

Dimeric Self-assembling via Hydrogen Bonding and Emissive Behavior of a New Copper (I) Complex

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Abstract: This work describes the synthesis, structural characterization and emissive behavior of a new copper (I) complex based on 1-thiocarbamoyl-5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1H-pyrazole ligand. A dimeric self-assembling via hydrogen bonding was determined by analyzing the short contacts present in the solid-state structure by means of X-ray crystallography. The spectroscopic properties were determined using UV-Vis and fluorescence experiments and an interesting behavior as bluish luminescence was assigned mainly to the mixed (MLCT + IL) electronic transitions of the Cu(I)d¹⁰ → (S=C–N_{ligand}) type. The complete characterization of the new copper (I) complex also included elemental analyses and IR spectroscopy.

Keywords: copper (I) complex; luminescent materials; X-Ray diffractometry

1. INTRODUCTION

The study of Copper (I) compounds has been an attractive field of investigation around the world for many reasons such as relevance of their metal complexes in biological systems [1-3], potential application in solar energy conversion [4], light emitting diodes (OLEDs) [5-7] and sustainable light emitting cells (LECs) [8] for example. In this context, the development of closed shell d¹⁰ Copper (I) complexes has been presented as an attractive and justifiable field of investigation for the prospecting of new luminescent materials due to their low cost, less toxicity and eco-friendly features when compared to the third-row noble metal complexes. On this way, a variety of emissive compounds based on Copper (I) phosphine, bidentate-NN' donor ligands and mixed halide-phosphine-NN' complexes have been synthesized [9-13]. Recently, tetrahedral Copper (I) compounds containing halide, phosphane and other ligands have shown intense blue/green emission ranging from 486 to 541 nm when excited at 360 nm in the solid state. The emission processes were assigned

to the metal-to-ligand charge transfer (MLCT) transitions involving the ligands and the Copper (I) atom present in those structures [14]. Mixtures of intraligand charge-transfer (ILCT) and ligand-to-ligand charge-transfer (LLCT) excitations have been correlated to the emission presented by green/emissive Copper (I) compounds based on heteroleptic coumarin (N,N' bidentate)/triphenylphosphine ligands [15]. DFT calculations have shown a possible mixture of metal-ligand orbitals in these complexes, which are responsible for longer permanence time of electronic density in the excited state (S₁) and consequently higher intensity and lifetime of fluorescence (τ) presented by these complexes when compared to the free ligands. Recently, Chavan and collaborators [16], have shown that the complexes containing monodentate ancillary phosphines like PPh₃, have shown higher quantum efficiencies (φ) relative to the Copper (I) complexes with bidentate (dppe) ancillary ligand. The authors reported that this trend would be correlated to the enlargement of the energy gap that decreases the non-radiative rate constant of the Copper

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(I) compounds. Finally mixed-ligand Copper (I) complexes bearing heteroleptic phosphane/thione ligands also have been subject of investigation due to interesting luminescent properties, antibacterial activity and DNA membrane damage [17]. These complexes presented an intense green emission ($\lambda = 534$ nm) when the solid samples were exposed at 410 nm. The broad emission bands, were assigned to the mixed metal-to-ligand (MLCT type $\text{Cu} \rightarrow \pi^*$ (ligand based orbitals)) with intraligand (IL type $\pi \rightarrow \pi^*$) electronic transitions. On this way, our research group started studying the preparation and characterization of Copper (I) luminescent compounds based on sulphur donor thiocarbamoyl-pyrazoline ligands. In order to enrich the literature and to contribute to development of Copper (I) chemistry, we present in this paper the communication of the synthesis, solid state structural characterization and emissive behavior of the first synthesized Copper (I) complex based on 1-thiocarbamoyl-3,5-substituted pyrazoline ligand.

