SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF COPPER THIOSEMICARBAZONE COMPLEXES AND THEIR OXIDES IN THE REDUCTION OF NITROAROMATIC COMPOUNDS

OMAR ABDULLAHI WAFUDU HANDY

UNIVERSITI TEKNOLOGI MALAYSIA

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DEDICATION

This thesis is dedicated, to my late father, Ladan Abdullahi Wafudu, who taught me that the best kind of knowledge to have is learning for its own sake. It's also, dedicated to my late mother Kyallu Ladan Abdullahi, who taught me that even the most extensive task could be accomplished if it is done one step at a time. I am also dedicated to my beloved wife Hajiya Amina Ibrahim Wazu Omar, my children Mohammed Auwal, Haruna, Ibrahim Aji, Medugu Abdullahi, and Suleiman, Kyallu Zakiya Ummi, Nuruddin Dan Auta and Mustapha Auta for their encouragement, patience and moral support during this PhD study.

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ABSTRACT

This study involves the synthesis, characterization and evaluation of the catalytic activity of copper thiosemicarbazone complexes and their copper oxides derivatives in the reduction of nitroaromatic compounds. A series of copper complexes of thiosemicarbazone ligands have successfully been synthesized, in which six of them are copper(I) complexes; 2- acetylpyridine-N(4)-(R)-thiosemicarbazone-tris-(triphenylphosphine)copper(I) nitrate {R = methoxyphenyl (**19**), R = methylphenyl (**20**), R = phenyl (**21**) and pyrrole-2-carboxaldehyde- N(4)-(R)-thiosemicarbazone-bis(triphenylphosphine)copper(I) nitrate {where R = phenyl (**22**), R= methoxyphenyl (**23**), R = methylphenyl (**24**)} and another six copper(II) complexes; 2- acetylpyridine-N(4)-(R)-thiosemicarbazone-triphenylphosphine-copper(II) chloride; {R = methoxyphenyl (**25**), R = methylphenyl (**26**), R = phenyl (**27**)} and pyrrole-2-carboxaldehyde- N(4)-(R)-thiosemicarbazone-triphenylphosphine-copper(II) chloride (R = phenyl (**28**), R = methoxyphenyl (**29**), R = methylphenyl (**30**)}. These complexes were characterized using Fourier transform infrared (FTIR), UV-visible (UV-Vis) and proton nuclear magnetic resonance (^{1}H-NMR) spectroscopic techniques. Single crystal X-ray diffraction analysis on complex **23** showed that the complex adopted a distorted tetrahedral geometry, where the central copper(I) ion is bonded to nitrogen and sulphur atoms of thiosemicarbazone bidentate ligand and two phosphorus atoms from two triphenylphosphine monodentate ligands while a nitrate ion acted as the counter ion. Molar conductivity value of the complex indicated a 1:1 electrolytic nature which supported the single crystal X-ray diffraction data. The copper complex **23** was converted into copper oxide by means of thermal decomposition. Evaluation of the catalytic performance of the copper(I) complex and copper oxide in the reduction of 4- nitrophenol (4-NP) to 4-aminophenol (4-AP) shows that copper oxide has a higher catalytic activity (98.7%) compared to the copper(I) complex (78.2%). Optimization of the catalyst loading revealed that 1.0 mol% of the catalyst was the most optimized amount with the highest conversion (98.7%). Reproducibility and recyclability tests of the copper oxide catalyst proved that the catalyst exhibits consistent catalytic performances and could be reused four times without a significant decrease. On the other hand, the copper(I) complex required a more prolonged reduction time and a higher amount of catalyst loading due to its insolubility in an aqueous solution. The product from the catalytic reduction, 4-AP was isolated, purified and characterized using FTIR and ^{1}H-NMR spectroscopic techniques. The catalytic activity of the copper oxide catalyst was also evaluated in the reduction of other nitroaromatic compounds with various substituent groups. In these reactions, the copper oxide maintained its excellent catalytic activity and showed consistent results.

