



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

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Abstract

Since the first ruthenium catalyst containing N-heterocyclic ligands was synthesized in 1982, many of them have been developed looking for a great performance in water oxidation catalysis and to get a better understanding of its mechanisms, which produces O₂ through a PCET reaction in the catalytic cycle. In this project, we are working with a new complex [Ru(H₂dimp)(phen)Cl](PF₆) (where H₂dimp = 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. Here we also focused on DFT calculations to obtain accurate theoretical results from its energy and geometry.

Key words:

water oxidation, water splitting, ruthenium(II) complexes

Introduction

In the last years, as the world's population grows, it is also notorious for an increase in energy demand and consumption all over the globe. Gas emission in the atmosphere such as carbon dioxide (CO₂) is one of the biggest concerns nowadays, especially because of its negative effects like greenhouse and global warming. 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 water oxidation¹. 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 well known that complexes bearing good electron-donor ligands may improve complex performance in water oxidation catalysis increasing its TOF and TON. Besides, it is important to determine the complex energy and geometry using DFT calculations to better elucidate the catalytic cycle and its intermediates.

Results and Discussion

The synthesis of the [Ru(H₂dimp)(phen)Cl](PF₆) was made from the precursor [Ru(H₂dimp)Cl₃] and 1.0 equivalent of phenanthroline in DMF solvent. The reaction was run under reflux for 4 hours at 150 °C and monitored by UV-vis with an yield of 93%. The ¹H NMR spectrum in Image 1 confirms the success of the synthesis of [Ru(H₂dimp)(phen)Cl](PF₆).

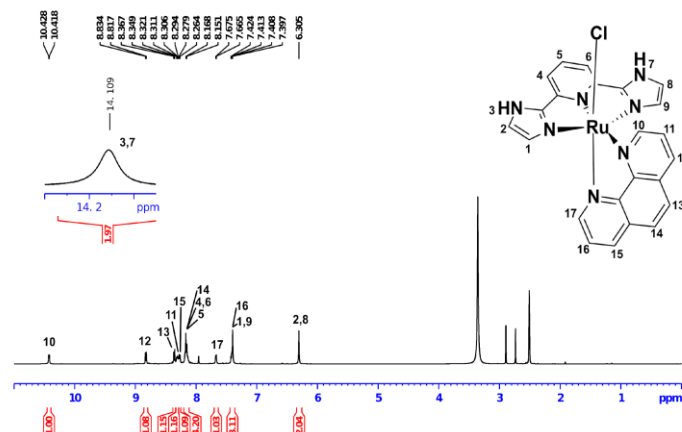


Image 1. ¹H NMR spectrum of [Ru(H₂dimp)(phen)Cl]PF₆ with zinc powder in DMSO-d₆.

It was possible to verify and determine some small changes on the chemical and spectroscopic properties of the [Ru^{II}(H₂dimp)(phen)Cl](PF₆) complex when compared to its precursor [Ru(H₂dimp)Cl₃] and the phenanthroline ligand itself. The UV-vis spectra (Image 2) was taken from the two ligands and our complex and shows a right-shifted MLCT band at λ = 475nm and H₂dimp ligand at λ = 288nm compared to its precursor. The phenanthroline band is exactly at λ = 265nm for both spectra.

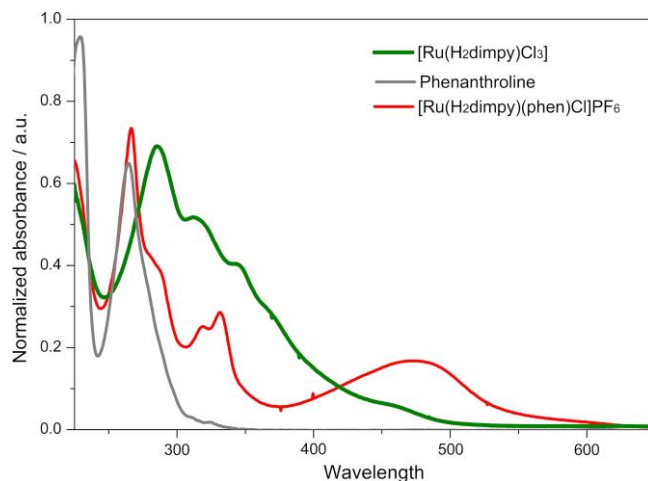


Image 2. UV-vis spectra of [Ru(H₂dimp)Cl₃], phenanthroline and [Ru(H₂dimp)(phen)Cl](PF₆) in MeOH.

DFT calculations were performed using Orca software for the [Ru(H₂dimp)(phen)Cl]⁺ complex which has converged. The def2-svp basis set used to perform these calculations is well recognized to obtain good geometrical optimization, so as peb0 functional that was chosen in this method. Image 3 shows the optimized molecular structure and all its atoms arrangement. Mulliken atomic charges analysis showed that most of the negative charge density is located on nitrogens and chloride atoms and positive on ruthenium as expected.

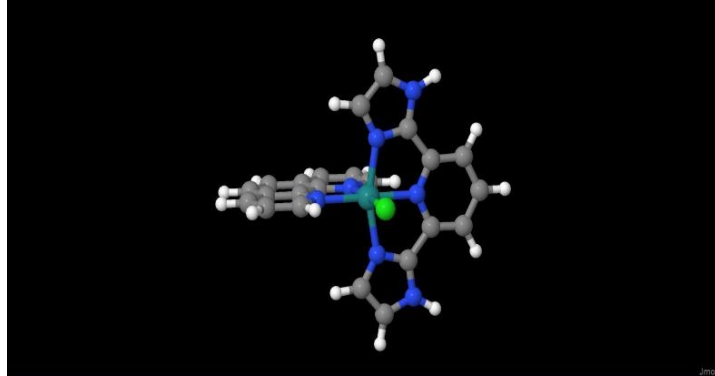


Image 3. $[\text{Ru}(\text{H}_2\text{dimpy})(\text{phen})\text{Cl}]^+$ geometry optimized using DFT calculations.

Conclusions

The successful synthesis of $[\text{Ru}(\text{H}_2\text{dimpy})(\text{phen})\text{Cl}]\text{PF}_6$ with a 93% yield led to the formation of the expected compound which was proved by ^1H NMR and UV-vis spectra. Through DFT calculations, it was possible to obtain good geometry

optimization and other important parameters such as electronic density on each atom and the complex final energy. On the next steps, the synthesis and characterization of $[\text{Ru}^{\text{II}}(\text{H}_2\text{dimpy})(\text{phen})\text{OH}_2](\text{PF}_6)_2$ are essential to study the water oxidation catalysis through electrochemical experiments and determine its kinetics by stopped-flow. DFT calculations will determine theoretical pK_a values and oxidation potential for each intermediate on the Pourbaix diagram to help understand the better catalytic path for water oxidation catalysis.

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¹ Kreuter, W. and Hofmann, H. *Int. J. Hydrog. Energy*, **1998**, *23*, 601.

² Liu, Feng.; Concepcion, J. J.; Jurss, J. W.; Cardolaccia, T.; Templeton, J. L.; and Meyer, T. J. *Inorg. Chem.* **2008**, *47*, 1729.