

# A new copper(II) complex with a pyridine/acac based ligand as a potential catalyst for “click-chemistry” reactions.

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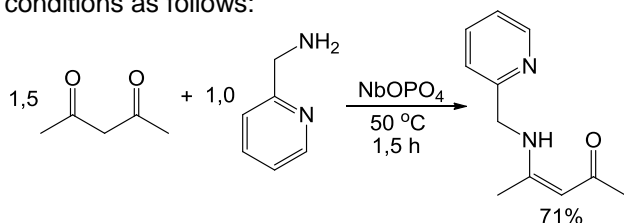
## Introduction

Click chemistry reactions are defined by the simplicity to perform, giving rise to their intended products in very high yields with little or no byproducts. They work well under many conditions, and are unaffected by the nature of the groups being connected to each other. Among them, the azide-alkyne cycloaddition (AAC) reactions, producing 1,2,3-triazoles, occupy a special place, once they are high in chemical potential energy, and their fusion to make triazoles are spontaneous. However, the rate of these reactions is quite slow, normally requiring prolonged heating for unactivated alkynes.

In this sense, the copper-catalyzed (CuAAC) version has been the most widely used in order to afford the desired products faster and in mild conditions.<sup>1</sup> Here we present the synthesis and characterization of a new copper(II) complex based on bidentate ligand (*Z*)-4-((pyridin-2-ylmethyl)amino)pent-3-en-2-one (**L**).<sup>2</sup>

## Results and Discussion

Although the bidentate ligand was already described in the literature<sup>2</sup>, we present here a new niobium-catalyzed methodology in mild and solvent free conditions as follows:



The organic product was characterized by GC-MS, <sup>1</sup>H and <sup>13</sup>C-NMR.

Copper(II) metal complex (**1**) was synthesized adding in a methanolic solution (5 mL) of the ligand in a methanolic solution (5 mL) of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in a 2:1 stoichiometric ratio respectively, under magnetic stirring and mild heating (45 °C). After 15 minutes, the green solution was cooled to room temperature, filtered and left for crystallization. After 48 h, bluish crystals were obtained. Complex **1** was characterized by IR and UV-Visible spectroscopy, Molar conductivity and electrochemistry.

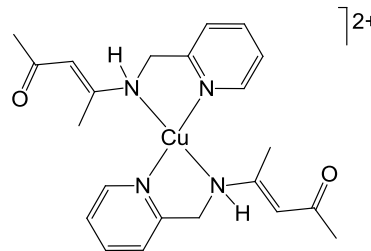
IR spectra (KBr) of **1** is comparable with the free ligand itself, however the N-H stretching are sharper and more intense in **1** indicating the presence of a rigid structure. The region between 1600 and 1450 cm<sup>-1</sup> indicates the aromatic C-N and C-C bonds while in **1** a strong absorption in 1087 cm<sup>-1</sup> (absent in the ligand) correspond to the Cl-O stretch of the perchlorate counterions.

Molar conductivity ( $\Lambda_M$ ) of a 1×10<sup>-3</sup> M solution in DMF (170 μS cm<sup>-1</sup>) agrees with a 2:1 electrolyte ratio, confirming the presence of two perchlorate ions and therefore the following aimed structural unit: [CuL<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.

The UV-Vis-NIR spectrum of **1** in DMF (1.0×10<sup>-3</sup> M) shows one broad absorption at 618 nm horough ( $\epsilon = 131 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) and no charge transfers which agrees with the idea of a *N*-rich coordination environment.

Cyclic voltammogram of the complex (DMF; TBAPF<sub>6</sub> 0.1 M; WE-C, CE-Pt; RE-Ag/AgCl; 100 mV·s<sup>-1</sup>) reveals a *quasi*-reversible wave (-0.23 V vs NHE) ascribed to redox pair Cu<sup>II</sup>/Cu<sup>I</sup>.

Based on these data we propose the following structural unit for the cation complex of **1**:



## Conclusions and Future Directions

A new solvent-free synthetic procedure for the ligand **L** was presented and its novel copper(II) complex was prepared. After thorough characterization a structural unit was proposed. Chemical tests using **1** as a catalyst for click-chemistry reactions are underway and they will be presented later.

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<sup>1</sup> Finn, M. G.; Fokin, V. V. *Chem. Soc. Rev.* **2010**, *39*, 1231.

<sup>2</sup> Lee, D. H.; Park, S. E.; Cho, K.; Kim, Y.; Athar, T.; Lee, I. M. *Tetrahedron Lett.* **2007**, *48*, 8281.