Physical Properties and Reactivities of Peroxomanganese(III) Complexes

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Our goal is to contribute to an understanding of H₂O₂ activation by manganese centers by generating and characterizing catalytically-relevant intermediates, such as peroxomanganese(III) adducts.

1) Enhanced thermal stability of second generation Mn³⁺ intermediates and their activation by acid chlorides.

\[
\begin{align*}
[Mn^{II}(L'\text{BQ})(\text{OTf})_2]^+ & \quad \text{5 eq. } H_2O_2/1.5 \text{ eq } \text{Et}_3\text{N} \quad \text{MeCN/ }-40 \degree \text{C} \\
[Mn^{III}(O)(L'\text{BQ})]^+ & \quad \text{Electronic Absorption}
\end{align*}
\]

\[
\begin{align*}
\text{0.5 eq. CH}_3\text{COCl} & \quad \text{MeCN/ }-40 \degree \text{C} \\
\text{Electronic Absorption} & \quad \text{Absorbance (A.U.)}
\end{align*}
\]

2) The reaction landscape of a Mn²⁺ complex with superoxide and hydrogen peroxide, which features the conversion of a peroxomanganese(III) adduct to a bis(μ-oxo)dimanganese(III,IV) species was determined.

\[
\begin{align*}
[Mn^{II}N4py(\text{OTf})]^+ & \quad \text{X-band EPR (5 K, parallel mode)} \quad \text{[Mn^{III}(O)(N4py)]}^+ \\
& \quad \text{KO}_2 \quad \text{MeCN} \\
& \quad \text{X-band EPR (5 K, parallel mode)} \\
[Mn^{III}(O)(N4py)]^+ & \quad \text{KO}_2 \quad \text{MeCN}
\end{align*}
\]

\[
\begin{align*}
[Mn^{II}N4py(\text{OTf})]^+ & \quad \text{Electronic Absorption} \\
0.5 \text{ eq. CH}_3\text{COCl} & \quad \text{MeCN/ }-40 \degree \text{C} \\
& \quad \text{Electronic Absorption}
\end{align*}
\]

\[
\begin{align*}
& \quad \text{EPR (20 K)} \\
& \quad \text{Absorption (A.U.)}
\end{align*}
\]