.

**Reactivity of 1MeOpy with Dioxygen.** Like complexes 1Mepy and 1Quino, reduced 1MeOpy rapidly reacts with O2 (Scheme 1) under ambient conditions to ultimately afford binuclear mono oxo-bridged [{MnIII(LMeOpy)}2(μ-O)]2+ (6MeOpy), characterized by its λmax = 565 nm (ε = 1030 M−1 cm−1) in the electronic absorption spectrum (Figure S25), the ORTEP of which is shown in Figure 6. The mean Mn···NAr separation in 6MeOpy is 0.15 Å shorter than that of 6-Me-pyridine 6Mepy, and 0.18 Å longer than that of 6-H-pyridine 6Py (Table 1), indicating, based on previously established trends,54 that the corresponding peroxo derivative should have a weaker O–O bond, but will likely be observable (vide supra). In addition, the more electron-rich metal ion should be capable of stabilizing high-valent intermediates (vide infra). Consistent with this, four metastable intermediates are observed en route to mono oxo-bridged 6MeOpy. At low temperatures (−73 °C) a metastable green intermediate, 3MeOpy, (λmax(CH2Cl2) = 630 nm, Figure 6), and O2 (Figure 7). Given the similarity of this spectrum (Figure 7) to that of peroxo-bridged 3Mepy (λmax = 640 nm, Figure 2) and peroxo-bridged 3Quino (λmax = 660 nm, Figure 2), this intermediate was tentatively assigned as a peroxo-bridged dimer, [{MnIII(LMeOpy)}2(μ-O2)]2+ (3MeOpy). DFT and TD-DFT calculations were found to support this assignment. Metrical parameters (Table S6) for the DFT optimized structure, calculated using the spin-unrestricted B3LYP hybrid functional and the 6-311G basis set, are consistent with 3MeOpy being a trans-μ-1,2-peroxo-bridged MnIII dimer (Figure 8), analogous to 3Mepy and 3Quino. The TD-DFT calculated electronic absorption spectrum (Figure S26) is in good agreement with the experimental spectrum of Figure 7, and...
Figure 8. DFT optimized structure of peroxo-bridged \( \text{3MeOpy} \). O−O = 1.518 Å, Mn−O=1.86 Å, Mn−S=2.33 Å; Mn(1)−Mn(2) = 4.361 Å, Mn−O−O=106°.

The calculated exchange coupling constant, \( J^\text{calc} = -0.53 \) cm\(^{-1} \), indicates that the two MnIII ions are essentially uncoupled. The calculated O−O bond length (1.518 Å) is 0.02 Å longer than that of \( 3\text{Quino} \), and 0.07 Å longer than that of \( 3\text{MeOpy} \) (O−O = 1.452(5) Å), indicating that this bond should cleave more readily in \( 3\text{MeOpy} \). Consistent with this, \( 3\text{MeOpy} \) is less stable than \( 3\text{MeOpy} \) and \( 3\text{Quino} \), and is not readily observed at temperatures above −73 °C unless a stopped-flow instrument is used.

Kinetics data for O₂ binding to MnII \( \text{3MeOpy} \) and the formation of putative peroxo \( \text{3MeOpy} \) were collected at low temperatures using a stopped-flow instrument. The build-up and decay of putative superoxo \( \text{2MeOpy} \) was followed at 504 nm. As illustrated in the time-resolved electronic absorption spectra of Figure 9, the calculated exchange coupling constant, \( J^\text{calc} = -0.53 \) cm\(^{-1} \), indicates that the two MnIII ions are essentially uncoupled. The calculated O−O bond length (1.518 Å) is 0.02 Å longer than that of \( 3\text{Quino} \), and 0.07 Å longer than that of \( 3\text{MeOpy} \) (O−O = 1.452(5) Å), indicating that this bond should cleave more readily in \( 3\text{MeOpy} \). Consistent with this, \( 3\text{MeOpy} \) is less stable than \( 3\text{MeOpy} \) and \( 3\text{Quino} \), and is not readily observed at temperatures above −73 °C unless a stopped-flow instrument is used.

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the higher the redox potential, the higher the barrier to \( \text{O}_2 \) binding (Figure 11). This indicates \( \text{O}_2 \) binding is coupled with the oxidation of the metal ion, as one would expect for a process that converts \( \text{O}_2 \) to superoxide, \( \text{O}_2^- \). Peak potentials, as opposed to \( E_{1/2} \) values are compared in Figure 11, since the cyclic voltammogram wave associated with the 1Quino is irreversible.55 In addition, comparison of the steric properties shows that the activation barrier decreases as the metal ion becomes more accessible (Figures 12, 13, and S34). The Mn(II) ion is more accessible in 1MeOpy, less so in 1Quino, and least accessible in the more sterically encumbered 1Mepy. A similar correlation is observed between the redox potential and the kinetic barrier to the conversion of superoxo 2 to the corresponding peroxo 3 (Figure 13).

