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Theoretical study of a new diarylic ligand for M^{2+} cations detection.

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Abstract: A novel byphenyl hydrazone ligand developed as chemosensor for the detection of Cu^{2+} was studied by a theoretical analysis based on the density functional theory (DFT) and time-dependent DFT (TD-DFT). The geometries of the ligand (L) and the Cu^{2+}-ligand complex were optimized at the CAM-B3LYP/631+G(d,p) level of theory in dimethyl sulfoxide using the conductor like polarizable continuum model. The adsorption spectra of these molecular systems were analyzed and compared with the experimental data. Theoretical study of the structural, electronics and optical properties allowed to understand the chemical changes that the ligand suffers in the complexation process with the Cu^{+2} ion.

Keywords: chemosensor, DFT, Cu^{2+} ion.

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1. Introduction

The design and development of selective chemosensors of cations that are biologically important, has gained considerable attention. In particular, copper is the third most abundant essential trace element in the human body and is commonly found as Cu^{2+} in natural water. While excessive intake of Cu^{2+} in the body can cause serious health effects, such as respiratory ailments, gastrointestinal problems, kidney damage, Alzheimer's disease or Wilson's disease [1]. Moreover, copper is also widely used in industry and agriculture, and consequently could cause some significant environmental pollution. Therefore, exploring new detection methods for Cu^{2+} that allow us a simple, fast and selective determination, is very important.

Some analytical methods for Cu^{2+} detection such as inductively coupled plasma-optical emission spectrometry, atomic absorption spectrometry, and atomic emission spectrometry were widely used.

But these methods often require expensive instrumentation and consume a lot of time. Therefore, in recent years, the identification of various heavy metal ions by fluorogenic and colorimetric chemosensors has drawn much attention due to their selectivity, sensitivity, low cost, operability, and velocity of detection [2,3].

Fluorogenic chemosensors are attractive and versatile tools for analytical sensing because of their high sensibility, fast response time, and technical simplicity [3]. In this sense, we have recently reported the design and synthesis of a novel chemosensor derived from 5,5′-*bis*-vanillin for the determination of Cu^{2+} [4].

In this work, we realized a theoretical study of this chemosensor using Density Functional Theory (DFT) and time-dependent DFT (TD-DFT) to understand the chemical changes that occurred in the ligand in the complexation process with the Cu^{+2} ion. We used the experimental data from UV-Vis spectroscopy and compared them with the theoretical data obtained by simulations to study the chelation phenomenon between the ligand and Cu^{2+}.

2. Computational methods

The ground state geometry optimizations of the ligand and complex Cu-ligand were carried out at the DFT level of theory using the CAM-B3LYP functional and the 6-31G(d,p) basis set. The excited states of these compounds were calculated by time-dependent DFT (TD-DFT) method using the same functional and basis set as in the ground state calculations (TD CAM-B3LYP/6-31G(d,p)). These calculations were performed with solvent models for dimethyl sulfoxide (DMSO) using the conductor-like polarizable continuum model (CPCM) [5]. Frequency calculations allowed us to verify that the currently located geometries are minimal.

The molecular orbital calculations and natural orbital (NBO) analysis were performed to characterize the exited-state properties. All of these calculations were developed using the Gaussian 09 program package [6].

3. Results and discussion

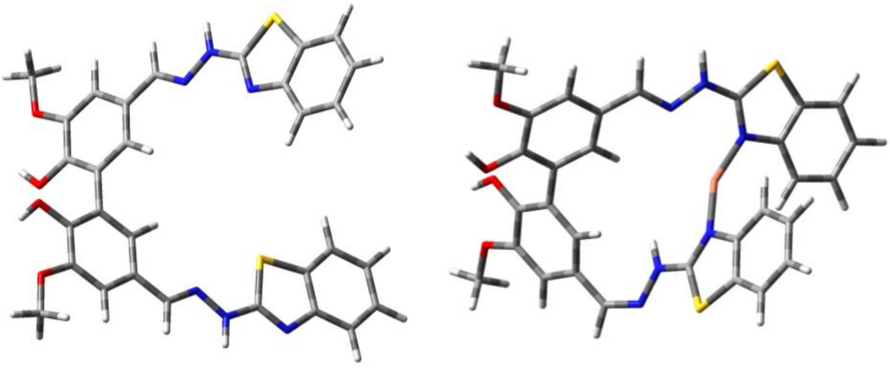
3.1. Ground state geometry

The optimized structures of Ligand (L) and L-Cu^{2+} complex molecules obtained with CAM-B3LYP/6-31G(d,p) level are presented in Figure 1. It is important to consider the solvent effect on theoretical calculations when seeking to compare the experimental data, in this way, CPCM is an effective tool to treat bulk solvent effects. Also, the CAM-B3LYP is recommended to get a good prediction of the excitation states of the aromatic system.

