Environmentally Benign Catalysts by Design: Functional Mimics of Metalloenzymes

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Background

- Bio-inspired catalytic systems have the potential to reduce chemical waste by performing efficient reactions under benign conditions.
- Enzymes can serve as an inspiration for the development of these methodologies. They carry out a wide variety of redox processes at high efficiency, employing a wide array of earth-abundant transition metals.
- Metabolic processes incorporating C-H bond oxidation can serve as inspiration for developing eco-friendly pathways for obtaining synthetic chemicals.
- Mimicking enzymes active site nature complexes with tetradeinate ligands with amine and pyridine functionalities (N2/Py2) have received significant attention for their role in hydrocarbon oxidation with high selectivity.
- Studying the structural and spectroscopic features as well as reactivity profiles of such biomimetic complexes can provide good insights for designing bio-inspired catalysts.
- Current efforts in the group are focused on investigating the reactivity of the nickel (II) complexes in hydrocarbon oxidation using environmentally benign oxidants and correlating structure and function.

Synthesis and Characterization

- Five Nickel complexes were synthesized from the reactions of N2-tetradeinate ligands with NiCl₂·6H₂O salt in methanol.

![Complexes 1-5](image)

- UV-Vis Spectroscopic studies of complexes 1-5 in methanol, gave colored solutions with optical bands in the visible region with weak intensities.

![UV-Vis Spectra](image)

- Single crystals suitable for X-ray diffraction studies were obtained for the complex 2 from methanol. 2 showed nickel in a pseudo-octahedral geometry with four coordination sites occupied by the nitrogen atoms of the ligand and the two other coordination sites were occupied by chloride ions.

Substrate Reactivity

- Complexes 1-3 were allowed to react with 2,4,6-Tri-tert-butyphenol (2,4,6 TTPB) in the presence of the oxidant KO₂ in methanol at room temperature.
- The reactions were monitored by UV-Vis Spectroscopy.

![UV-Vis Spectra](image)

<table>
<thead>
<tr>
<th>Complex</th>
<th>2,6 DTBQ (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>30%</td>
</tr>
<tr>
<td>2</td>
<td>15%</td>
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<tr>
<td>3</td>
<td>32%</td>
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- GC-MS analysis of the product solutions show 2,6-Di-tert-butyl-1,4-benzoquinone (2,6 DTBQ) as the product and the quantification was performed by GC-FID Spectrometry.

![GC-MS](image)

Summary

- Complexes 1-3 were able to perform phenol oxidation using KO₂ as an oxidant.
- Both 1 and 3 showed similar amounts of oxidation but 2 gave less yield in comparison.
- Overall these mononuclear nickel (II) complexes have the potential to serve as homogeneous catalysts.

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References