

Spectroscopic Properties and Reactivity of a Mn^{III}-hydroperoxo Complex that is Stable at Room Temperature

Jackson Group
KU Chemistry

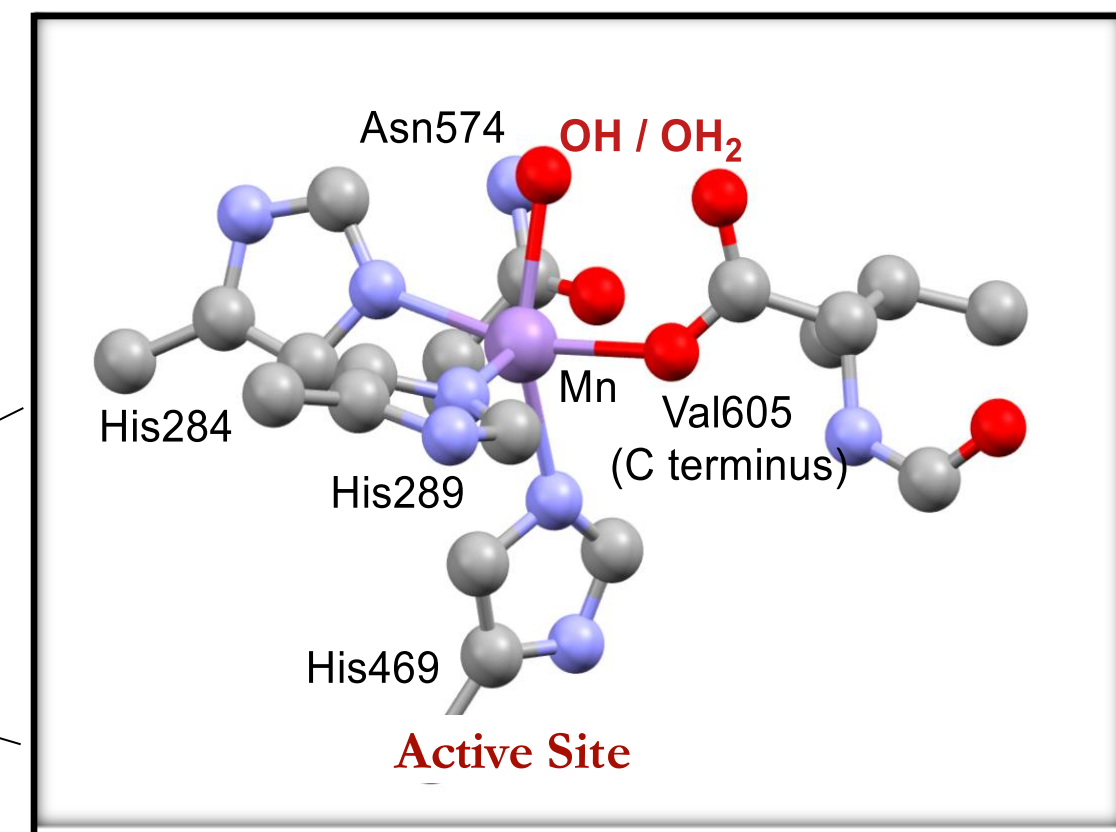
Zahra. Aghaei, Elizabeth N. Grotemeyer, and Timothy A. Jackson
Department of Chemistry, University of Kansas, Lawrence



