Faculty of Resource Science and Technology

Synthesis and Characterization of Transition Metal(II) Complexes of Bidentate and Tetradeutate Schiff Base Ligands

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Synthesis and Characterization of Transition Metal(II) Complexes of Bidentate and Tetradentate Schiff Base Ligands

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This project is submitted in partial fulfillment of the requirements for the Degree of Bachelor of Science with Honours (Resource Chemistry)

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DECLARATION

No portion of the work referred to this dissertation has been submitted in support of an application for another degree of qualification of this or any other university of institution of higher learning.

________________________________________
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Synthesis and Characterization of Transition Metal(II) Complexes of Bidentate and Tetradentate Schiff Base Ligands

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ABSTRACT

Two Schiff base ligands have been derived from the condensation reaction of 1,2-ethylenediamine with 2-acetylpyridine and benzophenone in 1:2 mole ratio, respectively. Five transition metal(II) {Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)} complexes of 1,2-ethylenediamine-bis(2-acetylpyridine) ligand (I) have been synthesized by direct reaction of ligand (I) and transition metal(II) salts in 1:1 (metal:ligand) mole ratio in absolute ethanol. Another three transition metal(II) {Co(II), Cu(II) and Zn(II)} complexes of N,N’-bis(benzophenone)-1,2-diiminoethane ligand (2) have been synthesized by the procedure similar to ligand (1). Schiff base ligands (1-2) and their transition metal(II) complexes (3-10) have been characterized using elemental (CHN) analysis, UV-Visible and IR spectral studies. Among them, ligand (1) and its Zn(II) complex (6) have also been studied by 'H NMR spectra. All transition metal complexes are non electrolytic in nature. Spectral studies suggested that Schiff base ligand (1) acts as a neutral tetradentate (NNNN) chelating agent and Schiff base ligand (2) acts as a neutral bidentate (NN) chelating agent towards transition metal(II) ions.

Keywords: Schiff base ligands; transition metal(II) complexes; spectral studies.

ABSTRAK

Dua ligan bes Schiff telah disintesis daripada proses kondensasi 1,2-etelinadiamina dengan 2-asetilpiridina dan benzofenon dalam 1:2 nisbah mol, masing-masing. Lima kompleks logam(II) {Co(II), Ni(II), Cu(II), Zn(II) dan Cd(II)} peralihan daripada ligan (I) iaitu 1,2-etelinadiamina-bis(2-asetilpiridina) telah disintesis dengan tindak balas terus campuran ligan (I) dan garam logam(II) peralihan dengan 1:1 nisbah mol di dalam ethanol. Tiga kompleks logam(II) {Co(II), Cu(II) dan Zn(II)} peralihan daripada ligan (2) N,N’-bis(benzophenone)-1,2-diiminoetana telah disintesis berdasarkan kaedah yang sama dengan ligan (I). Kedua-dua ligan bes Schiff (1-2) dan kompleksnya (3-10) telah dikenal pasti dengan analisis elemen (CHN), sinar cahaya nampak UV dan juga kajian spektra IR. Antaranya, ligan (1) dan semua kompleks logam kumpulan peralihan yang terhasil adalah bukan elektrolit. Kajian spektra yang telah dilakukan menunjukkan bahawa ligan bes Schiff (1) bertindak sebagai neutral tetrudentet (NNNN) dan ligan bes Schiff (2) bertindak sebagai neutral bidentet (NN), kepada ion logam peralihan.

Kata kunci: Ligan bes Schiff; kompleks logam(II) peralihan; kajian spektra.

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CHAPTER 1

1. INTRODUCTION

1.1 Schiff base ligands and metal complexes

Schiff base is a chemical compound which contains carbon-nitrogen double bond with the connection of nitrogen atom to aryl group or alkyl group but not hydrogen atom (Parker, 1993). Schiff bases are typically formed by the condensation reaction of a primary amine and an aldehyde or ketone. The resultant functional group, \( \text{R' R'' C=N-R} \), is called an imine and is particularly readily to bind with metal ions via lone pair electron of nitrogen atom, especially when used in combination with one or more donor atoms to form polydentate chelating ligands. Schiff base ligands can form very stable complexes compare to some other ligands. Schiff base ligands have the chelating properties which make the coordination system resistant to the attack of non-chelating ligands.

\[
\begin{align*}
\text{R' R'' O} & + \text{R- NH}_2 & \Leftrightarrow & \text{R' R'' NR} & + \text{H}_2\text{O} \\
\end{align*}
\]

Scheme 1: General reaction for condensation process.

