

SYNTHESIS, CHARACTERIZATION AND SPECTRAL ANALYSIS, OF PYRROLE -2-CARBOXALDEHYDE-4-(4-METHOXYPHENYL)-THIOSEMICARBAZONE-BIS(TRIPHENYLPHOSPHINE)COPPER(I)NITRATE

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Abstract

Thiosemicarbazones (TSCs) have been discovered as an essential class of nitrogen-sulphur donor ligands. In this study, pyrrole-2-carboxaldehyde-4-(4)(methoxyphenyl)-thiosemicarbazone-bis(triphenyl-phosphine) copper(I)nitrate has successfully been synthesized from pyrrole-2-carboxaldehydethiosemicarbazone and copper(I) nitrate with bis triphenylphosphine as precursor. This ligand and its complex was characterized using various spectroscopic techniques such as Fourier transform infrared (FTIR), UV-visible, (UV-Vis) and proton nuclear magnetic resonance (¹H-NMR) spectroscopies. The ligand and its corresponding complex are coloured, stable at room temperature, soluble in most organic solvents and insoluble in water, hexane, diethyl ether etc. The spectroscopic study of the ligand is expected to form a tridentate to the copper ion through azomethine, pyrrole nitrogen atoms and a sulphur atom. However, single crystal x-ray studies of the copper(I) nitrate complex, showed that the complex's molecular structure exhibits a distorted tetrahedral geometry, where the copper centre are bonded to nitrogen and sulphur atoms of thiosemicarbazone bidentate ligand and two phosphorus atoms of triphenylphosphine.. In addition, thermo-gravimetric analysis (TGA) and molar conductivity of the complex have also been analysed to study their properties. The complex exhibits high molar conductivity indicating electrolytic nature of 1:1, complex due to the presence of nitrate ion as a counter ion in the proposed structure with d¹⁰ configuration. The elemental analysis for both the ligand and complex has agreed well as compared with the theoretical values. The ligand can be used for coordination in many transition metals, as a result of its bidentate behaviour and binding modes. The complex and its oxide would be essential in biological and catalytic activities. Also due to the excellent performance of copper complex and copper oxide nanoparticles, their application can be used for removal of water pollutant, such as nitrophenol and this will give significant advantage for the environment also for some organic transformation, and drug design.

Key words: Copper(I) complex, Thiosemicarbazone, Spectroscopy, Copper oxide,

Introduction

Schiff base ligands constitute a class of ligands that have attracted many researchers, owing to their versatile coordination behaviour and various applications, such as in biological and catalytic activities.. Schiff base ligands can be prepared from the reaction of amine and corresponding aldehyde or ketone, as depicted in **Fig 1.1** [1]. They are considered a sub-class of imines, either secondary ketamine or secondary aldimines, depending on their structure [2].

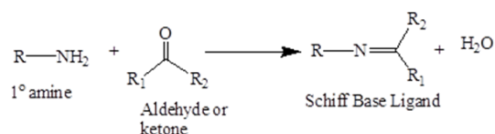


Fig 1.1 General route for the formation of Schiff base ligand (R is an alkyl or aryl group (not a hydrogen), whilst R¹ and R² may be hydrogen)

Schiff base ligands (SBLs) are condensation products of aliphatic or aromatic amines with carbonyl compounds [3] with C=N linkage that provides a binding site for metal ions via nonbonding electrons of nitrogen, [4]. Owing to the presence of a lone pair of electrons in the nitrogen atom of the amine group –C=N, numerous studies showed its biological relevance [5]. SBL, of thiosemicarbazones (TSCs), are versatile ligands coordinating to metal ions. On deprotonation, the complexes can adopt a variety of coordination,[6],[7] consistent with the fascinating properties of transition metal complexes that have garnered the attention of many researchers, [8] [9], especially for the application of catalytic-oxidation reactions for compounds such as alkane and alkene,[11]. Many Schiff base metal complexes (SBMCs) show excellent catalytic activity in various reactions at high temperature and in the presence of moisture. They have several applications in homogeneous and heterogeneous catalysis [12]. In the past years, thiosemicarbazone (TSCs) have been a focus, and many researchers have diverted their attention towards it, due to the full range of uses in biological activities [13] pharmaceuticals, agrochemicals and as an industrial catalyst, [8] [8],[9], [14].

