

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 oxidation¹. 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 purpose². 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)Cl₃] and 1.0 equivalent of phenanthroline in DMF solvent. The reaction was run at reflux for 8 hours at 150 °C 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.

It was possible to verify and determine some small changes on the chemical and spectroscopic properties of the [Ru^{II}(H₂dimpy)(phen)Cl]PF₆ complex when compared to its precursor [Ru(H₂dimpy)Cl₃] 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.

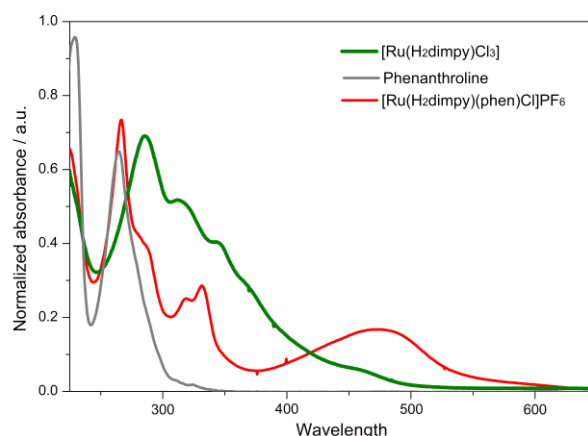


Image 2. UV-vis spectra of [Ru(H₂dimpy)Cl₃], phenanthroline and [Ru(H₂dimpy)(phen)Cl]PF₆ in MeOH.

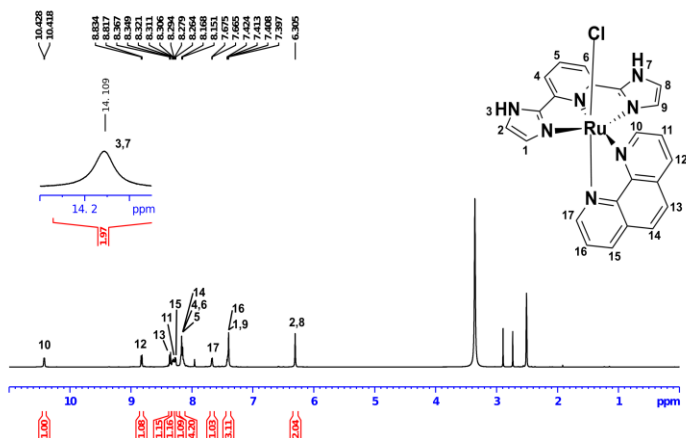


Image 1. ¹H NMR spectrum of [Ru(H₂dimpy)(phen)Cl]PF₆ with zinc powder in DMSO-d₆.

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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