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Acknowledgements

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Electrochemistry and Spectroscopy of a Molybdenum Porphyrin Compound

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ABSTRACT Carbon dioxide has been a problematic greenhouse gas since the beginning of the industrial age. In an effort to remediate its effects on the climate, multiple techniques have been utilized in the chemical and electrochemical reduction of CO₂. Homogeneous electrocatalysis for carbon dioxide reduction has been a topic of increasing interest. However, a full examination of the catalytic performance of early transition metals supported by macroligands has yet to be done. The research reported involves synthesis of a chelate of molybdenum within a tetraphenylporphyrin, and then synthesis, purification, and characterization of its ability to reduce carbon dioxide. The complex was found to be air-stable and robust. However, it was paramagnetic and not found to be an efficient electrocatalyst for CO₂ reduction.

INTRODUCTION

Since the late 1960's, various fields of chemistry have attempted to convert carbon dioxide into useful products through a variety of strategies. This aim is to thereby reduce the detrimental effects of the greenhouse gas on the climate and create a renewable source of fuel. Previous studies have shown that carbon dioxide can be reduced by means of homogenous catalysis in hydrogen-rich environments to produce formate.¹

Given that formate is a precursor to methanol, this allows for a feasible pathway from carbon dioxide to methanol, producing a potential renewable source of liquid fuel from a waste product, CO₂. For these reasons the industrial reduction of carbon dioxide requires the development and synthesis of efficient, stable homogenous electrocatalysts. Electrocatalysts lower the activation energy for the transfer of electrons and subsequently allow for accelerated reduction of CO₂. Catalytic reduction can be

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examined through cyclic voltammetry (CV), by observing the electrocatalytic current under CO₂. In this work, a metal-ligand complex was synthesized and examined as a potential electrocatalyst for CO₂ reduction. The complex consisted of molybdenum (a second-row transition metal) bound within a porphyrin supporting molecule. This approach was inspired by various studies wherein metal-porphyrin compounds were shown to be good CO₂ reduction catalysts. Prior research done by the Kubiak group demonstrated that molybdenum and tungsten complexes of bipyridine were effective catalysts for carbon dioxide reduction.² In addition, the Saveant group showed that Iron(0) porphyrins yield unprecedented turnover rates and efficiencies.³ This led us to examine the synthesis of a molybdenum center complexed inside of a porphyrin ligand in an attempt to combine the two separate electrocatalysts and observe the net electrocatalytic efficiency. In addition, we drew inspiration from nature, where highly specialized mechanisms of CO₂ reduction by carbon dioxide dehydrogenases involve molybdenum, as described by the Dobbek group.⁴

Several techniques were used in the synthesis and purification of the MoX(TPP), a compound with a molybdenum ligated within a porphyrin ring. The porphyrin was prepared according to known reactions and allowed to react with various molybdenum starting materials under thermal conditions. The product was then purified and characterized by means of proton Nuclear Magnetic Resonance (NMR), Ultraviolet-visible spectroscopy (UV-Vis) and electrochemistry. Finally, the compound was examined for electrocatalytic behavior under CO₂ using cyclic voltammetry.

METHODS

Synthesis and Characterization of MoX(TPP)

The synthesis was adapted from a literature report by Harvey and coworkers.⁵ An excess of molybdenum hexacarbonyl (186 mg, 1.52×10^{-3} mmol) was combined in a 5:1 ratio with the tetraphenylporphyrin (400 mg, 3.03×10^{-4}

mmol) and suspended in a 50 mL solution of decalin. The solution was refluxed for 72 hours under a steady stream of nitrogen to ensure an anaerobic environment. The crude solid was isolated with rotary evaporation at 80 °C. The resulting residue was then rinsed with pentane and a crude yield of 219 mg was recorded.

