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Synthesizing Ni-compounds for Homogenous Catalysis

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Project Summary

Synthesizing Ni-compounds for homogeneous catalysis

Our growing global demand for energy has promoted an urgent search for a clean, safe, sustainable energy solution. Over the past decades, great strides have been made to develop technology utilizing solar and wind power.¹ However, the intermittent nature of these renewable energy sources makes energy storage a requirement for a continuous and sustainable energy supply. Molecular fuels that can be produced by harnessing solar energy offer an attractive solution to this challenging problem. Among other options, hydrogen is an ideal solution, since the combustion is essentially pollution free. In order to shift from fossil fuels to a H₂ fuel economy, an energy-efficient, cost-neutral technological advancement is needed that will produce H₂. Splitting of water using solar energy to produce hydrogen in an integrated artificial device will be a perfect solution to this challenge, as the overall process will be completely carbon neutral.² Noble metals like platinum have been long used for producing hydrogen, but its low abundance makes it an unattractive catalyst. However, alternative earth-abundant metals or mixed metal alloys are a potential solution. In this project, I intend to synthesize catalysts comprising earth-abundant metals that will work in aqueous media and produce hydrogen using water as proton source. In order to gain better understanding of the mechanism of a water soluble catalyst, I propose to initiate the study by *synthesizing Ni-centered molecular catalysts that will reduce protons to produce H₂*.

So, I propose to investigate a set of N5-polypyridyl Ni-complexes (Figure 1) for H₂ production. Synthesis of the Ni-N5polypyridyl ligand is known in literature and the variation of the ligand will be accomplished by following published procedures. The compounds will also be made to compare and contrast the effect of ligand electronics on activity of the model complexes and understand the mechanism of proton reduction. In order to characterize these model complexes, standard instrumentation facility (Mass Spectroscopy, NMR, elemental analyses) will be used. Ni-complexes are colored, so they will be strongly influenced by their oxidation states and coordination environment. UV-Visible spectroscopy will be used once the complexes are made to characterize them and also will be used to monitor the spectroscopic changes in progress.

Student Prerequisites: Student should be familiar with organic chemistry laboratory, techniques. This is usually covered by course CH-335 and/or CH-336.

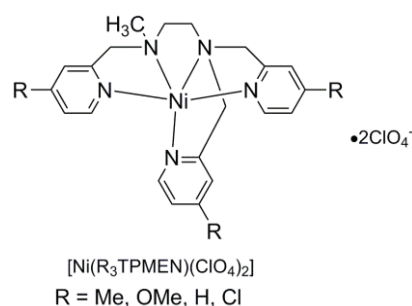


Figure 1: Ni-complexes for solar fuel

Student Duties: The student will be responsible to synthesize these complexes. In this project, new ligands will be synthesized following standard procedure published in the literature. Students will enhance their skills in organic synthesis. In parallel, student will make Nickel compounds from with the newly designed ligand once it is synthesized. This will give the student the opportunity to learn inorganic chemistry techniques and allow them to characterize the compounds. The ligand synthesis will be characterized by NMR, mass spectroscopy, so student will learn to analyze these spectra. In addition student will use UV-visible spectroscopy to monitor reaction between Ni-complexes and substrates. The product of these reactions will be analyzed by gas-chromatography-mass-spectroscopy technique. Many of these techniques are new to the students so they will be introduced to many new techniques. At the end of the term student should be able to make one designed ligand(R= H) and the corresponding nickel-complex and explore their reactivity toward proton.

This project allows a student to pick-up skills necessary to be successful for higher education or industrial careers. The techniques mentioned above are routinely used in analytical laboratories and industry research environments. In this project, student will also be trained to some computer software specific to this research-data analysis. Working in a small research project also gives student the exposure to do literature search, using scientific databases. Furthermore, they learn how to define a problem and how to approach a solution that a standard laboratory experiment does not teach. Research experience further enhances student's knowledge on fundamental topics of chemistry covered in lecture close. Organic chemistry course teaches a student condensation reaction, which he/she uses to make a ligand. Inorganic chemistry course covers topic like chelate effect that will be a principle applied once you make the nickel-complex. Finally, student learns to present their data in form of a poster that significantly improves student's communication skills.

Mentor Supervision and Interaction

Student will be closely supervised in this project by Dr. Mukherjee. Currently, Dr. Mukherjee has two graduate students in the laboratory so the student will never work without supervision. In the first few days student will be shown common laboratory techniques and given literature to study. These materials and instructions will be given to the student directly by Dr. Mukherjee. One graduate student will be assigned to the student as a direct mentor and she will assign the student daily responsibilities. The student will work closely with the graduate student, she will help him/her to set up experiments, show how to measure different spectra. Dr. Mukherjee will hold weekly meeting with the student in her office, where student will present the data he/she collected in that week. Dr. Mukherjee will help the student to analyze his/her data in these weekly meetings. These weekly meetings will allow Dr. Mukherjee to evaluate the student's progress and give directions for the next week. Mukherjee group usually meets every Wednesday to discuss research progress of every individual, so this will be also attended by the student. Dr. Mukherjee will teach the student to use chemical soft-wares to make quality figures for scientific poster. She will provide feedback on that poster. In the group meeting, student will present his/her data at the end of the summer term and Dr. Mukherjee and other group members will provide feedback to the student so that he/she is better prepared for the actual RCEU poster session. In summary, the student will interact with the PI every week and with the direct mentor on daily basis.

Reference

- (1) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 15729.
- (2) Thoi, V. S.; Sun, Y.; Long, J. R.; Chang, C. J. *Chem. Soc. Rev.* **2013**, *42*, 2388.

Faculty-Student meeting:

I am glad three students showed interested in my project, I chose two of them to have one-to-one interview. Both of the students showed sincere interest in the project, Hayden was looking for other offers so she declined to work on my RCEU project. Ashley, showed interest and her interest is reflected strongly, when she asked me, “why am I interested in this project?” This question showed that she really is interested in the research. She does not just want to use this opportunity as a research experience, she is interested in solar energy research. I was impressed, moreover her letter states that she is interested in industry jobs for future. Research capabilities in my group will give her expertise in synthesis and analytical techniques, those two skills are very valuable for research laboratory in industry. She took the CH-335 lab in Fall 2015, that makes her qualified to work in my lab under supervision. In summary, she will fit nicely in my group and I think this RCEU project will be a good opportunity for her, reflected in her email response “[I wanted to email you and let you know that I would love to work on this project with you this summer. I think this project would be a great experience and thank you so much for considering me. If given the option, I would like to commit to your RCEU project](#)”.