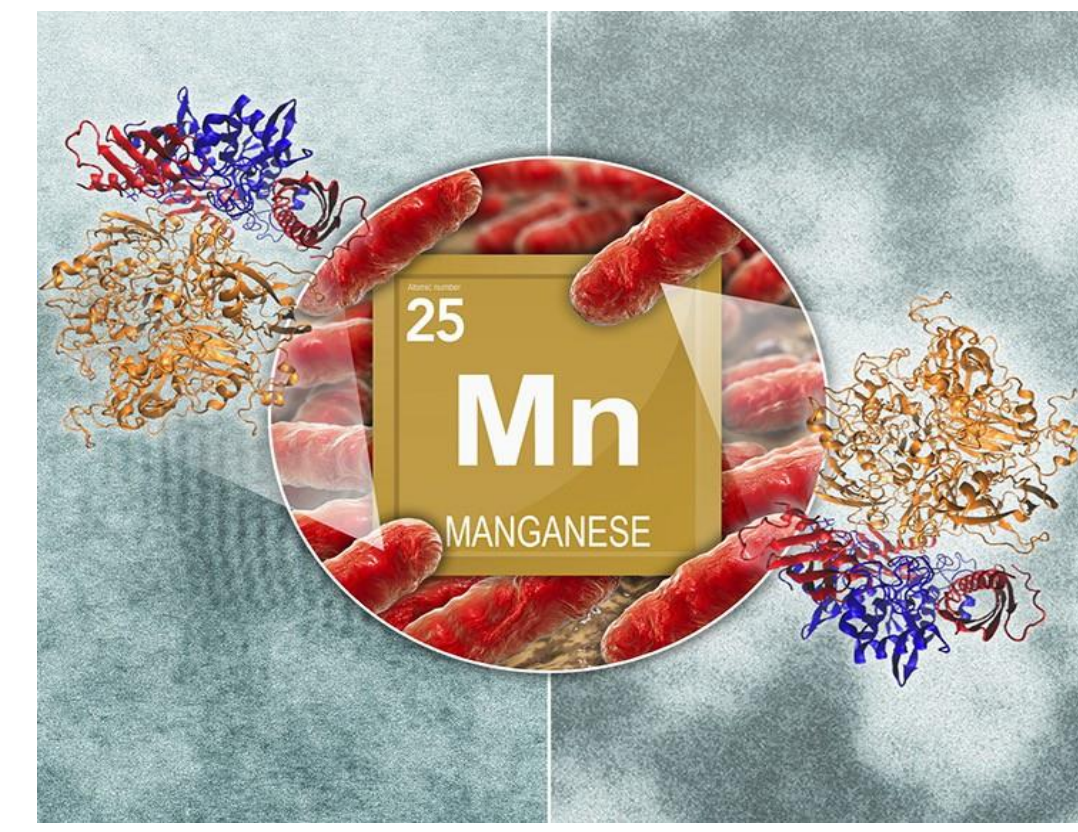
Motivation: Mn Enzymes in Nature

Manganese Lipoxygenase

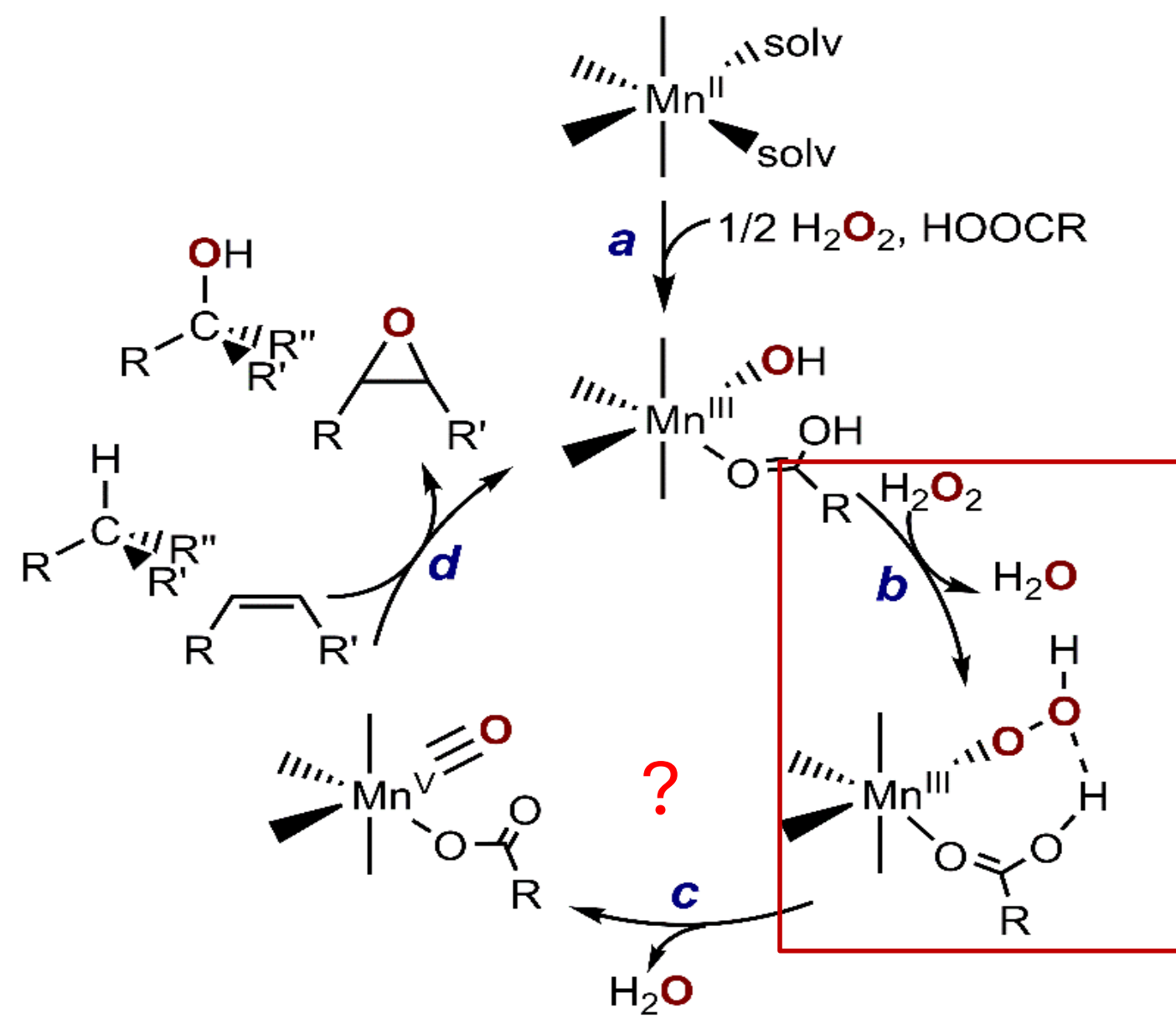
Synthesize hormones in plants and humans that helps wound healing