The Schiff base ligands can also be found in monodentate, bidentate, tetradentate and so on. The polydentate Schiff base ligands are known to form very stable metal complexes with transition and heavy metal ions (Atwood, 1997). These ligands played important roles in the development of coordination chemistry as they can readily form stable complexes with most of the transition metals.
Coordination compound can be defined as complex compound that consist of central atom which is usually metal ion or atom and attached group are known as ligands (Hill and Petrucci, 2002). Complex compound formation may be regarded as a reversible association of one or more metal ions and ligands. For example,

\[
\text{Ni(ClO}_4\text{)}_2 + 6\text{NH}_3 \rightleftharpoons [\text{Ni(NH}_3\text{)}_6\text{]}(\text{ClO}_4\text{)}_2
\]

Ligand is defined as the neutral molecules or ions (usually anions) which has the capability to attach at the central metal ion in the formation of complex compound. In Lewis sense, the ligands act as Lewis bases (electron pair donor) and the central metal ion acts as Lewis acid (electron pair acceptor).

The coordination chemistry of metal complexes has received great attention over the last few years. This is mainly due to the potential application of these complexes in various types of processes (Kia et al., 2007).

A large number of Schiff bases and their metal complexes have been studied for their interesting and important properties. Metal complexes of Schiff bases have attracted great interest due to their remarkable antifungal, antibacterial and antitumor activities (Garg and Kapur, 1990) and have pharmacological as well as physiological activities (El-hendawy et al., 1992).

Metals complexes such as copper(I) with N-, S- and P-donor ligands are of growing interest owing to their wide variation in structural formats and rich chemical properties (Zhou
et al., 2005). Many of these complexes have been reported to be luminescent and their emission behavior varies with structures, identities of halides, and steric and electronic effects of used ligands (Zhou et al., 2005).

The Schiff base ligands are one of the most widely used ligands to form metal complexes due to the ease of formation and remarkable versatility. Schiff base ligands have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals (Kandar et al., 2005). In the area of bioinorganic chemistry, Schiff base complexes are interesting synthetic models for investigation of the similar metal containing sites in proteins and enzymes (Kandar et al., 2007).

Metal complexation is of widespread interest. It is studied not only by inorganic chemists, but also by physical and organic chemists and by biochemists, pharmacologists, molecular biologists and environmentalists.

1.2 Chelate effects

The term chelate was first applied by Morgan and his co-worker (1920), who stated: ‘The adjective chelate, derived from the great claw or chela (chela – Greek word) of the lobster or other crustaceans, is suggested for the capiler like groups which function as two associating units and fasten to the central atom so as to produce heterocyclic rings’. The term chelate is referred to the improvement of stability of the complex systems that contain chelate
rings as compared to the stability of system similar as possible but contain none or fewer rings.

The chelate effect means the enhanced stability observed in a complex formed from bidentate or polydentate ligands compared with similar complex formed from the corresponding monodentate ligands. As the result, the complexes which have chelating properties ligands can form more stable complex compared to none chelating ligands. Chemical equation below shows the chelating properties that affected the equilibrium constants of complexes:

\[
\begin{align*}
\text{Ni}^{2+} (aq) + 6 \text{NH}_3 &\rightarrow [\text{Ni(NH}_3)_6]^{2+} \quad \log \beta = 8.61 \\
\text{Ni}^{2+} (aq) + 3 \text{en} &\rightarrow [\text{Ni(en)}_3]^{2+} \quad \log \beta = 18.28
\end{align*}
\]

Scheme 2: Different value of equilibrium constants affected by chelating properties.

The chelate effects can be seen by comparing the reaction of the chelating ligands and a metal ion with the corresponding chemical reaction involving comparable monodentate ligands. The system where in there are chelate rings are formed is almost 100 times more stable than the system that have no such ring formed. It has been known for many years that the complexes containing chelating ligands are more stable thermodynamically.

Obviously the complex of \([\text{Ni(en)}_3]^{2+}\) is much more stable than \([\text{Ni(NH}_3)_6]^{2+}\), since the former complex contains chelate ring while the other has no chelate ring. The chelate effect is also evident from the fact that the stability of \(\text{NH}_3\), ethylenediamine (en) and
triethyleneamine, $\text{NH}_2-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$ (trien) complexes of Cu$^{2+}$ ion are in order:

$$[\text{Cu(NH}_3)_4]^{2+} < [\text{Cu(en)}_2]^{2+} < [\text{Cu(trien)}]^{2+}$$

$$\log \beta = \begin{array}{l} 12.7 \\ 19.7 \\ 20.5 \end{array}$$

Figure 1: Log $\beta$ values of Cu(II) with different types of ligands.