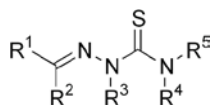


Fig 1.2 General structure of thiosemicarbazone (R¹, R², R³, R⁴ and R⁵ is an alkyl or aryl group or hydrogen)

Thiosemicarbazone has been widely used due to their coordination versatility, in which they can coordinate to metal centres through the nitrogen atoms of azomethine, hydrazine, and

sulphur atoms. Previous studies reported that copper complexes containing thiosemicarbazone ligands have been developed for biological studies.

In this paper, we described the synthesis, characterization and spectral analysis of copper(I) complex of pyrrole-2-carboxaldehyde-4-(4-methoxyphenyl)-thiosemicarbazone which will be further to evaluate the catalytic activity of its oxide on the reduction of nitroaromatic compounds in presence of sodium borohydride as a reducing agent.

3.0. Materials and methods

All the chemicals and reagents used were commercially purchased from Sigma-Aldrich, Fluker, Merck, Fisher Scientific, and used as received without further purification. All reliable products obtained were characterized by melting point electro-thermal digital melting point apparatus and were not corrected. The Fourier Transform Infrared (FTIR) PerkinElmer Frontier American model, UV-Visible (UV-Vis), Spectrophotometer. Shimadzu UV-1800. Japan, ¹H-NMR, (NMR spectrometer Bruker Avance 400 MHz, Germany), All the analysis were conducted at Universiti Teknologi, Malaysia, Johor Bahru - Malaysia.

3.1 Preparation of thiosemicarbazide derivative

4-(4-methoxyphenyl)-3-thiosemicarbazide a precursor was prepared by mixing 4-(methoxyphenyl)isothiocyanate (3 mL, 3.54 g, 21.46 mmol) with hydrazine (5 mL, 5.15 g, 100 mmol). The reaction mixture was stirred at room temperature for two hours. A white precipitate formed was collected via vacuum filtration, washed with cold diethyl ether, and dried in a desiccator over silica gel, affording white powder with good yield (0.156 g, 83.9%). This compound was characterized using IR and NMR spectroscopies and the characterization data were in good agreement with the literature values [10]

3.2 Synthesis of pyrrole-2-carboxaldehyde-4-(4-methoxyphenyl)-3-thiosemicarbazone ligand

Pyrrole-2-aldehyde-4-(4-methoxyphenyl)-3-thiosemicarbazone was prepared by mixing 4-(4-methoxyphenyl)-3-thiosemicarbazide (1 mmol, 0.1972 g) in ethanol (20 mL) with pyrrole-2-carboxaldehyde (1 mmol, 0.095 g) in a 100 mL round bottom flask. The product was collected as yellow powder with good yield (0.2376g, 86.6%). Melting point: 178-179° C. Elemental analysis (CHNS), Anal. Calcd. for C₁₄H₁₄N₄S (%): C, 62.19; H, 5.21; N, 20.72; S, 11.85. Found: C, 62.39; H, 5.44; N, 26.37; S, 11.74. UV-Vis, (λ_{\max} /nm) 253 ($\pi \rightarrow \pi^*$), 320 ($n \rightarrow \pi^*$). IR, (KBr discs, ν/cm^{-1}), 3383, 3362: (NH); 1584: (C=N) of pyridine; 1537: (C=N) of azomethine moiety; 782: (C=S) of the thiolate. ¹H NMR (CDCl₃) (δ /ppm): 2.5 (s, 3H, CH₃), 6.6 -8.7 (m, 8H, Ar), (s, 1H N-NH-C), 9.5 (s, 1H, Ar-NH)

