



# Copper(II) complex of chloro pyrrole-2-carboxaldehyde -N(4)-(methoxyphenyl)-thiosemicarbazone, synthesis, characterization and spectral analysis.

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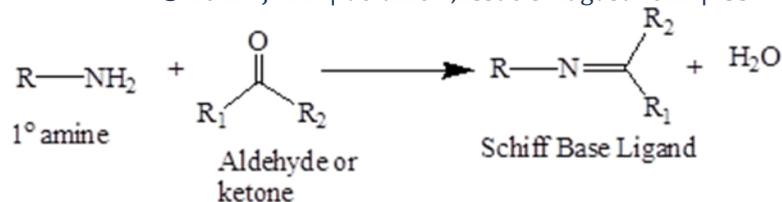
## Abstract.

This study is centered on the synthesis, characterization and spectral analysis of chloropyrrole-2-carboxaldehyde-N(4)(methoxyphenyl)thiosemicarbazone copper (II) complex. The complex was synthesized and characterized using spectroscopic methods such, IR, UV-Vis, <sup>1</sup>H-NMR and their elemental were found. The ligand is yellow in colour, while the complex is greenish yellow. Both the ligand and the complex are soluble in most organic solvents. From the spectral analysis the ligand was found to coordinate in a bidentate manner monobasic chelating ligand through nitrogen and sulphur despite its tridentate mode of coordination which could be via nitrogen of azomethine, pyrrolic nitrogen and thiolate sulphur.

**Key words:** Synthesis, Copper(II) complex, , Thiosemicarbazone, Spectroscopy.

## 1.0 Introduction

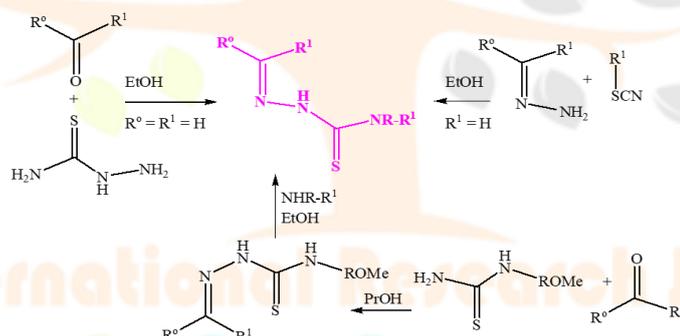
Transition metal complexes containing mixed ligands with N, N and S or N, and donors exhibit interesting stereochemical, electrochemical, and electronic properties. Derivatives of semicarbazones and thiosemicarbazones are amongst the most widely studied nitrogen and oxygen/sulfur ligands. [1]. The study of pyrrole -2-carboxaldehyde Schiff base ligand of thiosemicarbazone found a class of ligands that have fascinated so many researchers, owing to their convenient coordination behaviour toward metal ions [2]. As a result of the azomethine or hydrazine linkage with the general reaction  $R_2C=NR'$  pyrrole Schiff base metal complexes have been reported, [3], to show important biological and catalytic activities. They are considered a sub-class of imines, either secondary ketamine or secondary aldimines, depending on their structure [4]. Pyrrole-2-carboxaldehyde Schiff base ligand of thiosemicarboxaldehyde is synthesized by condensation of either aldehydes or ketones with various aromatic amine [5].



**Figure 1.1** General reaction for the formation of Schiff base ligand

Schiff base ligand as an industrial catalyst exhibits a broad range of biological activities, [6] [7], including, antifungal [8], antibacterial, antimalarial [9], anti-proliferative, anti-inflammatory [10]. Schiff bases are also used as pigments and dyes, intermediates in organic synthesis, polymer stabilizers, and corrosion inhibitors [11]. Schiff base of thiosemicarbazone is a versatile ligand. they coordinate to metal ions in neutral, or anionic and adopt a variety of coordination on deprotonation.[12], [13]. Many Schiff base metal complexes (SBMCs) show excellent catalytic activity in various reactions such as oxidation of sulphides, thioanisole, aldehydes, phenol, styrene, and the decomposition of hydrogen peroxide at high temperatures and in the presence of moisture [14]. Schiff base ligands have been used as chelating ligands in the area of coordination chemistry, and their metal complexes are applied widely in synthesis and catalysis. [15].

Thiosemicarbazone, which originates from thiosemicarbazides, is condensation products of aliphatic or aromatic amines **Figure 1.2** shows the synthetic route of thiosemicarbazones [16], [17]. Transition metal complexes of thiosemicarbazone have attracted chemists due to the presence of nitrogen and sulphur donor atoms which allows coordination between the metal ions in various binding modes [18].



