SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF COPPER(II) COMPLEXES CONTAINING SCHIFF BASE LIGAND IN THE REDUCTION OF 4-NITROPHENOL

HASSAN WAFI GARBA

UNIVERSITI TEKNOLOGI MALAYSIA

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HASSAN WAFI GARBA

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ABSTRACT

This thesis describes the preparation of a series of Schiff base ligands, N'-salicylidene-2-aminophenol [L1], N'-salicylidene-2-aminothiazole [L2], and N,N'-bis(salicylidene)-o-phenylenediamine [L3] and their corresponding copper(II) complexes; N'-salicylidene-2-aminophenol copper(II) acetate [C1], N'-salicylidene-2-aminothiazole copper(II) acetate [C2] and N,N'-bis(salicylidene)-o-phenylenediamine copper(II) acetate [C3]. The synthesized ligands and their copper(II) complexes were characterized using fourier transform infrared (FTIR), nuclear magnetic resonance (NMR) and ultraviolet-visible (UV-Vis) spectroscopy. The catalytic activities of the synthesized copper(II) complexes were evaluated in the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in the presence of sodium borohydride which acts as reducing agent. The progress of reaction was monitored using UV-vis spectroscopy and the percentage conversion was determined from the spectroscopy data. The results showed that N,N'-bis(salicylidene)-o-phenylenediamine copper(II) acetate [C3] has the highest catalytic activities with 97.5% conversion, followed by N'-salicylidene-2-aminothiazole copper(II) acetate[C2] complex with 95.2% conversion, then N'-salicylidene-2-aminothiazole copper(II) acetate [C1] complex with 90.8% conversion in the order C3>C2>C1. The rate of reaction for the reductions of 4-NP catalyst by copper(II) complexes shows that C3 complex is faster than C2 and C1 complex. The optimization of the catalyst amount shows that 1.0 mg of the catalyst dose was the most optimized amount with the highest conversion of 94.6% than other dose of 0.5 mg (92.4%) and 1.5 mg (91.4%). Recyclability and reproducibility tests of copper(II) complexes confirmed that all the three complexes were active, efficient and possess excellent reproducibility with consistent catalytic performances and could be re-used again without major decrease in the catalytic activities.

ABSTRAK

Tesis ini menerangkan penghasilan ligan Schiff base, N'-salicylidene-2-aminophenol [L1], N'-salicylidene-2-aminothiazole [L2] dan N,N'-bis(salicylidene)-o-phenylenediamine [L3] serta kompleks kuprum(II); N'-salicylidene-2-aminophenol copper(II) [C1], N'-salicylidene-2-aminothiazole copper(II) [C2] dan N,N'-bis(salicylidene)-o-phenylenediamine copper(II) [C3]. kesemua ligan dan kompleks ini telah diperincikan melalui beberapa kaedah spektoskopi, iaitu fourier transform infrared (FTIR), nuclear magnetic resonance (NMR) dan ultraviolet-visible (UV-Vis). kegiatan pemangkin kompleks kuprum (II) ini dinilai dalam tindakbalas pengurangan 4-nitrophenol (4-NP) menjadi 4-aminophenol (4-AP) dengan kehadiran natrium borohidride yang bertindak sebagai agen pengurangan. Kemajuan tindakbalas ini dipantau menggunakan spektroskopi UV-Vis dan peratusan pertukaran 4-NP to 4AP ditentukan dari data spektroskopi. Hasil kajian menunjukkan bahawa kompleks to N,N'-bis (salicylaldehyde) -o-phenylenediamine (II) [C3] mempunyai aktiviti pemangkin tertinggi dengan 97.5% diikuti oleh kompleks N'-salicylidene-2-aminothiazole (II) [C2] dengan 95.2% manakala kompleks N'-salicylidene-2-aminothiazole (II) [C1] dengan 90.8%. Pengoptimuman kuantiti pemangkin menunjukkan bahawa kuantiti 1.0 mg pemangkin adalah kuantiti yang paling dioptimumkan dengan penukaran tertinggi 94.6% daripada kuantiti-kuantiti lain 0.5 mg (92.4%) dan 1.5 mg (91.4%). Ujian kitar semula dan kebolehulangan kompleks tembaga (II) mengesahkan bahawa ketiga-tiga kompleks ini aktif, cekap dan mempunyai kebolehulangan yang sangat baik dengan prestasi pemangkin yang konsisten dan dapat digunakan semula tanpa penurunan yang signifikan dalam aktiviti pemangkin.