3.3 Preparation of precursor. was prepared according to the literature procedures [15]. In a beaker, copper(I) nitrate trihydrate (0.365 g, 1.5 mmol) was dissolved in ethanol (10 mL). In another beaker, triphenylphosphine (1.965 g, 7.5 mmol) was also dissolved in ethanol (30 mL). The two solutions were mixed in a 100 mL round bottom flask and refluxed for 1 hour. The resulting mixture was allowed to cool to room temperature. The resulting product was filtered, washed with cold ethanol and dried in a desiccator over silica gel. The product was collected as white powder with good yield (0.7796 g, 85.4%) The product of the reaction was characterized using IR and NMR spectroscopies and the characterization data were in good agreement with the literature values [16]

3.4 Synthesis of pyrrole-2-carboxaldehyde-4-(4-methoxyphenyl)-3-thiosemicarbazone-bis(triphenylphosphine)copper(I) nitrate

Pyrrole-2-aldehyde-4-(4-methoxyphenyl)-3-thiosemicarbazonetris(triphenylphosphine)-copper(I)nitrate was prepared by reacting tris-(triphenylphosphine)copper(I) nitrate (0.912g, 1.00 mmol) in dichloromethane (10 mL) with pyrrole-2-aldehyde-4-(4-methoxyphenyl) -3-thiosemicarbazone (0.258 g, 1 mmol) in dichloromethane (10 mL). Yield (0.412 g, 76%). Melting point: 231-232°C. Anal. Calcd. for $CuC_{49}H_{44}N_5SO_4P_2$ (%) : C, 63.66; H, 4.80; N, 7.57; S, 3.47. Found : C, 65.01; H, 4.92; N, 7.54; S, 3.50. UV-Vis, (λ_{max} /nm) : 266 ($\pi \rightarrow \pi^*$), 364 ($n \rightarrow \pi^*$). IR (KBr discs, ν/cm^{-1}), 3395, 3224: (NH), 1600: (C=N) of azomethine moiety, 1508: (C-N) of pyrrole nitrogen, 744: (C=S) of the thiolate. 1H -NMR ($CDCl_3$) (δ/ppm), 3.8 (OCH_3 , s, 3H), 6.0-7.8 (Ar-H, m, 38H), 8.4 (Ar-NH, s, 1H), 10.8 (pyrrole-NH, s, 1H).

4.4. Single-crystal X-ray diffraction analysis was used to investigate the molecular structure of the complex, A suitable single crystal of $[C_{49}H_{44}CuN_5O_4P_2S]$ was selected and on an XtaLAB AFC12 (RINC): K_{α} single diffractometer. The crystal was constant at 302.7(5) K during data collection. Using Olex2, the structure was solved with the Olex2 solve structure solution program using Charge Flipping and refined with the Olex2 refinement package using Gauss Newton minimization.

4.0.Result and discussion

In this study, the Ligand and its complex was synthesized and characterized following a modified literature procedure.[8],[17],[18]. The data for analyzed ligand and its complex agreed well with the theoretical value and revealed the general formulae of HL1 proposed for the ligand and its complex.

4.1 Synthesis of Ligand

The first stage involves the preparation of thiosemicarbazone ligand, from thiosemicarbazide. Thiosemicarbazide starting material was prepared by reacting 4-(4-Methoxyphenyl)-

isothiocyanate with hydrazine monohydrate at room temperature for 2 hours. The preparation scheme is shown in **Fig. 1**. The resulting product, 4-(4-methoxyphenyl)thiosemicarbazide was then reacted with pyrrole-2-carboxaldehyde in ethanol for 4 hours, as depicted in **Fig. 2**. This ligand was characterized using UV-Vis, IR and NMR spectroscopies.