ABSTRAK

Kajian ini melibatkan sintesis, pencirian dan penilaian aktiviti pemangkinan kompleks kuprum tiosemikarbazon dan terbitan kuprum oksida dalam tindakbalas penurunan sebatian aromatik nitro. Satu siri kompleks kuprum dengan ligan tiosemikarbazon telah berjaya disintesis, yang terdiri daripada enam kompleks kuprum(I); 2-asetilpiridin-N(4)-(R)- tiosemikarbazon-tris-(trifenilfosfin)kuprum(I) nitrat {R = metoksifenil (**19**), R = metilfenil (**20**), R = fenil (**21**) dan pirola-2-karboksialdehid-N(4)-(R)-tiosemikarbazon- bis(trifenilfosfin)kuprum(I) nitrat {R = fenil (**22**), R = metoksifenil (**23**), R = metilfenil (**24**) manakala enam lagi kompleks kuprum(II); 2-asetilpiridina-N(4)-(R)-tiosemikarbazon- trifenilfosfinkuprum (II) klorida; {R = metoksifenil (**25**), R = metilfenil (**26**), R = fenil (**27**) dan pirola-2-karbokaldehid-N(4)-(R)-tiosemikarbazon-trifenilfosfinkuprum (II) klorida {R = fenil (**28**), R = metoksifenil (**29**), R = metilfenil (**30**)}. Kesemua kompleks ini telah dicirikan menggunakan teknik spektroskopi inframerah transformasi Fourier (FTIR), ultralembayung- nampak (UV-Vis) dan resonans magnetik nuklear proton (^{1}H-NMR). Analisis pembelauan sinar-X hablur tunggal kompleks **23** menunjukkan kompleks ini mempamerkan geometri tetrahedron terherot, yang mana ion kuprum(I) pusat terikat kepada atom nitrogen dan sulfur daripada ligan bidentat tiosemikarbazon dan dua fosforus atom daripada dua ligan monodentat trifenilfosfin manakala ion nitrat bertindak sebagai ion lawan. Nilai kekonduksian molar kompleks menunjukkan sifat elektrolit 1:1 yang menyokong data pembelauan sinar-X hablur tunggal. Kompleks kuprum **23** ini telah ditukar menjadi kuprum oksida melalui kaedah penguraian haba. Penilaian prestasi pemangkinan kompleks kuprum(I) dan kuprum oksida dalam tindak balas penurunan 4-nitrofenol (4-NP) kepada 4-aminofenol (4-AP) menunjukkan kuprum oksida mempunyai aktiviti pemangkinan yang lebih tinggi (98.7%) berbanding dengan kompleks kuprum (78.2%). Pengoptimuman muatan mangkin menunjukkan 1.0 mol% mangkin adalah muatan yang paling optimum dengan peratus penukaran paling tinggi (98.7%). Ujian kebolehulangan dan kebolehkitaran mangkin kuprum oksida ini membuktikan mangkin ini menunjukkan aktiviti pemangkinan yang konsisten dan boleh diguna semula sebanyak empat kali tanpa penurunan aktiviti yang ketara. Walau bagaimanapun, kompleks kuprum mengambil masa yang lebih lama dan muatan mangkin yang lebih banyak disebabkan ketidak larutan di dalam larutan akues. Produk daripada tindak balas penurunan ini, 4-AP telah diasingkan, ditulenkan dan dicirikan menggunakan teknik spektrokopi FTIR dan ^{1}H-NMR. Aktiviti pemangkinan kuprum oksida juga dinilai dalam tindak balas penurunan sebatian aromatik nitro yang lain yang mengandungi pelbagai kumpulan penukarganti. Dalam semua tindakbalas ini, kuprum oksida menunjukkan aktiviti pemangkinan yang sangat baik dan keputusan yang konsisten.

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LIST OF ABBREVIATIONS

UV-Vis	Ultraviolet-visible
IR	Infrared
^{1}H-NMR	Proton nuclear magnetic resonance
TGA	Thermogravimetric analysis
FTIR	Fourier-transform infrared
XRD	X-Ray diffraction
FWHM	Full width half maximum
JCPDS	Joint Committee on Powder Diffraction Standards
UTM	Universiti Teknologi Malaysia
$NaBH_4$	Sodium borohydride
SBL	Schiff base ligand
Ar	Argon
EtOH	Ethanol
MeOH	Methanol
DCM	dichloromethane
DMF	Dimethylformamide
DMSO	Dimethylsulphoxide
$CHCl_3$	Chloroform
THF	Tetrahydrofuran
KBr	Potassium bromide
TMS	Tetramethylsilane
MA	Milliampere
CPLX	Complex
MHz	Megaherz
kV	Kilovolt
PPh_3	Triphenylphosphine
R.T.	Room temperature
cm	Centimeter
cm^{-1}	wavenumber
g	gram

mg	milligram
ml	millilitre
min	minute
h	hour
s^{-1}	per second
$pmol^{-1}$	per millimole
nm	Nanometre