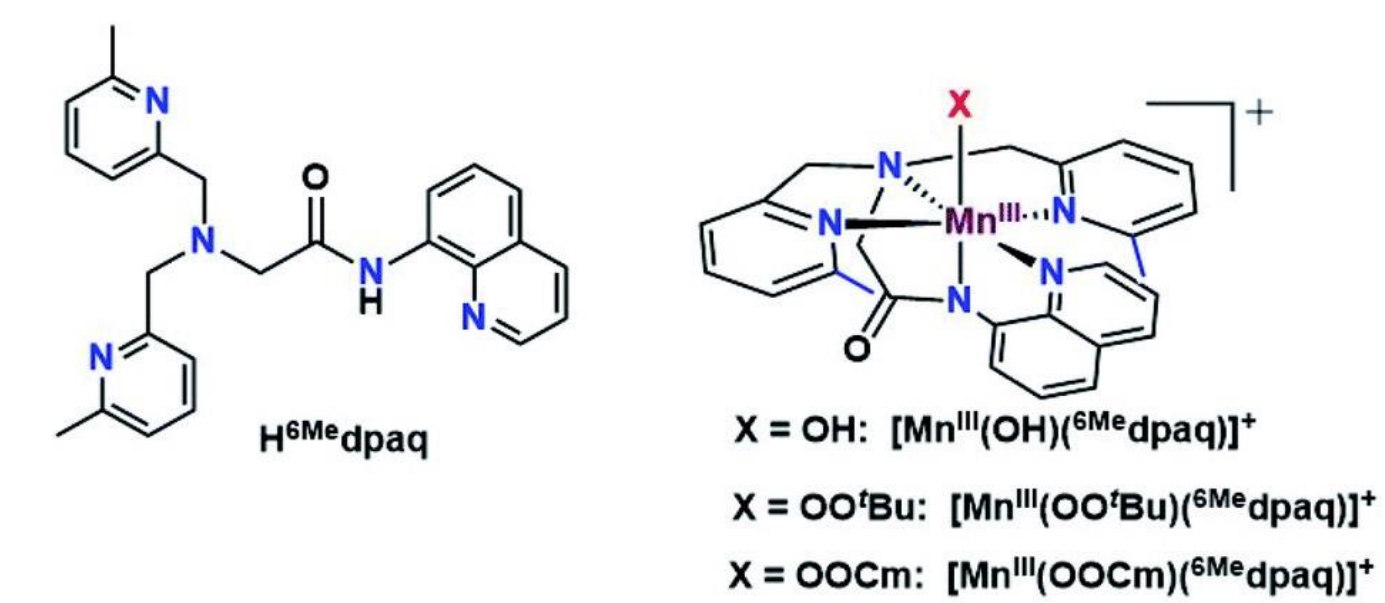
Biochem. Biophys., 2014, 555-556, 9.