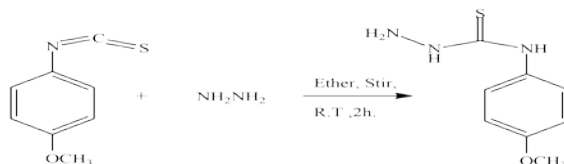


Fig 1. Preparation of starting material 4-(4-methoxyphenyl)thiosemicarbazide

The Schiff base ligands of pyrrole-2-carboxaldehyde-4-(4-methoxyphenyl)-thiosemicarbazone and its copper(I) complex in **Fig 2** are coloured which indicates the characteristics of thiosemicarbazone complex [19] stable at room temperature and soluble in most organic solvents [20],[21]

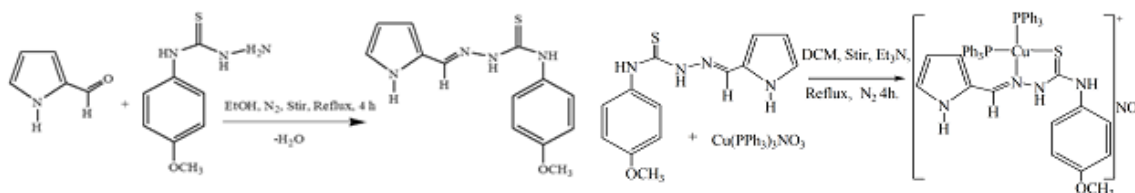


Fig. 2. Synthesis of pyrrole-2-carboxaldehyde-4-(4-methoxyphenyl)-thiosemicarbazone and its copper(I) complex

Characterization of thiosemicarbazone ligand and its complex

The CHN elemental analyses data of the ligand and complex are consistent with the calculated data, as shown in **Table 1**. The structures of the ligand and its complex are presented in **Fig.2**

Table.1: Elemental analysis of CHNS of ligands and their complex [C₄₉H₄₄CuN₅O₄P₂S]

Chemical Formula.	M. mass (gmol ⁻¹)	Elements: calculated / found (%)			
		C	H	N	S
Ligand	258.343	60.44, (60.39)	5.46, (5.48)	21.69, (21.72)	12.41, (12.45)
Complex	924.477	63.66, (63.68)	4.80, (4.83)	7.57 (7.60)	3.46, (3.49)

4.2 UV-Vis spectroscopic of ligand and its copper (I) complex.

The absorption spectra of the ligand and its complex was recorded in a solution of chloroform (CHCl₃) (10⁻³ M) in the wavelength range of 200 – 600 nm. **Fig 4.1** shows the absorption spectra of thiosemicarbazone ligand of pyrrole derivative. In the spectrum of the free ligand, only a single absorption band can be observed. This absorption was assigned to the transition of the imine function of the thiosemicarbazone moiety which can be observed at 340.50 nm, corresponding to n – π* transition which agrees with other reported similar N(4)-substituted-Isatin-3-thiosemicarbazones [22] [23]. with other similar compound that have been reported [24]

[25] [26]. **Fig. 4.1** shows the electronic spectrum of pyrrole ligand and its copper(I) complex. In the free ligand spectrum, only one band at 343 nm corresponds to $n - \pi^*$ transition of the pyrrole ring and azomethine is observed. Meanwhile, the electronic spectrum of the complex exhibits two absorption bands, centred at 266 nm due to $\pi - \pi^*$ transition and at 390 nm, which corresponds to $n - \pi^*$ transition. The wavelength shift of $n - \pi^*$ transition from 343 nm in the free ligand to a higher value of 390 nm in the complex indicates and supports the formation of the complex also coordination of the ligand to the copper ion. These findings are consistent with literature data for similar copper complexes [25] [16].