2. MATERIAL AND METHODS

2.1. Chemicals and measurements

The starting materials $(\text{PPh}_3)\text{CuCl}$ and the ligand L1 = (1-thiocarbamoyl-5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole) were prepared according to methods reported in the literature [18,19]. Solvents (AR grade) were obtained commercially and used in the synthesis without further purification. Elemental analyses (CHN) were performed using a Perkin-Elmer 2400 analyser. FT-IR spectra were acquired on a JASCO-4100 spectrophotometer using KBr pellets. The emission spectra were acquired on Cary Eclipse/Varian Fluorimeter by using quartz cuvetts (3 mL) containing solution of the ligand or complex in a 5.0×10^{-5} M. Melting points were determined using an Instruterm DF-3600 apparatus and

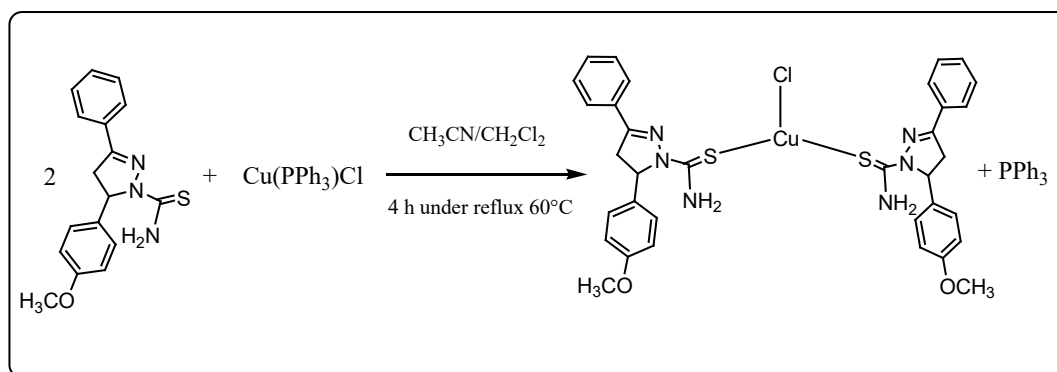
are uncorrected. The X-ray data were collected using a Bruker APEX II CCD area-detector diffractometer with graphite-monochromatised Mo $K\alpha$ radiation. The crystal structures of the complexes was solved using the SHELX package [20]. All non-hydrogen atoms were refined with anisotropic displacement parameters, and the hydrogen atoms were included at their theoretical ideal positions. More detailed information about the structure determinations is given in Table S1.

2.2. Preparation of the complex 1

The synthesis of the copper(I) complex was carried out in accordance with the methodologies already published by our research group [21].

Complex 1: According to the reaction scheme presented below (Scheme 1), a solution containing $(\text{Ph}_3\text{P})\text{CuCl}$ 0.036 g (0.1mmol) in 6 mL CH_2Cl_2 was mixed to a solution of the ligand (L1) 0.062 g (0.2 mmol) previously dissolved in 6 mL of acetonitrile. The pale yellow resulting solution was maintained under magnetic stirring and refluxed at 60 °C during 4h. Afterwards, the obtained solution was filtered off and after four days, prismatic pale yellow crystals were isolated from the mother solution.

Complex $([\text{Cu}(\text{L})_2\text{Cl}]\cdot\text{CH}_3\text{CN})$: Pale yellow and air stable crystalline substance, (Yield 0.057g (58%) of crystals based on Copper (I) precursor used; M.p. 255-257 °C; FW = 762.84 g/Mol, $\text{C}_{36}\text{H}_{37}\text{ClCuN}_7\text{O}_2\text{S}_2$: calcd.(%) C 56.68, H 4.89, N 12.85; found (%) C 59.79, H 4.78, N 12.68. IR (KBr, v/cm^{-1}): 3436-3200 [$\text{v}(\text{N-H})$], 3049 [$\text{v}(\text{C-H})$], 1588 [$\text{v}(\text{C=N})$], 1509-1433 [$\text{v}(\text{C=C})$], 1369 [$\text{v}(\text{C=S})$], 1247 [$\text{v}(\text{C-O})$] [22,23].



Scheme 1. Reaction scheme for the obtention of the Copper (I) complex.

