

Synthesis of Chemically Active Models of the Oxygen Evolving Complex

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Introduction and Background

With the constantly increasing dependence humanity places on technology with each passing year, the necessity to find more sustainable forms of energy to keep everything running is becoming increasingly necessary. Fossil fuels served as a crucial energy source for a long time, but over time, they deplete and renewable sources are needed. One of these essential sources is solar energy, the most exploitable energy source, yet one that has quite a few barriers to success. These barriers to success include a need to find efficient mechanisms for both (1) **solar capture and conversion** and (2) storage¹.

Equation for Photosynthesis: $6\text{CO}_2 + 6\text{H}_2\text{O} + \text{light energy} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$

The equation above is that of Photosynthesis, an essential process for life. Being able to create an 'artificial' photosynthetic pathway is the key to unlocking solar energy, but in order to be able to do that, we need to first look at Photosystem II, a protein complex that is essential for this process to occur.

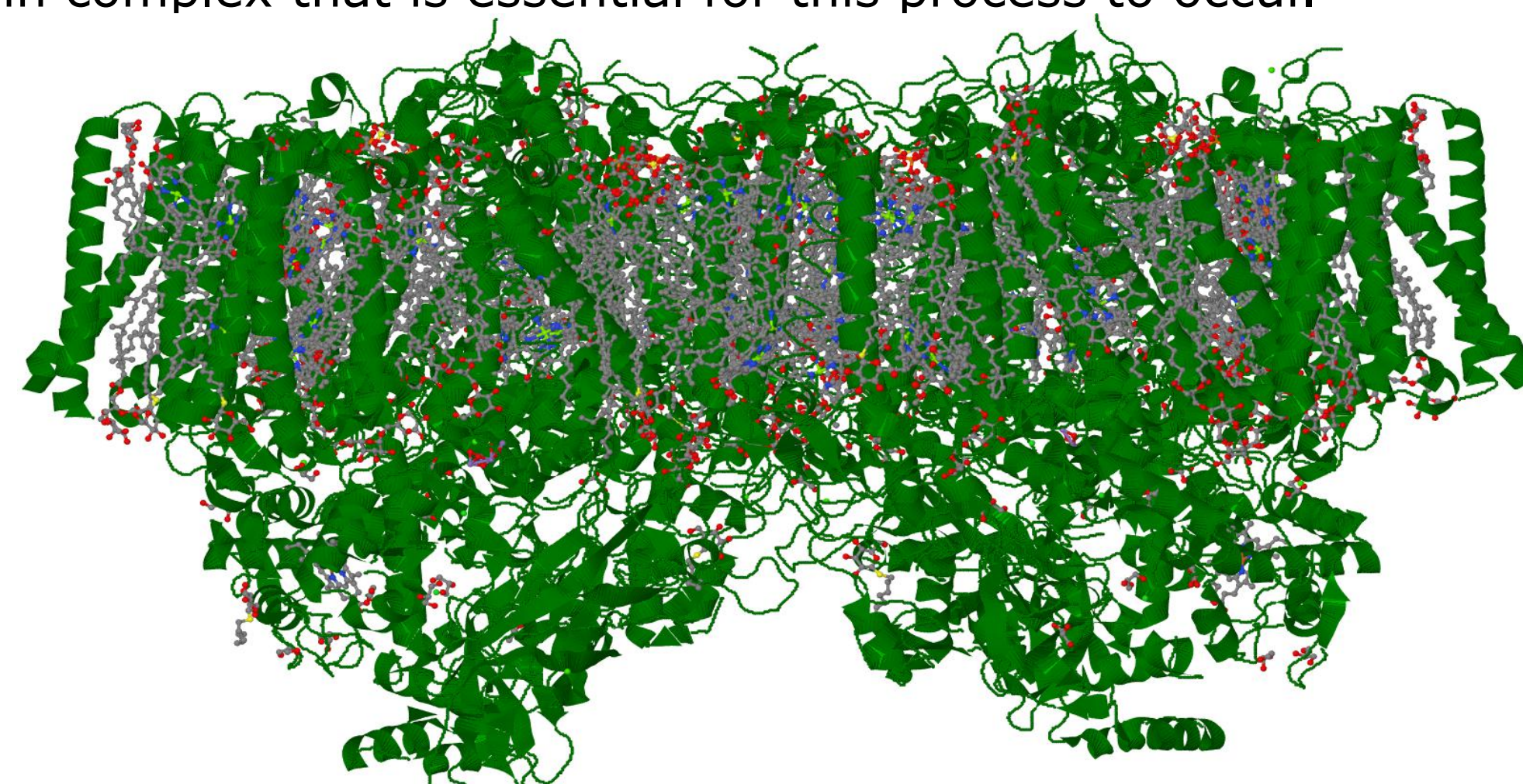


Figure 1. Structure of Photosystem II.²

Photosystem II utilizes a Mn/Ca cuboidal structure known as the Oxygen-Evolving Complex, which catalyzes the reaction that takes light energy and oxidizes water, releasing O_2 .³ The exact mechanism of this process, known as **water oxidation** is unknown at this point, but our project's goal is to mimic this with synthetically similar compounds.