LIST OF SYMBOLS

Δ	-	Delta
π	-	Pi
θ	-	Theta
Λ	-	Lambda
Ǻ	-	Angstrom
%	-	Percent
^{o} C	-	degree Celsius
δ	-	Chemical shift
2θ	-	Bragg angle
ν	-	absorption frequency
^{0}	-	degree angle
λ_{max}	-	maximum absorption wavelength
λ	-	Wavelength
ε	-	molar extinction coefficient

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

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 (Hosseini-Yazdi *et al.,* 2017). Schiff base ligands can be prepared from the reaction of amine and corresponding aldehyde or ketone, as depicted in **Figure 1.1** (Yadav *et al*., 2015). They are considered a sub-class of imines, either secondary ketamine or secondary aldimines, depending on their structure (Adekunle *et al*., 2019).

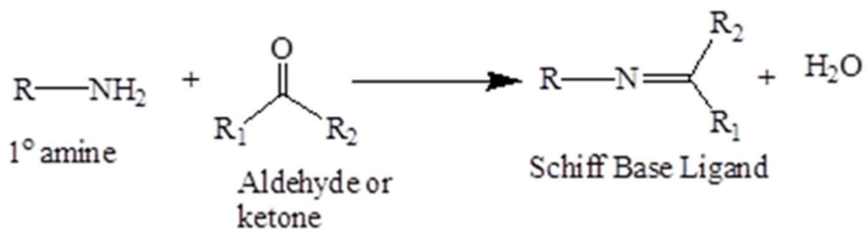

Figure 1.1 General route for the formation of Schiff base ligand (R is an alkyl or aryl group (not a hydrogen), whilst R^1 and R^2 may be hydrogen)

One class of Schiff base compound that has emerged rapidly is thiosemicarbazone, as shown in **Figure 1.2.** Thiosemicarbazone can be prepared from the condensation reaction of thiosemicarbazide and aldehyde or ketone (Scovill *et al*., 1982 and Reppert *et al*., 2016). Thiosemicarbazones have attracted the attention of chemists due to the presence of nitrogen and sulphur donor atoms which allows coordination between the metal ions in various binding modes (Salam *et al*., 2012). Thiosemicarbazone is an attractive class of metal-chelating agents and offer a numerous possibility to easily modify their molecular backbone.

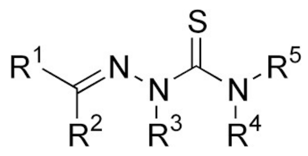

Figure 1.2 General structure of thiosemicarbazone (R^1, R^2, R^3, R^4 and R^5 is an alkyl or aryl group or hydrogen)

Thiosemicarbazones have been widely used due to their coordination versatility, in which they can coordinate to metal centres through the nitrogen atoms of either azomethine, hydrazine, and sulphur atoms (Bahron *et al*., 2019). Previous studies reported that copper complexes containing thiosemicarbazones ligands have been developed for biological studies, such as those shown in **Figure 1.3** (Cherchiaro and da Costa, 2006). These copper complexes have been intensively studied as inducing agents of apoptosis. Despite their advantages in biological applications, however the catalytic application of these copper complexes are not well-studied, as opposed to other metal complexes, like palladium, rhodium and gold (Ibrahim *et al*., 2017 and Zhu *et al*., 2017).

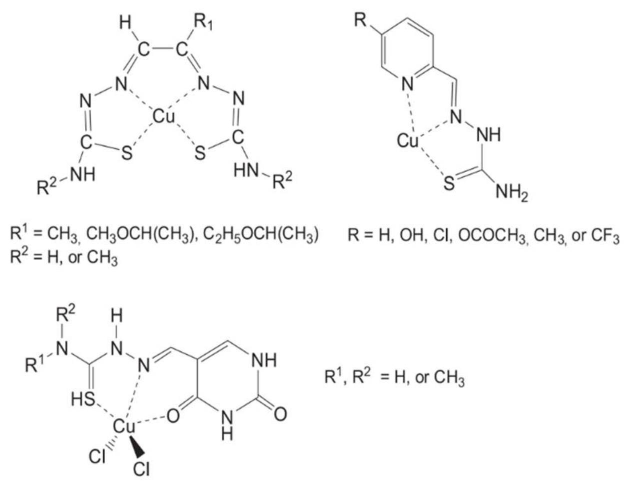

Figure 1.3 Some reported copper complexes containing thiosemicarbazone ligands. (Cherchiaro and da Costa, 2006).

The reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride is an excellent reaction which is used as a model to test the catalytic activity of a catalyst.