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LIST OF ABBREVIATIONS

^{1}H-NMR		Proton Nuclear Magnetic Resonance
$CDCl_3$	-	Deuterated Chloroform
FTIR	-	Fourier Transform Infrared
TMS	-	Tetramethylsilane
UV-Vis	-	Ultraviolet-visible
DMSO-d_6	-	Deuterated dimethylesulfoxide
HCl	-	Hydrochloric acid
KBr	-	potassium bromide
Abs	-	Absorbance
4-NP	-	4-Nitrophenol
4-AP	-	4-Aminophenol

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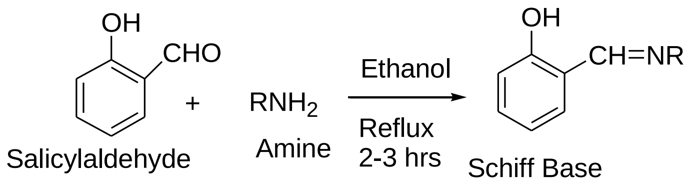
CHAPTER 1

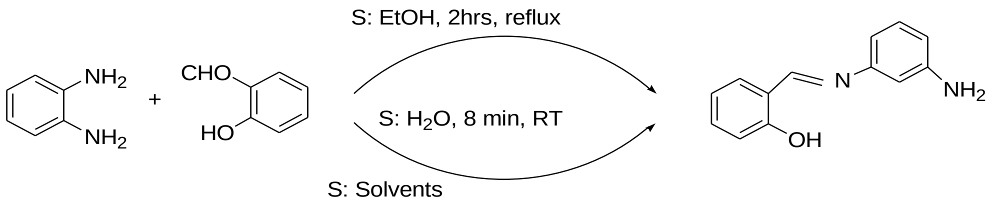
INTRODUCTION

1.1 Background of the Study

Schiff bases are compounds derived from carbonyl compounds in which the functional group of the carbonyl compounds is substituted by an imine or azomethine group (Silva *et al.*, 2011). Typically, Schiff bases are prepared through condensation reaction of amine and an aldehyde in presence of organic solvents such as, tetrahydrofuran (THF), methanol and 1, 2-dichloroethane (Abdel-Magid *et al.*, 1996). Figure 1.1 shows the preparations of Schiff base (a) without refluxing the solvent and (b) with refluxing the solvent.



(a)



(b)

Figure 1.1 Preparations of Schiff base ligands via the reaction of salicylaldehyde and a primary amine (a) without refluxing the solvent) and (b) with refluxing the solvent).

Schiff bases are among the most commonly used ligands due to their sigma donations and pie acceptor attributes and their reactivity relationship as well as the bonding mode features of Schiff base ligands with metal complexes derived great influence in coordination chemistry (Çalik *et al*., 2015). They coordinates easily with diverse range of transition metal ions, resulting in stable and deeply coloured metal complexes with impressive properties (Banasz and Chorab, 2019). The properties associated with the Schiff base ligands, such as catalytic, magnetic, fluorescent as well as electrochemical, make the transition metal complexes of Schiff-base ligands extremely interesting (Majumdar *et al*., 2020).

Many metal complexes containing Schiff base ligands such as palladium, gold, and silver complex have been reported but they are expensive and the synthetic route are complicated. Copper complexes is a promising alternative to chemist owing to its abundance and preparatory parts are environmental friendly (Cohen *et al*., 2016).

Copper metals can form complexes with neutral or anionic ligands and possess multiple oxidation states essential for their reactivity. Such coordination complexes serve as catalysts for substrates activation and reaction accelerations and contributes to the formations or cleavage of a number of chemical bonds. The behaviour and selectiveness of these complexes are closely related to ligands design (Dursch, 2019). Reactions involving catalyst and transition metal, most essential factors in determining the role of catalyst is the accessibility of catalyst, less expensive metals such as copper have gained attention in the development of catalytic system (Osgood *et al.*, 2016). The effect of ligands on the structure and reactivity of transition metal complexes is an important area of research in coordination and organometallic chemistry as well as in catalysis (Mantellini and Uniti, 1987).