3. RESULTS AND DISCUSSION

3. 1. Crystalline Structure and Dimeric Self-assembling

Figure 1 shows the molecular and crystalline structure of the copper (I) complex. The copper(I) complex has been presented as a neutral mononuclear compound, which contains two pyrazoline ligands and a chlorine atom bonded to the copper (I) atom. The complex **1** also presents an acetonitrile (CH_3CN)

molecule which is acting as a solvate in the crystalline packing in a 1:1 molar ratio. From the analysis of the bond angles (S2-Cu-S1 of $118.76(2)^\circ$, S2-Cu-Cl of $119.76(2)^\circ$ and S1-Cu-Cl of $121.36(2)^\circ$) (figure 2) a trigonal-planar coordination geometry occurs around the copper (I) atom. The Cu-S bond lengths presented by the complex **1** (Cu-S1 of $2.2184(6)$ and Cu-S2 $2.2057(5)$ Å) are in accordance to the values already published in the literature by Akrivos and coworkers in their studies on the copper/thione compounds [24].

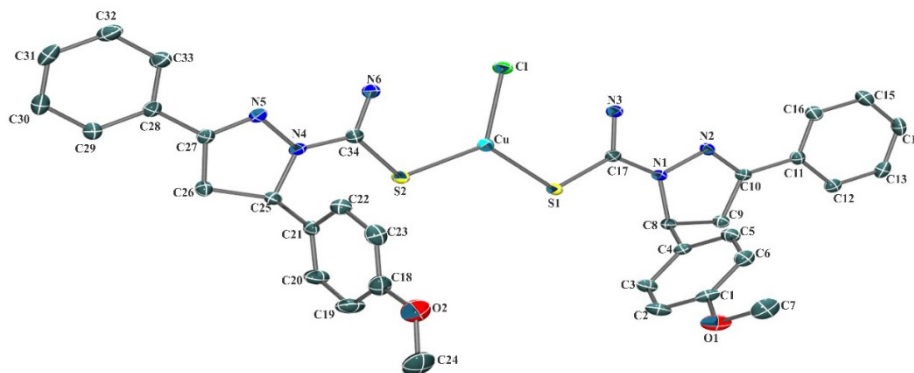


Figure 1. Molecular structure of the Copper(I) complex. Hydrogen atoms and CH_3CN (solvate) were omitted for clarity. Thermal ellipsoids were drawn at 50% probability level.

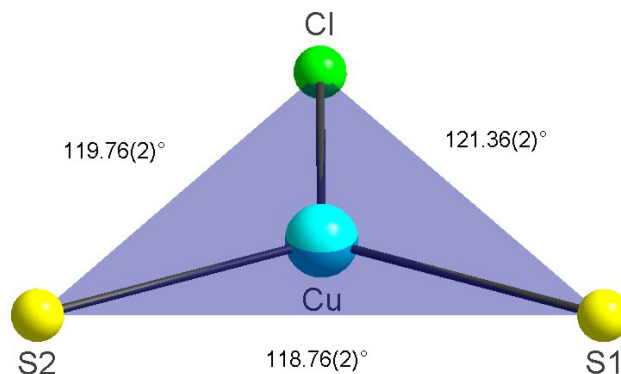


Figure 2. Trigonal-planar coordination geometry presented by the Copper(I) metallic center. Selected bond and angles: Cu-S1 of $2.2184(6)$ Å, Cu-S2 of $2.2057(5)$ Å, Cu-Cl $2.2741(6)$ Å; S2-Cu-S1 of $118.76(2)^\circ$, S2-Cu-Cl of $119.76(2)^\circ$ and S1-Cu-Cl of $121.36(2)^\circ$.

Two different types of hydrogen bonds were found by analyzing the intra and intermolecular contacts presented in the crystalline structure. The copper (I) complex presents intramolecular hydrogen bonding of 2.3700 Å involving $\text{N(3)-H(3B)}\cdots\text{Cl(1)}$ and $\text{N(6)-H(6B)}\cdots\text{Cl(1)}$ atoms and an intermolecular hydrogen bonding ($\text{N(3)-H(3A)}\cdots\text{Cl(1)\#1}$) of 2.6300 Å which is achieving the dimeric self-assembling array

presented by the copper (I) complex in the solid state (Figure 3). These hydrogen bonds take place from intra and intermolecular contacts between the $-\text{NH}_2$ moiety of the ligand and the chlorine (Cl) atom bonded to the Cu(I) center. The neighboring molecule is generated by a crystallographic inversion center, which belongs to the $P\bar{1}$ space group of the triclinic crystalline system. Hydrogen bonds present in the solid-state crystalline packing are summarized in Table S2.