The crude product was purified by means of flash column chromatography using a Teledyne Isco Combiflash Rf. A gradient was utilized with a hexane and ethyl acetate solvent mixture. This allowed for the separation of products yielding a final dark green solution of the (presumed) pure product as based on spectral analysis from UV-Vis within the Combi-Flash Rf system. This product was then isolated as a dark green powder (99 mg) using rotary evaporation.

Proton NMR characterization of the solid did not yield any signals, likely indicating that the compound was paramagnetic. The green product was examined using UV-Vis spectroscopy and compared with the spectra of the starting materials.

Electrochemistry of MoX(TPP)

Electrochemistry was performed in dimethylformamide (DMF) under argon and carbon dioxide using 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. A glassy carbon working electrode, a Ag/AgCl pseudo-reference electrode, and a platinum wire counter electrode were used. Ferrocene (Fc) was added to reference the peaks.

RESULTS AND DISCUSSION

The synthesis of the MoX(TPP) was performed by refluxing excess Mo(CO)₆ with H₂TPP in decalin, which has a boiling point of 186 °C. The H₂TPP makes a dianionic ligand when bound to metals, and therefore the oxidation state of the Mo in the product is likely changed from that of the starting material (Mo(0)). The product was isolated with flash chromatography using a Combiflash Rf to yield a green solid. A vapor diffusion crystallization was attempted

with a pentane and dichloromethane mixture (25%, 75%), but crystals were not obtained. As a result, X-ray crystallography could not be utilized for structural determination.

The purified complex was then characterized by NMR and UV-Vis spectroscopy. An initial proton NMR of the species in deuterated chloroform yielded no peaks for the compound, leading to the conclusion that the compound was likely paramagnetic (*e.g.* Mo(V)). The UV-Vis spectrum of tetraphenylporphyrin (H₂TPP), when observed as a dilute solution in toluene (magenta-colored solution) yielded a unique fingerprint region from 450 nm to 700 nm, as shown in Figure 1. This was compared to the UV-Vis spectra of a solution of the purified sample in toluene (green solution) and a complete change of the “fingerprint” region was observed (Figure 2), indicating that a reaction had taken place and that the purified sample was free of uncomplexed H₂TPP.

This green product was confirmed to be paramagnetic when it was observed to be NMR inactive. Paramagnetism makes the structural assignment more difficult, however does not impact the efficacy of the product. However, it can be assumed to be supported by the tetraphenylporphyrin ligand because the large 400 nm Soret peak that is common to all porphyrin compounds in the UV-Vis spectrum of the product.⁷ It is likely that there are axial ligands perpendicular to the plane of porphyrin in the molybdenum complex, based on other known molybdenum complexes being octahedrally coordinated. However the identities of these ligands remain unknown due to the paramagnetic nature of the compound.

To further characterize the synthesized molybdenum compound, electrochemical analysis was performed for H₂TPP and the green product. The analysis of H₂TPP via cyclic voltammetry yielded reductions at -1.42, -1.78, and -2.30 V under argon wherein the downward peaks denote reductions and the upward peaks represent the oxidations of each species (Figure 3). The synthesized molybdenum species was observed in the same cyclic voltammetry cell and referenced with ferrocene in a solution of DMF.

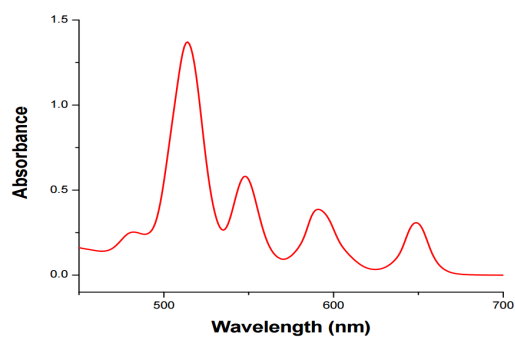


Figure 1. UV-Vis of the fingerprint region H₂TPP in toluene. The large Soret peak at 400 nm is off of the scale to the left.

