Synthesis and Characterization of Mn(salpn) Complexes. ¹

The experiments that we will be performing this quarter are based upon two articles from the Journal of the American Chemical Society. You are required to obtain a copy of each of these articles and read them prior to coming to the lab. You may also need to look up referenced articles in order to complete the pre-lab assignments. Quizzes will be given on information contained in these papers. The references are listed below and can be obtained in the library or online from the American Chemical Society (http://pubs.acs.org), click on “Journals and Magazines”, select “Journal of the American Chemical Society, click on “back issues”.


Week 1 Introduction, Handouts, Equipment check-in Ligand synthesis
Week 2 Synthesis of Mn^{III}(salpn)(AcAc) and Mn^{III}(salpn)(H_2O)_2(CF_3SO_3)
Week 3 Reactions of Mn^{III} complexes with H_2O_2 to form [Mn^{IV}(salpn)(\mu-O)]_2
Week 4-6 Protonation reactions of [Mn^{IV}(salpn)(\mu-O)]_2
Week 4-6 Recrystallization of [Mn^{IV}(salpn)(\mu-O)]_2 from DMF
Week 4-6 Synthesis of Mn^{IV}(salpn)(AcAc)(PF_6) by Bulk Electrolysis of Mn^{III}(salpn)(AcAc)
Week 7-9 Cyclic voltammetry of Mn complexes
Week 7-9 Reaction of [Mn^{IV}(salpn)(\mu-O)]_2 with excess H_2O_2 in methylene chloride (manometry)
Week 7-9 Magnetic susceptibility of Mn complexes

Grading scheme

15% Pre-lab write-ups
25% Post-lab write-ups
20% Lab work
20% Laboratory Notebook
15% Final written assignment
5% Quizzes

**Formal report of experimental activities**

At the end of this experiment, you will hand in a formal written report of your activities for the quarter. This report will be in the format of a chemistry journal article like the *J. Am. Chem. Soc.* articles used in this class. It will cover all of the work together, not as individual experiments. The article should reflect what you personally did and observed during your lab work, with comparison to the published journal articles. Your article should include:

- **Introduction**

  Discussion of the background to the bioinorganic problem addressed in these studies. *(Read, reference, and incorporate information from at least two reviews or articles other than those used in the class on this subject in your introduction).*

  Any necessary chemical background to place the experiments in context. Answer the question “*Why are the experiments significant?*”

- **Experimental Procedures**

  Descriptions of the syntheses and methods employed. Write it so that someone else can read it and reproduce your results. Routine measurements such as recording the UV/visible spectrum do not need detailed descriptions. Answer the question: “*What did you do?*”

- **Results**

  Observations and experimental results, including descriptions of the compounds made

  Answer the question: “*What did you make and what did you see happen?*”

- **Discussion**

  Interpret your results in terms of their chemical implications and the broader context. Make comparisons between observations for different complexes, and correlate results from different experimental methods (i.e., UV/vis energies and electrochemical potentials). Compare your results to the literature results. Do your results agree? Answer the question: “*What did these results mean?*”
**Pre-lab Write-ups**

At the beginning of each lab period, hand in a detailed description of how you plan to accomplish the goals for that lab period. Use the two JACS articles and any other sources of information you need (other articles, lab texts, etc.). Be sure to include amounts of reagents and expected yields both in grams and for the millimolar amounts indicated below (which may be different from those in the articles), and write balanced equations for all reactions. You should also look up the MSDS information for all the reagents that you will be using. It is important to be aware of potential hazards prior to beginning work in the lab. Chemical safety information is available online from chemical vendors such as Fisher scientific (www.fishersci.com). The Merk Index is also a good source for chemical safety information. Include hazard information in your pre-lab assignment.

**Week 1: Check-in, ligand synthesis**

- Synthesize 40 mmol H₂salpn ligand

**Week 2: Synthesis of Mn₃ Complexes**

- Synthesize 40 mmoles of Mn₃(salpn)(AcAc) using the H₂salpn you prepared in week 1.
- Use Mn₃(salpn)(AcAc) to synthesize 3 mmol of [Mn₃(salpn)(H₂O)₂](CF₃SO₃)
  The synthesis of complex 13 in the 1991 JACS paper actually gives this product.

**Why don’t we use the similar complex 1 instead?**

**Week 3: Hydrogen Peroxide Reactions of Mn₃ Complexes**

- Synthesize 10 mmoles of [Mn(IV)(salpn)(µ-O)]₂ by reaction of Mn₃(salpn)(AcAc) with hydrogen peroxide. Note the stoichiometry of reactants and product in this reaction.
- Try the same reaction with 0.5 mmole of [Mn₃(salpn)(H₂O)₂](CF₃SO₃).