Proposed Mechanisms

In order to create a synthetic replica of the Oxygen-Evolving Complex (OEC), we first had to analyze its structure and determine the pieces that were most important.

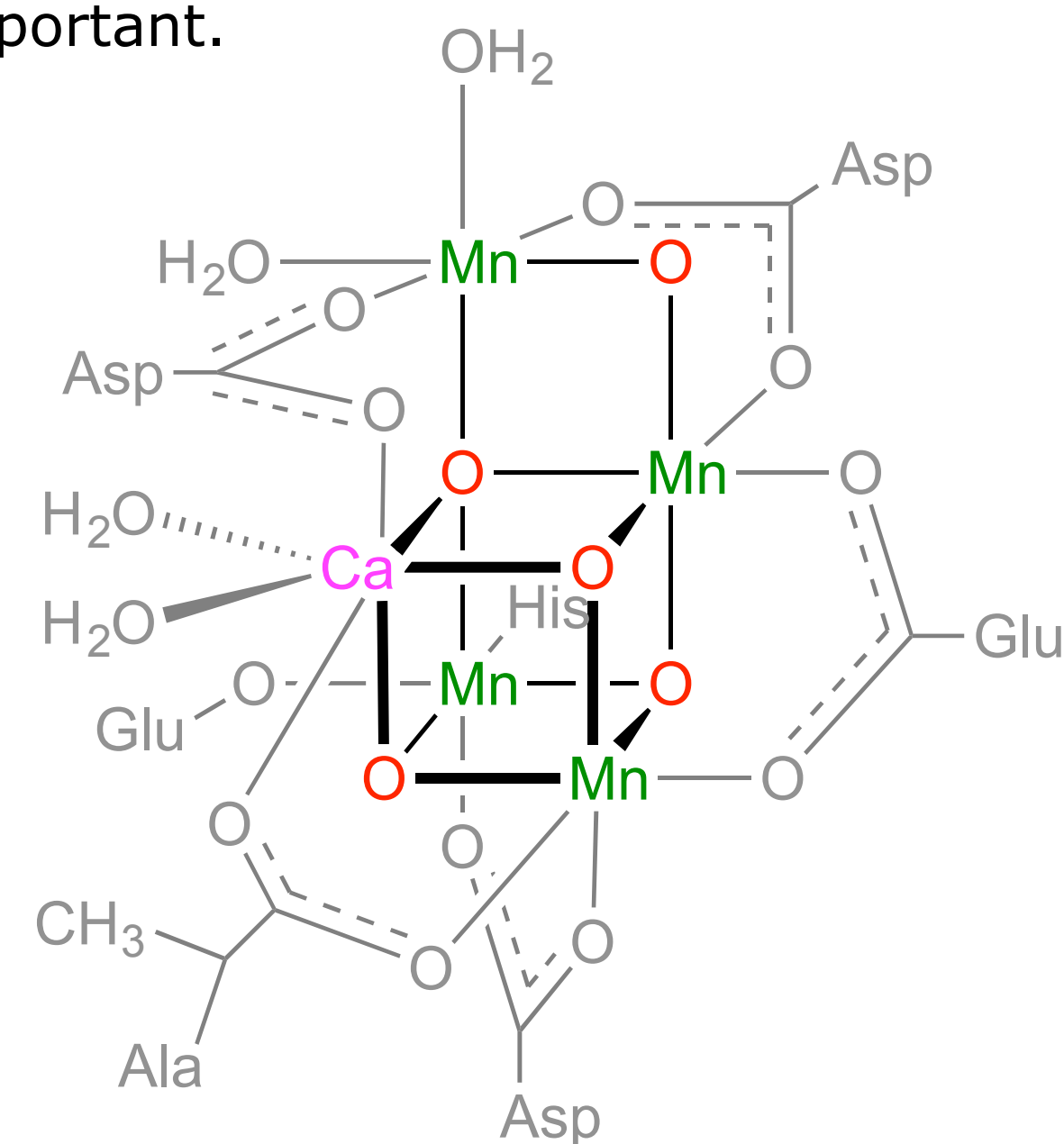
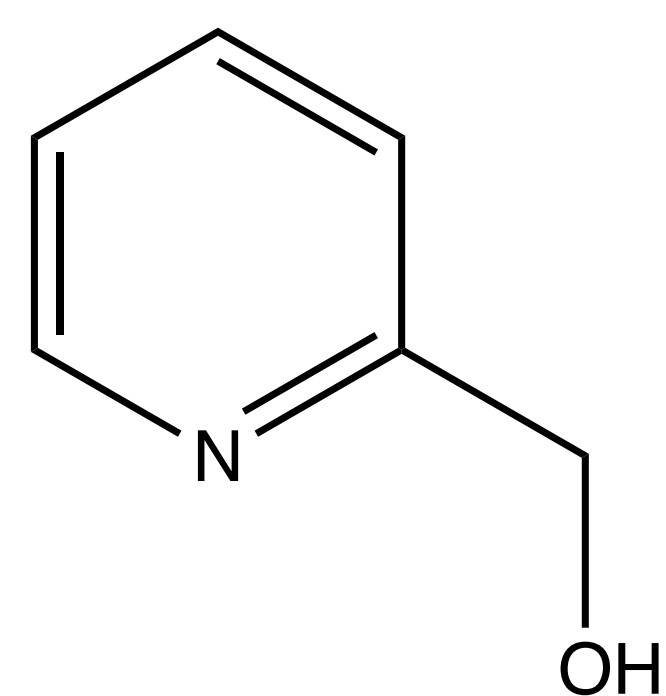