ACS Catalysis 8, no. 5 (2018): 4528-4538.



Synthesized Mn-complexes



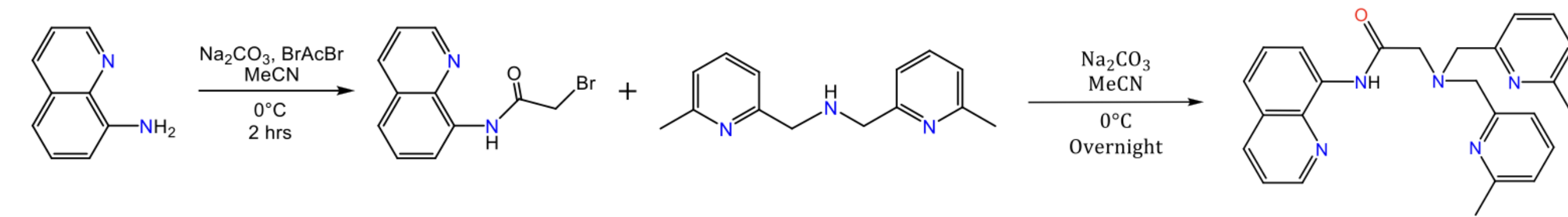
Chemical Science 12:38 (2021): 12564-12575.

To activate hydrogen peroxide with manganese centers, we pursue three objectives:

1. Characterize Mn^{III}-hydroperoxo adducts.
2. Define factors in reductive activation of Mn^{III}-hydroperoxo and Mn^{III}-peroxo adducts.
3. Develop Mn^{III}-alkylperoxo adduct structure-function relationships.