**Figure 1.2** Synthesis route of thiosemicarbazones

Thiosemicarbazones have been widely used due to their structural flexibility and versatility and are an excellent catalyst in carbon-carbon cross-coupling reactions [19], [20]. The thiosemicarbazones also have applications as analytical reagents, and their metal complexes, especially copper(II) complexes, possess a wide range of biological activities [19]. Thiosemicarbazones clinically have been developed for various diseases, including tuberculosis, viral infections, malaria, and cancer [21]. Mixed- ligand copper complexes of phosphines derived from N(4)-Substituted-thiosemicarbazones contained NSN, NN, NS, and the P of the triphenylphosphine form variety of chelation to metal atoms. Examples of a popular phosphine complexes are bis(triphenylphosphine)palladium(II) chloride, tris(triphenyl-phosphine)rhodium(I) catalyst of Wilkinson and tris(triphenyl-phosphine)copper(I) nitrate.

Henceforth, this paper purposes and reports the synthesis and characterization of an aromatic bidentate Schiff base ligand and its copper(II) complex derived from chloropyrrole-2-carboxaldehyde-N(4)-(methoxyphenyl)thiosemicarbazone ligand having methoxy as substituent which will further be used as catalyst in the reduction of aromatic compounds.

## 2.0. Materials and methods

### 2.1. Materials.

All the chemicals and reagents used in this study were commercially purchased and used as received without further purification. These include N(4)-(methoxyphenyl)isothiocyanate, hydrazine monohydrate pyrrole-2-carboxaldehyde copper(II) chloride, potassium bromide (KBr), diethyl ether, methanol, ethanol, acetone, glacial acetic acid, dichloromethane, benzene, dimethylsulfoxide, dimethylformamide, acetonitrile, chloroform, hexane and cyclohexane.

### 2.2 starting materials

The first stage involves the preparation of N(4)-(methoxyphenyl)-thiosemicarbazone was from N(4)-(methoxyphenyl)-thiosemicarbazide by reacting N(4)-(methoxyphenyl)-isocyanate with hydrazine monohydrate adopting literature procedure,[22], [18],[23], [24].

### 2.3 Preparation of N(4)-(methoxyphenyl)thiosemicarbazide starting material

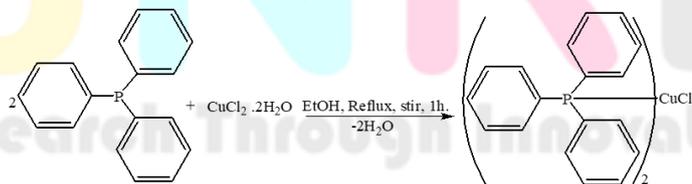
The starting material N(4)-(methoxyphenyl)thiosemicarbazide was prepared by mixing N(4)-(methoxyphenyl)isothiocyanate (3 mL, 3.54 g, 21.46 mmol), with hydrazine monohydrate (5 mL, 5.15 g, 100 mmol). The reaction mixture was stirred at room temperature for two hours shown in **Figure 2**. A white precipitate formed was collected via vacuum filtration, washed with cold diethyl ether, and dried in a desiccator over silica gel. The silky white product recrystallized from methanol. yield 83.9%), [C<sub>8</sub>H<sub>11</sub>N<sub>3</sub>OS, (197.3 g/mol)], melting point: 152 - 153°C. This value is consistent with the previously reported data [25].

### 2.4. Synthesis of pyrrole-2-carboxaldehyde-N(4)(methoxyphenyl)-thiosemicarbazone

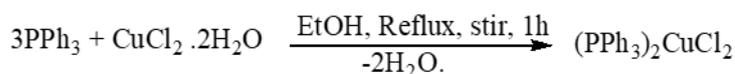
The ligand Pyrrole-2-carboxaldehyde-N(4)(methoxyphenyl)thiosemicarbazone was prepared by mixing N(4)-(methoxyphenyl) thiosemicarbazide (1 mmol, 0.1972 g) in methanol (20 mL) with Pyrrole -2-carboxaldehyde (1 mmol, 0.095 g) in a 100 mL round bottom flask Colour yellow, yield: 0.2376g, 86.6%, Melting point, 172-173°C.