Figure 2. Structure of the OEC and photosystem II.⁴

Considering that this natural structure consisted primarily of Manganese atoms, there was no doubt about the necessity in **starting with a Mn backbone for synthetic models**. While other transition metals could be potential options for further analysis, the evolutionary selection for Mn by plants made it a priority. We hypothesized that if we **reacted Manganese compounds with compounds containing Calcium, in varying equivalents, that we could create clusters that would be structurally similar to the OEC**. However, in order to do this, we needed a suitable ligand that would react in a comparable fashion.

Proposed Ligand: 2-PyrMeOH



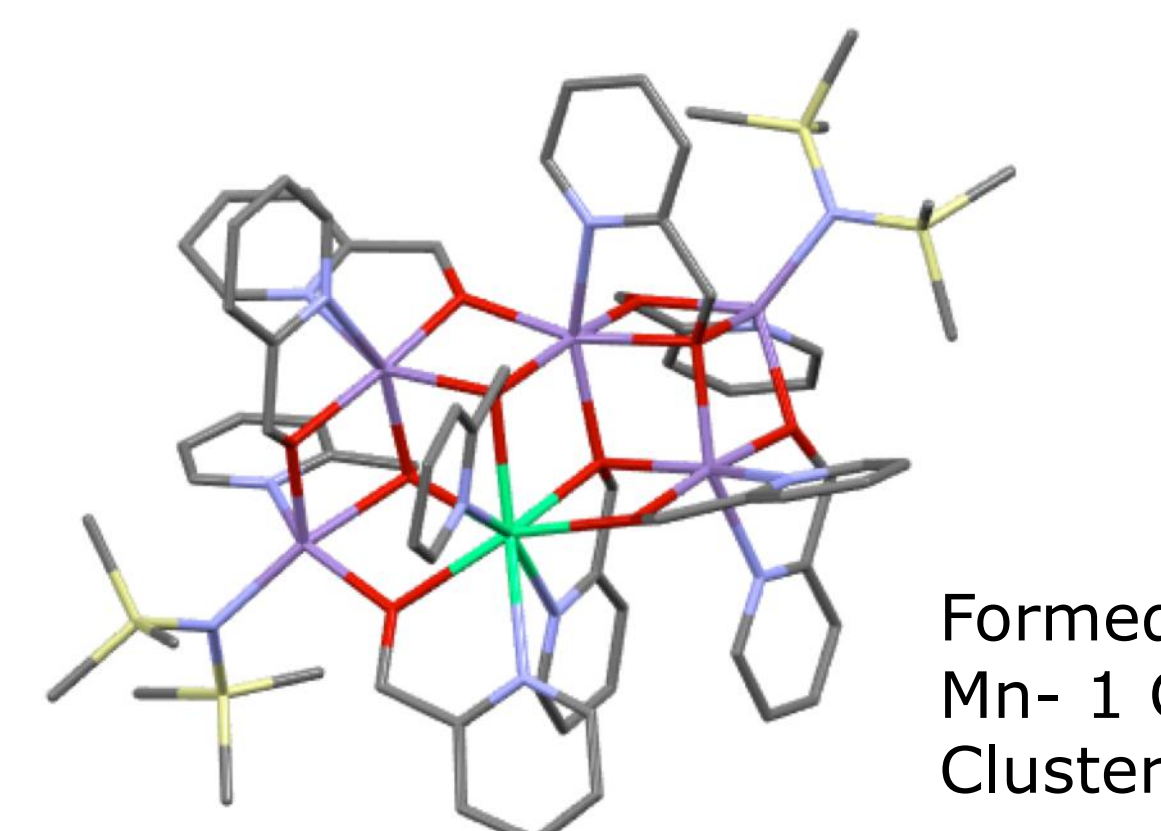
The ligand we chose was 2-Pyridine Methanol (pictured to the left). This ligand was chosen as it is relatively reactive with our starting material, and dissolves in Tetrahydrofuran, our solvent of choice as it does not interfere with the reactions in any way, yet still manages to dissolve all the reactants.