From these geometry optimizations, the values of the dihedral angle of the biphenyl structures were obtained. The dihedral angle for L and L-Cu^{2+} are 62.65° and 53.05°, respectively. These results demonstrate that the dihedral angle decreases (~10°) because of L chelation with Cu^{2+}, increasing the conformational rigidity of the ligand. This effect will be responsible for the bathochromic shift of L-Cu^{2+} in the UV-vis spectra and it also can be responsible of the enhanced fluorescence intensity of this complex [7].

It is found that Cu^{2+} is coordinated to both -N sites of benzothiazoles as shown in Figure 1(b), forming two coordinate bonds. The Cu^{2+}-N bond length value is 1.93 Å and 1.92 Å for each -N. The total energy of optimized structures of L and L-Cu^{2+} are -2582.60 and -4222.71 Hartree, respectively. The optimization energy values suggest that the total energy of the complex was lower compared to L indicating higher stability of the L-Cu^{2+} complex.

The complexation energy (E_C) of L-Cu^{2+} was evaluated according to the following total energy difference: $E_c = E(L\text{-}Cu^{2+}) - E(L) - E(Cu^{2+})$, whose value was -159.13 Kcal/mol. The negative value of E_C indicated exothermic processes.



(a) **(b)**

Figure 1. Optimized geometries of (a) ligand L and (b) L-Cu^{2+} complex.

3.2. Electronic properties and charge distribution

To understand the electrical transport properties, HOMO-LUMO gap of L and L-Cu^{2+} have been also estimated using the same DFT method. The negative energy values for HOMO and LUMO in L and in L-Cu^{2+} signifies that both molecules are stable. The energy gaps between the HOMO and LUMO (ΔE_{H-L}) in L and L-Cu^{2+} are 146.21 Kcal/mol and 67.44 Kcal/mol respectively. It shows that the complexation decreases the HOMO-LUMO energy gap, stabilizing the system. It also suggested the process of electron transfer from electron rich L to electron deficient Cu^{2+}.

The NBO charge distributions of L and L-Cu^{2+} were calculated and the most important differences of charge was observed in region of Cu-N bonds compared with charges of L free. In L the N atoms of the benzothiazoles presented the same charge (-0.55), while in L-Cu^{2+} the charge of these atoms increased (-0.58 and -0.65). The Cu^{2+} ion charge is 2.00 for free state, while in L-Cu^{2+} decreased to 0.67 due to the charge in the complex is delocalized.

3.3. *Optical properties*

To understand the electronical transitions from of these compounds, the quantum calculation on electronic absorption spectra in DMSO were perfermed using TD CAM-B3LYP/6-31G(d,p) level obtained the main vertical exitation energies of L and L-Cu^{2+}.

The UV-Vis absorpion spectrum of L in DMSO solution exhibits two band at 257 and 360 nm. After adding Cu^{2+} to the solution, the band of L at 360 nm gradually decreased and moves to a new wideband at 460-490 nm [3].

According to preliminary TD-DFT calculations, the main vertical exitation energies of L are 254 and 322 nm for excited states, and the absorption wavelengths of these states lie relatively closely and agree with the experimental absorption data.

For L-Cu^{2+} complex, the mail vertical exitate energies calculated were 599, 564, 553 and 475 nm corresponding at different exited states. As was observed with data analysis of L, the theoretical absorption data are in agreement with the experimental absorption wavelengths.

4. Conclusions

We have used the density functional theory method to investigate the geometries and electronic properties of a novel chemosensor derived from 5,5′-bis-vanillin for detection of Cu^{2+}. The energy of the ligand-Cu^{2+} complex in relation 1:1 presented more stability than the ligand free indicading that the formation of the complex is thermodinamically favored with a complexation energy of -159.13 Kcal/mol.

The coordination of Cu^{2+} with the ligand occurs throught the nitrogen atoms of the heterocyclic moiety of the corresponding hydrazone generating two new bond Cu-N. The GAP value of the ligand decreases with the complexation with cupper, increasing the stability of the system. Due to the chemical changes produced in the system, charges delocalization is observed in the atoms that are involved in the formation of the complex.

The TD-DFT calculations were used to replicate the necessary optical transitions to predict the excited states. The predicted results of the absorption wavelengths for the ligand and L-Cu^{2+} complex agree with the experimental data.

Acknowledgments

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