### 2.5. Preparation of bis(triphenylphosphine)copper(II) chloride a precursor.

A precursor bis(triphenylphosphine)copper(II) chloride [Cu(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], was prepared by dissolving copper(II) chloride dihydrate, (0.2 g, 1.5 mmol) and triphenylphosphine (0.525 g, 2.0 mmol). White powder product was washed with ethanol, followed by diethyl ether. yield: 0.573 g, 87%. melting point: 153-154°C.



**Figure 2.1.**Preparation of bis(triphenylphosphine)copper(II) chloride



Equation 0. Preparation of bis(triphenylphosphine)copper(II) chloride

## 2.6. Synthesis of Chloropyrrole-2-carboxaldehyde-N(4)(methoxy-phenyl)-thiosemicarbazone(triphenylphosphine)copper(II) complex.

Chloropyrrole-2-carboxaldehyde-N(4)(methoxyphenyl)thiosemicarbazone-tri (triphenylphosphine)copper(II) complex, was synthesized by reacting pyrrole-2-carboxaldehyde - N(4)(methyl-phenyl)thiosemicarbazone, (1mmol, 0.2743g,) and solution of bis(triphenylphosphine)copper(II) chloride (1mmol, 0.6591g). The reaction mixture was refluxed under N<sub>2</sub> flow and continuously stirred using a magnetic stirrer for 4 hours, represented in **Figure 4**. It was then allowed to cool at room temperature. The green product formed, was filtered and washed with ethanol followed by diethyl ether, then dried over silica gel in a desiccator. Green colour, yield 82%, melting point 213-214°C. The data is in good agreement with those reported in the literature.

## 2.7. Preparation of ligand and its complex for UV-Visible

UV-Vis spectroscopy is a type of absorption spectroscopy which can provide valuable information for a preliminary evaluation of the interaction between ligand and metal ion [26]. The absorption spectra of the N(4)-methoxythiosemicarbazone ligand and its complex was prepared in a solution of chloroform (CHCl<sub>3</sub>) (10<sup>-3</sup> M) in the wavelength range of 200 – 600 nm and recorded on UV-Vis spectroscopy Shimadzu 1800 model.

## 2.8. Molar conductivity measurement

Molar conductance studies of electrolytic solutions have always been exciting for chemists. The study of electrolytic behaviour of metal complex solutions provide brief insights into their nature and composition, provide a clue of the number of ions present in particular and predict geometries of metal complexes. Hence, Molar conductance data are explored to ascertain the electrolytic and non-electrolytic nature of metal complexes. Molar conductivity of copper(II) complex was measured on a Mettler Toledo 730 Series conductivity meter at room temperature in chloroform (CHCl<sub>3</sub>), at 1 x 10<sup>-3</sup> M.

## 3.0. Result and discussion

### 3.1. Synthesis of chloropyrrole-2-carboxaldehyde-N(4)-(methoxyphenyl)-thiosemicarbazone.

Pyrrole-2-carboxaldehyde-N(4)-(methoxyphenyl)thiosemicarbazone, yield: 0.2376g, 86.6%, yellow solid; melting point, 172-173°C. Anal Calcd. for [C<sub>13</sub>H<sub>14</sub>N<sub>4</sub>OS] (274.34 g/mol): C :56.92; H: 5.14, N : 20.42; S :11.69 (%). Found: C: 56.54; H : 5.11, N : 20.39; S : 11.66 (%). UV-Vis, ( $\chi_{\max}$  nm/ $\epsilon$ ), 343 nm, ( $\pi \rightarrow \pi^*$ ). IR, (KBr discs,  $V_{\max}/\text{cm}^{-1}$ ), 3344, 3325, 316:  $\nu(\text{NH})$ ; 1614: azomethine  $\nu(\text{C}=\text{N})$ ; 785: thiolate  $\nu(\text{C}=\text{S})$ . <sup>1</sup>H-NMR, (CDCl<sub>3</sub>, ppm)  $\delta$ , 3.8, OCH<sub>3</sub> (s, 3H); 6.3, ar-H (s, 1H); 6.6, ar-H (s, 1H); 6.9, ar-H (d, 2H); 7.2, ar-H (d, 2H); 7.4, ar-H (s, 1H); 7.5, ar-H (d, 2H); 7.8, ar-H (s, 1H); 8.9 (s, 1H, ph-NH); 9.2 (s, 1H, pyrrole-NH), 9.5 (s, 1H, azomethine-H).