Experimental Data and Results

General Reaction Scheme: $\text{Mn}(\text{SiMe}_3)_2\text{N} + \text{Ca}(\text{SiMe}_3)_2\text{N} + 2.5 \text{ PyrMeOH}$

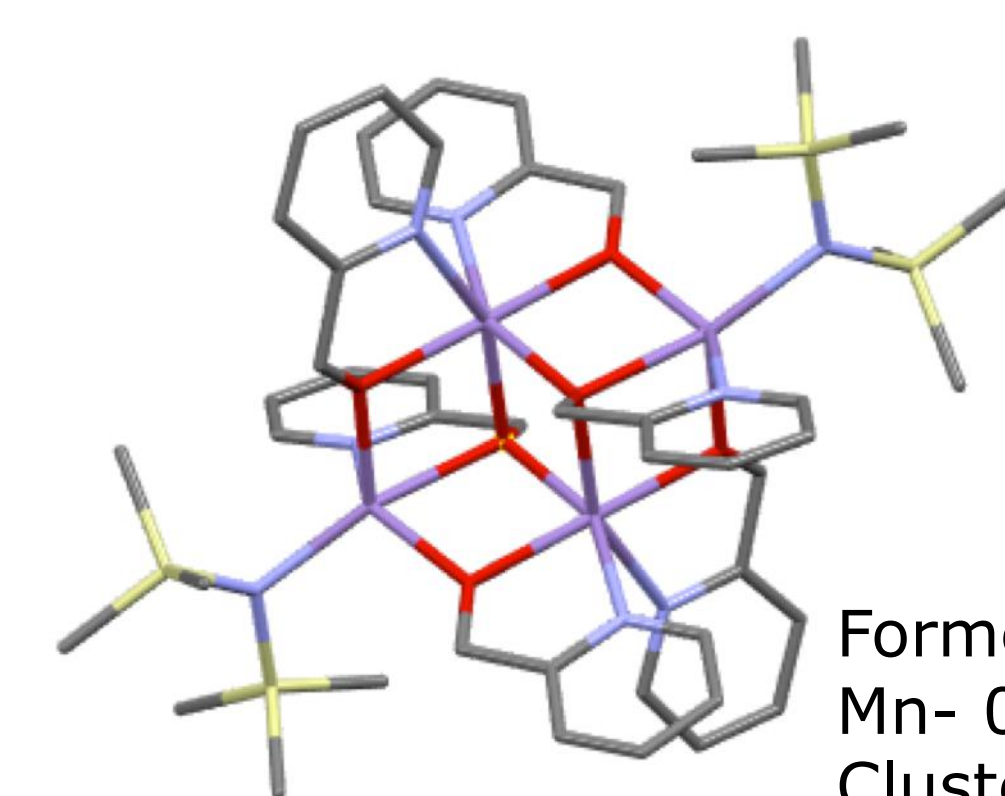
Each reaction was run as a vapor diffusion, which consists of an inner vial consisting of the reactants dissolved in minimal THF, placed into a larger outer vial with a relatively equal height of pentane. This vial combination was capped and placed in the freezer at -35°C , and allowed to sit for several days without any disturbance. The goal of each of these reactions was to create crystals, which were then indexed using the **X-Ray Diffractometer** in order to find their true crystal structures. An outline and subsequent structure for several different reactions are pictures below. As a guideline, the reactions were carried out using 180 mg of $\text{Mn}(\text{SiMe}_3)_2\text{N}$, also known as Mn(Bis), and the other reactants were carried out in a stoichiometric fashion from that point.