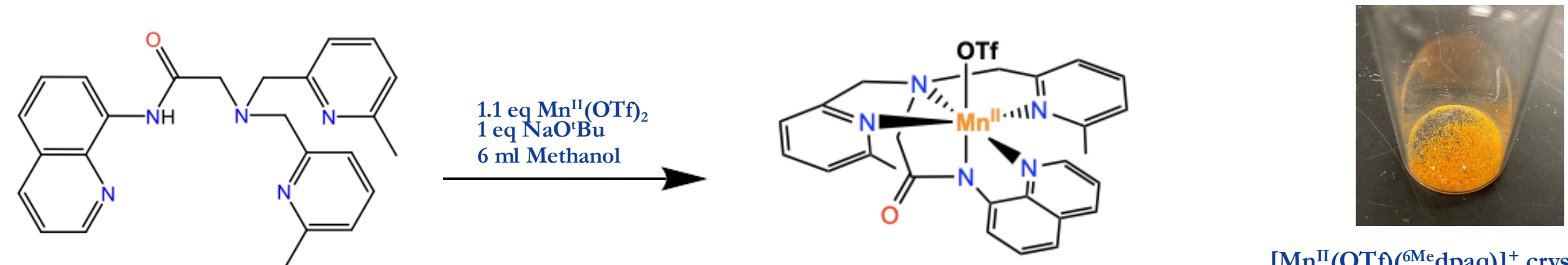
Synthesis of [Mn^{III}(OH)(⁶MeDpaq)]⁺

Synthesis of H⁶MeDpaq Ligand

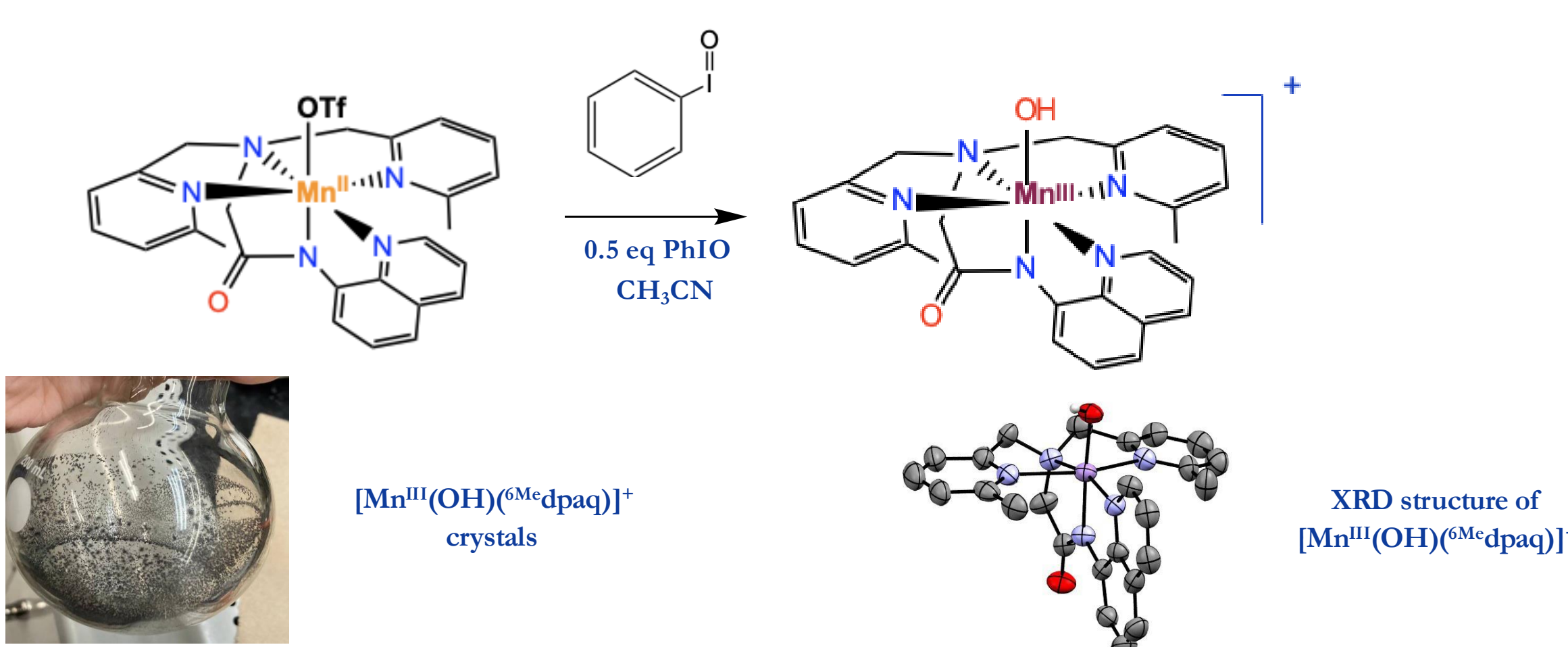