This reaction can be catalyzed using metal-based compounds, such as metal complexes and metal nanoparticles, including gold, silver, platinum, and palladium (Ibrahim *et al*., 2017 and Zhu *et al*., 2017). Despite the advantages of these metal compounds, however some of them are relatively expensive (Gebel, 2000). In contrast, copper compounds are relatively cheap and their preparation methods are quite simple and straightforward, compared to other metals. (Chavan *et al*., 2011). In addition to copper complexes, copper oxide also exhibits good catalytic properties.

Surprisingly, there is no reported study involving copper complexes of thiosemicarbazone in the reduction of nitroaromatic compounds. Due to this lack of information, it is interesting to investigate the catalytic activity of copper complexes containing thiosemicarbazone ligands in this reaction. More recently, a study by Nordin and co-workers has shown the excellent catalytic performance of copper oxide nanoparticles in reducing 4-nitrophenol to 4-aminophenol in the presence of sodium borohydride (Nordin and Shamsuddin, 2019). Based on this finding, it would be beneficial to convert the copper complexes to copper oxides and test the resulting product in the similar reaction. Hopefully, the results obtained from this study can be used to evaluate the catalytic activity of copper complexes of thiosemicarbazone ligands and their oxide in the reduction of 4-nitrophenol.

1.2 Problem Statement

Nitroaromatic compounds and their derivatives, such as 4-nitrophenol (4-NP) are one of the common discharge of agricultural wastes, which are toxic and hazardous (Henary et al., 1997) . Researchers have described many ways to convert 4-nitrophenol into a safer and environmentally friendly compound, such as 4-aminophenol. One of the methods that have been reported is the reduction reaction using metal compounds. (Al-hassani and Ahmedzeki, 2014) (Magdy *et al*., 2018).

Metal and their derivatives have been widely used in catalysis and organic reactions, and some of them involving precious metals, such as ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, and silver. (Olszewski *et al*., 2019). However the major drawback is in term of the cost and availability of the metals.

(Ahmad *et al*., 2018). Hence, there is a need to find a cheaper option and more-abundantly available metal, such as copper and their compounds. Recently, there is a report that described the biosynthesis of copper(II) oxide nanoparticles using *Murayya koeniggi* aqueous leaf extract and its catalytic activity in 4- nitrophenol reduction, which was cost-effective and efficient (Nordin and Shamsuddin, 2019).

Based on these findings, copper oxide nanoparticles are good candidates for the reduction of 4-nitrophenol, in addition to other metal compounds. It will be interesting to study whether copper oxide nanoparticles derived from copper complexes can act similarly as what has been described in the previous studies. Copper oxide nanoparticles has high catalytic activity due to its small sizes and large surface area (Nasrollahzadeh *et al*., 2015; Burke *et al*., 2019). Various methods for preparing copper oxide nanoparticles have been reported, such as sonochemical method (Angeline Mary *et al*., 2019), pyrolysis (Li *et al*., 2019), sol-gel process (Kayani *et al*., 2015) and electrochemical (Khatoon *et al*., 2018). However, a more simple and direct approach could be used, such as thermal degradation of copper complexes to obtain copper oxide nanoparticles. Eventually, the catalytic activity of both copper complexes and oxides can be investigated in the reduction of 4-nitrophenol in search of better catalysts that are efficient and effective.

1.3 Research Objectives

The objectives of the research are:

i. To synthesize and characterize N-(4)-substituted-thiosemicarbazone ligands of pyridine and pyrrole derivatives.

ii. To prepare and characterize copper(I) and copper(II) complexes of N(4)-substituted-thiosemicarbazone ligands and to convert the copper complexes into their oxides through thermal decomposition.

iii. To evaluate the catalytic activities of the copper complexes and copper oxide in the reduction of 4-nitrophenol to 4-aminophenol and other nitroaromatic compounds in the presence of sodium borohydride ($NaBH_4$).