If either of these reactions does not give a product consistent with the appearance described in the literature for [Mn(IV)(salpn)(µ-O)]₂, add one equivalent of base such as triethylamine per Mn.

**Week 4-6: Protonation Reactions**

- Add 1 equivalent of triflic acid (1M in acetonitrile) to 0.025 mmole [MnIV(salpn)(µ-O)]₂ in CH₂Cl₂.
- Add 2 equivalents of triflic acid to 0.025 mmole [MnIV(salpn)(µ-O)]₂ in CH₂Cl₂.
- Repeat each of the above experiments with the solution cooled to -78 °C (dry ice/acetone bath).
- To each of the above solutions, add one equivalent of triethylamine for each proton you added.
- Prepare 2 mmole of [MnIV(salpn)]₂(µ-OH)(µ-O)(CF₃SO₃).
Week 4-6: Recrystallization

- Recrystallize 1 mmole of [Mn^{IV}(salpn)(\mu-O)]_2 (see 1994 paper).

Week 4-6: Bulk Electrolysis

- Use bulk electrolysis to synthesize 0.5 mmoles of Mn^{IV}(salpn)(AcAc)(PF_6) from Mn^{III}(salpn)(AcAc).

Week 7-9: Cyclic Voltammetry

- Determine the electrochemical potentials for the Mn^{3+}/Mn^{4+} couple and the resting potential of:
  Mn^{III}(salpn)(AcAc)
  [Mn^{III}(salpn)(H_2O)_2](CF_3SO_3)
  [Mn^{IV}(salpn)(AcAc)](PF_6)
  [Mn^{IV}(salpn)(\mu-O)]_2
  [Mn^{IV}(salpn)]_2(\mu-OH)(\mu-O)(CF_3SO_3)

Week 7-9: Hydrogen Peroxide Reactions of Mn(IV) Complexes

- Make 0.05 mM solutions of [Mn^{IV}(salpn)(\mu-O)]_2 and [Mn^{IV}(salpn)]_2(\mu-OH)(\mu-O)(CF_3SO_3) (10 ml each in CH_2Cl_2) and observe what happens when you add a drop of 50% H_2O_2.
- Using a manometer, determine how many equivalents of gas are evolved when a 50-fold excess of hydrogen peroxide is added to the [Mn^{IV}(salpn)(\mu-O)]_2 solution.

Week 7-9: Magnetic Susceptibility

- Determine the room temperature magnetic moment by a modified Gouy method for:
  Mn^{III}(salpn)(AcAc)
  [Mn^{III}(salpn)(H_2O)_2](CF_3SO_3)
  [Mn^{IV}(salpn)(AcAc)](PF_6)
  [Mn^{IV}(salpn)(\mu-O)]_2
  [Mn^{IV}(salpn)]_2(\mu-OH)(\mu-O)(CF_3SO_3)
- In your prelab write-up, predict the “spin only” magnetic moment for each (based on the number of unpaired electrons):
  \[
  \mu_{\text{spin only}} = g_e \mu_e \sqrt{S(S+1)}
  \]
  where \(g_e\) is the electron g factor (\(g_e = 2.00\) for simplicity), \(\mu_e\) is the Bohr magneton (\(\mu_e = 9.274 \times 10^{-24} \text{ J T}^{-1}\)) and \(S = \frac{1}{2}\) for a single unpaired electron. All complexes are high spin. For example, high spin Fe^{2+} in an octahedral field has four unpaired electrons and the spin only magnetic moment is equal to 2.00\mu_e[2(2+1)]^{1/2} = 4.90 Bohr magneton.
**Post-Lab Write-ups**

At the beginning of the following lab period, hand in a discussion of the previous week’s experiments (including what you did and your observations) using the following as a guide. Be sure to answer all of the questions in your discussion.

**Week 1**

What is the correct full name for the ligand H$_2$salpn? Draw a picture of the ligand. What part of the ligand is deprotonated to give salpn$^{2-}$? What is the difference between salpn and the commonly used ligand salen? Write the balanced chemical equation for the synthesis of H$_2$salpn.

**Week 2**

Write the balanced equations for the synthesis of each of the two Mn(III)salpn complexes. What does HAcAc look like? What position on AcAc$^-$ is deprotonated? What is the chemical driving force for the conversion of Mn$^{III}$(salpn)(AcAc) to the Mn$^{III}$(salpn)(solvent)$_2^{2+}$ complex?