(1) 1 Mn(Bis) + 1/8 Ca(Bis) + 2.5 2-PyrMeOH



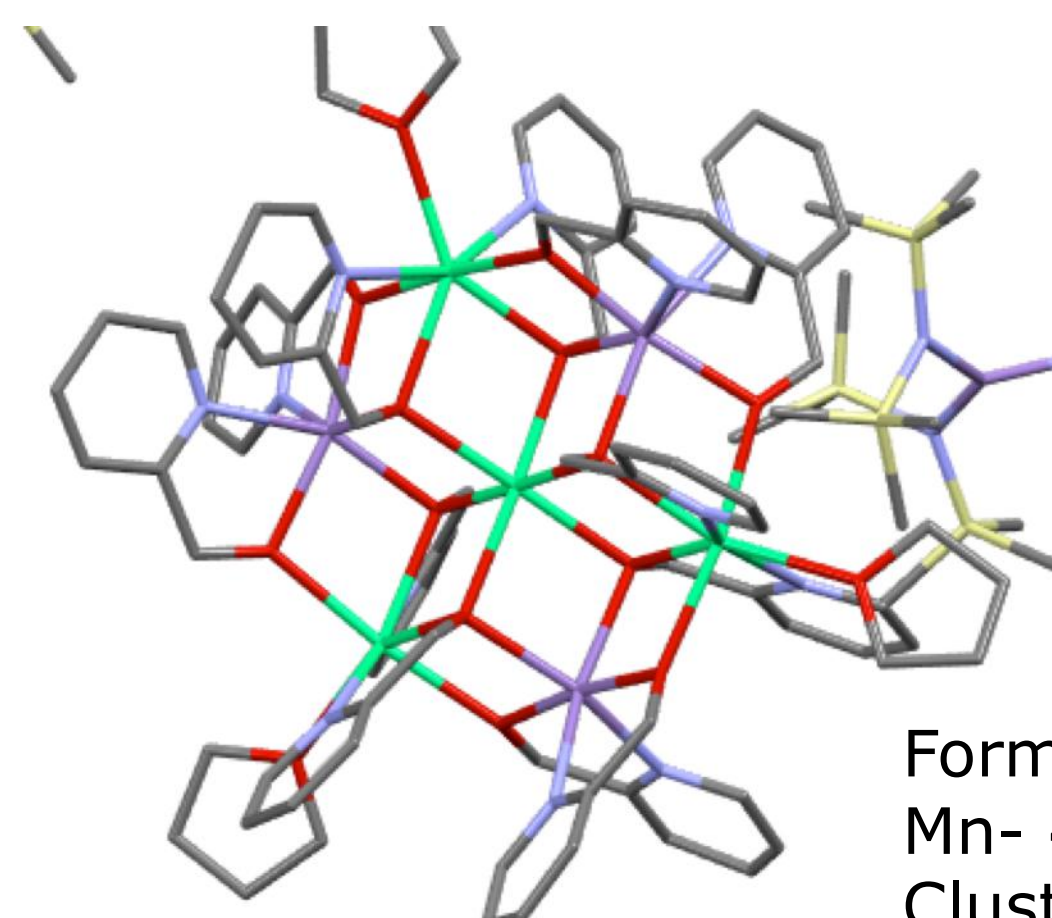
Formed 5
Mn- 1 Ca
Cluster

(2) 1 Mn(Bis) + 2.5 2-PyrMeOH



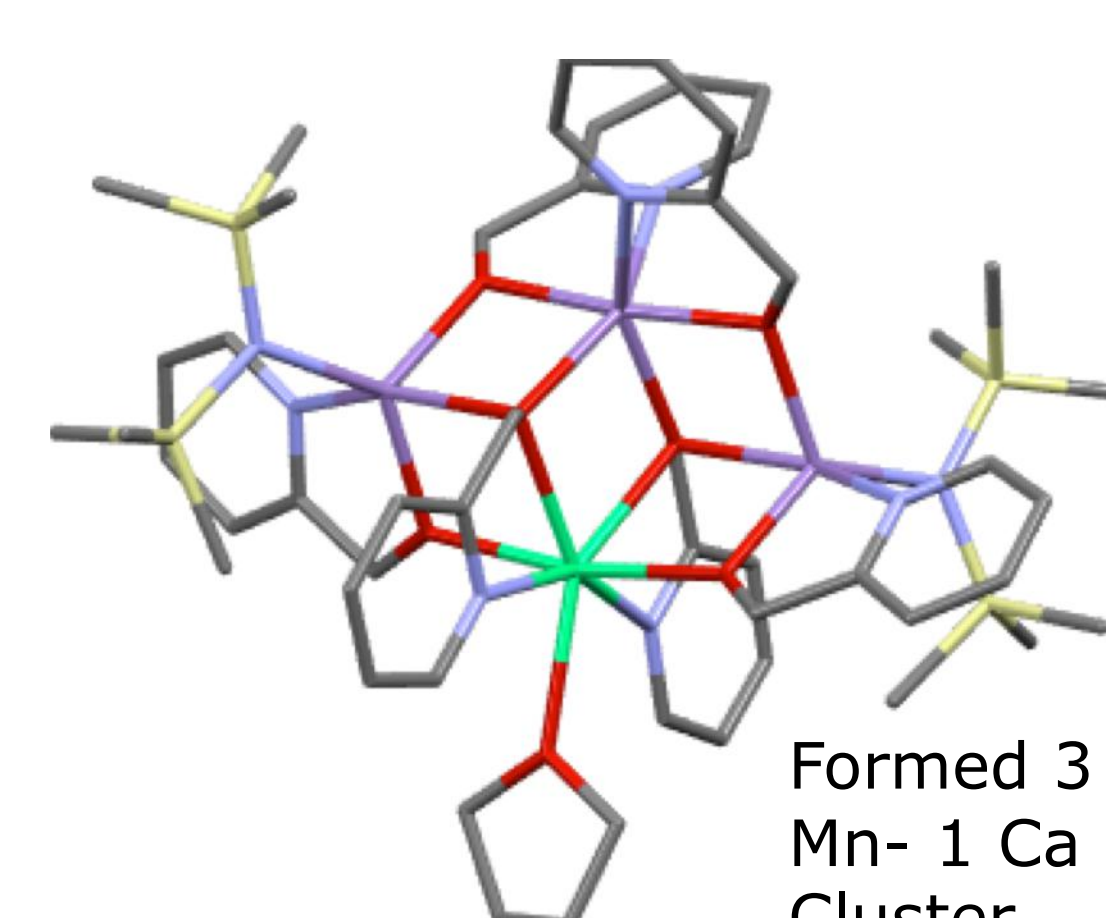
Formed 4
Mn- 0 Ca
Cluster

(3) 1 Mn(Bis) + 1 Ca(Bis) + 2.5 2-PyrMeOH



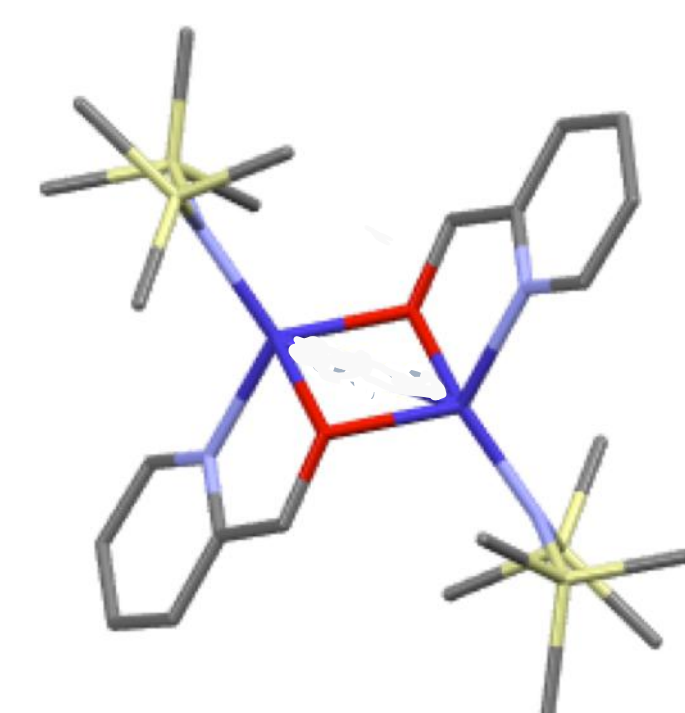
Formed 3
Mn- 4 Ca
Cluster

(5) 1 Mn(Bis) + 1/5 Ca(Bis) + 2.5 2-PyrMeOH



Formed 3
Mn- 1 Ca
Cluster

(5) 1 Co(Bis)₃ + 1/3 Ca(Bis) + 2.5 Pyr-MeOH