Barrier to \( \text{O}--\text{O} \) Bond Cleavage and the Observation of Additional Intermediates. As noted in the introduction, the steric properties of the substituted N-heterocycles differ dramatically, and have been shown to influence the barrier to alkylperoxo \( \text{O}--\text{O} \) bond cleavage.6 The least sterically encumbered complexes contain shorter Mn···NAr distances and weaker alkylperoxo O--O bonds. This is because the metal ion becomes less Lewis acidic as the Mn···NAr distance decreases, and this decreases \( \pi \)-interaction between the peroxo \( \pi^* \)(O--O) orbital and the metal ion d-orbital. X-ray emission (XES) spectroscopically calibrated calculations showed that peroxo 3Mepy adheres to this correlation, as well.11 Presumably this also applies to the other dioxygen-derived peroxos, 3Quino and 3MeOpy, described herein (Scheme 1). Kinetic studies were used to determine whether this was indeed the case.

Observation of peroxo 3MeOpy, and the metastable intermediates that follow, is optimized when excess amounts of \( \text{O}_2 \) ([\( \text{O}_2 \]) = 8.8 mM vs [1MeOpy] = 0.375 mM) and higher temperatures (\(-44^\circ \text{C}\)) are used (Figure 14). These conditions speed up the formation of superoxo 2MeOpy and its conversion to peroxo 3MeOpy. Under these conditions, peroxo 3MeOpy forms within 1.2 s (Figure 14), and then converts within 21 s to a metastable species, 4MeOpy. There is a clean isosbestic point at 730 nm, indicating that at most two species contribute to the absorbance at higher wavelengths. However, at wavelengths below 525 nm, the isosbestic points are less clear because several species (including superoxo 2MeOpy, and peroxo 3MeOpy) contribute to this region of the spectrum. On the basis of global fits to the data, 4MeOpy possesses absorption bands at 805 and 497 nm, and a shoulder at 532 nm (Figure 14).

According to the reaction scheme of Figure 10, the species most likely to form following peroxo 3MeOpy, would be a high-valent bis \( \mu-\text{oxo} \), \([[(\text{LMeOpy})\text{Mn}^\text{IV})_2(\mu^-\text{O})_2]^2+\) (4MeOpy). Conversion of 3MeOpy to 4MeOpy would involve peroxo \( \text{O}--\text{O} \) bond cleavage, explaining why higher temperatures are required. Rate constants for the conversion of 3MeOpy to 4MeOpy were obtained
from Global fits to the data. A comparison of the half-lives of 3MeOpy ($k_{3MeOpy} (193 \text{ K}) = 0.06(3) \text{ s}^{-1}, t_{1/2} = 11.5 \text{ s}$), 3Quino (Table S10), and 3Mepy (Table S10), shows that there is a correlation between the barrier to peroxo O–O bond cleavage and the experimentally measured redox potential, $E_{p,c}(\text{MnIII/II})$. This effect is enhanced if one takes into account the fact that these half-lives were measured at different temperatures, due to the fact that peroxo-bridged 3MeOpy is not observed above 233 K, and temperatures below 233 K were required for an accurate determination of rate constants for 3Quino due to its instability. The higher the redox potential, the more Lewis acidic the metal ion, and the more $\pi$-interaction with the filled peroxo $\pi^*$ orbital is facilitated. Redox potentials for the MnIII/II couple are used, as opposed to the MnIV/III couple, because our Mn(IV) derivatives are too reactive (vide infra) to obtain the latter. The metastable, reactive nature of 4MeOpy contrasts with the majority of bis-oxo bridged MnIVMnIV dimers, likely reflecting the electron donating properties of the thiolate.