### 1.3 Objectives of the project

The main objectives of this research are:

- to synthesize bidentate and tetradentate Schiff base ligands derived from 1,2-ethylenediamine.
- to synthesize transition metal(II) complexes from the above Schiff base ligands.
- to characterize bidentate and tetradentate Schiff base ligands and their metal(II) complexes by CHN analyses, UV-Visible, FTIR and $^1$H NMR spectra analyses.
- to determine the molar conductivity of the synthesized transition metal(II) complexes.
CHAPTER 2

2. LITERATURE REVIEW

2.1 Schiff base ligands and their transition metal complexes

The most common form of polydentate ligands is bidentate, that is having two possible points of attachment to a central metal ion. Tridentate ligands are less common compared to bidentate and tetradentate ligands. However, they are quite useful for binding with metal ions that can form stable 5-coordination complexes with sufficiently bulky partner ligands or indeed the Schiff base itself. Pyridine-2-carbaldehydezine is one of tetradentate N-donor ligand, which having pyridyl backbone. These are some of the example of bidentate N-donor ligands.

Figure 2: Examples of bidentate and tetradentate ligands.
A lot of studies undergo by chemists to determine how these types of ligands can form a very useful complexes with transition metals. In 2006, Gupta and his co-workers were trying to strengthen the facts from Sacconi et al. that the NNO-tridenetate Schiff base complexes of cobalt can bind with DNA to work as an antitumor therapy. This is an interesting finding that can be applied to bioinorganic chemistry to prevent tumor from spreading at the early stages. As part of a study, Gupta and his co-workers have synthesis a diamagnetic octahedral $\text{Co}^{\text{III}}$ complex.

![Octahedral compounds of Co(III) with NNO-donor ligands.](image)

Tetradentate Schiff bases with $\text{N}_2\text{O}_2$-donor atom set are well known to coordinate with various metal ions. Three $\text{N}_2\text{O}_2$-donor ligands have been derived from the condensation of $o$-phenylenediamine with salicylaldehyde, 2-hydroxy-1-naphthaldehyde, or $o$-hydroxyacetophenone (Ahd-Elzaher, 2001).
Salvati-Niasari et al., 2005, reported the synthesis of new square planar Mn(II), Co(II), Ni(II) and Cu(II) complexes with tetradentate Schiff base ligand \( N,N'-\text{bis}(\alpha\text{-methylsalicylidene})-2,2\text{-dimethylpropane}-1,3\text{-diamine} \). The Schiff base ligand was derived from the condensation process of 2-hydroxyacetophenone with 2,2-dimethyl-1,3-propanediamine under refluxing condition in ethanol as shown in Scheme 3.
Scheme 3: Condensation process of 2-hydroxyacetophenone with 2,2-dimethyl-1,3-propanediamine.

Another type of tetradentate Schiff base ligand has been reported as isatin-hydrazone ligand (Rodrigues-Arguelles et al., 2004). They have also described the reactions of nickel(II), copper(II) and zinc(II) ions with equimolar amount of isatin-hydrazone to afford the six-coordinated complexes.

Figure 5: Ni(II) complex with isatin-hydrazone ligand.
The hexadentate Schiff base ligand containing two N-donor atoms and four O-donor atoms was reported can form stable metal complexes depend on what kind of metal ion that is used. Synthesis, characterization and X-ray crystal structure of copper(II) and nickel(II) complexes with potentially hexadentate Schiff base ligands (Khandar et al., 2005) that form from 5-phenylazo and 2-[2-(2-aminophenoxy)ethoxy]aniline as shown in Scheme 4.

\[
\begin{align*}
2 \text{PhN}_2\text{-PhO} + & \quad \text{(CH}_2\text{)}_2\text{O} \quad \text{NH}_2 \quad \text{H}_2\text{N} \\
\rightarrow & \quad \text{(CH}_2\text{)}_2\text{O} \quad \text{O} \quad \text{N} \quad \text{N} \quad \text{OH} \quad \text{HO} \quad \text{N}_2\text{Ph} \\
\text{PhN}_2\text{-PhO} & \quad \text{HO} \\
\text{N}_2\text{Ph} & \text{N}_2\text{Ph}
\end{align*}
\]

Scheme 4: Hexadentate Schiff base ligand containing ON-donor atoms.

Cisplatin (cis-diamminedichloroplatinum(II)) is one of the transition metal complexes that is currently used clinically and is one of the most effective anticancer drugs in the treatment of variety of human solid tumors, such as genitourinary tumor. The ligand that attached to the platinum(II) is N-donor ligand and has very useful biological activity especially for the DNA. Miernicka and his co-workers had done some tests on this complex.
compound to ensure the side effects and the effectiveness of cis-diamminedichloroplatinum(II) (Miernicka et al., 2007).