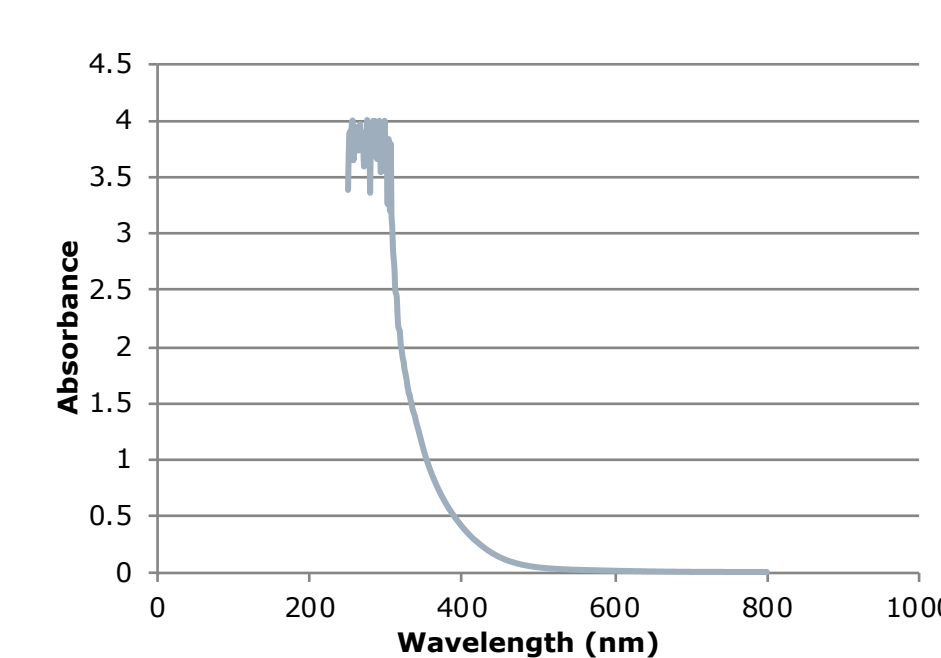


Formed 2
Mn- 0 Ca
Cluster

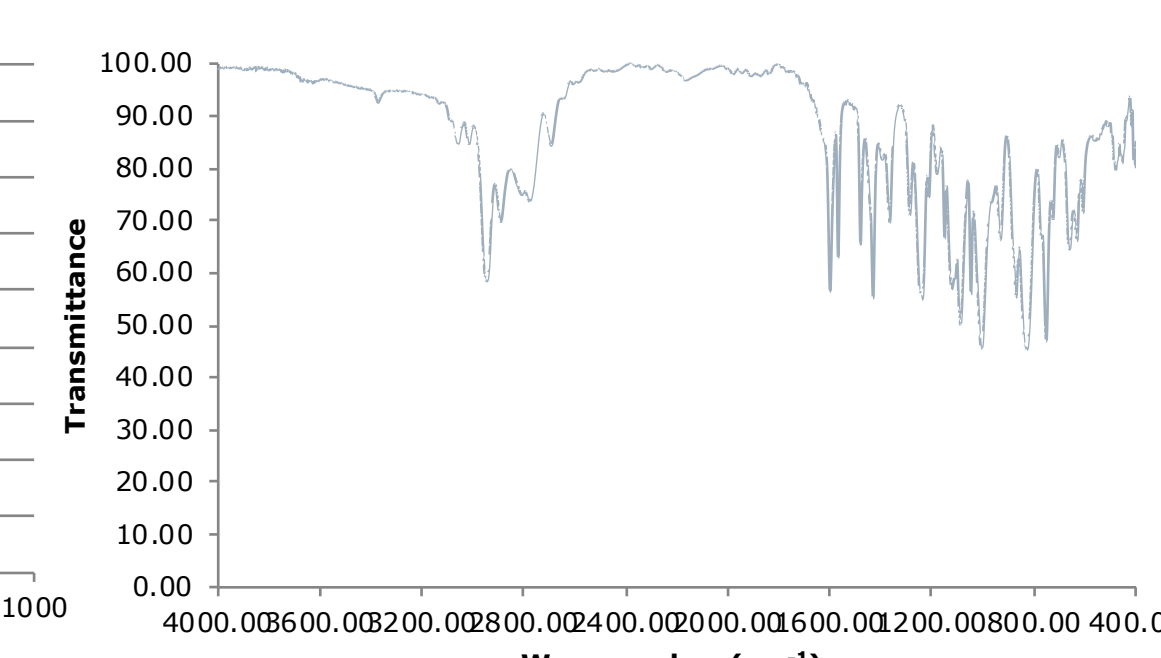
Note: This last structure (5) is the exception to the pattern displayed in all the reactions above. Rather than use Mn(Bis) for this reaction, we decided to try using a different transition metal, Co. The full formula for $\text{Co}(\text{Bis})_3$ is $\text{Co}(\text{SiMe}_3)_3\text{N}$. This reaction was also set up with a vapor diffusion with pentane, however.

After determining each compound's crystal structure, a series of tests were conducted on each sample to help characterize them. These included the following three types of testing that are also listed below: UV-Visible Light Spectroscopy (UV-Vis), Infrared Spectroscopy (IR), and Electron Paramagnetic Resonance (EPR). CHN analysis was also performed, and several structures have passed, but the results are not reported below. A sample is shown for each, from **reaction (3)**.

