Physical Properties and Reactivities of Peroxomanganese(III) Complexes

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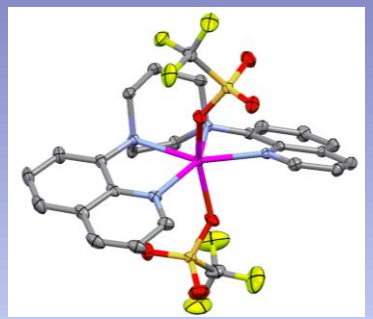
Our goal is to contribute to an understanding of H_2O_2 activation by manganese centers by generating and characterizing catalytically-relevant intermediates, such as peroxomanganese(III) adducts.

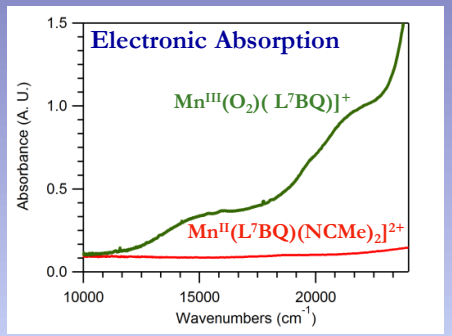
1) Enhanced thermal stability of second generation Mn^{III} intermediates and their activation by acid chlorides.



$[Mn^{II}(L^7BQ)(OTf)_2]$

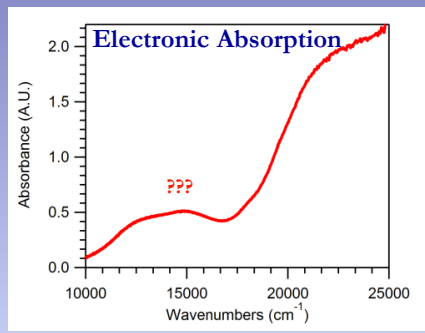
5 eq. H_2O_2/ 1.5 eq Et_3N

MeCN/ -40 °C

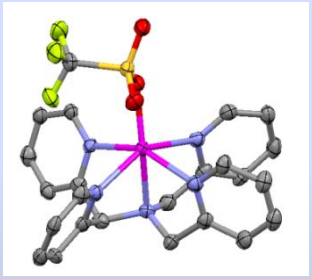


0.5 eq. CH_3COCl

MeCN/ -40 °C



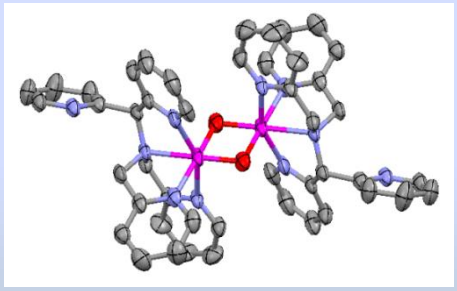
2) The reaction landscape of a Mn^{II} complex with superoxide and hydrogen peroxide, which features the conversion of a peroxomanganese(III) adduct to a bis(μ-oxo)dimanganese(III,IV) species was determined.



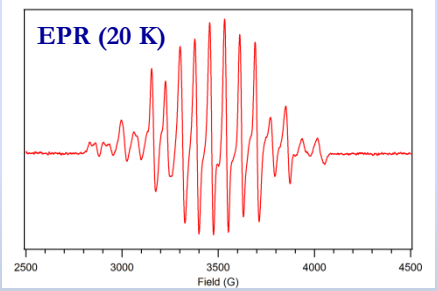
$[Mn^{II}(N4py)(OTf)]^+$

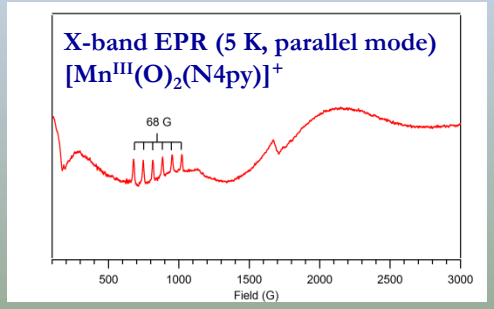
H_2O_2, Et_3N

MeCN



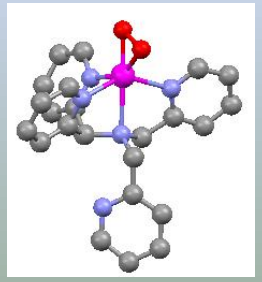
$[Mn^{III}Mn^{IV}(\mu\text{-}O)_2(N4py)_2]^{3+}$





KO_2

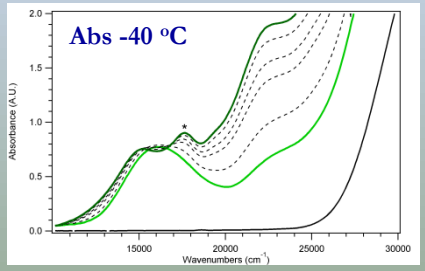
MeCN



$[Mn^{III}(O)_2(N4py)]^+$

DFT Model

+ $[Mn^{II}(N4py)(OTf)]^+$



Leto, D. F., Day, V. W. and Jackson T. A. *Manuscript in preparation.*