6-[bis(6-methylpyridine-2-ylmethyl)amino-N-quinoline-8-yl-acetamide] = 6MeDpaq

Metalation of H⁶MeDpaq

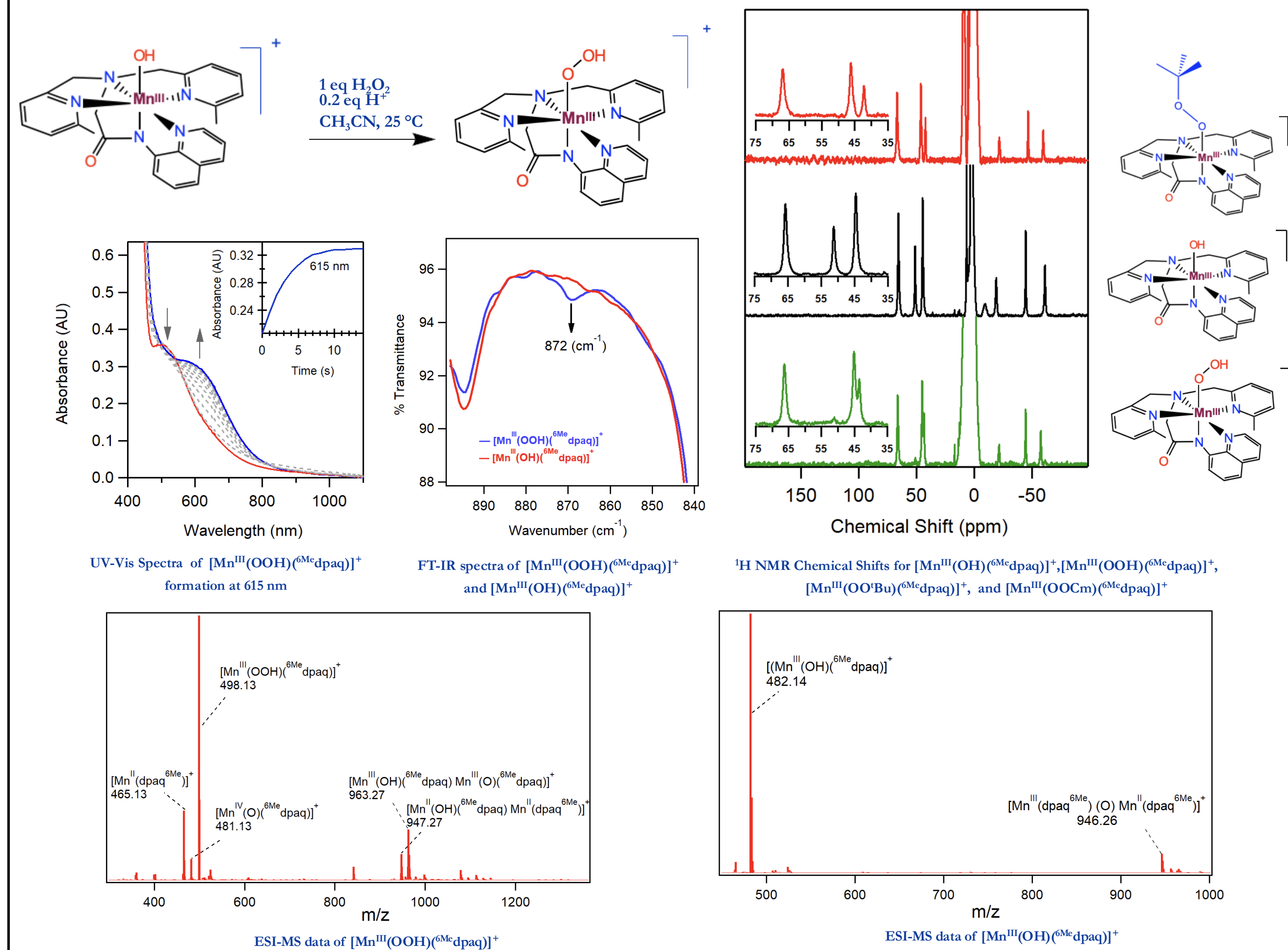


Oxidation of Mn^{II}(OTf)(⁶MeDpaq)