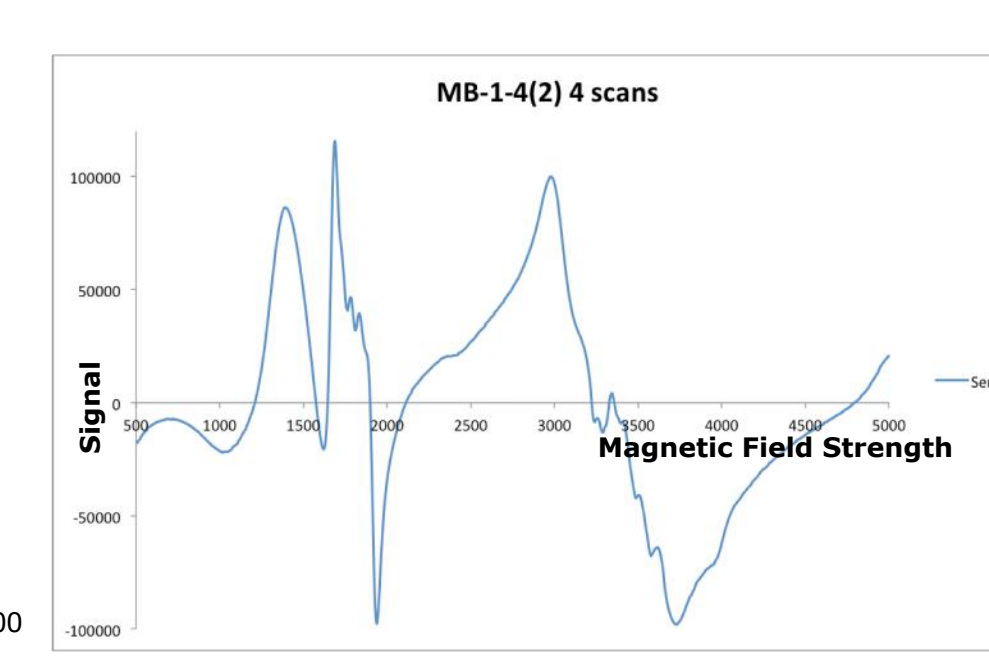
(1) UV-Vis Analysis



(2) IR Analysis

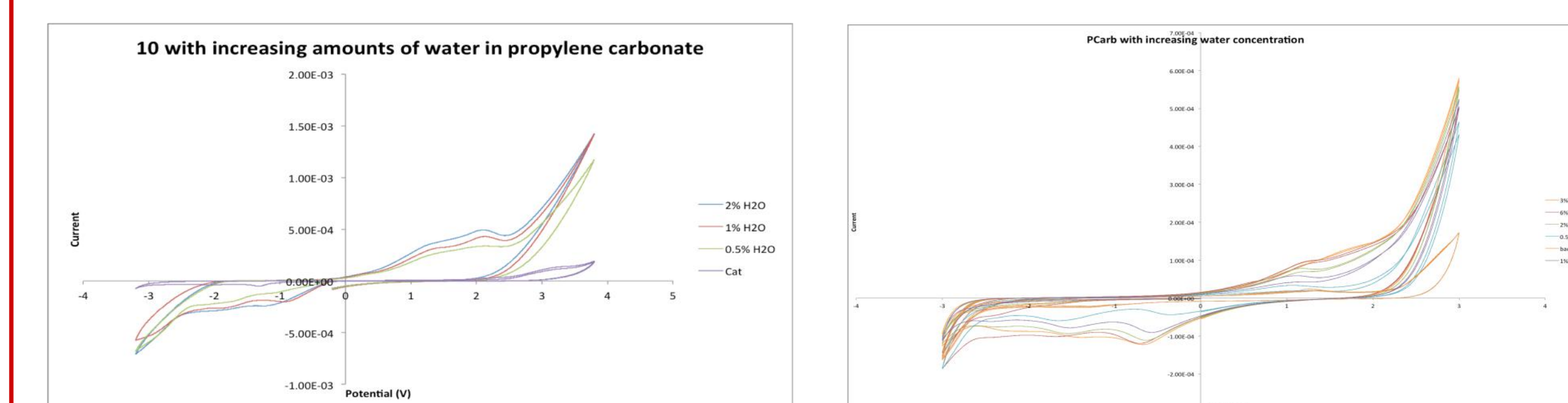


(3) EPR Analysis



Testing Chemical Activity

After finishing with the synthesis and basic characterization steps, there was only one remaining thing to test: the chemical nature of these clusters. While their physical structure at least somewhat resembles the OEC (with the exception of the Cobalt cluster, which is quite different, the chemical activity is completely unknown. In order to test this, **Cyclic Voltammetry** was run on one of the clusters, specifically a 2 Mn- 1 Ca structure that is not pictured on the left. Results were as follows.



The CV on the left was extremely promising, showing that as water was added to the structure (dissolved in Propylene Carbonate), the oxidation levels went up by quite a bit. However, they **did not go up proportionally to the amount of water added**, which was the first major problem. This led to the second CV on the right, which was one of just the solvent P-Carb in water. Surprisingly, the trend on this graph, with one exception of the 6% trial (likely due to decomposition of the substances), **was also showing oxidation without any catalyst present**. To determine what exactly was showing on the oxidation side of the CV graph, we ran a GC with Propylene Carbonate, which is when we found out that what we were seeing was **really decomposition of the solvent P-Carb into a Carbon Dioxide peak, not water oxidation**.

Conclusion and Future Work

In conclusion, our results up until this point were able to create several various clusters that are **structurally similar to the Oxygen-Evolving Complex** from Photosystem II. However, while physical structure may be similar, we have not gotten closer yet to determining whether water oxidation is possible with these structures. While extensive testing has been done regarding their electrochemical activity, current methods seem to prove that **water oxidation is not yet being catalyzed**. However, it is important to note that since the clusters do not dissolve in water, our methods of testing water oxidation are extremely limited, and not entirely conclusive.

Going forward, there are multiple paths to expand the scope of this research. First, I would like to continue to **explore Cobalt clusters** in order to see the extent of clusters that can be formed with a different transition metal from that found in nature. Additionally, in order to keep working on these prior clusters, I would like to devise a way to **make them water soluble**. This could theoretically be done by binding them to a water-soluble group like a sulfonyl, and doing so would make testing for water oxidation far more feasible.

References

1. Lewis, N. S.; Nocera, D. G. Proc. Natl. Acad. Sci. 2006, 103, 15729-15735.
2. Umena, Y et al. Nature 2011, 473, 55.
3. Kawakami, K.; et al. Photochem. Photobiol., 2011, 104, 9.
4. Photosynthetic Water Oxidation: Insights from Manganese Model Chemistry Karin J. Young, Bradley J. Brennan, Ranitendranath Tagore, and Gary W. Brudvig Accounts of Chemical Research 2015 48 (3), 567-574.

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