

Characterization and Investigation of a Binuclear Manganese(III)-Peroxo Metastable Intermediate

As you have seen to this point in the semester, coordination environments around metal centers in biological macromolecules are difficult to study due to the fact that they make up only a small portion of the overall structure. The metal is often buried in the middle of the protein structure and is not amenable to study via traditional spectroscopic methods.

One way that we can gain insight into metal centers in biological macromolecules is to study model complexes to give us information about the possible structural and spectroscopic properties of the metals in similar coordination environments. Recently an excellent article by Solomon, Rybak-Akimova, and Kovacs was published in the *Journal of the American Chemical Society* and we will be discussing it in an upcoming class.

Coggins, M.K.; Sun, X.; Kwak, Y.; Solomon, E.I.; Rybak-Akimova, E.; Kovacs, J.A. "Characterization of Metastable Intermediates Formed in the Reaction between a Mn(II) Complex and Dioxygen, Including a Crystallographic Structure of a Binuclear Mn(III)–Peroxo Species" *J. Am. Chem. Soc.* **2013** *135*, 5631. <http://dx.doi.org/10.1021/ja311166u>

To guide your reading of this article, I have a list of questions that will help you find the important points in this article. These questions need to be submitted before class and late assignments will not be accepted.

Your answers to these questions will be the basis of our in-class discussion. Our discussion of the article will not just be limited to these questions, but we have more in-depth discussions about the results reported in the article. I do not expect that you will give a fully correct answer to every question as you complete this assignment and you will not be penalized for incorrect responses. I do expect that you make a reasonable attempt to answer every question and submit a response to every question. I also expect that you will participate in the in-class discussion and if you are not present in class you will not receive any credit for this assignment.

Introduction

1. Why is it important to study the structure and properties of metal peroxo complexes?
2. Why is it important to investigate manganese-peroxo complexes specifically?
3. How do metals facilitate the O-O bond cleavage?
4. What other Mn-peroxo complexes have been characterized?
5. What is significant about the results reported in this article?

Experimental Section

6. How were the UV-vis spectra recorded?
7. What was the reaction that they used to detect hydrogen peroxide that could be produced from intermediate **3**?
8. How were the kinetics of the reaction studied? Under what conditions were the kinetic data obtained?

Results and Discussion

General

9. What is the d electron count on the manganese in complex **1**? How many electrons are on that metal center when both the metal d electrons and ligand electrons are taken into account?
10. What did the use of ^{18}O labeling prove in the reaction of **1** with O_2 ?
11. What does it mean that intermediate **3** is metastable? (You may need to use a dictionary to answer this question.)

Resonance Raman Spectroscopy

12. What information does the Resonance Raman spectrum shown in Figure 2 provide?
13. What does the $\nu_{\text{O-O}}$ stretching frequency suggest about the structure of the intermediate **3**?

X-ray Crystallography

14. How did they grow crystals of the intermediate **3**?
15. What crystallographic data was strong evidence that the O_2 molecule was reduced to O^{2-} ?
16. How do they describe the bonding of peroxo to the manganese ions? How do the Mn-O and Mn-Mn distances support this description?

Magnetic Susceptibility

17. The effective magnetic moment can be related to the number of unpaired electrons according to the equation provided below. How many electrons give rise to the μ_{eff} for **3** reported in the article? (You can solve this by trial and error.)

$$\mu_s = \sqrt{n(n+2)}$$

18. How is this magnetic moment indicative of the two manganese ions being magnetically uncoupled?

Kinetic Studies

19. What did the authors suggest was the likely mechanism for the reaction between **1** and O₂?

20. Why is a stopped flow instrument used to investigate the kinetics of the reaction? (For some further information, you can look at the two websites listed below.)

https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Kinetics/Reaction_Rates/Experimental_Determination_of_Kinetics/Stopped_Flow

<https://www.hi-techsci.com/techniques/stopped-flow/>

21. How was it identified that the intermediate **4** was formed before **3**?
22. What were the two rate laws determined for steps (1) and (2) in Scheme 2?
23. How did they determine the activation parameters (ΔH^\ddagger and ΔS^\ddagger) for steps (1) and (2) in the mechanism?
24. What did the negative entropy values suggest about the mechanism of steps (1) and (2)?

Conclusions

25. After reading the conclusion, please list three reasons why the results presented in this article are important?