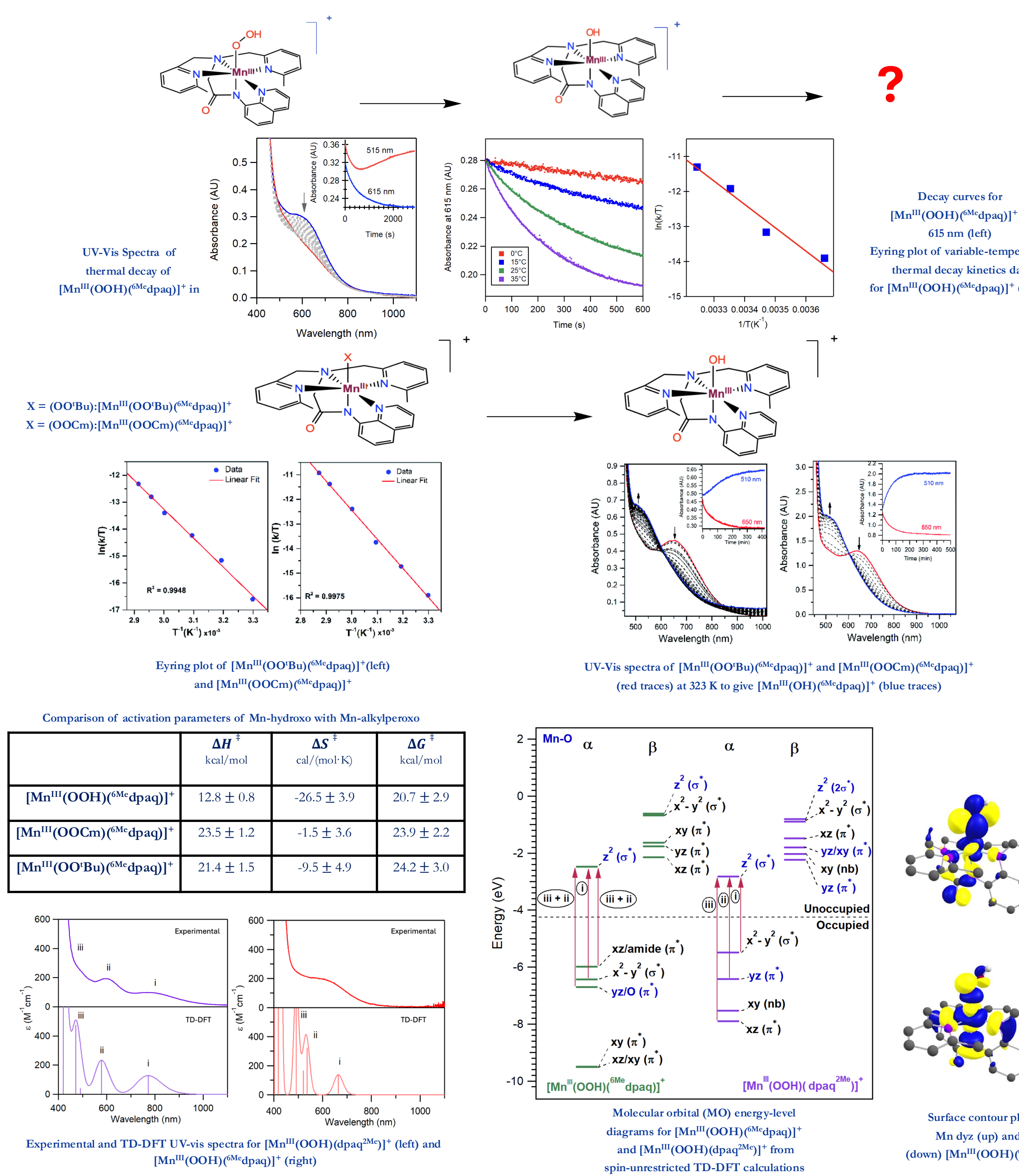


XRD structure of [Mn^{III}(OH)(⁶MeDpaq)]⁺

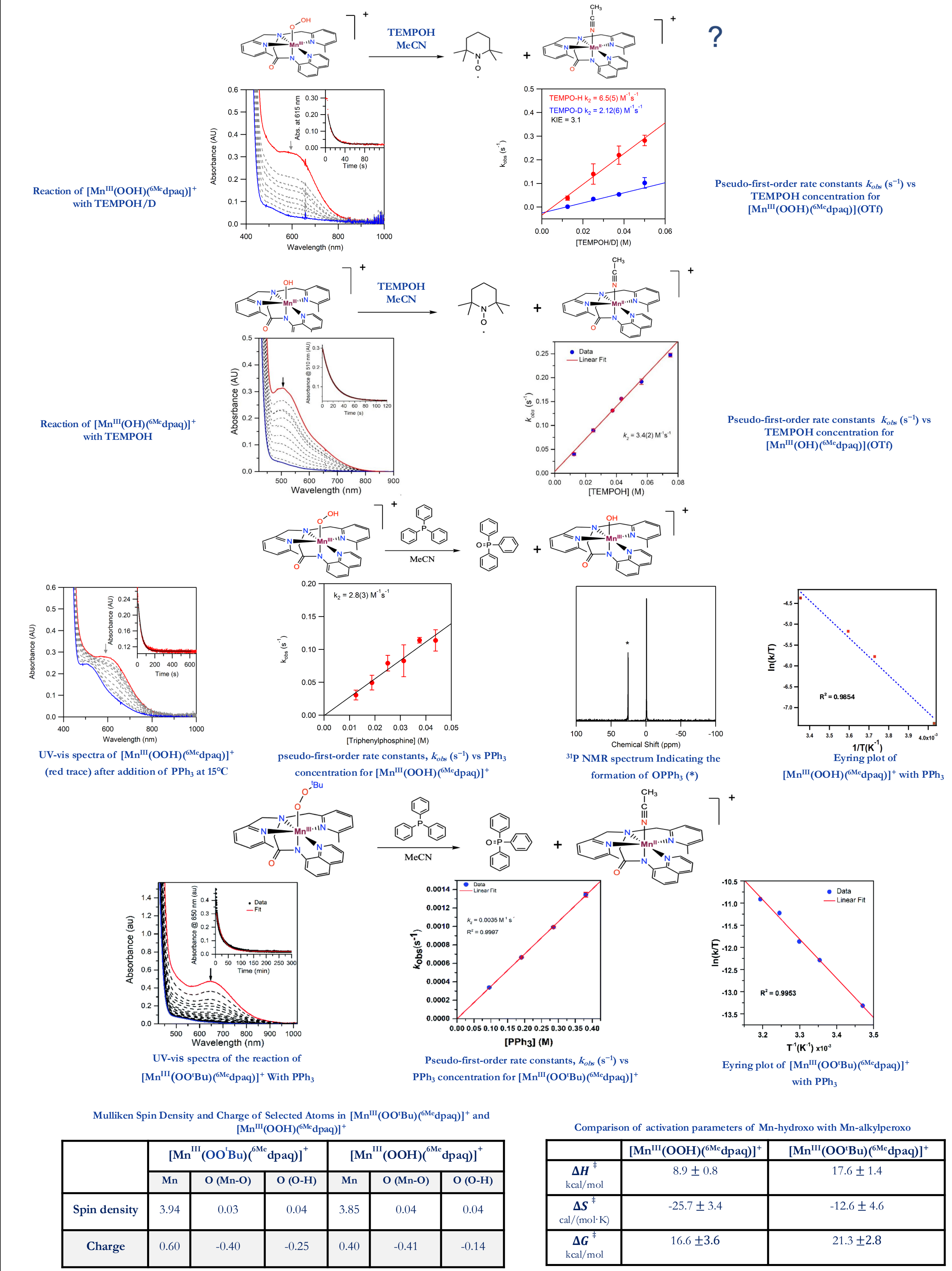
Reactivity of [Mn^{III}(OH)(⁶MeDpaq)]⁺ with Hydrogen Peroxide and Acid