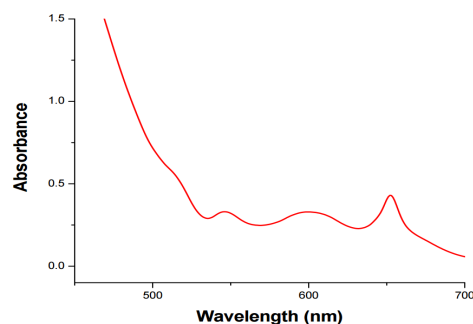


Figure 2. UV-Vis of the fingerprint region of the MoX(TPP) species in toluene. Note the significant difference between this spectrum and that of H₂TPP in figure 1.

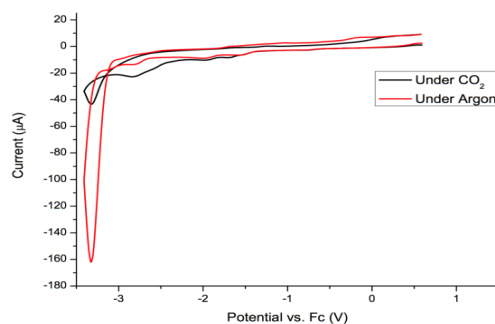


Figure 3. CV of H₂TPP in DMF. The difference between inert gas and CO₂ shows that H₂TPP reacts with CO₂ upon reduction.

This was observed to have reductions at -1.56, -1.87, and -2.76 V under argon (Figure 4). The differences in the electrochemical behaviors of the two samples offer additional support that the synthesized compound did not contain H₂TPP.

Each of the samples were prepared at ca. 1 mM concentrations and referenced to a ferrocene (Fc) standard. For the molybdenum complex, 1 mM was calculated based on the assumption of a theoretical molecular weight (~754 amu) for a Mo(TPP)(O)(OH) species, which would be paramagnetic.

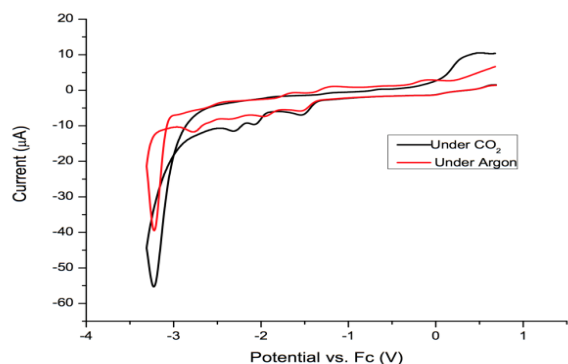


Figure 4. CV of MoX(TPP) in DMF. The addition of CO₂ altered the current of the third reduction at -2.76 V.

The electrochemistry of H₂TPP and the molybdenum complex was then examined multiple times under CO₂ to assess if either compound reacted with CO₂. Both species

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AUTHOR CONTRIBUTIONS

Both K. A. Grice and J. S. Bhanot contributed to the research. K. A. G. designed the experiments and helped process data. J. S. B. conducted the research to synthesize, purify and characterize the MoX(TPP) compound, as well as writing the manuscript. K. A. G. provided revisions and editorial assistance.

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showed changes under CO₂ that suggested a reaction between the reduced species and CO₂, but significant catalysis was not observed. The most notable difference in the two species is the increase in current for the third reduction in the presence of carbon dioxide, which was larger for the molybdenum compound. In addition, the molybdenum complex appeared to degrade or plate on the electrode, as repeated electrochemical scans resulted in decreased signal intensities.

CONCLUSIONS AND FUTURE DIRECTIONS

In conclusion, a molybdenum complex was synthesized from H₂TPP and Mo(CO)₆ and purified by flash chromatography. The synthesized complex was paramagnetic, but exhibited differences in its UV-Vis spectra and electrochemistry as compared to H₂TPP. The complex did not exhibit effective catalysis under CO₂, but did show reaction with CO₂ at reducing potentials. Future studies will include structurally characterizing the molybdenum compound and synthesizing modified ligands to determine if stability and activity can be improved.

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