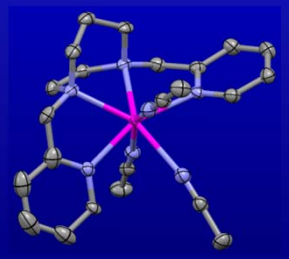
Physical Properties and Reactivities of Peroxomanganese(III) Complexes

Timothy A. Jackson, Department of Chemistry, University of Kansas, Lawrence, KS 66045.

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) A series of tetradentate aminopyridyl ligands with a range of steric and electronic properties were used to generate nine Mn^{III}-O_2 adducts by reacting Mn^{II} complexes with H_2O_2.

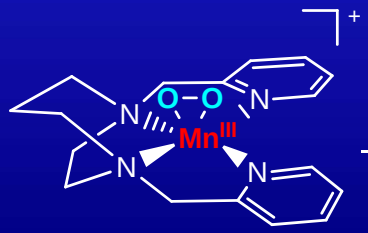
2) Reactivity studies using cyclohexanecarboxaldehyde (CCA) deformylation as a benchmark showed ligand sterics control the reaction rate, with $[Mn^{III}(O)_2(L^7py_2{}^H)]^+$ being among the most reactive Mn^{III}-O_2 species observed to date.



$[Mn^{II}(L^7py_2{}^H)(CH_3CN)_3]^{2+}$

5 eq H_2O_2 / 0.5 eq Et_3N

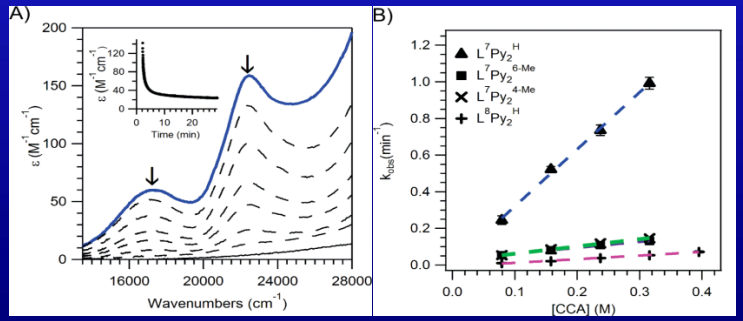
-40 °C / MeCN



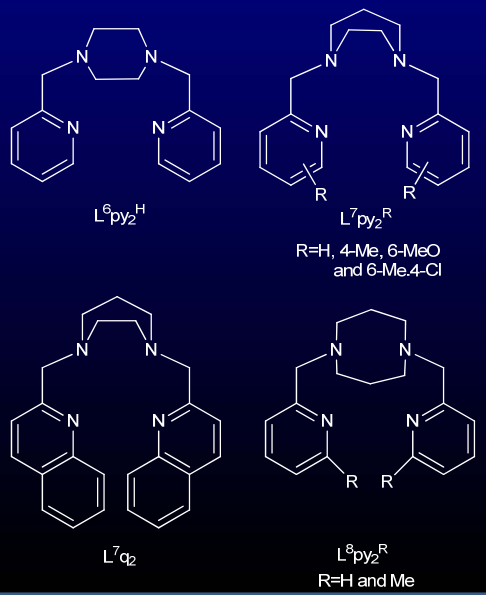
$[Mn^{III}(O)_2(L^7py_2{}^H)]^+$

excess CCA

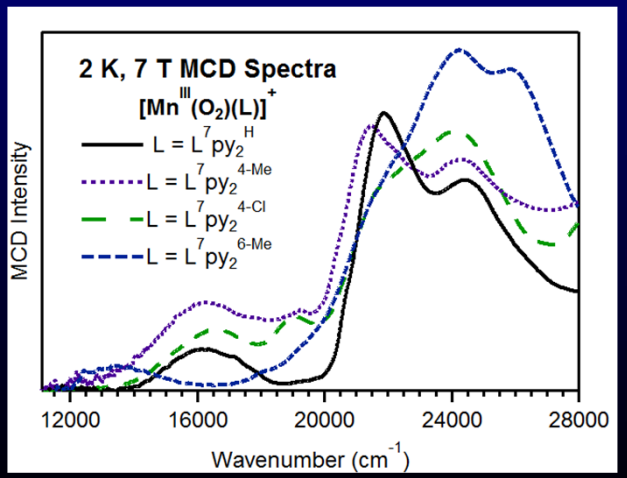
-40 °C / MeCN



Geiger, R. A., Chattopadhyay, S., Day, V. W. and Jackson T. A. *Dalton Trans.*, **2011**, *40*, 1707.



3) Electronic absoprtion, magnetic circular dichroism (MCD), EPR, and computational studies of a series of Mn^{III}-O_2 adducts (see ligands to the left) show that the steric effects of the ligand exert a larger influence on the Mn-O_{peroxo} binding mode than do electronic perturbations.



Geiger, R. A., Wijeratne, G. B., Day, V. W. and Jackson T. A. *Manuscript in preparation.*