Project 1: Mimicking MnLOX, Thermal-decay and Electronic Features of [Mn^{III}(OOH)(⁶MeDpaq)]⁺



Project 1: Mimicking MnLOX, Reactivity of [Mn^{III}(OOH)(⁶MeDpaq)]⁺



Project 1: Conclusions

1. [Mn^{III}(OOH)(⁶MeDpaq)]⁺ is stable at room temperature, then decays over the course of several hours, which allows for the study of the reactivity of this complex.
2. The reaction of [Mn^{III}(OOH)(⁶MeDpaq)]⁺ with PPh₃ is well fit by a pseudo-first order kinetic model. By varying the concentration of substrate, a second order rate constant of 2.8(3) M⁻²s⁻¹ for this reaction was determined. This rate is 600-fold faster than that of the [Mn^{III}(OOBu)(⁶MeDpaq)]⁺ complex with PPh₃ (k₂ = 4.7 × 10⁻³ M⁻²s⁻¹ at 15°C).
3. The reaction of [Mn^{III}(OOH)(⁶MeDpaq)]⁺ with TEMPOH follows a pseudo-first order model. By varying the concentration of TEMPOH a second order rate constant of 6.5(5) M⁻²s⁻¹ for this reaction was obtained. This rate is almost double that of [Mn^{III}(OOH)(⁶MeDpaq)]⁺ with TEMPOH under identical conditions (k₂ = 3.4(2) M⁻²s⁻¹). Reactions with TEMPOD gave a kinetic isotope effect of 3.1, which is consistent with an HAT reaction mechanism.
4. The variations in the electronic absorption spectra of [Mn^{III}(OOH)(⁶MeDpaq)]⁺ and [Mn^{III}(OOH)(dpaq^{2Me})]⁺ was attributed to perturbations in interactions with pyridine groups of the supporting ligands. Consequently, the electronic absorption spectra of Mn^{III}-hydroperoxo complexes not only reflect Mn-hydroperoxo bonding interactions, also are extremely sensitive to the entirety of the Mn coordination environment.

Acknowledgment



Current Members:
Markell Lomax
Anagha Puthiyadath
Purvi Patel
Brandon Nguyen
Natalie Scholz
Andrew Farrar
Delara Mafi

Previous Member:
Dr. Elizabeth Grotemeyer
Dr. Priya Singh
Dr. Sam Brunclik



National Science Foundation:
CHE-2154955