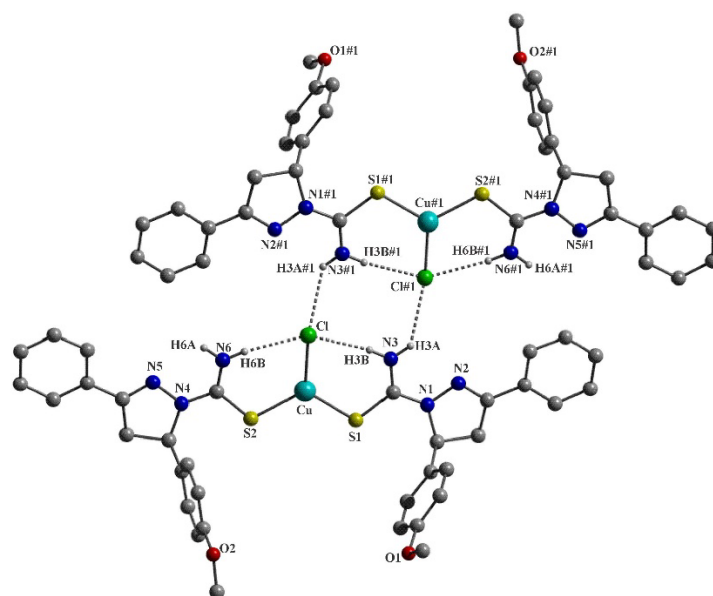


Figure 3. Dimeric self-assembling via hydrogen bonding present in the crystalline packing of the prepared Copper (I) complex. Symmetry operator to generate equivalent atoms #1 -x,-y,-z+2

3. 2. Absorption and Emission Behavior

Usually thiocarbamoyl-pyrazoline ligands have been presented two absorption shoulders in the UV-Vis range, which are related to the Intraligand (IL) electronic transitions [21]. The absorption shoulder that appear centered at ca. 325 nm (figure 4) is assigned to an IL electronic transition of the type $n \rightarrow \pi^*$ involving the $-N-C=S$ (thiocarbamoyl moiety) of the ligand as well as the absorption shoulder at shorter wavelength at ca. 255 nm is also assigned to the $\pi \rightarrow \pi^*$ electronic transitions from the aromatic system present in the structure of the ligand. An hyperchromic

effect was observed at ca. 325 nm in the UV-Vis spectrum of the copper (I) complex. This effect should be related to the appearing of the metal to ligand charge transfer (MLCT) type $Cu(I)d^{10} \rightarrow (S=C-N_{ligand})$ electronic transitions that are expected after coordination of the ligand to the copper (I) center. Intraligand (IL) electronic transitions also should not be ruled out for the copper (I) complex in this region of the spectrum, on this way we found it reasonable to attribute the absorption band that appear at c.a. 325 nm in the complex spectrum as a mixture of (MLCT + IL) electronic transitions.

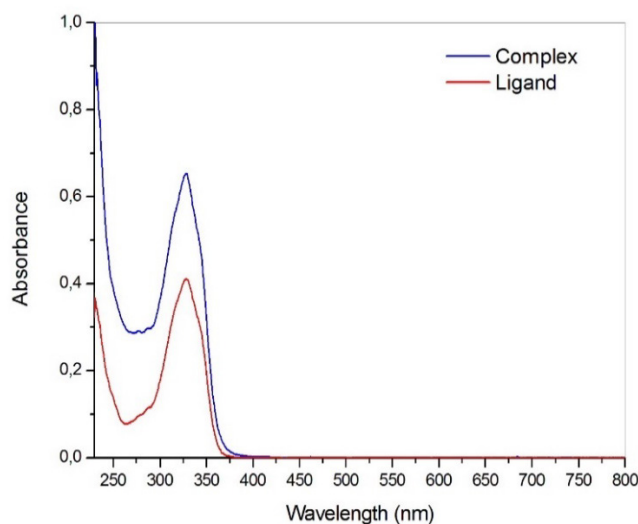


Figure 4. Absorption spectra of the copper (I) complex and ligand measured at 298 K in CH_2Cl_2 solution.

