UNIVERSITI TEKNOLOGI MARA

SYNTHESIS, CHARACTERIZATION, COMPUTATIONAL, CATALYTIC AND ANTIBACTERIAL STUDIES OF Pd(II), Ni(II) AND La(III) SCHIFF BASE COMPLEXES DERIVED FROM ALIPHATIC AND CYCLIC DIAMINES

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Thesis submitted in fulfilment
of the requirements for the degree of
Doctor of Philosophy
(Chemistry)

Faculty of Applied Sciences

July 2025

ABSTRACT

Schiff base metal complexes have attracted considerable interest due to their catalytic and biological application. However, studies on Pd(II), Ni(II) and La(III) complexes derived from aliphatic and cyclic Schiff bases remain underexplored, particularly in catalytic studies involving Sonogashira reaction and in antibacterial study. Moreover, there is a lack of comprehensive investigations combining these experimental studies approaches such as Density Functional Theory (DFT) and Response Surface Methodology (RSM) for reaction optimization and mechanistic insights. To address these gaps, ten (10) Schiff bases derivatives (AD1 and AD2 series) were synthesized via condensation of five salicylaldehyde derivatives (X = H, F, Cl, CH_3 and OCH_3 at the *meta* position to C=O) with two primary amines, 2,2-dimethyl-1,3-propanediamine (DMPD) and 1,2-cyclohexanediamine (CHD), in 2:1 molar ratio. These Schiff bases reacted with Pd(II), Ni(II) and La(III) salts in a 1:1 molar ratio to form 26 metal complexes. Six Schiff bases and 13 metal complexes were identified as new compounds indicated through comparison with reported structures in the Cambridge Structural Database (CSD). The compounds were characterized via elemental analysis (CHNS), melting point, FTIR, ^{1}H and ^{13}C NMR, UV-Visible spectroscopy, magnetic susceptibility and thermogravimetric analysis (TGA). Single crystal X-ray diffraction confirmed the structures of eight (8) Schiff bases and five (5) metal complexes. Spectral data revealed significant shift in FTIR, UV-Vis, and NMR spectra upon complexation, particularly a 3 to 36 cm^{-1} shift in the C=N stretching band, confirming azomethine nitrogen and phenolic oxygen coordination. Using Pd(AD1) series complexes as catalysts, the optimum conditions were determined to be KOH as the base, 2.0 mmol% catalyst, and 120 °C reaction temperature. Pd(II) complexes exhibited the highest percent conversion of iodobenzene compared to Ni(II) and La(III) complexes, with 100% selectivity for the coupling product and no detectable byproducts. Aliphatic (AD1) complexes outperforming cyclic (AD2) complexes due to greater ligand flexibility, enhancing substrate access. Under these conditions, Pd(AD1F) achieved a 100% conversion of iodobenzene in 3 hours, in agreement with the RSM calculation, except for the reaction time. The isolated yield of diphenylacetylene was 14.3% of yield, attributed to purification losses, leading to lower turnover number (TON) and turnover frequency (TOF) values with values of 7.1 and 2.4 h^{-1}, respectively. The diphenylacetylene was characterized using CHN analysis, FTIR and ^{1}H NMR spectroscopy. Kinetic studies showed Pd(AD1F) catalyzed reaction twice as fast as uncatalyzed one. Substitution of iodobenzene with bromobenzene resulted in a slightly reduced conversion of 92.0%. DFT studies on selected compounds, namely Pd(AD1F), Pd(AD1Me), Ni(AD1Me), AD2Cl and AD2OMe supported the experimental findings. Pd(AD1F) exhibited favourable electronic properties with high ionization potential and low electron affinity, enhancing its catalytic efficiency. Conversely, large HOMO-LUMO energy gap in AD2Cl (4.615 eV) and AD2Me (4.589 eV) supports their inactive antibacterial activity. Antibacterial screening revealed Pd(AD1F) exhibited significant inhibition against *Streptococcus mutans* (90.87%), while Pd(AD2OMe) was active against *Proteus vulgaris* (93.99%). This work highlights Schiff base Pd(II) complexes, particularly Pd(AD1F), as efficient catalysts and potential antibacterial agents, with promising applications in green chemistry and medicine.