Finally, this research work covered the used of copper(II) complexes as a catalyst containing Schiff-base ligands and the applications of the synthesized copper(II) complex in the catalytic reductions of 4-nitrophenol with the intentions to achieves a shorter reactions time and excellent yields during catalytic reductions. Therefore, this research work aimed at synthesis, characterizations and catalytic applications of copper(II) complexes.

1.2 Problem Statement

Previously, the applications of copper oxide and copper oxide nanoparticles as catalyst for the reductions of aromatic compounds were reported, little attentions has been given for the use of copper(II) complex for similar purpose. Therefore, in other to contributes to this scope of study, a copper catalyst was developed using copper(II) complexes containing Schiff base ligands for the reduction of 4-nitrophenol in presence of sodium borohydride as a reducing agent using UV-visible spectroscopy to monitor the progress of reactions.

However, the problems associated with metal complexes such as palladium, gold and silver complexes are expensive and complicated synthetic route as compared to copper complex which is cheaper, abundance and synthesis methods are environmental friendly (Patent, 2012). Furthermore, reduction of 4-nitrophenol required extreme reaction condition such as high temperature and hydrogen pressure as compared to reduction in aqueous solution and milder reaction condition (Araynet, 1994). Among the types of ligand, Schiff base ligands has been extensively studied and proved to be suitable for copper complex species (Sunatsuki *et al.*, 2002).

As a results of large interests in the synthesis of new catalytic process for higher activity, stability and substrates tolerance as well as good selectivity, copper complex is the most widely used transition metals for catalytic activity (Zhang *et al.*, 2018) as compared to other type of complex such as palladium complex (Patent, 2012).

1.3 Research Objectives

The objectives of this research are:

a. To synthesize the Schiff base ligand from salicylaldehyde and amino derivatives.

b. To synthesize the copper(II) complexes from the above Schiff base ligand and copper acetate.

c. To characterize the synthesized Schiff base ligands and copper(II) complexes using infrared (FTIR), ^{1}H NMR and UV-visible spectroscopy.

d. To evaluate the catalytic activity of copper(II) complexes in the reduction of 4-nitrophenol.

1.4 Scope of the Study

This thesis has covered the preparations of copper(II) complexes from corresponding Schiff base ligands. The Schiff base ligands were synthesized by condensations reaction between salicylaldehyde and amino derivatives (2-aminophenol, 2-aminothiazole and ortho-phenylenediamine). The corresponding copper(II) complexes was obtained by treating the synthesized ligands with copper acetate in presence of organic solvents such as methanol (MeOH), tetrahydrofuran (THF) and 1,2-dichloroethane. The synthesized ligands and its copper(II) complexes were structurally characterized by infrared (FTIR), UV-visible and proton NMR spectroscopy. The catalytic activities of the prepared copper(II) complexes was evaluated to study the possibility in the catalytic reductions of 4-nitrophenol to 4-aminophenol in presence of reducing agent such as sodium borohydride ($NaBH_4$).
The progress of reactions was monitored by UV-visible spectroscopy and the percentages conversions was determined from the spectroscopic data.

1.5 Significant of the Study

This research works was chosen as a model to demonstrate the catalytic efficiency of a series of synthesized copper(II) complexes derives from Schiff base ligands in the reduction of 4-nitrophenol.

Global industries are facing severe problems of designing efficient processes of improved selectivity and minimized by-products. Catalysis plays an essential part in the creation of improved chemical processes where developments in catalyst design are critical components to be considered. In particular, chemical industries can generate ultimate benefits by lowering the energy barrier of chemical reactions during productions and conversions of raw material into finish products.

Therefore, this study has endeavour to developed a new model for the reduction of aromatic compounds (4-nitrophenol) using copper(II) complexes as active catalyst to achieves better yield and shorter reaction time during catalytic reactions

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