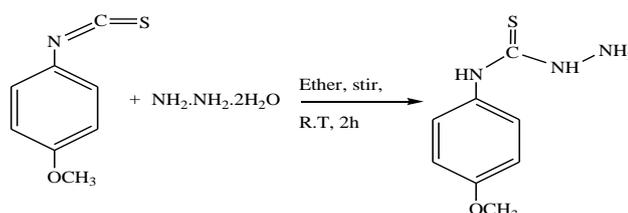


Figure 3.1. Preparation of chloropyrrole-2-carboxaldehyde-N(4)-(methoxyphenyl) -thiosemicarbazone.

### 3.2. Synthesis of chloropyrrole-2-carboxaldehyde-N(4)-(methoxyphenyl)-thiosemicarbazone(triphenylphosphine)copper(II) complex.

Greenish colour, yield 73%, melting point 210-211°C. [CuC<sub>31</sub>H<sub>28</sub>N<sub>4</sub>SOPCl] (molar mass 634.65 g/mol), UV-Vis, ( $\lambda_{\max}$  (nm)/ $\epsilon$ ): 266 nm, ( $\pi - \pi^*$ ), 390 nm, ( $n - \pi^*$ ). Anal cald. C: 58.67, H: 4.45, N: 8.83, S:5.05 %. IR: (KBr discs,  $\nu_{\max}/\text{cm}^{-1}$ ), 3352, 3125: (NH), 1590: (C=N) of azomethine moiety, 1557: (C-N) of pyrrole, 740: (C-S) of the thiolate; <sup>1</sup>H-NMR (CDCl<sub>3</sub>), 6.8-7.8 (aro-H m, 27H), 8.4(NH, s, 1H), 3.5 (OCH<sub>3</sub> s, 3H), 2.3 (CH<sub>3</sub> s, 3H)

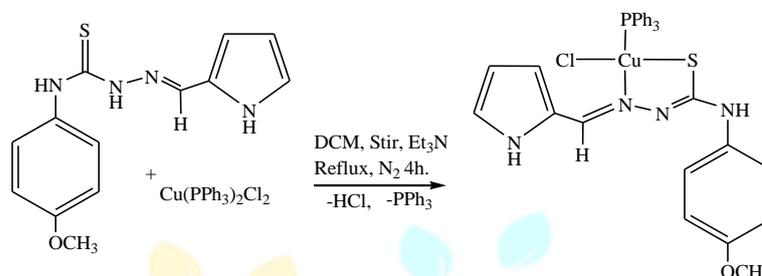


Figure 3.2. Synthesis of chloropyrrole-2-carboxaldehyde-N(4)-(methoxyphenyl)-thiosemicarbazone(triphenylphosphine)copper(II) complex

**3.3.** UV-Vis spectroscopy is a type of absorption spectroscopy which can provide valuable information for a preliminary evaluation of the interaction between ligands and metal ion [26]. The absorption spectra of the N(4)- (methoxyphenyl)thiosemicarbazone ligand, was recorded in a solution of chloroform (CHCl<sub>3</sub>) (10<sup>-3</sup> M) in the wavelength range of 200 – 600 nm, The free ligand UV-Vis spectra gave one band each at 341nm, while in the complex bands of 266 nm and 390 nm respectively are observed. These band is assigned, to  $n - \pi^*$  transition due to azomethine ring, which agrees with other reported similar compounds N(4)-substituted-Isatin-3-thiosemicarbazones, with values 320 nm and 270 nm [27], [28].

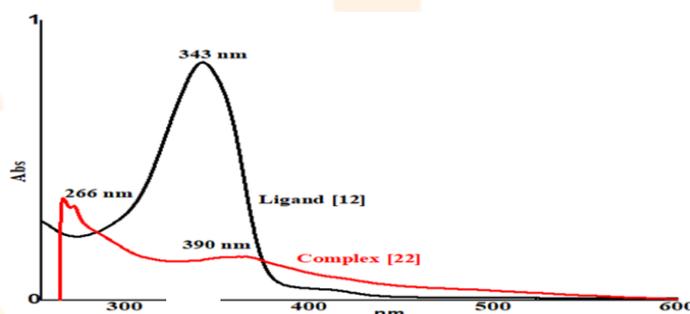
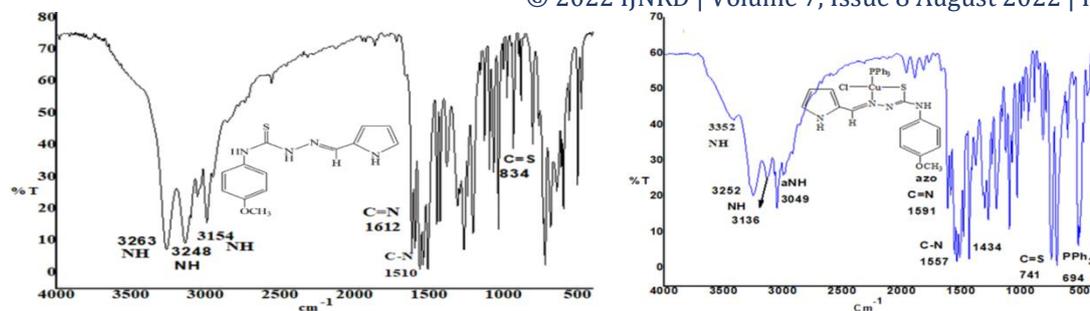