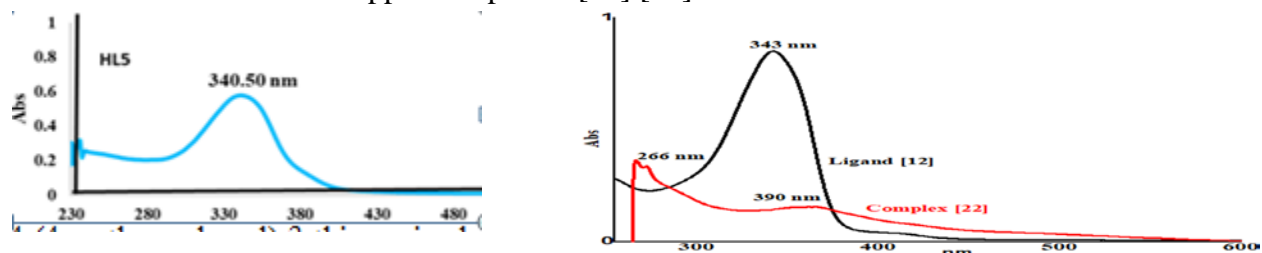


Figure 4.1 UV-Visible absorption spectra of pyrrole ligand and its copper(I) complex.

4.2 IR spectra of thiosemicarbazone ligand and its copper(I) complex

The IR spectra of thiosemicarbazone ligand and its copper(I) complex was obtained as KBr disc in the range of $4000-400 \text{ cm}^{-1}$. IR spectral data for thiosemicarbazone pyrrole ligand and its copper(I) complex. In the pyrrole derivative ligand, the bands at 3263 , 3248 and 3154 cm^{-1} are assigned to $\nu(\text{N-H})$ vibrations. **Fig 4.2** shows the IR spectrum of the free ligand and its copper(I) complex. In the IR spectrum of the free ligand, the two absorption bands observed at 1612 cm^{-1} and 1510 cm^{-1} , corresponds to azomethine $\nu(\text{C=N})$ and pyrrole $\nu(\text{C-N})$ respectively. A vibrational band at 834 cm^{-1} is assigned to $\nu(\text{C=S})$ of the thiosemicarbazone. As seen in the spectrum of the copper(I) complex, the band at 1591 cm^{-1} is attributed to azomethine moiety $\nu(\text{C=N})$ whilst the band at 743 cm^{-1} is attributed to thione $\nu(\text{C=S})$. The shift of the $\nu(\text{C=N})$ and $\nu(\text{C=S})$ stretching to a lower frequency probably indicating coordination of the ligand to copper ion through the azomethine nitrogen and thiol sulphur atoms. Also, a band observed at 1384 cm^{-1} is typical of free nitrate NO_3 which acted as counter ion.

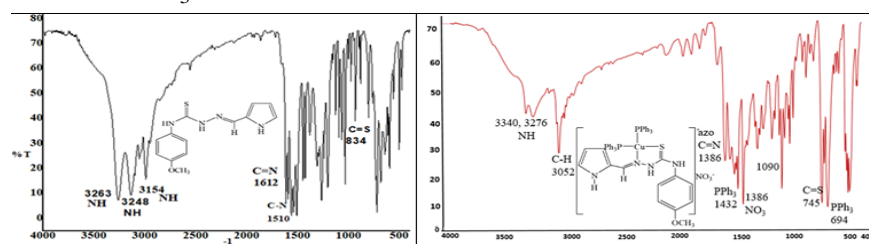


Fig. 4.2 shows the electronic spectrum of pyrrole ligand and its copper(I) complex

4.3 $^1\text{H-NMR}$ spectra of the ligand and its copper(I) complex

In the spectrum of the ligand **Fig 4.3** singlet resonance at 9.8 ppm is due to the hydrazinyl proton resonance while, the phenyl imino proton resonated as a singlet at 8.9 ppm. The sharp singlets appeared at 3.8 ppm, is assigned to the methoxy (C-OCH_3) equivalent proton. In the spectrum of the copper(I) complex, the hydrazinyl proton resonance had shifted downfield 9.2 to 9.80 ppm, indicating coordination of the ligand to the copper ion. Compared to the spectrum of the free ligand, the complex's hydrazinyl proton downfield shift is attributed to the deshielding

effect. The electron density around the proton decreases upon coordination of the ligand to copper ion. This data are consistent with other similar compounds such as the heteroleptic copper(I)phosphine-thiosemicarbazone reported in the literature [27], [28].