Emissive behavior of copper(I) complexes bearing (S)-donor ligands has been subject of great interest, once in some cases they could present biological activities and bluish luminescence in the same molecule [25]. On this way, (S)-donor thiocarbamoyl-pyrazolines copper(I) complexes, have been presented as a good opportunity of investigation to produce blue emitting materials which could find future application as new emitters materials or dopants for MOLEDs (metal-organic light-emitting devices) [5]. Motivated by these studies, our attention was focused on the emissive behavior presented by the copper (I) complex when excited at $\lambda_{\text{ex}} = 320$ nm, once the luminescence profile did not change significantly when the sample was excited at other wavelengths ($\lambda_{\text{ex}} = 290, 320$ and 380 nm). This trend is in accordance to

the Kasha's rule where the emission wavelength does not depend on the excitation wavelength [26]. Figure 5 shows the emission spectra of the copper (I) complex and the corresponding ligand under excitation at $\lambda_{\text{ex}} = 320$ nm. Both molecules presented bluish luminescence as a broad band centered at c.a. $\lambda_{\text{em}} = 440$ nm of the electromagnetic spectrum. The bluish emission presented by the copper (I) complex was mainly assigned to the (MLCT + IL) excitations arising from $\text{Cu(I)}d^{10} \rightarrow (\text{S}=\text{C}-\text{N}_{\text{ligand}})$ orbitals according to the UV-Vis experiments. This emission is also supported by the observation that the complex has presented higher emission intensity when compared to the free ligand, which has presented its emission attributed only to the intraligand (IL) excitations.

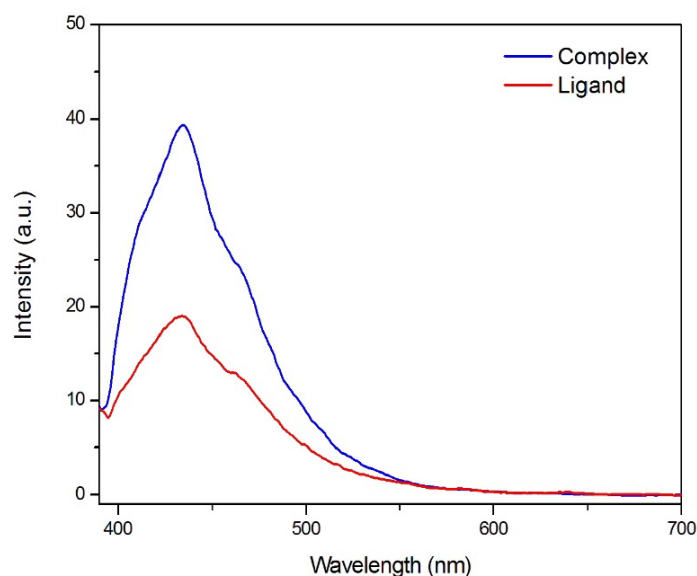


Figure 5. Emission spectra of the copper (I) complex and ligand measured at 298 K ($\lambda_{\text{ex}} = 320$ nm) in CH_2Cl_2 solution.

4. CONCLUSION

A new copper (I) complex based on 1-thiocarbamoyl-5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole was prepared and characterized. A dimeric structure generated by the self-assembling via hydrogen bonding was determined throughout the solid-state crystallographic studies. Good correlations were found between UV-Vis and luminescence experiments as well as the new material showed interesting luminescence behavior presenting bluish emission arising from mixed (MLCT + IL) electronic transitions under excitation at $\lambda_{\text{ex}} = 320$ nm. On this way, we believe that the emission behavior presented

by the synthesized copper (I) complex would qualify it as a promising compound for application in luminescent devices.

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