Figure 3.3. Overlay electronic spectra of Chloropyrrole-2-carboxaldehyde-N(4)-(methoxyphenyl)-thiosemicarbazone-(triphenylphosphine)copper(II) complex

### 3.4. Infra-Red (IR) Spectroscopy

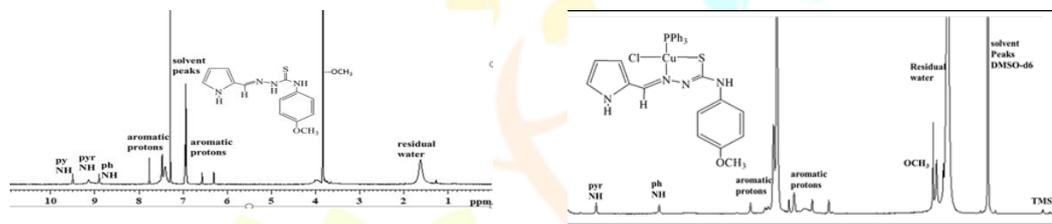
IR spectroscopy is an excellent technique to determine functional groups in compounds and molecules. In this study, IR spectra of the pyrrole ligand and its copper(II) complex, was obtained at the range of 4000-400cm<sup>-1</sup>. IR frequencies of selected functional groups in both the ligand and its copper(II) complex. **Figure 3.4**



**Figure 3.4.** IR Spectra of the ligand and its complex Chloropyrrole-2-carboxaldehyde-N(4)(methoxyphenyl)thiosemicarbazone-triphenylphosphine-copper(II) complex

### 3.5. $^1\text{H-NMR}$ Spectroscopy

$^1\text{H-NMR}$  spectroscopy is an instrument used to determine a molecule's chemical structure. In this study, solution-state the  $^1\text{H-NMR}$  of ligand and its corresponding complex **figure 3.5**, recorded in deuterated chloroform ( $\text{CDCl}_3$ ) and dimethylsulphoxide ( $\text{DMSO-d}_6$ )



**Figure 3.6.**  $^1\text{H-NMR}$  spectra of the ligand and its copper(II) complex

### 3.6. Molar conductivity analysis

The molar conductance studies of electrolytic solutions have always been exciting for a chemist. The electrolytic behaviour of the copper complex provides brief insights into their nature and composition. It gives a clue of the number of ions present in a particular solution responsible for the conduction analysis of the show high value, which indicates its electrolytic nature to be 1:1 metal to a ligand, providing important structural information. Besides, molar conductance data is applied to predict geometries of metal complexes, efforts are made to estimate the size of complexes, and used to determine metal-ligand stoichiometry [29].

However, the molar conductivity values of the copper(II) complex is below  $20 \text{ mol}^{-1}\text{cm}^2 \text{ ohm}^{-1}$  suggesting that the complex is either non or week electrolyte. These values agreed well to thus reported in the literature [3] Also the presence of chloride ions within the coordination sphere Cu(II) complex [30].

### 4.0. Conclusion

The complex chloropyrrole-2-carboxaldehyde-N(4)(methoxyphenyl)-thiosemicarbazone copper(II), was successfully synthesized and characterized by elemental and spectroscopic methods such, IR, UV-Vis,  $^1\text{H-NMR}$ . The ligand is yellow in colour, while the complex is greenish yellow. Both the ligand and the complex are soluble in most organic solvents. From the spectral analysis the ligand was found to coordinate in a bidentate manner monobasic chelating ligand through nitrogen and sulphur despite its tridentate mode of coordination which could be via nitrogen of azomethine, pyrrolic nitrogen and thiolate sulphur.

## 5.0. Recommendations

The ligand could be used to chelate other metal atoms beside copper.

The complex could go further for its catalytic activity.

The complex could be recommended for reduction of aromatic compounds.

The complex could be recommended for other organic transformations.

## 6.0. Acknowledgement

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