**Week 3**

What differences do you observe between the reactions of Mn$^{III}$(salpn)(AcAc) and Mn$^{III}$(salpn)(solvent)$_2^{2+}$ with H$_2$O$_2$? Based on this difference, write a balanced equation for the reaction of each Mn$^{III}$ complex to give the Mn$^{IV}$ dimer. Discuss the importance of the acid/base chemistry in the oxidation/reduction reaction. Propose a reasonably detailed mechanism for the reactions of the Mn$^{III}$ complexes with H$_2$O$_2$.

**Week 4-6 Protonation Reactions**

Discuss your observations regarding the acid/base chemistry of the Mn$^{IV}$ dimer, including stoichiometry, reversibility, and temperature effects. What do you conclude happened in each case? Where do you think the complex gets protonated? What are other possible (and chemically reasonable) positions that could be protonated? Given the information that the lowest energy (highest wavelength) intense absorption band in the UV/vis spectrum is a phenolate-to-Mn charge transfer*, argue in favor of your assignment of the protonation position based on the direction that the transition shifts upon protonation of the complex.

* The lowest energy (= highest wavelength) intense (ε > 1,000 M$^{-1}$ cm$^{-1}$) absorption feature in these Mn complexes is a transition in which an electron is moved from the highest occupied molecular orbital (HOMO) that is mostly located on the phenolate group and is moved to the lowest unoccupied molecular orbital (LUMO) that is located mostly on the manganese atom. Thus, the changes in energy of this transition depends on changes in the energies of one or both of these molecular orbitals. Shifts of the transition to higher energy indicates that the energies of these MO’s move farther apart, while shifts to lower energy indicate that they move closer together. The transition energies do NOT say anything about the stability of the complex as a whole.
**Week 4-6 Recrystallization**

What is the point of recrystallizing a material? Why is DMF (N,N-dimethylformamide) a good solvent for recrystallizing \([\text{Mn}^{IV}(\text{salpn})(\mu-O)]_2\)? Discuss this in terms of the general solvent characteristics you would want with respect to your product and the impurities you want to remove. Why is the DMF solution of your complex heated in a double boiler/water bath rather than just heating up the DMF to boiling? According to the literature, is there anything in the crystals made in this way besides \([\text{Mn}^{IV}(\text{salpn})(\mu-O)]_2\)? [Note that there is an inconsistency between the two papers on the details of this point…the 1994 paper is correct.] If so, how does this affect your calculation of the yield?

**Week 4-6 Bulk Electrolysis**

Describe your observations during this experiment. Do you think the bulk electrolysis was successful? Why or why not? Discuss the change in the absorption spectrum with respect to the energies of the orbitals involved in the lowest energy charge transfer transition.* What are possible advantages and disadvantages of this method of oxidation as a synthetic method compared to use of a chemical oxidant?

*See note above following “protonation reactions”.

**Week 4-6 Cyclic Voltammetry**

Describe what happens, chemically, during the course of the CV experiment. Use one of the CVs you collected as a specific example so that you can refer to specific potentials along the course of the voltammogram in your discussion, but include data for all of them. Be sure to note the significance of the resting potential. Compare the reduction potentials of all of the complexes you study in terms of the chemical attributes of the complexes. Do these reduction potentials seem to correlate to the charge transfer energies you discussed previously? Why would it make sense or not make sense for these different kinds of data to correlate with each other?

**Week 7-9 \(\text{H}_2\text{O}_2\) Reactions with \(\text{Mn}^{IV}\)**

Describe your observations upon addition of \(\text{H}_2\text{O}_2\) to solutions of \([\text{Mn}^{IV}(\text{salpn})(\mu-O)]_2\) and \([\text{Mn}^{IV}(\text{salpn})_2(\mu-\text{OH})(\mu-O)(\text{CF}_3\text{SO}_3)\]. How are they different? Define a catalyst. For each, are your observations consistent with the Mn complex being a catalyst for a reaction of \(\text{H}_2\text{O}_2\)? Calculate the number of moles of \(\text{H}_2\text{O}_2\) used and \(\text{O}_2\) generated, and compare to the amount of catalyst used. What is the significance of the amount of gas produced in the manometry experiment in terms of the definition of a catalyst and the stoichiometry of the \(\text{H}_2\text{O}_2\) reaction? Write a balanced equation for the \(\text{H}_2\text{O}_2\) reaction.

**Week 7-9 Magnetic Susceptibility**

Compare the magnetic moments determined for each complex in terms of the number of unpaired electrons you expect the complex to have. How close is each moment to the predicted “spin only” value? What contributions might cause the moment to be higher than predicted, and what might cause it to be lower, other than impurities.