Study of the water oxidation mechanism by ruthenium(II) complexes containing N-heterocyclic ligands

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Abstract
Recent researches and elucidation of new ruthenium catalysts containing N-heterocyclic ligands have shown great importance and relevance in the study of water oxidation kinetics and its mechanisms, which produces O2 coupled with protons and electrons transfer through the catalytic cycle. In this project, we are working with a new complex [Ru(H2dimpy)(phen)Cl]PF6 (where H2dimpy = 2,6-bis(1H-imidazol-2-yl)pyridine and phen = 1,10-phenanthroline), which was synthesized and characterized by 1H NMR, FTIR, UV-vis and elemental analysis.

Key words:
water oxidation, water split, ruthenium(II) complexes

Introduction
The search for new sources of sustainable energy that are free of pollutants such as carbon dioxide which is responsible for the greenhouse effect has been the subject of much research efforts. The water splitting theme emerged as an alternative to the demand for a new cheap and clean energy source, since O2 and H2 can be obtained from the water oxidation. In order to understand more deeply the mechanisms, intermediates and kinetics of water electrolysis, ruthenium(II) catalysts containing N-heterocyclic ligands have been used for this purpose. It is already known that these catalysts containing different kind of σ-donor ligands may affect spectroscopically the catalyst stability. The main objective of this project is to contribute to the current studies based on these various catalysts in order to improve their efficiency in the catalytic water oxidation.

Results and Discussion
The synthesis of the [Ru(H2dimpy)(phen)Cl]PF6 was made from the precursor [Ru(H2dimpy)Cl] and 1.0 equivalent of phenanthroline in DMF solvent. The reaction was run at reflux for 8 hours at 150 ºC and monitored by UV-vis with a yield of 93%. The 1H NMR spectra in Figure 1 shows the molecular structure of [Ru(H2dimpy)(phen)Cl]PF6.

![Image 1. 1H NMR spectrum of [Ru(H2dimpy)(phen)Cl]PF6 with zinc powder in DMSO-ds.](image)

It was possible to verify and determine some small changes on the chemical and spectroscopic properties of the [RuII(H2dimpy)(phen)Cl]PF6 complex when compared to its precursor [Ru(H2dimpy)Cl2] and the phenanthroline ligand itself. The UV-vis spectra (Figure 2) was taken from the two ligands and our complex in which shows a MLCT band at λ = 475nm and also the other peaks at λ = 265nm and λ = 288nm corresponding to the phenanthroline and H2dimpy ligands, respectively.

![Image 2. UV-vis spectra of [Ru(H2dimpy)Cl2], phenanthroline and [Ru(H2dimpy)(phen)Cl]PF6 in MeOH.](image)

Conclusions
The successful synthesis of [Ru(H2dimpy)(phen)Cl]PF6 with a 93% yield led to the formation of the expected compound which was proved by 1H NMR and UV-vis spectra. On the next steps, further studies are necessary for evaluation of the electrocatalyst properties for water oxidation.

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