

PRF # 56706, UR-3

Project Title: Neutral Dinuclear Iron Complexes Supported by $N_{\text{amido}} - \text{Metal Bonds}$

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Overview

The goal of this project is to prepare a series of metal complexes (with a focus on the Fe(II) metallic center), then investigate their propensity activate molecular oxygen and, in the case of iron, to form oxygen adducts. The ligands we proposed to use for this chemistry are built around a $N_{\text{amido}} - O_{\text{phenoxo}} - N_{\text{amido}}$ core, having either the N-H or C=O group directly attached to the phenyl ring, respectively. Their side-arms are further functionalized with a bis-(pyrazolyl)methane donor set.

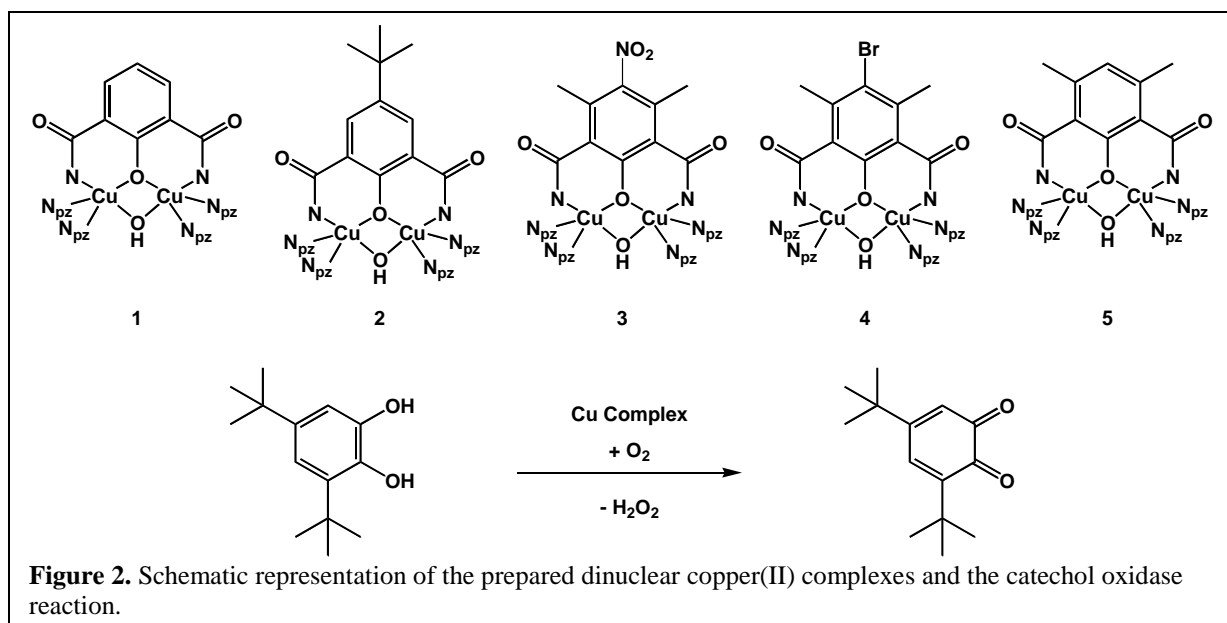
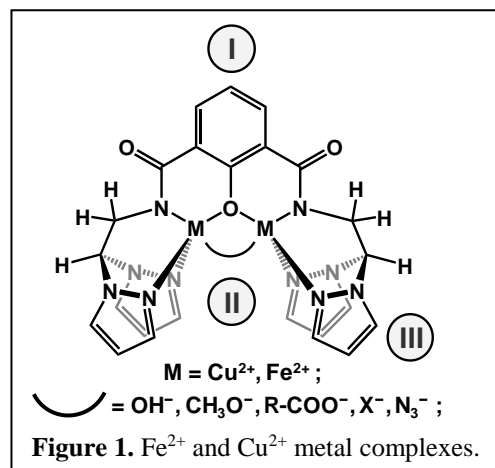
The **specific objectives** of this project are:

1. Synthesis and characterization of the ligands.
2. Synthesis and characterization of Fe(II) dinuclear complexes.
3. Synthesis and characterization of high-valent diiron-oxo complexes.

Progress report

During the second year of the grant, we have successfully expanded our library of ligands capable of supporting dinuclear metal complexes. The idea behind this work was to prepare a set of metal complexes that can be finely tuned in their structure, as depicted in Figure 1, then study their catalytic activities. In region I, it is possible to change the electronic properties of the complexes by grafting electron donating or withdrawing groups on the central arene ring. In region II, a large variety of exogenous bridges can be selectively placed within these complexes, either by choosing a suitable starting material or by exchanging one bridge with another. The steric demand around the active site of these complexes (region III) can be modified by attaching substituents of various sizes, such as methyl or *t*-butyl groups on the 3 and 5 positions of the pyrazolyl moieties.