1.4 Scope of the Research

This research involves the synthesis of six N(4)-substituted-thiosemicarbazone Schiff base ligands, namely: 2-acetylpyridine-N(4)(methoxyphenyl)thiosemicarbazone **[8]**, 2-acetyl-pyridine-N(4)(methyl phenyl)-thiosemicarbazone **[9]**, 2-acetylpyridine-N(4)-(phenyl)thiosemicarbazone **[10],** pyrrole-2-carboxaldehyde-N(4)-(phenyl)thiosemicarbazone **[12]**, pyrrole-2-carboxaldehyde-N(4)(methoxyphenyl)thiosemicarbazone **[13]** pyrrole-2-carboxaldehyde-N(4)(methylphenyl)thiosemicarbazone **[14].** From these six ligands, a new set of twelve copper(I) and copper(II) complexes have been synthesized from copper precursors. The synthesized complexes were analyzed and characterized using various techniques such as melting point, molar conductivity, elemental analysis, spectroscopies (IR, UV-Vis and ^{1}H-NMR) TGA, and X-ray crystallography. Copper complexes were converted into their oxide using a thermal decomposition method. The catalytic activity of copper oxide was evaluated in the reduction of nitroaromatic compounds; such compounds are 2-hydroxy-5-nitrobenzaldehyde, 2-methyl-4-nitrophenol, nitroaniline, and nitrobenzene. The catalytic reduction reactions were evaluated using a UV-Vis spectrometer. The product from the catalytic reduction reaction of 4-nitrophenol to 4-aminophenol was isolated and structurally characterized using FT-IR and ^{1}H-NMR spectroscopic techniques.

1.5 Research Flowchart

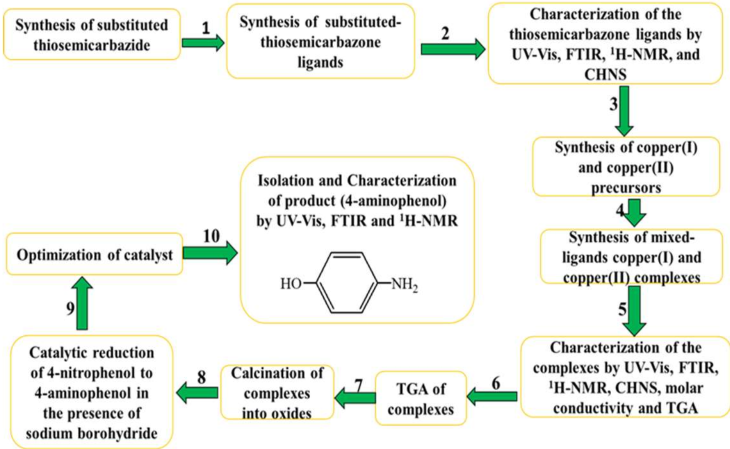

Figure 1.4 Research flowchart

1.6 Significance of Research

In this study, a series of six novel substituted-2-acetylpyridine and substituted-pyrrole-2-carboxaldehyde thiosemicarbazone ligands and twelve new copper(I) and copper(II) complexes of N(4)-substituted-thiosemicarbazone ligands were successfully synthesized and characterized by various spectroscopic techniques such as Fourier transform infrared (FT-IR), UV-visible (UV-Vis) and proton nuclear magnetic resonance (^{1}H-NMR). Thermogravimetric analysis (TGA) and molar conductivity were performed to investigate the properties of the complex. The copper complexes were successfully converted to copper oxide nanoparticles via thermal decomposition method. This method proved to be easy, direct and effective way to obtain copper oxide nanoparticles.

The results from catalytic studies showed that both copper complexes and copper oxide exhibited good catalytic activity in the reduction of 4-nitrophenol. Recyclability and reproducibility tests were performed and the results proved that copper oxide was easily recovered, maintained high and consistent catalytic activities over four cycles without any significant decrease in the conversion of the product. Due to the excellent performance of copper complex and copper oxide nanoparticles, their applications can be used for removal of water pollutant, such as 4-nitrophenol and this will give a significant advantage for the environment.

1.7 Thesis Outline

This thesis consists of five main chapters, namely Chapter 1, which provides a brief framework of the research background, the problem statement, and the objectives of this thesis. Chapter 2 lays out the literature review that is related to this research. Experimental methods are written in Chapter 3, while detailed discussions of results and data are presented in Chapter 4. Chapter 5 provides a conclusion for the whole thesis and recommendation for future works.

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LIST OF PUBLICATIONS

1. Omar Abdullahi Wafudu Handy, 7th International *Conference* and Workshop on Basic and Applied Sciences (*ICOWOBAS* 2019). "Synthesis, Characterization of 2-acetylpyridine-N(4)-(methoxyphenyl)-thiosemi-carbazonecopper(I) complex and Catalytic Activity of its oxide."

2. Omar Abdullahi Wafudu Handy, Mohamad Shazwan Shah Jamil, Mustaffa Shamsuddin (2020). Copper oxide derived from copper(I) complex of 2-acetylpyridine-N(4)-(methoxyphenyl)thiosemicarbazone as an efficient catalyst in the reduction of 4-nitrophenol: *Malaysian Journal of fundamental and applied sciences (MJFAS}* Vol, 16 No 3. Available online.