From the literature review, there are some research have been done on the Schiff base ligands and their transition metal complexes, but still not enough to cover up all the characterization of Schiff base complexes. That is why this research needs to be done to get more information about Schiff base ligands and their metal complexes properties. From this study, it is hope that a successful synthesis and characterization of Schiff base ligands and also their transition metal complexes can be achieved. Therefore, it has been considered to synthesize and characterize the transition metal complexes with the proposed Schiff base ligands.
CHAPTER 3

3. MATERIALS AND METHODS

3.1 Physical measurements

The main research was conducted in Inorganic Research Laboratory at UNIMAS. All the chemicals were purchased from Fluka, Aldrich or J.T Baker. Schiff base ligands and their transition metal complexes were characterized by using CHN analyses, UV-visible, FTIR and \(^1\)H NMR spectral analyses. The CHN analyses were recorded with FlashEA 1112 Series CHN elemental analyzer at UNIMAS. Infrared spectra were recorded as KBr disc using Perkin Elmer Spectrum GX Fourier-Transform Spectrometer (4000–370 cm\(^{-1}\)). \(^1\)H NMR spectra were recorded in DMSO-\(d_6\) solution on a Jeol 500 MHz FT-NMR spectrophotometer at UNIMAS. Electronic spectra were recorded with a suitable solvent on a Perkin Elmer Lambda 25 UV-Visible Spectrometer at UNIMAS. Molar conductance of the ligands and their transition metal complexes were measured at room temperature using Jenway 4510 conductivity meter at UNIMAS.

3.2 Laboratory work

Purifying of solvents, Schiff base ligands and their transition metal complexes were synthesized according to Kia \textit{et al.}, 2007 and Affan \textit{et al.}, 2007.

3.3 Solvent distillation

All solvents were distilled according to the published methods by Amergo \textit{et al.}, 1996.
3.4 Synthesis of Schiff base ligands (1-2)

3.4.1 Synthesis of 1,2-ethylenediamine-bis(2-acetylpyridine) ligand \([C_{16}H_{18}N_4] \(1\))

The tetradebate Schiff base ligand, 1,2-ethylenediamine-\textit{bis}(2-acetylpyridine) was prepared by direct condensation reactions of 1,2-ethylenediamine (0.120 g, 0.001 mole) in 3 mL of absolute ethanol and 2-acetylpyridine (0.484 g, 0.002 mole) in 10 mL absolute ethanol in 1:2 mole ratio. The mixture was stirred and heated under reflux condition for 3 hours. The ligand formed is in liquid state which has brown in colour with b.p. >130 °C.

\[
\begin{align*}
\text{H}_2\text{N} & + \text{NH}_2 \\
1,2\text{-ethylenediamine} & + 2 \text{CH}_3\text{O} \\
2\text{-acetylpyridine} & \text{Abs. ethanol} \\
& \text{Refuxed and Stirred for 3 hours} \\
\text{H}_3\text{C} & + 2\text{H}_2\text{O} \\
\text{N} & \text{N} \\
(1) & \text{N=N} \\
\text{N} & \text{N} \\
\text{N} & \text{N} \\
\end{align*}
\]

Scheme 5: Tetradebate Schiff base 1,2-ethylenediamine-\textit{bis}(2-acetylpyridine) ligand (1).
3.4.2 Synthesis of \(N,N'-\text{bis}(\text{benzophenone})-1,2\text{-diiminoethane ligand} \ [C_{28}H_{24}N_{2}] \) (2)

\(N,N'-\text{bis}(\text{benzophenone})-1,2\text{-diiminoethane ligand} \ (2)\) were synthesized by adding benzophenone (1.72g, 0.010 mole) in 15 mL of absolute ethanol to the solution of 1,2-ethylenediamine (0.30g, 0.005 mole) in 5 mL absolute ethanol. The resulting solution was stirred and refluxed for 5 hours. Then the mixture volume was reduced to half of its original volume by using rota vapor. The product mixture was left at room temperature for overnight. \(N,N'-\text{bis}(\text{benzophenone})-1,2\text{-diiminoethane ligand} \ (2)\) was formed as white micro-crystals. The micro-crystals were filtered and washed several times with absolute ethanol and dried in vacuo. Yield 1.46g, 72.56\%, m.p. 55-57 °C.

\[
\text{NH}_2 \text{NH}_2 + \text{Benzophenone} \rightarrow \text{N,N'-bis(benzophenone)-1,2-diiminoethane ligand (2)} + 2\text{H}_2\text{O}
\]

Scheme 6: Bidentate Schiff base \(N,N'-\text{bis}(\text{benzophenone})-1,2\text{-diiminoethane ligand (2)}\).