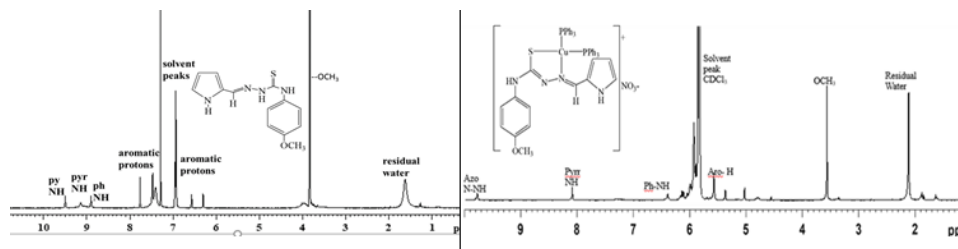


Fig. 4.3 ¹H-NMR spectra of the pyrrole ligand and its corresponding copper(I) complex

4.4 Molar conductivity analysis

The molar conductance studies for the complex electrolytic behaviour in solution was investigated in order to estimate the number of ions present responsible for the conduction, thereby determine the metal : ligand stoichiometry thus providing important structural information [29]. In this research, the molar conductance (Λ_M) for the complex was measured as a 1 mM solution in chloroform (CHCl_3) at room temperature. the molar conductivity value of the copper(I) complex is in the range of $71 - 85 \text{ mol}^{-1}\text{cm}^2 \text{ ohm}^{-1}$ which are in close agreement with literature values for a 1: 1 electrolyte [23] [29][30] The 1:1 electrolyte behaviour strongly suggests that the structure of the Cu(I) metal complex consisted of one nitrate ion acting as counter ion and is located outside of the coordination sphere of the copper ion.

4.4 Single-crystal X-ray diffraction analysis was used to investigate the molecular structure of the complex, $[\text{C}_{49}\text{H}_{44}\text{CuN}_5\text{O}_4\text{P}_2\text{S}]$.

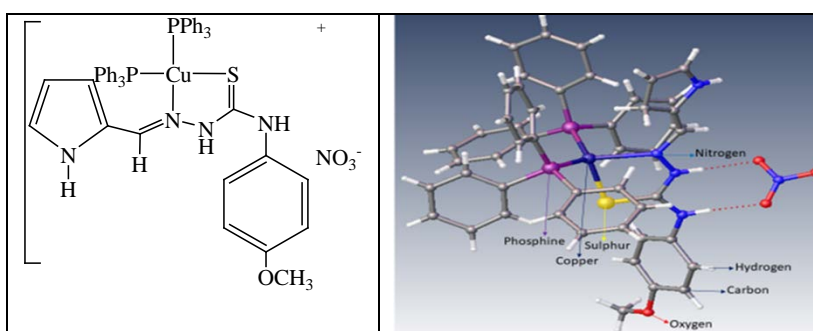


Fig.4.6 Chemdraw and Single crystal x-ray structure of pyrrole-2-carboxaldehyde-4-(4-methoxyphenyl)-thiosemicarbazone-bis(triphenylphosphine)copper(I)nitrate. $[\text{C}_{49}\text{H}_{44}\text{CuN}_5\text{O}_4\text{P}_2\text{S}]$

CONCLUSION

In this study, thiosemicarbazone ligand of pyrrole-2-carboxaldehyde has been prepared, alongside with corresponding N(4)-thiosemicarbazone copper(I) complex. The spectroscopic analysis of this compound had agreement with the proposed molecular formula. Structurally, the substituted-pyrrole-2-carboxaldehyde which supposed to have tridentate mode shows different observation, in which it coordinated as bidentate in the copper(I) complex. This is because the

distance of pyrrole-nitrogen atom, which is far away from the metal centre. Also, a single crystal x-ray crystal spectroscopic analysis has further revealed bidentate structure of the pyrrole derivative of a copper (I) complex,

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