ACKNOWLEDGEMENT

First and foremost, all praises and thanks to Allah, the Almighty, for His countless blessings in allowing me to complete this project, even though it was slightly later than expected. Upon completing this work, I would like to express my deep gratitude to many individuals and parties who have directly and indirectly contributed to the successful completion of this project.

I extend my heartfelt thanks to my supervisor, Dr Shahrul Nizam Ahmad, for his patient guidance, enthusiastic encouragement, and valuable critiques of this research. His invaluable help, constructive comments, and suggestions throughout both the experimental and thesis works have greatly contributed to the success of this research. I am also deeply grateful to my co-supervisors; Professor Dr Hadariah Bahron, Dr Nor Mas Mira Abd Rahman and Dr Nor Saadah Mohd Yusof, for their pieces of advice and assistance in guiding me through the analysis of my study results, as well as for their generosity in sharing their knowledge. I would also like to acknowledge the laboratory assistants of Faculty of Applied Sciences for their cooperation throughout my study. Special thanks go to my supportive and helpful labmates, Dr. Solihah, Mr. Azwan, Ms. Balqis, Ms. Nabihah, Dr. Ummi, Ms. Sufi, Mrs. Nurul and Ms. Siti, for their encouragement and companionship throughout this long journey.

I gratefully acknowledge Dr. Nurul Aili and Siti Sarra from Faculty of Applied Sciences, Universiti Teknologi MARA, for their assistance with antibacterial screening. Appreciation is also extended to Mrs. Nova Pratiwi Indriyani (Bandung Institute of Technology, Indonesia), Dr. Aditya Wibawa Sakti (Waseda University, Japan), and Dr. Siti Syaida Sirat (Universiti Teknologi MARA) for their contributions in DFT calculations. I also thanks the Laboratory of Microbiology, Faculty of Applied Sciences, UiTM Shah Alam, and the Natural Approach to Oral Health (NAtOH), Faculty of Dentistry, UiTM Sungai Buloh, for providing bacterial strains.

My deepest gratitude goes to my beloved parents, Mr. Nasaruddin Bin Mohd Nor and Mrs. and to my siblings, for their endless love, prayers and unwavering encouragement. This thesis is specially dedicated for my parents, with the hope that this achievement will inspire them to continue their fight for better health. My love and prayers will always be with them, and may Allah grant the best for all of us.

TABLE OF CONTENTS

CHAPTER 1
INTRODUCTION

1.1 Research Background

1.1.1 Aliphatic and Cyclic Schiff Bases

Schiff bases are compounds that contain azomethine (C=N) functional groups. These compounds can be produced through a condensation reaction between primary amine with either aldehyde or ketone. Such compounds have fascinated the scientific community's interest due to their ease of synthesis and metal complexation (Boulechfar et al., 2023). Most often, Schiff bases are solids that are transparent and coloured. The precise melting points of Schiff bases make them valuable for identifying carbonyl compounds and quantifying metal content due to their stability and sensitivity to structural variations (Subasi, 2022). Schiff base formation can be confirmed through spectroscopic analysis such as FTIR, ^{1}H and ^{13}C NMR, UV-Visible spectroscopies and X-ray crystallography. The appearance of azomethine chromophore in the Schiff base can be detected through these analyzes.

A stable Schiff base can be formed from aromatic aldehyde with an effective conjugation system such as salicylaldehyde and its derivatives (Xavier & Srividhya, 2014). Schiff bases can be categorized into aliphatic and cyclic based on the type of carbon skeleton which can vary by changing the amine bridging groups (Figure 1.1). Aliphatic Schiff bases can be derived from aliphatic diamines, i.e. 2,2-dimethyl-1,3-propanediamine, while the cyclic Schiff bases can be derived from cyclic diamines, i.e. 1,2-cyclohexanediamine. Aliphatic diamine has a linear or branched carbon skeleton, while cyclic diamine has a ring structure. Their structure differences can affect their physical and chemical properties, including their stability, reactivity, and solubility. Cyclic Schiff bases tend to be more stable than their aliphatic counterparts, due to the cyclic structure's rigidity, which reduces the likelihood of decomposition. Due to higher molecular weight and stability, cyclic compounds tend to have higher melting and