Following its formation, putative high-valent bis oxo Mn$^{\text{III}}$Mn$^{\text{IV}}$ (4MeOpy, $\lambda_{\text{max}} = 805 \text{ nm}$) converts more slowly (Table S9) to a metastable red species with $\lambda_{\text{max}} = 505 \text{ nm}$, and a reproducibly observed multiline $\perp$-mode EPR signal (Figure 15). The spectrum of Figure 15 is well simulated with an $S = \frac{1}{2}$ system with a rhombic g tensor with principal values 1.994, 2.004, and 2.016 coupled to two $^{55}\text{Mn}$ nuclei with isotropic hyperfine couplings of 325 and 180 MHz. These values are consistent with an antiferromagnetically coupled Mn$^{\text{III}}$Mn$^{\text{IV}}$ dimer. If the reaction between 1MeOpy and $\text{O}_2$ is carried out in the presence of 100 equiv of 1,4-cyclohexadiene (CHD), and then quenched immediately upon the formation of the red, EPR-active intermediate, then 0.5 equiv of benzene is detected by GC-MS (Figure S35). This indicates one H atom is abstracted en route to the red intermediate. If the same reaction is followed to its completion (Figure 10), then 1.0 equiv of benzene is detected, indicating that two H atoms in total, one before, and the other after the red intermediate (Figure S36), are abstracted en route to mono oxo-bridged 6MeOpy. In the absence of a sacrificial H atom donor the yield of 6MeOpy decreases if it is carried out in CH$_2$Cl$_2$ solvent (Figure 16). In this solvent, with its strong C–H bonds (98 kcal/mol), near quantitative yields of 6MeOpy are only observed when sacrificial H atom donor TEMPOH is added. If TEMPOD is used in place of TEMPOH, then a deuterium isotope effect ($k_H/k_D = 3.5$) is observed (Figure 17). Together these results indicate that the O$_2$-promoted conversion of 1MeOpy to 6MeOpy requires two e$^-$ and two H$^+$. (Figure 10).

Figure 14. Conversion of peroxo 3MeOpy to a metastable species, 4MeOpy, with $\lambda_{\text{max}} = 805 \text{ nm}$ monitored by transient absorption spectroscopy in CH$_3$CH$_2$CN at $-44 \, ^\circ\text{C}$. $[\text{O}_2] = 8.8 \text{ mM}$, [1MeOpy] = 0.375 mM, after mixing.

Figure 15. Low temperature (6.6 K) perpendicular-mode X-band (9.645 GHz) EPR spectrum of the MnIII/MnIV intermediate, 15, observed following peroxo 12. Microwave power = 0.2 mW, modulation amplitude = 0.75 mT.

Figure 16. Comparison of the rates of formation and yield of 6MeOpy in CH$_2$Cl$_2$, both in the absence (green) and presence of sacrificial H atom donors CHD (red) or TEMPOH (blue).
CONCLUSIONS

With this study, we have shown that the relative stability of metastable dioxygen intermediates can be tuned by adjusting the supporting ligands. Whereas $\text{O}_2$ binds irreversibly to 1-MeOpy, kinetics data shows that $\text{O}_2$ binding is less favored for the less Lewis acidic complexes 1-Quino and 1-MeOp, and the microscopic reverse process involving $\text{O}_2$ release from superoxo 2-Quino and 2-MeOp is more favorable. The Mn$^{III}$ complexes 1-MeOp and 1-Quino are complementary in that the initial $\text{O}_2$ binding step to form a superoxo intermediate is observable with 1-MeOp, but not with 1-Quino information regarding the barrier to $\text{O}_2$-O bond cleavage can be obtained for peroxo 3-Quino, but not for 3-MeOp or 3-MeOpy because they are too slow or too fast, respectively. The incorporation of a more electron rich, less sterically encumbering ligand (6-MeO-pyridine) ligand decreases the barrier to $\text{O}_2$ binding and release, as well as $\text{O}_2$-O bond cleavage, relative to the other derivatives. A strong correlation between the Mn$^{II/III}$ redox potential and the ligand-dependent activation barrier to $\text{O}_2$ binding and the conversion of superoxo to peroxo 3 is observed. The reaction landscape for the dioxygen chemistry of 1-Quino and 1-MeOp is shown to be relatively flat, compared to that of 1-MeOp, with respect to the barriers separating metastable intermediates. With this study, we have shown that the relative stability of metastable dioxygen intermediates can be tuned by adjusting the supporting ligands. With TEMPOH, the reaction is shown to be relatively flat, compared to that of 1-MeOp, with respect to the barriers separating metastable intermediates. With this study, we have shown that the relative stability of metastable dioxygen intermediates can be tuned by adjusting the supporting ligands. With TEMPOH, the reaction is shown to be relatively flat, compared to that of 1-MeOp, with respect to the barriers separating metastable intermediates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b04729.

Experimental section, crystallographic tables for 1-MeOp, 6-MeOp, and 3-Quino; $k_{obs}$ and DFT optimized metrical parameter tables, $k_{obs}$ vs [O$_2$] or [Mn] plots, van’t Hoff plot for O$_2$ binding to 1-MeOp, Eyring and Arrhenius plots, DFT calculated structures and Mulliken charges, TD-DFT calculated spectra for 3-Quino and 3-MeOp, ORTEP, ESI-MS, and EPR of 1-MeOp, quantitative UV–vis of 6-MeOp (PDF)

Crystal data (CIF)

Crystal data (CIF)

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Notes

The authors declare no competing financial interest.

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