Following this idea, we have prepared five copper(II) complexes pictured in Figure 2 – top. All complexes have either electron donating or withdrawing groups grafted onto the central arene ring.

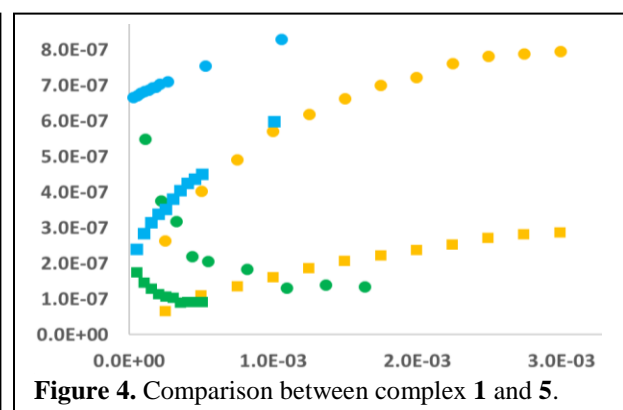
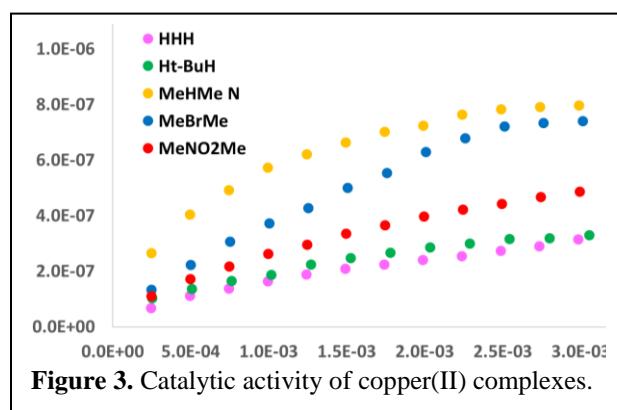


We have studied the catechol oxidase activity of these complexes, using 3,5-di-tert-butyl-catechol (DTBC) as a substrate, with the formation of 3,5-di-tert-butyl-quinone (DTBQ) as a product (the reaction is depicted at the bottom of Figure 2). We have found that in methanol and in the presence of dioxygen, all five complexes follow a Michaelis-Menten type kinetics. Furthermore, their catalytic activity is influenced by the substituents of the central phenol ring: as depicted in Figure 3, the activity increases from complex **1** to complex **5** (see Figure 2 for numbering scheme).

We have also found that this catalytic process produces hydrogen peroxide as a byproduct, in contrast to the natural enzyme, which produces water. The catalytic activity of these complexes is influenced by the presence of increased amounts of hydrogen peroxide: addition of increasing amounts of H₂O₂ to the reaction mixture leads to a significant increase in the catalytic activity of the complexes, suggesting that the hydrogen peroxide is involved in the catalytic process.

In contrast, the product of the reaction has little influence on the activity of the complexes: addition of increasing amounts of DTBQ to the reaction mixture, after causing an initial small decrease in activity, has no further influence on the activity of our copper(II) complexes.

These findings are graphically represented in Figure 4, where the circles represent the findings of the most active complex (**5**), and the squares the results obtained after investigating the least active complex (**1**). The orange color represents the catalytic activity, the blue color the same in the presence of increasing amounts of H₂O₂, and the green color the influence of the DTBQ byproduct. As it can be seen, both complexes have a similar behavior, as described above.



Impact of funding

The funding of this proposal had an important impact on the PI's career. The research component of this project provided the PI with the opportunity to study and understand the factors that govern the synthesis and characterization of metal complexes supported by N_{amido}-Metal bonds, as well as the influence of this type of bond on the catalytic activity of the resulting complexes. It also provided him with the opportunity to engage in new collaborations with research groups having similar research interests from other Universities.

During the summer of 2018, four students (three undergraduates and one masters) were supported by this grant. During their time in the PI's lab, the students were trained in synthetic design, and accumulated experience in ligand and metal complex syntheses (including those requiring the handling of air and moisture sensitive compounds), instrument operation, and spectral interpretation. In the same time, they were able to identify, acquire and describe information pertaining to the synthetic and characterization methods used in this particular field, and integrate the principles learned in various chemistry lectures with the laboratory experiences. The experiments performed by the PI's students reinforced a broad range of fundamental principles covered in regular inorganic, organic, and physical chemistry courses.

The results obtained during this year have been collected in a paper accepted for publication (pending minor revisions) in *Inorganica Chimica Acta*; furthermore, one more paper is in preparation and will be submitted soon.